1 Fundamentals

1.1 What is a surfactant?

1.1.1 Physical and chemical properties

"Surfactants, what on earth are they? Yes, I've heard of them, aren't they found in washing powders?"

"What are they called again...?"

An alternative term for a surfactant, «tenside», goes back to the Latin «tensio», which means tension and refers to the alteration in surface tension under the influence of surfactants¹. This is why surfactants are also called «surface-active substances». Such a surface could be, for example, a water surface forming the boundary between water, the liquid medium and air, the gaseous medium. The surface of a potato in a cooking pot can also be the boundary surface between the solid medium (potato) and the liquid medium (water). Naturally there are also boundary surfaces between two liquids such as fat droplets floating in a soup. If vegetable oil and water are brought together then the two immiscible liquids separate out and a boundary surface forms between them. It is exactly this boundary surface on which the surface-active substances, the surfactants, act. If a suitable surfactant is added then products such as mayonnaise or margarine can be formed from the immiscible components vegetable oil and water.

All typical surfactant properties can be traced back to their amphiphilic structure, i.e. to the presence of hydrophilic (water-loving) and hydrophobic (water-repellent) groups in the molecule. This structure has the ability to lower the surface tension. An example of this is the molecular structure of dodecyl sulphate in Fig. 1.

In the literature a simplified representation of the so-called surfactant pins or surfactant matches (Fig. 2) can often be seen.

1.1.2 Surfactants and foam

Once you start foaming... and who doesn’t think about foam when reading or hearing the term «surfactant»: foam in the washing machine or the dishwasher, foam in the bubble bath or under the shower. In all these cases the foam has something to do with the presence of surfactants. Readers who lived in the Federal Republic of Germany (FRG) during the hot summer of 1959 may remember the giant mountains of foam that could be seen on lakes and rivers, particularly near barrages. Above and below weirs these foam mountains were often as high as houses. In those days the foam was caused by the surfactant tetrapropylenebenzene sulphonate (TPS) (Fig. 3), a «hard», i.e. non-degradable surfactant. Industry and government reacted quickly and in 1964 detergent regulations were introduced in the FRG that banned the use of non-degradable surfactants. The industry developed the linear alkylbenzene sulphonate (LAS) (Fig. 4), a soft, i.e. biodegradable surfactant.

Since 1st January 1990 the new law on the biodegradability of detergents has been in effect in the FRG. It contains minimum requirements regarding the biodegradability of surfactants contained in aqueous cleaning agents, washing agents and detergents.

According to the Council Directive of the of the European Union dated 23rd November 1973, only those detergents that are eliminated from wastewaters to at least 90% within 28 days may be sold.

In this way the analytical circle was closed right from the very start, as whether a surfactant is biodegradable or not is a question that can only be solved by analytical means.

A small laboratory sewage treatment plant is used and the surfactant concentration in the inflow and outflow of this plant is determined under specified conditions and applying defined procedures. From the analytical results obtained the biodegradability can be determined. At least three sewage disposal plants are required; one for the surfactant under investigation, a further one with the «hard» standard TPS and the final one with the «soft» standard LAS.
1.1.3 Equilibria in surfactant solutions (micelle formation)

Up to now we have concerned ourselves primarily with the effect of surfactants on the boundary surfaces and their ability to reduce the interfacial tension. Let us now have a look at the behaviour of surfactants in aqueous solutions. They tend to accumulate at the boundary surfaces, i.e. the walls of the vessel containing the surfactant solution, and at the interfacial boundary water/air. As the surfaces of most vessels are negatively charged, the orientation of the surfactant molecules at the surface depends on the type of surfactant, as shown in Fig. 5.

In this respect surfactants clearly differ from all other substances, as neither common salt nor alcohol, etc., will orient themselves with respect to a surface. This unusual behaviour compared to other substances is even more pronounced within the solution. Surfactants form micelles. Micelle formation describes the interesting property of the surfactant to form different molecular aggregates depending on its concentration. Only surfactants in the strict sense of the term have this distinctive feature. However, surface-active compounds are also known in the fields of biology and biochemistry. These are structurally similar to surfactants but will not be discussed any further here.

The type of molecular aggregate formed by the surfactant depends on its concentration and the structure of the surfactant molecule. At lower concentrations real solutions are formed in addition to enrichment at the surface. Above a defined point, the so-called CMC (Critical Micelle Concentration) the tendency of the hydrophobic components of the surfactant to no longer interact with the water becomes so pronounced that they join together to form micelles (Fig. 6).

In the example shown a sphere is formed in which all hydrophilic (water-loving) heads are oriented towards the aqueous phase. In the interior of this sphere the hydrophobic alkyl groups of the surfactant are found. The number of surfactant molecules which join together to form a micelle depends on the type of surfactant and starts at about 50 for ionic surfactants of low molecular mass. Micelles need not be spherical; they can also assume other shapes. A micelle should not be thought of as being just a static aggregate. The average lifespan is just a few milliseconds. Then it dissociates and another aggregate forms with different surfactant molecules. The CMC is an important feature for characterising a surfactant. The CMC of a pure-chain dodecyl sulphate is about 700 ± 100 mg/L.

1.1.4 History

The German chemist Justus von Liebig once said «The more educated and well-off the people, the greater their soap consumption». Soaps also belong to the large surfactant family and form their own sub-group within it. Other personalities have also pointed out that the standard of living and cultural performance of a people develop in parallel to their soap consumption.

In the second century AD the Romans already manufactured soap from oils and ashes (potash) and used it chiefly for body cleansing purposes, but also for washing clothes.

Industrial soap manufacture only started after the French chemist Nicolas Leblanc (1742 to 1806) developed a method of manufacturing soda.

For a long time soap remained the only surfactant available. Only the scarcity of raw materials during the Second World War, which also affected vegetable oils, which were used for soap manufacture, caused the German industry to look for alternatives. The use for cleaning purposes of an emulsifier normally used in the emulsion polymerisation of buna (synthetic rubber) produced promising results. A practical application to the requirements of the population was not permitted by those then in power, as buna production was declared to be more important.

Immediately after the war development was taken up again and pursued more strongly; in a short time marketable products were introduced.

The manufacturers received whole sacks of thank-you letters from the population. In the Ruhr region in particular it was again possible to clean oneself and one’s dirty working clothes properly. A special advantage was that the new surfactants, as opposed to soap, were not rationed and could be bought in almost any quantity. Chemically speaking the first surfactants used were alkylbenzene sulphonates, fatty alcohol ethoxylates, fatty alcohol sulphonate ethoxylates and alkyphenol ethoxylates.

The first alkylbenzene sulphonate in the world was sold in 1936 by the National Aniline Chemical Company, New York, under the name «Nacconol». The successors to IG Farben brought it onto the market shortly after the war under the
name «Igepal NA» and in 1948 Hüls introduced it under the trade name «Marlon», which is still in use today. Alkylalkylbenzene sulphonate was produced in parallel to it. In those days the raw materials benzene and naphthalene were still raw products from the coking process. Alkylbenzene sulphonate established itself very rapidly against alkylalkylbenzene sulphonate, because its washing activity was clearly greater. The first generation of alkylbenzene sulphonates consisted exclusively of products with a strongly branching alkyl group, mainly tetrapiropylene benzene. Only the problems encountered during the hot summer of 1959 with its very low water levels in some places led to the development of the linear alkylbenzene sulphonates, which were available from 1963 onwards. On 1st October 1964 the new law on Detergents came into effect and banned the use of non-biodegradable surfactants (detergents). In the fifties and sixties pride was still taken in the fact that the new generation of surfactants were manufactured solely from synthetic raw materials and thus the natural fat resources were conserved.

However, in 1959 the first green environmental initiative occurred with its demand «back to soap».

About 100 years ago the Berlin chemist C. Scheibler discovered a unique substance in the juice of the sugar beet. He named it beta-in, which corresponds to the Latin name for beets. Its analysis produced an interesting result: This substance was the salt of an acid and simultaneously the salt of a base. The carboxylate group and the quaternary ammonium compound are the particular features of betain. This is thus a so-called zwitter ion, an internal salt. The chemical name of the betain isolated by Scheibler is trimethylaminoaetic acid. Its trivial name is beet betain.

Today the name betain stands for a whole class of surfactants. It is used whenever cationic quaternary nitrogen and an anionic carboxylate group are present in a single molecule. This surfactant group has a large number of interesting properties, which made betains particularly interesting to dermatologists and biologists at the end of the sixties. At this time Messrs. Th. Goldschmidt AG in Essen began with the production of the first betain, TEGO Betain L7, based on Patent 1.172.802. TEGO Betain L7, a cocamidopropyl betain, still forms part of the wide range of betains offered by Th. Goldschmidt AG today. Research, development and applications technology have continually developed, improved and optimised this product. As a result these products enjoy worldwide esteem today.

1.1.5 Natural and synthetic surfactants

The word «surfactant» has an involuntary association with chemistry. Surfactants are «artificial». However, surfactants can also be completely «natural». This is always the case when they are synthesised by Mother Nature, i.e. by a living organism. Practically all living organisms produce tailor-made surfactants, which are synthesised to fulfil a particular task for the organism. Wherever boundaries in the body have to be crossed, surfactants help to make these boundaries permeable. For example, when food is to be transferred from the digestive system to the blood circulation or atmospheric air to the lungs, special surfactants provide vital assistance.

The best-known surfactant occurring in nature is certainly lecithin which, to name just one example, makes up about 10% of an egg yolk. Quantitatively the surfactants produced by the liver play a far more important role. These are collected in the gall bladder and are of decisive importance for the digestion of fats. In this connection it is interesting that the human livers of the 80 million German citizens and the chemical industry in Germany take part in a neck-and-neck race to produce the highest annual surfactant tonnage. If animals are also included then the notion of the predominantly artificial synthetic surfactants has to be revised.

1.1.6 Surfactants as aids

One could almost say that surfactants have a helper syndrome. And it is just as well. Have you ever tried to rinse the soiled lunch-time plates without the help of surfactants? It is hardly possible without the few but so important drops of detergent, which lower the surface tension of the water so much that rinsing the plates can be carried out without any problems; indeed, it almost takes place by itself. In this case the surfactants accumulate almost exclusively where their help is required, namely at the interfacial boundary between the rinsing water and the soiled plates. As a result of the lowered surface tension a thin film of water can penetrate between the soil and the plate and carry off the soil. A German advertising slogan in the sixties explained this in the following manner: «Pril relaxes the water, makes it softer, more liquid, wetter».

1.2 Dividing the surfactants into classes

The hydrophilic group of a surfactant primarily determines its application as well as its analytical properties. This is why the hydrophilic group also forms the basis for the division into various subgroups. According to this principle the arrangement shown in Fig. 7 is obtained:

1.2.1 Anionic surfactants

These are substances which form ions in aqueous solution and in which the anion has the surface-active properties.

Within this group there are both natural and synthetic surfactants. Excellent properties for technical applications such as good solubility in water, high cleaning efficiency, but also a favourable price are the basis for the prominent role played by anionic surfactants. They occur in the industrial sector, but also in the household, e.g. in washing agents, household detergents and body care products (Figs. 8 to 10).
1.2.2 Cationic surfactants

These are substances which form ions in aqueous solution and in which the cation has the surface-active properties. An important feature of the cationic surfactants is their ability to accumulate substantively on negatively charged surfaces such as textiles, metals or even on cell membranes and change the properties of the surface. This ability is the main reason for the use of cationic surfactants. They are used as anti-rust additives for metals, as fabric softeners, as conditioners after hair washing or as disinfectants in cleaning agents (Figs. 11 to 14).

1.2.3 Nonionic surfactants

These are substances which possess surface-active properties without dissociating into ions in aqueous solution. This group also contains substances such as the polyethylene glycols, which only exhibit their surface-active properties after hydration (Fig. 15).

In nonionic surfactants the water solubility results from polar but not dissociable groups, often OH functions or polyglycol substituents (POE adducts). The hydrophilic and oleophilic properties are influenced by varying the POE units in the molecule (HLB system). As the number of POE units in the molecule increases the hydrophilicity also increases. This is due to hydration of the polyglycol chain (POE units), which projects into the aqueous phase for quite some distance.

As in all technically manufactured surfactants, particularly in the POE adducts, a very wide distribution of the homologues can be found both in the alkyl chains, which influence the oleophilic properties and in the POE chains, which influence the hydrophilic properties.

Other important representatives of the group of nonionic surfactants are the alkylpolyglucosides or the fatty acid partial esters of multivalent alcohols such as glycerol, polyglycerol, sorbitans or other sugar alcohols. These are chiefly used as emulsifiers in the pharmaceutical, cosmetics or food industry sectors (Fig. 16 to 19).
1.2.4 Amphoteric surfactants

Those surfactants which can react nonionically, cationically or anionically depending on the pH of the aqueous phase belong to this group. They contain both an anionic group as well as a cationic group in a single molecule, which cannot be separated from each other by dissociation in aqueous solution. Both ampholytes as well as betains (Fig. 20) belong to the group of amphoteric surfactants.

Ampholytes are compounds which contain both cationic and anionic hydrophilic groups in a single molecule. These can be ionised in aqueous solution and yield a substance with either anionic or cationic properties, depending on the pH of the solution. The most important representatives of the ampholyte group are the amino carboxylic acids. At the isoelectric point these are present as internally balanced salts, at low pH values they are cationic and at pH values above the isoelectric point they are anionic, as shown in Figs 21 and 22.

Betains are true zwitter ions which take on a cationic character in strong acids. In the alkaline range there are no anionic properties as the internally molecularly balanced condition prevails.

The group of amphoteric surfactants contains substances with very different chemical structures. Nevertheless the common properties predominate, such as lower sensitivity to water hardness and lime soap, compatibility with electrolytes or even bactericidal properties. In the body care sector they are well tolerated by the skin and mucous membranes. In particular betains such as TEGO Betain L7 or F50 can significantly reduce the skin-irritating properties of the anionic surfactants so that by using a suitable combination it is possible to manufacture body care agents which are very gentle to the skin. Additionally the betains offer further interesting properties for the production of shampoos and shower gels, such as increasing their viscosity. This has led to betains becoming the most important co-surfactants in this sector. The sulphobetains (Fig. 23) are important special surfactants for technical applications. As the terminal sulphonic acid is markedly more acidic than the carboxylate group normally present in betains, the protonation of the sulphonic group (to convert the sulphobetain into a cationic surfactant) is made difficult and can only be achieved at a sulphuric acid concentration of 2 mol/L.
1.2.5 Soaps
From a chemical point of view soaps are salts of fatty acids (Fig. 24). Basically soaps are also anionic surfactants. They only possess their anionic properties in the alkaline range. Under acidic conditions they are present as undissociated fatty acids. Soap manufacture, soap boiling, belongs to the oldest chemical reactions carried out by humans. Soaps are very sensitive to hard water and form insoluble calcium or magnesium soaps. In the cleaning agent sector soaps have largely been replaced by synthetic surfactants. In many areas such as washing agent formulations, general purpose cleaners, etc. soaps still have an important function.

1.3 Qualitative examination
Qualitative analysis is particularly important when an analyst inexperienced in this field is called upon to carry out a complete analysis. Many experienced analysts prefer to make their preliminary examination both qualitative and quantitative. Many of the essential separations for qualitative purposes must be repeated later on a quantitative basis and the reluctance to repeat these steps has led experts to the conclusion that time can be saved by adopting quantitative separations and reactions at the outset and to use the separated fractions for qualitative identification. It is assumed at this stage that the analyst approaching this field for the first time will prefer to confine his energies to a qualitative identification.

By far the most useful qualitative test is the determination of the infrared spectrum of the ethanol-extractable matter, but this will normally require the isolation of the organic fraction before any reliable identification of the components can be made. This will identify most of the functional groups present.

1.3.1 Behaviour on acidification
The first step in the qualitative examination is to acidify an aqueous solution of the product with hydrochloric acid (colour change of methyl orange, i.e. pH ≤ 3). Note whether or not the lather is completely destroyed. If it collapses and there is simultaneous precipitation, then soap only or soap containing only a very minor proportion of detergent is present. If the lather persists the presence of a surfactant is indicated.

1.3.2 Test for elements
If a surfactant is present, a filtered ethanol extract of the product is tested for sulphur, nitrogen, phosphorus and halogens either by the sodium-fusion method or preferably by the zinc dust-sodium carbonate fusion method (Middleton). If chlorine is found this may be due to contamination of the active matter with sodium chloride and this should be checked. If, however, both organic nitrogen and organically combined halogen are present, then the product may contain either a quaternary ammonium salt, a tertiary amine hydrohalide, an organic chlorine bleach or a germicidal agent. Subsequent tests will confirm whether or not a quaternary ammonium constituent is present. If none is present but the product liberates iodine from a solution of potassium iodide acidified with sulphuric acid then a nitrogenous organic bleach based on chlorine is probably present. If the product contains no nitrogen but still liberates iodine with the acidified potassium iodide solution, a halogen-substituted perbenzoic acid could be present.

1.3.3 Test with mixed dimidium bromide-disulphine blue dyes
Disulphine blue VN 150
Dimidium bromide, available from Burroughs, Wellcome Co. Ltd.

Mixed indicator stock solution
Weigh 0.5 – 0.05 g dimidium bromide into a 50 mL squat beaker. Weigh 0.25 – 0.005 g disulphine blue into a second 50 mL beaker. Add 25 mL of hot 10% aqueous ethanol solution to each beaker, stir to dissolve and transfer each to a 250 mL graduated flask. Rinse the beakers into the graduated flask with the aqueous ethanol solution and dilute to volume.

Acidic indicator solution
Add 200 mL of distilled water and 20 mL of the above mixed indicator solution to a 500 mL stoppered graduated flask, add 20 mL of 2.5 mol/L sulphuric acid solution, mix and dilute to volume with distilled water. Store in an amber glass vessel out of direct sunlight.

Chloroform A.R., washed free from ethanol.

Sulphuric acid, 2.5 mol/L aqueous solution.

Phenolphthalein indicator solution
Dissolve 1 g phenolphthalein in 50 mL of ethanol and add 50 mL of water while stirring.

Sulphuric acid solution, 0.5 mol/L.

Sodium hydroxide, 1 mol/L aqueous solution.

Test
First dissolve a little of the product in water, divide it into two fractions, adjust one solution to pH = 1 and the other to pH = 11. To each add 5 mL of dimidium bromide-disulphine blue VN 150 mixed indicator solution and 10 mL of chloroform.
Shake and allow to settle so that the colour in the chloroform phase can be observed. In the presence of an anionic surfactant this indicator imparts a pink colour to the chloroform phase. In the presence of cationic material the chloroform phase is coloured blue. These reactions hold for acidic and alkaline conditions. Some constituents react either anionically or cationically in both acid and alkaline media, others give a positive reaction only in one or the other, whilst some show no reaction at all. The data in Table 1 is given as a guide.

Table 1: Response of surfactants to dimidium bromide-disulphine blue VN 150 mixed indicator

<table>
<thead>
<tr>
<th>Active species</th>
<th>Colour response</th>
<th>Acid solution (pH = 1)</th>
<th>Alkaline solution (pH = 11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactant</td>
<td></td>
<td>pink</td>
<td>pink</td>
</tr>
<tr>
<td>Cationic quaternary ammonium salts</td>
<td>blue</td>
<td>blue</td>
<td></td>
</tr>
<tr>
<td>Tertiary amines and their hydrohalides</td>
<td>blue</td>
<td>negative</td>
<td></td>
</tr>
<tr>
<td>Amine oxide</td>
<td>blue</td>
<td>negative</td>
<td></td>
</tr>
<tr>
<td>Quaternary ammonium hydroxamates</td>
<td>blue</td>
<td>negative</td>
<td></td>
</tr>
<tr>
<td>Hydroxyalkyl methyltauride</td>
<td>negative</td>
<td>pink</td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactants</td>
<td>negative</td>
<td>negative</td>
<td></td>
</tr>
<tr>
<td>Alkyl quaternary sulphobetains</td>
<td>negative</td>
<td>negative</td>
<td></td>
</tr>
<tr>
<td>Pyridinium sulphobetains</td>
<td>negative</td>
<td>negative</td>
<td></td>
</tr>
<tr>
<td>Alkyl quaternary betains</td>
<td>negative</td>
<td>blue</td>
<td></td>
</tr>
<tr>
<td>Sarcosinates</td>
<td>negative</td>
<td>pink</td>
<td></td>
</tr>
<tr>
<td>Soap</td>
<td>negative</td>
<td>pink</td>
<td></td>
</tr>
</tbody>
</table>

1.3.4 Test with methylene blue solution

A similar test can be carried out with acid methylene blue indicator. Similar volumes of the indicator solution and chloroform are added. If the chloroform phase is colourless, the aqueous phase is blue, and the effect is unaltered by the addition of 0.15 mL of 0.2% aqueous solutions of anionic active material such as sodium dodecyl sulphate, then the surfactant is cationic. If the colour is transferred to the chloroform phase by the addition, a nonionic surfactant may be present. If the blue colour is initially in the chloroform phase and after the addition of 0.15 mL of 0.2 aqueous cetylbenzylidemethylammonium chloride (CBC) or Hyamine 1622 the colour still remains in the chloroform layer, then the surfactant is anionic; if it is transferred to the aqueous phase a nonionic surfactant may be present.

1.3.5 Differentiation of soap and sarcosinates

Soap and alkoxyl sarcosinates, although nonionic, behave as nonionic detergents under the above conditions. This is simply because under acidic conditions neither soap fatty acids nor sarcosinic acids are capable of forming a salt complex with the dyes present. These sarcosinates can be distinguished from soap by the fact that the former contain nitrogen, they are less prone to formation of scum in hard water and in the form of the free acid they can be removed from petroleum spirit (b.p. 40...60 °C) solution by washing with 70% aqueous ethanol. This latter technique can be used for the isolation of sarcosinic acids from fatty acids. Some secondary fatty amine derivatives such as fatty acid alanides are amphoteric in character and under the acidic conditions of this test act as cationic surfactants. Ampholytes will behave anomalously, the response depending upon the nature of the substituent groups. The sulphobetain zwitter ions give no response.

1.3.6 Test for POE-based nonionic surfactants

Qualitative test for nonionic surfactants using modified Dragendorff reagent 5. This reagent forms a precipitate with even small amounts of polyaloxylates 5.

Reagents

Solution A: Dissolve 1.7 g basic bismuth nitrate, (BiO.NO₃ x H₂O), in 20 mL glacial acetic acid. Make up to 100 mL with water.

Solution B: Dissolve 40 g KI in 100 mL water.

Test solution

Mix 10 mL each of solution A and B with 20 mL acetic acid and 60 mL water. Add 50 mL 20% BaCl₂ solution and store in an amber bottle. Discard when the colour changes from red-orange to brown (after about 2 weeks). Note: This solution is commercially available, generally without BaCl₂.

Procedure

The test is performed in a small centrifuge tube. Equal volumes of sample solution and test solution are combined and shaken vigorously. The presence of nonionic surfactant is shown by the formation of a precipitate. Small quantities of precipitate are more easily detected if the solution is centrifuged.
1.4 Classification by acid and alkaline hydrolysis

General
Differentiation of surfactant mixtures can often be achieved by time-proven acidic or basic hydrolysis. This applies to both qualitative tests and to quantitative determination by means of surfactant titration. Initially the total surfactant content of a formulation is titrated and then, after acidic or basic hydrolysis, a second titration is carried out to determine the remaining amount of surfactant.

Acid hydrolysis is carried out by boiling under reflux in aqueous hydrochloric or sulphuric acid solution. Boiling for 2 h in 1.0 mol/L hydrochloric acid or 0.5 mol/L sulphuric acid will completely hydrolyse alkyl sulphates, alkylether sulphates, sulphated alkylphenol ethoxylates and the sulphate groups of alkanolamide sulphates, but other functional groups may take much longer. It is possible to use more dilute acid, but the hydrolysis time is then longer; in 0.1 mol/L acid several hours' boiling may be needed. Excessive foaming often occurs in the early stages; this can be avoided by heating on a steam bath for 20...30 min before starting to boil. If acid hydrolysis is done in alcoholic solution then any fatty acid liberated may esterify with the solvent, and subsequent alkaline hydrolysis is then necessary.

Amides in general can be hydrolysed, but with difficulty. N-acryltaurates and methyltaurates, sulposuccinamates and sarcosinates are hydrolysed by boiling under pressure for 6 h at 150...160 °C in 6 mol/L hydrochloric acid. Alkanolamides require rather less extreme conditions; boiling for 8 h with 6 mol/L hydrochloric acid is adequate.

Alkaline hydrolysis is usually carried out in ethanolic solution under mild conditions, typically boiling for 1 h or less in 0.5 mol/L alkali, although high molecular weight esters may require more concentrated alkali or a longer boiling time. Hydrolysis with aqueous acid is of fairly general application, but hydrolysis with alcoholic alkali is better for carboxylate ester groups.

The sulphonate group itself is generally very resistant to hydrolysis, but in the case of fatty ester a-sulphonates the sulphonate group is removed by several hours' boiling with 1 mol/L alkali. Acid hydrolysis, however, has no effect.

ISO 2869 and ISO 2870 deal with the determination of alkali- and acid-hydrolysable detergents, respectively. ISO 2589 prescribes boiling 25 mL of a 0.003...0.005 mol/L solution for 30 min with 5 mL of aqueous 10 mol/L sodium hydroxide. ISO 2870 prescribes boiling a similar sample for 3 h with 5 mL of aqueous 5 mol/L (40 g/L) sulphuric acid. In both cases the hydrolysed solution is neutralised and titrated with Hyamine 1622. In the acid treatment, the H⁺ concentration is only 1.67 mol/L, and this may be insufficient for complete hydrolysis of the more resistant titratable species. Both methods should be used where appropriate, but ISO 2870 may not be universally valid and, if it is used for products containing amides, it is advisable to carry out a second experiment with a longer hydrolysis time. Hydrolysis of unknown formulations is best done in duplicate at least, the second sample being hydrolysed for 1 h longer than the first. If the results show that further hydrolysis has occurred during this time, repeat, again in duplicate, but for longer times, until the second experiment confirms that hydrolysis is complete.

Alkyl sulphates, alkylether sulphates and sulphated alkylphenol ethoxylates

Acid
All sulphates yield an alcohol, a sulphate ion and a hydrogen ion, regardless of the structure of the rest of the molecule.

Alkyl sulphates yield the fatty alcohol. Alkylether and ethoxylated alkylphenol sulphates yield the ethoxylated alcohol and ethoxylated alkylphenol respectively.

Alkali
Sulphates are not hydrolysed by alkalis under mild conditions.

Sulphonated esters

Acid
Conversion to carboxylic acid and alcohol takes place. The sulphonate group may be on either of these. Thus acyl isethionates yield a fatty acid and isethionate ions, mono- and di-alkyl sulphosuccinates yield fatty alcohols and sulphosuccinic acid, and a-sulphonated fatty esters yield the a-sulphonated fatty acid and a low-molecular-weight alcohol.

Alkali
The results are similar, but fatty acids appear as soap. Alkaline hydrolysis is generally to be preferred for esters, but fatty ester a-sulphonates undergo rapid hydrolysis of the ester group accompanied by slower hydrolysis of the sulphonate group, so this is not a practical method for their determination.
Sulphonated hydrocarbons
Sulphonated hydrocarbons are not hydrolysed by either acids or alkalis.

Carboxylates
Sarcosinates are hydrolysed under the same conditions as methyltaurates to give a fatty acid and sarcosine. Other carboxylates are not hydrolysed by either acids or alkalis.

Alkyl phosphates and alkylether phosphates
Phosphates are not hydrolysed by either acids or alkalis.

Nonionic esters
This category includes polyoxyethylene glycol esters, sorbitan esters, fatty acid esters of glycols and glycerol, including ethoxylated derivatives, and sugar esters.

Acid
Conversion to fatty acid and alcohol takes place, i.e. polyoxyethylene glycol, sorbitan, glycol or glycerol, sugar.

Alkali
Conversion to soap and alcohol takes place. Alkaline hydrolysis is of more practical use.

Quaternary ammonium salts

Acid
The quaternary ammonium group is not hydrolysed by acids, but ester or amide groups in the alkyl chain may be hydrolysed.

Alkali
Conversion to olefin and tertiary amine or pyridine takes place.

There are, however, apparently no reports in the literature of the use of this hydrolysis for analytical purposes.

Imidazolinium salts

Acid
Imidazolinium salts are not hydrolysed by acids under mild conditions.

Alkali
Ring opening occurs, with formation of an ethylenediamine derivative.

The product is a tertiary base, which is cationic in acid solution and can still be titrated with sodium dodecyl sulphate.

Amphoteric
Alkylglycines, alkylaminopropionates and alkylidimethyl betains are not hydrolysed by either acids or alkalis. Imidazoline derivatives are hydrolysed by acids to fatty acid and an ethylenediamine derivative. Alkylamidobetains are converted by acids to fatty acid and a short-chain dimethylbetain.

To classify an unknown surfactant, either acid or alkaline hydrolysis or both are carried out, and the reaction products are examined. Procedures for this examination are discussed later; quantitative analysis of hydrolysis products is usually necessary. Comparison against the previously mentioned lists will in most cases identify the class of surfactant. Mixtures may present difficulties.

A systematic scheme for identifying a very wide range of surfactants has been devised by Rosen and Goldsmith.

1.5 Declaration of surfactants in finished formulations
In most cases the chemical names of surfactants are ambiguous. The same substance is often found hiding behind different chemical names. This is the reason for the adoption of a standard nomenclature, the CTFA adopted names. CTFA is the American Cosmetics, Toiletry and Fragrance Association in Washington DC, an American cosmetics association which has issued the International Cosmetic Ingredient Dictionary. This is today the standard according to which the ingredients of cosmetic formulations are to be declared. This is carried out in many countries throughout the world according to the CTFA nomenclature and according to diminishing amounts of the ingredients in the product. This means that from the sequence given in the declaration of a cosmetic product it is possible to recognise whether a
surfactant is a basic surfactant or a co-surfactant. The CTFA names have sometimes been used in this publication so that the English names are used for the ingredients in cosmetic formulations. Since 14th January 1997 information about the ingredients of all body care agents must be provided throughout the European Union. The markings will be carried out according to an EU nomenclature, which consists of a list of all cosmetic ingredients and standardised names. This nomenclature is based on the previous CTFA system, which has been harmonised throughout the world. The future nomenclature for identification will be known as the INCI Nomenclature (International Nomenclature Cosmetic Ingredients) 13.

This declaration forms the basis for the selection of suitable titration parameters. If this information is not provided then chromatographic or spectroscopic methods must be included for qualitative surfactant analysis.

1.5.1 Cosmetics

The regulations governing the declaration of the ingredients of cosmetic formulations are currently being amended in Europe; the following information is therefore based on the current situation. The regulation about the identification of ingredients applies to all products brought onto the EU market after 14th January 1997. The declaration is made on the outer packaging in descending order of ingredient concentration. Constituents with a concentration of less than 1% are listed in any order. The colours are listed at the end. The nomenclature corresponds to the INCI names (previously CTFA names). Standard names for the ingredients used are published in the so-called Inventory by the European Commission.

The identification of the ingredients of cosmetic agents guarantees "transparency" for the consumer, who should thus receive reasonable information about the product. Additionally it will be possible for consumers, by studying the substances identified on the cosmetic's packaging, to avoid purchasing products containing ingredients to which they are allergic.

For the analysts this means that in many cases it is no longer necessary to make qualitative investigations into the composition of a formulation and that useful information is obtained for the quantitative determination of individual components. This also applies to potentiometric surfactant titrations, where it is possible to recognise very quickly whether one is dealing only with a surfactant from a particular group or a mixture of surfactants. In many cases this means that by knowing the qualitative composition, an interference-free method of determination can be selected. According to section 27 of the Food and Consumer Goods Law (LMBG – Lebensmittel- und Bedarfsgegenständegesetz) and section 3 of the Law against Unfair Competition (UWG – Gesetz gegen den unlauteren Wettbewerb) all ingredients must be listed on the packaging in Germany. An incomplete list is regarded as being misleading. The following substances do not need to be declared:

- contaminants in the raw materials used
- technical auxiliaries used during the manufacturing process which are no longer present in the finished product
- substances used in the minimum amounts necessary as solvents or carriers for aroma chemicals or flavours.

Trade names or trademarks must in no circumstances be used for identifying ingredients.

1.5.2 Declaration of cleaning and washing agents

In contrast to cosmetics, the recommendation of the EC Commission from 13th September 1989 about the identification of cleaning and washing agents was published on 10th October 1989 in Official Journal no. L 291 of the European Community and came into force on 15th October 1989.

The recommendation governs the information provided about the contents of cleaning and washing agents and the recommended dosages for household textile washing agents.

The EC Commission recommended giving the contents on the packaging of cleaning and washing agents according to the following percentage values:

- below 5%
- 5...15%
- 15...30%
- above 30%

The following ingredients have to be declared if their content exceeds 0.2%:

- phosphates
- phosphonates
- anionic surfactants
- cationic surfactants
- amphoteric surfactants
- nonionic surfactants
- oxygen-based bleaching agents
- chlorine-based bleaching agents
- EDTA
- NTA
- phenols and halogenphenols
- paradichlorobenzene
- aromatic hydrocarbons
- aliphatic hydrocarbons
- halogenated hydrocarbons
- soaps
- zeolites
- polycarboxylates
The following categories, if present, should be listed regardless of their concentration:

- enzymes
- preservatives
- disinfectants

For cleaning and washing agents that are intended exclusively for industrial use, the above requirements do not need to be fulfilled provided that equivalent information is given in technical data sheets, safety data sheets or another suitable form.

The recommendation of the EU Commission is not binding; however, it is accepted and used by the overwhelming majority of manufacturers of cleaning and washing agents in the European Union.

1.6 Methods for surfactant analysis

Practically the whole range of instrumental analytical techniques is used for the analysis of surfactants, depending on the class of surfactant and the problem to be solved.

A differentiation must be made as to whether the analysis is to be carried out within the framework of

- control of incoming raw materials
- quality assurance of manufactured ionic surfactants
- quality assurance of manufactured nonionic surfactants
- monitoring competitors
- quality assurance of formulations
- monitoring competitors' formulations
- environmental samples
- investigating electroplating baths
- checking the surfactant content of water-soluble cooling lubricants
- anionic surfactants and soaps in washing powders
- etc.

In the context of quality assurance the specifications of the raw materials used are already checked before they are used in the production process so that during the production process itself only simple summation parameters such as surfactant content by potentiometric titration, the hydroxyl number or the saponification number need to be determined.

In the context of monitoring competitors the task is more complicated. In many cases the type of raw material used and the manufacturing process are unknown, so that considerably more comprehensive (as well as more expensive) instrumental analytical methods must be used.

«Analysis of Surfactants» by Thomas M. Schmitt, Surfactant Science Series, Volume 40, published by Marcel Dekker Inc., may be considered the standard up-to-date textbook for details about general instrumental surfactant analysis. The information is given in a well-structured manner together with a comprehensive bibliography for all groups of surfactants.

The following methods are used for surfactant analysis:

1.6.1 Chromatography

Chromatographic methods are used in a wide variety of ways for characterising surfactants. Column chromatography is mainly used for the analysis of formulations and environmental samples (sample preparation, enrichment). That this method is still up-to-date and unavoidable was again demonstrated by Krusche in his plenary lecture at the conference of the German Chemists’ Association (GDCh), expert group for washing agents, in May 1995. A systematic separation process for washing agents was presented in which the components were systematically separated and thus made available for further qualitative or quantitative determination methods. GC and HPLC methods, which are particularly relevant for checking raw materials, are also used for further characterisation and the quantitative determination of these surfactant fractions, e.g. for GC determination of the fatty alcohol or fatty acid distribution, high-temperature GC for determining the degree of oligomerisation of alkyl poly glucosides (APG), or HPLC for determining the degree of ethoxylation.

Supercritical fluid chromatography (SFC)

A few years ago a great deal was expected of SFC as an alternative to HPLC methods in the analysis of nonionic surfactants, particularly for POE adducts. It was thought that one could explore the molecular range that is not accessible to GC. However, reality has turned out to be different; competitive methods such HT-GC and MALDI/TOF-MS (matrix-assisted laser desorption ionisation – time of flight) could be used with greater versatility. Today silence reigns over this special field of separation methods.

Thin layer chromatography (TLC)

In the surfactant sector TLC has never quite lost its position of being an important analytical method, but particularly in the last few years it has received a new impetus. The formulations sector in particular can hardly be imagined without it. This rapid and economical method supplies a first fingerprint of a formulation and the data for drawing up an analytical program to investigate it. The use of various group-specific chromogenic reagents allows ever more precise statements to be made, even where the separations as such cause problems.
1.6.2 Molecular spectroscopy

NMR
In surfactant analysis NMR retains its classical role of being an instrument for structural elucidation; however, NMR technology is being increasingly used for the quantitative or semi-quantitative determination of individual components, particularly for those components that are difficult to determine with other methods. An example of this is the determination of trimethylaminocetic acid, the so-called beet betain, in a cocamidopropyl betain. Even other additives in such a cocamidopropyl betain, such as citric acid or NTA, can be recognised from the NMR spectra; trained NMR analysts can do this quickly and reliably. In this case it must be taken into account that the spectrum of the basic substance, cocamidopropyl betain, itself changes according to the pH. This is why the interpretation of the NMR spectra of surfactant-like substances requires a certain experience. The cocamidopropyl betain content in a commercial product can be determined by NMR spectroscopy. Even for classes of substances which are relatively difficult to analyse, such as the alkylpolyglycosides, NMR spectroscopy provides valuable information. Quantitative measurements are carried out by addition of an internal standard. The NMR spectra can be obtained by measurements of the $^1$H or $^{13}$C nuclei.

IR

IR spectroscopy is chiefly used in surfactant analysis for structural elucidation. It carries out similar tasks to NMR spectroscopy. Both methods complement each other with a synergistic effect.

UV-VIS

UV-VIS spectroscopy does not have a very large role in surfactant analysis. It is mainly used for quantitative measurements, particularly for trace analysis and for the determination of surfactants in water. Extraction-photometric measurements such as of the methylene blue active substance (MBAS) are mainly carried out as summation parameter for anionic surfactants or of the disulphine blue active substance (DSBAS) as summation parameter for cationic surfactants.

NIR

The near-infrared technique is certainly an extremely interesting analytical method for determining quantitative parameters. At the moment it is the «Super Star» among the analytical methods used for carrying out a rapid analysis in the context of quality assurance. It can always be used with great efficiency whenever a large number of repetitive samples with a fixed matrix are to be analysed. The near-infrared technique is the epitome of a relative method and is also the epitome of what is known as a «Black Box», as none of the group-specific bands that are normally employed are used here for the analysis, but the total spectrum is scanned for a correlation to the measured data. A multivariable regression technique has been developed which can process this type of spectra. The sample must undergo a complicated calibration before the analysis is carried out. The samples used for the calibration should be a representative cross-section of those samples which are later to be analysed. In this respect, cross-section applies both to the matrix and to the results. The NIR spectra recorded are then stored together with the analytical results obtained by other methods. 40 to 60 samples are required for a good calibration. Only then can this technique be used to determine many parameters such as hydroxyl number, iodine number, acid number, saponification number, anionic or cationic surfactant contents, water viscosity, etc. The analysis can be carried out in the laboratory or online at a production plant via fibre-optic light guide system.

Mass spectroscopy

The latest mass spectroscopic method MALDI/TOF-MS (matrix-assisted laser desorption ionisation – time of flight) is an extremely rapid method providing much information for the qualitative identification of raw materials and surfactant fractions following surfactant separation. Alkyl chain distributions and degree of ethoxylation can be analysed particularly well with this method. It is ideal for combined use with TLC and column chromatography. This method provides the real masses of the unfragmented molecule.

1.6.3 Potentiometric titration

Potentiometric surfactant titration

Potentiometric surfactant titration is a purely quantitative analytical method. This analytical method provides the main theme of this monograph and is used for recording the summation parameter «total surfactant content». Assignment of the type of surfactant or the alkyl chain distribution is therefore not possible. The two-phase titration is the classical method for titrating ionic surfactants. It is used today whenever this method is specified in the delivery conditions, or where potentiometric surfactant titration cannot be carried out, e.g. with washing agents in powder form.

1.6.4 Characteristic quantities

Characteristics such as hydroxyl number, saponification number, iodine number or acid number are simple properties with which nonionic surfactants, in particular those based on esters and/or POE, can be characterised and specified. These quantitative analytical methods are used particularly in the quality assurance sectors for raw materials and finished products. The Karl Fischer water determination method is an important method in the formulations sector.

1.6.5 Miscellaneous

The so-called ethanol-soluble content is still determined today in many raw materials and dewatered formulations. It is also used indirectly for determining the so-called «wash-active substance» (WAS). Many other determination methods can be carried out on this ethanol-soluble content as it is free from inorganic salts and fillers.
There are also a number of other parameters which do not record any surfactant constituents, but which nevertheless are determined in raw materials or formulations. Standard methods of the German Society for Fat Research (Deutsche Gesellschaft für Fettwissenschaften – DGF) exist for many of these parameters. Examples are:

- determination of residue on drying
- determination of sodium chloride by argentometric titration
- determination of sodium sulphate
- determination of neutral oil content

The selection of a suitable analytical method depends largely on the problem to be solved.

Today analysis certificates are provided by the manufacturers for many surfactant raw materials. These also contain the methods used to determine the parameters and are often a part of the contract between the manufacturer and the purchaser.

Complicated questions, e.g. the complete analysis of a washing or cleaning agent or a rinse off formulation can only be answered by the use of several of the analytical methods mentioned above.

1.7 Which surfactants can be titrated?

As later described in detail in section 7, many different surfactant classes can be titrated today. By far the greatest number of the potentiometric surfactant titrations which concern us here belong to the large group of precipitation titrations. This means that the surfactant molecule (the analyte) can be precipitated out with a different and oppositely charged molecule (titrant) quantitatively, i.e. the resulting compound has an extremely low solubility product. This explains the possibilities but also the limitations of potentiometric surfactant titration. Ionic surfactants are titrated with a surfactant having the opposite charge. A cationic analyte is thus titrated with an anionic titrant and an anionic analyte with a cationic titrant. The most important selection criterion for the titrant is as high a purity as possible, also as regards the equal length of the alkyl chains, and a chemical structure that allows most analytes to be precipitated out quantitatively during the titration. This is more difficult for amphoteric surfactants; although they can be converted to cationic surfactants by protonation, quantitative precipitation with an anionic surfactant is hardly ever possible. These special features are discussed in more detail in section 7.6. Nonionic surfactants cannot be titrated; as their name suggests, they have no ionic group which would allow them to be precipitated out with an oppositely charged ion. To date the only exception is the subgroup of polyoxyethylene adducts which, however, represent the most important subgroup of the nonionic surfactants. By means of a simple trick, the addition of selected metal salts, these nonionic surfactants can be converted into pseudocationics which can then be titrated with a large anion. All other nonionic surfactants have been regarded until now as being untitratable; however, it must be expected that further developments will occur in this field with the aim, for example, of converting the OH groups of such a nonionic surfactant into cationic or anionic groups by means of suitable derivatisation reagents; these could then be analytically determined as such. Developments in this direction are just beginning.

The solubility product of an adduct of anionic and cationic surfactant, which is formed during the titration with a titrant, depends very strongly on the length of the alkyl chain of the analyte. It seems that most ionic surfactants with an alkyl chain length of C_{16} or more are precipitated quantitatively, while with smaller alkyl chains it is quite possible that only partial precipitation occurs, or even that no precipitation at all is obtained with chain lengths of C_{10} or less. However, by selection of a suitable titrant improvements are possible. Further details can be found in section 5.4. The market introduction of the surfactant electrode Metrosensor Surfactrode Resistant (SR) by Metrohm Ltd. during the Achema trade fair in Frankfurt, Germany in June 1997 has meant that the white spots on the surfactant titration applications map have become much smaller. This applies in particular to the field of problematic formulations as well as samples containing solvents, fats or oils. The ranges of application of the various surfactant electrodes only overlap in a small area. This means that the SR can be regarded as complementing the proven electrodes.

1.8 Two-phase titration

1.8.1 Early work

Wash-active substances underwent a dynamic development in the thirties and forties although there were hardly any recognised analytical methods for their quantitative determination in those days. This is why titration methods were developed in this field to follow the development of the surfactants. The demand was made that a whole group of wash-active substances should be determined with this method and that normal additives should not interfere. The analysis should be carried out with easily available means and without complicated calculations.

The first titration method which was based on the reaction of an anionic substance with a cationic substance was developed by Hartley and Runnicles. They titrated an anionic surfactant with cetylpyridine chloride in aqueous solution and used bromthymol blue as the indicator. The colour changed from purple–red to blue when the reaction approached the equivalence point. However, this equivalence point was very poorly defined and depended to a large extent on the judgement and experience of the operator.

An improvement was obtained by Preston, who used the alteration of the surface tension of the solution to determine the endpoint. During the titration he determined the pressure required for the formation of air bubbles. However, this method did not enter general use as it was influenced by the presence of electrolytes, among other things.

In parallel to this, Jones developed a colorimetric method for the determination of anionic surfactants. He extracted an aqueous solution of the anionic substances by shaking out with chloroform and methylene blue. The anionic substances formed a salt together with the methylene blue that was quantitatively soluble in the chloroform phase and gave it a blue colour. The amount of anionic surfactant could be determined colorimetrically from the intensity of the colour of the solution. Jones also noticed that the extraction was inhibited if the aqueous solution contained a cationic surfactant.
1.8.2 The classical two-phase titration developed by Epton

The observations by Jones led Epton\(^{53,54}\) to develop a two-phase titration method. In this method an anionic substance is pipetted into a sealable vessel and then a solution of methylene blue in dilute sulphuric acid and chloroform is added. By vigorously shaking the solution a salt is formed which is extracted into the chloroform phase and colours it blue. The mixture is then titrated with cetylpyridine bromide. As the titration proceeds the blue colour wanes into the aqueous phase slowly at first but then quicker and quicker until the colour of each phase is the same. This is regarded as being the equivalence point of this titration.

In parallel to the publication of Epton’s work two other two-phase titrations were described. The first method of Barr, Oliver and Stubbings\(^{54}\) is similar to that of Epton and used methylene blue as the indicator. The endpoint is reached here when all the colour from the chloroform phase has been transferred to the aqueous phase. The second method used bromophenol blue as the indicator; the endpoint is reached when the first blue colouration appears in the chloroform phase.

1.8.3 The two-phase titration according to DGF

For a long time the Epton titration was the most-used method\(^{55}\). In the sixties, however, the usefulness of the Epton titration was called into question because of its susceptibility to interference. Moreover, the often-mentioned difficulty of visual endpoint recognition led to demands for better indicators. Complaints were often made about the lack of a standardised method. This is the reason why both the International Analytical Commission (CIA) of the International Committee for Surface-Active Substances (CID) and the DGF expert group «Standard Methods» in Germany concerned themselves with the problem\(^{56}\). The improvement of the Epton method consisted in replacing methylene blue by a mixed indicator (disulphine blue VN 150 / dimidium bromide), developed by Holness and Stone\(^{57}\) for qualitative analysis and suggested for two-phase titration by Herring\(^{58}\). This indicator yielded a clearly improved endpoint recognition as the colour change is only observed in the chloroform phase, which is coloured red-violet in the presence of excess anionic surfactant ions and blue in the presence of excess cationic surfactant ions. Additionally the classical cationic surfactant cetylpyridine bromide was replaced by Hyamine 1622 (N-benzyl N,N-dimethyl N-[4-(1,1,3,3-tetramethylbutyl) phenoxyethoxy ethyl] ammonium chloride) as, in contrast to cetylpyridine bromide, this is available commercially at a very high degree of purity and is very soluble in water so that loss of activity as a result of crystallising out is no longer to be feared. Dodecyl sulphate sodium salt is used as the reference substance for standardisation of the Hyamine 1622 solution. This modified two-phase titration was then accepted as a DGF standard method\(^{59}\) and as an ISO standard\(^{60}\). This method determines the anionic component of «wash-active substances» and is known as the classical two-phase titration.

1.8.4 Characteristics of the DGF two-phase titration

The standard method for the titration of anionic surfactants is the two-phase titration with the mixed indicator system disulphine blue and dimidium bromide\(^{59}\). However, this method has many disadvantages.

1. It is hardly possible to automate it.
2. Chloroform or other chlorinated hydrocarbons are required; their use is now being called into question from an environmental point of view.
3. Endpoint recognition is sometimes difficult.
4. Nonionic surfactants contained in formulations have an emulsifying effect and make the endpoint recognition more difficult.
5. It only meets a few of the modern requirements according to ISO 900X.

In addition, interference from betains should be mentioned; today these are used as co-surfactants in virtually all rinse formulations. According to the standard, the mixed indicator used in the standard method contains approx. 0.1 mol/L sulphuric acid in addition to the two indicators. This produces a pH of approx. 1 during the titration so that the betain is largely protonated and thus behaves like a cationic surfactant (Fig. 29). This neutralises a corresponding amount of the anionic surfactant being determined so that only the remaining free anionic surfactants can be determined by the titration, i.e. the result obtained is too low. For this reason many laboratories that carry out quality control on formulations containing betains routinely do not determine the actual content of anionic components, but only carry out an empirical titration against a standard product.

Two-phase titration is certainly the classical titration method for the determination of ionic surfactants. It is also known as the Epton titration\(^{55}\). The first works carried out in this field all used a single indicator (Fig. 30), which possessed an opposite charge to the analyte and thus had the same charge as the titrant. The reactions occurring during the two-phase titration are shown schematically in the diagram.

In this case the titration of a cationic surfactant is used as an example of the reaction mechanism, e.g. the disinf ectant benzalkonium chloride (alkyl(dimethylbenzyl)ammonium chloride) with the anionic titrant dodecyl sulphate sodium salt and the anionic indicator bromophenol blue. Buffered bromophenol blue solution and a layer of chloroform are added to the aqueous sample solution of the analyte. The free bromophenol blue indicator is insoluble in chloroform and therefore
remains in the aqueous phase. After intensive shaking the cationic analyte and the anionic indicator react with each other. The polar groups of these two ionic compounds are blocked by the so-called colour-salt formation; the oleophilic character predominates and the colour-surfactant associ- ate can be extracted into the chloroform. This causes the chloroform phase to have an intensive blue colour; the aqueous phase is colourless. If the titration is now started by adding the titrant dodecyl sulphate sodium salt then the dodecyl sulphate sodium salt displaces the indicator from the existing ion associate. This occurs because the new ion associate which is formed by the cationic and anionic surfactant is less dissociated than the associate of the cationic surfactant and anionic indicator previously present. The bromophenol blue indicator which is released by this process is again water-soluble. The chloroform phase thus becomes increasingly decoloured, while the colour intensity of the aqueous phase increases correspondingly. The total decolouration of the chloroform phase indicates that the required ion associate of analyte and titrant has been formed quantitatively, i.e. that the endpoint of the titration has been reached.

Today two-phase titration using a mixed indicator has established itself. (Figs. 31 and 32). This technique is based on work by Reid and Longman. As has been done above for the simple Epton titration, the determination of alkyltrimethylammonium chloride is also described here as an example. The mixed indicator solution is added to the aqueous solution of the analyte in an Erlenmeyer flask and a chloroform layer is added. During the intensive shaking an ion associate is formed by the cationic analyte and the anionic indicator disulphine blue. This complex is now soluble in chloroform and colours the chloroform phase an intensive green-blue. The dodecyl sulphate sodium salt titrant also displaces the disulphine blue indicator from the existing indicator-surfactant ion associate here because of the lower dissociation of the complex it forms (Fig. 32). The endpoint of the titration is reached when the whole of the disulphine blue indicator has been displaced from the complex. The first slight excess of the dodecyl sulphate sodium salt titrant and the cationic dini- dium bromide indicator (Fig. 33) then form a different ion associate. As here the pink-coloured dini- dium bromide indicator is involved this causes a colour change in the chloroform phase from green-blue to pink. This colour change is the exact endpoint of the two-phase titra- tion.

In most cases the titration described here allows a simpler and more accurate endpoint recognition than can be achieved with a single indicator system. However, even here a strong dependence on the structure of the analyte can be recognised. If, for example, approx. 10 mL of the titrant is consumed then with some surfactants an endpoint recognition to an accuracy of approx. 2 µL is possible; with other surfactants the endpoint recognition is only possible to approx. 200 µL. In the first case a clear colour change from pink to green-blue or vice-versa can be recognised. In the second case the colour change occurs with slowly-changing mixed tones so that the endpoint recognition depends on the routine of the operator.

The last determination method described can also be found in the DGF standard methods and corresponds to the DIN method for the determination of ionic surfactants. The more marked the surfactant properties of the analyte, which are characterised by a hydrophilic head and a sufficiently long oleophilic remainder in the surfactant molecule, the better the titration can be carried out and the better the endpoint can be recognised. However, if apart from the hydrophilic groups that determine the surfactant properties there are other hydrophilic groups present in the surfactant molecule, such as ester groups or ether groups, then this means more difficult endpoint recognition and a larger error range for the titration.
Another disadvantage of two-phase titration is that intensive shaking must be carried out continuously. If there is no intensive shaking after each titrant addition then inaccurate results will be obtained. This is why Hoffmann developed a semi-automatic method which meant that the operator no longer had to carry out the shaking himself. Intensive mixing is performed with a motor-driven blade stirrer. This two-phase titration has proved itself in some analytical laboratories and replaced the classical shaking method. Many laboratories completely reject this method. One of the reasons is that stirring in a special apparatus is at variance with the method which has been standardised in Germany and can lead to irregular results with some substances.

Recently it has been possible to find publications concerned with the topic of two-phase titration. Cohen tested a new method alongside the classical mixed indicator system by carrying out additional titrations with bromocresol green and phenol red indicators. This should allow individual components in mixtures with soaps as well as soaps themselves to be titrated better. Reports have also been made about the differentiation between secondary alkansulphonates and mono, di, and polysulphonates.

1.8.5 Two-phase titration of soaps: the dichlorofluorescein method

The virtue of this method is that soap is titrated quantitatively along with anionic surfactants. Consequently the technique can be used in conjunction with any method which assesses anionic surfactants exclusively. This allows to deduce the content of both soaps and anionic surfactants.

Reagents

Cetyldimethylbenzylammonium chloride (CBC); approximately 0.003 mol/L solution obtained by dissolving 1.25 g of its monohydrate in 1 L of distilled water.

Chloroform, A.R.

Dichlorofluorescein solution; dissolve 0.05 g of dichlorofluorescein in 3 mL of 0.1 mol/L aqueous sodium hydroxide solution and add 50 mL of distilled water. Filter if necessary and keep in a stoppered bottle – the solution will remain stable for two weeks.

0.1 mol/L aqueous sodium hydroxide solution.

Procedure

Weigh out a quantity of sample accurately and make up to 200 mL in a glass-stoppered measuring flask. The amount taken should give an approximately 0.003 mol/L solution. Pipette 10 mL of this solution into the titration vessel (150 mL glass-stoppered cylindrical glass bottle), add 12 mL 0.1 mol/L aqueous sodium hydroxide solution so that the pH of the solution is and remains at least 9.0. Now add 8 mL distilled water, 6 drops of the dichlorofluorescein solution and 15 mL of chloroform; shake well. Add the standard CBC solution whilst swirling the flask. Near the endpoint a transient pink colouration appears in the aqueous phase. At this stage add the titrant one drop at a time, shaking after each addition and allowing the chloroform phase to separate. The endpoint is indicated by the first permanent appearance of a pink colour in the chloroform phase when viewed by transmitted light. A test solution in which the chloroform phase has developed the correct first pink shade should be used for comparison. The colour of the chloroform layer is best observed with the bottle held about 3 cm away from a white surface evenly illuminated by daylight. Viewing should take place at about 40 °C laterally to the white surface. The anionic surfactant content is then determined on a fresh solution by the standard methylene blue technique. The difference between the two titrations gives a measure of the soap content and the content of each fraction is calculated. A correction factor of 0.4 mL is added to the dichlorofluorescein titration. This is because the CBC titration observed is higher for the anionic surfactant content than when methylene blue solution is used as indicator.

Standardisation of the cetyldimethylbenzylammonium chloride solution against soap

Unsaponifiable and unsaponified fatty matter is removed from a sample of soap by diethyl ether extraction from a 30% aqueous ethanol solution of the soap. The fatty acids are liberated with sulphuric acid and extracted with diethyl ether, dried and neutralised to reconvert them to the sodium soap. The soap is then dissolved in water and titrated with the CBC solution.

Procedure

Weigh out sufficient soap to produce a 0.03 mol/L solution when dissolved in water and diluted to 1 L. Dissolve this weight of soap base in about 50 mL of 30% aqueous methanol in a 250 mL conical flask and transfer to a 500 mL glass-stoppered separating funnel. Wash the flask with 15 mL and then 10 mL portions of 30% aqueous ethanol and transfer each in turn to the separating funnel. Extract with 75 mL of diethyl ether, allow the phases to separate, run off the aqueous ethanolic phase into a second separating funnel and extract with 50 mL diethyl ether. Repeat the extraction in a third separating funnel with a further 50 mL diethyl ether. Combine the ether extracts and wash three times with 10 mL portions of distilled water and then three times alternately with 10 mL of 0.5 mol/L aqueous sodium-hydroxide solution and 10 mL of distilled water. Discard the ether phase and collect the aqueous ethanolic phase and washes. Transfer these to an evaporating basin and evaporate off ethanol completely from the solution. Transfer the remaining solution to
a 500 mL round-form separating funnel, wash with distilled water to transfer all soap to the separating funnel, add a few drops of methyl orange indicator and acidify by the addition of a 50% aqueous sulphuric acid solution until the colour is distinctly pink. Extract the liberated fatty acids three times, each with a 50 mL volume of diethyl ether, combine the three extracts, wash with 10 mL aliquots of distilled water until the wash liquor is neutral to methyl orange. Transfer this ether extract to a tared 200 mL wide-neck flask and distil off the diethyl ether. Add 10 mL of dry acetone and again distil off the solvent. Dissolve the residue in 25 mL of 95% neutral ethanol, warm to dissolve the fatty acids and titrate with 0.2 mol/ L ethanolic sodium hydroxide solution until pink to phenolphthalein sodium indicator. Evaporate off the ethanol on the steam bath, dry the residue with 5 mL dried distilled acetone and again evaporate off the solvent, rotating the flask on the steam bath during this operation. Remove the last traces of acetone with a stream of dry air, dry the flask and its contents in an oven at 105 °C for 20 min, cool in a desiccator and weigh. Place the flask in an oven at 105 °C for a further 10 min, blow out with dry air, again cool in the desiccator and weigh. Repeat this procedure until the difference in weight between two consecutive weighings is less than 2 mg.

Dissolve the accurately weighed soap in 100 mL of distilled water, transfer quantitatively to a 1 L graduated, glass-stoppered flask and dilute to 1 L with distilled water. Mix thoroughly. Pipette a suitable aliquot of this solution and the requisite volume of normal sodium hydroxide solution and titrate with CBC solution as described for the test solution. Calculate the factor for CBC from the weight of soap taken and the volume of solution used.

1.9 Comments on the accuracy of potentiometric surfactant titrations

In this monograph information is supplied at various places about the titration of raw materials or different types of formulations. Not only very different types of samples have been titrated, but also every effort has been made to treat the results critically and to check their accuracy.

An important point before the start of a titration is in each case a critical examination of the sample to be analysed. All available information should first be evaluated. The INCI or CTFA declaration of a cosmetic formulation shows e.g. the type of surfactants used. This makes it easier for the analyst to determine the optimal detection method and also the correct pH for the surfactant titration. In this way the first and very important step towards obtaining a correct result has already been taken.

With many samples classical two-phase titrations were carried out in parallel to the potentiometric surfactant titrations. Wherever possible the results are compared and evaluated. This method has natural limits and, for example, cannot be used for most cosmetic rinse off products. The reason for this is the co-surfactants in these formulations. The classical two-phase titration is associated with a very particular pH value at which the surfactant titrations must be carried out. However, at this pH the betains contained in virtually all formulations interfere. These have a partially cationic reaction which produces erroneous results. As this problem can be completely avoided in the potentiometric surfactant titration of anionic surfactants simply by adjusting the pH, it would not make sense to use two-phase titration as a reference method in such cases.

In our laboratory we have naturally gone even further. We have prepared our own model mixtures which are very similar to the samples to be investigated. We have then compared the theoretical and actual values of the titrations. We have received a great amount of help and support from the various application technology laboratories of the Surfactants Division of Th. Goldschmidt AG in Essen, Germany. Typical formulations were also prepared here and the accuracy of the analytical data produced by us was assessed.

Often friendly companies have provided us with samples whose theoretical values were known. This is an extremely interesting and often exciting way of checking the accuracy of surfactant titrations. The results obtained were often so interesting for the companies providing the samples that many of them have included potentiometric surfactant titration in their quality control testing plan and use the potentiometric surfactant titration method for monitoring their competitors.

Particular thanks are also due to the colleagues of the analytical expert group of the German Society for Scientific and Applied Cosmetics (DGK – Deutsche Gesellschaft für wissenschaftliche und angewandte Kosmetologie). Many relevant products from various sectors were analysed, and we could share in the special knowledge of our colleagues in this particular field.

For completely unknown analytical samples a classical spectroscopic method was first used for structural elucidation; this then showed us what the sample to be analysed actually was. It was then much easier to determine the correct detection method, the optimal pH and the most suitable titrant.

«Unfortunately» formulations differ in different parts of the world. Sometimes these differences are significant, sometimes they are only slight. Wherever possible we have tried to obtain typical samples from all important markets throughout the world. In this way at the end of a foreign holiday my luggage would usually contain a packet of washing powder, a bottle of dishwashing agent, an all-purpose cleaner or a bottle of shower gel. The representatives of Metrohm Ltd. have also used their knowledge of the local market to send me typical products. Many characters on the sample bottles could not be deciphered because we had no knowledge of the local language, but thankfully the signals produced by the spectroscopic method for structural elucidation speak a language which is understood by chemists throughout the world.

This has meant that a wide range of methods has been used in order to guarantee that the accuracy of practically all the results has been checked critically. Wherever differences in evaluation have occurred these are always indicated in this monograph. All these efforts were made so that I can say with a clear conscience that this is «a monograph by a practitioner for practitioners». 
1.10 Potentiometric surfactant titration

1.10.1 General considerations

Potentiometric titration is an alternative to the titration of surfactants with visual indication. As early as the beginning of the sixties the first «do-it-yourself instructions» could be found in the literature. These self-made electrodes sometimes functioned quite well. Often, however, attempts to reconstruct the electrodes described in the literature met with great problems. Apart from this, many laboratories in which large numbers of surfactant titrations were carried out simply did not have the time or the technical possibilities for constructing their own surfactant electrodes. It was therefore no surprise that these self-made indicator electrodes for surfactant titrations could not establish themselves. A first practical application was offered by some of the so-called liquid-membrane electrodes, e.g. fluoroborate (BF$_3^-$), calcium (Ca$^{2+}$) or nitrate (NO$_3^-$). With some of these electrodes cross-sensitivities to ionic surfactants were observed. This cross-sensitivity was to some extent exploited by using the appropriate electrode for surfactant determinations. In particular, the BF$_3^-$ electrode gained a certain importance for this type of analysis in the seventies and up to the first half of the eighties. It seems certain that at least 90% of all BF$_3^-$ electrodes sold throughout the world were used as indicator electrodes for potentiometric surfactant titration. A serious disadvantage was that these ion-sensitive electrodes were really intended for perfume oils or other oils. However, they also solubilise the anionic surfactants which are to be analysed. This is why it was necessary to optimise the electrode for determination of an ion, e.g. NO$_3^-$ for making other types of measurements and that the electrode manufacturers had only tested them for these applications. A serious disadvantage was that these ion-sensitive electrodes were really intended for perfume oils or other oils. However, they also solubilise the anionic surfactants which are to be analysed. This is why it was necessary to optimise the electrode for determination of an ion, e.g. NO$_3^-$ for making other types of measurements and that the electrode manufacturers had only tested them for these applications. This meant that an improved, optimised electrode for determining an ion, e.g. NO$_3^-$ or BF$_3^-$ suddenly became virtually unsuitable for surfactant determinations. It was also often noted that two electrodes of an identical type differed from each other so much that one was very suitable for surfactant titration but the other was totally unsuitable. This led very quickly to the demand that suitable electrodes specially for surfactant titration should be developed and marketed. This also happened at a time when catch phrases such as ISO 900X, GLP, GMP and EN 45000 were penetrating ever further into normal laboratory life. At the start of the nineties the Swiss firm Metrhom Ltd. brought a special surfactant electrode onto the market. In the meantime the number of surfactant electrode manufacturers has expanded further.

As previously mentioned, all these electrodes are so-called liquid-membrane electrodes with a PVC base. The name «liquid-membrane electrode» is somewhat misleading, as we are not dealing with a real liquid but with soft and flexible but non-flowing membranes. A typical electrode of this type consists of approx. 1/3 PVC; 1/3 of the total weight being made up of plasticiser. The so-called ion carrier, the electroactive component which is responsible for the detection of the surfactant ions and potential formation, is present at a concentration of only 0.1 to 1%.

Although the basis for all surfactant electrodes on the market is similar or identical, the properties of surfactant electrodes from different manufacturers differ significantly. Important criteria, e.g. the response time or the slope of the potential jumps which occur during titration differ in part very strongly from each other for different electrodes. It can even happen that an analytical method which was worked out with an electrode of company A can hardly be carried out with an electrode from company B. The whole set of titration parameters often needs to be changed. Some applications that can be carried out with a surfactant electrode from company A without any problems cannot be carried out with any other electrode. The fact that the individual electrodes from different manufacturers show such clear differences is certainly one of the reasons why this new technique has up to now not been incorporated in any standards. It would be beneficial and sensible if this were to happen. The potentiometric surfactant titration method has considerable advantages compared to two-phase titration. These are apparent from both an ecological as well as an economic point of view. The only partial success in this respect is «The determination of the active content of anionic surfactants by potentiometric titration, indicated by surfactant electrodes», DGK method AO11.1.

Potentiometric surfactant titration is generally carried out in aqueous media. The use of a solvent, such as the chloroform required in the two-phase titration, is neither necessary nor must it be disposed of when the titration has been completed. The titration of surfactants with the surfactant electrode can also be easily automated by the use of microprocessor-controlled titrators which are in common laboratory use today. If sample changers are included in the system then series of samples can be processed unattended overnight.

From the point of view of ISO 9000 or EN 45000 potentiometric surfactant titration offers considerable advantages. All parameters can be documented clearly and unambiguously. The automatic titrators in use today record the sample weight, the titration conditions, the raw data obtained during the titration as well as the result. Suitable interfaces allow all required data and information to be transferred to LIMS systems and in this way the requirements for a quality assurance system are fulfilled.

The basis of potentiometric surfactant titration is a precipitation titration, in which the analyte is precipitated out with the titrant. All surfactant electrodes in use today are sensitive to both cationic and anionic surfactants. This means that the titration produces optimal S-shaped titration curves; these can often be easily evaluated by normal titrators. Cationic analytes are titrated with anionic titrants, anionic analytes with cationic titrants. Both titrations can be carried out in the dynamic mode, in which the added volume increments are calculated by a microprocessor according to the change in electrode potential and then added. The aim of a dynamic titration is to obtain constant mV increments. In most surfactant titrations this dynamic mode is the method of choice.

1.10.2 Potentiometric titrations using Metrosensor surfactant electrodes

A surfactant electrode – e.g. the Metrosensor «High Sense» surfactant electrode or the NIO electrode shown in Figs. 35 and 36, respectively – initially detects the sample surfactant ion. This is precipitated during the titration with the surfactant-like titrant, whose ionic charge is opposite to the sample surfactant. After the titration endpoint the titrant determines the potential at the electrode. From this it can be seen that it is of the greatest importance that the ion associate of sample surfactant and titrant should be present in as undissociated a form as possible. The dependence on the surfactant structure has been thoroughly investigated by Schulz and Gerhards.

Apart from ionic surfactants, many finished products containing surfactants also contain nonionic surfactants based on POE adducts. These POE adducts act either as a wash-active substance (WAS), as refattng agent or also as solubiliser for perfume oils or other oils. However, they also solubilise the anionic surfactants which are to be analysed. This is why
in the quantitative determination of anionic surfactants in formulations which also contain nonionic surfactants it is particularly important that a titrant is used which possesses a high reaction speed and has a high affinity to the analyte surfactant. TEGO trant A100 (1,3-didecyl-2-methylimidazolium chloride) has proven itself to be extremely suitable in such cases. As a great number of formulations are extremely complex, the qualitative composition of the sample must be known.

The special titrant TEGO trant A100 for the titration of anionic surfactants has significantly extended the range of surfactants and surfactant mixtures that can be determined. This titrant produces larger potential differences between the start of the titration and its end, the largest potential changes occurring in the region of the equivalence point. The derivative curve is steeper and also narrower by several orders of magnitude (Figs. 37 to 39). This results in excellent standard deviations and a high degree of accuracy. Metrohm Ltd. has secured the exclusive worldwide sales rights for the titrant TEGO trant A100, a product of the research department of Th. Goldschmidt AG in Essen, Germany.
The Metrohm 6.0733.100 reference electrode was specially selected for the requirements of surfactant titration. It enables a high sample throughput in sample changer operation and, in combination with the Ionic Surfactant Electrode, ensures that smooth, low-noise titration curves can be recorded.

For surfactant titration in two-phase media the Metrohm 6.0726.100 reference electrode, a so-called double-junction electrode, has proved to be particularly suitable as its ground-sleeve diaphragm does not get blocked by crystallising KCl or AgCl.

It is recommended that, for each titration, the titration curve and the first derivative are printed out as well as the results. In particular, the derivative curve allows the titration to be critically evaluated and errors and interferences to be reliably recognised. In an ideal case the derivative curve should show a mirror image arrangement in the increasing and decreasing regions, i.e. in the regions above and below the equivalence point (Fig. 40). If this is not the case, and if the titrator algorithm recognises more than one equivalence point, then there are two different possibilities. There may be homologues of the surfactant being analysed producing two different endpoints. The phenomenon may also be the result of an interference caused, e.g., by a titrator whose parameters are not optimally adjusted. In order to solve the problem, the derivative curves of two or more titrations carried out consecutively are evaluated. If these are identical, as shown in Fig. 41, then it can be assumed that the titrations carried out are correct. This means that the endpoints are split up, e.g. due to the presence of homologues in the analyte. However, if the split up is not reproducible this can almost always be traced back to spikes, i.e. an interference during measurement recording, as shown in Fig. 42. Such titration curves should not be used for calculating results. If a titration curve with only one equivalence point is expected but two or more are observed, then it is almost 100% certain that none of the detected endpoints is correct. Such results should be rejected.

The Ionic Surfactant Electrode is a PVC membrane electrode whose membrane composition has been specially optimised for the determination of ionic surfactants. Potential formation is due to a specific interaction between the ion carrier (ionophore) contained in the PVC membrane and the ions to be determined in the sample solution. At equilibrium this interaction leads to a potential transfer of the measuring ions from the sample solution to the membrane and – linked to this – the formation of an electrical at the sample phase boundary solution / membrane. This potential difference can be measured versus a reference electrode potentiometrically, i.e. at virtually zero current. The extent of ion transfer from the solution to the membrane depends on the concentration.

The particular properties of surfactants, such as surface activity, substantivity, micelle formation, etc., mean that surfactant electrodes do not show Nernstian behaviour. In practice this means that:
1. The electrode is not suitable for direct potentiometric concentration determinations.
2. Titrations should always be evaluated using the inflection point of the S-shaped titration curve.
3. Titrations to a fixed potential (fixed endpoint titrations) are not recommended.

The determination of the active content of anionic surfactants by potentiometric titration indicated with surfactant electrodes is the subject of standards, e.g. DGK method AO11.1.

1.10.3 Metrosensor surfactant electrodes and their abbreviations

- IS Ionic Surfactant Electrode
- NIO NIO (nonionic) Surfactant Electrode
- SR Surfactrode Resistant
- HS High Sense Surfactant Electrode

1.11 Two-phase titration compared to potentiometric surfactant titration

1.11.1 Titrations in aqueous media

Although two-phase titration and potentiometric surfactant titration appear very similar at first glance, they differ significantly in important aspects. Both titration methods use the same chemical method, the titration of a analyte having surfactant properties with an oppositely charged surfactant titrant as the basic reaction. The basis of the two-phase titration is the displacement of a surfactant-indicator ion associate by the less dissociated surfactant-surfactant ion
associate and also the distribution equilibrium between the aqueous and the chloroform phase. A limiting factor here is the extractability into chloroform. A particular surfactant can be analysed by two-phase titration if the following conditions are fulfilled:

1. The analyte must form a chloroform-soluble associate with the corresponding indicator.
2. The titrant must be able to displace this indicator from the complex.
3. The surfactant-surfactant ion associate must be extractable in chloroform without any problems as only this prevents dissociation occurring in the aqueous phase that could lead to renewed colour-salt formation with the oppositely charged indicator molecule, which in turn would result in unreliable and indistinct endpoints.

As mentioned several times, the basis of potentiometric surfactant titration is a precipitation reaction. As in this case the intermediate step of complex formation with the indicator plays no role, the system as a whole is more manageable and also more predictable. In this case the limiting factor is the dissociation constant of the associate formed between analyte and titrant, which should be as small as possible.

Whereas in two-phase titration the type of titrant has no great influence on the result, in potentiometric surfactant titration this is an extremely important factor. Results differing considerably from each other can be obtained when two different titrants are used. In one case a particular chain section may either not be determined or only partially determined, in a second case the use of a different titrant guarantees the quantitative determination of all relevant alkyl chains of the surfactant in question. The question of the accuracy of the method is very difficult to judge, as even the two-phase titration according to DIN does not necessarily provide the correct values because even here not all surfactants are determined to the same extent. This method also has particular limitations. These could include, for example, the length of the alkyl chain or the number of hydrophilic groups in the molecule, such as the number of POE units in an ether sulphate. Further hydrophilic groups, e.g. ester groups in an esterquat, can also cause problems in two-phase titration. A disadvantage is seen in the fact that two-phase titration only allows an assessment of quality up to a certain point. The colour change, i.e. the indicated endpoint, appears at some stage; assessing whether this is a relevant endpoint is extremely difficult. In potentiometric surfactant titration not only the endpoint is obtained, but the titration also produces a complete titration curve, which can be printed out both in the original form or also as the first derivative curve. These titration curves, the derivative curves in particular, allow a trained surfactant analyst to assess the quality. Irregular curves also provide certain information about possible errors or interferences.

Let us ask Radio Eriwan a question:

Can two-phase titration be used to determine correct and real surfactant concentrations?

In principle no…, but the claim is made time and time again. The good old Radio Eriwan jokes are called to mind whenever discussions about the accuracy of two-phase titrations are heard. Many attempts carried out today with surfactant electrodes under optimised conditions show that values obtained by two-phase titrations are not correct in the classical sense of the word. Two-phase titration has the decisive advantage that it has been standardised and is a DIN method, which means that alternative methods are measured against it.

For the reasons mentioned above the analytical results obtained by two-phase titration and potentiometric surfactant titration in aqueous media may not always be the same. For a large number of clearly defined compounds, e.g. dodecyl sulphate with an alkyl chain length of C\textsubscript{12} or more, or with linear alkylbenzene sulphonates the agreement between the analytical results is good, as shown in Table 2.

### Table 2: Comparison of titrations of alkyl sulphates with two-phase titration and potentiometric surfactant titration

<table>
<thead>
<tr>
<th>Chemical designation</th>
<th>Potentiometric surfactant titration</th>
<th>Two-phase titration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lab 1</td>
<td>Lab 2</td>
</tr>
<tr>
<td>Na-decyl sulphate C\textsubscript{10}</td>
<td>29.07</td>
<td>0.33</td>
</tr>
<tr>
<td>Na-dodecyl sulphate C\textsubscript{12}</td>
<td>93.53</td>
<td>0.52</td>
</tr>
<tr>
<td>Na-alkyl sulphate C\textsubscript{12}-C\textsubscript{14}</td>
<td>36.13</td>
<td>0.17</td>
</tr>
<tr>
<td>Na-alkyl sulphate C\textsubscript{12}-C\textsubscript{18}</td>
<td>90.80</td>
<td>0.15</td>
</tr>
<tr>
<td>Na-alkyl sulphate C\textsubscript{12}</td>
<td>15.37</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Significant variations in the titration results of surfactant raw materials are given in section 7 for all important substance classes.
1.11.2 Titration with the Metrosensor Surfactrode Resistant

If two-phase titration according to Epton is compared with two-phase titration using the Surfactrode Resistant as indicator electrode, then the pictures are very similar. The detection principle of both methods is almost identical. In contrast to potentiometric surfactant titration in aqueous media, in which the analyte is precipitated out by the titrant, the ion associate formed by the analyte and titrant is extracted into the second, organic phase in the titration with the Surfactrode Resistant as indicator (Fig. 44). The only difference is that the role of the indicator is not taken into account as it is not required in this case. As the formation of the associate of analyte and indicator is only temporary, it has virtually no importance at the end of the titration. This is why the absence of the indicator is hardly noticed. If the comparability of the methods is to be increased still further then the corresponding indicator can also be added here without causing any interference.

As a result of the similarity of the two detection methods there is a very high degree of comparability in the analytical results. This is particularly noticeable with surfactant raw materials such as secondary alkane sulphonates or α-olefin sulphonates; but even complex formulations such as concentrated dishwashing liquids or washing powders show identical results.

Table 3: Comparison of the results of two-phase titrations using the Metrosensor Surfactrode Resistant (SR)

<table>
<thead>
<tr>
<th></th>
<th>Result of classical two-phase titration in mmol/100 g</th>
<th>Result of potentiometric titration in a two-phase medium with SR in mmol/100 g</th>
<th>Relative standard deviation obtained from potentiometric titration in two-phase medium with SR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Linear alkylbenzene sulphonate (A)</strong></td>
<td>43.10</td>
<td>43.30</td>
<td>0.60%</td>
</tr>
<tr>
<td><strong>Linear alkylbenzene sulphonate (B)</strong></td>
<td>104.00</td>
<td>104.30</td>
<td>0.47%</td>
</tr>
<tr>
<td><strong>Fatty alcohol sulphate C&lt;sub&gt;12&lt;/sub&gt;</strong></td>
<td>52.78</td>
<td>52.88</td>
<td>0.34%</td>
</tr>
<tr>
<td><strong>Fatty alcohol ether sulphate C&lt;sub&gt;12&lt;/sub&gt;14&lt;sub&gt;4&lt;/sub&gt; POE units (A)</strong></td>
<td>69.68</td>
<td>69.75</td>
<td>0.29%</td>
</tr>
<tr>
<td><strong>Fatty alcohol ether sulphate C&lt;sub&gt;12&lt;/sub&gt;14&lt;sub&gt;4&lt;/sub&gt; POE units (B)</strong></td>
<td>155.5</td>
<td>155.8</td>
<td>0.13%</td>
</tr>
<tr>
<td><strong>Fatty alcohol ether sulphate C&lt;sub&gt;12&lt;/sub&gt;14&lt;sub&gt;2&lt;/sub&gt; POE units (A)</strong></td>
<td>70.46</td>
<td>70.61</td>
<td>0.50%</td>
</tr>
<tr>
<td><strong>Fatty alcohol ether sulphate C&lt;sub&gt;12&lt;/sub&gt;14&lt;sub&gt;2&lt;/sub&gt; POE units (B)</strong></td>
<td>143.1</td>
<td>143.7</td>
<td>0.32%</td>
</tr>
</tbody>
</table>
Dissociated then the equal charges would immediately repel each other and destroy the micelle structure. So that their hydrophilic heads are arranged alongside one another. If the surfactant molecules in such a micelle were to come together to form aggregates, they are present in an undissociated form, as in such micelles the surfactants are oriented concentration. At concentrations above the critical micelle concentration (CMC), i.e. when the surfactant molecules join solution for detection by the electrode. This produces two low results, whose extent depends on the total surfactant molecules. A large number of surfactant molecules are required for this which are then no longer available within the several times, the surface activity of a surfactant has the effect that initially all surfaces become saturated with surfactant. For direct potentiometry 100% of the ion to be determined must be present in the ionised form. As has been reported feared that this dream will continue to be dreamed for a long time yet and remain unfulfilled. The surfactant analyst’s dream of simply connecting an electrode to a modern microprocessor-controlled ion meter which, with its previously stored calibration curves, would immediately allow the surfactant concentration to be read off. It must be fact that this dream will continue to be dreamed for a long time yet and remain unfulfilled. It is also known that many large, voluminous ions are also detected by the surfactant electrodes and cause a baseline shift. By adding a particular interfering substance the initial potential can be shifted, for example, by 20 mV. In most cases this means that the endpoint potential is also shifted by a similar amount. In an endpoint titration this would produce a significant error. On the other hand, in a potentiometric titration carried out completely this would not produce any incorrect results because the inflection point of a titration curve does not depend on the initial potential. Potentiometricendpoint titration, at least wherever we are not talking about a constantly performed titration of the same product with a very large number of samples, can be compared to flying blind to Venus. Titrations to a fixed endpoint can be sensible and necessary if the normal potentiometric surfactant titration only produces very flat curves and the exact evaluation of these curves by the titrator is not possible. Titrimetric determination of surfactants and pharmaceuticals 33

Table 3: Comparison of the results of two-phase titrations using the Metrosensor Surfactrode Resistant (SR) (continued)

<table>
<thead>
<tr>
<th>Fatty alcohol ether sulphate C_{12,14} 0.8 POE units</th>
<th>Result of classical two-phase titration in mmol/100 g</th>
<th>78.41</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Result of potentiometric titration in a two-phase medium with SR in mmol/100 g</td>
<td>78.35</td>
</tr>
<tr>
<td></td>
<td>Relative standard deviation obtained from potentiometric titration in two-phase medium with SR</td>
<td>0.09%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Secondary alkane sulphonate (A)</th>
<th>Result of classical two-phase titration in mmol/100 g</th>
<th>45.17</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Result of potentiometric titration in a two-phase medium with SR in mmol/100 g</td>
<td>45.44</td>
</tr>
<tr>
<td></td>
<td>Relative standard deviation obtained from potentiometric titration in two-phase medium with SR</td>
<td>0.58%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Secondary alkane sulphonate (B)</th>
<th>Result of classical two-phase titration in mmol/100 g</th>
<th>98.33</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Result of potentiometric titration in a two-phase medium with SR in mmol/100 g</td>
<td>99.02</td>
</tr>
<tr>
<td></td>
<td>Relative standard deviation obtained from potentiometric titration in two-phase medium with SR</td>
<td>0.41%</td>
</tr>
</tbody>
</table>

1.12 Titration to a fixed endpoint (endpoint titration)

Titration to a fixed endpoint means that initially a normal potentiometric surfactant titration is carried out. When the titration has been completed the titrators in use today provide the operator with a report which, apart from the volume recorded at the endpoint, additionally contains the measured potential in mV. Endpoint titration means that a complete titration curve is not recorded, as in the first case, but that the titration mode is altered. Titration is only carried out up to the potential which was recognised as the endpoint potential in the first titration. The precondition for this method is an absolutely stable endpoint potential during a large number of titrations. However, this can only be expected if the same surfactant electrode is always used for the titration of a particular surfactant. In the raw material control sector, and particularly for anionic surfactants, many users aware by the advantages of this method. As opposed to the normal potentiometric surfactant titration, no meaningful titration curve, which would allow the trained operator to critically assess the quality of the titration, is obtained in endpoint titration. Such endpoint titrations are not possible with the Metrosensor High Sense Electrode, Ionic Surfactant Electrode, NIO Surfactant Electrode or Surfactrode Resistant; they are recommended by neither the author nor the manufacturer. For example, if twenty consecutive surfactant titrations with an identical titrant are carried out under the same, reproducible conditions, it can be seen that the endpoint potential continually changes, particularly during the initial titrations. The more titrations carried out, the smaller the subsequent changes. However, these changes can always be measured and when they are plotted a trend can be made out. This trend can be interpreted as being a measure for the conditioning of the electrode during a titration series.

It is also known that many large, voluminous ions are also detected by the surfactant electrodes and cause a baseline shift. By adding a particular interfering substance the initial potential can be shifted, for example, by 20 mV. In most cases this means that the endpoint potential is also shifted by a similar amount. In an endpoint titration this would produce a significant error. On the other hand, in a potentiometric titration carried out completely this would not produce any incorrect results because the inflection point of a titration curve does not depend on the initial potential. Potentiometric endpoint titration, at least wherever we are not talking about a constantly performed titration of the same product with a very large number of samples, can be compared to flying blind to Venus.

Titrations to a fixed endpoint can be sensible and necessary if the normal potentiometric surfactant titration only produces very flat curves and the exact evaluation of these curves by the titrator is not possible.

1.13 Direct potentiometry

In recent times reports are being constantly made about the development of completely new surfactant electrodes. These are said to be particularly suitable for direct potentiometry of ionic surfactants at extremely low concentrations. The question as to whether surfactants can be measured by direct potentiometry is not so much a question of a special electrode but rather a physicochemical problem of the surfactants themselves. That is, unless these electrodes turn out to be magic wands that can abolish all the special «surfactant properties». This would be the fulfilment of every sur-

For direct potentiometry 100% of the ion to be determined must be present in the ionised form. As has been reported several times, the surface activity of a surfactant has the effect that initially all surfaces become saturated with surfactant molecules. A large number of surfactant molecules are required for this which are then no longer available within the solution for detection by the electrode. This produces two low results, whose extent depends on the total surfactant concentration. At concentrations above the critical micelle concentration (CMC), i.e. when the surfactant molecules join together to form aggregates, they are present in an undissociated form, as in such micelles the surfactants are oriented so that their hydrophilic heads are arranged alongside one another. If the surfactant molecules in such a micelle were dissociated then the equal charges would immediately repel each other and destroy the micelle structure.
For direct potentiometry a Nernstian relationship should exist between the potential and the activity (concentration) of the ion to be measured. This relationship is described by the Nernst equation (Equation 1), which is certainly one of the most important electrochemical equations.

In the Nernst equation, the quantity s represents the slope of the electrode. Ideally for monovalent ions at 25 °C this should be approx. 59 mV per activity (concentration) decade. In practice lower slopes are often determined. \( E_0 \) is the standard potential of the electrode, \( a_M \) the activity of the surfactant ions and \( E \) the measured potential.

Up to now, such a Nernstian relationship has not been recorded in the direct potentiometry of surfactant solutions. Only if the surface activity could be eliminated by means of a suitable additive which, however, must itself have no effect on the potential to be measured, would it be possible to carry out direct potentiometry. The addition of alcohols is known to reduce the surface activity, but not to eliminate it completely. On the contrary, too high alcohol concentrations would counteract dissociation again.

Even if some companies describe their surfactant electrode as an ion-selective electrode, this is not correct. All electrodes found on the market today respond to large voluminous ions. This means that other voluminous ions also cause an alteration in the potential. Most ionic dyes and many pharmaceuticals fulfil this condition; they have large voluminous ions and also affect the potential. In many cases this property is so clearly noticeable that these products can also be titrated potentiometrically using a surfactant electrode as the indicator.

\[
E = E_0 + s \cdot \log a_M
\]

Equation 1 Nernst equation
2 Surfactants and their special properties from the analyst's point of view

2.1 Surface activity

The concentration of solutions which are used as titrants, auxiliary or sample solutions is — after they have been prepared and thoroughly mixed — normally the same at each point, i.e. the solution is homogeneous. From whatever point a partial volume of the solution is removed, be it from the bulk or from the edges, they will have identical concentrations. This is an extremely important fact for analysts, who must rely on it in almost all areas, no matter whether for solutions of acids, bases, salts, alcohols, etc. in water or other common solvents.

With surfactants this is not the case, because surfactants are surface-active, i.e. they enrich themselves at all surfaces or interfaces. To make this clear a surfactant molecule can be thought of as being like a matchstick (Fig. 2); it consists of a water-loving (hydrophilic) head and a stick which is water-repellent (hydrophobic). The opposing properties of the two groups, the hydrophilic and the hydrophobic, form the basis of the surface-active properties of the surfactant molecule. The hydrophobic stick (e.g. the alky1 chain) will have nothing to do with the water and tries to escape from it. The hydrophilic head (e.g. a sulphate or sulphonate group) loves the water and wants to remain in it. This is why the surfactants first arrange themselves according to the old nursery rhyme «heads in the water, tails (sticks) in the air»; the complete water surface is perforated by the hydrophobic parts of the surfactant molecule, which causes the water surface to lose its cohesion. The water becomes «relaxed», i.e. the surface tension of the water is reduced significantly. For the analyst this also means that at this location the surfactant concentration is higher than in the aqueous phase beneath. If during the homogenisation of the solution a head of foam was formed by gentle or vigorous shaking then this means that the surfactant concentration here is also significantly higher than in the aqueous phase beneath. Surfactants also enrich themselves on the glass surfaces of, for example, a volumetric flask. The lower the surfactant concentration, the more clearly these effects can be seen. In dilute surfactant solutions of 1 mg/L or lower a large proportion of the surfactant molecules can be found in the surface area. If an aliquot of such a solution is removed with a pipette then a large error is to be expected. This has the following consequences:

1. Surfactant solutions must be homogenised very carefully, i.e. not with vigorous shaking.
2. Surfactant solutions should not be used at too low concentrations.
3. Whenever possible a little alcohol, such as methanol, ethanol or isopropanol should be added to the solution, as this at least reduces the surface-active properties. This can also be recognised by the fact that a head of foam formed on a surfactant solution spontaneously collapses when a few drops of alcohol are added. It must be ensured, however, that the added alcohol has no negative influence on the subsequent determination.
4. Unnecessary surfactant dilution steps should be avoided as some surfactant loss must be expected at each dilution step.
5. Intermediate dilutions or stock solutions should not be purely aqueous but should, if possible, always be prepared with the addition of some methanol or possibly even with pure methanol.

2.2 Substantivity

Substantivity means the tendency of surfactants to migrate to surfaces and remain there permanently, see Fig. 5. The tendency towards substantivity depends on many factors. Most solid surfaces such as glass, plastics, metal, etc. have a «weakly negative charge», which means that cationic surfactants in particular can concentrate on these surfaces. From the technical applications point of view this property of the cationic surfactants is greatly desired, e.g. for fabric softeners. As a result of its carboxylate functions, a cotton fibre has a negative charge. If, after the washing process, a fabric softener such as an esterquat is added to the last rinsing cycle then the negative charges of the cotton fabric combine with the positive charges of the esterquat. A thin layer of the quaternary ammonium compound becomes attached to the fibres so that these can no longer stick together. This is why the fibres feel soft.

Correct dosage produces the ideal case in which there is no free esterquat left in the aqueous phase but all has been substantively attached to the fibres.

Something similar happens if a titrant based on a quaternary ammonium compound is prepared. A part of this cationic surfactant molecule is used to saturate the negative charge of the volumetric flask. That is the case that can be seen from the fact that volumetric flasks in which surfactant solutions have been stored for some time have a greasy appearance. Remember that the surface of the glass has a weakly negative charge, i.e. the surfactant molecules orient themselves so that their hydrophilic parts point towards the glass surface and their hydrophobic parts project into the aqueous phase. If the cationic solution is poured away after a contact time of two days and the glass flask is then rinsed out a few times with water it will still have a greasy appearance. This means that the substantive coating of cationic surfactants cannot be removed from the surface of the glass by rinsing. This effect can only be reversed by the addition of detergents containing anionic surfactants or by rinsing with alcohol. In strongly acidic solutions this substantive behaviour of surfactants is more noticeable than in neutral or strongly alkaline solutions. The amount of surfactant attracted to the surface depends on the latter’s condition. With glass apparatus in particular the frequent washing in washing machines, use of aggressive cleaning agents and rinsing with ion-deficient distilled water all damage and consequently increase the glass surface. Twenty washing cycles in a normal laboratory washing machine with the usual laboratory cleaning agents, followed by a threefold rinse with hot deionised water, alters and enlarges the glass surface significantly. This in turn increases the proportion of quaternary ammonium compounds which can attach themselves to glass surfaces damaged in this way. Our own experiments have demonstrated than an increase of the substantivity by a factor of approximately 10 is possible.
As a consequence no more apparatus than is absolutely necessary should be used for surfactant analysis. Glass apparatus with intact surfaces should be preferred to that with damaged ones. The substantiveity of the surfaces should be reduced by addition of alcohol.

The substantive properties of anionic surfactants are considerably smaller than those of cationic surfactants.

For amphoteric surfactants it depends very strongly on the pH whether they show any substantive behaviour; in the neutral range substantiveity is very low, under strongly acidic conditions, where the amphoteric surfactants are present in their cationic form, the substantiveity is comparable with that of the cationic surfactants. Among cationic surfactants with identical functionality but different alkyl chain lengths, those with the longer alkyl chain are attracted to the surface to a larger degree and with greater stability.

2.3 Micelle formation

Whereas in the previous sections the main emphasis has been placed on the way in which surfactants behave at surfaces, in this section we are concerned with what occurs in the bulk of the solutions. A very interesting surfactant phenomenon is also observed here; this is the ability of the surfactants to form—depending on their concentration—widely differing molecular aggregates called micelles. Only surfactants have this tendency to form micelles; this feature allows them to be easily characterised and a large number of technical properties for various applications are derived from it. The type of molecular compound found in the aqueous phase depends very strongly on the surfactant concentration. At lower concentrations the surfactants dissolve in water and get enriched at the surfaces as described above. However, this is only possible up to the point where a monomolecular layer has formed. The equilibria within the surfactant solution can be seen in Figure 6.

The micelles are in dynamic equilibrium with the dissolved individual molecules, i.e. they are not stationary, but continually dissolve and reform, possibly in new formations. This is very important for surfactant analysts, particularly for those who carry out surfactant titrations with surfactant electrodes. The surfactant electrode needs a dissociated surfactant molecule to be able to form a potential. In the micelle the surfactants are present in a non-dissociated form as otherwise the opposing charges would repel each other. During the titration the dissociated surfactant molecules are detected by the surfactant electrode and precipitated by the titrant. As this causes the concentration of dissociated molecules in the aqueous phase to decrease, micellar compounds break up and produce newly dissociated surfactant molecules in the aqueous solution that are available for further titration. This is one of the reasons why surfactant titrations should not be carried out too quickly. The system must be given enough time for the micellar compounds to break up and release ions which can then react with the titrant. As the average life span of a micelle is only of the order of a few milliseconds, the necessary waiting period should be kept within reasonable limits.

When planning suitable conditions for carrying out a potentiometric surfactant titration in aqueous solution this tendency towards micelle formation must not be neglected under any circumstances. The conditions must always be selected so that the tendency to form micelles is reduced right from the start. This can be achieved by the addition of justifiable amounts of suitable alcohols to the surfactant solution. It is important to state once more that no surfactants are lost to the titration as a result of micelle formation but that micelle formation can reduce the reaction rate. However, if other surfactants apart from the one to be analysed are present when planning and carrying out the titration. In a shower gel which, apart from the anionic surfactants to be determined, normally also contains nonionic surfactants and/or betaines, it must be taken into consideration that mixed micelles can be formed and that in this case the removal from the micelles and the precipitation with the titrant of all the anionic surfactants may take somewhat longer. This results in a slower titration process; a check should also be made as to whether the use of an increased amount of alcohol is necessary.

In the analytical determination of ionic surfactants these are always precipitated out with a surfactant of the opposite charge. In this case the hydrophilic part of a surfactant is blocked by a reaction similar to that of salt formation so that the hydrophilic parts of the associate dominate. This ionic association thus no longer behaves like a surfactant, it is no longer surface-active and it cannot form any more micellar compounds.

2.4 Foam formation

There is a causal connection between foam formation in an aqueous surfactant solution and the surface activity of the surfactant. By the formation of a head of foam the active surface of a surfactant solution is increased significantly. This gives considerably more surfactant molecules the possibility of orienting themselves at this surface in a natural manner, i.e. with the hydrophilic head towards the aqueous phase and the hydrophobic stick projecting into the air. For the analyst this means that the surfactant concentration is considerably higher in the foam phase than in the aqueous solution beneath. The previously mentioned relationship also applies in this case: The lower the surfactant concentration in the aqueous phase, the more clearly the influence of the foam on the concentration can be seen. In general, surfactant solutions with a head of foam on top should only be used for analysis when the foam has collapsed, either of its own accord or as a result of some suitable measure. If this is not taken into account then incorrect analysis results must be expected.

2.5 Water quality

The use of a particular water quality for dilution in potentiometric surfactant titration is not really very important. There is no reason for thinking that tap water will contain any surfactants or other substances that could interfere with the surfactant titration. If no other water is available then normal tap water can be used to prepare solutions or make dilutions for surfactant titration.

Normally fully deionised water from an ion-exchanger system is used in laboratories. The ion-exchanger resins are polymers that contain either sulphonate groups (cation exchangers) or quaternary ammonium compounds (anion exchangers). It can happen that monomers may be released from the resin into the water, particularly after a regeneration
cycle or if rinsing has been insufficient. In this case large voluminous cations or anions are present, i.e. two classes of substance which the surfactant electrode can potentially react to. This means that under unfavourable conditions incorrect results could be obtained. Accordingly, the deionised water should be checked by placing some of it in a clean glass vessel and shaking it vigorously. If even slight foam formation is observed the water should not be used until further checks have been carried out. If possible distilled water should be used rather than deionised water obtained from an ion exchanger system.

2.6 Demands placed on glass apparatus and cleaning processes

The cleaning of glass apparatus, the «how and with what» has a great influence on surfactant titration.

1. Cleaning agents

Almost all cleaning agents used today contain surfactants. Cleaning agents for cleaning dishes by hand contain large amounts of anionic surfactants. The cleaning agents used in washing machines, such as those used in dishwashers, also contain surfactants, but in considerably lower amounts and usually in the form of nonionic surfactants. They additionally contain polycarboxylates and other substances which could interfere with or influence surfactant titrations.

2. Dishwashers

Laboratory dishwashing machines usually clean at a temperature of 80 °C or even higher which, combined with the strongly alkaline detergents and the subsequent multiple rinsing with deionised water, also at high temperature, clearly damages the surface of the glass. In this way the active surface of the glass can be increased by several hundred percent. As a result the substantivity of cationic surfactants in particular has a very negative effect on the surfactant titration. After such a cleaning process it is quite likely that minute amounts of cleaning agent adhere to the glassware. This is why particular attention should be given to the cleanliness of the glass apparatus used for surfactant titration. If a large number of surfactant titrations are carried out then the setting apart of glass apparatus for use in surfactant titration only and for nothing else should be considered.

For example, when a cationic surfactant is titrated with an anionic surfactant then, when the titration is finished, it is sufficient to pour off the solution, rinse once or twice with normal tap water and possibly rinse once more with deionised or distilled water. Glassware cleaned in this way can be used for the next titration and no interferences are to be expected. In the case of surfactant titration a cleaning process such as is normally carried out in laboratories only brings additional problems into the system. If anionic surfactants are titrated with a cationic titrant then – in order to avoid an excess of cationic surfactant in the solution – the titration should not be continued unnecessarily beyond the endpoint as this could cause the glass surface to become coated. Titrated solutions should not be allowed to stand for unnecessarily long periods. Before reuse the glassware should, if possible, be rinsed with a few mL alcohol. If mechanical cleaning is preferred for rationalisation purposes then the cleaning temperature should be drastically reduced and the cleaning agent concentration reduced to 10...15% of the usual amount. The glassware is not soiled in the normal sense of the word, but it contains substances which are normally contained in cleaning agents. Volumetric flasks which are often used, e.g. for making up titrants, should never be cleaned but only marked accordingly and always used for this particular purpose only. Particularly for the preparation of cationic surfactants this has the additional advantage that the surface of the volumetric flask is saturated substantively by the cationic surfactant and that the solution can therefore be used immediately after it has been prepared, without waiting until the equilibration period which is otherwise required has elapsed.
Potentiometric surfactant titrations

3 Possible surfactant electrode applications

The development of surfactant electrodes in the potentiometric surfactant titration sector has led to a wide acceptance of this new analytical method. In contrast to the BF$_4^–$, Ca$^{2+}$ or NO$_3^–$ electrodes which were previously used for surfactant titration and which only had a cross-sensitivity to surfactants, the new generation of surfactant electrodes were developed specifically for this purpose. This means that operators no longer have to reckon with having to modify all their methods when an old, unusable electrode is exchanged for a new one because the response behaviour of the old electrode differs significantly from that of the new one. The new surfactant electrodes have been tested by the electrode manufacturers for surfactant titration applications and only then released. With regard to the amount of time required and the reliability of the analysis this is really a great advantage, particularly in quality assurance laboratories. The fact that surfactant electrodes from different manufacturers differ significantly from each other is detrimental to the general acceptance of the analytical method described here. This is why it is barely possible today to carry out a method, developed with an electrode from manufacturer A, using an electrode from manufacturer B. However, it cannot be expected that the manufacturer of the better electrode would pass on his know-how to the manufacturer of the poorer electrode.

The great differences between the various surfactant electrodes are certainly one of the reasons why this analytical method, although it is so widely accepted and has established itself, has found so little incorporation into standardisation.

3.1 Anionic surfactants

The anionic surfactants group is certainly the one in which the surfactant electrode finds its greatest use as the indicator electrode for potentiometric surfactant titration. Now that it is possible to review approx. eight years’ application of potentiometric surfactant titration it can be said that this method established itself. In particular, it is hard to imagine the field of raw materials analysis without the surfactant electrode for ionic surfactants. Only the two product groups sec. alkane sulphonates and field of raw materials analysis without the surfactant electrode for ionic surfactants. Only the two product groups sec.

Potentiometric surfactant titration of sec. alkane sulphonates, results that are too high by 8 to 10% are found when compared with two-phase titration; for α-olefin sulphonates the corresponding range is 2 to 4%. The causes of these too high results are known. They result from the proportion of di- or polysulphonates in the sec. alkane sulphonate. In the α-olefin sulphonates the proportion of disulphonate is also responsible for the too high results. Further information can be found in chapter 7, sections 7.2.5 and 7.2.6.

The standardisation committees should concern themselves with these problems. In the potentiometric surfactant titration of these sulphonates the sulphonate group present in each molecule forms a corresponding ion associate with the titrant. This means that 1 mol of cationic titrant is consumed per mol alkane monosulphonate, 2 mol cationic titrant per mol alkane disulphonate and 3 mol cationic titrant per mol alkane trisulphonate. Nobody would reject the titration of sulphuric acid with sodium hydroxide just because 2 mol sodium hydroxide are required to neutralise one mol sulphuric acid.

3.2 Cationic surfactants

The potentiometric surfactant titration of cationic surfactants has also been the state of the art for a long time and has replaced the classical two-phase titration for routine applications. This has certainly to do with the fact that in potentiometric surfactant titration, in contrast to two-phase titration, there is the possibility of differentiating between quaternary ammonium compounds and, e.g., surfactant-like parent amines by selecting a suitable pH value. It is exactly this possibility of carrying out titrations at any pH that has considerable advantages with cationic surfactants. As an example, the titration of hydrolysis-sensitive esterquats is difficult with two-phase titration. With potentiometric surfactant titration this determination can be carried out without any problems if certain conditions are fulfilled.

3.3 Betains

Betains are not as easy to titrate as anionic or cationic surfactants. This is related to the structure of the betains, see Fig. 29.

At neutral pH values, where the betain is present in the internally neutralised form, there is no possibility of carrying out a titration. Only in the protonated region is there a chance of carrying out a titration. This is best achieved by dissolving the betain in 0.1 mol/L HCl. The betain is now quantitatively present as a cationic surfactant. Even in this condition a potentiometric surfactant titration analogous to that for a cationic surfactant, i.e. by titration with an anionic surfactant, is not possible. This has several reasons. The betain is often a cocamidopropyl betain, as shown in Fig. 20. In this case the basic raw material is natural or hardened (hydrogenated) coconut oil with a wide alkyl chain distribution from C$_6$ to C$_{18}$. With short-chain betains in particular, i.e. those with C$_6$ or C$_7$ alkyl residues, the ion associates formed with the classical anionic surfactants do not precipitate. On top of this the betain molecule contains not just one but three polar groups: the amide group, the quaternary nitrogen and the carboxylate group. During titration with an anionic surfactant only the polarity of the quaternary nitrogen group is blocked by the ion association formation; that of the carboxylate and amide groups remains. The remaining polarity ensures that precipitation with an anionic surfactant is only partially possible. A possibility for titrating amphoterics surfactants is only provided if the anionic surfactant titrant is exchanged for a different large, voluminous anion. Sodium tetraphenylborate (NaTPB) has proved itself to be best for this purpose. A corresponding method was described by Gerhards et al. However, this titration cannot be carried out with a normal surfactant electrode intended for the determination of ionic surfactants. The NIO Surfactant Electrode mentioned in section 3.4 below is more suitable for this purpose. The determination is relatively complicated and requires that all the given parameters are observed. Only in this way can it be guaranteed that in this titration all the alkyl chains contained in a
The surfactant-like pharmaceuticals of group 1 are, like other ionic surfactants, titrated with the Ionic Surfactant Electrode. The non-surfactant-like pharmaceuticals, i.e. large, voluminous cations or anions that can be precipitated out with a surfactant electrode, are divided into two large groups: surfactant-like pharmaceuticals, e.g. benzalkonium chloride, that can be used either as an active ingredient in lozenges or as a preservative in many aqueous preparations. Other surfactant-like pharmaceuticals are cetylpyridinium chloride or amine fluoride, octadecyltrimethylenediamine-N,N'-tris-(2-ethanol) dihydrogenfluoride. Anionic indicators are titrated with a cation-active titrant, preferably TEGO trant A100 (1,3-didecyl-2-methylimidazolium chloride), cationic indicators are titrated with an anion-active titrant, preferably dodecyl sulphate sodium salt or bis-2-ethylhexylsulphosuccinate. As a whole the analysis of ionic indicators is considerably easier and less complicated than the titration of surfactants, as many of the surfactant-specific problems such as surface activity, micelle formation or costs and handling. A feature of the new electrode is its specific adaptation to the requirements of NIO titration in respect of rapid response and good reproducibility. With typical nonionic surfactants, e.g. fatty alcohol, fatty acid or an alkyl phenol with 10 to 50 POE per molecule, standard deviations of <0.5% can be achieved (Fig. 45). This means that this titration method is able to replace the much-disliked BIAS determination (bismuth-active substance) throughout a wide range. This BIAS analytical method requires an extremely long time and special safety measures. The range of surfactants that can be determined with the new surfactant electrode and the BIAS method is practically the same. This also means that the cross-sensitivity to polyethylene glycols (PEGs) is the same. This must be taken into account, e.g. in the determination of nonionic surfactants in wastewaters, as here the non-surfactant-like PEGs must not be determined. Accordingly, whenever the separation of PEGs by the blow-out method is required for the BIAS determination, this step must also be carried out for the potentiometric titration. On the other hand the applicability of the NIO Surfactant Electrode is mainly limited to POE-containing surfactants. A general sensitivity to all nonionic surfactants, as postulated by Ulrich, at least does not apply to APGs or other sugar surfactants that have recently achieved particular importance among the nonionic surfactants. Despite the limitations the NIO Surfactant Electrode represents an enormous progress in the field of surfactant analysis. Its possibilities, peculiarities and limits are described below with practical examples.

The subgroup with by far the largest production share of all nonionic surfactants are the alkylene oxide derivatives. These are addition products of ethylene oxide (POE) and propylene oxide (POP) on hydrophobic parent molecules such as fatty alcohols, fatty acids or the fatty acid partial esters of polyvalent alcohols such as glycerol, etc.

3.4 Nonionic surfactants

In the determination of ionic surfactants, surfactant electrodes today offer in many cases a rapid, cost-saving, environmentally acceptable and easily automated alternative to the classical two-phase titration according to Epton. The modern generation of these electrodes is characterised by their high performance and long working life. In recent times a surfactant electrode for the titration of nonionic (NIO) surfactants based on polyoxyethylene (POE) adducts (section 4.3) has been introduced. Carrying out a NIO titration is extremely simple and is comparable to the titration of ionic surfactants with regard to costs and handling. A feature of the new electrode is its specific adaptation to the requirements of NIO titration in respect of rapid response and good reproducibility. With typical nonionic surfactants, e.g. a fatty alcohol, a fatty acid or an alkyl phenol with 10 to 50 POE per molecule, standard deviations of <0.5% can be achieved (Fig. 45). This means that this titration method is able to replace the much-disliked BIAS determination (bismuth-active substance) throughout a wide range. This BIAS analytical method requires an extremely long time and special safety measures. The range of surfactants that can be determined with the new surfactant electrode and the BIAS method is practically the same. This also means that the cross-sensitivity to polyethylene glycols (PEGs) is the same. This must be taken into account, e.g. in the determination of nonionic surfactants in wastewaters, as here the non-surfactant-like PEGs must not be determined. Accordingly, whenever the separation of PEGs by the blow-out method is required for the BIAS determination, this step must also be carried out for the potentiometric titration. On the other hand the applicability of the NIO Surfactant Electrode is mainly limited to POE-containing surfactants. A general sensitivity to all nonionic surfactants, as postulated by Ulrich, at least does not apply to APGs or other sugar surfactants that have recently achieved particular importance among the nonionic surfactants. Despite the limitations the NIO Surfactant Electrode represents an enormous progress in the field of surfactant analysis. Its possibilities, peculiarities and limits are described below with practical examples.

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3.5 Ionic dyes

Although ionic indicators are not surfactants they are often large, voluminous cations or anions and therefore substances which a surfactant electrode can detect. Indeed, many ionic indicators can be titrated just like surfactants. Anionic indicators are titrated with a cation-active titrant, preferably TEGO trant A100 (1,3-didecyl-2-methylimidazolium chloride), cationic indicators are titrated with an anion-active titrant, preferably dodecyl sulphate sodium salt or bis-2-ethylhexylsulphosuccinate. As a whole the analysis of ionic indicators is considerably easier and less complicated than the titration of surfactants, as many of the surfactant-specific problems such as surface activity, micelle formation or substantive properties do not appear there.

The experiments were all performed using the Ionic Surfactant Electrode from Metrohm; approx. sixty to seventy percent of the indicators tested could be titrated without any problems. The indicator titration is also a precipitation titration and it is therefore necessary for the indicator to precipitate out with the titrant. Whether and how this happens can easily be determined by a qualitative preliminary test. This is carried out by preparing a stock solution of the indicator to be analysed, placing aliquots of it into different beakers and precipitating the titrant. Whether and how this happens can easily be determined by a qualitative preliminary test. This is carried out by preparing a stock solution of the indicator to be analysed, placing aliquots of it into different beakers and precipitating the titrant. The titrant with which the precipitation is seen to proceed best and with which the precipitation is seen to proceed best and with the best reproducibility. With typical nonionic surfactants, e.g. fatty alcohol, fatty acid or an alkyl phenol with 10 to 50 POE per molecule, standard deviations of <0.5% can be achieved (Fig. 45). This means that this titration method is able to replace the much-disliked BIAS determination (bismuth-active substance) throughout a wide range. This BIAS analytical method requires an extremely long time and special safety measures. The range of surfactants that can be determined with the new surfactant electrode and the BIAS method is practically the same. This also means that the cross-sensitivity to polyethylene glycols (PEGs) is the same. This must be taken into account, e.g. in the determination of nonionic surfactants in wastewaters, as here the non-surfactant-like PEGs must not be determined. Accordingly, whenever the separation of PEGs by the blow-out method is required for the BIAS determination, this step must also be carried out for the potentiometric titration. On the other hand the applicability of the NIO Surfactant Electrode is mainly limited to POE-containing surfactants. A general sensitivity to all nonionic surfactants, as postulated by Ulrich, at least does not apply to APGs or other sugar surfactants that have recently achieved particular importance among the nonionic surfactants. Despite the limitations the NIO Surfactant Electrode represents an enormous progress in the field of surfactant analysis. Its possibilities, peculiarities and limits are described below with practical examples.

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3.6 Pharmaceuticals

Pharmaceuticals that can be titrated with a surfactant electrode are divided into two large groups:

1. Surfactant-like pharmaceuticals, e.g. benzalkonium chloride, that can be used either as an active ingredient in lozenges or as a preservative in many aqueous preparations. Other surfactant-like pharmaceuticals are cetylpyridinium chloride or amine fluoride, octadecyltrimethylenediamine-N,N'-tris-(2-ethanol) dihydrogenfluoride.

2. The non-surfactant-like pharmaceuticals, i.e. large, voluminous cations or anions that can be precipitated out with oppositely-charged anions or cations.

The surfactant-like pharmaceuticals of group 1 are, like other ionic surfactants, titrated with the Ionic Surfactant Electrode. For the titration of group 2 pharmaceuticals the Metrohm NIO Surfactant Electrode is mainly used. As reference electrode an Ag/AgCl electrode with aqueous 3 mol/L sodium chloride as the electrolyte has proved itself. Pharmaceuti
tical titrations, like all titrations using surfactant electrodes, belong to the group of precipitation titrations. Anionic pharmaceuticals are best titrated with a large cation, e.g. TEGO tram A100 (1,3-didecyl-2-methylimidazolium chloride). For the titration of cationic pharmaceuticals, sodium tetraphenylborate (NaTPB) has proved to be the best large anion. The following preconditions for titrating non-surfactant-like pharmaceuticals must be met:

1. The pharmaceutical must have a solubility in water of at least 50 mg/100 ml. To improve the solubility, the titrant solution can be made acidic or basic.

2. The pharmaceutical itself must have a cationic or an anionic group within the molecule.

3. It must form an insoluble ion associate with the oppositely-charged titrant.

With non-surfactant-like pharmaceuticals the interferences or limitations which occur as a result of surfactant-like properties are not to be expected. There are therefore no problems with surface activity, micelle formation or similar surfactant-specific characteristics. This is why pharmaceutical titrations show a very good linearity between sample weight and titrant consumption throughout a very wide range. As a result good titration curves and correct results can be obtained even with low titrant consumption. The titration takes place stochiometrically and is therefore easy to evaluate. The pharmaceutical titration is a true absolute method. The surfactant electrode, which is used as the indicator electrode in surfactant titration, has a similar response sensitivity to the pharmaceutical analytes and to the titrants. This results in very good, symmetrical and S-shaped titration curves that can be evaluated by the modern titrators without any problems. This new technique for the determination of pharmaceuticals can be regarded as being exceptionally friendly to the environment because no organic solvents are required and the titration is carried out in a purely aqueous medium. Toxic pharmaceuticals are precipitated during the titration and can thus be easily disposed of. This means that pharmaceutical titration is quick, simple and economical. It can also be easily automated and allows the use of sample changers so that a large number of titrations can be carried out unattended. The determination of pharmaceuticals can be used both as a quality check for incoming raw materials and for the quality control of finished pharmaceuticals. Among the finished pharmaceuticals that have been investigated are solutions, drops and also cough syrups with an extremely high sugar content. Tablets, injection solutions, creams or gels also present no problems. Difficulties were only experienced with dragees in which the active ingredient is bonded to an ion exchanger resin. Even somewhat problematic matrices such as a cream containing the fungicide clotrimazole in a concentration of 1.0% require no complicated sample preparation. Weigh approx. 2 g of the cream directly into the titration vessel, add a few mL alcohol, warm the mixture until the emulsion has broken down, fill up with water, add a few drops of dilute acetic acid to convert the clotrimazole into the more soluble acetate, and titrate immediately with sodium tetraphenylborate. Even ingredients that cause problems in HPLC analysis, e.g. chlorhexidine in the form of its digluconate or hydrochloride salt or the active ingredient chlorhexidine contained in many gargling solutions can be titrated with this new method without any problems. Approx. 15 min are required for carrying out a double determination. The titration of pharmaceuticals is highly suitable for use with standard sample changers which can be connected to many titrators. Special electrode conditioning or cleaning is not required even with large titration series, as the ion associates formed during the titration do not deposit on the electrodes. The titration of pharmaceuticals is a simple, quantitative determination method for checking active ingredients and auxiliaries in formulations or determining the purity of raw materials. The ingredients to be determined must be known as well as their molar masses. The titration cannot be used to identify the ingredients in any way.
4 The sensors

The question of what causes the potential at a surfactant electrode can – despite far-reaching literature searches and many investigations by the author – still not be clearly answered today. This is why an attempt is made here to provide general information about the detection principle.

4.1 Fundamentals of potentiometry; detection principle

The endpoint of a surfactant titration is detected potentiometrically by means of a surfactant electrode. The potential obtained at the indicator electrode is measured against the constant potential of a second electrode, the so-called reference electrode. This combination of indicator electrode and reference electrode is also known as a measuring chain.

The difference in potential depends on the electrodes used and the composition of the solution. If the composition of the solution alters during the titration, e.g. by the addition of the titrant, then this causes a measurable change in the potential. This change in potential is used to follow the course of the titration. The following requirements must therefore be fulfilled before a potentiometric surfactant titration can be carried out:

- The equilibrium must clearly be on the side of the reaction products.
- The reaction must be sufficiently rapid.
- The reaction must take place with a clear quantitative relationship, i.e. stoichiometrically.
- The potential jump must exclusively be determined by the substances that take part in the titration reaction.

About the indicator electrode

An indicator electrode is immersed in the sample solution together with the reference electrode and has the task of following changes in the potential of the measuring system.

In the sample solution cations and anions are uniformly distributed, the solution is therefore electrically neutral. In the area of the phase boundary the charges are separated as the electrode surface has completely different properties than the bulk of the solution. The result of this anisotropy at the phase boundary is a re-orientation of the particles affected by these forces. This is because in the altered force field the particles try to achieve the condition of lowest energy. Larger or smaller dipole orientations of the solvent molecules may occur. The oriented dipoles at the electrode surface can be thought of as being a charged condenser plate at a distance from the surface. In this way an electrical double layer is formed which would work like a condenser in an electrical circuit. This layer is known as the Helmholtz double layer.

In contrast to this the inner Helmholtz layer is formed by the specifically absorbed ions, which at the electrode side have stripped off their solution shell, and their oriented solvent molecules at the electrode surface.

As the distance from the electrode increases the double layer becomes an increasingly diffuse layer. At a sufficiently large distance a local separation of the charge carriers can no longer be observed.

The separation of the charge carriers is seen in the appearance of a potential difference between the solid electrode and the solution. The potential that is established at the electrode depends on the type of ion and its concentration. The type of ion that displaces the greatest number of charge carriers at this phase boundary determines the electrode potential.

Principles of precipitation titration

The basis of almost all surfactant titrations is a precipitation titration. As an example the anionic surfactant analyte is precipitated out with the cationic surfactant titrant. This means that during the titration the analyte is transformed into a sparingly soluble compound with a defined composition. The endpoint of the titration is reached when an equivalent amount of the precipitation agent contained in the titrant has been added. If the measured potential is plotted against titrant concentration then the point of inflection of this curve corresponds to the equivalence point, which is also known as the endpoint. When precipitation has occurred there is an equilibrium between the precipitate and the supernatant liquid. The liquid is a saturated solution, i.e. it contains the precipitated substance in the highest possible concentration, the saturation concentration. The precipitation reaction is also reversible to a certain extent. From these observations it can be seen that all precipitation titrations have a source of error. This is because an absolutely insoluble compound does not exist. In the surfactant titration sector, for example, the precipitated ion associate from an octylsulphate and TEGO trantr A100 has a higher solubility than a reaction product from a dodecyl sulphate and TEGO trantr A100.

The alterations in the concentration of the ion to be determined that occur during precipitation are reflected by the titration curve. The titration curve is obtained by plotting the measured potential changes against the consumption of standard solution. The titration curve is S-shaped; the point of inflection of the curve corresponds to the equivalence point. The first derivative of the curve (dU/dV) shows a peak whose maximum corresponds to the equivalence point.

The accuracy of a precipitation titration increases as the solubility product of the precipitate decreases. The smaller the solubility product, the steeper the slope of the titration curve, i.e. the steeper its first derivative.

The field of surfactant precipitation titration is characterised by several additional features.

Surfactants form micelles. Precipitates formed during the titration can be solubilised in these micelles. If before the point of inflection only the analyte is present as a surfactant, then its concentration and therefore the ability to undergo micelle formation and solubilisation will decrease continuously. In this case a relatively steep titration curve with good potential differences is usually produced. However, if apart from the analyte, e.g. an anionic surfactant, there is another one present, e.g. the nonionic surfactant alkyl phenol ethoxylate, then the concentration of this nonionic surfactant will remain constant throughout the titration. This means that during the titration there is the possibility of solubilising both the analyte and the precipitate and, at the end of the titration, the titrant. If there is a sufficiently high concentration of alkyl phenol ethoxylate this could mean that a precipitation titration could be carried out without a precipitate being...
formed. A better and more accurate way of putting things would be to say that no visible precipitate is formed, as the anionic analyte forms an insoluble ion associate with the cationic titrant which, however, is immediately solubilised. This type of titration can be immediately recognised from the titration curve produced. The transition interval of this titration curve covers a volume range at least four times as large as it would be in the absence of the nonionic surfactant. The total potential difference, i.e. the difference between the start of the titration and the end also decreases by approximately 20 to 40%.

**Surfactant electrodes**

Electrodes can thus be used to detect charge separations and charge transfers which originate at the solid/liquid interface. A potential is generated because at the phase boundary between the electrode and the sample solution there is an orientation of the particles on the surface. During surfactant titration this takes place at the surfactant electrode, i.e. at the interface between the PVC membrane and the sample solution.

In order for a difference in potential to be formed there must be an undissolved ion in the electrode membrane in addition to the ion to be measured, which is present in the sample solution in dissociated form. In the PVC membrane electrode this condition is fulfilled by the presence of an organic water-insoluble phase, the ion carrier dissolved in plasticiser, which is stabilised by the PVC matrix. The interaction between the ion carrier in this organic phase with the sample ion in the solution produces a defined chemical potential of the ion to be measured. See also Fig. 46.

Potential formation now occurs by an interaction between the ion carrier in the PVC membrane and the ion to be determined in the sample solution. This interaction in an equilibrium reaction causes a potential transfer from the ion in the sample solution to the membrane and leads to the formation of a potential difference at the interfacial boundary. In the type of surfactant electrode that is used for the titration of ionic surfactants both the analyte and the titrant are responsible for the potential formation.

### 4.2 Surfactant electrodes for ionic surfactants and dyestuffs

#### 4.2.1 Comparing the High Sense Surfactant Electrode with the NIO Surfactant and the Ionic Surfactant Electrode

The continuing development of surfactant electrodes can be seen in the fact that, in the third quarter of 1996, Metrohm brought the second special electrode for the titration of ionic surfactants onto the market. This NIO Surfactant Electrode differs from the initially introduced High Sense Surfactant Electrode chiefly in its design.

The older design, the High Sense Surfactant Electrode, had an exchangeable sensor tip. If the sensor was no longer working properly then only the tip had to be exchanged, which saved money. Unfortunately this exchangeability also created problems. The most important characteristic property of the surfactants is their ability to reduce the surface tension of water. This meant that the surfactants also had the possibility of penetrating the electrode at the point where the tip was screwed on, which caused problems.

In the new NIO Surfactant and Ionic Surfactant Electrodes the sensor rod is permanently connected to the electrode body. No problems have occurred with this new construction. The manufacturer will continue to offer the High Sense Surfactant Electrode for some time longer so that operators who have validated their surfactant titrations with the High Sense Surfactant Electrode can still obtain this electrode. However, conversion to the Ionic Surfactant Electrode is possible without any problems. In many thousand comparative investigations in our laboratory both electrodes have proved to be both comparable and interchangeable as regards results and handling. In these comparative investigations the new electrode, the Ionic Surfactant Electrode has proved to be the better electrode for the determination of ionic surfactants in aqueous media; it is also easier to use. The author and his laboratory team are convinced that the new Ionic Surfactant Electrode will establish itself.
If ionic silicon surfactants are to be titrated as well as the classical ionic surfactants and the Surfactrode Silicon is not available (see also section 4.4), then the High Sense Surfactant Electrode should be used. For this special application it has considerable advantages when compared with the Ionic Surfactant Electrode.

### 4.2.2 Resistance, service life, storage and maintenance

#### Maintenance

The Ionic Surfactant Electrode requires no particular maintenance.

If an anionic analyte is titrated with a cationic titrant then the combination of Ionic Surfactant Electrode and reference electrode should not be left unnecessarily long in the titrated solution. This attracts the substantive titrant to the membrane surface and covers it with a monomolecular layer. This layer negatively affects the response of the electrode. If this nevertheless should happen then the surfactant layer can be removed by rinsing once or twice with a few mL methanol. After rinsing with water the electrode is then again ready for use.

When a titration or a series of titrations has been completed and whenever there are no further titrations to be carried out in foreseeable time on the same working day then the electrodes should be rinsed once or twice with a few mL methanol and then rinsed off with distilled water. The Ionic Surfactant Electrode is then stored dry and the reference electrode is placed in a vessel containing 3 mol/L potassium chloride solution.

#### Conditioning

The Metrosensor High Sense Surfactant Electrode, in contrast to other surfactant electrodes, does not need conditioning. The best method is to carry out titrations with the new electrode immediately. The first two or three titrations are conditioning titrations and their results should not be used. It may also be necessary to carry out these two or three titrations when the electrode has not been used for a long time or if the titration conditions have significantly altered. This means that the High Sense Surfactant Electrode is able to adapt itself to special samples or special sample problems.

It is also possible to carry out a special conditioning procedure; however, this is not required for normal routine use. In the research sector, when a newly developed surfactant is to be analysed or if one with special properties is to be titrated the following conditioning technique has proved useful.

Pipet approx. 0.04 mmol (10 mL of a 0.004 mol/L solution) of the surfactant to be analysed into a beaker, add approx. 5 mL methanol followed by 75 mL water and 10 mL of the buffer solution to be used in the subsequent titrations. Then add 10 mL of the titrant with a concentration of 0.004 mol/L under stirring. An equimolar ion associate is formed by the analyte and the titrant. It is important that neither a large excess of analyte nor titrant is present. Continue stirring and immerse the High Sense Surfactant Electrode in this solution. A contact time of at least 1 hour is necessary; overnight immersion is preferable. If during this conditioning phase the turbidity in the solution caused by precipitation of the ion associate should disappear or become visibly reduced then the process should be repeated, several times if necessary. When the conditioning process is finished the High Sense Surfactant Electrode is rinsed twice with a few mL methanol and then rinsed off with water; it is immediately ready for the titration of the special surfactant.

The Metrosensor Ionic Surfactant Electrode requires no conditioning at all. After delivery or after a longer storage period it is immediately ready for use without any preparation being required. This fact can and should be used to advantage in laboratories in which the time factor is important. The quality of the results does not suffer because of it.

The Metrosensor Surfactrode Resistant also needs no conditioning and is ready for use as soon as it is unpacked®.

#### Resistance

All the following information refers to the High Sense Surfactant Electrode and the Ionic Surfactant Electrode from Metrom.

In general these electrodes are only resistant in water or aqueous solutions. These may contain the following alcohols up to the volume fractions given.

- up to 30% methanol
- up to 15% ethanol
- up to 10% 2-propanol
- up to 10% glycerol
- up to 10% 1,2-propanediol
- up to 10% 1,3-propanediol
- up to 10% sorbitol and other sugar alcohols

The electrodes can tolerate these alcohol concentrations being exceeded by approx. 25%; however, the working life of the electrode is shortened.

Higher alcohol concentrations or other solvents, particularly those which dissolve PVC or cause it to swell up, or which dissolve the plasticiser must not be present.

**SUCH SOLVENTS CAN DESTROY THE SURFACTANT ELECTRODE MEMBRANE IN A VERY SHORT TIME!**

Surfactant titration in 0.1 mol/L hydrochloric acid or in alkaline media up to pH = 11 is tolerated by the electrode even in continuous operation. Should it be necessary, titrations can also be carried out in, e.g., up to 1 mol/L sulphuric acid. In this case, when two titrations have been carried out the electrode should be immersed in water for approx. 15 minutes. The same applies for titrations in 0.1 mol/L sodium or potassium hydroxide.

#### Service life

In our laboratory we have several surfactant electrodes that have been in constant use for more than 2 years without their performance being affected. Please also see the information provided by the electrode manufacturer.
4.2.3 Prevention of contamination

As already described, potentiometric surfactant titration is a precipitation titration in which the analyte is precipitated out by the oppositely-charged titrant (Fig. 48). This takes place in a chemical reaction similar to salt formation between the positive charge of the polar group of the cationic surfactant and the negatively charged polar functional group of the anionic surfactant.

The ion associate produced is insoluble both in water and the permitted concentrations of alcohol. The long alkyl groups do not allow crystallisation to occur; instead, finely divided particles float in the aqueous solution and produce a Tyndal effect. These particles do not precipitate out, even after standing for a long time, e.g. overnight. Attempts to filter off this precipitate also fail owing to the precipitate rapidly blocking all common filtering media. Something similar also seems to happen on other surfaces, the ion associate attaching itself to the glass surface of the titration beaker or the reference and indicator electrodes. This clearly interferes with the indicator signal. Initially the response time becomes longer and at some stage potential differences are no longer detected. This means that the electrode combination either needs to be cleaned or that deposit formation on the electrodes must be prevented by a suitable additive.

In the literature\textsuperscript{77} nonylphenol-10 POE, e.g. Triton X 100, is often recommended as an additive to the sample solution.

As an example, Fig. 49 clearly shows the effect of Triton X 100 on a potentiometric surfactant titration, in this case the determination of sodium laureth sulphate with TEGOtrant A100. The basic titration without the addition of nonylphenol-10 POE shows a total potential difference from the start of the titration to its end of 325 mV. The curve is ideally S-shaped and the changes in potential occur almost exclusively in the region of the inflection point. Such a titration curve can be processed by the evaluation algorithm of the titrator and is the guarantee for good reproducibility and low standard deviations.

The titration curves obtained when nonylphenol-10 POE was added show clearly the negative influence, which increases with the concentration of the nonionic surfactant. The potential difference drops to 150 mV and in the region of the inflection point the curve becomes markedly flatter than in the titration without addition of Triton X 100.

If the recommendations in the literature about the addition of nonylphenol-10 POE to the titration solution are followed, the surface stability of the electrode membrane is indeed improved; however, at the same time, the detection sensitivity and, above all, the accuracy diminish. The addition apparently causes strong fluctuations of the potential in the course of a titration and therefore a larger standard deviation in the results.

The addition of 5% methanol to the titration solution has proved to be more suitable. The influence and the advantages of methanol have been described in detail by Schulz and Gerhards\textsuperscript{66}.

Methanol in particular, but also ethanol and 2-propanol prevent electrode contamination by the ion associate without causing interferences themselves at the given concentrations.

4.3 Surfactant electrodes for nonionic surfactants, betains and pharmaceuticals

The Metrosensor NIO Surfactant Electrode is suitable for the titration of

1. Nonionic surfactants
2. Pharmaceuticals not having surfactant properties
3. Betains
4. Soaps

However, when one of these four applications has been selected it is important to mark the electrode with a sticker and use it only for this application. Changing between the different applications causes problems and shortens the life of the electrode.

The new NIO Surfactant Electrode has a design different from that of other surfactant electrodes that have been on the market for a longer time. Electrodes of this type are known under the name of coated wire electrodes. Fig. 50 shows such an electrode. The PVC membrane is attached here to a rod of approx. 2 mm diameter and 50 mm length. This electrode is outstandingly stable, both as regards the mechanical properties and the attached PVC membrane substance.
4.3.1 Resistance, service life, storage and maintenance

Before its first proper use the NIO Surfactant Electrode is conditioned by carrying out two or three titrations whose results are then discarded. These conditioning titrations may also be necessary if the electrode has not been used for a long time, e.g. over the weekend. This ensures that in any case the electrode is again in an optimal condition. Furthermore it is advisable to wait about 30 s at the start of each titration so that the electrode can adapt itself to the particular sample matrix.

When the titration or series of titrations has been completed the electrode is wiped with a tissue moistened with methanol, rinsed two or three times with a few mL methanol from a wash bottle, then rinsed with distilled water and stored dry.

The electrode can also be stored in a 1% aqueous solution of PEG 1000. This type of storage is always recommended when nonionic surfactant titrations are often carried out. An electrode stored in this way is ready for immediate use, without the preliminary titrations mentioned above having to be carried out.

Apart from this the NIO Surfactant Electrode needs no special care or maintenance.

The NIO Surfactant Electrode is a coated wire type electrode and is extremely robust and stable. It tolerates careful mechanical cleaning with a Kleenex tissue moistened with methanol as described above.

If the electrode is treated properly its service life is at least six months. In our laboratory we often work with electrodes which are more than one year old and which cause no problems (please also see the information provided by the electrode manufacturer).

4.3.2 Prevention of contamination

The product precipitated during the titration of the pseudocationic nonionic surfactant with NaTPB has a very sticky consistency and tends to attach itself to any available surfaces, including the surfactant electrode and the reference electrode, from which it is difficult to remove because of its greasy and sticky consistency. For this reason it is absolutely necessary to add additives to the NaTPB titrant in order to convert the precipitate to a fine colloidal form which only attaches itself to the electrodes to a small extent (see section 6.4.2). If normal aqueous sodium tetraphenylborate solution is used as titrant then the surfactant electrode and reference electrodes must be cleaned after every single titration.

If the titration is carried out with the modified NaTPB solution described in section 6.4.3 then the electrode still needs cleaning after every three or four titrations. This is best carried out by rinsing the electrodes with methanol or carefully wiping them with a tissue moistened with methanol. They are then rinsed with distilled water and are again immediately ready for use.

Checking and then removing the coatings from the electrodes is one of the most important aspects of nonionic surfactant titration. The coatings significantly lengthen the response time of the electrode and the titration becomes too long for good results still to be obtained. The coating on the electrode surface means that titrant consumption almost always will be too high. Unfortunately this cannot be recognised from the shape of the titration curve; on the contrary the titration curve appears to be ideal. The coating can be detected from multiple determinations that show very poor agreement.

In the meantime there are special sample changers on the market, e.g. the Metrohm 730 Sample Changer. During the development of this sample changer the electrode coating problem occurring during the titration of nonionic surfactants was taken into account. This sample changer is equipped with an improved rinsing device in which a spray jet ensures optimal electrode cleaning. In addition, the technology of this sample changer allows not only a cleaning beaker filled with methanol to be brought into position after each titration or when several titrations have been carried out, but also a second beaker containing water. In this way the electrodes can be cleaned after every single titration and are in an optimal condition for the next nonionic surfactant titration to be carried out. This technology is currently the best available for carrying out large numbers of nonionic surfactant titration.

In pharmaceutical titration the special NaTPB solution (see section 6.4.3) should also be used. The reaction products of the pharmaceutical and NaTPB precipitated out in this titration do not have such negative properties as those produced by the nonionic surfactant titration. They also do not have such a strong tendency to deposit on the electrode surfaces. In this case it is possible to carry out 10 to 20 titrations on the sample changer without intermediate cleaning being necessary.

In betain determination with NaTPB other additives are added to the titration solution to prevent the electrodes becoming coated. Details can be found in section 7.6.1.
4.4 Titration of ionic silicon surfactants with the Surfactrode Silicon

When compared to classical ionic hydrocarbon surfactants, ionic organically modified siloxanes exhibit different physical-chemical properties. This can also be clearly seen during the analysis and in most cases prevents the direct transfer of determination methods. The higher the siloxane proportion in the molecule, the more noticeable the deviation. A wide range of organically modified siloxanes with an anionic, cationic or betain basis are currently available on the market. They have been specially prepared for a range of different applications in the pharmaceuticals, cosmetics or technology sectors.

A special surfactant electrode called the Surfactrode Silicon allows almost all ionic organically modified siloxanes currently found on the market to be determined potentiometrically in an easy way.

For the quantitative determination of ionic surfactants the two-phase titration according to Epton\(^6\) as modified by Reid\(^5\) is normally used\(^1\). The basis of this determination method is the formation of a chloroform-soluble coloured salt from the surfactant to be determined and an oppositely charged indicator substance. During the titration with a standard surfactant, whose charge is opposite to that of the surfactant to be determined, the indicator is displaced from the ion associate by the standard surfactant. The ionic indicator substance released is no longer soluble in chloroform and therefore the end of the titration is indicated by the decolouration of the chloroform phase. This determination method, which is relatively easy to carry out, cannot be used with most ionic organically modified siloxanes. These do form an ion associate with the indicator substance but this is not soluble in chloroform. This can be clearly recognised because, after the chloroform and aqueous phases have been vigorously shaken, the coloured salt accumulates at the phase boundary. This can be explained by the pronounced hydrophobicity and non-existent oleophilicity. Exchanging the chloroform for a different water-immiscible solvent does not improve this situation. Even attempts with low-viscosity siloxanes as extraction agents, using e.g. octamethyltetrcyclosiloxane, the so-called D4, have had no success.

All surfactant electrodes consist of a PVC matrix with a high plasticiser content (mass fraction above 50%). This matrix also contains an ionophor, which can be imagined as being an ion exchanger. The ionophor is responsible for the potential formation. Unfortunately the commercially available surfactant electrodes cannot be used for the potentiometric titration of ionic organically modified siloxanes. The reason seems to be the lacking oleophilicity of the siloxane base. This prevents the penetration of the ionic organically modified siloxanes into the membrane surface. This interferes with the potential formation to such an extent that the titration curves obtained cannot be evaluated.

The Surfactrode Silicon was developed at Th. Goldschmidt AG and is optimally oriented towards the demands of the potentiometric titration of ionic organically modified siloxanes, whereby the siloxanes can be mono- or polyfunctional. The ionic groups may be attached to the end groups or to the ionic groups of the siloxane backbone.

During the development of the electrode special attention was given to allowing the titrations to be carried out with an automatic sample changer, i.e. no coating of the electrodes was to take place, as this would require intermediate rinsing or conditioning phases. In sample changer operation we have carried out more than 100 titrations one after another without a deterioration of the titration curves becoming evident. For series of titrations in particular the necessary pH adjustment should be carried out immediately before the titration, preferably via an automatic dosing device, e.g. a Dosimat which can be addressed by the titrator program. In addition the electrode combination should be given the opportunity of adapting itself to the sample solution by including a waiting period of 30 seconds.

Tables 4 and 5 show some examples of titrations with the Surfactrode Silicon.

<table>
<thead>
<tr>
<th>Product name</th>
<th>pH during Titration</th>
<th>Quaternary N (%)</th>
<th>No. of determinations (n)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon quat A</td>
<td>10</td>
<td>1.97</td>
<td>11</td>
<td>0.130</td>
</tr>
<tr>
<td>Silicon quat A</td>
<td>7</td>
<td>2.02</td>
<td>12</td>
<td>0.076</td>
</tr>
<tr>
<td>Silicon quat B</td>
<td>10</td>
<td>0.74</td>
<td>12</td>
<td>0.020</td>
</tr>
<tr>
<td>Silicon quat B</td>
<td>7</td>
<td>0.83</td>
<td>12</td>
<td>0.018</td>
</tr>
<tr>
<td>Silicon quat C</td>
<td>10</td>
<td>0.36</td>
<td>12</td>
<td>0.012</td>
</tr>
<tr>
<td>Silicon quat C</td>
<td>7</td>
<td>0.41</td>
<td>11</td>
<td>0.004</td>
</tr>
<tr>
<td>Silicon quat D</td>
<td>10</td>
<td>1.83</td>
<td>12</td>
<td>0.020</td>
</tr>
<tr>
<td>Silicon quat D</td>
<td>7</td>
<td>1.91</td>
<td>12</td>
<td>0.018</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product name</th>
<th>pH during Titration</th>
<th>Surfactant S (%)</th>
<th>No. of determinations (n)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon anionic E</td>
<td>5</td>
<td>7.87</td>
<td>12</td>
<td>0.185</td>
</tr>
<tr>
<td>Silicon anionic F</td>
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<td>7.78</td>
<td>12</td>
<td>0.158</td>
</tr>
<tr>
<td>Silicon anionic G</td>
<td>5</td>
<td>7.65</td>
<td>12</td>
<td>0.294</td>
</tr>
<tr>
<td>Silicon anionic H</td>
<td>7</td>
<td>5.56</td>
<td>12</td>
<td>0.081</td>
</tr>
<tr>
<td>Silicon anionic I</td>
<td>7</td>
<td>6.64</td>
<td>10</td>
<td>0.292</td>
</tr>
</tbody>
</table>

The electrode was systematically investigated using the ionic organically modified siloxanes that are shown in Figs. 51 and 52.
4.4.1 Resistance, service life, storage and maintenance

**Maintenance**

The Surfactrode Silicon requires no special care or maintenance. The coated wire form of this electrode should only be cleaned with methanol or water from a washing bottle. Mechanical stress, such as wiping with a cloth, should be avoided.

If an anionic silicon surfactant is titrated with a cationic titrant then the combination of the Surfactrode Silicon and reference electrode should not be left unnecessarily long in the titrated solution. Otherwise the substantive titrant may coat the membrane surface. This would cause a considerable deterioration of the electrode responsive. If this should happen then the coating can be removed by rinsing once or twice with a few mL methanol. After rinsing with water the electrode is again ready for use.

When a titration or a series of titrations has been completed and whenever there are no further titrations to be carried out in foreseeable time on the same working day then the electrodes should be rinsed once or twice with a few mL methanol and then with distilled water. The electrode is then stored in a dry condition and the reference electrode is placed in a vessel containing 3 mol/L potassium chloride solution.

**Resistance**

The Surfactrode Silicon is considerably more sensitive towards ionic hydrocarbon surfactants than the normal surfactant electrode. The Surfactrode Silicon is only stable for long periods in water or aqueous solutions. The presence of the following alcohols up to the given volume fractions is also tolerated:

- up to 15% methanol
- up to 10% ethanol
- up to 5% 2-propanol

Higher alcohol concentrations or other solvents, particularly those which dissolve PVC or cause it to swell, or which dissolve the plasticiser must not be present.

**SUCH SOLVENTS CAN IRREVERSIBLY DESTROY THE ELECTRODE MEMBRANE IN A VERY SHORT TIME!**

Titration in 0.1 mol/L hydrochloric acid (pH = 1) or in alkaline media up to pH 10 is tolerated by the electrode, even in continuous operation. Higher concentrations of acids and, in particular, alkalis are not tolerated by the electrode. Solutions whose pH value is above 10 destroy the silicon structures in the electrode membrane.

**Service life**

In its current form the Surfactrode Silicon has a service life of approx. 3 to 6 months. During electrode storage «bleeding» is observed. Within the given service life of 3 to 6 months this has no observable effects on the use of the electrode.

**Availability**

The Surfactrode Silicon is being further optimised. At the time that this monograph is being printed, it is not yet commercially available. Interested parties should contact the author.

4.4.2 Prevention of contamination

The contamination problems affecting the Surfactrode Silicon electrode and measures for their prevention correspond to those affecting the normal surfactant electrode for ionic surfactants, which are treated in section 4.2.3.
4.5 Potentiometric two-phase titration

4.5.1 The Metrosensor Surfactrode Resistant

In recent years potentiometric surfactant titration using surfactant electrodes such as the High Sense Surfactant Electrode or the Ionic Surfactant Electrode has increasingly established itself. However, in some cases this method has limitations which can be overcome with the Metrosensor Surfactrode Resistant (SR). A completely new design of membraneless electrode means that this sensor is now suitable for use in two-phase media. If required, potentiometric titrations can now also be carried out in an analogous way to two-phase titrations. Even when the solvent chloroform is replaced by less toxic solvents the results correlate to a high degree with those obtained by the classical Epton titration.

The new Metrosensor Surfactrode Resistant (SR) allows titrations of difficult-to-analyse surfactants in problematic media which could not even be imagined with previously available electrodes.

The extension of the range of applications relates to the following sectors in particular:

1. The titration of ionic surfactants in a matrix which would cause the destruction of a classical surfactant electrode membrane. This could be, e.g., a solvent or a mineral oil. As an example it can be used to determine the content of anionic surfactants in water-soluble cooling lubricants or in alkaline, oil-contaminated cleaning baths, a range of applications for potentiometric surfactant titrations which is absolutely new. An example is shown in Fig. 53.

The determinations can be carried out without any problems for both cooling lubricant concentrates and products which have been in use for some time. In most cases titration curves are recorded which can be easily evaluated by the titrator. The analysis duration corresponds to that of other surfactant titrations. A further reduction in the time required is also possible. Whereas in surfactant titrations in aqueous media the preliminary dosing technique should not be used (section 5.7), this time-saving technique can be used with the Surfactrode Resistant for titrations in two-phase media in many cases.

According to our experience the method of potentiometric determination of ionic surfactants in cooling lubricants only fails when the sample of the used cooling lubricant has a too high salt content.

2. To a potentiometric surfactant titration with an extended analogy to classical two-phase titration. Whereas the normal potentiometric titration methods belong to the group of precipitation titrations, in two-phase titration with the Metrosensor Surfactrode Resistant the ion associate formed from the analyte and titrant is extracted into the organic phase, which corresponds to the conventional Epton titration.

3. To those surfactants whose hydrophilic groups prevent the precipitation of the analyte-titrant complex in water in the conventional titration and thus either considerably worsen the detection by the electrode or even make it impossible. By the use of the Surfactrode Resistant and an organic phase, the adducts formed during the titration can in many cases transfer to the organic phase so that they are removed from the aqueous phase in which the detection takes place. This means that even those analytes that react with the titrant but do not form an insoluble ion associate can be titrated with the Surfactrode Resistant.

4. The determination of ionic surfactants together with large concentrations of nonionic surfactants based on POE adducts and particularly with alkyl polyglucosides causes problems. These problems are pointed out several times in this monograph, e.g. in the determination of anionic surfactants in liquid light-duty or wool washing agents, or also in the determination of anionic surfactants in rinse-off products. The problems in the determination of cationic surfactants together with nonionic surfactants in high concentrations, e.g. in some disinfectant cleaners are known. The content of these nonionic surfactants remains practically constant during the whole titration. This means that they have the possibility of solubilising the analyte, as well as the ion associate formed during the titration. In these determinations sometimes no turbidity can be recognised. A value for the quantitative ratio of ionic surfactant to nonionic surfactant above which a determination can no longer be carried out cannot be given because the chemical structure of the nonionic surfactant has a great influence. The higher the proportion of POE groups in the molecule, the greater the interference can be. When the Surfactrode Resistant is used in a two-phase medium, the ratio of ionic to nonionic surfactant in a formulation is far less important than for a conventional surfactant electrode. This means that in formulations which contain 10 times as much nonionic surfactant as ionic surfactant the content of the ionic surfactant can still be determined accurately without any problems. The nonionic surfactants have a solubilising effect on the analyte, on the precipitate formed during the titration and later also on the titrant. This causes the total potential difference to become smaller and in the inflection point region the titration curve becomes wider, until a point is reached at which the titration curves can no longer be evaluated. Additionally, in the determination of cationic surfactants a high content of the nonionic surfactants described can lead to incorrect results. If the Surfactrode Resistant is used then these problems are either minimised or disappear completely.

A further large advantage of the Surfactrode Resistant is its universal and unproblematic use. In surfactant titrations in aqueous media numerous factors must be taken into consideration, and different substances often require different titrator settings. In potentiometric two-phase titration with the Surfactrode Resistant this is fundamentally different. More than 90% of the samples analysed to date could be titrated with a single standard method. The knowledge of other matrix constituents in the sample, which is normally required, is in most cases not necessary at all. Using shampoo and shower gel preparations as an example, it was possible to analyse all the approx. 100 samples investigated with one single method at pH = 3.
This results in considerable advantages, particularly for quality assurance laboratories. The time required for the preparation of a titration is decisively reduced. Once the method has been set up on a titrator it can be carried out by semiskilled personnel.

As described in detail in section 4.5.7, the Surfactrode Resistant is not affected by chloroform and other chlorinated hydrocarbons. This means that not only can a titration be carried out in the presence of a solvent, but the addition of a solvent immiscible with water is an absolute necessity. The solvent is highly important for the detection.

However, one of the main demands placed on potentiometric surfactant titration was the avoidance of the use of chloroform, because its classification as a very toxic and also a carcinogenic substance is still valid*. For this reason alternative organic solvents should be used.

The following have proved to be particularly suitable:

- methyl isobutyl ketone
- n-hexane
- cyclohexane

The use of chloroform has no advantages when compared with these solvents. There are only a small number of special applications where the use of chloroform is essential.

Methyl isobutyl ketone (MIBK) has an intensive and unpleasant smell. However, up to now it has proved to be the most universal of the solvents used.

It results from the above that the Surfactrode Resistant perfectly complements potentiometric surfactant titration in aqueous media.

In this method the surfactant analyte is also titrated with an oppositely-charged standardised surfactant titrant. Anionic analytes are titrated with a cationic titrant and cationic analytes with an anionic titrant.

The Application Bulletin describes a wide range of substances and formulations which can be determined better with the Surfactrode Resistant and mentions the particular working conditions and parameters.

Electrode theory

The Surfactrode Resistant is based on a completely different concept from the other surfactant electrodes in use up to now. It differs from these in that it possesses no membrane based on plasticised PVC. The electroactive substance responsible for the detection is permanently attached to a carrier material by a completely new technique. In practice this results in numerous advantages compared with the classical surfactant electrodes.

By the addition of suitable solvents titrations analogous to the classical two-phase titration can be carried out. The detection principle of this electrode is very similar to that used in two-phase titration.

The addition of solvent removes virtually all the negative matrix effects caused by other formulation constituents of the analyte.

This is why this electrode can also be used to titrate washing powders, cosmetic oil baths and even cooling lubricants which previously could not be determined potentiometrically with electrodes based on PVC membranes.

Potential formation occurs by a specific interaction between the ion carrier (electroactive substance) attached to the carrier material and the ions to be determined (surfactants) in the sample solution. In an equilibrium reaction this interaction leads to a potential transfer of the sample ions from the sample solution to the surface layers of the carrier material and linked to this the formation of an electrical potential difference at the phase boundary. This is measured in the virtual absence of current (potentiometrically) against a reference electrode. The extent to which the ions are transferred from the sample solution to the carrier material depends on the concentration.

The relationship between the sample ion concentration and the electrical potential is described by the Nernst equation; see section 1.13.

As a result of the special properties of surfactants, such as surface activity, substantivity (the tendency to be attracted to surfaces) and micelle formation, it cannot be assumed that the electrode described shows Nernstian behaviour. In practice this means that

- the electrode is not suitable for direct potentiometric concentration determinations, and
- the titration should always be evaluated according to the point of inflection of the S-shaped titration curve. Endpoint titrations are not recommended.

4.5.2 Reagents

Hydrochloric acid c(HCl) = 2 mol/L and c(HCl) = 0.1 mol/L, sodium hydroxide c(NaOH) = 2 mol/L and c(NaOH) = 0.1 mol/L, for adjusting the pH values

methanol, analytical grade and distilled or deionised water

ethanol, denatured

titrant

a solvent such as methyl isobutyl ketone (MIBK) or cyclohexane or n-hexane

If required, chloroform or another chlorinated hydrocarbon can be used.

TEGO add is a new additive developed especially for surfactant titrations using the Surfactrode Resistant. This additive has a positive influence on the whole course of the titration and keeps the electrodes clean. When titrating washing

We have deliberately not included the current classification of chloroform as an alteration is probably about to take place. Please obtain any information required from up-to-date safety data sheets.
powders, toothpastes, scouring agents, etc., or analytical samples containing other insoluble cleaning substances the addition of TEGO add is an absolute necessity.

For many other substances the addition of TEGO add also has a positive influence on the course of the titration. TEGO add has a positive effect on the fine and uniform distribution of the aqueous and organic phases during the titration and ensures smooth titration curves, particularly in the region of the point of inflection. The technique of adding TEGO add has proved particularly beneficial in the titration of raw materials.

Experimental investigations into the analysis of powder-form washing agents have also shown that the quality of the titration curves does not decrease as the number of titrations increases. The titration curve of a new electrode is directly comparable to one made 160 titrations later, provided that TEGO add has been added to each of these titrations of powder-form washing agent. If TEGO add is not used then after a few titrations a flattening of the titration curves is to be expected. The builders contained in the powder coat the electrode surface and subsequently are almost impossible to remove.

If the sample to be titrated itself contains a high percentage of nonionic surfactants, TEGO add is normally not required. Throughout the whole world TEGO add can only be obtained from Metrohm.

In practice the preparation of a solvent mixture of ethanol : methyl isobutyl ketone (1 : 1) has proved advantageous; TEGO add is added to this mixture so that 20 mL of the mixture contain 200 µL TEGO add. This is done by placing in a 1 L beaker 495 mL ethanol, 495 mL methyl isobutyl ketone and 10 mL TEGO add and mixing them thoroughly. This solvent mixture should always be used when the titrations can or must be carried out with the addition of TEGO add.

Experience gained recently by different users shows that TEGO add diluted 1 : 5 to 1 : 10 with water can be used for storing the Surfactrode Resistant.

**TEGO add was developed exclusively for use in potentiometric two-phase titration.** This is the only titration in which the use of this nonionic emulsifier is sensible and necessary.

In titrations in aqueous media TEGO add should not be added under any circumstances. This will always cause problems and produce poorer standard deviations and incorrect results. When used in aqueous media the interference from TEGO add could be so extensive that no evaluable titration curves at all are obtained.

This ban on the addition of TEGO add applies to all surfactant titrations carried out in aqueous media, regardless of what type of surfactant electrode or photometric detection method is used.

Apart from the selection of the correct titrant the thorough mixing of the sample is of very great importance. Titrations with the Surfactrode Resistant are performed in a two-phase medium. It is particularly important that the two phases are mixed together so thoroughly that an emulsion is formed without too many air bubbles becoming entrained or without the formation of a vortex. A magnetic stirrer is completely unsuitable for this purpose. The propeller 722 Rod Stirrer, e.g. as used in the 727 Titration Stand or in sample changers has proven to be satisfactory for this purpose. The addition of TEGO add also has a positive influence here.

### 4.5.3 Preparation, maintenance and storage of the surfactant electrode

- The Surfactrode Resistant is immediately ready for use and requires no conditioning.
- The pH adjustment of the titration solution should not be carried out in the normal way by using a buffer solution. We recommend to adjust the pH by adding sodium hydroxide or hydrochloric acid. This can be carried out manually with the aid of a pH meter, or the titrator can carry out an endpoint titration to the required pH.
- A solution of 20% ethanol in water is recommended for rinsing the electrodes. With modern sample changers, e.g. Metrohm 730 and 717, the electrodes should be immersed in a rinsing beaker containing 20% ethanol in water after each titration. After this, the stirrer should be switched on for a short time.
- After a titration or series of titrations has been finished the electrodes are rinsed briefly with ethanol and then with distilled water and then, if necessary, wiped carefully with a soft paper tissue soaked in ethanol.
- The electrode is stored in a dry condition.
- As has been found recently, the electrode can also be stored in a TEGO add solution diluted at a ratio ranging from 1 : 5 to 1 : 10.
- The electrode must never be stored in KCl solution c = 3 mol/L or in any other solutions with a high salt concentration!
- The service life of the electrode is approx. 1 year.

### 4.5.4 Analysis

- For the potentiometric two-phase titration with the Surfactrode Resistant the dynamic titration mode is most suitable. This titration mode is to be preferred. If it is required or absolutely necessary the titration can also be carried out in a monotonic mode with fixed volume increments.
- The titrant consumption should amount to about 10 to 15 mL. A corresponding amount of sample is weighed out into a beaker and dissolved in about 50 mL distilled water. Then 20 mL of a solvent mixture consisting of ethanol and a solvent immiscible with water (e.g. methyl isobutyl ketone, n-hexane, chloroform) is added. Distilled water is then added to give a total volume of approx. 100 mL, the pH adjusted with NaOH or HCl and the titration started. If the sample does not dissolve in water very well the ethanol-solvent mixture can also be used. For raw materials and
concentrates it is recommended that a dilution is first made for reasons of accuracy. An aliquot portion of this dilution is then used for the titration.

- 100 to 200 µL TEGO add are added to the titration solution.

4.5.5 Remarks

- It is recommended that the electrode is always immersed in the sample solution for about 20 to 40 s before each titration to guarantee adaptation to the sample matrix.

- The titrant TEGO trant A100 produces much steeper titration curves and larger potential jumps than other titrants. This advantage is seen particularly well with surfactants and soaps, which only produce weak, poorly evaluable potential jumps with Hyamine 1622, for example. As opposed to Hyamine 1622, TEGO trant A100 can be used to determine more hydrophilic surfactants, i.e. those with shorter alkyl chains or with hydrophilic components in the molecule (e.g. ester groups, amide groups, POE groups).

- If enough of the sample is available then a sample weight should be used which gives a titrant consumption of at least 10 mL. Only in this way can it be guaranteed that the total amount of surfactants is determined. Smaller sample weights produce nicer titration curves, but to some extent also produce low-bias results.

4.5.6 Titration parameter selection with the Surfactrode Resistant

For titrations with the Surfactrode Resistant three titration methods are normally sufficient; one method each for titrations with c = 0.004 mol/L and c = 0.02 mol/L titrant, and one method for titrating soaps.

<table>
<thead>
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<th>Table 6 Parameters for the 736 DMS Titrino as an example(^a).</th>
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<td>min.incr.</td>
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</tr>
<tr>
<td>signal drift</td>
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<tr>
<td>pause</td>
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</tbody>
</table>

All in all surfactant titration with the Surfactrode Resistant can be said to be relatively free from problems. Compared with the classical surfactant electrodes for use in purely aqueous media there are only a few influences here that need to be taken into account. This results in great advantages; in particular, for unknown samples in an unknown matrix good results can be obtained.

4.5.7 Resistance, service life, storage and maintenance

The technical outlay for the manufacture of the Surfactrode Resistant is very high. The monomer of an ion carrier based on an organically modified siloxane is polymerised by a beam of electrons and fixed to a carrier. The electrode made in this way is then inert to virtually all solvents. Chloroform or other chlorinated hydrocarbons can be used, even for longer periods, without any problems. Even after boiling the electrode in chloroform for 12 hours the functions of the Metrosensor Surfactrode Resistant remain fully intact for use in a two-phase medium.

Oils, fats, solvents or other oleophilic substances in analytes cannot destroy the electroactive substance nor can they remove it from the carrier material.

The electrode is resistant against all solvents which are relevant for the titration. This means that the sample can contain the following solvents:

- all chlorinated hydrocarbons including chloroform, 1,1,1 trichloromethane, dichloroethane, etc.
- aromatic hydrocarbons
- aliphatic hydrocarbons such as hexane, cyclohexane
- benzene, kerosene, fuel oil, etc.
- fats, oils and greases, cooling lubricants
- ethers
- water-immiscible ketones such as methyl isobutyl ketone

Scouring agents or abrasives in the sample and even metallic particles that could be contained in a typical sample have, within limits, no negative influence on the electrode surface.

Even samples containing free active chlorine or hydrogen peroxide can be titrated with this electrode. These substances do not damage the electrode in any way.

The Surfactrode Resistant is not affected by the chemicals mentioned above. However, it is not resistant to mechanical stress, which therefore should be avoided. If the electrode is treated, for instance, in the same way that a glass electrode is treated then nothing can happen.

Just like a glass electrode, however, the Metrosensor Surfactrode Resistant can be destroyed if it is allowed to fall to the ground.

The Surfactrode requires no special care. At the end of work the electrode should be rinsed with a mixture of 20% ethanol in distilled water. It is then stored dry. Overnight, the electrode should always be stored dry.

Under no circumstances should the electrode be allowed to stand in solutions containing salts for any length of time.
4.5.8 Stability of the Metrosensor Surfactrode Resistant towards alkalis

The electroactive substance of the Surfactrode Resistant is based on a polymeric silicone acrylate. It is a well-known fact that silicone polymers can be broken down by bases. This is why the Metrosensor Surfactrode Resistant only has a limited resistance to basic solutions. This is the reason why the alkalinity limitations given for potentiometric two-phase titration with the Surfactrode Resistant must be observed under all circumstances. Titrations can only be carried out in solutions whose pH value does not exceed 10. For safety the pH should be adjusted with a buffer, pH adjustment by the addition of potassium hydroxide or sodium hydroxide cannot be recommended.

pH values above 10 significantly shorten the service life of the electrode and can only be recommended when the operator is fully aware of the risk of destroying the electrode.

4.5.9 Prevention of contamination

In potentiometric two-phase titration contamination only plays a subordinate role. The solvent added to allow the electrode to function in the titration simultaneously ensures that the electrode remains clean. When samples are to be analysed that contain insoluble components, e.g. the builders in a powder-form washing agent, the addition of TEGO add prevents or reduces the contamination of the Surfactrode Resistant.

A TEGO add solution diluted at a ratio ranging from 1 : 5 to 1 : 10 can also be used to store the Surfactrode Resistant. This results in a «gentle» cleaning of the electrode. According to recent investigations, this form of storage offers several advantages. Before the electrode stored like this is used again as an indicator electrode, it should be rinsed with a 20 : 80 ethanol : water mixture.

If the electroactive part of the electrode should nevertheless become coated then this can be wiped off or rubbed off with a moist or dry cosmetic tissue.

It is important to ensure that the graphite surface of the Surfactrode Resistant does not become polished by this cleaning procedure. The response of a polished electrode surface is markedly worse than that of a rough one. Should polishing have occurred just the same, the graphite part of the electrode can be roughened up again by means of a sand paper of medium granulation.

If the Surfactrode Resistant has been accidentally left for a long time in a salt solution then it will no longer function as an indicator electrode for potentiometric two-phase titration. However, the electrode can be reactivated by placing it in distilled water overnight or, if necessary, over the weekend.

4.5.10 The Metrosensor Surfactrode Refill (this sub-chapter has been added in proof)

The Surfactrode Refill is an additional special electrode for determining ionic surfactants in a two-phase medium. It is the ideal supplement to the Surfactrode Resistant and has its main advantages where the latter has its weaknesses, i.e. in the alkaline region, in the titration of soaps and salt-containing samples. In contrast to the Surfactrode Resistant the Surfactrode Refill has no hard core consisting of sensor material, but is filled with a sensor paste that is used up during surfactant titration and is periodically renewed.

Scope of delivery
6.0507.140 Metrosensor Surfactrode Refill
6.2319.000 Surfactrode Refill paste
6.2826.010 Filling tool

Principle

The Surfactrode Refill is an alternative design of the Surfactrode Resistant. Both types of electrodes have been developed for use in potentiometrically indicated surfactant titrations in two-phase systems. In the Surfactrode Resistant the ionophore is polymerised in the carrier material in a homogeneous and solvent-resistant manner which guarantees a long working life. In the Surfactrode Refill the sensor material is constantly consumed. Its composition has been selected so that it is removed layer by layer by the solvent used in the potentiometrically indicated two-phase titration. This means that as the titrations are carried out a new sensor surface is continually being formed, which results in rapid response as well as a high tolerance towards sample components that might coat the sensor surface.

The sensor material of the Surfactrode Refill has a plastic, moldable consistency and can be refilled or exchanged easily and whenever required. At the base of the shaft there is a small opening into which the sensor material can be pressed with a simple tool. After the filling process the electrode is immediately ready for use; however, a control titration is recommended. One filling of sensor material is sufficient for at least one day’s continuous use. If the Surfactrode Refill is used continually, e.g. during a week, possibly with a sample changer, then the sensor material should be refilled daily.

Filling the Surfactrode Refill with sensor material

For filling or refilling the Surfactrode Refill with sensor material the connection cable is screwed off and the protective cap screwed on. The shaft is then placed vertically on a hard surface with the base pointing upwards. A spatula is used to fill the sensor material into the opening provided in the base of the electrode and this is pressed firmly into position with the tool supplied (any residues of the old sensor material in the electrode opening do not need to be removed before refilling). When refilling the electrode it is important that the electrode with protective cap is held firmly on the hard surface and that the pressing tool is pressed in until the built-in spring reaches its stop. If the filling level is not sufficient the filling and pressing processes are repeated. In an electrode that has been properly filled the filling level of the compacted sensor material is slightly below the electrode base and its surface is uniformly smooth. Any sensor material remaining on the electrode after the filling process can be simply wiped off. The sensor material has a storage life of several years.
Remarks concerning the potentiometric titrations

For general information consult Application Bulletin No. 269. The following titration parameters are recommended for the 716, 736 and 751 Titinos and the 726 Titroprocessor:

- DET mode, time-controlled
- Meas. point density 2
- Signal drift Off
- Equil. time 15 s
- Min. increment 50 µL
- Start volume* 6 mL or less
- Pause after start volume 30 s

* Expected titration volume >10 mL

4.6 Use of light-guide photometers

4.6.1 Titration in aqueous media

As surfactant titration is normally a precipitation titration in which the ion associate from cationic and anionic surfactant is insoluble, it is also possible to use the degree of turbidity as a detection method. This technique is generally known as turbidity titration or turbidimetry. A sensor is immersed in the solution to be titrated and measures the alterations in the optical density which are caused as the turbidity increases.

Two variants are commercially available for carrying out turbidity titrations.

The principle of the first variant, the so-called light-guide photometer, is shown in Fig. 54.

The light-guide photometer can be universally used for the detection of all titrations that can be photometrically indicated. It is without doubt the more expensive variant for surfactant titration, but also capable of more universal use. For example, the Metrohm instrument is a complete photometer with monochromator for the visible range. This means that in any type of photometrically indicated titration it is possible to set exactly that wavelength which is optimal for the titration. In our laboratory we have found that a wavelength of 420 nm is optimal for turbidity titrations. In principle a turbidity can, of course, be observed throughout the whole visible range. Light from a lamp is led via a fibreglass light guide into the titration solution and, after a path length of exactly 1 cm, is reflected from a mirror and led back to the photomultiplier via a second fibreglass light guide. This means that the total path length is 2 cm. Before the start of the titration, 100% light transmittance is calibrated as 0 mV and 0% light transmittance as 2000 mV, so that the normal range for a potentiometric titration is obtained. The light-guide photometer works with pulsed light so that interference from external light sources is eliminated.

4.6.2 Titration in two-phase media

This section was written in cooperation with G. Wulk, Kao Chemicals, D-46446 Emmerich, Germany

In a workshop G. Wulk reported an extremely interesting instrumental titration method for the determination of ionic surfactants.

The method normally used for the determination of anionic surfactants is the two-phase titration (water-chloroform) according to Epton with benzethonium chloride (Hyamine 1622) as titrant. Normally a mixed indicator of dimidium bromide and disulphine blue VN 150 is used. This method is described in a long series of national and international standards, e.g. in DGF standard method H-III 10 (94) or DIN ISO 2271 in Germany. In practice the method has been shown to have several disadvantages.

Wulk informed that several years ago, the task was set of developing an instrumental method which avoided or at least reduced as many of the disadvantages as possible of the two-phase titration. On the other hand the method should not depart too far from the standardised methods in order to keep validation expenditure within tolerable limits. As a result a turbidimetric titration was developed. The idea could be implemented with standard equipment for photometric titration. In the context of further automation the method was revised and extended.

As in the conventional Epton two-phase titration we use a two-phase titration based on a liquid-liquid extraction. The ion associates formed during the titration are extracted with a mixture of chloroform and methanol. The ratio of the aqueous phase to chloroform and methanol, and also the ratio of chloroform to methanol are important parameters in this titration method. For different types or classes of surfactant it may be necessary to optimise these ratios again.

c(\text{Hyamine 1622}) = 0.01 \text{ mol/L} \text{ in aqueous solution is used as the titrant. The solution was standardised with dodecyl sulphate sodium salt according to DGF H-III 10. The use of TEGO trant A100 as titrant is also possible. The titrant is added by a Dosimat. A magnetic stirrer or other suitable mixer is used to mix the sample solution. The endpoint recognition is not based on a colour change but on measuring the turbidity during the titration. A photometer equipped with fibre optics (e.g. the Metrohm 662 Photometer) is used. Photometric sensors with a fixed wavelength such as the Spectrode are also suitable for endpoint indication. According to Wulk the light-guide photometer is more suitable for the indication as this is the variant with the higher light intensity.}

In contrast to similar methods described in other places, the diffuse reflection of the solution is measured rather than the transmission. This is achieved by removing the reflection cap, i.e. the mirror, from the light guide. In this way interfer
ences to the titration caused by air bubbles can be avoided. The abrupt alteration of the reflection at the endpoint of the titration is evaluated.

In the titration of surfactant-like raw materials such as fatty alcohol sulphates or fatty alcohol ether sulphates the method produces results that agree with those obtained by the reference method for the surfactant content of a sample. However, in the method proposed by Wulk a considerably improved reproducibility is achieved, accompanied by a clear reduction in the amount of work required.

The method is suitable for the determination of sulphates (from C₁₀), ether sulphates (from C₁₀ to 15 mol POE) and sulphonates as well as for the determination of ether carboxylic acids (from C₁₀ to 25 POE) and carboxylates.

If dodecyl sulphate sodium salt solution is used as a titrant the method is also suitable for the determination of cationic surfactants.

The titration must always be carried out in the monotonic mode. A volume increment of 15 µL has proved effective. In the method described by Wulk the measurements are accepted after a fixed waiting period of 3 seconds. It has been shown experimentally that in this titration method an initial titrant addition can be made. This means that an analysis time of 10 to 15 minutes is required for one determination. The method can easily be automated by the use of sample changers.

The evaluation should not be carried out according to the standard algorithms for S-shaped titration curves, but according to the maximum turbidity. Mathematically this endpoint can be regarded as being the extrapolated intersection of the increasing turbidity curve with the line of constant or weakly falling turbidity. The PC software Metrodata TiNet 2.2 and higher offers the corresponding evaluation software for this purpose.

The use of the normal evaluation algorithm of the titrator for S-shaped titration curves can only be accepted if the determination of the titrant’s accurate content has been carried out under exactly the same conditions.

4.6.2.1 Determination of the active anionic content of alkyl ether sulphates

4.6.2.1.1 Applications

The method is used for determining the content of anionic surfactants in alkyl sulphates from C₁₀, alkyl ether sulphates (AES) from C₁₀, and an ethoxylation degree up to 20, alkyl benzene sulphonates (LAS) from C₈, and sulphonated ethoxylated alkyl phenols from C₁₀. The method is also suitable for determining the content of these surfactants in preparations.

This method is not suitable for the determination of alkyl sulphonates and sec. alkyl sulphonates (SAS). These surfactants require the use of solvent ratios different from those used in this method.

4.6.2.1.2 Principle

Anionic surfactants can be selectively determined in acidic media (pH = 2 to 3) by ion pair titration with benzethonium chloride (Hyamine 1622). The automated method used here is indicated photometrically. The diffuse reflection of the sample solution is recorded. The very sharp potential jump at the end of the titration is evaluated.

4.6.2.1.3 Safety

Carrying out this analytical method involves handling chemicals which are hazardous to health (chloroform) or toxic (methanol) and flammable (methanol). All necessary protective measures should be taken when the method is used. The titration should be carried out in a fume cupboard. Modes of action and countermeasures are contained in the Ecomed list of poisons.

**Note:** Chloroform and methanol may affect the foetus. Protective measures for mothers-to-be must be observed.

4.6.2.1.4 Reagents

- Hyamine solution in water c = 0.015 mol/L
- deionised water
- buffer solution pH = 2
- methanol, pure
- chloroform, pure
- sodium n-dodecyl sulphate (Merck 13760) for determining the molarity of the titrant

4.6.2.1.5 Instruments

- Metrohm 670 Titroprocessor with dosing and titration stands or Metrohm 716 or 736 Titrino with 728 stirrer stand (with stirrer bar 30 mm x 6 mm, PTFE-coated) or 730 Sample Changer
- Exchange Unit 20 mL
- Metrohm 662 Photometer with light-guide sensor (without reflector cap)
• analytical balance
• 150 mL and 100 mL tall form beakers, 250 mL volumetric flask, 25 mL pipet

4.6.2.1.6 Instrument and solvent parameters

Solvent parameters

In comparison to DGF method H-III 10 (94), correct values are obtained with this method if the following solvent ratio is observed at the start of the titration:

chloroform: 1.00 parts
methanol: 1.25 parts
aqueous phase: 3.75 parts

Note: Instead of the Hyamine 1622 c = 0.0015 mol/L used here a solution with a strength of 0.0010 or 0.0005 mol/L can also be used. However, the solvent ratio mentioned above must be strictly observed. The sample weight should be selected so that a Hyamine solution consumption of approx. 12.5 mL is achieved.

Instrument parameters

<table>
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<th>Parameter</th>
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<td>Titration mode</td>
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<tr>
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<td>Measurement drift</td>
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</tr>
<tr>
<td>Waiting time</td>
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<td>3 s</td>
</tr>
<tr>
<td>Initial dosing volume</td>
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<td>10 mL</td>
</tr>
<tr>
<td>Delay after initial dosing</td>
<td>200 s</td>
<td>200 s</td>
</tr>
<tr>
<td>EP criterion</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>

The parameters volume increment and waiting time must be set so that a reciprocal titration rate of not less than 200 s per mL titrant results. The parameter «volume increment» should be between 10 and 20 µL, depending on the steepness of the titration curve.

If a Metrohm 728 Titration Stand is used the stirrer speed must be set to 3 to 4. A list of parameters for titration with a 716 Titrino can be found below in section 4.7.1.

4.6.2.1.7 Procedure

Sample weight

The sample weight should be selected so that a consumption of approx. 12.5 mL titrant is achieved. The sample weight can be estimated by using the following equation:

\[
sample\ weight\ in\ g = \frac{12.5 \times \text{molarity}\ of\ titrant \times \text{molar mass of sample}}{10 \times \text{estimated}\ %\ contend\ of\ sample}
\]

Equation 1

Dilution

The sample is weighed into a 100 mL beaker with an accuracy of 0.1 mg. It is then dissolved in a little deionised water – under gentle warming if necessary – and transferred quantitatively to a 250 mL volumetric flask and filled up to the mark with deionised water. 25 mL of the sample solution is pipetted into a 150 mL (tall form) beaker and 5 mL buffer solution pH = 2 as well as 15 mL deionised water and a magnetic stirrer bar are added.

Titration

The beaker containing the sample solution is placed on the 728 Magnetic stirrer. The stirrer is set to step 3 to 4. The sensor is immersed in the sample solution. The sample weight and the sample data are entered into the entry mask (TiNet). The titration is started when the data have been entered. If required (blinking display on 662 Photometer) the photometer is set to 0. The addition of 12 mL chloroform and 15 mL methanol is carried out automatically, as is the rest of the titration.

Preparation of the titrant c(Hyamine 1622) = 0.015 mol/L

Weigh out 6.72 ± 0.1 g of Hyamine 1622 dried overnight at 105 °C and dissolve in 500 mL deionised water. The solution is transferred to a 1000 mL volumetric flask and filled up to the mark with deionised water. The solution is thoroughly mixed. For determining the factor 517.5 ± 5 mg SDS (sodium n-dodecyl sulphate, Merck) is weighed out accurately to 0.1 mg and the consumption determined as described above under «Dilution» and «Titration». The molarity of the solution is obtained from the mean consumption of 3 determinations. The molarity is calculated as follows:

\[
molarity = \frac{\text{sample weight (in g) \times % SDS}}{\text{mean consumption of SDS}}
\]

Equation 2
The content and mean molar mass of the SLS are determined according to DGF H-III 18 (94).

**Preparation of a pH 2 buffer solution**

Using a buffer concentrate for 500 mL buffer solution, e.g. Titrisol (Merck), proceed as follows: add ca. 300 mL deionised water to a 500 mL volumetric flask. Pour the contents of the vial into the flask and rinse the vial well. Fill up the volumetric flask to the mark and mix well.

**4.6.2.1.8 Calculation**

\[
\text{WAS in mmol/g} = \frac{\text{ml consumed} \times \text{molarity} \times \text{dilution}}{\text{sample weight in g}}
\]

**Equation 3**

\[
\text{WAS in } \% = \frac{\text{ml consumed} \times \text{molarity} \times \text{dilution} \times \text{molar mass}}{\text{sample weight in g} \times 10}
\]

**Equation 4**

**4.6.2.1.9 Statistical information**

<table>
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<tr>
<th></th>
<th>SLS</th>
<th>SLES 2 POE</th>
<th>SLES 3 POE</th>
<th>LAS</th>
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<td>Within-run standard deviation (Sr)</td>
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<td></td>
<td>0.06</td>
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<tr>
<td>Reproducibility (2.8 x S&lt;sub&gt;r&lt;/sub&gt;)</td>
<td>0.04</td>
<td>0.17</td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>Coefficient of variation (CV&lt;sub&gt;r&lt;/sub&gt;)</td>
<td>0.04</td>
<td></td>
<td></td>
<td>0.06</td>
</tr>
</tbody>
</table>

**4.6.2.1.10 Known interferences**

This method always determines the total amount of all surfactants that are present in the sample solution and are titratable under these conditions.

Sulphonates of toluene, xylene and cumol interfere if present in amounts above 15%. Free chlorine and peroxides do not interfere.

**4.7 Use of the Spectrode**

An alternative method uses an optical sensor whose compact construction means that it resembles an electrode and only works with one fixed wavelength. Recently Metrohm has offered such a compact design under the name Spectrode. The Spectrodes are available with wavelengths of 610 nm and 525 nm.

The field of use of such compact sensors is really the detection of an indicator colour change, so that they do not operate at the optimal wavelengths for measuring turbidities. However, this does not appear to be a particular disadvantage for turbidity measurements as the effect measured is very pronounced (a change from a transparent solution to a turbid one). As a result the Spectrodes are often used for surfactant titrations and there are several application reports.

The formation of a turbidity as detected by the systems described above does not take place in parallel to the titrant consumption. At the start of the titration, when there is still a relatively high analyte surfactant concentration, the analyte present in the micellar structures has a solubilising effect on the ion associate formed during the titration so that the titration solution remains clear at the start or is only very slightly turbid. As the titration continues there are increasingly fewer of the analyte micelles present so that the turbidity increases disproportionally and an S-shaped curve is obtained, similar to that one gets in potentiometric titrations using surfactant electrodes. This does not mean that a turbidity titration can also be evaluated like an S-shaped potentiometric titration curve. The endpoint of a turbidimetric surfactant titration is the point of maximum turbidity, i.e. the break after which the titration curve becomes almost horizontal. Mathematically this point corresponds to the intersection of the tangents to the curve of increasing turbidity and to the turbidity line remaining constant or decreasing slightly.

The basis of a photometrically indicated surfactant titration is identical with that of a potentiometrically indicated titration in aqueous media, with the requirement that insoluble ion associates are formed between the analyte and titrant. As a result there is the same dependence on the selection of a titrant as described for potentiometric titration. All in all several special influences act on the method of photometrically indicated surfactant titration and these exclude the general use of this analytical determination method.

1. In turbidity titration the surfactants are also titrated according to falling oleophilicity; however, only the more oleophilic surfactants form insoluble complexes with the titrant. For example, if an alkyl sulphate based on natural coconut fat is titrated with Hyamine 1622 as titrant then it is known that the C<sub>8</sub> alkyl sulphates will not be precipitated out. However, these are still fully capable...
of solubilising an existing ion associate, which means that incorrect endpoints can be obtained.

2. If surfactant raw materials contain large amounts of free fatty acids, as is the case with isethionates, then this could also cause problems. At the start of the titration the free fatty acids are at least partially held in solution by the solubilising ability of the isethionate. During the titration the turbidity will increase not only as a result of the formation of the ion associate from analyte and titrant but also additionally by the fatty acids, which are no longer solubilised. As a consequence, the degree of turbidity is affected by two different influences and the endpoint determined does not necessarily have to coincide with the real endpoint of the neutralisation of the isethionate with a cationic surfactant.

3. Larger amounts of nonionic surfactants as contained, e.g., in household cleaning agents or other formulations, can strongly influence the photometric titration of anionic surfactants. Depending on the amount and type of the nonionic surfactants, no turbidity at all may form because the nonionic surfactants immediately solubilise the ion associate. The higher the share of nonionic surfactants and the higher their degree of ethoxylation, the more readily this happens. In some experiments this influence was so great that the turbidity titration yielded completely false results. A large content of highly ethoxylated nonionic surfactants or also of APG can completely prevent any turbidity from occurring.

Fig. 58 shows the influence of increasing amounts of the nonionic surfactant PEG-40 hydrogenated castor oil on the titration of sodium lauryl sulphate. Approx. 15 mg sodium lauryl sulphate in 100 mL water were titrated with Hyamine 1622.

Fig. 59 shows the influence of increasing amounts of the nonionic surfactant lauryl glucoside (APG) on the titration of sodium lauryl sulphate. Approx. 15 mg sodium lauryl sulphate in 100 mL water were titrated with Hyamine 1622.

Fig. 60 shows the influence of increasing amounts of the amphoteric surfactant cocamidopropylbetain on the titration of sodium lauryl sulphate. Approx. 15 mg sodium lauryl sulphate in 100 mL water were titrated with Hyamine 1622.

If sodium lauryl sulphate is exchanged for an anionic surfactant that itself has POE units in the molecule, e.g. sodium laureth sulphate or disodium laureth sulphosuccinate, then the nonionic surfactants or the betain interfere to a considerably higher degree. The degree of interference is greater by a factor of approx. 5. This means that the photometrically indicated surfactant titration of formulations in aqueous media should only be used with reservations. Apart from the interference to the turbidity, which makes detection either difficult or impossible, the graphs also show that in some cases incorrect results may be obtained.

1. Larger amounts of alcohols in a formulation also have a significant influence on the formation and type of precipitate and can therefore influence the results of the turbidity titration.

2. The particle size of the ion associate from analyte and titrant changes in the course of the titration. This naturally influences the optical density and therefore also the detection. In titrations it is often possible to observe a phenomenon that occurs in the region of the equivalence point, sometimes just before it but sometimes just after it. The ion associate formed during the titration suddenly «coagulates». This leads to an offset in the titration curve. If this point lies in the endpoint region of the titration curve then the calculation of the equivalence point will be incorrect.
3. When photometrically indicated surfactant titrations are carried out then the titration curve obtained should always be examined closely. The endpoint of a turbidity titration is reached when the turbidity reaches its maximum. However, only a few of the titrators available on the market possess the ability to find this maximum by means of a suitable algorithm, as almost all titrators determine the point of inflection of the normal S-shaped titration curve as the endpoint of a titration. If during the examination of the titration curve it is obvious that the endpoint calculated by the titrator significantly differs from the optically recognisable point of maximum turbidity then other methods, e.g. manual evaluation or special software packages should be used to calculate the endpoint.

4. The total potential difference resulting from a photometrically indicated surfactant titration is considerably larger than in a normal potentiometric titration. The titration almost always starts with a clear solution, i.e. with a mV value of around 0. The resulting turbidity in a titration with a 0.004 mol/L solution is so large that an absorption of almost 100% or a transmission of 0% is achieved, which means that work is carried out with a total potential difference of 2000 mV. This potential difference is higher by a factor of 4 to 5 than that of a normal potentiometric surfactant titration. All the parameters of the titrator must therefore be set completely new for this special method, otherwise the danger exists that the large potential differences will cause the titrator to recognise several points of inflection in a single titration. This means that completely different methods must be developed for such a photometrically indicated titration.

5. The mixing of the titration solution is also very critical in this titration method, as with too slow stirring the mixing process lasts too long and with rapid mixing air bubbles are easily entrained which, as shown by experience, usually settle in the optical area of the sensor and therefore cause interferences.

In conclusion it can be stated that photometrically indicated surfactant titration is very suitable for use with some products. However, many influences are present that preclude the universal use of this method. Its use in the titration of raw materials that contain only small amounts of secondary constituents is more likely to be successful than its use in formulations of any type.

4.7.1 Determination of sodium laureth sulphate with the Spectrode

**Instruments and chemicals**

- 716, 736 or 751 Titrino
- Titration stand with propeller stirrer
- Dosimat with Exchange Unit
- Spectrode 610 nm
- Buffer pH = 3
- Titrant c(TEGO trant A100) = 0.004 mol/L or 0.005 mol/L
- Distilled or deionised water

**Titration parameters**

<table>
<thead>
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<th>DET</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Meas.pt density</td>
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</tr>
<tr>
<td>Min.increment</td>
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</tr>
<tr>
<td>Signal drift</td>
<td>30 mV/min</td>
</tr>
<tr>
<td>Equilibr.time</td>
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<tr>
<td>Meas.input</td>
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<td>Dos.rate</td>
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<tr>
<td>Pause</td>
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</tr>
<tr>
<td>Stop EP</td>
<td>9</td>
</tr>
<tr>
<td>Filling rate</td>
<td>max. ml/min</td>
</tr>
</tbody>
</table>

**Procedure**

The titrant consumption should be approx. 10 mL. With raw materials, a stock solution should be used for reasons of accuracy. An appropriate weight of sample is either weighed directly into a 150 mL beaker or pipetted in as an aliquot of the stock solution.

10 mL buffer pH = 3 is added and the solution made up to a total volume of approx. 60 mL with water. The titration is then carried out against the 0.004 mol/L TEGO trant A100 using the parameters given above.

4.8 Use of the RI sensor

This section could be subtitled «The Emperor’s new clothes» or «The Prince who never was».

The so-called RI sensor is an instrument which measures changes in the refractive index. This would be a completely new method for the indication of a surfactant titration. However, as the experiments we have carried out clearly prove, this is not the case. In numerous surfactant titrations an external Abbe refractometer was used to measure changes in the refractive index in steps corresponding to 1 mL titrant addition. During the whole titration, i.e. during the twenty individual steps investigated, no measurable change in the refractive index was observed. The alterations in potential measured by the RI sensor during this titration must therefore be caused by something other than the change in the refractive index. In order to strengthen these findings the titration of a dilute barium chloride solution with dilute sulphuric
Acid was carried out. In this titration there can be no change
in the refractive index. When this titration was carried out
the RI sensor did record a potential change during the ti-
tration that was very similar to that of a surfactant titration.
It must therefore be assumed that the so-called RI sensor
simply measures the alterations in the optical density and
that it is used in a very similar way to the light-guide pho-
tometer described in section 4.6. Whereas the light-guide
photometer sensor has a mirror at the sensor end which
reflects the light, this is different on the RI sensor. Only
that light is returned to the photomultiplier which is reflected
from the insoluble ion associates formed by the analyte
and titrant. The proportion of light reaching the
photomultiplier is thus considerably smaller than when a
light-guide photometer is used. This means that the meas-
uring signal must be amplified to a far higher degree, which
can easily be seen from the noise on a curve recorded
with an RI sensor. An RI sensor also does not work with
pulsed light so that a negative influence from external light sources cannot be ruled out. The fact that the RI sensor only
sees reflected light also makes it relatively sensitive to influences which would otherwise be unimportant. This means
that the distance of the sensing probe of the RI sensor from the base or side walls of the beaker is very important, as
these beaker surfaces also cause reflections.

If the technique of photometrically indicated surfactant titration on the basis of reflected light appears to make sense for
a particular application, then this titration mode can also be carried out with a light-guide photometer, by removing the
mirror at the end of the sensing probe so that the photomultiplier only uses reflected light for evaluation of the measure-
ments.

There are doubtlessly good reasons for using the RI sensor for the titration of ionic surfactants in cooling lubricants that
are miscible with water; one of these is the robustness of this detector. On-site use, directly on the production line and
away from a laboratory is easily possible. A high percentage of the determinations of ionic surfactants in cooling lubri-
cants are carried out using the RI sensor. See also section 4.9.

4.8.1 Influences on the measuring signal of the RI sensor
As the RI sensor is a largely unknown detector and little is known of its measuring behaviour in surfactant analysis
general investigations were first carried out. Clarification was sought as to which physical and chemical influences would
influence the measuring signal to different extents.

Influence of the experimental setup
The RI sensor is an optical detector which recognises changes in the reflection and refractive index in its surroundings
(see following points). In order to achieve reproducible measurements it is therefore necessary to optimise the measur-
ing arrangement and then to keep it constant.

Simple experiments in a beaker filled with water show that the RI sensor reacts to alterations in the
• distance from the beaker base
• distance from the beaker wall
• distance from the liquid surface
• distance from the magnetic stirrer bar
• stirrer speed.

Influence of air bubbles
During surfactant titration rapid stirring is used to obtain an optimal mixing of the titrant and sample solution and there-
fore to achieve a rapid precipitation reaction. Vortex formation and air dissolved in water lead to increased bubble
formation. The air bubbles settle on the glass tip of the RI
sensor and produce spurious measuring signals. This is
seen by an increase in the baseline. When the gas bub-
bles leave the glass tip the measuring signal decreases
again.

Influence of the refractive index
As the name RI sensor already states, it can be used to
measure the refractive index of a solution. However, inves-
tigations have shown that only alterations in the refrac-
tive index and not the absolute refractive index can be
measured (Fig. 63). The cause is found in the measuring
electronics, which compensate to approx. 1000 mV each
time the RI sensor is immersed. There is therefore no lin-
ear relationship between the refractive index and the mV
signal. However, as no actual refractive index is neces-
sary for the evaluation of a titration but only the alterations
are to be detected, this has no negative influence on car-
rying out the titration.

From the curves it can be seen that the RI sensor reacts to the alterations of the refractive index. The received signal is
inversely proportional to the refractive index. However, no linear behaviour can be seen. This can be attributed to the
sensitivity of the detector being too low.
Influence of the turbidity

During the titration of an alkyl benzene sulphonate with 0.004 mol/L TEGO trant A100 solution the refractive index was determined with an Abbe refractometer after the addition of each increment of the titrant. During the precipitation titration no measurable alteration in the refractive index was observed.

In the following experiment – the titration of a barium chloride solution with sulphuric acid – only the turbidity of the solution altered. The refractive index remained practically constant.

Experimental conditions:

10 mL 0.05 mol/L barium chloride solution were diluted with water to 20 mL and titrated with 0.05 mol/L sulphuric acid. After each addition, 50 µL of the solution were removed and the refractive index determined with an Abbe refractometer (Fig. 64).

The refractive index remains constant during the titration. The RI sensor produces a jump in the region of the equivalence point. As the turbidity increases, the measuring signal decreases.

The behaviour of the RI sensor when only the turbidity is altered is shown in the following experiment.

Experimental conditions:

Solid barium sulphate is suspended in water and the signal changes are monitored (Fig. 65).

The reduction in the measuring signal as the turbidity increases can be seen clearly. The sinking of the particles when the stirrer is switched off and the associated clearing of the solution can also be clearly observed.

The experiments show that the RI sensor reacts to an alteration in the turbidity. This occurs because of an increase in the reflection of emitted light by the precipitate particles.

This reflection from the particles has the effect that the signal is extremely dependent on the type of precipitate. Before the equivalence point of a precipitation titration is reached, the precipitate is still charged by adsorbed sample molecules and is therefore finely distributed or colloidal. At the equivalence point all charges are balanced and the precipitate can form larger aggregates. It is therefore present in a coarser form. The reflection suddenly decreases. After the equivalence point there is a surplus of standard solution molecules. As a result of their adsorption on the precipitate, repulsion occurs and there is again a finer distribution. The reflection properties change again. A silver chloride precipitation shows this phenomenon.

Experimental conditions:

20 mL of a 0.1 mol/L silver nitrate solution is added to 20 mL of 0.1 mol/L hydrochloric acid. Then 1 mL of a dilute ammonia solution is added. The changes in turbidity are followed with the RI sensor (Fig. 66).

The increase in turbidity and the onset of precipitation can be recognised from the decreasing measuring signal. Fine and coarse precipitates are present. After addition of the ammonia the finely distributed precipitate dissolves. Only coarse particles of silver chloride are now present. The signal of the RI sensor increases. Different types of precipitate have different reflection properties. A finely distributed precipitate reflects the emitted light of the RI sensor better than a coarse precipitate.

For surfactant precipitation this means that the shape of the curve changes. At the equivalence point the precipitate forms aggregates. The previously falling jump in the titration curve changes to a rising one. As the surfactant concentration increases this may proceed to such an extent that the falling part of the curve may no longer be obvious beside the large increase and therefore a false endpoint is indicated.
Experimental conditions:
1.7 mL of a 0.04 mol/L dodecyl sulphate sodium salt solution were titrated with 0.04 mol/L TEGO tran A 100 solution (Fig. 67).

Depending on the precipitation conditions the precipitate forms aggregates after the equivalence point and produces different titration curves under the same concentrations and experimental conditions.

4.9 Comparison between the RI sensor, photometer and Ionic Surfactant Electrode

Does the endpoint at the maximum turbidity correspond to the electrochemically detected endpoint?

In order to answer this question a surfactant titration was carried out with simultaneous detection by all three types of detector (Figs. 68, 69 and 70). Metrohm Ltd., Herisau (Switzerland) provided a special software which allowed this technique to be used.

Different weights of alkyl benzene sulphonate were used as the sample surfactant.

The curves for the highest concentration show the maximum turbidity at the equivalence point of the potentiometric curve. The electrochemical endpoint agrees with the maximum turbidity and the maximum reflection. The detector sensitivity increases from the RI sensor through the photometer to the Ionic Surfactant Electrode. In dilute solution potential changes occur even when there is no clear turbidity change.

The advantages of the optical sensors are found in their mechanical robustness. There is no PVC membrane that can be destroyed mechanically or chemically, e.g. by solvents. Conditioning runs are also not required for optical detectors.

A disadvantage of the RI sensor is its complicated handling, as reproducible values can only be obtained under reproducible experimental setups. The photometer is not affected by this disadvantage because of its defined lightpath.
**Determination of ionic surfactants**

**5 Factors influencing surfactant titration**

5.1 Titration procedure

Special sample preparation is seldom required for potentiometric surfactant titration. In the majority of cases it is possible to weigh the sample directly into the titration vessel. The next step is the addition of the amount of methanol set down in the test method, either 5 or 10 mL, but in special cases even 20 mL or more, to the concentrated sample. The solubility of the surfactants is often better in methanol than in water and therefore the methanol is used at this point either to dissolve the sample or to extract the surfactant from the sample. The necessary amount of water is added and the optimal pH for the titration is set by addition of a buffer solution. In most cases it is not necessary to check the pH again. Only in particular cases where the sample is extremely acidic or basic should the pH be rechecked. In such cases it is better to adjust the pH by the addition of alkalis or acids. If a sample in which the anionic surfactant content is to be determined also contains soaps then it has also proved useful to adjust the pH by the direct addition of an acid. In this case the use of a buffer solution has not been successful.

The titration itself can now be started; it must always be carried out on a modern titrator. In the early days a simpler technique was often used in potentiometry, just as in redox or halide titrations. An electrode was simply connected to a pH or mV meter, equal volumes of titrant added from a burette and the resulting potentials were noted by hand. From the \( x \) (mL) and \( y \) (mV) data a graph was then plotted on graph paper and the point of inflection of the titration curve determined. This technique cannot be used for a potentiometric surfactant titration. The person carrying out such a titration is simply not able to acquire the measured values in the way which is required for the calculation of a surfactant titration because the chemical reaction during a surfactant titration and the response of the surfactant electrode are considerably slower than one is accustomed to from an acid-base titration or a chloride titration.

Surfactant titrations can be carried out without any problems, as is mentioned over and over again in this monograph, but they require the observance and optimisation of all parameters involved. Even details which appear trivial, such as correct stirring and correct mixing with an optimised stirrer, are extremely important in surfactant titration. These parameters can be decisive for the success or failure of a potentiometric surfactant titration. This is why it is absolutely necessary that, if potentiometric surfactant titrations are to be carried out successfully, the contents of the following section, which treats the factors influencing the titration, are taken to heart.

For titration with the Surfactrode Resistant several peculiarities must be taken into account; these are described in detail in section 4.5, which covers the Metro sensor Surfactrode Resistant and explains the general context more closely.

5.2 pH value of the titration

If a two-phase titration is carried out according to the German standard, then the pH is determined by the mixed indicator solution used, which is acidic. If the most important aim of a potentiometric surfactant titration is to achieve results that are as close as possible to those of a two-phase titration, then the same pH as found in the two-phase titration should be maintained. This is best achieved by preparing a dilute sulphuric acid solution similar to the indicator solution used in two-phase titration. The same amount of this acidic solution is added to the diluted sample solution as is used in the DGF two-phase titration test method.

In contrast to two-phase titration, in potentiometric surfactant titration it is possible to adapt the pH of the titration solution to the sample matrix or to optimise it in order to solve a particular problem. This means that there are many new possibilities of determining surfactants better, more optimally and more specifically. Even in mixtures it may be possible to achieve a differentiation by carrying out different titrations at different pH values. The two following tables for anionic (Fig. 71) and cationic surfactants (Fig. 72) show in traffic-light form the ranges in which titrations can be carried out.

![Fig. 71](image1) pH recommendations for the titration of anionic surfactants

![Fig. 72](image2) pH recommendations for the titration of cationic surfactants

The yellow area indicates a range in which a titration can be carried out in principle, green indicates a range in which a titration can be carried out particularly well and which the author can recommend from his own experience. The red bar in the diagram indicates the area in which a titration is not possible or cannot be recommended owing to possible interferences or sensitivity to hydrolysis.

Surphates such as fatty alcohol sulphates or fatty alcohol ether sulphates are anionic over the whole pH range from 1 to 14, and in theory can be analysed at any pH. However, experience shows that a surfactant titration can be carried out particularly well at \( \text{pH} = 2 \) to 4 and optimally at \( \text{pH} = 3 \). The lower pH range of \( \text{pH} = 1 \) or less should be avoided as sulphates can undergo hydrolysis here. The products formed from the fatty alcohol sulphate, fatty alcohol and sulphuric acid no longer have any surfactant properties and lead to low-bias results.
The large group of sulphonates, i.e. alkyl benzene sulphonates, alkane sulphonates, α-olefin sulphonates, are also anionic surfactants over the whole pH range from 1 to 14. Therefore they can also be analysed throughout the whole pH range. Just like the sulphates, an optimal determination can also be carried out at values around pH = 3. Sulphonates cannot be hydrolysed even in strongly acidic solutions so that, if a particular problem makes it necessary, titrations can be carried out in acidic solution, e.g. 0.1 mol/L hydrochloric acid or 0.1 mol/L sulphuric acid solution. This technique can be useful and important, particularly for surfactants such as sec. alkane sulphonates or α-olefin sulphonates. More details are given in sections 7.2.5 and 7.2.6.

Carboxylates, i.e. soaps, can only be titrated in alkaline solutions when they have formed the corresponding salts. The pH above which free fatty acids (Fig. 73) are present as soaps depends very largely on the sample matrix and other constituents in a sample or formulation. To be on the safe side carboxylates should be titrated at approx. pH 10 (Fig. 74). If, for example, a differentiation of soaps in combination with sulphonates or sulphates is to be carried out then two titrations are normally required. A total activity titration is first carried out at pH = 10 in which the total of carboxylate and classical anionic surfactants is titrated. In a second titration the pH is adjusted to 2 and now only the sulphates or sulphonates are titrated. The soap content can be obtained from the difference between the two titrations.

Sulphosuccinate monoesters contain two potentially surfactant-like anionic groups in their molecule. See Fig. 115.

If only the sulphonate group is to be determined in a sulphosuccinate monoester then the pH should be adjusted to 3. The best titration curves are obtained at this pH value: see section 7.2.8. When acidifying the sulphosuccinate great care should be taken because strongly acidic solutions can easily cause ester hydrolysis whereby anionic activity is lost. If several titrations are to be carried out in sequence then pH adjustments should be carried out just before the titration. This means that if a sample changer is used, a second dosing device is required to add the acid or buffer to the sample solution immediately before the titration. If, however, the carboxylate and sulphonate groups of a sulphosuccinate monoester are to be titrated then a pH of between 8 and 10 is necessary. In our laboratory we have made our best experiences at about pH = 9. Care should also be taken here because the ester group of such a sulphosuccinate monoester can also be hydrolysed under alkaline conditions. This is why the same recommendation is made as for titration under acid conditions: pH adjustment should only be carried out immediately before the titration. This technique of carrying out the titration under alkaline conditions can always be recommended whenever a mixture of sulphate or sulphonate is present together with a sulphosuccinate monoester. Two titrations can also be carried out here to obtain a differentiation of the two surfactants; one under acidic and the second under alkaline conditions.

Quats, used here to denote the classical quaternary ammonium compounds such as alkyltrimethylbenzylammonium chloride, dialkyldimethylammonium chloride, cetpyridinium chloride or quaternary imidazolium compounds are cationic throughout the whole range, i.e. they can in theory be determined from pH = 1 to 14. In our laboratory we have made our best experiences with titrations at about pH = 10. An advantage is that at this pH (above 7) only true quats are determined and any remaining non-quaternary starting amine contained in the sample is not determined. This provides a simple possibility for quality assurance or incoming goods control of such a quaternary ammonium compound by carrying out two titrations, one at approx. pH = 10 and the other at pH = 2 to 3. This means that the content of quaternary ammonium compounds and the starting compounds can be obtained by calculating the difference.

Just like the previously described QACs, esterquats are actually cationic throughout the whole pH range and it ought to be possible to determine them throughout this range. Unfortunately the stability of an esterquat is very low in most pH ranges so that an optimal titration of most esterquats can only be carried out in a pH range of 1 to 2. More details are given in section 7.5.5. In contrast to the method described above, in this case the pH should be adjusted as early as possible to ensure the stability of the product up to the titration. There are also special esterquats whose pH-stability is found in a different pH range; these are then to be determined at the pH at which they exhibit their greatest stability. In this case the data sheet provided by the raw material manufacturer should be studied to obtain information about its stability as a function of the pH value.

Fatty amines and fatty amine ethoxylates are only cationic in the pH range in which they are present as a salt in protonated form. Most representatives of this class of products can be titrated best in a pH range of 3 to 4. There is also the possibility that they must be more strongly acidified. With fatty amine ethoxylates, i.e. addition products of polyoxymethylene and fatty amines, some care should be taken because these only possess cationic properties up to a certain number of POE groups in the molecule and only these can be titrated. If the proportion of POE groups in the molecule becomes too large then these behave like nonionic surfactants and can also only be determined in this form. If fatty amine ethoxylates are to be determined in formulations then the pure product must in any case be titrated to see whether it fulfills the titrability criteria.

Betaines cannot be titrated under the conditions described here. If, however, anionic surfactants are to be determined in formulations which also contain betaines then the betain may interfere. However, this can only occur in the range in which the betain is protonated, which is partially the case at pH = 2.5; at pH = 1 and below, protonation is quantitative. If a titration solution containing both a betain and an anionic surfactant in which the anionic content is to be determined is set to a pH between 3 and 5 then an interference-free titration is guaranteed.
5.3 Sample weight

In a potentiometric surfactant titration the correct sample weight is very important for the attainment of a correct result. If the sample weight is too small the possibility of errors is ever-present; these errors always manifest themselves in the form of low-bias results.

Fig. 75 shows this using an approx. 25% commercially available fatty alcohol ether sulphate 2.5 POE as an example. A two-phase titration was first carried out and the determined content of 26.6% was used as the 100% value in the graph.

From the graph it can be seen that approx. 40 mg of the fatty alcohol ether sulphate must be weighed in to obtain correct and constant results comparable with the results of a two-phase titration. A further difficulty is that the corresponding titration curves become increasingly worse as the sample weight increases. This means that if the connections between the sample weight and the correctness of the analytical results are not known it is very easy to make mistakes. If only a small amount of the sample substance is weighed in to obtain good curves then low-bias analytical results are obtained. Fig. 76 shows some of the 1st derivative curves of the titration of fatty alcohol ether sulphate with TEGO tranA100.

The relationship between the results and the sample weight depends to a large extent on the hydrophilic groups in the molecule. The higher the number of hydrophilic groups in the molecule, in this case the number of POE units, the higher must the sample weight be in order to obtain correct results.

An additional criterion is the alkyl chain distribution in the oleophilic part of the molecule. The shorter the alkyl chain and the wider the range of distribution of the various alkyl chains, the higher the sample weight which must be selected in order to obtain correct results.

A crass dependence on sample weight, practically the «worst case» model, is found with ammonium cocoylsulphate (Table 9), a fatty alcohol sulphate based on natural coconut oil, with ammonium as counter ion (see also section 7.2.3).

Table 9 Titration of alkyl sulphates C₈-C₁₈ distribution (coco)

<table>
<thead>
<tr>
<th>Sample weight (mg)</th>
<th>Endpoints (from 1st derivative)</th>
<th>WAS content (mean value, %)</th>
<th>Standard deviation (%)</th>
<th>Rel. standard deviation (%)</th>
<th>No. of titrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1/1</td>
<td>24.71</td>
<td>0.80</td>
<td>3.22</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>1/1</td>
<td>27.15</td>
<td>0.73</td>
<td>2.70</td>
<td>6</td>
</tr>
<tr>
<td>15</td>
<td>1/1</td>
<td>28.46</td>
<td>0.19</td>
<td>0.66</td>
<td>6</td>
</tr>
<tr>
<td>22</td>
<td>1/1</td>
<td>28.97</td>
<td>0.25</td>
<td>0.85</td>
<td>6</td>
</tr>
<tr>
<td>30</td>
<td>1/2</td>
<td>28.92</td>
<td>0.12</td>
<td>0.41</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2/2</td>
<td>33.50</td>
<td>0.17</td>
<td>0.52</td>
<td>6</td>
</tr>
<tr>
<td>45</td>
<td>1/2</td>
<td>28.95</td>
<td>0.03</td>
<td>0.12</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2/2</td>
<td>33.01</td>
<td>0.06</td>
<td>0.18</td>
<td>6</td>
</tr>
<tr>
<td>60</td>
<td>1/3</td>
<td>25.12</td>
<td>0.08</td>
<td>0.32</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2/3</td>
<td>29.00</td>
<td>0.07</td>
<td>0.24</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>3/3</td>
<td>33.12</td>
<td>0.06</td>
<td>0.17</td>
<td>6</td>
</tr>
</tbody>
</table>

All titrations were carried out with TEGO tranA100 as titrant, and all titrated solutions had a total volume of 100 mL.

In these titrations it is also very noticeable that sometimes several points of inflection were detected which are not artifacts but have an astonishing reproducibility, as can be seen from the standard deviations given in Table 9.

This is why several significant titration curves in this series should be examined carefully (Figs. 77, 78, 79 and 80).
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Fig. 77: Titration of alkyl sulphate C₈-C₁₈ distribution (coco) with a sample weight of 5 mg

Fig. 78: Titration of alkyl sulphate C₈-C₁₈ distribution (coco-) with a sample weight of 10 mg

Fig. 79: Titration of alkyl sulphate C₈-C₁₈ distribution (coco) with a sample weight of 15 mg

Fig. 80: Titration of alkyl sulphate C₈-C₁₈ distribution (coco-) with a sample weight of 20 mg
It is plain to see that with lower sample weights, i.e. at lower concentrations, only 1 point of inflection is detected. At a larger sample weight of approx. 15 mg the titrator already detects 2 points of inflection, and 3 points of inflection are only detected from a sample weight of approx. 20 mg. If the sample weight is increased still more no further alterations occur, neither to the shape of the curve nor to the result. According to the theory that in potentiometric surfactant titrations the titration is carried out according to decreasing oleophilicity these 3 points of inflection can be characterised as follows:

1st point of inflection = alkyl sulphate C<sub>10</sub> (dodecyl sulphate) and higher than C<sub>12</sub>.  
2nd point of inflection = alkyl sulphate C<sub>12</sub> (decyl sulphate)  
3rd point of inflection = alkyl sulphate C<sub>8</sub> (octyl sulphate)

To confirm these findings we carried out an acidic sulphate decomposition on the ammonium cocoyl sulphate and examined the resulting fatty alcohols by gas chromatography. In this way the results of the titration regarding the definition of the three points of inflection found could be confirmed.

If instead of TEGO trant A100 the titrant Hyamine 1622 is used then the results are markedly lower because the approx. 8% octyl sulphate found in the sample is either not determined at all, or only partially.

It is not a dependency on the sample weight, as described here, but rather more of a dependency on the concentration. However, as sample weight and concentration are linked to each other we have chosen to use the term sample weight dependency, particularly as surfactant titration is normally carried out using a sample changer. In order for the electrodes to be properly immersed in the sample solution and for the stirrer to function optimally a total titration solution volume of 100 mL has proved itself in practice for many years. If a total titration solution volume of only 50 mL is used instead of the 100 mL solution we use then the sample weight must also be reduced by half in order to obtain correct results.

The conclusion to be drawn from the many thousand titrations carried out in our laboratory is that if 100 mL sample solution is used together with a titrant solution of 0.004 mol/L then the sample weight should be selected so that a titrant consumption of about 10 mL or more is obtained. The ideal range has proved to be 10 to 16 mL. This applies to 100 mL has proved itself in practice for many years. If a total titration solution volume of only 50 mL is used instead of the 100 mL solution we use then the sample weight must also be reduced by half in order to obtain correct results.

The low-bias results obtained by using too low sample weights have been determined in many investigations and agree with reports from other laboratories concerning the same problem. In contrast, Buschmann has reported a contrary finding, i.e. high-bias results with too low sample weights.

A sample weight dependency has been observed with almost all detection methods in titrations involving ionic surfactants. They occur in titrations in aqueous solutions with the High Sense Surfactant Electrode, the Ionic Surfactant Electrode, in potentiometric titration in two-phase media with the Surfactrode Resistant and in photometrically indicated surfactant titration in aqueous media.

We have no experience of our own concerning high-bias or low-bias results with low sample weights in titrations with the Refractrode, nor have we been able to find any references in the literature involving this topic.

5.4 The titrant

The titrant is extremely important in potentiometric surfactant titration. The titrant has the job of precipitating out the sample surfactant or analyte quantitatively. This quantitative precipitation is a precondition for a correct analysis. Only a complete precipitation produces large potential differences from the start to the end of the titration. The cationic titrant Hyamine 1622 or N-benzyl-N,N-dimethyl-N-[4-(1,1,3,3-tetramethylbutyl)-phenoxyethoxethyl] ammonium chloride, Fig. 81, which is used as the standard titrating agent in two-phase titration, is not particularly suitable for potentiometric surfactant titration.

Apart from the quaternary ammonium group, which provides the surfactant properties, there are two other polar groups in the molecule, the ether bonds.

In this case the titrant TEGO trant A100, 1,3-didecyl-2-methylimidazolium chloride, is far more suitable. With its excellent water solubility this product has a clearly defined hydrophobic part in the form of two decyl groups, as shown in Fig. 82.

Precipitation products with this cationic titrant and the anionic surfactants to be titrated are only slightly soluble, considerably less than those with Hyamine 1622, as shown in Figs. 83, 84 and 85. This product also has optimal properties concerning interactions with the oleophobic PVC membrane. This is particularly true for the Metrosensor Ionic Surfactant Electrode because the development and optimisation of this titrant was carried out particularly with the properties of the Ionic Surfactant Electrode in mind. Significant differences between the two titrants can be seen in the comparative titration of pure-chain fatty alcohol sulphates with an alkyl chain length of C<sub>8</sub>, C<sub>10</sub> and C<sub>12</sub>.

While the fatty alcohol sulphates (also known as alkyl sulphates) with a C<sub>8</sub> chain (octyl sulphates) cannot be determined at all with Hyamine 1622 as titrant, an easily evaluable potential jump is obtained with TEGO trant A100. Quantitative measurements have shown that up to 98% of the octyl sulphate is determined in this titration. In the titration of C<sub>10</sub> fatty alcohols (decyl sulphates) and C<sub>12</sub> alkyl sulphates (dodecyl sulphates) the advantages of using TEGO trant A100 as the titrant are even more obvious.
titrant are even more evident. The titration curves are steeper and the potential differences larger. A different titrant for anionic surfactants often mentioned in the literature is cetylpyridinium chloride. The potential differences and the slopes of the curves obtained with this titrant lie between those of Hyamine 1622 and TEGO trant A100.

A cationic titrant has to fulfill a number of requirements. On the one hand the alkyl chain must be uniform; this means that under no circumstances should there be a mixture of C_{12} or C_{14} alkyl groups, and on the other hand it is very important that the product has a degree of quaternisation of 100%. If this is not the case then the titre of the reagent depends on the pH at which the titration is carried out. If a degree of quaternisation of 95% is assumed, as is the case for a very large number of quaternary ammonium compounds, then this means that under alkaline conditions the titration is carried out with only this 95% while under acidic conditions the surfactant-like original amine is also involved. This means that the titres differ by approx. 5% between pH = 10 and pH = 2. This means that the titre must be determined for each pH range in which titrations are to be carried out. This is why only the three titrants described here should be used:

1. TEGO trant A100
2. Cetylpyridinium chloride
3. Hyamine 1622

TEGO trant A100 is a new titrant which has been developed specially for potentiometric titrations using surfactant indicator electrodes. Particularly interesting properties with truly synergistic effects result from its use with the Ionic Surfactant Electrode. Its applicability is clearly extended when compared with other titrants, particularly for surfactants which are difficult to titrate such as alkyl sulphates with lower alkyl chains or those with a higher hydrophilicity such as fatty alcohol ether sulphates. Even surfactants whose endpoints are difficult to recognise in two-phase titration can be easily titrated. Steeper titration curves mean better evaluation by the titrator algorithms and thus better standard deviations. By the selection of suitable titration conditions it is even possible, within certain limits, to differentiate between surfactants with different alkyl chain lengths.

The use of TEGO trant A100 makes it possible for the first time to learn more about potentiometric surfactant titrations. Thus, it has been clearly shown that surfactants are titrated according to decreasing oleophilicity. In our experience a 0.004 mol/L TEGO trant A100 has proven highly suitable for the titration of anionic surfactants, but 0.02 mol/L solutions are also occasionally used. Cationic surfactants of the quaternary ammonium compound type are very strongly substantive. In a way similar to the properties of fabric conditioners, which attach themselves to fibres during the rinsing process, cationic titration solutions also have the ability to attach themselves to glass or plastic surfaces (Fig. 5). If a solution of TEGO trant A100 or another cationic surfactant is prepared, filled into the exchange unit of an automatic burette and the titre of the solution is then determined immediately, then this titre will differ significantly from the value determined after a lapse of 24 hours. However, substantivity, i.e. the attractive behaviour, leads to the surfaces becoming saturated by the surfactant. Our experience has shown that it is a good idea to allow the apparatus coming into contact with the cationic titration solution to remain in contact with this solution for 24 hours. All the surfaces are then saturated, and this apparatus should then be used continually without rinsing. Waiting periods no longer need to be observed. During the attraction of the cationic surfactants to the negatively charged surfaces the ionic hydrophilic groups of the surfactant are oriented towards the surface and the hydrophobic alkyl chains towards the gas phase. This means that the apparatus has a greasy appearance. This apparent greasiness must be accepted. Rinsing with an anionic surfactant or an alcohol would remove the attached surfactant from the surface again.

Such a clear favourite as for the titration of anionic surfactants does not exist for titrating cationic surfactants. Dodecyl sulphate, which is available commercially at a high degree of purity, is often used. For some applications bis-2-ethylhexyl sulphosuccinate is more suitable. The use of linear alkylbenzene sulphonate has advantages for some samples. When a large number of different surfactant titrations are to be carried out in a single laboratory it is beneficial to have all three...
titration solutions ready for use. If only a few or only certain standard surfactants are to be titrated then dodecyl sulphate is recommended as it is the most universal of the three. Bio-2-ethylhexyl sulphosuccinate has the advantage that it produces correct results at very low concentrations.

In product development or for new substances a titration should always be carried out with each of the different titrants. The titrant that shows the largest potential jump from the start to the end of the titration and usually also has the greatest slope should then be used for subsequent titrations. The following method can be used for the rapid test of the suitability of a titrant:

Equal amounts of the surfactant to be titrated are added to three beakers, diluted with equal amounts of water and then the same amount of one of the three different titrants mentioned above is added to each beaker. The titrant which produces the greatest turbidity is usually the most suitable one for the titration.

No compromises whatsoever should be made when selecting the optimal titrant.

The best titration curves are produced when the analyte is dissolved in pure water and no other secondary constituents are present. In real samples this «stroke of luck» rarely happens and other constituents in the sample cause a reduction in the total potential difference and the slope of the curve so that the selection of the optimal titrant right from the very beginning is extremely important.

If the titration curves or, even better, the derivative curves of various surfactants recorded under fixed and reproducible conditions are examined closely, then it can easily be seen that these vary quite considerably from surfactant to surfactant. Some have very steep curves whereas some curves are so flat that excessive demands are placed on the titration algorithm. Examples of steep titration curves are alkyl benzene sulphonates or alkyl sulphates. Typical representatives of surfactant groups which produce flat titration curves are the paraffin sulphonates (sec. alkane sulphonates) or the sulphosuccinate monoesters.

However, if the structure of the surfactant to be titrated has such a large influence on the quality of the titration curve then it must be expected that the structure of the titrant has a similar influence. This means that there is an additional factor for improving titrations, as it is obvious that the evaluation algorithm of a titrator produces better results with steeper titration curves. During the development of the modern titrator generation, great attention was naturally given to the evaluation algorithms for titration curves as obtained, for example, in acid-base or redox titrations. Comparative measurements clearly show better standard deviations for steep titration curves, such as those shown in Fig. 87.

5.5 Sensors, surfactant electrodes

Naturally not all pH electrodes are the same. However, if an acid-base titration is to be carried out then pH electrodes from different manufacturers are interchangeable. This interchangeability is not possible between the surfactant electrodes currently on the market. This is why an application with a surfactant electrode made by X cannot be transferred to an electrode made by Y.

With surfactant electrodes we are dealing in virtually all cases with so-called liquid membrane electrodes based on plasticised PVC. The membrane contains an ion-active substance, the so-called ion carrier. Uniformity is limited to this single point. Surfactant electrodes from different manufacturers differ greatly in their response rate, the total potential difference during a surfactant titration, in their robustness and also in their service life. The first two points in particular, the response rate and the total potential difference, are extremely important criteria for the successful performance of a titration in an acceptable time span. It is also an advantage for the evaluation algorithm of the titrator if as large a potential change as possible takes place in as small a volume range as possible. These differences all result from the «fine differences» in the membrane composition, where the chemical structure of the ion carrier is naturally decisive for the detection mechanism.

There are also different designs of surfactant electrodes. The first is the standard electrode with a thin PVC membrane at its base; the other type on the market is the coated wire surfactant electrode. This latter is a relatively unusual design which, however, has clear advantages over the classical type for some applications. Which electrode type will establish itself still remains to be seen.

A reference electrode belongs to each surfactant electrode. The selection of a suitable reference electrode is just as important as the surfactant electrode itself for proper functioning and a good response during the titration. The less time available for the production of the analysis result, the more important the selection of the correct reference electrode. For surfactant titrations many authors recommend the double junction electrode, which has a large ground glass joint as the outer diaphragm. We do not think that this electrode is very suitable because it is exactly this rough, large ground surface which rapidly becomes coated by the ion associate that is precipitated out during the surfactant titration. This
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without knowing the chemical mechanism on which the detection was based. Even the ASTM lays down an NO₃-sensitive electrode for the potentiometric determination of anionic surfactants, although even here no mention is made of the detection method on which it is based. However, it seems to work. An astonishing number of literature references describe how it is possible to make surfactant electrodes by oneself. This allows conclusions to be drawn as to how interesting potentiometric surfactant titration methods appear to the authors. In our own tests we were quickly able to see that a lot of experience and routine were necessary before such electrodes could be made reproducibly. Many of these electrodes could not be used at all, or they only worked for a few titrations.

It was certainly a move in the right direction when commercial manufacturers started to produce surfactant electrodes. This guarantees that an analytical method can be carried out in the same manner after the electrode has been changed. This applies particularly with respect to GLP, ISO 900X and Quality Management (QM). In the meantime there are at least three commercially available special surfactant electrodes on the market which are called either surfactant-selective or surfactant-sensitive, depending on the manufacturer. The term «sensitive» is more correct as the electrodes respond to all large, voluminous ions that possess a certain degree of oleophilicity.

The membrane of a surfactant electrode consists of PVC, a plasticiser and a so-called ionophor or ion carrier. These represent the real electroactive components. Potential formation takes place owing to an interaction between the ion carrier in the membrane and the ions in the titration solution. In an equilibrium reaction this interaction leads to a potential difference at the phase boundary between the titration solution and the electrode membrane, which is measured in the virtual absence of current by a normal reference electrode. The extent of the ion transfer depends on the concentration. The relationships are described by the Nernst equation which is surely one of the most important equations in the field of electrochemistry (Equation 1, section 1.13).

Surfactant ions, no matter whether those of the surfactant to be determined or those of the titrant, must therefore have the possibility of penetrating into the membrane at the titration solution/electrode membrane phase boundary in order to create the potential differences that are necessary for detection. The membrane of a surfactant electrode for use in aqueous media consists at least 98% of PVC and plasticiser.

The Metro sensor Surfactrode Resistant does not have a PVC membrane. The electroactive substance is fixed in the graphite base. In this case the solvent which is present during every titration with the Surfactrode Resistant has the task of transporting the surfactant ions to be detected to the electroactive substance.

5.6 Titrator concept

It may sound a little dramatic, but the titrator and the correct titrator design play a highly important role in carrying out a surfactant titration without any problems. Knowledge about the titrator itself is also required as well as about the possibilities it offers for optimising the titrations such as, e.g., the titration mode: linear titration with constant volume increments or dynamic titration. It has been shown that dynamic titration is nearly always the best mode for performing surfactant titrations – simply because it yields interference-free curves that are easy to evaluate. The correct setting of the dynamic parameters, the criteria for the acquisition of the measured value, the observation of waiting periods, the definition of the smallest or largest volume increments to be added are of great importance.

The following graphs show the size of the volume increments for each titration step. Fig. 88 shows a poorly optimised titration. The size of the volume increments hardly decreases as the endpoint is approached, the first derivative is flat and broad, the evaluation is difficult and inexact. Fig. 89 shows a well optimised titration; the size of the volume increments clearly is at a minimum at the endpoint. In this case exact evaluation by means of the titrator algorithm is easily possible.

All these are factors that must be taken into account in order to carry out a titration in the acceptable time span of five to seven minutes with a low standard deviation. The inexperienced titrator operator has very little chance. This is why it would be a good idea if the titrator manufacturers were to supply methods for surfactant titration already implemented in the titrator system. Before you make a decision on the purchase of a titrator you should speak with the application chemists in the manufacturer’s laboratories and convince yourself that they have the required know-how for carrying out surfactant titrations and that you will receive application support in creating your own methods.

![Fig. 88: Example of a poor titration shown as a bar graph](image)

![Fig. 89: Example of a good titration shown as a bar graph](image)
The titration curves which may be produced in a surfactant titration with different products can be very different. However, they can be allocated to one of three large groups:

1. Titration curves that have a very steep slope and whose point of inflection corresponds to a sharp peak in the first derivative curve.
2. Those with a medium slope in which the peak of the derivative curve is somewhat more rounded.
3. Those with a slight slope in which the peak of the derivative curve covers a larger volume range.

For these three types of titration curves three different methods are required which clearly differ from each other in the criteria mentioned before such as measuring point density, dynamic control, smallest volume increment, etc.

The reaction rate of a surfactant titration is significantly lower than that of an acid-base or redox titration. The response characteristics of a surfactant electrode are also not comparable to that of a normal glass electrode. This is why you need a certain number of measuring points in the region around the inflection point. If this number is too low then the inflection point will either not be recognised at all or incorrectly determined. If the number of measuring points is too high it can easily happen that the titrator algorithm evaluates two or three inflection points instead of a single one. If the titrator algorithm splits a single inflection point into two or three then none of these will be correct. If you have this type of problem then you should optimise your method even further by reducing the measuring point density and then carry out a further titration.

Once the three methods discussed above have been stored in your instrument then, if the titration parameters are not optimal, you can simply switch to one of the other methods.

In order to assess a titration correctly both the original titration curve and the first derivative curve should be used for interpretation. This can either be carried out on the screen of the computer used to store the titration data or on the titrator printouts.

Most of the titrators on the market today are equipped with high-performance power processors. Today’s normal onboard technology ensures that the titrators are very rapid, often rather too quick for surfactant titration. In our laboratory we were faced with the problem that under drift-controlled measurement acquisition the titrator recognised constant measuring values which were below the drift values set on the instrument. In reality the potential change following addition of a volume increment had not yet occurred. This problem can be avoided by suitable titrator settings; it must not be ignored.

If the titrator is to be used for more than just routine titrations for the determination of surfactant concentrations then it is strongly recommended that the titrator be connected to a PC. Most titrator manufacturers offer special data communication programs for storing all raw data and measuring data of the titration. With values stored in this way the results can be transferred together with the required raw data, e.g. to a laboratory information management system (LIMS). Good programs such as Vesuv® or TiNet® include database systems that allow data storage and special evaluation procedures.

It is also important that all raw data that are measured while the titration curve is being recorded and that are used to calculate the titration curve remain available so that further operations can be carried out with this raw data. While the titration curves printed out by the titrator are always produced from smoothed, sometimes from strongly smoothed or even from “ironed” measuring data, the raw data are the original data. Only when original data are used is there any sense in producing the graphs shown above or the so-called GREX plot Figs. 90 and 91, which permits a critical assessment of the titration.

* GREX is a DOS software, but will shortly be available in a Windows™ version.

Only these data allow you to determine whether the titration parameters have been set optimally or whether further optimisation is necessary (Fig. 92 and Fig. 93).

The newest generation of programs under Windows, above all TiNet®, provide a large range of possibilities with which evaluations can be carried out according to different criteria. With such programs it is also possible to carry out evaluations as if “by hand”, by constructing tangents and allowing the program to calculate the endpoint of a titration with them. For each point in a titration curve calculated by the program it is possible to produce the corresponding data such as the potential in mV and titrant consumption in mL. Today it is a matter of course that all “manipulations” are documented in a manner conforming to GLP and that the original data remain unaltered. It is very useful to allow such a
program to be demonstrated to you; it is even more useful to own such a program and use it. Without the transfer of all titration data to a PC system and corresponding reprocessing with the above-mentioned programs, the development of the surfactant electrodes that are available today would not have been possible. The additional knowledge obtained from the titrations and presented in this monograph has only been gained by storing all raw data and subsequently processing them with special evaluation programs and improved possibilities for the assessment of the relevant facts.

5.7 Initial dosing

A start volume, also known as initial dosing, is to be understood as being the addition of the titrant at the start of a potentiometric titration. In normal titrations, such as acid-base or redox titrations, the start volume can equal 75 to 90% of the expected total titrant consumption. During addition of the start volume no measurements are made. This means that, apart from the total volume of the start increment, no other data that could be used for the evaluation of the titration are available. If the endpoint of the titration is already reached within this start volume then the microprocessor of the instrument will not notice it. This is why after a start volume has been added a test should always be carried out to check whether the measured mV value still signals a condition before the titration endpoint. This test is always a good idea in combination with an IF statement, in which depending on the measured potential a decision is made whether the titration should be carried on or broken off.

Working with a start volume has proved very useful in the daily routine of quality assurance laboratories. The time required for carrying out a titration is significantly reduced without any loss of accuracy. This is why working with a start volume is regarded as being the state of the art in all laboratories in which the same products are always titrated and whose specifications lie within a narrow range.

This is not the case in surfactant titrations. Here the technique of adding a start volume leads to incorrect results. The way in which this happens has not been completely explained up to now. However, it is a fact that the errors that occur after addition of a start volume increase as the range of alkyl chain distribution of the surfactant to be analysed increases. In the titration of surfactants with pure alkyl chains, such as are used for setting the titre, these errors practically never occur. The following reason for the occurrence of this error is conceivable. In potentiometric surfactant titrations the surfactants are titrated according to decreasing oleophilicity. It is possible that, if the titrant is added rapidly as when a start volume is added, there is a short-term local excess of titrant and this interferes with the precipitation reaction. This could already cause surfactants with shorter alkyl chains to be precipitated out. The remaining period for the titration may then be too short for the more stable condition to be achieved with the less dissociated ion associate formed of long chain sample surfactants and the analyte.

Our vast experience has shown that the technique of initial dosing cannot be recommended for surfactant titrations. It should only be used when, as a result of comparative titrations, it can be guaranteed that no error in the titration of the particular surfactant being analysed arises from the addition of a start volume. These comprehensive investigations are only worthwhile if particular surfactant samples are to be determined repeatedly in large numbers.

By optimising both the titration parameters and the titration process as a whole the time required for a titration is reduced to a reasonable value. In this way a double determination can be carried out in 10 to 15 minutes.

For a long time now the author has been asking the manufacturers of titrators to market a titrator that takes into account the distinctive features of surfactant titration. At the start of 1997 Metrohm Ltd. introduced their new flagship in the titration sector, the 726 Titroprocessor, which incorporates and fulfils almost all the author’s requirements. The creation as well as the optimisation of methods for surfactant titration has become extremely simple. It even allows an inexperienced operator to rapidly put together exactly the method required. This saving in time is a particular advantage for plant laboratories, where there is never a lot of time available for carrying out long experiments.

The compactness of the 726 also impresses. This titrator, which can be seen as the successor to the 670 Titroprocessor, allows a rapid switch-over to be made to one of the most modern titrators without having to completely revise one’s way of thinking. The 726 Titroprocessor is extremely well regarded in my laboratory.

However, life is unjust. Just as important requirements have been fulfilled new ones immediately appear. The 726 Titroprocessor and the 796 Titro have so-called memory cards. These are electronic storage media on which sample-specific data as well as complete methods can be permanently stored. The cards available today already have methods for surfactant titration stored on them. However, there is still room for improvement. The target must be that the operator has all relevant methods for surfactant titration stored on these cards together with all available detection methods. The optimisation work for the production of these titration methods should be carried out by the instrument manufacturers for the benefit of their customers. This would again provide particular help for the permanently overloaded quality assurance laboratories that could then again concentrate on their main task of carrying out quality assurance analyses as quickly as possible.
5.8 Stirrer requirements

The stirrer also has an important influence on carrying out a potentiometric surfactant titration. The optimal positioning of the stirrer ensures that the titration solution is rapidly and reliably mixed and that the added titrant volume increments are distributed as rapidly and uniformly as possible without the formation of a vortex and air entrainment. The magnetic stirrers used with many titrators, particularly those without a sample changer, do not fulfil this criterion. They distribute the volume increment much too slowly, and at increased stirrer speeds a vortex is easily formed with air entrainment. Air bubbles prefer to attach themselves firmly to the oleophilic PVC membrane and interfere with the acquisition of the measured value, which falsifies the measurement. Only propeller stirrers are suitable, but even here there are different designs whose suitability for surfactant titration differs from one to the other. The manufacturers of titration systems are aware of these special stirrer requirements for surfactant titration and will offer the correct stirrer. However, even the correct stirrer must have the correct settings. This is done when a titration is not being carried out by reducing the stirrer speed from its maximum until no vortex formation is observed. This stirrer setting should be noted or marked on the instrument. More modern stirrers have a scale division and this scale value should be included as a fixed value in your surfactant titration testing method, as this value is important for the optimal performance of the titration and for obtaining a correct result.

In titrations in two-phase media with the Surfactrode Resistant the stirrer is almost the decisive factor. In this type of titration the stirring must be so intensive that the aqueous phase and the water-immiscible organic phase form a stable emulsion. Only then can a good and sufficiently rapid detection and the resulting smooth titration curves be obtained. Such a titration cannot be carried out with a magnetic stirrer. The higher the proportion of solvent in the titration solution, the greater the demands placed on the stirrer.

5.9 Addition of alcohol

Many formulations contain alcohols, sometimes in considerable concentrations. Medical skin disinfectants contain up to 70% ethanol or also 2-propanol, with a quaternary ammonium compound content of only 0.1%. Even these products can be titrated without any problem with the Ionic Surfactant Electrode. The following limiting concentrations of alcohols, referring to solutions ready for titration, have been determined to be non-critical for approx. six titrations in sequence:

- 30% methanol
- 15% ethanol
- 10% 2-propanol
- 3% glycerol
- 3% 1,2-propanediol
- 3% 1,3-propanediol
- 3% benzyl alcohol
- 10% sorbitol

* In earlier publications the value given was 3%, but according to recent investigations 10% is practicable.

If you are using a surfactant electrode from a different manufacturer it is essential that you ask about the alcohol tolerance of the electrode. Take care because high alcohol concentrations can rapidly destroy an electrode.

Alcohol is also deliberately added to the sample solution because its addition can achieve a range of positive effects. Normally the alcohol used is methanol and corresponds to a volume concentration of approx. 5 to 10% of the titration solution. By addition of alcohol the special physicochemical properties of surfactants can be influenced in a positive way. A limitation of the surface-active properties and therefore a limitation of the substantivity can be achieved. Intermediate dilutions can also be more easily prepared and are simpler to handle if they contain alcohol. In addition the tendency for foam formation is much smaller, and any foam formed collapses more quickly. This means that long waiting periods are no longer necessary when an intermediate solution has to be filled up to the calibration mark. During the titration the alcohol additive has the effect that fewer air bubbles are entrained in the solution; any air bubbles which may be present exist for a shorter time and their tendency to deposit on the oleophilic membrane is minimised. This results in considerably reduced interferences during the titration; the electrodes remain cleaner and the handling as a whole is much simpler, both during the preparation of the titration solution as well as during the titration.

If the concentration of alcohols increases beyond the limits given then the titration curves become poorer, i.e. flatter, which leads to poorer standard deviations. The best experience has been made with a volume concentration of 5 to 10% methanol or from 3 to 5% ethanol by volume.

In titrations with the Surfactrode Resistant™ matters are again different. The electrode tolerates practically all solvents. Here it is important that the solvent in the sample or the deliberately added solvent and the water form two phases. This formation of two phases which are immiscible or only slightly miscible is the precondition for carrying out the analysis. This electrode cannot be used in purely organic solvents, not even in pure alcohol or acetone. The content of solvent immiscible with water should ideally amount to approx. 10% of the total titration volume. However, it can be increased up to almost 50%. This limit of 40 to 50% of the total titration volume has nothing to do with the stability of the electrode, but results simply from the ability of the stirrer system to mix the two phases to form a homogeneous emulsion. According to our experience this is no longer possible at higher concentrations.

5.10 Relationship between the chemical structure of a surfactant and the quality of a titration

If the chemical structure of the titrant used, as mentioned above, clearly influences the surfactant titration, then it is only natural that the chemical structure of the analyte also has an influence. Of course, in this case the analyst has no possibility of affecting any changes. Nevertheless it is important to know the relationships in order to be able to optimally adjust all those parameters that can be altered to suit the particular problem to be solved.

The differences that arise from the chemical structure in surfactant titration can be clearly indicated in a comparison between two fabric softeners. A first-generation fabric
softener based on dimethyldistearylammonium chloride is shown in Fig. 94.
In this molecule only the quaternary nitrogen acts as a hydrophilic group and provides the surfactant properties. There are two long, well-structured alkyl chains present as the oleophilic groups. In comparison the chemical structures of several esterquats, belonging to the modern generation of fabric softeners, are shown in Figs. 135 to 138.

In order to achieve better biodegradability and better wettability of treated textiles, a predetermined breakage point, a hydrophilic ester group, has been built into the alkyl chains of this fabric conditioner. However, this results in a better solubility of the ion associate formed during the titration and also a poorer interaction with the oleophilic PVC membrane of the surfactant electrode. The titration curves of the two compounds differ accordingly, see Figs. 95 and 96.

The dimethyldistearylammonium chloride produces a truly ideal titration curve with a slope which almost approaches that of an acid-base titration. The total potential difference here is approx. 250 mV. The titration curve of the esterquat recorded under comparable conditions is considerably flatter with an approx. 70 to 80 mV lower potential difference. In the derivative curves this variation can be seen even more clearly. The discontinuities in the esterquat curve are due to the fact that this fabric softener does not correspond to the ideal chemical structure shown but also contains considerable amounts of mono- and ternary-substituted quaternary ammonium compounds.

If the titration curve of a fatty alcohol sulphate is compared with that of a fatty alcohol ether sulphate then it can be clearly seen that the pure fatty alcohol sulphate gives the best titration curve, and that in the fatty alcohol ether sulphates the curves become increasingly poorer as the number of polyoxyethylene units in the molecule increases. To summarise it can be said that good or very good titration curves can always be expected if:

1. The hydrophilic group determining the surfactant activity is the only polar group in the molecule. The more polar groups in the molecule can be determined quantitatively and correctly. More highly ethoxylated fatty alcohol ether sulphates were also a poorer interaction with the oleophilic PVC membrane.
2. If the alkyl chain is too short or if the alkyl chain contains polar groups.
3. The product is readily soluble in water.

Poor titration curves can always be expected:

1. If other hydrophilic groups apart from those determining the surfactant activity are present in the molecule. The more polar groups the molecule contains, the poorer the titration curves to be expected. The same also applies for too many polyoxyethylene units in the molecule. Similar effects are also known from two-phase titrations. At some stage such products with a large number of POE groups no longer react as ionic but only as nonionic surfactants. A fatty alcohol ether sulphate with statistically 10 POE units in the molecule reacts analytically like a nonionic surfactant. Such a substance cannot be determined by either two-phase titration or potentiometric surfactant titration.
2. If the alkyl chain is too short or if the alkyl chain contains polar groups.

In titrations with the Surfactrode Resistant the influences are similar but much less marked. The fatty alcohol ether sulphates can be taken as an example. With the Surfactrode Resistant even fatty alcohol ether sulphates with statistically 12 mol POE in the molecule can be determined quantitatively and correctly. More highly ethoxylated fatty alcohol ether sulphates were not available for test measurements, so that it is not currently possible to make any statements. In almost all cases, even surfactants about which either only a little or nothing at all is known can be titrated correctly with the Surfactrode Resistant. This applies not only to raw materials but also to the far more important formulations. Information about the structure of the surfactant or surfactant mixture to be analysed is missing in many cases when competitors’ products are being analysed. In these cases a two-phase system titration with the Surfactrode Resistant is to be preferred to titration in aqueous media.

### 5.11 Influence of common salt and other electrolytes

**Titrations in aqueous media**

Like almost all substances present in a potentiometric surfactant titration, electrolytes such as sodium chloride also have a negative influence on surfactant titration. However, this influence is not relevant for most of the samples to be titrated because a salt concentration which would produce a measurable alteration is reached neither in the sample nor during the pH adjustment. Higher salt concentrations in the titration solution do not lead to incorrect results in the form of high-bias or low-bias results, but they do alter the slope of the titration curve. This usually causes the standard deviation to become worse. This also depends on the concentration of the electrolyte, just as for virtually all other substances that show this influence, as can be seen in Fig. 97.

Here it can be seen that a very steep titration curve is obtained in the titration where no common salt is added; addition of 0.2 g common salt, corresponding to a concentration of 0.2%, already produces a poorer curve. This tendency increases when 1 g of common salt, corresponding to 1.0%, is added. Two effects can be plainly seen:
1. The total potential difference between start and end of the titration becomes smaller.

2. The region around the endpoint becomes broader, i.e. the derivative curve also becomes flatter.

Titration curves with the addition of 1.0 to 5% common salt can still be evaluated by modern titrators without any problems. If all these determinations are carried out ten times then a slight worsening of the standard deviation can be recognised. The effect is even clearer when the salt concentration is increased so much that the saturation limit of sodium chloride in water is approached. Under these conditions the analyte is «salted out», i.e. it is present in the titration solution in a finely distributed form which is no longer dissolved nor dissociated, as shown in Fig. 98.

The non-dissociated surfactant cannot be detected by the surfactant electrode. Titrations carried out under these conditions produce unusual titration curves, which have nothing to do with the classical S-shape in the region around the endpoint.

Although there is a reaction between the analyte and the titrant, this requires considerably more time than in a low-electrolyte solution. Under no circumstances may such a titration be carried out in a dynamic titration mode. As the microprocessor can detect practically no alterations in the potential in such a case, the individual volume increments added would be very large and would not be any smaller in the region around the endpoint. This means that in a dynamic titration an endpoint will always be detected, but at a reagent volume that is considerably higher than the real value. In the classical sense there has been «over-titration». A surfactant titration in a solution with a high electrolyte load should only be carried out in the monotonic titration mode, i.e. with uniform volume increments. After each volume increment a waiting period of approx. 20 s should be observed before the measurement is accepted for calculation. Such a titration will last at least half an hour, but can be carried out with a standard deviation of less than 2%.

In reality it is quite possible that samples with a high electrolyte content have to be analysed. In the electroplating industry, for example, a very high content of metal salts, such as nickel or chromium salts, is completely normal. In order to obtain uniform metal deposition on the substrate during the electroplating process some electroplating baths contain surfactant additives whose concentration needs to be monitored.

To summarise it can be said that correct titrations can also be carried out in solutions rich in electrolytes but that poorer standard deviations must be expected, while with systems containing a very high amount of electrolytes a special technique in the form of an additional method specially adapted for this purpose must be used.

**Potentiometric two-phase titration**

While in titrations carried out in aqueous media electrolytes such as sodium chloride, potassium chloride, the corresponding sulphates or other salts only have a relatively slight effect on the titration, this is a completely different matter in titrations with the Surfactrode Resistant in two-phase media. In a titration with the Surfactrode Resistant, salts should only be present at low concentrations. Under no circumstances should salts be added deliberately; this also applies to the region around the endpoint. This means that in a dynamic titration an endpoint will always be detected, but at a reagent volume that is considerably higher than the real value. In the classical sense there has been «over-titration». A surfactant titration in a solution with a high electrolyte load should only be carried out in the monotonic titration mode, i.e. with uniform volume increments. After each volume increment a waiting period of approx. 20 s should be observed before the measurement is accepted for calculation. Such a titration will last at least half an hour, but can be carried out with a standard deviation of less than 2%.

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To summarise it can be said that correct titrations can also be carried out in solutions rich in electrolytes but that poorer standard deviations must be expected, while with systems containing a very high amount of electrolytes a special technique in the form of an additional method specially adapted for this purpose must be used.

**Fig. 98: Schematic diagram of the electrolyte influence**

**Fig. 97: Effect of adding NaCl in a titration with TEGO trant A100**
The newly developed Surfactrode Refill can be recommended for titrating surfactants that have a high salt content. According to recent experience this sensor tolerates significantly higher salt concentrations than the Surfactrode Resistant. Accordingly, the Surfactrode Refill is recommended as the indicator electrode for all those samples whose salt content in the titration solution exceeds 0.5 g per 100 mL.

5.12 Influence of insoluble pigments

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Titrination in aqueous media

Toothpastes contain abrasive particles based on silicates, aluminium oxide, phosphates, etc. These compounds are insoluble in water. Because of the surface-active properties of the surfactants it is to be expected that the surfactants contained in the formulations will be absorbed substantively on the surfaces of these pigments.

If 10% methanol is added to the titration solution then under time-controlled acquisition of the measured value and with the usual sample weight for toothpaste an interference-free quantitative determination of both cationic and anionic surfactants is possible.

Toothpastes mostly contain surfactants in the order of magnitude of between 1 and 2%; this means that a sample weight of 1 to 2 g should be used. The amount of insoluble pigments in this sample weight is tolerated by the electrode without any problems. This means that the preparation of the ethanol-soluble constituent which is usually necessary is no longer required; this leads to clear savings in time and costs.

Other formulations such as abrasive powders or scouring agents also contain considerable amounts of solid material. An abrasive powder consists mainly, i.e. to far more than 90%, of insoluble pigments. Only small amounts of surfactant are present. Nevertheless, anionic surfactants in an abrasive powder or in a scouring agent can be determined without previous separation or the usual and complicated preparation of the ethanol-soluble constituent. Sample preparation is practically no longer required. As the content of anionic surfactants in these products amounts to 1 to 2%, then 1 to 2 g are again weighed out and then approx. 10 mL methanol, 80 mL water and 10 mL buffer solution are added. After stirring for some time the titration is carried out in the dynamic mode, but also in this case the measurement should not be drift-controlled but time-controlled, and the time constant should be set somewhat higher than normal, e.g. to 20 to 25 seconds. Although such a titration takes 20 minutes it is carried out without any checks being required.

The materials in an abrasive powder or scouring agent have an abrasive effect on the electrode membrane. Accordingly, the service life of an electrode used only for this purpose will be approx. 50 to 75% less than that of a comparable electrode used only with pigment-free samples. Calculated back to a single titration this means an extra cost of below DM 1.00 (approx. 60 US cents in April 1998) and therefore a favourably priced alternative to the preparation of the ethanol-soluble constituent.

If, for example, the surfactant content of soil sediments, which are usually relatively coarse-grained, is to be investigated then this is not possible without previous separation. Titrination curves obtained from the original sample show very uneven potentials, which can be traced back to coarse-grained soil or sand particles impacting against the indicator or reference electrode and causing spikes. The surfactant content of such samples can only be determined from the ethanol-soluble constituent.

The PVC membrane that is used for the titration of surfactants in the presence of insoluble pigments rapidly becomes dull, but this has no effect on the functioning of such a PVC membrane. The coated wire type of surfactant electrode is more suitable for the titration of samples containing insoluble pigments than those of the conventional type. This is probably attributable to the considerably larger surface of a coated wire electrode.

Potentiometric two-phase titration

The MetroSensor Surfactrode Resistant does not have a PVC membrane and is therefore almost insensitive to insoluble pigments in formulations. This means that the materials in toothpastes or in a scouring agent and the silicates in washing powders cannot influence the functioning of the electrode even under continuous use.

Chloroform must always be used as the water-immiscible solvent for the determination of surfactants in scouring agents with the Surfactrode Resistant. However, as one of the targets of the potentiometric two-phase titration is the replacement of chloroform, which has fallen into disrepute together with other, non-chlorinated solvents such as methyl isobutyl ketone, it is better to determine the surfactants in scouring agents in aqueous media using the Ionic Surfactant as indicator electrode. A titration of the scouring agent in aqueous media is possible with relatively few problems.

Summary

The Surfactrode Resistant is insensitive to the abrasive properties of pigments or materials in the samples to be analysed. This is why the Surfactrode Resistant is certainly the electrode of choice when such samples are to be analysed. However, we have also analysed several systems in which the Ionic Surfactant Electrode produced better titration curves. This was the case for many toothpastes.

5.13 Influence of nonionic surfactants based on POE adducts

Titrination in aqueous media

The following examples of POE adducts have been selected: POE-20 sorbitan monolaurate, POE-40 hydrogenated castor oil and POE-7 glyceryl cocoate. All products exhibit similar behaviour in potentiometric anionic surfactant titration. Depending on the concentration of nonionic surfactants, the titration curves become poorer, i.e. the total potential difference and the slope of the first derivative become smaller and the point of inflection extends over a larger volume range than in the basic titration curve. The higher the degree of ethoxylation of a surfactant, the smaller the amount required to cause an alteration to the curve. The results obtained are still correct, but the standard deviation becomes poorer as the nonionic surfactant content increases. If this is limited to that concentration ratio between anionic surfactants and POE adducts that is normal in formulations then alterations to the titration curve can be recognised, but the alteration to the standard deviation is statistically of little significance. The use of TEGO trant A100 as titrant also brings advantages in
this case. If Hyamine 1622 is used the negative influences are considerably more noticeable, so that at higher concentra-
tions of POE adducts some titration curves may become so flat that they can no longer be evaluated. If the content of
nonionic surfactants is about double that of the anionic surfactants then the limit is reached at which a potentiometric
titration of the anionic surfactants makes sense. In such a case it is a good idea to use the Surfactrode Resistant; this
allows a titration to be carried out with the addition of a solvent which is immiscible with water and the interfering
influences of the nonionic surfactants are hardly noticeable.

Potentiometric two-phase titration

As a result of a different method of detection the influence of nonionic surfactants based on POE adducts is considerably
less in titrations in two-phase media than in titrations in aqueous media. If the Metrosensor Surfactrode Resistant is
used as the indicator electrode then a ratio of ionic surfactant to the nonionic surfactant based on POE adducts of 1:1
has no noticeable effect on the titration curve. But even at a ratio of 1:5, with some surfactants even 1:10, a titration can
still be carried out without any problems. This means that in almost all cases the relevant range for the analysis of
formulations is covered. In the majority of cases this advantage is utilised to titrate formulations with a high content of
nonionic surfactants based on POE adducts in a two-phase medium with the Surfactrode Resistant.

5.14 Influence of nonionic surfactants based on APG

Titration in aqueous media

In surfactant titrations in aqueous media alkyl polyglycosides show a influence on the titration of anionic surfactants
which is similar to that of the POE adducts; referred back to the concentration their influence is even more marked. If the
amount of APG is reduced to that which is realistic in, e.g., a rinse-off product, a rinsing agent or a household cleaner
then only a slight influence can be expected.

Recently (April 1996) we have tested formulations from North America in our laboratory, including both household
cleaners and cosmetic rinse-off formulations. The APG content in these formulations was considerably higher com-
pared to samples obtained in Spring 1993. Some disinfectant household cleaners in particular, which as well as quater-
nary benzalkonium chloride also contained the approx. 6-fold amount of nonionic surfactant as a mixture of fatty alcohol
POE and APG, produced titration curves in aqueous medium that were extremely difficult to evaluate. In a manual
graphical evaluation the results were clearly too high and noticeably dependent on the sample weight.

In many cases apparent high-bias results are obtained for anionic surfactants, as most alkyl polyglucosides still contain
a small amount of anionic detergents as a result of their manufacturing process. These high-bias results mostly lie in an
order of magnitude of about 1% referred to the APG used. When referred to the total formulation the error which this
causes is so small that it disappears within the normal error margin.

Potentiometric two-phase titration

Only when the new Metrosensor Surfactrode Resistant was used in a two-phase medium instead of the Ionic Surfactant
Electrode for the titration of these North American cleaners were normal, easily evaluable titration curves obtained.
Methyl isobutyl ketone at a concentration of 10% by volume was added as the organic solvent.

As the APGs exhibit extraordinarily positive properties as co-surfactants in a very large number of formulations it must
be expected that this surfactant raw material will continue to be used in many formulations and in increasing concentra-
tions.

As a result of a different method of detection the influence of nonionic surfactants based on APG is considerably less in
titrations in two-phase media than in titrations in aqueous media. If the Metrosensor Surfactrode Resistant is used as the
indicator electrode then a ratio of ionic surfactant to the nonionic surfactant based on APG of 1:1 has no noticeable effect
on the titration curve. But even at a ratio of 1:5, with some surfactants even 1:10, a titration can still be carried out without
any problems. This means that in almost all cases the relevant range for the analysis of formulations is covered. In the
majority of cases this advantage is utilised to titrate formulations with a high content of nonionic surfactants based on
APG in a two-phase medium with the Surfactrode Resistant.

In this case high-bias findings of anionic surfactant can also occur, because many alkyl polyglycosides often contain
some anionic surfactant as a result of their manufacturing process. This amount is usually so small that the anionic
surfactant content is only influenced slightly or perhaps not at all. This is only mentioned again to provide the operator
with an explanation if this problem is encountered.

5.15 Influence of betains

Titration in aqueous media

The influence of the betain depends very strongly on the pH at which the titration is carried out. The best results are
obtained at pH = 3 to 5, at which neither the slope of the curve not the results are affected. But even under slightly
alkaline conditions, anionic surfactant determinations can be carried out without interference from betains. At a pH value
of 1, at which the betain is present in its protonated form, the slope of the titration curve collapses rapidly and completely
and the results are incorrect, i.e. the betain, which has become cationic as a result of protonation, has neutralised an
equimolar amount of the anionic surfactant.

Betains and most of the other amphoteric surfactants cannot be determined with the normal surfactant electrode and the
titrant which is normally used. A determination is only possible under special conditions; these are described in section
3.3. Nevertheless a betain is able to interfere with the determination of other anionic surfactants. This is then particularly
relevant when formulations such as shower gels, shampoos, liquid soaps, etc. are concerned in which, apart from the
basic surfactants based on anionics, betains are normally contained as co-surfactants in almost all cases. If the anionic
surfactant content is to be determined for such a formulation then interference from betains must always be expected if
a pH is selected at which the betain is present in a protonated or even partially protonated form, i.e. when it will react like
a cationic surfactant. Quantitative protonation is the case at or below pH = 1; this means that it is impossible to carry out
an anionic surfactant titration in this range. The pH range between 1 and 2.5 must also be avoided because at least

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partial protonation must be expected in this range. Depending on the other formulation ingredients contained in the system the determination of the anionic surfactant content in a pH range between pH = 3 and 5 has proved effective. If the formulation also contains a sulphosuccinate, e.g. disodium laureth sulphosuccinate, then a titration can only be carried out at pH = 3. At a pH of 3 or more there is no negative influence from the betain. A negative influence on the titration, e.g. such as that of nonionic surfactants based on polyoxyethylene adducts as described in section 5.13, can hardly be recognised with betains or is only weakly developed. If the analytical determination of the anionics is to be performed under alkaline conditions then this can be carried out in the presence of betains without any problems because under alkaline conditions betains are present in an internally balanced molecular form. An additional titration under alkaline conditions can also be a good idea if two anionic surfactants are present together and one of them is e.g. disodium laureth sulphosuccinate.

**Potentiometric two-phase titration**

If the Surfactrode Resistant is used in a pH range of >3 then the betain is present in a non-protonated form. In this range the betain can also be described as being a nonionic surfactant. In this case the different detection mechanism also means that the influence of the betain is less noticeable than in titrations in aqueous media. This means that in almost all cases the relevant range for the analysis of formulations is covered. In the majority of cases this advantage is utilised to titrate formulations with a high content of betains or similar amphoteric surfactants in a two-phase medium with the Surfactrode Resistant.

### 5.16 Influences of fats and mineral oils

**Titration in aqueous media**

In potentiometric surfactant titrations indicated with a normal surfactant electrode fats and mineral oils should either not be present at all or only in small amounts. The apolar fats or oils can remove the plasticiser from the PVC membrane and thus destroy the electrode. The extent to which this is tolerated by the electrode membrane depends on the type of apolar substance. Some fats and oils are actually tolerated at a concentration corresponding to approx. 1 to 3% of the total volume without any problems. In such cases it must be expected, however, that the service life of the membrane will be reduced.

**Potentiometric two-phase titration**

If the Metrosensor Surfactrode Resistant is used as the indicator electrode for titrations in two-phase media, then fats and mineral oils, and also natural oils, present no problems. Cooling lubricants or even cosmetic shower oils with a natural oil content of more than 60% can be titrated without any problem at all. Nevertheless, a solvent immiscible with water must also be added in these cases. Oils and fats have no influence on the shape of the curve and no influence at all on the service life of the electrode throughout a very wide range.

### 5.17 Influence of organic solvents

**Titration in aqueous media**

Solvents immiscible with water, e.g. chloroform or other chlorinated hydrocarbons, but also aromatics, acetone, tetrahydrofuran, dimethylformamide, etc., must not be present during surfactant titration. All these solvents can remove the plasticisers and therefore the ion carrier from the membrane. The PVC itself can also swell up or be dissolved. This would allow to the rapid destruction of a normal surfactant electrode membrane. It would be impossible to regenerate such an electrode; it could only be written off. This is why the greatest possible care must always be taken with samples containing solvents.

**Potentiometric two-phase titration**

All solvents tested by us to date, even chlorinated or fluorinated hydrocarbons, have had no negative influence on titrations in two-phase media with the Surfactrode Resistant. These solvents are even absolutely necessary for the titration to be carried out. The amount of solvents immiscible with water should not exceed 40% of the titration solution. At higher amounts it is no longer possible for the stirrer to produce a homogeneous emulsion from the aqueous and solvent phases.

### 5.18 Influence of non-surfactant-like quats (polyquaternium 10 etc.)

Non-surfactant-like quats based on cellulose, e.g. Polyquaternium 4 or Polyquaternium 10 (Fig. 99), are an important conditioning ingredient of modern shower gel or shampoo formulations. These non-surfactant-like quats are inert during the potentiometric surfactant titration; this means that they can form no insoluble reaction products either with anionic, cationic or amphoteric surfactants. These polymer cellulose quats are not determined and do not interfere with the other determinations.

![Fig. 99: Structural formula of Polyquaternium 10: polyquaternium 10 cellulose parent substance from a natural raw material source; polymer quaternary ammonium salt from a reaction product of hydroxyethylcellulose and a trimethylammonium-substituted epoxide.](image)

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5.19 Influence of polymers
Polymers or copolymers such as those listed below, used widely, e.g., in rinse-off or also in cleaner formulations and further products have no negative influence on surfactant titration:

- Octylacrylamide-acrylate-butylaminoethyl-methacrylate copolymer
- Octylacrylamide-acrylate copolymer
- Vinylacetate-crotonic acid-vinyl neodecanoate copolymer
- Vinylacetate-crotonic acid copolymer, acrylate
- t-Octylpropenamide copolymer
- Starch-octenylsuccinate
- Corn starch
- Sodium polystyrene sulphonate
- Methylcellulose
- Hydroxyethylcellulose

They cannot be determined by potentiometric surfactant titration methods, are not determined when other surfactants are being determined and therefore cause neither high-bias nor low-bias results.

5.20 Influence of complexing agents
Most cleaner formulations contain complexing agents with different structures. All the tested types of complexing agents (see list below) have no influence at all on carrying out surfactant titrations:

- Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA)
- 1,2-cyclohexylenenitritetraacetic acid monohydrate
- N-(2-hydroxyethyl)-ethylenediamine-N,N',N'-triacetic acid trisodium salt
- Bis-(aminoethyl)-glycolether-N,N,N',N'-tetraacetic acid
- Diethyleneiaminepentaaacetic acid
- Nitrilotriacetic acid
- Ethylenedinitritetraacetic acid
- Triethylene tetraminehexaacetic acid
- Citric acid, etc.

5.21 Influence of hydrotropes
Hydrotropes such as toluene sulphonate, xylene sulphonate or cumol sulphonate, which are often contained in technical formulations, have a structure similar to that of the anionic surfactant dodecylbenzene sulphonate, but lack the necessary oleophilic alkyl group to become a surfactant.

Titration in aqueous media
In titration in aqueous media the missing alkyl group ensures that the hydrotrope cannot be precipitated out by the known titrant. Hydrotropes therefore cannot be determined under these conditions; they do not interfere with surfactant titration in aqueous media.

Potentiometric two-phase titration
In potentiometric surfactant titration in two-phase media the hydrotropes cannot form any reaction product with the surfactant titrant which is extractable in the solvent because of their missing oleophilic alkyl group. This results in the same consequences as for the titration in aqueous media: Hydrotropes cannot be determined and do not interfere with the determination of ionic surfactants.

Fig. 100: Structural formula of cumol sulphonate
Fig. 101: Structural formula of toluene sulphonate
Fig. 102: Structural formula of xylenen sulphonate

5.22 Influence of cleaning agent builders
The builder system has a very large influence on potentiometric two-phase titration.

The influence of builders and other cleansing agent ingredients is discussed in detail in chapter 8 and following.
6 Titrant preparation and titre determination

6.1 General; titrant concentration

In most cases the titrant solutions for the determination of ionic surfactants have a concentration of 0.004 mol/L. This concentration is found even in very old publications. In the titrations carried out in the author’s laboratory, on which this monograph is based, the titrant solution was also used at a concentration of 0.004 mol/L.

In parallel to this, other laboratories have successfully used a titrant solution concentration of 0.005 mol/L for the determination of ionic surfactants. All the applications mentioned in this monograph can also be carried out with a 0.005 mol/L titrant solution. The sample weight must be adjusted accordingly.

Titrations should not be carried out with more dilute solutions as the effect of the special physicochemical properties of the surfactants becomes even larger and linearity between the sample weight and titrant consumption can no longer be achieved.

Higher titrant solution concentrations up to 0.05 mol/L are possible. These produce steeper titration curves, but the results are no better. This is why this technique cannot be recommended for daily routine use if one works in aqueous solution. Only in cases where the use of 0.004 mol/L solutions results in flat titration curves which cannot be evaluated should more concentrated solutions be used. Another reason for the use of more concentrated solutions is a wide distribution of the alkyl chains of the surfactant, e.g. as may be found in surfactants based on natural coconut oil. For example, the quantitative determination of sodium cocoyl isethionates is only possible with 0.04 or 0.05 mol/L TEGO trant A100 solution.

During the development and test phase of the Surfactrode Resistant electrode it could be seen that it made more sense to titrate with a 0.02 mol/L solution for most cosmetic formulations as well as for washing and cleaning agents. This applies to both anionic and cationic titrants. In this way better, smoother and more typical titration curves could be obtained. In this case «typical» means that the titration curves approached the ideal S-shape and therefore the titrator algorithms could evaluate them better. By carrying out an extremely large number of experimental titrations in our laboratory we were able to prove that 0.02 mol/L titrant solutions yielded better standard deviations for the formulations mentioned above. In addition the higher titrant concentration allowed a single method to be used for almost all formulations without the need for having a lot of background knowledge of the products to be analysed. This has considerable advantages, particularly when competitors’ products are being analysed. This is the reason for my recommendation of a titrant concentration of 0.02 mol/L in such cases. For raw materials the 0.004 mol/L solution can and should still be used, aside from the exceptions described.

In many cases the question of which titrant concentration is the optimal one or just the most suitable one cannot be answered simply and sometimes it is a good idea to carry out the titration with different titrant concentrations. An assessment should then be made of which titrant concentration produces the better titration curves.

In this monograph a titrant concentration of 0.02 mol/L is often recommended for formulations. Of course, every rule has its exceptions. This became very clear to us when we investigated formulations found on the North American market. In the cosmetics sector new tendencies became apparent in rinse-off formulations. As an example we list hair & body shampoo and body shampoo formulations.

**Hair & Body shampoo**
- Water
- PEG-80 Sorbitan laurate
- Cocamidopropyl betain
- **Sodium trideceth sulphate**
- Glycerol
- Disodium lauroamphodiacetate
- PEG-150 distearate
- Sodium laureth-13 carboxylate
- Fragancem
- Polyquaternium-10
- Tetrasodium EDTA
- Quaternium-15
- Guar hydroxypropyltrimonium chloride
- Sodium hydroxide
- BHT
- Methylchloroisothiazolinone
- Methylisothiazolinone

**Body Shampoo**
- Water
- Cocamidopropyl betain
- Dimethicone
- **Sodium laureth sulphate**
- Ammonium sulphate
- Fragrance
- Laureth-4
- Laureth-23
- Carbomer
- Mica
- Titanium dioxide

In both formulations it can be recognised that nonionic surfactants are the basic surfactants used, e.g. those based on POE sorbitan fatty acid esters or betains. The anionic surfactants to be titrated are listed in the CTFA or INCI declarations only in the third place or even later. For these formulations better titration curves can be achieved with a 0.004 mol/L TEGO trant A100 solution as titrant. The reason for this is quite simple. The low titrant concentration results in a low sample weight. This means that smaller amounts of those surfactants that have a negative influence on the titration curve are found in the titration solution.
In classical formulations, as shown for example in these body shampoo and hair shampoo formulations, the 0.02 mol/L TEGO trant A100 solution has proved to be a suitable titrant.

**Body Shampoo**
- Water
- Ammonium lauryl sulphate
- Ammonium laureth sulphate
- Lauramide DEA
- Citric acid
- Hydroxypropyl methylcellulose
- Tetrasodium EDTA
- Ammonium chloride
- Benzophenone-4
- Methylchloroisothiazolinone
- Methyisothiazolinone
- DMDM Hydantoin
- Ammonium xylenesulphonate
- Fragrance
- D & C Red No. 33
- D & C Orange No. 4

**Hair Shampoo**
- Aqua
- Sodium laureth sulphate
- PEG-7 glyceryl cocoate
- Disodium cocoamphodiacetate
- Cocamidopropyl betain
- Laureth-2
- Perfume
- Glycol distearate
- Laureth-4
- Allantoin

In these formulations the anionic surfactant to be titrated is the first mentioned in the CTFA or INCI declaration and is therefore the primary surfactant in the formulation. These and similar formulations can be titrated better with a 0.02 mol/L TEGO trant A100 solution.

For the preparation of the titrants only the purest chemicals available on the market should be used. Many of the substances which are required here can be found in the catalogues of the well-known laboratory chemical companies. Merck (Darmstadt, Germany) offers chemicals with the quality description «for surfactant tests» as a speciality.

TEGO trant A100 is a research product of Th. Goldschmidt AG in Essen, Germany and was specially developed for the titration of anionic surfactants. It shows its strengths particularly when used with the High Sense Electrode, the Ionic Surfactant Electrode and also the Surfactrode Resistant. TEGO trant A100 is marketed worldwide exclusively by Metrohm Ltd., Switzerland and their suppliers abroad. This special titrant allows the range of potentiometric surfactant titration applications to be significantly extended.

### 6.2 Titrants for the determination of anionic surfactants

#### 6.2.1 General

The selection of a suitable titrant is of the utmost importance, particularly for cationic titrants. (see section 5.4)

Examples of suitable titrants are:
- TEGO trant A100 (1,3-didecyl-2-methylimidazoliumchloride)
- Hyamine 1622 = N-benzyl-N,N-dimethyl-N-[4-(1,1,3,3-tetramethylbutyl)-phenoxyethoxyethyl] ammonium chloride
- N-cetylpyridinium chloride

Extremely high demands must be placed on the purity of the titrants. Only the best quality obtainable should be used for the preparation of the titrant solutions. Quaternary ammonium compounds must additionally have a degree of quaternization of 100%. If this is not the case then a special titre must be determined for each pH value at which the surfactant titration is later to be carried out. For this reason most quaternary ammonium compounds are eliminated because without exception they only have a degree of quaternization of typically 92 to 98%. A further important demand to which the titrant must be subjected is that it must have a uniform alkyl chain distribution. If this is not the case then problems during the titration may occur. For example, a point of inflection in the titration curve may be split into two or more because the titration has not been carried out with a uniform titrant, but with a mixture of two or more homologues.

Care must also be taken as a large number of quaternary ammonium compounds in powder form contain water of crystallization or otherwise may have a constant residual moisture content.

Particular attention must be paid to the pronounced substantivity of cationic titrants to glass or other material surfaces during the preparation of cationic titrants. For example, if an exactly 0.004 mol/L TEGO trant A100 solution is prepared and the titre determined to be 1.000, then this titre will not be accurate only a short time later because the surfaces will have become coated with TEGO trant A100. The amount of substance required for this is removed from the titrant so that a renewed titre determination may possibly give a titre of 0.990 or similar. This fact may appear to be serious at first
This is why attention must be paid to the following points:

- The titrant should be prepared the day before being used in a special volumetric flask or a freshly prepared solution should be allowed to stand overnight in a volumetric flask before use.
- This volumetric flask, which now has a surface saturated with cationic surfactant, should be reserved only for the preparation of this one particular titrant and, as long as it is used for this purpose, should not be rinsed out.
- This solution is then filled into the Exchange Unit of the automatic piston burette and rinsed until all relevant parts of the Exchange Unit such as tubing and the burette tip have been wetted with the titrant. A waiting period of at least 2 hours (overnight is better) is now necessary. During this period saturation of the surface with the substantive cationic surfactant occurs. A further two cylinder fillings are rinsed through and rejected. A stable system now exists and the titre can be determined. The titre of a 0.004 mol/L TEGO trant A100 solution determined in this way is stable for a period of at least 3 months. The samples can then be titrated immediately.
- The storage bottle of this Exchange Unit and other components should also not be rinsed again as they are in optimal condition with a saturated surface.

The occupancy of the surface takes place with the hydrophilic part of the surfactant oriented towards the surface, e.g. glass and the oleophilic part away from the surface. This has the effect that the glass apparatus has an extremely «greasy» or soiled appearance. This state, which is anathema to a demanding analyst, must be unconditionally accepted. If cleaning were to be carried out then the surfaces would no longer be saturated with the cationic surfactant and the whole process would have to be carried out again.

6.2.2 Preparation and titre determination of a 0.004 mol/L TEGO trant A100 solution

**Materials and reagents**

- Dodecylsulphate sodium salt (Merck 12533.0050)
- TEGO trant A100 (Metrohm 6.2317.000 [6 g] or 6.2317.010 [60 g])
- Buffer solution pH = 3 (e.g. prepared from Titrisol, Merck 9883)
- Methanol analytical grade (e.g. Riedel-de Haén 32213)
- Analytical balance (e.g. Sartorius A 200)
- Automatic titrator with peripherals (e.g. Metrohm 726 Titroprocessor or 716, 736, 751 Titrino)
- 6.0507.120 Ionic Surfactant Electrode (Metrohm)
- 6.0733.100 Ag/AgCl reference electrode with ceramic diaphragm (Metrohm)
- Titrination beakers (matched to sample changer, if present)
- Measuring cylinders 5, 10 and 100 mL
- Volumetric flask 1 L
- Volumetric pipette 10 mL

**Procedure**

**General information**

The titration should be carried out using a titrator with which the titrant addition can be carried out dynamically, i.e. as a function of the variation of the electrode potential.

The dynamic control parameters of a titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be made out.

**Titration parameters**

The titration parameters for the Metrohm 726 and 670 Titroprocessors and 716, 736, 751 Titrinos are given below. If titrators from other manufacturers are used then the parameters should be adapted accordingly.

**670 Titroprocessor**

Measures

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meas 1</td>
<td>30 s</td>
</tr>
<tr>
<td>Quantity</td>
<td>U</td>
</tr>
<tr>
<td>Drift/min</td>
<td>off mV</td>
</tr>
<tr>
<td>M.Delay</td>
<td>32 s</td>
</tr>
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Dynamic parameters

<table>
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<tr>
<td>MPT.Density</td>
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<tr>
<td>Dos.Rate/min</td>
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</tr>
<tr>
<td>f.VResol</td>
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</tr>
<tr>
<td>TStop</td>
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</tr>
<tr>
<td>N.EPs</td>
<td>20.000 mL</td>
</tr>
<tr>
<td>Volume</td>
<td>Off</td>
</tr>
<tr>
<td>M.Value</td>
<td>Off</td>
</tr>
</tbody>
</table>

**716, 736, 751 Titrino**

Titration parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pause</td>
<td>30 s</td>
</tr>
<tr>
<td>V</td>
<td>20 mL</td>
</tr>
</tbody>
</table>

**Materials and reagents**

- Dodecylsulphate sodium salt (Merck 12533.0050)
- TEGO trant A100 (Metrohm 6.2317.000 [6 g] or 6.2317.010 [60 g])
- Buffer solution pH = 3 (e.g. prepared from Titrisol, Merck 9883)
IMPORTANT!!
Because of its large substantivity this solution should be filled into the Dosimat bottle one day before it is to be used so that all the tubing and vessels of the Dosimat with which this solution comes into contact are filled with it! Only when all surfaces have been saturated with the cationic surfactant will the solution have a stable titre for at least six months. The first time it is filled into the Dosimat the initial 40 mL of the solution which are dosed out should not be used for titration.

**Titre setting of the 0.004 mol/L TEGO trant A100 solution**

10 mL of the dodecylsulphate sodium salt solution are pipetted into a titration beaker from a volumetric pipette. 5 mL methanol, 75 mL water and 10 mL pH = 3 buffer solution are then added.

The titration against the 0.004 mol/L TEGO trant A100 solution is now carried out by the Titroprocessor using the above-mentioned titration parameters.

The measuring curve and the 1\textsuperscript{st} derivative are recorded.

The results may only be used if the titrator has recognised one single point of inflection. If this is not the case then further titrations must be carried out.

**Evaluation**

The titre of the TEGO trant A100 solution is calculated according to the following equation:

\[
\text{titre } t = \frac{10 \times E \times \omega}{V \times M \times 100 \times c_{\text{nom}}}
\]

where: E weight of dodecylsulphate sodium salt for 1 L solution in g
\(\omega\) purity of the dodecylsulphate sodium salt used in %
V consumption in mL of 0.004 mol/L TEGO trant A100 solution
M molar mass of dodecylsulphate sodium salt (288.4 g/mol)
\(c_{\text{nom}}\) nominal content of the TEGO trant A100 solution (0.004 mol/L)

The calculation formula must be converted into the form used by your particular titrator.

The determination should be made as a fourfold determination. The titre used for subsequent calculations is the mean value of the fourfold determination and is given to four decimal places.

**6.2.3 Preparation and titre setting of a 0.02 mol/L TEGO trant A100 solution**

**Materials and reagents**

- Dodecylsulphate sodium salt (Merck 12533.0050)
- TEGO trant A100 (Metrohm 6.2317.000 [6 g] or 6.2317.010 [60 g])
- Buffer solution pH = 3 (e.g. prepared from Titrisol, Merck 9883)
- Methanol analytical grade (e.g. Riedel-de Haen 32213)
- Analytical balance (e.g. Sartorius A 200)
- Automatic titrator with peripherals (e.g. Metrohm 726 Titroprocessor or 716, 736,751 Titrino)
- 6.0507.120 Ionic Surfactant Electrode (Metrohm)
- 6.0733.100 Ag/AgCl reference electrode with ceramic diaphragm (Metrohm)
- Titration beaker (matched to sample changer, if present)
- Measuring cylinders 5, 10 and 100 mL
- Volumetric flask 1 L
- Volumetric pipette 10 mL

**Procedure**

**General information**

The titration should be carried out using a titrator with which the titrant addition can be carried out dynamically, i.e. as a function of the variation of the electrode potential.

The dynamic control parameters of a titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be made out.

**Titration parameters**

The titration parameters for the Metrohm 726 and 670 Titroprocessors and 716, 736, 751 Titrinos are given below. If titrators from other manufacturers are used then the parameters should be adapted accordingly.
Preparation of a dodecylsulphate sodium salt solution

5.75 to 5.8 g dodecylsulphate sodium salt are weighed out exactly to 0.1 mg and dissolved in approx. 200 mL water. The solution is transferred quantitatively to a 1 L volumetric flask, made up to the mark with water and mixed. The weight used is later required for calculating the titre and must be noted.

Preparation of 0.02 mol/L TEGO trant A100 solution

8.7 g of the TEGO trant A100 are weighed out exactly to 0.1 mg and dissolved in approx. 150 mL water. The solution is transferred quantitatively to a 1 L volumetric flask and made up to the mark with water. This solution is then filled into a Dosimat bottle.

IMPORTANT!!

Because of its large substantivity this solution should be filled into the Dosimat bottle one day before it is to be used so that all the tubing and vessels of the Dosimat with which this solution comes into contact are filled with it! Only when all surfaces have been saturated with the cationic surfactant will the solution have a stable titre for at least six months.

The first time it is filled into the Dosimat the initial 40 mL of the solution which are dosed out should not be used for titration.

Titre setting of the 0.02 mol/L TEGO trant A100 solution

10 mL of the dodecylsulphate sodium salt solution are pipetted into a titration beaker from a volumetric pipette. 5 mL methanol, 75 mL water and 10 mL pH = 3 buffer solution are then added.

The titration against the 0.02 mol/L TEGO trant A100 solution is now carried out with the Titroprocessor using the above-mentioned titration parameters.

The measuring curve and the 1st derivative are recorded.

The results may only be used if the titrator has recognised one single point of inflection. If this is not the case then further titrations must be carried out.

Evaluation

The titre of the TEGO trant A100 solution is calculated according to the following equation:

\[
\text{titre } t = \frac{10 \times E \times \omega}{V \times M \times 100 \times c_{\text{nom}}}
\]

where: 
- \(E\) weight of dodecylsulphate sodium salt for 1 L solution in g
- \(\omega\) purity of the dodecylsulphate sodium salt used in %
- \(V\) consumption in mL of 0.02 mol/L TEGO trant A100 solution
- \(M\) molar mass of dodecylsulphate sodium salt (288.4 g/mol)
- \(c_{\text{nom}}\) nominal content of the TEGO trant A100 solution (0.02 mol/L)

The calculation formula must be converted into the form used by your particular titrator.

The determination should be made as a fourfold determination. The titre used for subsequent calculations is the mean value of the fourfold determination and is given to four decimal places.
6.2.4 Preparation and titre determination of a 0.004 mol/L Hyamine 1622 solution

**Equipment and reagents**

- Dodecylsulphate sodium salt (Merck 12533.0050)
- 0.004 mol/L Hyamine 1622 solution (ready-to-use titrant, Merck 15480.1000)
- or Hyamine 1622 solid substance (Merck 12058.0250)
- Buffer solution pH = 3 (e.g. prepared from Titrisol, Merck 9883)
- Methanol, analytical grade (e.g. Riedel-de Haën 32213)
- Analytical balance (e.g. Sartorius A 200)
- Automatic titrator with peripherals (e.g. Metrohm 726 Titroprocessor or 716, 736, 751 Titrino)

**Procedure**

**General information**

The titration should be carried out using a titrator with which the titrant addition can be carried out dynamically, i.e. as a function of the variation of the electrode potential.

The dynamic control parameters of a titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be made out.

**Titration parameters**

The titration parameters for the Metrohm 726 and 670 Titroprocessors and 716, 736, 751 Titrinos are given below. If titrators from other manufacturers are used then the parameters should be adapted accordingly.

**670 Titroprocessor**

- Meas 1: 30 s
- Quantity: U
- Drift/min: off mV
- M.Delay: 26 s
- DynT 1: 30 s
- MPT:Density: 3
- Dos.Rate/min: 30,000 ml
- f.VResol: 0.10%
- TStop: N.EPs: 8
- Volume: 20,000 ml
- M.Value: Off

**716, 736, 751 Titrino**

- Titration parameters: meas.pt.density 3
- min.incr. 50 µl
- titr.rate 30 ml/min
- signal drift 15 mV/min
- equilibr.time 26 s
- start conditions: pause 30 s
- evaluation: EP recognition all
- stop conditions: stop V 20 ml
- TStop: N.EPs: 8
- Volume: 20,000 ml
- M.Value: Off

**726 Titroprocessor**

- Pause: 30 s
- Meas.pt.density: 6
- Min.increment: 50 µl
- Titr. rate: max
- Signal drift: 20 mV/min
- Equilibr.time: 26 s

**Preparation of a dodecylsulphate sodium salt solution**

1.15 to 1.16 g dodecylsulphate sodium salt are weighed out exactly to 0.1 mg and dissolved in approx. 200 mL water. The solution is transferred quantitatively to a 1 L volumetric flask, made up to the mark with water and mixed. The weight used is later required for calculating the titre and must be noted.

**Preparation of the 0.004 mol/L Hyamine 1622 solution**

The 0.004 mol/L solution can either be obtained from Merck as a ready-to-use solution or the solid substance can be used.

If the ready-to-use solution is chosen its titre must still be determined. However, it is sufficient if the titre of one bottle in the batch is determined. As long as the ready-to-use solutions belong to the same batch this titre can be used. If a new batch is used then a new titre must be determined.

**Preparation of 0.004 mol/L Hyamine 1622 solution from solid substance**

1.79 g of the Hyamine 1622 are weighed out exactly to 0.1 mg and dissolved in approx. 150 mL water. This solution is transferred quantitatively to a 1 L volumetric flask and made up to the mark with water. Mixing should not be carried out by shaking the flask, but by means of a magnetic stirrer bar which is added to the flask after the solution has been made up to the mark.

**Titre determination of the 0.004 mol/L Hyamine 1622 solution**

10 mL of the dodecylsulphate sodium salt solution are pipetted into a titration beaker from a volumetric pipette. 5 mL methanol, 75 mL water and 10 mL pH = 3 buffer solution are then added.

The titration against the 0.004 mol/L Hyamine 1622 solution is now carried out by the Titroprocessor using the above-mentioned titration parameters.

The measuring curve and the 1st derivative are recorded.
The results may only be used when the titrator has recognised one single point of inflection. If this is not the case then further titrations must be carried out.

**Evaluation**

The titre of the Hyamine 1622 solution is calculated according to the following equation:

\[
titre \, t = \frac{10 \times E \times \omega}{V \times M \times 100 \times c_{\text{nom}}}
\]

*Formula 7*

where:
- \( E \): weight of dodecylsulphate sodium salt for 1 L solution in g
- \( \omega \): purity of the dodecylsulphate sodium salt used in %
- \( V \): consumption in mL of 0.004 mol/L Hyamine 1622 solution
- \( M \): molar mass of dodecylsulphate sodium salt (288.4 g/mol)
- \( c_{\text{nom}} \): nominal content of the Hyamine 1622 solution (0.004 mol/L)

The calculation formula must be converted into the form used by your particular titrator.

The determination should be made as a fourfold determination. The titre used for subsequent calculations is the mean value of the fourfold determination and is given to four decimal places.

**6.3 Titrants for the determination of cationic surfactants**

**6.3.1 General**

The titrants for cationic surfactants are normally anionic surfactants. In such cases the selection of a suitable titrant is particularly important. The following titrants have proved particularly suitable in practice:

- Lauryl sulphate, dodecylsulphate sodium salt, dodecylhydrogensulphate sodium salt, laurylsulphate sodium salt (or SDS = sodiumdodecyl sulphate).
- Dioctyl sodium sulphosuccinate, bis-2-ethylhexylsulphosuccinate (DOS =dioctylsulphosuccinate).
- Sodium dodecylbenzene sulphonate, linear alkylbenzene sulphonate sodium salt (LAS) (or dodecylbenzene sulphonate sodium salt).
- Tetrapropylbenzene sulphonate sodium salt.

It is also important that the best quality of the chemicals available on the market is used for the preparation of the titrants, and that the substances have absolutely pure alkyl chains. However, so-called 100% pure chemicals cannot be expected. As a result of the manufacturing process these substances always contain impurities. For the most often used titrant for cationic surfactants, dodecylhydrogensulphate Na salt, these are:

- free dodecyl alcohol
- inorganic sulphate (Na₂SO₄)
- water

As a first approximation for calculating the weight to be used, such a substance can be regarded as being 98 to 99% pure. The accurate content of the titrant is determined in the titre determination.

According to the criteria of the German Washing and Cleaning Agent Regulations (WRMG), anionic surfactants must be biodegradable. These are practically the same surfactants as are used here in a cleaner form as titrants. The concentration of 0.004 mol/L, which corresponds to an mass concentration of approx. 1.2 to 1.6 g/L, is relatively low so that growth of microorganisms and therefore biodegradation is to be expected. To avoid this, only boiled distilled water should be used for preparing the solution. In our laboratory the addition of 10 mL of a commercially available concentrated (approx. 35%) formaldehyde solution as preservative before filling the solution into the volumetric flask has proved beneficial. A titrant preserved in this way has a stable titre for more than three months.

**6.3.2 Preparation and titre determination of a 0.004 mol/L dodecylsulphate sodium salt solution**

**Equipment and reagents**

- Dodecylsulphate sodium salt (Merck 12533.0050)
- Formaldehyde solution min. 35% (e.g. Merck 4001)
- Distilled water
- Analytical balance (e.g. Sartorius A200)
- 250 mL beaker
- 1 L volumetric flask
- Graduated pipette 2 mL

**Preparation of the 0.004 mol/L dodecylsulphate sodium salt solution**

1.1629 g of the dodecylsulphate sodium salt are weighed out as accurately as possible into a beaker and dissolved in approx. 150 mL water. (The weight of 1.1629 g results from an assumed content of 99.2%. For the exact determination of the weight please refer to the section «Determination of the weight of dodecylsulphate sodium salt», which can be found below.)
This solution is then transferred quantitatively to a 1 L volumetric flask with distilled water. Then 10 mL of the min. 35% formaldehyde solution are added and the mixture is filled up to the mark with distilled water.

The addition of formaldehyde prevents bacterial decomposition of the dodecylsulphate sodium salt solution. The amount mentioned has an adequate disinfectant effect to keep the solution stable for at least three months without affecting the surfactant titration.

The solution must now be thoroughly mixed. In order to reduce foam formation to a minimum a magnetic stirrer bar is added to the flask. Mixing is carried out with a magnetic stirrer.

The solution is now filled into a Dosimat bottle.

**Titre determination of the 0.004 mol/L dodecylsulphate sodium salt solution**

**General information about the titre determination of anionic titrants**

A titre determination in the normal sense cannot be carried out for anionic titrants such as 0.004 mol/L dodecylsulphate sodium salt solution.

For a classical titre determination a titrimetric standard is required.

For the titre determination of an anionic titrant an oppositely-charged surfactant is necessary, i.e. a cationic surfactant or a quaternary ammonium compound.

Cationic surfactants are normally quaternary ammonium compounds which, however, cannot be manufactured with a sufficiently high purity for them to be used as titrimetric standards.

The degree of quaternization of a quaternary ammonium compound used for a titre determination must be 100%. This requirement is also not fulfilled by any of the compounds available.

In general, one of the requirements for a titrimetric standard is that its content does not change. This means that the substance must have a permanently defined composition which must not change even after a long storage period.

Most quaternary ammonium compounds are hygroscopic, i.e. in contact with air they take up moisture. This means that it is not possible to manufacture a quaternary ammonium compound with a defined content, as the water content changes during a long storage period and even each time the bottle is opened.

The fact that a titre determination for the 0.004 mol/L dodecylsulphate sodium salt is not possible means that the solid titrant must be weighed out as accurately as possible.

**Determination of the weight of dodecylsulphate sodium salt**

From many years’ experience the dodecylsulphate sodium salt content of the above-mentioned Merck product can be assumed to be 99.2%.

To obtain an accurate weight the possible impurities should be determined separately so that the purity of the dodecylsulphate sodium salt can be determined.

Secondary constituents of the dodecylsulphate sodium salt are:

- Sodium sulphate
- Water
- Dodecyl alcohol.

The sodium sulphate can be determined by a photometrically indicated titration, the water content by a Karl Fischer titration and the dodecyl alcohol content by gas chromatography.

The purity of the dodecylsulphate sodium salt is obtained from the difference between the total of secondary constituents determined and 100%.

When the purity of the dodecylsulphate sodium salt has been determined in this way the weight can be calculated exactly from the following equation:

\[
\text{Weight in g} = \frac{M \times c \times 100}{\omega}
\]

Formula 8

A purity of 99.2% results in the above-mentioned weight of 1.1629 g.

**Calculation of the titre of the 0.004 mol/L dodecylsulphate sodium salt solution**

The weight calculated according to the above equation should be weighed out as accurately as possible. When the exact purity of the dodecylsulphate sodium salt has been determined it is possible to calculate the titre of the 0.004 mol/L dodecylsulphate sodium salt from the purity and the actual weight used.

\[
\text{Titre} = \frac{E_{aw} \times \omega}{M \times c \times 100}
\]

Formula 9

The calculated titre is given to four decimal places.

The titre must be recalculated when a new dodecylsulphate sodium salt solution is made up and the Dosimat bottle is filled with this new solution. Before the new solution is added the bottle should be completely emptied.
### 6.3.3 Preparation and titre determination of a 0.02 mol/L dodecylsulphate sodium salt solution

#### Equipment and reagents

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecylsulphate sodium salt (Merck 12533.0050)</td>
<td>400 mL beaker</td>
</tr>
<tr>
<td>Formaldehyde solution min. 35% (e.g. Merck 4001)</td>
<td>1 L volumetric flask</td>
</tr>
<tr>
<td>Distilled water</td>
<td>Graduated pipette 2 mL</td>
</tr>
<tr>
<td>Analytical balance (e.g. Sartorius A200)</td>
<td></td>
</tr>
<tr>
<td>400 mL beaker</td>
<td></td>
</tr>
<tr>
<td>1 L volumetric flask</td>
<td></td>
</tr>
<tr>
<td>Graduated pipette 2 mL</td>
<td></td>
</tr>
</tbody>
</table>

#### Preparation of the 0.02 mol/L dodecylsulphate sodium salt solution

5.8145 g of the dodecylsulphate sodium salt are weighed out as accurately as possible into a beaker and dissolved in approx. 300 mL water. (The weight of 5.8145 g results from a content of 99.2% dodecylsulphate sodium salt. For the exact determination of the weight please refer to the section «Determination of the weight of dodecylsulphate sodium salt», which appears above.)

This solution is then transferred quantitatively to a 1 L volumetric flask with distilled water. Then 10 mL of the min. 35% formaldehyde solution are added and the mixture is filled up to the mark with distilled water.

The addition of formaldehyde prevents bacterial decomposition of the dodecylsulphate sodium salt solution. The amount mentioned has an adequate disinfectant effect to keep the solution stable for at least three months without affecting the surfactant titration.

The solution must now be thoroughly mixed. In order to reduce foam formation to a minimum a magnetic stirrer bar is added to the flask. Mixing is carried out with magnetic stirrer.

The solution is now filled into a Dosimat bottle.

#### Titre determination of the 0.02 mol/L dodecylsulphate sodium salt solution

**General information about the titre determination of anionic titrants**

A titre determination in the normal sense cannot be carried out for anionic titrants such as 0.02 mol/L dodecylsulphate sodium salt solution.

For a classical titre determination a titrimetric standard is required.

For the titre determination of an anionic titrant an oppositely-charged surfactant is necessary, i.e. a cationic surfactant or a quaternary ammonium compound.

Cationic surfactants are normally quaternary ammonium compounds which, however, cannot be manufactured with a sufficiently high purity for them to be used as titrimetric standards.

The degree of quaternization of a quaternary ammonium compound used for a titre determination must be 100%. This requirement is also not fulfilled by any of the compounds available.

In general, one of the requirements for a titrimetric standard is that its content does not change. This means that the substance must have a permanently defined composition which must not change even after a long storage period.

Most quaternary ammonium compounds are hygroscopic, i.e. in contact with air they take up moisture. This means that it is not possible to manufacture a quaternary ammonium compound with a defined content, as the water content changes during a long storage period and even each time the bottle is opened.

The fact that a titre determination for the 0.02 mol/L dodecylsulphate sodium salt is not possible means that the solid titrant must be weighed out as accurately as possible.

#### Determination of the weight of dodecylsulphate sodium salt

From many years’ experience the dodecylsulphate sodium salt content of the above-mentioned Merck product can be assumed to be 99.2%.

To obtain an accurate weight the possible impurities should be determined separately so that the purity of the dodecylsulphate sodium salt can be determined.

Secondary constituents of the dodecylsulphate sodium salt are:
- Sodium sulphate
- Water
- Dodecyl alcohol.

The sodium sulphate can be determined by a photometrically indicated titration, the water content by a Karl Fischer titration and the dodecyl alcohol content by gas chromatography.

The purity of the dodecylsulphate sodium salt is obtained from the difference between the total of secondary constituents determined and 100%.

When the purity of the dodecylsulphate sodium salt has been determined in this way the weight can be calculated exactly from the following equation:

\[
\text{Weight in g} = \frac{M \times c \times 100}{\omega}
\]

Formula 10

where:
- \(M\) molar mass of dodecylsulphate sodium salt (288.4 g/mol)
- \(c\) nominal content of dodecylsulphate sodium salt solution (0.02 mol/L)
- \(\omega\) purity of dodecylsulphate sodium salt
**Calculation of the titre of the 0.02 mol/L dodecylsulphate sodium salt solution**

The weight calculated according to the above equation should be weighed out as accurately as possible. When the exact purity of the dodecylsulphate sodium salt has been determined it is possible to calculate the titre of the 0.02 mol/L dodecylsulphate sodium salt from the purity and the actual weight used.

\[
\text{Titre} = \frac{E_{\text{eff}} \times \omega}{M \times c \times 100}
\]

*Formula 11*

where:
- \(E_{\text{eff}}\): weight of dodecylsulphate sodium salt
- \(M\): molar mass of dodecylsulphate sodium salt (288.4 g/mol)
- \(c\): nominal content of dodecylsulphate sodium salt solution (0.02 mol/L)
- \(\omega\): purity of dodecylsulphate sodium salt

The calculated titre is given to four decimal places. The titre must be recalculated when a new dodecylsulphate sodium salt solution is made up and the Dosimat bottle is filled with this new solution. Before the new solution is added the bottle should be completely emptied.

### 6.4 Titrants for the determination of nonionic surfactants and pharmaceuticals

#### 6.4.1 General

The sodium tetraphenylborate solution (NaTPB solution) described below was specially developed for the titration of nonionic surfactants indicated by the NIO Surfactant Electrode developed by Th. Goldschmidt AG and Metrohm Ltd. It has a stable titre and contains additives which significantly reduce deposition of the precipitates formed during titration on the electrode membrane and so permit an interference-free titration.

If differently manufactured sodium tetraphenylborate solution is used then the indicator and the reference electrode must be cleaned after each titration. Moreover, the titre should be checked at regular intervals.

Apart from the normal sodium tetraphenylborate it can sometimes be advantageous to use modified sodium tetraphenylborate. In particular, some fluoro-substituted derivatives exhibit a very interesting profile. Complexes of the barium nonionic associate with the fluoro-substituted sodium tetraphenylborate are more stable than with the standard sodium tetraphenylborate. This results in advantages in the titration of nonionic surfactants in the lower concentration ranges. Even in the titration of betains this substituted sodium tetraphenylborate has some advantages. However, the greatest disadvantage of this fluoro-substituted sodium tetraphenylborate is its very high price, which means that the cost of 1 L titrant may be more than 1000 $. It may be that price reductions are possible if the demand rises, so that this development should be closely observed.

During the titration the complexes formed with the fluoro-substituted sodium tetraphenylborate increase in stability as the degree of substitution increases. However, higher fluoro-substituted sodium tetraphenylborates are less water-soluble, which further reduces their applications.

**IMPORTANT NOTE**

The sodium tetraphenylborate solutions given below have only a limited shelf-life. Only that amount of sodium tetraphenylborate solution should be prepared which will be used within two to three months. Occasionally growth of microorganisms has been observed in the sodium tetraphenylborate solution. This can be avoided by adding 2 to 5 mL of a commercial formaldehyde solution for preservation when the titrant is being prepared. After this addition the sodium tetraphenylborate solution is filled up to the mark in the flask. The addition of formaldehyde solution has no negative influence on the titration. Other preservatives may be used after corresponding checks have been carried out.

The polyvinyl alcohol in the sodium tetraphenylborate solution can, if this is only very infrequently used, cause problems with the Dosimat stopcock, which may get stuck. This can be observed particularly when a ceramic stopcock is used. In order to protect the Exchange Unit and the Dosimat, stopcock switching should be checked manually after the Exchange Unit has not been used for a longer period. If it is found that switching is more difficult than normal then the flat stopcock should be removed from the Exchange Unit and cleaned.

#### 6.4.2 Preparation and titre determination of a 0.01 mol/L sodium tetraphenylborate solution

**Equipment and reagents**

- Sodium tetraphenylborate (e.g. Merck 1.06669.100)
- 0.1 mol/L aqueous sodium hydroxide (e.g. prepared from Merck Titrisol 9959)
- Polyvinyl alcohol protective colloid (e.g. Merck 114266100)
- Papaverine hydrochloride (e.g. Biochemika, Fluka)
- Hydrochloric acid 36 to 38% (e.g. Baker 6081)
- Distilled water
- Analytical balance (e.g. Sartorius A200)
- Automatic titrator with peripherals (e.g. Metrohm 726 Titroprocessor or 716, 736, 751 Titrimo)
- 6.0507.010 NIO Surfactant Electrode (Metrohm)
- 6.0726.100 Ag/AgCl reference electrode with intermediate electrolyte (double junction) and ground joint diaphragm (Metrohm)

**Note:** The intermediate electrolyte of the reference electrode must be replaced by aqueous 3 mol/L NaCl solution!

**Titration beaker, matched to sample changer, if present**

**Measuring cylinders 10, 50 and 100 mL**

**Beakers**
Preparation of the 0.01 mol/L sodium tetraphenylborate solution

Approx. 200 mL of water are heated to 60...70 °C in a suitable beaker. 10 g polyvinyl alcohol are slowly added to the hot water and stirred until an almost clear solution is obtained. This solution is allowed to cool down to room temperature and then transferred to a 1 L volumetric flask. 10 mL of 0.1 mol/L aqueous sodium hydroxide are added to this solution.

In a second beaker exactly 3.4223 g sodium tetraphenylborate are weighed in and dissolved in a little water. This solution is transferred quantitatively with water to the volumetric flask containing the polyvinyl alcohol solution and sodium hydroxide. Then the flask is filled to the mark with distilled water and mixed thoroughly. This solution is then filled into a Dosimat bottle.

The solution of the protective colloid must be cooled down to room temperature before addition of the sodium tetraphenylborate, as otherwise the titrant cannot be used!

Titre determination of 0.01 mol/L sodium tetraphenylborate solution

General points concerning the procedure

The titration should be carried out with a Titroprocessor with which the titrant addition can be carried out dynamically, i.e. as a function of the alteration of the electrode potential.

The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, are smooth and reasonably free of spikes.

Titration parameters

The titration parameters for the Metrohm 726 and 670 Titroprocessors and 716, 736, 751 Titrinos are given below. If titrators from other manufacturers are used then the parameters should be adapted accordingly.

<table>
<thead>
<tr>
<th>670 Titroprocessor</th>
<th>716, 736, 751 Titrino</th>
<th>726 Titroprocessor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Titration parameters</strong></td>
<td><strong>Titration parameters</strong></td>
<td><strong>Titration parameters</strong></td>
</tr>
<tr>
<td>Meas pt. density 4</td>
<td>Meas pt. density 4</td>
<td>Meas pt. density 4</td>
</tr>
<tr>
<td>Min. incr. 50 μl/min</td>
<td>Titr. rate 30 ml/min</td>
<td>Titr. rate 30 ml/min</td>
</tr>
<tr>
<td>Signal drift off</td>
<td>Signal drift off</td>
<td>Signal drift off</td>
</tr>
<tr>
<td>Equilibr. time 30 s</td>
<td>Equilibr. time 30 s</td>
<td>Equilibr. time 30 s</td>
</tr>
<tr>
<td>Start conditions pause</td>
<td>Start conditions pause</td>
<td>Start conditions pause</td>
</tr>
<tr>
<td>Stop conditions stop V 20 ml</td>
<td>Stop conditions stop V 20 ml</td>
<td>Stop conditions stop V 20 ml</td>
</tr>
<tr>
<td>726 Titroprocessor</td>
<td>716, 736, 751 Titrino</td>
<td>670 Titroprocessor</td>
</tr>
<tr>
<td>Meas pt. density 4</td>
<td>Meas pt. density 4</td>
<td>Meas pt. density 4</td>
</tr>
<tr>
<td>Min. incr. 50 μl/min</td>
<td>Titr. rate 30 ml/min</td>
<td>Titr. rate 30 ml/min</td>
</tr>
<tr>
<td>Signal drift off</td>
<td>Signal drift off</td>
<td>Signal drift off</td>
</tr>
<tr>
<td>Equilibr. time 30 s</td>
<td>Equilibr. time 30 s</td>
<td>Equilibr. time 30 s</td>
</tr>
<tr>
<td>Start conditions pause</td>
<td>Start conditions pause</td>
<td>Start conditions pause</td>
</tr>
<tr>
<td>Stop conditions stop V 20 ml</td>
<td>Stop conditions stop V 20 ml</td>
<td>Stop conditions stop V 20 ml</td>
</tr>
</tbody>
</table>

Carrying out the titre determination

Note: Papaverine hydrochloride is toxic. Corresponding safety precautions are to be taken when this substance is used.

0.04 g papaverine hydrochloride are weighed out exactly to 0.1 mg in the titration beaker, dissolved in 100 mL water and then 3 to 4 drops of the concentrated hydrochloric acid are added. The titration against the 0.01 mol/L sodium tetraphenylborate solution is now carried out by the titrator using the above-mentioned titration parameters.

Evaluation

The titre of the 0.01 mol/L sodium tetraphenylborate solution is calculated according to the following equation:

\[
Titre = \frac{E \times 1000}{M \times V \times c}
\]

where:

- \( V \) consumption of sodium tetraphenylborate solution (in mL)
- \( c \) nominal concentration of sodium tetraphenylborate solution (0.01 mol/L)
- \( M \) molar mass of papaverine hydrochloride (375.9 g/mol)
- \( E \) weight of papaverine hydrochloride (in g)

The determination should be made as a fourfold determination. The titre used for subsequent calculations is the mean value of the fourfold determination and is given to four decimal places.

The titre can also be calculated directly by the titrator, but the equation must then be converted into the form which the particular titrator requires.
6.4.3 Preparation and titre determination of a 0.1 mol/L sodium tetraphenylborate solution

Equipment and reagents

- Sodium tetraphenylborate (e.g. Merck 1.06669.100)
- 0.1 mol/L aqueous sodium hydroxide (e.g. prepared from Merck Titrisol 9959)
- Gum arabic (e.g. SIGMA G-9752)
- Hydrochloric acid 36 to 38% (e.g. Baker 6081)
- Papaverine hydrochloride (e.g. Biochemika, Fluka)
- Distilled water
- Analytical balance (e.g. Sartorius A200)
- Automatic titrator with peripherals (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736, 751 Titrino)

Preparation of the 0.1 mol/L sodium tetraphenylborate solution

34.223 g sodium tetraphenylborate are weighed out exactly into a suitable beaker and dissolved in approx. 200 mL water. This solution is then transferred quantitatively with water to a 1 L volumetric flask already containing 20 mL of 0.1 mol/L sodium hydroxide. The flask is filled up to the mark with distilled water and then thoroughly mixed. This solution is then filled into a Dosimat bottle.

Preparation of the gum arabic solution

In order to prepare 1 L gum arabic solution 50 g gum arabic powder are weighed out. Gum arabic is a very fine white powder (SIGMA). 1 L distilled water is heated in a suitable beaker almost to boiling point. The gum arabic powder is added under vigorous stirring. The powder immediately clumps but slowly dissolves under vigorous stirring. The solution is then allowed to cool down and preserved with 10 mL 30% formaldehyde solution (Merck). Preservation is necessary for increasing the useful life span of the solution. In this concentration formaldehyde does not interfere with the titration. The finished solution has a slight yellowish colour. A brown precipitate appears at the bottom of the beaker after standing overnight. This is removed by decanting off, but does not interfere with the titration. The solution is now ready for use.

Titre determination of the 0.1 mol/L sodium tetraphenylborate solution

General points concerning the procedure

The titration should be carried out with a titrator with which the titrant addition can be carried out dynamically, i.e. as a function of the alteration of the electrode potential.

The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, are smooth and reasonably free of spikes.

Titration parameters

The titration parameters for the Metrohm 726 and 670 Titroprocessor and 716, 736, 751 Titrinos are given below. If titrators from other manufacturers are used then the parameters should be adapted accordingly.

### 670 Titroprocessor

<table>
<thead>
<tr>
<th>Meas 1</th>
<th>30 s</th>
<th>titration parameters</th>
<th>meas.pt.density</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity</td>
<td>U</td>
<td>Drift/min</td>
<td>off mV</td>
<td></td>
</tr>
<tr>
<td>M.Delay</td>
<td>30 s</td>
<td>DynT</td>
<td>30 s</td>
<td></td>
</tr>
<tr>
<td>MPT.Density</td>
<td>4</td>
<td>Dos.Rate/min</td>
<td>30.000 ml</td>
<td></td>
</tr>
<tr>
<td>f.VResol</td>
<td>0.10%</td>
<td>TStop</td>
<td>evaluation</td>
<td></td>
</tr>
<tr>
<td>N.EPs</td>
<td>8</td>
<td>Volume</td>
<td>20,000 ml</td>
<td></td>
</tr>
<tr>
<td>M.Value</td>
<td>Off</td>
<td>TStop</td>
<td>stop conditions</td>
<td></td>
</tr>
</tbody>
</table>

### 716, 736, 751 Titrino

| Meas.pt.density | 4 | titr.rate | 30 µl/min | |
| M.Delay | 30 s | equilibr.time | 30 s | |
| signal drift | off | TStop | evaluation | |
| equilibr.time | 30 s | N.EPs | EP recognition | all |
| TStop | pause | Volume | 20,000 ml | |
| M.Value | Off | stop conditions | stop V | 20 ml |

### 726 Titroprocessor

| Pause | 30 s | Meas.pt.density | 4 |
| Min.increment | 50 µl | Titr. rate | 30 µl/min |
| Signal drift | off | Equilibr.time | 30 s |

Carrying out the titre determination

Note: Papaverine hydrochloride is toxic. Corresponding safety precautions are to be taken when this substance is used.

0.4 g papaverine hydrochloride are weighed out exactly to 0.1 mg in the titration beaker and dissolved in 90 mL water. 0.5 mL hydrochloric acid and 10 mL gum arabic are added and the titration against 0.1 mol/L sodium tetraphenylborate solution is carried out by the titrator using the above-mentioned titration parameters.
Evaluation

The titre of the 0.1 mol/L sodium tetraphenylborate solution is calculated according to the following equation:

\[
\text{Titre} = \frac{E \times 1000}{M \times V \times c}
\]

where:
- \(V\) consumption of sodium tetraphenylborate solution (in mL)
- \(c\) nominal concentration of sodium tetraphenylborate solution (0.1 mol/L)
- \(M\) molar mass of papaverine hydrochloride (375.9 g/mol)
- \(E\) weight of papaverine hydrochloride (in g)

Formula 13

The determination should be made as a fourfold determination. The titre used for subsequent calculations is the mean value of the fourfold determination and is given to four places after the decimal point.

The titre can also be calculated directly by the titrator, but the equation must then be converted into the form which the particular titrator requires.

6.4.4 Preparation and titre determination of 0.002 mol/L sodium tetraphenylborate solution

Equipment and reagents

Sodium tetraphenylborate solution 0.01 mol/L, prepared as described in section 6.4.2

0.1 mol/L aqueous sodium hydroxide (e.g. prepared from Merck Titrisol 9959)

Papaverine hydrochloride (e.g. Biochemika, Fluka)

Hydrochloric acid 36 to 38% (e.g. Baker Art. 6081)

Distilled water

Analytical balance (e.g. Sartorius A200)

Automatic titrator with peripherals (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736, 751 Titrinos)

6.0507.010 NIO Surfactant Electrode (Metrohm)

6.0726.100 Ag/AgCl reference electrode with intermediate electrolyte (double junction) and ground joint diaphragm (Metrohm)

Note: The intermediate electrolyte of the reference electrode must be replaced by aqueous 3 mol/L NaCl solution!

Titration beaker, matched to sample changer, if present

Measuring cylinders 10, 50 and 100 mL

Beakers

Preparation of 0.002 mol/L sodium tetraphenylborate solution

200 mL of the 0.01 mol/L sodium tetraphenylborate solution are added to a 1 L volumetric flask. After addition of 10 mL aqueous 0.1 mol/L sodium hydroxide the solution is filled to the mark with water and mixed thoroughly. The solution is then filled into the bottle of a Dosimat with 20 mL burette.

Titre determination of the 0.002 mol/L sodium tetraphenylborate solution

General points concerning the procedure

The titration should be carried out with a titrator with which the titrant addition can be carried out dynamically, i.e. as a function of the alteration of the electrode potential.

The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, are smooth and reasonably free of spikes.

Titration parameters

The titration parameters for the Metrohm 726 and 670 Titroprocessor and 716, 736, 751 Titrinos are given below. If titrators from other manufacturers are used then the parameters should be adapted accordingly.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>670 Titroprocessor</th>
<th>716, 736, 751 Titrino</th>
<th>726 Titroprocessor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meas 1</td>
<td>30 s</td>
<td>titration parameters</td>
<td>Pause 30 s</td>
</tr>
<tr>
<td>Quantity</td>
<td>U</td>
<td>meas.pt.density 4</td>
<td>Meas.pt. density 4</td>
</tr>
<tr>
<td>Drift/min</td>
<td>off mV</td>
<td>min.incr. 50 µl</td>
<td>Min.increment 50 µl</td>
</tr>
<tr>
<td>M.Delay</td>
<td>30 s</td>
<td>titr.rate 30 ml/min</td>
<td>Titr. rate 30 ml/min</td>
</tr>
<tr>
<td>DynT 1</td>
<td>30 s</td>
<td>signal drift equilibr.time 30 s</td>
<td>Signal drift off</td>
</tr>
<tr>
<td>MPT.Density</td>
<td>4</td>
<td>start conditions pause 30 s</td>
<td>Equilibr.time 30 s</td>
</tr>
<tr>
<td>Dos RATE/min</td>
<td>30.000 ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f.VResol</td>
<td>0.10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TStop</td>
<td>N.EPs 8</td>
<td>evaluation</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>20.000 ml</td>
<td>EP recognition all</td>
<td></td>
</tr>
<tr>
<td>M.Value</td>
<td>Off</td>
<td>stop conditions stop V 20 ml</td>
<td></td>
</tr>
</tbody>
</table>

Carrying out the titre determination

Preparation of a papaverine hydrochloride standard solution

0.16 g papaverine hydrochloride are weighed out into a 100 mL beaker and dissolved in 50 mL water. This solution is transferred quantitatively with water to a 500 mL volumetric flask, filled up to the mark with water and mixed thoroughly.

Note: Papaverine hydrochloride is toxic. Corresponding safety precautions are to be taken when this substance is used.
**Titre determination**

A volumetric pipette is used to pipette 25 mL papaverine standard solution into a titration beaker. 75 mL water and 3 to 4 drops of concentrated hydrochloric acid are added. Titration against the 0.002 mol/L sodium tetraphenylborate solution is now carried out by the titrator using the above-mentioned titration parameters.

**Evaluation**

The titre of the 0.002 mol/L sodium tetraphenylborate solution is calculated according to the following equation:

\[
\text{Titre} = \frac{E \times V_1 \times 1000}{V_2 \times M \times V \times c}
\]

where:
- \(V_1\) aliquot of papaverine hydrochloride standard solution (25 mL)
- \(V_2\) total volume of papaverine hydrochloride standard solution (500 mL)
- \(V\) consumption of sodium tetraphenylborate solution (in mL)
- \(c\) nominal concentration of sodium tetraphenylborate solution (0.002 mol/L)
- \(M\) molar mass of papaverine hydrochloride (375.9 g/mol)
- \(E\) weight of papaverine hydrochloride in the standard solution (in g)

The determination should be made as a fourfold determination. The titre used for subsequent calculations is the mean value of the fourfold determination and is given to four decimal places.

The titre can also be calculated directly by the titrator, but the equation must then be converted into the form which the particular titrator requires.

**6.5 Titrants for the determination of betains**

Only sodium tetraphenylborate can be considered for use as a titrant for the determination of betains. It is not possible to use the same solution as is used for the determination of nonionic surfactants. In this case the sodium tetraphenylborate solution does not contain the otherwise usual gel builders; these are added just before the titration of the sample solution. (See also section 7.6.1.) In addition it is important to use a concentrated NaTPB solution for the titration of betains.

**6.6 Titrants for the determination of dyes**

For the titration of ionic dyes no special titrants are required. They are titrated in exactly the same way as ionic surfactants, i.e. an anionic indicator is titrated with a cationic surfactant, usually TEGO trant A100. Accordingly, a cationic indicator is titrated with an anionic surfactant. Dodecylsulphate sodium salt and dodecyl benzene sulphonate have been successfully applied.
7 Raw materials

This chapter was produced in cooperation with Hubert Reger, Product Manager Titration, Deutsche Metrohm, D-70794 Filderstadt, Germany

Note added in proof:

Interlaboratory test on potentiometric two-phase titration

In spring 1998 interlaboratory tests were carried out concerning the potentiometric two-phase titration of surfactant raw materials and of a standard detergent. In Germany, these tests were supervised by GAT and in the rest of Europe by CESIO. The tests met with an enormous interest, which meant that many laboratories participated. Accordingly, there is now enough data available for performing statistical evaluations and drawing meaningful conclusions. The organisers report high-quality results and a good agreement with the classical two-phase titration. It has been decided to set up a DGF method for potentiometric two-phase titration and CESIO is going to publish a European standard on the subject.

The positive results of these interlaboratory tests and the standard methods that are being established will increase the importance of potentiometric surfactant titration and in particular that of two-phase titration. Please watch out for the relevant publications by the above organisations and in the technical journals.

Up-to-date information can be obtained from the Metrohm suppliers.

7.1 General

• The potentiometric surfactant titration of raw materials generally poses no problems if the parameters and procedures described in chapter 18 are strictly adhered to. Apart from the two subgroups of secondary alkane sulphonates (section 7.2.5) and alpha olefin sulphonates (section 7.2.6) the results are identical or at least comparable to those of the two-phase titration.

• The sample weight for all raw materials should be calculated so that a consumption of 0.004 mol/L titrant solution of between 10 and 18 mL results. If the titrant consumption is outside this range then the results should not be used and the titration repeated with a corrected sample weight. With a consumption of less than 10 mL significant low-bias results must be expected, depending on the surfactant being analysed.

• For most raw materials it does not make sense to weigh in the amount of sample required for the titration directly, because this amount is so low that an error of 1% or more would be the result. This is why an intermediate dilution should be made in a volumetric flask and an aliquot of this taken with a pipette. In order to eliminate or reduce surfactant properties such as attraction to the glass surfaces, etc., a 1:1 mixture of water and methanol should be selected to make the dilution. The simplest way is to select the aliquot so that the amount of methanol in the subsequent sample solution corresponds to a methanol volume concentration of 5%.

• For the determination of anionic surfactants TEGO trant A100 is the titrant of choice. The use of this titrant is absolutely necessary with all raw materials based on natural fats, e.g. coconut oil, soybean oil, etc. Even for raw materials containing POE units, as is the case with sodium laureth sulphate or disodium laureth sulphosuccinate, only TEGO trant A100 should be used as the titrant.

• All titrations in our laboratory were carried out with the 716 DMS Titrino and the Ionic Surfactant Electrode.

Some problems are encountered during the potentiometric titration of surfactants whose natural raw material is coconut oil in either its natural or hardened form (see Table 10):

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Coconut oil [%]</th>
<th>Hardened coconut oil [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₈</td>
<td>Caprylic acid</td>
<td>7</td>
</tr>
<tr>
<td>C₁₀</td>
<td>Capric acid</td>
<td>6</td>
</tr>
<tr>
<td>C₁₂</td>
<td>Lauric acid</td>
<td>50</td>
</tr>
<tr>
<td>C₁₄</td>
<td>Myristic acid</td>
<td>18</td>
</tr>
<tr>
<td>C₁₆</td>
<td>Palmitic acid</td>
<td>8.5</td>
</tr>
<tr>
<td>C₁₈</td>
<td>Stearic acid</td>
<td>3</td>
</tr>
<tr>
<td>C₁₈/₁₆</td>
<td>Oleic acid</td>
<td>6</td>
</tr>
<tr>
<td>C₁₈/₂</td>
<td>Linoleic acid</td>
<td>1</td>
</tr>
</tbody>
</table>

It is known that the C₈ components can only be determined to a limited extent in anionic surfactants based on coconut fats, and that sometimes even certain problems are encountered with the C₁₀ components. Synthetic mixtures of alkyl sulphates (fatty alcohol sulphates), made from the pure mono-substances octyl sulphate, decyl sulphate, dodecyl sulphate and myristyl sulphate (E.Merck AG, Darmstadt, Germany) show that in the two-phase titration of such a mixture carried out according to standard conditions the octyl sulphate is only partially recorded. This also applies to potentiometric surfactant titration, at least when Hyamine 1622 (N-benzyl-N,N-dimethyl-N-[4-(1,1,3,3-tetramethylbutyl)-phenoxyethoxyethyl] ammonium chloride) is used as titrant. This changes when TEGO trant A100 (1,3-didecyl-2-methylimidazolium chloride) is used as the titrant. The titration curves show the titration behaviour of the pure alkyl sulphates. Other surfactants also exhibit the same behaviour.
The titration results of a real sample should if possible correlate with those obtained by a two-phase titration. However, no agreement can be expected in this case as it must be assumed that the values obtained by the two-phase titration are too low, because the C₈ alkyl chain components cannot be determined or at least are not quantitatively determined.

This means that whenever surfactants based on natural raw materials are to be titrated or must be titrated that particular attention must be paid to whether these contain a C₈ alkyl chain component. If this is the case then the titration must be carried out with TEGO transt A100 as the titrant because only in this way can it be guaranteed that the whole of the alkyl chain sections are also quantitatively determined. For such a sample matrix the sample weight should also be selected so that a consumption of approx. 15 mL 0.004 mol/L titration solution is obtained.

With some surfactants based on natural coconut oil, e.g. sodium cocoyl isethionate (see section 7.2.7) a further step must even be taken. In this case correct values are only obtained from the titration curves evaluated by the titrator when the concentration of the titrant is increased to 0.02 mol/L.

**Potentiometric two-phase titrations**

If raw materials are to be determined with the Surfactrode Resistant in a two-phase medium then both 0.004 mol/L and also 0.02 mol/L titrant solutions can be recommended. In some cases these titrations are to be preferred to those carried out in aqueous media. This applies particularly to the two anionic surfactants sec. alkane sulphonate (section 7.2.5) and α-olefin sulphonate (section 7.2.6).

A further advantage is enjoyed by many of the users of 0.02 mol/L titrants. This is the fact that when this solution is used the sample weight can be 5 times higher than when the 0.004 mol/L solution is used. This means that in many cases it is no longer necessary to carry out a time-consuming intermediate dilution and that the sample can be weighed in directly. This can result in a saving in time which can be very important in the context of quality assurance or the incoming goods control of raw materials.

**7.2 Anionic surfactants**

**7.2.1 Alkyl benzene sulphonates (LAS)**

Table 11 shows the specifications of a typical alkyl benzene sulphonate.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance at 20 °C</td>
<td>Yellowish, separating paste</td>
</tr>
<tr>
<td>Wash-active substance (WAS)</td>
<td>Approx. 50%</td>
</tr>
<tr>
<td>Neutral oil (non-sulphonated portion)</td>
<td>Approx. 1%</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>Approx. 0.5%</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>Approx. 0.3%</td>
</tr>
<tr>
<td>Water</td>
<td>Remainder to 100%</td>
</tr>
<tr>
<td>Density at 20 °C</td>
<td>Approx. 1 g/cm³</td>
</tr>
<tr>
<td>pH value, 2% in deionised water</td>
<td>Approx. 8</td>
</tr>
<tr>
<td>Iodine number, 10% in deionised water</td>
<td>Approx. 1</td>
</tr>
</tbody>
</table>

There are also alkyl benzene sulphonates with a higher water content, but also products that are water-free, highly concentrated, in flakes or sprayed.

Alkyl benzene sulphonates are very easy to titrate potentiometrically. Their titration curves have relatively steep slopes with large potential differences. The neutral oil contained in the product, in this case the non-sulphonated alkyl benzene, does not affect the titration or the electrode membrane. The results of titrating alkyl benzene sulphonate by two-phase titration and potentiometric titration are identical.

The use of the Surfactrode Resistant (two-phase titration) has no advantages with this class of products.

**7.2.2 Titration of hydrotropes**

Sulphonic acid salts such as toluene sulphonate, xylene sulphonate and cumol sulphonate are numbered among the hydrotropes. They have a structure similar to that of the anionic surfactant dodecyl benzene sulphonate, but have no oleophilic alkyl group which would give them surfactant properties.
**Titrations in aqueous medium**

In titrations in aqueous medium the missing alkyl group ensures that the hydrotrope cannot be precipitated out with the known titrants. Hydrotropes therefore cannot be determined under these conditions.

**Potentiometric two-phase titrations**

In potentiometric surfactant titration in a two-phase medium the hydrotrope cannot form any reaction product with the surfactant titrant that could be extracted into the solvent because of the missing oleophilic alkyl group. This has the same consequences as in the titration in aqueous media. Hydrotropes cannot be determined and do not interfere with the determination of ionic surfactants.

### 7.2.3 Fatty alcohol sulphates (FAS)

Table 12 shows the specifications of a typical fatty alcohol sulphate.

<table>
<thead>
<tr>
<th>Table 12: Specifications of a fatty alcohol sulphate (base: fatty alcohol C&lt;sub&gt;12-18&lt;/sub&gt;SO₃Na)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance at 20 °C</td>
</tr>
<tr>
<td>Wash-active substance (WAS)</td>
</tr>
<tr>
<td>Neutral oil (non-sulphonated portion)</td>
</tr>
<tr>
<td>Sodium sulphate</td>
</tr>
<tr>
<td>Sodium chloride</td>
</tr>
<tr>
<td>Bulk density</td>
</tr>
<tr>
<td>pH value, 2% in deionised water</td>
</tr>
</tbody>
</table>

Other concentrations are available commercially, but also fatty alcohol sulphates based on a completely different fatty alcohol to that given here are available. Both fatty alcohol sulphates based on raw materials as well as those based on synthetic oxoalcohols are available.

Alkyl sulphates, also known as fatty alcohol sulphates, can be titrated very easily without any problem. The results obtained also agree very well with those obtained by two-phase titration. See Table 2 (chapter 1).

With fatty alcohol sulphates it can also be clearly recognised and confirmed that in potentiometric surfactant titration the titration is carried out according to diminishing oleophilicity. Fig. 105 shows titration curves for a fatty alcohol sulphate based on natural coconut oil in a comparison of the titrants TEGO trant A100 and Hyamine 1622. With the titrant TEGO trant A100 several points of inflection can easily be recognised in the derivative curve. The first inflection point corresponds to dodecyl sulphate (C₁₂) and higher alkyl sulphates (> C₁₂), the second to decyl sulphate (C₁₀) and the third to octyl sulphate (C₈). Titration at pH = 3 is recommended.

Fatty alcohol sulphates should preferably be titrated with TEGO trant A100 as titrant. The titration curves have an unusually steep slope and almost achieve the characteristics of an acid-base titration. However, it is necessary that the titrator is optimally set for these steep potential jumps as otherwise incorrect evaluations could occur.

![Comparison of the titrations of coco alkyl sulphate with TEGO trant A100 and Hyamine 1622](Fig. 105: Comparison of the titrations of coco alkyl sulphate with TEGO trant A100 and Hyamine 1622)

The use of the Surfactrode Resistant for the two-phase titration has no advantages with this class of products.
7.2.4 Fatty alcohol ether sulphate (FAES)

![Structural formula of a fatty alcohol ether sulphate](image)

Fig. 106: Structural formula of a fatty alcohol ether sulphate

Table 13 shows the specifications of a typical fatty alcohol ether sulphate.

**Table 13: Specifications of a fatty alcohol ether sulphate (base: synthetic fatty alcohol C\textsubscript{12-14} with approx. 3 mol POE)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance at 20 °C</td>
<td>Colourless to yellow liquid</td>
</tr>
<tr>
<td>Wash-active substance (WAS)</td>
<td>Approx. 28%</td>
</tr>
<tr>
<td>Neutral oil (non-sulphated portion)</td>
<td>Approx. 0.7%</td>
</tr>
<tr>
<td>Sodium sulphate, %</td>
<td>Approx. 0.3%</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>Traces</td>
</tr>
<tr>
<td>Water</td>
<td>Remainder to 100%</td>
</tr>
<tr>
<td>Density at 20 °C</td>
<td>Approx. 1 g/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>pH value, 2% in deionised water</td>
<td>7 to 7.5</td>
</tr>
</tbody>
</table>

The ease with which alkyl ether sulphates or also fatty alcohol ether sulphates can be titrated\cite{93, 94, 95, 96} depends to the greatest extent on the number of POE units in the ether portion of the surfactant. If e.g. a sodium laureth-2.5 sulphate is declared by the manufacturer as being a laureth sulphate with statistical 2.5 POE units, then a relatively complex mixtures of different substances is hidden behind this term.

![Maldi TOF spectrum of laureth-2.5 sulphate](image)

Fig. 107: Maldi TOF spectrum of laureth-2.5 sulphate

Fig. 107 shows the Maldi spectrum of such a compound. It can be clearly seen that the starting alcohol is a mixture of decyl, dodecyl or lauryl, myristyl and cetyl alcohols, of which lauryl and myristyl alcohols are the main components. The POE range from 0 up to 13. This means that the surfactant is a mixture of about 60 individual components which differ greatly in their hydrophilic-lipophilic balance. In order to be able to determine the more hydrophilic substances such as sodium decyleth-12 sulphate quantitatively it is also necessary to use TEGO trant A100 as the titrant. The following ether sulphates are often used in the cosmetics industry and can be titrated without interference:
• Sodium laureth-2 sulphate
• Sodium laureth-2,5 sulphate
• Sodium laureth-3 sulphate
• Magnesium laureth-2 sulphate
• Magnesium laureth-2,5 sulphate
• Magnesium laureth-3 sulphate
• MIPA laureth-2,5 sulphate
• MIPA laureth-3 sulphate

The results obtained agree with those of the two-phase titration. Titration at pH = 3 is recommended. Even those raw materials that contain mixtures of ether sulphates with a higher POE portion can still be correctly titrated. However, in this field there are only very few substances so that little experience has been made. Fig. 108 shows the titration of three different laureth ether sulphates:

- Sodium laureth-2 sulphate
- Sodium laureth-2,5 sulphate
- Sodium laureth-3 sulphate

All three are normal commercial products with a similar distribution of homologues to that shown in Fig. 107. The number of POE units which are given in the product names corresponds to the statistical mean value. It can be plainly seen here that as the number of POE units in the surfactant increases, the titration curves become flatter. If this trend is extrapolated further then it is conceivable that the titration of a lauryl ether sulphate with a higher number of POE groups will not be possible.

Fatty alcohol ether sulphates with a higher number of POE units also cause problems in classical two-phase titrations. Their other physicochemical properties also correspond more to those of the nonionic surfactants. This is why it is possible to determine higher ethoxylated fatty alcohol ether sulphates titrimetrically as nonionic surfactants (see also chapter 13).

Fatty alcohol ether sulphates with a statistical content of more than three POE units are better titrated with the Metrosensor Surfactrode Resistant™. With this electrode, the levelling-out influence of the POE units in the molecule is much less noticeable. The Surfactrode Resistant can also be used to titrate fatty alcohol ether sulphates with 8, 10 or 12 statistical POE units in the molecule simply and well. It is not yet possible to make any statement about even higher ethoxylated fatty alcohol ether sulphates as these have not been available for testing. In the titration of fatty alcohol ether sulphates in aqueous media the titration curves become ever flatter as the number of POE-units in the molecule increases. This trend is not observed in titrations with the Surfactrode Resistant in two-phase media. Both the titration curves and the derivative curves show only a very slight dependence on the degree of ethoxylation of the fatty alcohol ether sulphate.

7.2.5 Sec. alkane sulphonate (SAS)

Table 14 shows the specifications of a typical sec. alkane sulphonate.

<table>
<thead>
<tr>
<th>Appearance at 20 °C</th>
<th>Yellowish, separating paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wash-active substance (WAS) of which disulphonate</td>
<td>Approx. 60% approx. 7%</td>
</tr>
<tr>
<td>Neutral oil (non-sulphonated portion)</td>
<td>Approx. 0.6%</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>Approx. 4%</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>Approx. 0.2%</td>
</tr>
<tr>
<td>Water</td>
<td>Remainder to 100%</td>
</tr>
<tr>
<td>Density at 20 °C</td>
<td>1.1 g/cm³</td>
</tr>
<tr>
<td>pH value, 2% in deionised water</td>
<td>Approx. 7.5</td>
</tr>
<tr>
<td>Colour, 10% solution (ALPHA)</td>
<td>Approx. 40</td>
</tr>
</tbody>
</table>

Titration in aqueous media

Sec. alkane sulphonates, also known as n-paraffin sulphonates, belong to the problem cases of potentiometric surfactant titration in aqueous media, the results obtained here being between 5 and 10% (usually about 8%) higher than those obtained by the classical two-phase titration. Why this should be and why it perhaps must be will be explained here. This means, however, that this section has to be taken a little further.

The production of sec. alkane sulphonates involves the following steps: In a continuous sulphoxidation process the n-paraffin is first allowed to react with sulphur dioxide and oxygen under UV-radiation, whereby the paraffin sulphonatic acid
is formed. In order to prevent this paraffin sulphonic acid from being further sulphonated, it is continuously extracted from the production process with water. The alkane sulphonate is obtained as a result of various processing, separation and neutralization steps. In the production process it is obtained as a water-free, beeswax-like product which is either sold in the form of tablets or diluted with water as a solution. Although the paraffin sulphonic acid formed during the sulphonation process is continually removed from the production process by extraction with water, it still contains between 5% and 10% paraffin disulphonic acid and paraffin polysulphonic acid. Fig. 109 shows the chemical structure of the product and its by-products. When the raw material is later processed the paraffin disulphonic acid and paraffin polysulphonic acid are not separated off but remain in the product.

If the potentiometric surfactant titration, like most potentiometric surfactant titrations of anionic surfactants, is now carried out at pH = 3, then each sulphonate group present in the molecule reacts stoichiometrically with one mol titrant.

For 1 mol paraffin monosulphonate 1 mol cationic titrant is consumed. For 1 mol paraffin disulphonate 2 mol cationic titrant is consumed and for 1 mol paraffin trisulphonate 3 mol cationic titrant are consumed, and so on. It can be recognised here that the potentiometric surfactant titration of sec. alkane sulphonates follows the general stoichiometrical rules, similar to an acid-base titration in which 1 mol sulphuric acid reacts with 2 mol sodium hydroxide. If the titration curve for the potentiometric titration of a sec. alkane sulphonate shown in Fig. 110 is examined then, although it is obviously flatter than e.g. that of a linear alkyl benzene sulphonate, there are no other features which could indicate possible high-bias results.

If the pH of the potentiometric surfactant titration of sec. alkane sulphonates is reduced to pH = 1, then there are no significant differences in the results, as Table 15 shows.

<table>
<thead>
<tr>
<th>pH Value (buffer)</th>
<th>Value 1 (%)</th>
<th>Value 2 (%)</th>
<th>Value 3 (%)</th>
<th>Value 4 (%)</th>
<th>Value 5 (%)</th>
<th>Mean (%)</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 1 (buffer)</td>
<td>31.2</td>
<td>31.2</td>
<td>31.7</td>
<td>31.3</td>
<td>31.2</td>
<td>31.3</td>
<td>0.217</td>
</tr>
<tr>
<td>pH 3 (buffer)</td>
<td>31.2</td>
<td>31.1</td>
<td>31.5</td>
<td>30.9</td>
<td>31.1</td>
<td>31.2</td>
<td>0.219</td>
</tr>
<tr>
<td>pH 1 (H₂SO₄)</td>
<td>30.9</td>
<td>30.9</td>
<td>31.0</td>
<td>30.5</td>
<td>30.8</td>
<td>30.8</td>
<td>0.192</td>
</tr>
</tbody>
</table>

Only when the acid concentration is further increased, i.e. the pH lowered, do we obtain a different picture. If the titration is carried out in approx. 0.3 to 0.5 mol/L sulphuric acid, i.e. at the limit tolerated by the electrode, the resulting titration curve in Fig. 111 shows a different picture. These titrations were carried out with the Metrohm Ionic Surfactant Electrode. At this point is must be pointed out that this strongly acid range is far beyond the ranges given by other electrode manufacturers for use of their electrodes. Please note that this high concentration of sulphuric acid might destroy other surfactant electrodes.

In the derivative curve of the titration two points of inflection can be clearly seen. In the evaluation the first point of inflection corresponds approximately to the value which is also obtained by two-phase titration. The second point of inflection corresponds to the otherwise determined content which would contain an excess amount of approx. 7%. From approx. ten titrations carried out, a standard deviation of just over 1.2% can be obtained for the first point of inflection, while the standard deviation for the second point of inflection is approx. 0.3%. However, the value for the first point of inflection is too high for formulating a test procedure for the titration of sec. paraffin sulphonates based on titrations in media containing high sulphuric acid concentrations.

The classical two-phase titration of sec. alkane sulphonates is also not completely free from problems. If a titrant consumption of 10 mL is assumed for the two-phase titration then the point of inflection in the titration of a linear alkyl benzene sulphonate can be recognised with an accuracy of approx. 2 µL. For the titration of a sec. alkane sulphonate...
this value is considerably higher. In tests carried out for a thesis covering this topic, a value was obtained which was higher by a factor of 100 and more, with a range of variation of 0.3 mL. While in the titration of the alkyl benzene sulphonate the colour change from red to blue-green takes place without any intermediate steps, in the titration of the sec. alkane sulphonate this takes place in a range of approx. 0.3 mL, with a hardly imaginable number of intermediate colours and nuances. This means that different persons will assess the colour change differently. In many laboratories in which the two-phase titration of sec. alkane sulphonates is carried out, sodium sulphate is added to suppress the dissociation of the disulphonates and trisulphonates, so that it can be assumed that in two-phase titration virtually only the paraffin monosulphonate portion is titrated. The addition of sodium sulphate in potentiometric surfactant titration has no influence on the result.

Potentiometric surfactant titration will establish itself further. As the stricter regulations concerning industrial safety are becoming ever more important, it is to be expected that two-phase titrations based on toxic chloroform are on their way out. In the Journal of the American Oil Chemists’ Society (JAOCS) Buschmann recently reported about the potential carcinogenicity of the indicator used in two-phase titration, dimidium bromide. This article caused quite a sensation, particularly in the USA.

The high-bias results obtained in the potentiometric surfactant titration of sec. alkane sulphonates, which result from the fact that each sulphonate group in the molecule is titrated, cannot simply be ignored because if three sulphonate groups are titrated in a paraffin trisulphonate this does not mean that a threefold surfactant activity is also present. In the author’s opinion it would be necessary for the committee responsible for the standardisation of surfactant analyses to concern itself with this problem and produce a regulation. As the amounts of paraffin disulphonates and paraffin trisulphonates or polysulphonates are very similar for most manufacturers, it ought to be possible to agree to a reduced molar mass to be used for the calculation of the paraffin sulphonate contents.

The molar masses which are used to calculate the content of sec. alkane sulphonates in two-phase titrations are not the real and actual molar masses which are normal in stoichiometry. The expression «two-phase-titration equivalent» or «Epton equivalent» would certainly be more accurate. This is actually a calculated molar mass which, when used for a model substance, produces a result which correlates with that obtained by other analytical methods.

As often described, surfactant titration in aqueous media is based on a different detection principle. This is why in this case a corresponding electrode equivalent must be introduced. In many plants such correction factors are in use—with good results.

**Potentiometric two-phase titrations**

In potentiometric two-phase titration results are also obtained which are higher than those of the classical two-phase titration.

The results obtained in the titrations depend to a large degree on the alcohol content during the potentiometric two-phase titration. This applies both to the curve shape and to the result, the calculated sec. alkane sulphonate content. If the titration is carried out without any addition of alcohol at all then a separation according to degree of sulphonation is obtained. Polysulphonates and monosulphonates yield different potential jumps. However, the reproducibilities of these titration curves are not so good. The first potential jump in particular, corresponding to the monosulphonate, is weak. The results obtained in the titrations depend to a large degree on the alcohol content during the potentiometric two-phase titration. If the usual addition for potentiometric two-phase titrations of 10 mL methyl isobutyl ketone and 10 mL ethanol is made then very good and steep titration curves are obtained which can easily be evaluated by the titrator algorithm; relative standard deviations of 0.2% or even lower can be achieved. However, the results are clearly higher than those of the classical two-phase titration. Work should continue to be carried out with exactly these conditions.

### 7.2.6 α-olefin sulphonates

Table 16 shows typical specifications of an α-olefin sulphonate.

<table>
<thead>
<tr>
<th>Table 16: Specifications of an α-olefin sulphonate (base: α-olefin)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance at 20 °C</strong></td>
</tr>
<tr>
<td><strong>Washing active substance (WAS)</strong></td>
</tr>
<tr>
<td><strong>Neutral oil (non-sulphonated portion)</strong></td>
</tr>
<tr>
<td><strong>Sodium sulphate</strong></td>
</tr>
<tr>
<td><strong>Water</strong></td>
</tr>
<tr>
<td><strong>Density at 20 °C</strong></td>
</tr>
<tr>
<td><strong>pH value, 2% in deionised water</strong></td>
</tr>
</tbody>
</table>

**Titrations in aqueous media**

In a similar manner to sec. alkane sulphonate (SAS) in section 7.2.5, α-olefin sulphonate is also a “problem child” in potentiometric surfactant titration in aqueous media. High-bias results are also obtained for α-olefin sulphonate compared to the classical two-phase titration. These amount to about 3%. The reason for these high-bias results is the same as that for the sec. alkane sulphonates. The α-olefin sulphonates also contain a certain amount of disulphonates. In a
From other anionic surfactants based on coconut oil it is known that the C
octyl sulphate components are only partially determined. This also applies to potentiometric surfactant titration, at least when Hyamine 1622 (N-benzyl-N,N-dimethyl-N-[4-(1,1,3,3-tetramethylbutyl)-phenoxyethoxyethyl] ammonium chloride) is used as the titrant. However, this changes when TEGO trant A100 (1,3-didecyl-2-methylimidazolium chloride) is used. Other surfactants exhibit the same behaviour. Unfortunately pure-chain isethionates are not available, so that the model cannot be tested. However, it can be assumed that the isethionates behave similarly. This is why only TEGO trant A100 should be selected as the titrant for the determination of isethionates.

Agreement between the analytical results obtained with potentiometric surfactant titration and two-phase titration cannot be expected, as it must be assumed that the sodium octyl isethionate component cannot be quantitatively determined in the two-phase titration and that the values obtained are therefore too low.

As a result of the manufacturing process the normal sodium cocoyl isethionate products from different manufacturers contain about 10% or even more of free fatty acids. Under alkaline conditions these free fatty acids can react anionically as soaps and therefore lead to significant low-bias results in the titration of sodium cocoyl isethionates.

In similar cases the titration of the anionic surfactants at pH = 3 in a buffered medium has allowed the selective determination of surfactant sulphates or sulphonates apart from fatty acids. Attempts to titrate the raw material sodium cocoyl isethionate potentiometrically according to these experiences produced results with an unacceptably poor reproducibility. This was also the case when various other commercial sodium cocoyl isethionates were titrated. Tests at other acidic pH values showed a continuous reduction in the results obtained in multiple determinations, which indicates hydrolysis of the ester group of sodium cocoyl isethionate. A somewhat different trend is seen in titrations in a buffered solution at pH = 5. Here the results initially fall off and then slowly increase again.

If the sample is dissolved in water alone then results are obtained which, although they have a poor reproducibility, exhibit no statistical trend in any direction. This determination method cannot be used for checking production or for quality control because variations in the pH value resulting from the manufacturing process could immediately produce incorrect results.

A further explanation for the poor reproducibility is the limited solubility of the sodium cocoyl isethionate samples. The surfactant itself is easily soluble in water, but the high fatty acid content results in a poor total solubility. The fatty acids are strongly hydrophobic, so that the water can only make a very poor contact with the sample material. This is why it was a matter of priority to find a method for dissolving the surfactant to be titrated from the mixture with the fatty acids without attacking the sodium cocoyl isethionate.

In this case a simple but practical way has been found. The sample is weighed out directly into the sample vessel. 5 mL methanol and 5 mL water are added to it. The amount of methanol should not exceed 5 mL as otherwise the titration curve, which is already rather flat, will become even flatter and can no longer be evaluated. The suspension is then heated until all the sample has dissolved. Care must be taken that the sample is really completely dissolved, as otherwise widely varying results will be obtained. When it is dissolved approx. 80 mL cold water are added and the sample solution is allowed to stand for at least 3 minutes. The free fatty acids are precipitated out and can no longer influence the titration. For the titration of our samples the addition of 2 mL 0.1 mol/L hydrochloric acid solution has proved to be very advantageous. The titrated sodium cocoyl isethionate was most stable against hydrolysis under weakly acidic conditions. By addition of hydrochloric acid we avoided any salt loading from buffers which could negatively influence the titration curve. The free fatty acids present are insoluble under acidic conditions. By addition of hydrochloric acid we avoided any salt loading from buffers which could negatively influence the titration curve. The free fatty acids present are insoluble under acidic conditions.

A method for flat curves is selected for the titration. TEGO trant A100 in the higher concentration of 0.02 mol/L is used as the titrant in order to positively influence the non-optimal titration curve. Unfortunately the free fatty acids soil the electrodes so much that frequent cleaning of the electrodes cannot be avoided. This is the reason why we particularly recommend the Metrohm 730 Sample Changer, which is equipped for optimal electrode rinsing.
A total of twelve different sodium cocoyl isethionates from different manufacturers in Europe and North America was examined; these differed widely in their active substance content. All samples could be analysed according to the method described above. However, the given parameters must be strictly observed. The relative standard deviations that can be achieved are around 0.3% (n = 10).

7.2.8 Sulphosuccinate monoesters

The sulphosuccinates can be divided into two different groups which, on titration, behave in completely different ways:

- Sulphosuccinate monoesters
- Sulphosuccinate diesters

The distribution of sulphosuccinate monoesters is relatively small if one ignores the etherified versions, which are treated in section 7.2.9. The structure of the sulphosuccinate monoester shows two hydrophilic groups, the sulphonic and the carboxylate groups which, depending on the selected pH, can provide the surfactant properties of the sulphosuccinate monoester. Under acidic conditions the surfactant properties are defined by the sulphonic group; the sulphosuccinate monoester can be regarded as being monovalent. Under alkaline conditions the surfactant properties are defined by the sulphonic group and by the carboxylate group. Under these conditions the sulphosuccinate monoester can be regarded as being divalent. For the analyst this means that under acid conditions 1 mol of the titrant is required for 1 mol ester; under alkaline conditions 2 mol titrant are required. This peculiarity opens good differentiation possibilities if sulphosuccinate monoesters are present as well as classical anionic surfactants. This means that two different titrations can be carried out, one under acidic conditions and one under alkaline conditions. Under acidic conditions the sulphate or sulphonic groups of the classical surfactant and the sulphonic groups of the sulphosuccinate monoester are titrated; under alkaline conditions the carboxylate group of the sulphosuccinate monoester is additionally titrated.

Particularly for sulphosuccinates the «quality» of the titration curve depends very strongly on the pH at which the titration is carried out. This is why with a new, unknown raw material of this group it may be necessary to carry out titrations at different pH values and to examine the resulting original titration curves and first derivative curves critically before deciding on the pH range at which subsequent titrations are to be carried out. Not only the titration curves but also the result itself should be examined as the sulphosuccinate monoesters, like all other esters, have a tendency to ester cleavage. If ester cleavage occurs in a sulphosuccinate monoester, the surfactant properties are lost. This is why extreme pH values, both acidic and in particular alkaline, must be avoided. A result of the well-known hydrolysis instability of the sulphosuccinate monoesters is that, in series titrations carried out with a sample changer, the pH adjustment required for the titration must not be carried out at the same time for all samples but immediately before each individual titration. This requires a second automatic burette to either add a buffer or to titrate to a given pH value by addition of either acid or alkali. This means that a titrator is required that has a second electrode input to which a classical pH electrode can be connected.

Some highly crystallised sulphosuccinate monoesters are available on the market. These are very difficult to dissolve in water. To minimise the danger of ester hydrolysis these highly crystallised sulphosuccinate monoesters should be treated as follows. Approximately 25 times the calculated sample weight is weighed out into a beaker and 100 mL methanol are poured in. The mixture is carefully heated under continuous stirring until the substance has dissolved. The methanolic solution is then transferred with water to a 250 mL volumetric flask and filled up to the mark when the solution has cooled down to 20 °C. An aliquot of 10 mL is used for the titration.

7.2.9 Fatty alcohol ether sulphosuccinates

In the cosmetics industry the sulphosuccinate monoesters are the main items of interest. Disodium laureth-3 sulphosuccinate is often used in rinse off formulations as the basic surfactant or co-surfactant. In two-phase titration several problems are encountered with these substances, as a certain routine is necessary for recognition of the colour change. While with fatty alcohol sulphates the colour in the chloroform phase in the region of the point of inflection changes from blue-green to pink within a few µL, with disodium laureth sulphosuccinate this occurs within a few 100 µL and the colour nuances cover every imaginable intermediate colour. In potentiometric titration such raw materials can be
titrated relatively free from problems. In this case the adjustment to the correct pH is also important as, depending on the pH selected, the sulphosuccinate can have different structures.

Fig. 115 shows the different chemical structures of disodium laureth sulphosuccinate under acidic and alkaline conditions.

As expected, the titration curves have different shapes at different pH values and divergent results are obtained. Fig. 116 shows that a titration of this type of sulphosuccinate should not be carried out at pH 5 under any circumstances, because the titration curve cannot be evaluated. If the sulphosuccinate is to be titrated then the necessary pH adjustment is to be carried out immediately before the titration, i.e. when working with a sample changer an additional dosing device should be available to add the corresponding buffer immediately before the titration. This is necessary because disodium laureth sulphosuccinate can hydrolyse under both acidic and alkaline conditions. During saponification the sulphosuccinates lose their surfactant properties. Only TEGO trant A100 should be used as titrant for this group of products.

**Potentiometric two-phase titrations**

In the potentiometric two-phase titration of disodium laureth sulphosuccinate with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

### 7.2.10 Sulphosuccinate diesters

The sulphosuccinate diesters belong to that class of surfactants which can be titrated extremely well. In most cases very steep, easily evaluable potential jumps are obtained, and the titration curves almost have the characteristics of those obtained in acid-base titration. For the sulphosuccinate diester group TEGO trant A100 is also the suitable titrant. The sulphonate group is the surfactant-active group in the molecule. This can be titrated throughout the whole pH range. In contrast to the sulphosuccinate monoesters it is not possible to make any differentiations under acidic or alkaline conditions.

The best-known representative of the group of sulphosuccinate diesters is certainly dioctyl sodium sulphosuccinate or dioctyl sulphosuccinate (DOS); the correct name is: bis-2-ethylhexyl sulphosuccinate. This product, apart from its use in cleaning agent formulations, particularly glass cleaning agents, is also used in surfactant titration as a titrant for the determination of cationic surfactants.

The sulphosuccinate diesters also show a certain instability to hydrolysis, particularly under alkaline conditions. But even under acidic conditions this should not be neglected, so that in the selection of suitable titration conditions extreme pH values should be avoided.

### 7.2.11 Pearl lustre concentrates

The so-called pearl lustre concentrates are dispersions of glycol distearate in a basis of anionic surfactants. The amount of anionic surfactants in pearl lustre concentrates can be determined at pH = 3 without interference. The insoluble glycol distearate, which is finely distributed during the titration, has no negative influence on the titration or the detection. Titrations at pH = 7 or more cannot be recommended as here the stearic acid present in the glycol distearate as a minor component acts as an anionic surfactant (soap) and would lead to high-bias results.

### 7.2.12 Taurodies

![Structural formula of sodium cocoyl taurate](image1)

![Structural formula of sodium methyl cocoyl taurate](image2)
Titrimetric determination of surfactants and pharmaceuticals

Fundamentals

Titrimetric determination of surfactants and pharmaceuticals

Titration in aqueous media

Taurides and also methyl taurides cannot be titrated in aqueous media. The titration curves resulting from the titration are very flat, too flat to be evaluated by the titrators. Our attempts at altering the titration conditions to obtain an improvement were not successful. The use of TEGO trant A100 as titrant also brought no significant alteration.

Potentiometric two-phase titrations

Potentiometric two-phase titration with the Surfactrode Resistant is possible. However, it is absolutely necessary to use TEGO trant A100 as the titrant. The difference in potential from the start to the end of the titration is considerably lower than for other anionic raw materials and amounts to approx. 80 mV. The titration curves are also less steep than one has come to expect from other raw materials. Titrators such as the 726 Titroprocessor, 736 GP Titrino, 716 DMS Titrino, etc., can still handle these curves well. However, only relative standard deviations of approx. 1.6% can be achieved. The titrations are carried out at pH = 3 with the addition of TEGO add.

7.3 Soaps

Fig. 120: Structural formula of a soap, acidic form

Fig. 121: Structural formula of a soap, alkaline form

7.3.1 Possibilities and limits for the determination of soaps

Titrations in aqueous media

Soaps, i.e. fatty acid salts, only exist under alkaline conditions. In acidic media the free fatty acids are again formed which are insoluble and therefore cannot exhibit any surfactant activities. As soaps only exist under alkaline conditions, they can only be determined under alkaline conditions. Seen as a whole the potentiometric surfactant titration for the determination of soaps, similar to the determination in two-phase titration, is only possible to a limited extent. A limitation is given by the too high solubility product of the ion associate formed by the soap and the titrant. This applies particularly to soaps in the lower alkyl chain range.

As shown by Figs. 122 and 123, determination with Hyamine 1622 is only possible from a chain length of C_{16}. If TEGO trant A100 is used a determination is possible from a chain length of C_{12}, i.e. lauric acid.

The titration curves in the graph were recorded with the NIO Surfactant Electrode, which has a better response to the soaps than the Ionic Surfactant Electrode. In this connection it is important to repeat that a NIO Surfactant Electrode which is used for the determination of soaps should only be used for this type of titration.

Soaps with an alkyl chain length of C_{12-18} are often used. Lower units of the fatty acid series have no surfactant properties. This means that soaps which are used technically and have surfactant-like properties can only be determined with TEGO trant A100 as titrant. If the soap involved is a so-called «toilet soap», which contains coconut oil as a raw material, then such a soap cannot be titrated potentiometrically.

In potentiometric surfactant titration soaps generate potential jumps separated according to alkyl chain lengths to a particularly high degree.

Fig. 124 shows the titration of a synthetic mixture of C_{10-16} fatty acids. In this case the titration is again carried out according to decreasing oleophilicity; this means that the most apolar, i.e. the C_{16}, then the C_{14} and finally the C_{12} fatty acids or fatty acid salts will be titrated, while the C_{10} acids, as mentioned above, will not be determined. The separation of the fatty acids according to decreasing oleophilicity depends on the amount of alcohol that has been added to the sample solution. If no separation is desired then either no alcohol at all or only a little should be added.
added. Even the use of this method cannot prevent separation in some cases. The only remaining possibility is to use the last of the potential jumps obtained as the final consumption for calculating the soap content.

**Potentiometric two-phase titrations**

The potentiometric two-phase titration with the Surfactrode Resistant is more suitable for the determination of soaps than titration in aqueous media. The titration curves produced by the potentiometric two-phase titration are steeper and the peaks of the derivative curves narrower than in the titration in aqueous media. However, it is easier to recognise the limits of the potentiometric two-phase titration in the titration of soaps than it is with classical anionic surfactants. Thus the quantitative titration of fatty acid salts is only possible from a chain length of \( C_{12} \), i.e. from lauric acid. Soaps with a shorter chain length also cannot be determined using potentiometric two-phase titration this method. As is known, these fatty acid salts exhibit no surfactant activities.

Soaps should only be titrated with TEGO trant A100 as titrant, because this is the only way in which a fatty acid chain length of \( C_{12} \) can be titrated. In experimental tests a titrant concentration of TEGO trant A100 of \( c = 0.004 \text{ mol/L} \) or \( c = 0.005 \text{ mol/L} \) has proved to be optimal. A more concentrated TEGO trant A100 solution of \( c = 0.02 \text{ mol/L} \) was significantly less suitable.

Exchanging the water-immiscible solvent methyl isobutyl ketone for chloroform in the potentiometric two-phase titration produced significantly better titration curves. When chloroform is used as the solvent, soaps with a chain length of \( C_{10} \), i.e. from capric acid, can be titrated. In contrast the titration curves become poorer when methyl isobutyl ketone is replaced by hexane or cyclohexane as solvent.

Under optimised conditions the potentiometric two-phase titration of soaps yields relative standard deviations of approx. 0.3 to 0.4\%. These are clearly better than the relative standard deviations that can be achieved in aqueous media.

In the potentiometric two-phase titration of soaps with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

### 7.3.2 Determination of soaps in formulations

The determination of soaps in soap products and also in other formulations that contain anionic or nonionic surfactants in addition to soaps is possible.

Figs. 125, 126 and 127 are only intended to show the possibility for titrating soaps.

The titration of soaps is handled in the section on formulations, e.g. the titration of soaps in powder-form washing agents in section 8.1.2, liquid universal washing agents in section 8.1.3 or in all-purpose detergents in section 8.2.4.

In the potentiometric two-phase titration of soaps in formulations with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

### 7.3.3 Titration of lauroyl sarcosinate

A typical commercial lauroyl sarcosinate has the following characteristic composition

- Water 68\%
- Sodium lauroyl sarcosinate 30\%
- Sodium laurate 1 to 2\%

Because of their chemical structure sarcosinates can only be titrated under alkaline conditions. Most of the

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**Fig. 125:** Titration of a soft soap  
**Fig. 126:** Titration of a liquid soft soap  
**Fig. 127:** Titration of a bar soap  
**Fig. 128:** Structural formula of lauroyl sarcosinate
sarcosinates found on the market contain free fatty acid residues. In the alkaline titration of sarcosinates attention must be given to the fact that soaps are formed from these fatty acids which are then determined together with the sarcosinates. Whether it makes sense to determine soaps and sarcosinates together as a total simply depends on the problem to be solved.

Apart from lauroyl sarcosinates, cocoyl sarcosinates are also commercially available. These cannot be titrated. The reason is probably the amount of C\textsubscript{8} and C\textsubscript{10} sarcosinates present.

**Titration in aqueous media**

Because of their soap-like structure sarcosinates cause similar problems to those known from the titration of soaps. Only TEGO trantr A100 can be used as titrant. The titration curves with Hyamine 1622 are so flat that they cannot be evaluated. Even when TEGO trantr A100 is used as titrant the «standard conditions» of the method must be altered because otherwise results are obtained that are clearly too low. If TEGO trantr A100 \(c= 0.05\) mol/L is used then correct results are obtained which even have a good reproducibility. The titration is carried out at \(pH = 10\). Relative standard deviations of 0.74% \((n=10)\) can be achieved.

Particularly on the North American market sarcosinates are used as co-surfactants in various cosmetic formulations; see also section 9.1.6.1.

**Potentiometric two-phase titrations**

The potentiometric two-phase titration of lauroyl sarcosinates is easier to carry out with the Surfactrode Resistant. If TEGO trantr A100 \(c= 0.02\) mol/L is used as titrant the titration gives easily evaluable titration curves and correct results.

The titrations are carried out at \(pH = 10\) as described in section 18.2.2.

In the potentiometric two-phase titration of lauroyl sarcosinates with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The \(pH\) should only be set by adding a buffer solution and \(pH = 10\) must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

### 7.3.4 Titration of ether carboxylic acids

From the amounts produced, ether carboxylic acids can be described as niche products. Nevertheless they play an important role in many formulations and in special applications. This is also reflected in the very wide range of products produced. Ether carboxylic acids can be supplied both as free acids and in the form of salts, usually the sodium salts. From the wide range of ether carboxylic acids available a representative cross-section of commercial products has been titrated.

- Capryleth-6 CA + Hexeth-4 CA
- Capryleth-9 carboxylic acid
- Laureth-4 carboxylic acid
- Laureth-6 carboxylic acid
- Laureth-11 carboxylic acid
- Sodium PEG-4 lauramide carboxylate
- Sodium PEG-6 cocoamide carboxylate

**Titrations in aqueous media**

No evaluable titration curves are obtained.

**Potentiometric two-phase titrations**

It is only possible to titrate the ether carboxylic acids in the form of their salts. This has been confirmed by taking some of the above-mentioned ether carboxylic acids as examples. The best and steepest titration curves were obtained at \(pH = 10\).

All the ether carboxylic acids mentioned above can be determined by a potentiometric two-phase titration. However, the resulting potential curves differ significantly depending on the chemical structure. The longer the C chain in the starter molecule and the lower the number of POE units in the molecule, the better and steeper the titration curve. Further hydrophilic groups in the starter, e.g. the amide group in sodium PEG-4 lauramide carboxylate or in sodium PEG-6 cocoamide carboxylate have a levelling influence on the titration curves.

Products with a short, less defined oleophilic starter and a larger number of POE units in the molecule can be titrated better if the MIBK is exchanged for chloroform.

The achievable relative standard deviations also depend on the chemical structure of the ether carboxylic acid. With laureth-4 carboxylic acid as an example the following statistical data were obtained.
### 7.4 Phosphoric surfactants

**Titrations in aqueous media**

Many surfactants based on phosphoric acid esters are insoluble in water. They therefore cannot be titrated in aqueous media with existing surfactant electrodes.

**Potentiometric two-phase titrations**

Potentiometric two-phase titration of this class of surfactants can be performed with the Surfactrode Resistant without problems. This is carried out by making the samples slightly alkaline with sodium hydroxide and then titrating in the usual way with the addition of MIBK and ethanol.

In the potentiometric two-phase titration of phosphoric acid esters with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

A 0.02 mol/L TEGO trant A100 solution is suitable for use as the titrant. The relative standard deviations which can be achieved are approx. 1%.

### 7.5 Cationic surfactants

#### 7.5.1 General

In principle cationic surfactants can be titrated in the same way as anionic surfactants, except that in this case a cationic analyte is titrated with an anionic titrant. Problems may occur in the titration of quaternary ammonium compounds. These may appear as flat, poorly evaluable titration curves, as incorrect results or in the form of poor reproducibilities. The cause is either an alkyl residue in the molecule that is too short or the presence of other polar groups apart from the hydrophilic groups that provide the surfactant properties. Unfortunately no anionic titrant is known that can solve these problems or that has good properties similar to TEGO trant A100 used in the determination of anionics. In some cases sodium tetraphenylborate can be used as the titrant, but under no circumstances should it be regarded as being an all-round titrant for the determination of cationic surfactants. The reaction is less specific and there are several potential sources of interference. This is true to a particular degree for its use as a titrant for the determination of cationic surfactants in complex formulations.

Particular caution is required if a formulation contains nonionic surfactants based on POE adducts. The additional presence of bivalent cations in the formulation, such as Ca²⁺, can produce significant high-bias results; see section 13.1.2.

The substantivity of the cationic surfactants must also be taken into account. This is why the concentration of methanol in the solution to be titrated should be higher than in the titration of anionic surfactants and should not be less than 10%. For the «quats» that are used, for example, as fabric conditioners the methanol concentration must be increased or, if unsatisfactory solubility makes it necessary, a switch should be made to ethanol or 2-propanol. Note that 2-propanol in particular reduces the quality of the titration curve. Please also note that the working life of a surfactant electrode is shortened if it is constantly used in solutions with an alcohol concentration of more than 10%. However, this shortening is not so dramatic that this aid should not be used.

The substantivity of a quaternary ammonium compound (QAC) also affects a surfactant electrode. If a surfactant electrode is left overnight in a sample solution containing a cationic surfactant it can happen that no more potential alterations are indicated or that the response to an alteration is very slow. The reason is that a very thin monomolecular layer of the cationic surfactant is deposited on the membrane surface and interferes with the detection. In this case both the reference electrode and the SE must be cleaned by rinsing with a few mL methanol and then with water. The electrode is then immediately ready for use again.
If an intermediate dilution is required for the sample weight, for example with highly concentrated raw materials, then this should always be carried out with the addition of methanol. In this way errors which could be caused by the substantivity of the QAC affecting volumetric flasks, pipettes, etc. can be avoided or minimised. An addition of 25% is required. If these solutions are to be stored for a longer period of time then the methanol concentration should be further increased.

### 7.5.2 Dialkyl dimethyl ammonium halides

The best-known technical representatives of this group are:

- Distearyl dimethyl ammonium chloride, the first generation fabric conditioner, which because of its poor biodegradability is no longer used today.
- Didecyl dimethyl ammonium chloride, a well-known and highly effective disinfectant.

In surfactant chemistry we are always dealing with technical compounds that cannot be regarded as being so defined as the correct chemical name would appear to indicate. These are always mixtures which contain different alkyl chain distributions as well as appreciable amounts of monoalkyl trimethyl ammonium chloride and trialkyl monomethyl ammonium chloride.

These factors play no special role in the product distearyl dimethyl ammonium chloride. All the individual substances imaginable are very hydrophobic, so that they are always determined in the total and in the titration only a single, well defined point of inflection is obtained.

For didecyl dimethyl ammonium chloride this is not the case. Tridecyl monomethyl ammonium chloride and didecyl dimethyl ammonium chloride are found in a single jump, but monodecyl trimethyl ammonium chloride is separated and there is a further potential jump in the titration. Whether and how this happens also depends on the alcohol content. The higher the alcohol content, the better the separation. It is also important that sufficient substance is weighed out for the titrant consumption to be large enough and that the titrator algorithm recognises the second potential jump as such and that it is not smoothed out by the smoothing algorithm. When working out an analytical method for this product the raw data obtained during the titration should be stored in a PC and the titration curve shown graphically for data analysis with a standard spreadsheet program such as Excel, etc. For this purpose the unsmoothed raw data should of course be used. This technique allows breaks in the derivative curve to be recognised more easily.

### 7.5.3 Benzalkonium halides

The main field of use of the benzalkonium halide or alkyl dimethyl benzyl ammonium chloride type of quaternary ammonium compound is in disinfectants or similar applications in which bacteria, fungi or similar organisms are to be eliminated, i.e. where microbicidal properties are required. The standard product often used in such applications has the following alkyl chain distribution:

- 40% C\textsubscript{12}
- 50% C\textsubscript{14}
- 10% C\textsubscript{16}

Other benzalkonium chlorides have different alkyl chain percentage distributions, but because of the microbicidal properties these are always in the range from C\textsubscript{12} to C\textsubscript{16}. For benzalkonium compounds with alkyl chains mentioned above there are no problems in potentiometric surfactant titration, e.g. with the Ionic Surfactant Electrode. The analytical results obtained correlate well with those of the two-phase titration.

### 7.5.4 Imidazolium quats

No problems have been encountered with the imidazolium quats tested up to now. The titration curves have good slopes, can be evaluated without problems and the results show a good comparability with those of the two-phase titration.

Fabric conditioners based on imidazolium quats should be titrated with the addition of 20% methanol. Intermediate dilutions for this type of product should either be made in pure methanol or, if necessary because of problems with poor solubility, prepared with the addition of 2-propanol. Dialkylimidazolium quats produce extremely steep titration curves on titration. This must be taken into account when the titrator parameters are set, because otherwise faulty evaluations may be obtained as a result of a simulated second endpoint.
7.5.5 Esterquats

**Titration in aqueous media**

The main problem in the determination of esterquats is their great sensitivity to hydrolysis, which is more or less strongly present in all the various structures. Some of these esterquats hydrolyse so rapidly that after merely half an hour under neutral or weakly alkaline conditions more than 20% of the starter substance may exhibit ester group cleavage. Upon cleavage the esterquat loses its cationic properties and can no longer be titrated as a surfactant.

In principle the cationic activity of this product group is present throughout the whole pH range from strongly acidic to strongly alkaline. However, because of the tendency to undergo hydrolysis, in practice only a very narrow pH range remains in which the titration can be carried out.

This results in a great advantage for the potentiometric surfactant titration method. In contrast to two-phase titration, in which the use of the mixed indicator solution means that a particular acidity is required, in potentiometric surfactant titration the pH can be optimally adapted to the requirements of the sample.

The esterquats used chiefly as fabric conditioners have their greatest stability under acidic conditions at a pH value between 2 and 4. The titration should also be carried out in this pH range. The total of the esterquat and the unquaternised, possibly surfactant-like starter amine is determined.

If serial titrations are carried out using a sample changer then it is important that the pH is set when the sample is dissolved.

In this way ester cleavage before the start of the titration is avoided.

Other esterquats also exist whose stability could lie in a completely different range. Information about this can be found in the corresponding product data sheets or inquiries can be sent to the manufacturers or suppliers.

**Potentiometric two-phase titrations**

The titration of esterquats can also be carried out very well with the Surfactrode Resistant as indicator electrode in two-phase media. The resulting titration curves appear to have a better shape than those obtained by titration in aqueous media. The titration curve also has a typical S-shape, which in principle allows a better and correct evaluation of the endpoint by the titrator algorithm. A splitting up of the endpoint, such as is normally seen in titrations in aqueous media, is only rarely seen in titrations in two-phase media with the Surfactrode Resistant.

The use of 0.02 mol/L dodecyl sulphate sodium salt solution as titrant is also recommended for this titration. An extremely important point which needs to be observed in the titration of esterquats is their great sensitivity to hydrolysis. The sample is weighed out directly into the beaker in which the titration will later be carried out. An intermediate dilution is not necessary and cannot be recommended. Immediately after it has been weighed out the sample should be diluted with water. We have obtained good results by immediately acidifying the solution with 2 mL 25% acetic acid. After the addition of 10 mL MIBK and 10 mL ethanol the titration is immediately carried out with 0.02 mol/L dodecyl sulphate sodium salt solution.

As in all potentiometric surfactant titrations, including those with the Surfactrode Resistant, the sample weight should be selected so that a minimum titrant consumption of 10 mL is obtained. This is the only way to obtain correct results. In this titration relative standard deviations of approx. 1% can be achieved.
7.5.6 Fatty amines

In the neutral form in which these fatty amines are normally supplied these products do not possess surfactant properties. The surfactant-like cationic form is only formed on protonation, i.e. salt formation. A potentiometric titration can therefore only be carried out in this protonated state. The pH range in which the amine is present in the protonated form depends largely on the structure of the amine and the pKₐ value of the amine, but also on the acids used for the salt formation and their pKₐ values. In order to be sure that the fatty amines are analytically determined or determined in a mixture a pH value of 4 or less should be selected. If the fatty amine content in a mixture is not to be determined and if the surfactant activities of the other surfactants permit it then it is recommended that the titration is carried out at a pH value of 9 or more.

Fatty amines based on coconut oil as the raw material cause problems as a result of their share of C₈ alkyl chains. The other fatty amines can be determined without any problems. The addition of methanol is usually required to improve the solubility.

7.5.7 Fatty amine ethoxylates

Titrations in aqueous media

Not all fatty amine ethoxylates can be titrated, neither by potentiometric surfactant titration nor by two-phase titration. The decisive factor is the number of POE units in the molecule. From a certain number of POE units which, however, cannot be exactly defined the fatty amine ethoxylates behave like nonionic compounds. It is not just the number of POE units alone that determines whether a fatty amine ethoxylate can be titrated; but also the chain length of the alkyl chain or chains in the molecule is decisive. As a result there is no sharp separating line concerning the determination of this class of products by titration.

The fatty amine ethoxylates are also technical compounds with a large range of homologue distribution. As a guideline it can be said that the longer the alkyl chain and the smaller the number of POE units in the molecule, the better the chance of being able to titrate the substance.

The quality of the titration curve obtained in the titration also reflects this trend. A stearyl amine with 2 POE units shows a very steep, ideal titration curve. With a POE number of 5 the curve is already clearly flatter, both in the potential difference and in the width of the derivative curve in the inflection point region. Titration curves of a stearyl amine with 10 to 12 mol POE in the molecule can no longer be evaluated. These substances can only be determined like a nonionic surfactant.

Just like fatty amines, fatty amine ethoxylates in the neutral form in which they are normally supplied do not possess surfactant properties. The cationic form is only formed on protonation, i.e. salt formation, and a potentiometric titration can only be carried out in this protonated state. The pH range in which the amine is present in the protonated form depends largely on the structure of the amine and its pKₐ value, the number of POE units in the compound, and also on the acids used for the salt formation and their pKₐ values. In order to be sure that the fatty amine ethoxylates are analytically determined or determined in a mixture a pH of 3 or less should be selected.

Fatty amine ethoxylates based on coconut oil as a raw material cause a large number of problems so that their analytical determination as cationic substances cannot be recommended. This class of substances should either be determined as nonionic surfactants if a sufficiently large number of POE units is present or, if this is not the case, by other means, e.g. chromatographic methods.
Potentiometric two-phase titrations

The use of the Surfactrode Resistant as the indicator electrode in two-phase medium extends the range of POE fatty amines which can be titrated.

Stearyl, lauryl or oleyl amines with up to 10 mol POE in the molecule can still be titrated easily, correctly and without any problems. Before the titration the POE fatty amines were adjusted with acetic acid to a pH of 2 to 3. The titration curves obtained could be easily evaluated by the titrator algorithm. The relative standard deviations achieved were again about 1%.

As in all potentiometric surfactant titrations, including those with the Surfactrode Resistant, the sample weight should be selected so that a minimum titrant consumption of 10 mL is obtained. This is the only way to obtain correct results.

7.6 Amphoteric surfactants

7.6.1 Betains

The name betain comes from Latin and means beet.

About 100 years ago a substance with a betain structure was isolated from sugar beet for the first time and then named. Today this is still known as original betain; its chemical name is trimethylaminoacetic acid.

Today the name betain primarily refers to a class of surfactants with similar structural properties. A betain is understood to be a chemical substance that contains a quaternary nitrogen and an anionic carboxylate group in the molecule. Neither the cationic quaternary nor the anionic carboxylate group can be separated from each other by dissociation.

Two classes of betain products are of great commercial interest today. These are the alkylbetains and the alkylamidobetains. While the alkylbetains are primarily used in specialty cleaning agents, the alkylamidobetains have achieved a great significance as being the most important co-surfactants in the rinse off formulation sector.

The acid amide group (1) shown in Fig. 145 is related to the peptide bond, a component of all natural proteins. The quaternary ammonium group (2) is to a slight degree microbicidal and substantive (see section 2.2). The carboxylate group (3) is a general characteristic of soaps.

The alkylamidobetains used in formulations differ greatly in the alkyl chain distribution. Which alkyl chain section is preferred here depends mainly on the type of the formulation to be prepared from it. The most often used betain is cocamidopropyl betain whose raw material base is hardened coconut oil (see also Table 10).

In other places in this monograph, e.g. in the analysis of fatty alcohol sulphates based on coconut oil or for sodium cocoyl isethionate, a description has already been given of how the analysis of those products based on natural coconut oil with a proportion of lower alkyl chains is considerably more complicated than the analysis of products with higher alkyl chain distributions.

All in all the analysis of such cocamidopropyl betains is relatively problematic. The titration methods used up to now for betain analysis were mostly too non-specific to be considered as real betain determinations. Titration with perchloric acid in a non-aqueous medium, which is certainly the most frequently used betain titration, is primarily a method for the determination of basic components in a sample.

The perchloric acid titration of betains, in which the sample is dissolved in glacial acetic acid and then titrated with acetic perchloric acid, is based on the fact that betain present in the internally balanced betain-like form is converted to the protonated form by the perchloric acid. This method always produces incorrect results if the betain is not present in exactly the internally balanced form at the start of the titration, but as a result of pH adjustments during the production process is already present to some extent in the protonated form. In the same way all other basic compounds that could be present in a betain also interfere, e.g. the starter amine, sodium monochloroacetate, sodium acetate, sodium gluconate, etc. A further difficulty is that if these low-molecular substances are present and also determined in the titration and then evaluated in the calculation equation with the high molar mass of the betain then significantly incorrect results can be obtained. In this way, for example, 1% sodium acetate can simulate the presence of 4% betain.

It is relatively uncommon to find betain titration methods in which the surfactant activity is used as a basis for the determination. Normally all cationic surfactants are determined by titration with an anionic surfactant. After corresponding protonation, betains are present in hydrochloric acid solution as cationic surfactants and it must be possible theoretically to determine them as such. For betains this is not possible, neither in a two-phase titration nor in a potentiometric titration using surfactant electrodes. In the literature mention is made of potentiometric surfactant titrations in which sodium tetraphenylborate is used as titrant instead of the anionic surfactant and this titration is also indicated with an surfactant electrode89. If an attempt is made to reproduce the work in this publication then the results show significant differences from the theoretical content in the form of low-bias results in a range from 10 to 20%. This is caused by the alkyl chain share of the C₈ and C₁₀ betains in the original coconut oil which is not determined in this method. This has been proved by comparative titrations with pure-chain C₈ and C₁₀, C₁₂, C₁₄ and C₁₆ betains.
In our laboratory we have recently worked out and published several new betain analysis methods. A method has also been described that is based on converting the betain to a cationic form by the addition of hydrochloric acid and then titrating with sodium tetrphenylborate solution. Working out this analytical method took a great deal of time and its execution is not without problems. This is why this betain determination method should only be used when the new, modified perchloric acid titration also described in these pages cannot be carried out. The great advantage of this method is that really only the cationic surfactants are determined and other possible additives, e.g. trimethylaminoacetic acid or other amino acids have no interfering influences. With this analytical method for determining the betain content correct results can only be obtained if the test method described in section 18.6 is strictly followed. 0.1 mol/L hydrochloric acid is used as the medium for the titration. Only the Metrohm NIO Surfactant Electrode can be used for the indication of this betain titration. As already described elsewhere, the NIO Surfactant Electrode can be used for a wide range of titrations, but a particular electrode should always be used for a particular application. This means that under no circumstances should an electrode that has been used for a long time for titrating soaps under alkaline conditions, be used for the titration of betains under acidic conditions. No satisfactory results will be achieved if this is done. Other critical factors in this betain titration are the correct sample weight of betain and an optimised content of the added colloid former. Only if the testing method described in section 18.6 is strictly adhered to, particularly with respect to these two points, can correct values with an acceptable standard deviation be achieved. The relative standard deviation that can be achieved with this method if the process has been optimised is 1.0%.

As a variation from the subject of this monograph the optimised perchloric acid titration is mentioned here. The speciality of this perchloric acid titration is that it is no longer a non-specific betain determination in which the alkalinity of a sample is determined but has been modified so that under the conditions given for the test method in section 18.7 only betains or other substances that have a betain or amino acid structure are determined. The method is based on the fact that initially the addition of sodium hydroxide converts all the betain present in the sample into a form in which the quaternary ammonium compound and the carboxylate structure are internally balanced. In order to ensure this an excess of sodium hydroxide is added. By selection of an optimised solvent mixture for the analyte and by selection of a special solvent for the titrant a high resolution of the substances present in the sample according to their pK values is achieved. In this way both the alcalis as well as any free amidamines, free fatty acids and other substances which may be present in the sample are separated from the betain to be determined. The last potential jump in this titration corresponds to the betain to be analysed. The volume consumed between the last but one and the last potential jump is used to calculate the betain content. With this betain determination method standard deviations can be achieved that are better than those of the sodium tetrphenylborate titration by a factor of 3 to 4. This method can also be carried out quickly and safely. A double determination required approx. 15 minutes. This method can be easily automated and if a sample changer is used, 100 titrations in sequence can be carried out without any problems, so that this method can also be performed unattended by laboratory personnel, e.g. overnight. The analytical results are then available or, if one has the corresponding facilities, can be transferred by a computer system to the appropriate division. The test method for this betain determination can be found in section 18.7. Table 17 provides information about the determination of betains and the differing influences of interfering substances in these two methods.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEGO Betain L7</td>
<td>yes</td>
</tr>
<tr>
<td>TEGO Betain F</td>
<td>yes</td>
</tr>
<tr>
<td>TEGO Betain F50</td>
<td>yes</td>
</tr>
<tr>
<td>TEGO Betain CK</td>
<td>yes</td>
</tr>
<tr>
<td>TEGO Betain HS</td>
<td>yes</td>
</tr>
<tr>
<td>Betain C8</td>
<td>yes</td>
</tr>
<tr>
<td>Betain C10</td>
<td>yes</td>
</tr>
<tr>
<td>Betain C12 and higher</td>
<td>yes</td>
</tr>
<tr>
<td>Amidamine</td>
<td>no</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>no</td>
</tr>
<tr>
<td>Glycerol</td>
<td>no</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>no</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>no</td>
</tr>
<tr>
<td>Monochloroacetic acid</td>
<td>no</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td>no</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>no</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>no</td>
</tr>
<tr>
<td>Na-acetate</td>
<td>no</td>
</tr>
<tr>
<td>K-sorbate</td>
<td>no</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>no</td>
</tr>
<tr>
<td>NaCl</td>
<td>no</td>
</tr>
<tr>
<td>EDTA</td>
<td>interferes</td>
</tr>
<tr>
<td>NTA</td>
<td>interferes</td>
</tr>
<tr>
<td>Aminoacetic acid</td>
<td>interferes</td>
</tr>
<tr>
<td>Dimethylaminoacetic acid</td>
<td>interferes</td>
</tr>
<tr>
<td>Trimethylaminoacetic acid</td>
<td>interferes</td>
</tr>
<tr>
<td>Surfactant-like quats</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 17: Interferences in betain determinations
7.6.2 Amphoglycinates

Amphoglycinates can be titrated with sodium tetraphenylborate and with the perchloric acid titration in a similar way to betains. No experience has been made concerning the ability of cocoamphodiglycinates to be titrated, nor do any results exist.

The structural formulas of two different amphoglycinates are shown in Figs. 21 and 22 (chapter 1).

7.6.3 Disinfectants based on amphoteric surfactants

The betain determination of disinfectants based on amphoteric surfactants, e.g. TEGOL 2000, TEGO 51 or products from the TEGO 103 range cannot be carried out with either of the two methods.

![Fig. 146: Structural formula of a disinfectant based on an amphoteric surfactant](image)

Formulations

Table 18 shows the surfactants mainly used in Europe and their principal applications. The table is only intended as a general guide; it is by no means complete.

Table 18 Use of surfactants in European cleaning agents

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>All-purpose washing agents</th>
<th>60 °C washing agents</th>
<th>Light duty/wool washing agents</th>
<th>Liquid washing agents</th>
<th>Carpet cleaners</th>
<th>Dishwashing agents</th>
<th>Cleaning agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl benzene sulphonates</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Alkane sulphonates</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Olefin sulphonates</td>
<td>(+)</td>
<td>(+)</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Fatty alcohol sulphates</td>
<td>+</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>+</td>
<td>(+)</td>
<td>(+)</td>
</tr>
<tr>
<td>Fatty alcohol ether sulphates</td>
<td>+</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>+</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>Sulphosuccinic acid esters</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Soaps</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>(+)</td>
<td>−</td>
<td>−</td>
<td>+</td>
</tr>
<tr>
<td>Natural alkyl polyglycol ethers</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Synthetic alkyl polyglycol ethers</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Alkyl phenolpolyglycol ethers</td>
<td>(+)</td>
<td>(+)</td>
<td>(+)</td>
<td>(+)</td>
<td>(+)</td>
<td>(+)</td>
<td>+</td>
</tr>
<tr>
<td>Fatty acid alkanolamides</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>(+)</td>
<td></td>
</tr>
<tr>
<td>APG</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Legend

+ used
(++) used only in certain products
− not used
8 Washing agents and cleaners

The analysis of washing powders by titration in aqueous media, using surfactant electrodes, was and is not possible. In a very few cases where the washing powder has a simple composition the anionic surfactant content can be determined. The determination of soaps in washing powders by titration in aqueous media, using surfactant electrodes, was and is not possible.

Titration concentration

In most cases titrant solutions with a concentration of 0.004 mol/L have been successfully used for the determination of ionic surfactants. This concentration is also found in very old publications. In all the titrations carried out in the author's laboratory, which form the basis of this monograph, a titrant concentration of 0.004 mol/L was used.

In parallel to this other laboratories have also established a titrant concentration of 0.005 mol/L for the determination of ionic surfactants. All the applications mentioned in this monograph can also be carried out with a 0.005 mol/L titrant solution. The sample weight must be adjusted accordingly.

Higher titrant concentrations up to 0.05 mol/L are possible. They produce steeper titration curves, but the results are no better. This is why this technique cannot be recommended for routine daily use where titrations are always carried out in aqueous solution. Only in cases where the use of 0.004 mol/L solutions results in flat titration curves which cannot be evaluated should more concentrated solutions be used. Another reason for the use of more concentrated solutions is a wide distribution of the alkyl chains of the surfactant as may be found, e.g., in surfactants based on natural coconut oil. Thus, the quantitative determination of sodium cocoyl isethionates is only possible with 0.04 or 0.05 mol/L TEGO trant A100 solution.

During the development and test phase of the Surfactrode Resistant it could be seen that it made more sense to titrate with a 0.02 mol/L solution for most cosmetic formulations as well as for detergents and detergents. This applies to both anionic and cationic surfactants. In this way better, smoother and more typical titration curves can be obtained. «Typical» here means that the titration curves approach the ideal S-shape and therefore the titrator algorithms can evaluate them better. By carrying out an extremely large number of experimental titrations in our laboratory we were able to prove that better standard deviations could be achieved for the formulations mentioned above. In addition, the higher titrant concentration allowed a single method to be used for almost all formulations without the need for having a lot of background knowledge of the products to be analysed. This is the reason for my recommendation of a titrant concentration of 0.02 mol/L in such cases.

In many cases the question of which titrant concentration is the optimal one or even the most suitable one cannot be answered simply. Sometimes it is a good idea to carry out the titration with different titrant concentrations. An assessment should then be made of which titrant concentration produces the better titration curves.

In this monograph a titrant concentration of 0.02 mol/L is often recommended for the formulations sector. Of course, every rule has its exceptions. This became very clear to us when we investigated modern, really new formulations found in both the European and North American markets. In several sectors new formulation trends can be seen. As in the case of detergents and detergents the products are normally not declared at all or only according to a coarse framework. In this way it is more difficult to make a recommendation.

In formulations that contain either nonionic surfactants as the basic surfactant or betains a potentiometric two-phase titration with a 0.004 mol/L solution has proved to be better in practice. The reason for this is quite simple. The lower titrant concentration also means a lower sample weight. This means that smaller amounts of surfactants are found in the titration solution and therefore have a smaller negative influence on the titration curves.

In the titration of powder-form detergents a 0.004 mol/L TEGO trant A100 solution as titrant has been successfully used in the vast majority of cases.

With the Surfactrode Resistant used in two-phase media an important and interesting unmapped region has vanished from the applications chart. It is now finally possible to analyse a wide range of washing powders. The results that are obtained in titrations with the Metrosensor Surfactrode Resistant are, as shown here, to a large extent identical with those obtained in the classical two-phase titration using the mixed indicator system disulphine blue/dimidium bromide.

8.1 Washing agents

8.1.1 Powder-form washing agents

The development of branded detergents started in Germany in 1878 with the introduction of Henkel’s «Bleichsoda» (bleaching soda), which was followed in 1907 by «Persil», a word created from perborate and silicate. In those days «Persil» naturally contained soap as the washing-active substance. A disadvantage was, however, that the soap solution had an alkaline reaction owing to hydrolysis and combined with the hardeners in the water to form wash-inactive lime soap. In 1917 it became possible to synthesise short-chain alkyl naphthalene sulphonates. This class of compounds had very good wetting properties, but an unsatisfactory cleaning effect. In 1928 fatty alcohol sulphates were manufactured for the first time as synthetic surfactants for detergents which, apart from their neutral reaction, effectiveness under acidic conditions and resistance to hardness, also had a high washing performance. In 1932 the first synthetic household detergent was brought onto the market in Germany under the «Fewa» trade mark. Since then a whole range of different household detergents has entered the market for a wide range of different applications.

Because of the extremely complex composition of such powder form detergents the author cannot recommend anybody to determine the surfactant content, i.e. anionic surfactant content, in such a formulation by a potentiometric surfactant titration. Naturally some specialists in the large detergent manufacturing companies carry out their anionic surfactant determinations using a surfactant electrode. These specialists also know what is contained in the detergent and which interferences have to be taken into account. But even these absolute specialists only concern themselves with their
competitors’ products on rare occasions. In their own production control procedures the surfactant electrode is used for both the determination of the classical anionic surfactants and the determination of soaps.

It is more common and makes more sense to determine the anionic surfactants in detergents by two-phase titration. Promising approaches have also been made by the use of the new MetroSensor Surfactrode Resistant which, as its name implies, is solvent-resistant.

The short passage printed above in italics about the titration of anionic surfactants in powder-form detergents appeared in the first, German language edition of my book «Titration von Tensiden und Pharmaka (Titration of Surfactants and Pharmaceuticals)». But revolutions do not only take place in the washing tub; things have also happened in the analytical laboratory. The new solvent-resistant surfactant electrode, the Surfactrode Resistant has, with respect to the titration of powder-form detergents, fulfilled everything that was expected of it after its development. We can now proudly assert that the anionic surfactant content in powder-form detergents can be determined easily and correctly with the Surfactrode Resistant.

The interferences in the potentiometric titration of powder-form detergents in aqueous media can chiefly be traced back to the following ingredients: silicate builders, nonionic surfactants and inorganic salts. Interactions between surfactants and silicates, restriction of the dissociation of the surfactants as a result of the high electrolyte content by, e.g., sodium sulphate and the solubilisation of the precipitated ion pair by a high nonionic surfactant content are the causes for the above-mentioned effects. In addition the silicates destroy the electrode membrane in the long run. These effects can be compensated by extracting the ion pair into an organic phase, i.e. by applying the two-phase principle.

Table 19: Typical formulations of all-purpose washing powders used in Europe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Example</th>
<th>Composition in Western Europe with phosphate [%]</th>
<th>Composition in Western Europe without phosphate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactant</td>
<td>Alkyl benzene sulphonate</td>
<td>5-10</td>
<td>5-10</td>
</tr>
<tr>
<td>Fatty alcohol sulphate</td>
<td>1-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactant</td>
<td>Alkyl polyethyleneglycol ether</td>
<td>3-11</td>
<td>3-6</td>
</tr>
<tr>
<td></td>
<td>APG</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N-methyl gluconamide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antifoam agent</td>
<td>Soap</td>
<td>0.1-3.5</td>
<td>0.1-3.5</td>
</tr>
<tr>
<td></td>
<td>Silicone oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Paraffin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foam regulator</td>
<td>Fatty acid monoethanolamide</td>
<td>0-2</td>
<td></td>
</tr>
<tr>
<td>Complexing agent</td>
<td>Sodium triphosphate</td>
<td>20-40</td>
<td></td>
</tr>
<tr>
<td>Ion exchanger</td>
<td>Zeolite 4A</td>
<td>2-20</td>
<td>20-30</td>
</tr>
<tr>
<td></td>
<td>Polyacrylic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkali</td>
<td>Sodium carbonate</td>
<td>0-15</td>
<td>5-10</td>
</tr>
<tr>
<td>Co-builders</td>
<td>Sodium nitriolacetate</td>
<td>0-4</td>
<td>0-4</td>
</tr>
<tr>
<td></td>
<td>Sodium citrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleaching agent</td>
<td>Sodium perborate</td>
<td>10-25</td>
<td>20-25</td>
</tr>
<tr>
<td></td>
<td>Sodium percarbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleach activator</td>
<td>Tetraacetyl ethylene diamine</td>
<td>0-5</td>
<td>0-2</td>
</tr>
<tr>
<td>Bleach stabiliser</td>
<td>Ethylenediamine tetraacetate</td>
<td>0.2-0.5</td>
<td>0.2-0.5</td>
</tr>
<tr>
<td>Phosphonate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Greying inhibitor</td>
<td>Cellulose ether</td>
<td>0.5-1.5</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>Enzymes</td>
<td>Protease Amylase</td>
<td>0.3-0.8</td>
<td>0.3-0.8</td>
</tr>
<tr>
<td></td>
<td>Cellulase Lipase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optical brightener</td>
<td>Stilbene disulphonic acid</td>
<td>0.1-0.3</td>
<td>0.1-0.3</td>
</tr>
<tr>
<td></td>
<td>Bis-(styryl)biphenyl derivates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion protection</td>
<td>Sodium silicate</td>
<td>2-6</td>
<td>2-6</td>
</tr>
<tr>
<td>Fragrance</td>
<td></td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Colourant</td>
<td></td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Filler and water</td>
<td>Sodium sulphate</td>
<td>rest up to 100</td>
<td>rest up to 100</td>
</tr>
</tbody>
</table>

Fig. 147: Titration of a washing powder in an aqueous phase
Titrations with the Metrosensor Surfactrode Resistant

All titrations were carried out in the two-phase system water/methyl isobutyl ketone under the following conditions:

**Instruments**
- 670 Titroprocessor with 665 Dosimat and 674 Sample Changer (Metrohm Ltd.)

**Electrodes**
- Metrosensor Surfactrode Resistant (Metrohm Ltd.)
- Ag/AgCl reference electrode (Metrohm Ltd.)

**Stirrer**
- 722 Propeller blade stirrer (Metrohm Ltd.)

**Titrant**
- 0.005 mol/L Hyamine 1622 solution
- pH value: 2 to 3; adjusted with 0.5 mol/L hydrochloric acid

8.1.1.1 Titration of surfactant raw materials

The following commercial surfactant raw materials, which are used in washing and cleaning agents, were titrated:
- Fatty alcohol sulphate
- Fatty alcohol ether sulphates with different POE distributions
- Alkyl benzene sulphonate (15% LAS)
- Secondary alkane sulphonate (30% SAS)

The aim was to establish universal titration conditions under which all these anionic surfactants, which are relevant for washing and cleaning agents, could be determined with a good reproducibility, recovery rate and sensitivity. Moreover, the influence of the most important detergent ingredients on the titration should be determined. As a measure for the evaluation of the titration results classical two-phase titrations were carried out in parallel for all the potentiometric titrations. These two-phase titrations were performed according to DGF standard H III 10, the established method for the determination of ionic surfactants in complex matrices.

**Influence of the pH value**

The pH value has an important influence on the shape of the curve and the slope of the potential jump.

As the pH increases there is a clear improvement in the titration curve and thus an increased slope of the curve. At pH = 1 the surfactants are no longer present in a completely dissociated form. This results in a very low slope of the curve.

**Table 20:** pH dependence for LAS

<table>
<thead>
<tr>
<th>pH</th>
<th>Mean value [mmol/100 g]</th>
<th>Standard deviation [mmol/100 g]</th>
<th>Relative standard deviation [%]</th>
<th>Recovery rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 1.0</td>
<td>No inflection point determined</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 2.0</td>
<td>42.96 ± 0.30</td>
<td>0.70</td>
<td>99.80</td>
<td></td>
</tr>
<tr>
<td>pH = 2.5</td>
<td>43.02 ± 0.08</td>
<td>0.19</td>
<td>99.91</td>
<td></td>
</tr>
<tr>
<td>pH = 3.5</td>
<td>43.02 ± 0.14</td>
<td>0.33</td>
<td>99.91</td>
<td></td>
</tr>
</tbody>
</table>

Basic value from classical two-phase titration = 43.06 mmol/100 g

**Table 21:** pH dependence for C_{12/14}-FAEOS 2 POE

<table>
<thead>
<tr>
<th>pH</th>
<th>Mean value [mmol/100 g]</th>
<th>Standard deviation [mmol/100 g]</th>
<th>Relative standard deviation [%]</th>
<th>Recovery rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 1.0</td>
<td>No inflection point determined</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 2.0</td>
<td>71.41 ± 0.12</td>
<td>0.17</td>
<td>101.38</td>
<td></td>
</tr>
<tr>
<td>pH = 2.5</td>
<td>69.94 ± 0.20</td>
<td>0.29</td>
<td>99.29</td>
<td></td>
</tr>
<tr>
<td>pH = 3.5</td>
<td>70.46 ± 0.35</td>
<td>0.50</td>
<td>100.03</td>
<td></td>
</tr>
</tbody>
</table>

Basic value from classical two-phase titration = 70.44 mmol/100 g
Table 22: pH dependence for C\textsubscript{12}-FAS

<table>
<thead>
<tr>
<th>pH</th>
<th>Mean value [mmol/100 g]</th>
<th>Standard deviation [mmol/100 g]</th>
<th>Relative standard deviation [%]</th>
<th>Recovery rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 1.0</td>
<td>No inflection point determined</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 2.0</td>
<td>54.34 ± 0.22</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 2.5</td>
<td>54.62 ± 0.14</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 3.5</td>
<td>54.80 ± 0.14</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Basic value from classical two-phase titration = 54.95 mmol/100 g

Table 23: pH dependence for C\textsubscript{12/14}-FAPOES 0.8 POE

<table>
<thead>
<tr>
<th>pH</th>
<th>Mean value [mmol/100 g]</th>
<th>Standard deviation [mmol/100 g]</th>
<th>Relative standard deviation [%]</th>
<th>Recovery rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 1.0</td>
<td>No inflection point determined</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 2.0</td>
<td>77.84 ± 0.35</td>
<td>0.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 2.5</td>
<td>77.14 ± 0.32</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 3.5</td>
<td>77.82 ± 0.32</td>
<td>0.41</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Basic value from classical two-phase titration = 77.36 mmol/100 g

Table 24: pH dependence for C\textsubscript{12/14}-FAPOES 4 POE

<table>
<thead>
<tr>
<th>pH</th>
<th>Mean value [mmol/100 g]</th>
<th>Standard deviation [mmol/100 g]</th>
<th>Relative standard deviation [%]</th>
<th>Recovery rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 1.0</td>
<td>No inflection point determined</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 2.0</td>
<td>70.81 ± 0.20</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 2.5</td>
<td>69.74 ± 0.11</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 3.5</td>
<td>70.31 ± 0.27</td>
<td>0.38</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Basic value from classical two-phase titration = 69.89 mmol/100 g

Generalising it can be said that a titration can be carried out at pH = 2, 2.5 and 3.5. The largest total potential difference and slope of the titration curve is reached for all surfactants at pH = 2.5 – 3.5. The relative standard deviations at pH = 2 are minimally worse than at pH = 2.5 and pH = 3.5 and are comparable at these two pH values.

A pH value of 1 or less should be avoided as under these conditions sulphates are sensitive to hydrolysis. Their breakdown products no longer have any surfactant properties.

The pH value for the conventional two-phase titration according to the DGF method is fixed at pH = 2. The aim of potentiometric two-phase titration is to imitate the DGF two-phase titration and achieve results which are as close as possible to those of the two-phase titration. This is why pH = 2 was used for the investigations described below, despite the slightly better results obtained at the higher pH values.

8.1.1.1 Results of the raw material titrations

The investigations carried out have shown that the mixing of the two-phase system and the titrant consumption have a decisive influence on the ability to carry out the potentiometric two-phase titration.

Titration curves that are easy to evaluate can only be obtained under optimal mixing conditions; the total potential difference reaches a maximum.

The recovery rates depend on the titrant consumption. For all surfactants with the exception of the secondary alkane sulphonates the recovery rates lie between 99.5% and 101% at a titrant consumption between 10 mL and 15 mL. The relative standard deviations are in the range from 0.2% to 0.7% (see Table 25).

Table 25: Potentiometric two-phase titration of commercial surfactant raw materials

<table>
<thead>
<tr>
<th>Surfactant raw material</th>
<th>DGF H III 10</th>
<th>Potentiometric two-phase titration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Content [mmol/100 g]</td>
<td>Content [mmol/100 g]</td>
</tr>
<tr>
<td>LAS (approx. 15%)</td>
<td>43.1</td>
<td>43.2</td>
</tr>
<tr>
<td>SAS 30 (approx. 30%)</td>
<td>97.5</td>
<td>97.6</td>
</tr>
<tr>
<td>Texapon K 14-S (approx. 73%)</td>
<td>155.2</td>
<td>155.7</td>
</tr>
<tr>
<td>Texapon NSO (approx. 27%)</td>
<td>69.7</td>
<td>69.7</td>
</tr>
<tr>
<td>Texapon K 12 (approx. 15%)</td>
<td>52.2</td>
<td>52.6</td>
</tr>
</tbody>
</table>
The contents given in the table are mean values from tenfold determinations. The given recovery rates refer to the result of the classical two-phase titration according to DGF H III 10.

As can be seen from Table 25, the results of the potentiometric two-phase titration are comparable to those obtained by the classical method. The slightly higher recovery rate observed in most cases is insignificant with respect to the anionic surfactant content present in detergents of max. 20% and the relative accuracy of 5% required in the context of product analyses.

8.1.1.2 Influence of the ingredients

In the development of methods for analysing products, matrix effects must be taken into account. Powder-form detergents contain, apart from anionic surfactants, even larger amounts of nonionic surfactants, water-insoluble sodium aluminium silicates as builders and sodium sulphate as an additive. Potentiometric surfactant titrations of ionic surfactants in aqueous solution carried out with the current surfactant electrodes are disturbed by high concentrations of nonionic surfactants, electrolytes and water-insoluble substances, among others. Low-bias results are obtained and the titration curves can hardly be evaluated. This is caused by salting-out effects and adsorption effects, among others.

The way in which these substances influence surfactant titration with the Metrosensor Surfactrode Resistant was investigated using the titration of alkyl benzene sulphonate as an example; this is still the most often used anionic surfactant in powder-form detergents. The concentrations of nonionic surfactants found in powder-form detergents do not interfere with the titration with the Surfactrode.

8.1.1.2.1 Influence of sodium sulphate

Sodium sulphate is added to washing powders to maintain their flow characteristics and prevent them from caking. Alkyl benzene sulphonate was titrated after the addition of various amounts of sodium sulphate. The titration curves are shown in Fig. 149.

As can be seen, as the sodium sulphate concentration increases the total potential difference becomes smaller and the curves become flatter. However, the curves can still be easily evaluated. Realistic maximum concentrations of sodium sulphate in washing powders lie around 30%; under the selected experimental conditions this corresponds to an added amount of 0.07 g sodium sulphate. At this concentration no visible alteration to the titration curve can be seen. The above-mentioned effect is first seen when 3 times the maximum concentration is added. As a result the additive in powder-form detergents has no effect on the titration of these products.

8.1.1.2.2 Influence of the builders

Apart from the insoluble sodium aluminium silicates mentioned, in particular zeolite A and P, soluble crystalline disilicates are also used in powder-form detergents while phosphates are used as builders in special products. The influence of these common detergent builders on the titration curve of alkyl benzene sulphonate can be seen in Fig. 150.

Compared to the amount of LAS, the builder concentrations used were twice as high as the maximum concentrations found in washing powders; i.e. in the titration of washing powders the effects seen should be less noticeable.

There is a lowering of the total potential difference, which with the insoluble zeolite-type builders is stronger than with the soluble builders. The titration curves are, however, easy to evaluate; there is no significant worsening in the quality of the results.

The stronger, concentration-dependent influence of the insoluble builders on the titration curve in comparison to soluble builders is reflected in the examples of zeolite 4A «Sasil» and Na-SKS 6 in Fig. 151.
Concentration-dependent influences of a soluble and an insoluble builder system on the titration curves

Both the soluble builder Na-SKS 6 and the insoluble builder «Sasil» have a concentration-dependent influence on the titration curves and their derivative. If the concentration-dependent alteration of the titration curves due to the water soluble builder Na-SKS 6 (Fig. 152) and the water-insoluble builder «Sasil» (Fig. 153) are compared then it is clear that the total potential difference and the slope of the «Sasil» curves obtained when doubling the builder weight are clearly worse than those obtained with the doubled weight of Na-SKS 6.

8.1.1.2.3 Influence of the bleaching system

Bleaching agents, bleach activators and complexing agents are further important ingredients of powder-form detergents. Their contents may be as high as 20%. Their influence on the titration of alkyl benzene sulphonate has also been investigated and is shown in Fig. 154.

The bleaching system in particular (activator and perborate) causes a lowering of the potential jump; however, this has no significant influence on the result. Curves that are easy to evaluate are still obtained.

Influence of detergent ingredients – results

All tested washing powder ingredients caused the total potential difference to be lowered to varying extents and the titration curves to become flatter. These effects were often only noticeable at the maximum concentrations of the particular ingredient in the washing powder, so that for powder-form detergents flatter titration curves must be expected; however, these can still be easily evaluated.

8.1.1.3 Titration of washing powders

Thirty-one washing powders based on current formulations on the European market were titrated: all-purpose washing agents, light-duty washing agents and washing agents for coloured fabrics. The various products mainly differed in the type and amount of the surfactants contained, builders and bleaching agents. Some typical formulations are listed in Table 26.

For sample preparation of the washing powders all products were first passed through a sample divider to obtain a representative amount which was then homogenised in an ultracentrifugal mill.

Table 26: Typical formulations of powder-form washing agents*, composition in %

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Light-duty and colour washing agents</th>
<th>All-purpose washing agents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional powder</td>
<td>Superconcentrate</td>
</tr>
<tr>
<td>Anionic surfactants (alkyl benzene sulphonate, fatty alcohol sulphate, fatty alcohol ether sulphate)</td>
<td>5-20</td>
<td>10-20</td>
</tr>
<tr>
<td>Nonionic surfactants</td>
<td>1-5</td>
<td>2-10</td>
</tr>
<tr>
<td>Soaps</td>
<td>1-5</td>
<td>0.1-4</td>
</tr>
<tr>
<td>Builders (zeolite, disilicate, phosphate)</td>
<td>10-35</td>
<td>20-35</td>
</tr>
<tr>
<td>Bleaching agent</td>
<td>-</td>
<td>10-20</td>
</tr>
<tr>
<td>Na silicate</td>
<td>0-7</td>
<td>2-6</td>
</tr>
<tr>
<td>Greying inhibitors</td>
<td>0-5</td>
<td>0-1</td>
</tr>
<tr>
<td>Enzymes</td>
<td>0-1</td>
<td>0.3-0.8</td>
</tr>
<tr>
<td>Optical brighteners</td>
<td>0</td>
<td>0.1-0.3</td>
</tr>
<tr>
<td>Additives</td>
<td>+</td>
<td>0.2-20</td>
</tr>
</tbody>
</table>

Fig. 152: Titration of LAS, influence of Na-SKS 6

Fig. 153: Titration of LAS, influence of «Sasil»

Fig. 154: Titration of LAS, influence of further detergent ingredients

Light-duty and colour washing agents
In Table 27 examples of some European product formulations declared according to the EU directives are given.

**Table 27: Typical formulations for European all-purpose washing agents**

<table>
<thead>
<tr>
<th>Formulation</th>
<th>A in %</th>
<th>B in %</th>
<th>C in %</th>
<th>D in %</th>
<th>E in %</th>
<th>F in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactants</td>
<td>5-15</td>
<td>5-15</td>
<td>5-15</td>
<td>5-15</td>
<td>5-15</td>
<td>5-15</td>
</tr>
<tr>
<td>Oxygen-based bleaching agents</td>
<td>5-15</td>
<td>15-30</td>
<td>15-30</td>
<td>5-15</td>
<td>&gt;30</td>
<td>5-15</td>
</tr>
<tr>
<td>Nonionic surfactants</td>
<td>&lt;5</td>
<td>5-15</td>
<td>5-15</td>
<td>5-15</td>
<td>&lt;5</td>
<td>5-15</td>
</tr>
<tr>
<td>Cationic surfactants</td>
<td>&lt;5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soaps</td>
<td></td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>5-15</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Polycarboxylates</td>
<td>&lt;5</td>
<td>5-15</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>5-15</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Phosphonates</td>
<td>5-15</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td></td>
</tr>
<tr>
<td>Protease</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Lipase</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amylase</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Cellulase</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

As an example, Fig. 155 shows the titration curves of four different washing agents whose compositions differ greatly from each other.

In general, titration curves that were easy to evaluate were obtained for all the products analysed. The standard deviations lay between 0.2 and 0.8 mmol/100 g. The recovery rates were determined relative to the results of the classical two-phase titrations. They ranged from 98% to 102%. In Table 29 the essential titration results for the different types of product are listed.

**Table 28: Typical formulations for European light-duty washing agents**

<table>
<thead>
<tr>
<th>Formulation (declaration according to EU recommendation)</th>
<th>A in %</th>
<th>B in %</th>
<th>C in %</th>
<th>D in %</th>
<th>E in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolites</td>
<td>15-30</td>
<td>15-30</td>
<td>&gt;30</td>
<td>&gt;30</td>
<td>15-30</td>
</tr>
<tr>
<td>Nonionic surfactants</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>15-30</td>
<td>15-30</td>
</tr>
<tr>
<td>Soaps</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Polycarboxylates</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Protease</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Lipase</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Amylase</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Cellulase</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

![Fig. 155: Titration curves obtained with different all-purpose washing agents](https://example.com/fig155.png)

**Table 29: Potentiometric anionic surfactant titration in powder-form washing agents**

<table>
<thead>
<tr>
<th>Product type (builder)</th>
<th>Potentiometric two-phase titration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Content acc. to DGF H III10 [mmol/100 g]</td>
</tr>
<tr>
<td>All-purpose washing agent (phosphates)</td>
<td>61.8</td>
</tr>
<tr>
<td>All-purpose washing agent (zeolite P)</td>
<td>49.4</td>
</tr>
<tr>
<td>Colour washing agent (zeolite A)</td>
<td>51.6</td>
</tr>
<tr>
<td>All-purpose washing agent (zeolite P)</td>
<td>29.3</td>
</tr>
<tr>
<td>Light-duty washing agent (zeolite P)</td>
<td>33.4</td>
</tr>
<tr>
<td>All-purpose washing agent (disilicate/ zeolite A)</td>
<td>32.2</td>
</tr>
</tbody>
</table>
Depending on the product composition there are clear differences in the titration curves (Fig. 155). In particular, products which contain insoluble builders provide relatively flat curves with low potential differences. In such cases the pH value has a decisive influence. For all analysed products the steepest curves with the largest potential differences were obtained at pH = 3. In Fig. 156 this phenomenon is illustrated using an all-purpose washing agent as an example.

### 8.1.1.3.1 Rationalisation of sample preparation

Potentiometric two-phase titration offers, apart from the classical sample preparation – preparation of a stock solution, titration of an aliquot – the option of weighing the sample directly into the titration vessel and titrating it, i.e. one working step is saved. The two types of sample preparation were compared using four different products. The analytical results from both methods can be seen in Tables 30 and 31.

#### Table 30: Titration of directly weighed-in washing powders

<table>
<thead>
<tr>
<th>Product</th>
<th>Content acc. to DGF H III 10 [mmol/100 g]</th>
<th>Content [mmol/100 g]</th>
<th>Standard deviation [mmol/100 g]</th>
<th>Coefficient of variation [%]</th>
<th>Recovery rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product A</td>
<td>31.3</td>
<td>30.8</td>
<td>0.67</td>
<td>2.2</td>
<td>98.4</td>
</tr>
<tr>
<td>Product B</td>
<td>29.9</td>
<td>30.5</td>
<td>0.23</td>
<td>0.76</td>
<td>102.0</td>
</tr>
<tr>
<td>Product C</td>
<td>52.2</td>
<td>52.4</td>
<td>0.50</td>
<td>0.95</td>
<td>100.5</td>
</tr>
<tr>
<td>Product D</td>
<td>60.6</td>
<td>61.7</td>
<td>0.69</td>
<td>1.11</td>
<td>101.9</td>
</tr>
</tbody>
</table>

#### Table 31: Titration of washing powders from a stock solution

<table>
<thead>
<tr>
<th>Product</th>
<th>Content acc. to DGF H III 10 [mmol/100 g]</th>
<th>Content [mmol/100 g]</th>
<th>Standard deviation [mmol/100 g]</th>
<th>Coefficient of variation [%]</th>
<th>Recovery rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product A</td>
<td>31.3</td>
<td>31.1</td>
<td>0.16</td>
<td>0.51</td>
<td>99.2</td>
</tr>
<tr>
<td>Product B</td>
<td>29.9</td>
<td>29.5</td>
<td>0.19</td>
<td>0.64</td>
<td>98.9</td>
</tr>
<tr>
<td>Product C</td>
<td>52.2</td>
<td>52.4</td>
<td>0.67</td>
<td>1.28</td>
<td>100.4</td>
</tr>
<tr>
<td>Product D</td>
<td>60.6</td>
<td>60.4</td>
<td>0.57</td>
<td>0.94</td>
<td>99.8</td>
</tr>
</tbody>
</table>

Titrination from a stock solution tended to supply more reproducible results which were comparable to the classical method.

However, within the context of the accuracy required for product analysis the results obtained by the two sample preparation methods can be regarded as being comparable. The decisive factors for the selection of the type of sample preparation are the amount of time which can be spent and the stability of the Surfactrode Resistant electrode.

#### 8.1.1.3.2 Stability of the Surfactrode Resistant

If the samples are weighed out directly into the titration vessel and then titrated automatically the amount of time required, particularly for larger series of samples, is clearly less than when a stock solution has to be prepared. However, the Surfactrode is so contaminated after approx. 60 measurements that the titration curves obtained can no longer be evaluated. If an aliquot is taken from a stock solution then the electrode can be used for approx. 150 measurements.

The performance of the Surfactrode Resistant is noticeably enhanced by the addition of TEGO add. 160 directly weighed-in samples of a washing agent containing zeolite were measured nonstop with the same Surfactrode. As shown in Fig. 157, the titration curves obtained gave no indication that the electrode was contaminated.

In general the addition of TEGO add can be recommended to minimise deposits. If, however, the electrode is coated with washing agent only mechanical cleaning is effective, see section 4.5.9.

![Fig. 156: Titration of an all-purpose washing agent, influence of pH](image)

![Fig. 157: Stability of the Surfactrode Resistant after addition of TEGO add; long-term measurements with an all-purpose washing agent](image)
8.1.1.3.3 Summary
A potentiometric titration method for the determination of anionic surfactants in powder-form detergents is now available for the first time. In an analogy to the classical two-phase titration the anionic surfactants in the two-phase system are titrated in water/methyl isobutyl ketone at pH = 3 with Hyamine 1622. The new solvent-resistant surfactant electrode Surfactrode Resistant provides the indicator signal.

The titration can be universally used for all washing powder formulations, regardless of their other ingredients. Individual adaptation of the titration conditions for individual product types is no longer necessary. Advantages of this method are that it can be automated and that it uses a non-critical solvent.

The matrix effects which, depending on the product formulation, appear more or less strongly in the form of lower potential differences have no significant influence on the result.

The method is extremely robust and therefore suitable for routine use if TEGO add is used as an additive to increase the stability of the Surfactrode.

8.1.1.4 Titration of North American powder-form washing agents
A total of seven different powder-form washing agents were available for our investigation: all-purpose washing agents, light-duty washing agents and washing agents for coloured fabrics. One of the powder-form washing agents was marked «with bleach» on the package. This is probably a bleaching agent based on oxygen, e.g. percarbonate or perborate with the corresponding bleach activator.

None of the washing powder packages had a usable declaration of the ingredients or contained any other information that would allow conclusions to be made about the composition of the powder. We have attempted to titrate them in an analogous way to European formulations; see section 8.1.1.3. All titrations were carried out as potentiometric two-phase titrations with the Metrosensor Surfactrode Resistant as indicator electrode and TEGO trant A100 as titrant. It rapidly became clear to us that it was not possible to titrate the powder-form washing agents if the sample was weighed out directly into the titration vessel. This produced titration curves that could simply not be evaluated. Often it was not even possible to recognise an S-shaped curve over a very wide region. Variations in the titration conditions and exchanging the water-immiscible MIBK for chloroform or other solvents brought no improvement.

The titration curves look much better when a stock solution is used. Approx. 50 times the amount of the powder-form washing agent is weighed out into a beaker, approx. 200 mL of water are added and the mixture heated to approx. 80 °C under stirring. After cooling down the solution is transferred to a 500 mL volumetric flask and filled up to the mark. A short time is allowed for the insoluble builders to settle out and then 10 mL of the supernatant solution is pipetted off and used for potentiometric surfactant titration. The titration is carried out at pH = 3, with the addition of 200 μL TEGO add, as described in section 18.2.1. Under these conditions all seven powder-form washing agents from the North American market could be titrated by potentiometric two-phase titration using the Metrosensor Surfactrode Resistant as indicator electrode without any problems. The titration curves resulting from these titrations were all very good. The typical relative standard deviation for all these products was <0.5%.

We have attempted to determine the anionic surfactant content of these powder-form washing agents by the classical two-phase titration using the mixed indicator system disulphine blue/dimidium bromide. Unfortunately we did not succeed. The builders contained in these samples caused extreme interference in the chloroform phase, so that the colour change could not be recognised. Two-phase titration on the supernatant solution, which is also used for potentiometric two-phase titration, produced identical results between the classical two-phase titration and the potentiometric two-phase titration.

8.1.1.5 Titration of powder-form washing agents from the Asian/Pacific* markets
A total of seven different powder-form washing agents were available for our investigation: all-purpose washing agents, light-duty washing agents and washing agents for coloured fabrics.

These commercially available powder-form washing agents came from various countries in the Asian/Pacific region. None of the washing powder packages had a usable declaration of the ingredients or contained any other information that would allow conclusions to be made about the composition of the powder. We also attempted to titrate them in an analogous way to European formulations; see section 8.1.1.3. All titrations were carried out as potentiometric two-phase titrations with the Metrosensor Surfactrode Resistant as indicator electrode and TEGO trant A100 as titrant. But, just as for the North American powder-form products, we also found that it was not possible to titrate powder-form washing agents from the Asian/Pacific region by weighing in the sample directly.

We therefore also had to use a stock solution for these powders. The preparation of the stock solution and the titration of the anionic surfactants were carried out in a similar manner to that used for the North American powder-form washing agents.

The titration curves resulting from these titrations were all very good. The typical relative standard deviation for all seven titrated samples was below 0.5%.

* Hong Kong, Taiwan, Singapore, Malaysia, Japan, Indonesia, China, Philippines, Australia, New Zealand

Fig. 158: Titration of an all-purpose washing agent from the Asian/Pacific market at pH = 3 and pH = 10
In contrast to the sample preparation procedures used for the European powder-form washing agents, the samples analysed above were not prepared optimally. These powder-form washing agents were not divided up and homogenised in special machines. As this homogenisation process would also destroy any coating present on the powder-form washing agent it is possible that the titration behaviour of these powder-form washing agents could also be completely different when weighed in directly.

8.1.1.6 Titration of powder-form washing agents from Saudi Arabia

Two different powder-form washing agents were investigated, a light-duty washing agent and an all-purpose washing agent.

Because of the almost completely water-soluble builder system the titrations for the determination of the anionic surfactants content could be carried out without any problems. The titration was possible both in an aqueous medium with the Ionic Surfactant electrode and in potentiometric two-phase titration indicated with the Metrosensor Surfactrode Resistant. Both methods gave identical results that correlated with those of the classical two-phase titration. TEGO trant A100 c = 0.004 mol/L was used as titrant. The relative standard deviations were about 0.8%.

8.1.2 Titration of soaps in powder-form washing agents

Apart from the anionic surfactant content, the soap content in powder-form washing agents is an important parameter for quality assurance and also for the general assessment of a powder-form washing agent. The fact that this product group is made up of complex formulations was described at length in section 8.1.1. Among the many ingredients of a powder-form washing agent there are also some which could interfere with the determination of soaps or whose influence on the joint titration of anionic surfactants and soaps has not yet been explained. The most important group of substances that could cause interferences during the titration of soaps are the polycarboxylates, which form part of the builder system of powder-form washing agents.

Titrations in aqueous media

The state of the art is that soaps can be titrated together with the classical anionic surfactants under alkaline conditions at pH = 10 to give a total joint content, provided that the soaps have at least 12 carbon atoms in the molecule. This condition applies to those soaps that are used in powder-form washing agents.

Problems occur if an attempt is made to carry out the joint titration in an aqueous medium using classical surfactant electrodes such as the High Sense or the Ionic Surfactant as indicator electrodes. The titration curves are very flat and can only be evaluated poorly or not at all; the results obtained are also too high. These high-bias results are caused by the polycarboxylates, which to some extent are titrated together with the soaps; this effect is independent of the type of polycarboxylate used.

Potentiometric two-phase titrations

Potentiometric two-phase titration of the anionic surfactants in powder-form washing agents is also the method of choice for the determination of anionic surfactants. This is the reason why it is only natural that this determination method was also tested for the joint titration at pH = 10. At the copy deadline for this monograph the experiments had not been concluded so that no final conclusions can yet be made about the applicability of this method. As this method is very important for many operators the current situation is explained here.

In potentiometric two-phase titration at pH = 10 titration curves that were easy to evaluate were obtained in almost all cases. Relative standard deviations of approx. 1% could be achieved.

The «quality» of the titration curve depends on the builder system, exactly as in the titration of anionic surfactants in powder-form washing agents. With soluble builders the derivative curves of the surfactant titration are steeper, with insoluble builders they are flatter.

Carrying out the surfactant titration on an aliquot of a stock solution is a great advantage. This basically results in better, steeper titration curves with lower standard deviations than when the sample is weighed in directly.

Up to now it has not been proved that the technique of using an aliquot of a stock solution produces correct results. Polycarboxylates do not interfere in the potentiometric two-phase titration of powder-form washing agents. Only TEGO trant A100 should be used as the titrant. A titrant concentration of c = 0.004 mol/L has proved to be best in practice.

The use of TEGO add is absolutely necessary.

8.1.3 Liquid all-purpose washing agents

8.1.3.1 Liquid washing agents

The titration of liquid washing agents with a surfactant electrode in aqueous media is possible. Fig. 159 shows the titrations of a liquid washing agent at pH = 3 for determining the anionic surfactants content and at pH = 10 for determining the sum of anionic surfactants plus soaps.

Origin: Europe

Ingredients according to EU recommendation:

- <5% nonionic surfactants and soap
- 5 to 15% anionic surfactants
- Enzymes
- Citrate
- Alcohol
- Foam regulators
- Optical brighteners
- Perfume oils
The results obtained suggest that all the liquid washing agents tested in the branded goods sector as well as the no-name products supplied evaluable titration curves for all titrations at pH = 3 and pH = 10. Care must be taken when interpreting the titration curves obtained at pH = 10. The fact that polycarboxylates are partially determined here and will therefore simulate a too high soap content must be taken into account.

As an alternative, whenever the nonionic surfactant content is very high and clearly exceeds the anionics content, the new Metrosensor Surfactrode Resistant can be used.

Liquid all-purpose washing agents on the Asian/Pacific market and the North American market did not have any ingredients or the types of surfactants used declared. In potentiometric two-phase titration these behaved in a similar manner to the European products so that all explanations and information given for them can also be applied to the products on the Asian/Pacific market and the North American market.

8.1.3.2 Liquid light-duty washing agents

Ingredients according to EU recommendation:
- 5 to 15% anionic surfactants
- 15 to 30% nonionic surfactants
- Alcohol
- Fragrances

In these special liquid washing agents the concentration of the nonionic surfactants is higher than that of the anionic surfactants, but a titration of the anionic surfactants in this formulation could nevertheless be carried out easily. The relative standard deviation obtained was about 1.5%.

Liquid light-duty washing agents on the Asian/Pacific and North American markets had no declarations as to the ingredients or classes of surfactants used. In potentiometric two-phase titration they behaved in a similar manner to the European products so that all information given for them can also be applied to the products on the Asian/Pacific market and the North American market.

8.1.3.3 Liquid washing agents for coloured fabrics

Ingredients according to EU recommendation:
- <5% polycarboxylates
- 5 to 15% anionic surfactants
- 5 to 15% soaps
- 15 to 30% nonionic surfactants
- Enzymes
- Colour transfer inhibitors
- Borax
- Fragrances
- Glycerol
- Sodium citrate

This is a complicated formulation. However, it can still be easily titrated provided that one or two points are observed. The titration of the anionic surfactants in this formulation is carried out at pH = 2. The pH is adjusted with dilute hydrochloric acid. Only TEGO trant A100 is suitable for use as the titrant; the added methanol should remain in the normal range of about 5%. An additional titration to determine the soap content is only recommended in the quality assurance sector if the type of polycarboxylate used is known and its behaviour during the soap titration can be assessed. The titration of soaps at pH = 10 can then be recommended. The pH adjustment is made with dilute sodium hydroxide, preferably controlled by a pH meter.

The analysis by potentiometric surfactant titration of such a liquid washing agent for coloured fabrics with an unknown formulation cannot be recommended if the analyst does not know what type of polycarboxylate and which anionic surfactants or nonionic surfactants it contains.

Liquid washing agents for coloured fabrics on the Asian/Pacific and North American markets had no declarations as to the ingredients or classes of surfactants used. In potentiometric two-phase titration they behaved in a similar manner to the European products so that all information given for them can also be applied to the products on the Asian/Pacific market and the North American market.
8.1.3.4 Wool washing agents

Formulation 1
Origin: Europe
Ingredients according to EU recommendation:
• <5% amphoteric surfactants
• <5% nonionic surfactants
• 15 to 30% anionic surfactants
• Preservatives
• Keratin hydrolysate
• Polypeptides
• Auxiliaries
• Preservatives
• Fragrances

Formulation 2
Origin: Europe
Ingredients according to EU recommendation:
• <5% nonionic surfactants
• 5 to 15% anionic surfactants
• Fragrances

These two special washing agents for washing fine and sensitive textiles that contain wool, angora or mohair as well as textiles made of silk are, as the name wool shampoo suggests, particularly mild surfactants. Fatty alcohol sulphates or fatty alcohol ether sulphates are often used as the anionic surfactants.

The determination of the anionic surfactants in the presence of the other ingredients does not cause any problems. The titration curves are good and have enough slope for the titrators to evaluate them. In this case titration at pH = 3 is also recommended. With formulations containing betains in particular the pH value must not fall below 3 under any circumstances, as otherwise interference from the betain occurs. As in the majority of the surfactant titrations, approx. 5% methanol should be added to the titration solution in order to achieve better values. The relative standard deviation for the determination the anionic surfactants in the above-mentioned formulations is <1%.

The statistical distribution of the fatty alcohol can be seen in Fig. 160.

Fig. 160: Maldi TOF spectrum of a wool shampoo

methanol should be added to the titration solution in order to achieve better values. The relative standard deviation for the determination the anionic surfactants in the above-mentioned formulations is <1%

The statistical distribution of the fatty alcohol can be seen in Fig. 160.
Wool washing agents on the Asian/Pacific and North American markets had no declarations as to the ingredients or classes of surfactants used. In potentiometric two-phase titration they behaved in a similar manner to the European products so that all information given for them can also be applied to the products on the Asian/Pacific market and the North American market.

8.1.3.5 European liquid washing agents

Potentiometric two-phase titrations

The formulations listed in Table 32 have been titrated.

Table 32: Typical formulations for European liquid washing agents

<table>
<thead>
<tr>
<th>Formulation</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing agent type</td>
<td>All-purpose</td>
<td>All-purpose</td>
<td>Colour</td>
<td>Colour</td>
<td>Wool</td>
<td>Wool</td>
</tr>
<tr>
<td>Ingredients according to EU recommendation</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Anionic surfactants</td>
<td>15-30</td>
<td>15-30</td>
<td>5-15</td>
<td>5-15</td>
<td>&lt;5</td>
<td>15-30</td>
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<td>Cationic surfactants</td>
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<tr>
<td>Amphoteric surfactants</td>
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</tr>
<tr>
<td>Soaps</td>
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<td>Polycarboxylates</td>
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</tr>
<tr>
<td>Phosphonates</td>
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</tr>
<tr>
<td>Enzymes</td>
<td></td>
<td>X</td>
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</tr>
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<td>X</td>
<td>X</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Cellulase</td>
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<td></td>
</tr>
<tr>
<td>Lipase</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Protease</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Potentiometric two-phase titration with indication by the Metrosensor Surfactrode Resistant can be carried out without any problems with all the formulations described above. Both classical liquid washing agents and washing gels were investigated. These did not differ in their behaviour in the titrations.

The titrations were carried out as described in section 18.2.2 with the addition of 200 µL TEGO add.

The anionic surfactants were titrated at pH = 3 as usual. The pH was adjusted with sulphuric acid c = 0.05 mol/L. Particularly for liquid washing agents with a high soap content care must be taken that the pH of the titration solution does not exceed 3 under any circumstances. The other ingredients could otherwise have a negative influence, which could also cause the soaps to react at lower pH values. It is advantageous to wait for about 5 min after the pH has been adjusted before starting the titration.

The sum of the anionic surfactants and soaps is determined by a titration at pH = 10. The pH is adjusted with sodium hydroxide c = 0.1 mol/L. The polycarboxylates contained in the sample interfere with the titration neither at pH = 3 nor at pH = 10.

Care must be taken because the soap content of the liquid washing agent is sometimes significantly higher than the classical anionic surfactants content.

In all cases TEGO trant A100 c = 0.02 mol/L is used as the titrant.

The relative standard deviations for the titration at pH = 3 were 0.3%, those for titrations at pH = 10 between 0.5 and 0.6%.

In the potentiometric two-phase titration of liquid washing agents with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

8.1.4 Other washing agents

8.1.4.1 Travelling and hand washing agents

Titrations in aqueous media

The travelling washing agent product group has a less complicated formulation and can be determined with very few problems using a surfactant electrode. Fig. 161 shows the titration of such a travelling washing paste.

Origin: Europe

Ingredients according to EU recommendation:

![Fig. 161: Titration of a travelling washing paste](image-url)
Because of the excellent and very steep titration curves it must be assumed that the anionic surfactants are either an alkyl benzene sulphonate, a fatty alcohol sulphate or a mixture of both.

**Potentiometric two-phase titrations**

The powder-form washing agents or washing pastes listed in Table 33 were titrated using the Metrosensor Surfactrode Resistant as indicator electrode.

Table 33: Formulations of some travelling washing agents

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pa = Paste; Po = Powder</td>
<td>Pa</td>
<td>Pa</td>
<td>Pa</td>
<td>Po</td>
<td>Po</td>
<td>Po</td>
</tr>
<tr>
<td>15-30% anionic surfactants</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-15% anionic surfactants</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>5-15% nonionic surfactants</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Below 5% nonionic surfactants</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Preservatives</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foam regulators</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Auxiliaries</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Soap</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Polycarboxylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15-30% zeolites (Sasil®)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The titrations were carried out as described in section 18.2.2 with the addition of 200 µL TEGO add. This addition is strongly recommended.

The anionic surfactants were titrated at pH = 3 as usual. The pH was adjusted with sulphuric acid c = 0.05 mol/L

The sum of the anionic surfactants and soaps were determined by a titration at pH = 10.

In the potentiometric two-phase titration of travelling washing agents and washing pastes with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

The polycarboxylates contained in the powder-form washing agent interfere with the titration neither at pH = 3 nor at pH = 10; in the titrations given above polycarboxylates are not taken into account.

In all cases TEGO trantr A100 c = 0.02 mol/L was used as the titrant.

The relative standard deviations for the titrations at pH = 3 were 0.3%, those for titrations at pH = 10 between 0.5 and 0.6%.

**8.1.5 Fabric softeners**

**Titration in aqueous media**

The fabric softeners that are added in the final rinsing cycle after the washing process itself has been completed are exclusively quaternary ammonium compounds. However, in recent years the structure of these quaternary ammonium compounds has greatly changed. At the start of the eighties these were still of the dialkyl type, primarily distearyldimethylammonium chloride. These were criticised because of their poor degradability and were replaced by quaternary imidazolium compounds. Currently the formulations contain primarily esterquats with widely differing structures and methosulphates as counter-ions.

Origin: Europe

A typical formulation contains:

- Nonionic surfactants
- Cationic surfactants
- Preservatives
- Fragrances
- Auxiliaries
- Colourants
- Water

The nonionic surfactant content is usually below or about 5%. The cationic surfactant content varies from 5 to 30%, depending on whether the fabric softener is an «original», a «concentrate» or a «superconcentrate».
The esterquats contained in the fabric softeners are sensitive to hydrolysis; see also section 7.5.5. This is why a titration under acidic conditions, preferably at pH = 2 or 3, is recommended. Because of their long alkyl chains, which the esterquats need for good substantivity to the fibres, they are not particularly soluble in water. This means that the titration should be carried out in the presence of large amounts of alcohol. Methanol in concentrations between 15 and 25% is recommended. As some of the esterquats are mixtures that have one, two or three alkyl groups attached to the quaternary nitrogen, each of them with an ester function, several endpoints may be found in the titration. The oleophilicity of these products differs significantly depending on whether they are mono-, di- or tri-substituted.

If the splitting up of the endpoint shown in Figs. 162 and 163 is not wanted then the alcohol content should be reduced as much as possible.

As with all products that contain esterquats, the pH adjustment should always be carried out immediately after preparation of the solution as this simultaneously stabilizes it. Under no circumstances should esterquats in the fabric softeners be titrated under alkaline conditions as the alkalinity causes immediate ester cleavage. This ester cleavage causes the products to lose their cationic activity and they can no longer be determined.

Potentiometric two-phase titrations

The titration of esterquats in fabric softeners can be carried out very well in a two-phase medium with a Surfactrode Resistant as the indicator electrode. The resulting titration curves have a better shape than those obtained by titration in an aqueous medium. Additionally the titration curve has the typical S-shape, which in principle allows a better and more correct automatic evaluation of the endpoint by the titrator algorithm. A splitting up of the endpoint, which is normal in titrations in aqueous media, is very seldom seen in titrations in a two-phase medium using the Surfactrode Resistant. From the author's point of view the titration of esterquats in fabric softeners with the Surfactrode Resistant in a two-phase medium can be recommended and should be preferred to a titration in an aqueous medium.

A 0.02 mol/L dodecyl sulphate sodium salt solution is also recommended as titrant for these titrations. A very important point in esterquat titrations is the observance of the great sensitivity to hydrolysis. The sample is weighed out directly into the beaker in which the titration is later carried out. An intermediate dilution is not necessary and cannot be recommended. The sample should be diluted with water as soon as it has been weighed out. We have had great success when the solution is then immediately acidified with 2 mL 25% acetic acid. After addition of 10 mL MIBK and 10 mL ethanol the titration is carried out immediately with 0.02 mol/L dodecyl sulphate sodium salt solution.

As in all potentiometric surfactant titrations, including those with the Surfactrode Resistant, the sample weight should be selected so that a minimum titrant consumption of 10 mL results. This is the only way to obtain correct results.

In the titration of esterquats in fabric softeners relative standard deviations of approx. 1% can be achieved.

8.1.6 Stain removers

In Europe stain removers are a standard additional product containing a high proportion of oxygen-based bleaching agents, often with percarbonates as oxygen carriers. These products also contain special bleach activators and anionic surfactants.

Origin: Europe

A stain remover could have the following formulation and declaration:

- <5% anionic surfactants
- <5% nonionic surfactants
- 15-30% oxygen-based bleaching agent (percarbonate)
- Tetra acetyl ethylene diamine (TAED), silicates, soda and auxiliaries

The anionic surfactants content in stain remover formulations can be determined in two-phase media with the Metrosensor Surfactrode Resistant. The high proportion of oxidants such as perborates or percarbonates has no interfering influence on the titration. The titration is best carried out at pH = 2. This is done by adjusting the pH of the stain remover sample with 0.25 mol/L sulphuric acid.

As a result of the large proportion of salts in stain removers reduced potential differences are to be expected. In order to keep the influence small it is better in this case to use a 0.004 mol/L TEGO trant A100 solution, as described in section 18.2.1. The relative standard deviations that can be achieved in this titration are about 0.7%.
8.1.7 Liquid oxygen-based bleaching agents

Table 34: Typical formulations of some liquid bleaching agents

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen-based bleaching agent</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Nonionic surfactant &lt;5%</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Anionic surfactant</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The anionic surfactant content in these liquid bleaching agents is quite small, so that the sample weight must be approx. 5 to 6 g. Accordingly the sample will contain a large amount of oxygen-based bleaching agent (hydrogen peroxide). Fig. 164 shows again very clearly that oxidants have no negative influence on potentiometric two-phase titrations using the Metrosensor Surfactrode Resistant as the indicator electrode.

The titration was carried out after the addition of 200 µL TEGO add as described in section 18.2.1, using TEGO tran A100 as the titrant. The relative standard deviation was 0.24%.

8.2 Diswashing agents and cleaners

8.2.1 Dishwashing agents for manual cleaning

Titrations in aqueous media

As most detergents for household use, manual dishwashing agents are commercially available in versions with different concentrations. As well as the standard manual dishwashing agents, which have been available for many years, concentrates or three-fold concentrates are now commercially available. The anionic surfactants in these detergents can be determined very well by potentiometric surfactant titration. As an example two concentrates from different manufacturers are shown; both have the same declaration.

Origin: Germany

Ingredients according to EU recommendation:

- >30% anionic surfactants
- <5% nonionic surfactants
- <5% betains
- Alcohols
- Fragrances
- Colourants
- Preservatives

Although the declaration of both detergents is identical, the two titration curves obtained from the anionic surfactant titration differ quite significantly, as Fig. 165 shows. These differences can be traced back to the different types of anionic surfactants used. In order to rule out any interference from the betains contained in the formulation the titration was carried out at pH = 5.

8.2.2 Dishwashing agent concentrates for manual cleaning

Potentiometric two-phase titrations

For dishwashing agents in particular the declaration according to the EU recommendation does not give very much information about the ingredients contained in the formulation. The concentration information covers a relatively wide range and only gives the totals within a group. The information 5-15% anionic surfactants can mean 5.0% on one occasion and 15.0% the next. This could be fatty alcohol sulphates, fatty alcohol ether sulphates, sec. alkane sulphonates or also alkyl benzene sulphonates. It is also possible that only one of the surfactants mentioned is present in the formulation or, as in most cases, a mixture of two or more of them. The same also applies to the other groups of nonionic or amphoteric surfactants. The nonionic surfactants are usually POE fatty alcohols or APG, or a mixture of both.

This is the reason why a potentiometric two-phase titration using the Metrosensor Surfactrode Resistant has many advantages. Good and correct results can be obtained even when there is no exact knowledge about the composition of the sample.

Origin: Europe
The ingredients according to the EU recommendation are given in Table 35.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactants 5-15%</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anionic surfactants 15-30%</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Anionic surfactants &gt;30%</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactants &lt;5%</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactants 5-15%</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactants 15-30%</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Amphoteric surfactants &lt;5%</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Preservatives</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Alcohol</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Auxiliaries</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The determination of the anionic surfactants should be carried out at pH = 3 because of the amount of amphoteric surfactants contained in almost all the samples. All the formulations of dishwashing agents listed in the table could be titrated in a two-phase medium with the Metrosensor Surfactrode Resistant. The relative standard deviations were 0.6% or less. Depending on the surfactant used and the nonionic surfactant content the derivative curves were narrower or, in some formulations, wider. However, all curves could be easily evaluated by the titrator algorithm.

In all cases TEGO tran t A100 with a concentration of 0.02 and 0.004 mol/L was used as the titrant for these dishwashing agent concentrates. Titration curves that could be evaluated were obtained with both titrant concentrations. In many cases the titration curves obtained with the 0.004 mol/L TEGO tran t solution were better to evaluate and showed lower relative standard deviations. For this reason the more dilute 0.004 mol/L TEGO tran t A100 can be recommended as the titrant solution.

**North American formulations**

Table 36: North American formulations of manual dishwashing agents

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium laureth sulphate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Ammonium laureth sulphate</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Ammonium linear alcohol ether sulphate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzenesulphonate</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Magnesium dodecylbenzenesulphonate</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Sodium cocoamphoacetate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Cocamide diethanolamid (DEA)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Lauryl polyglucose</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Triclosan</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>SD Alcohol 3-A</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Sodium xylenesulphonate</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Lauramide/myristamide MEA</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Magnesium sulphate</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Quaternium-15</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Alcohol</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Lauryl alcohol</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Hydroxypropyl guar hydroxypropyltrimonium chloride</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

A total of ten different dishwashing concentrates was examined, of which only the two appearing in Table 36 had a full declaration. However, in all tested dishwashing concentrates the anionic surfactants content could be determined by potentiometric two-phase titration with the Metrosensor Surfactrode Resistant as described in section 18.2.1. In other respects the samples behaved similarly to those on the European market. **Dishwashing agent formulations from the Pacific market**

A total of six different dishwashing agent formulations from various countries were investigated. The results were comparable in all points with those from Europe and North America.
8.2.3 Dishwashing agents for manual cleaning, sensitive products

Potentiometric two-phase titration

Origin: Europe

The ingredients according to the EU recommendation are given in Table 37.

Table 37: Typical formulations of some sensitive products

<table>
<thead>
<tr>
<th>Formulation</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactants 5-15%</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anionic surfactants 15-30%</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactants &lt;5%</td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactants 15-30%</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Amphoteric surfactants &lt;5%</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Preservatives</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Skin protection component</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

The potentiometric determination of the anionic surfactants in a two-phase medium in the above-mentioned formulations is possible in all cases. However, in formulation B the titration curves were very flat and the relative standard deviation in this case was 2.1%. With the other dishwashing agents relative standard deviations of between 0.45 and 1.1% were achieved. Otherwise the same explanations as given for dishwashing agent concentrates apply.

8.2.4 All-purpose cleaners

By way of example we have examined two commercially available all-purpose cleaners.

All-purpose cleaner A (Fig. 167) was a standard product with the following composition:

Origin: Germany

Declaration according to EU recommendation:
- <5% anionic surfactants
- <5% nonionic surfactants
- <5% soaps
- Alcohols
- Fragrances
- Colourants
- Preservatives

All-purpose cleaner B (Fig. 168) was a so-called concentrate.

Origin: Germany

Declaration according to EU recommendation:
- 5% to 15% anionic surfactants
- 5% to 15% nonionic surfactants
- <5% soaps
- Alcohols
- Fragrances

Two titrations were carried out for each version, one at pH = 5 to determine the anionics content and the second at pH = 10 to determine the sum anionics plus soaps.

8.2.5 All-purpose cleaner with insoluble cleaning crystals

Potentiometric two-phase titration

Origin: Germany

Ingredients according to EU recommendation:
- 5-15% anionic surfactants
- <5% nonionic surfactants
- Soap, preservatives
• Cleaning crystals
• Fragrances

The titration is carried out as described in section 18.2.2 with the addition of 200 µL TEGO add.

The anionic surfactants were titrated at pH = 3 as usual. The pH adjustment was carried out with sulphuric acid \( c = 0.05 \) mol/L. The resulting titration curves are flatter than usual, but can still be evaluated well by the evaluation algorithm.

The sum of anionic surfactants and soaps is determined by a titration at pH = 10. The titration curves are also flatter than normal here. In each case TEGO trant A100 \( c = 0.02 \) mol/L was used as titrant. The relative standard deviation for the titration at pH = 3 was 0.6%, at pH = 10 it was 1.0%. In the potentiometric two-phase titration of all-purpose cleaners with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

The addition of 200 µL TEGO add is recommended.

### 8.2.6 Phosphate-based cleaners

**All-purpose cleaners**

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Origin</th>
<th>Ingredients according to EU recommendation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Great Britain</td>
<td>&lt;5% anionic surfactants &lt;5% nonionic surfactants Phosphates Preservative</td>
</tr>
<tr>
<td>B</td>
<td>Great Britain</td>
<td>&lt;5% amphoteric surfactants &lt;5% anionic detergent &lt;5% phosphates Preservatives &lt;5% tetrapotassium pyrophosphate</td>
</tr>
</tbody>
</table>

**Bathroom cleaner**

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Origin</th>
<th>Ingredients according to EU recommendation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Great Britain</td>
<td>&lt;5% amphoteric surfactants &lt;5% anionic detergent &lt;5% phosphates Preservatives &lt;5% tetrapotassium pyrophosphate</td>
</tr>
<tr>
<td>B</td>
<td>Great Britain</td>
<td>&lt;5% nonionic surfactants &lt;5% anionic surfactants &lt;5% phosphates Preservatives</td>
</tr>
</tbody>
</table>

**Bathroom gel**

<table>
<thead>
<tr>
<th>Origin</th>
<th>Ingredients according to EU recommendation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Great Britain</td>
<td>&lt;5% nonionic surfactants &lt;5% anionic surfactants &lt;5% phosphates Preservatives</td>
</tr>
</tbody>
</table>

**Antibacterial Multi Surface Cleaner**

<table>
<thead>
<tr>
<th>Origin</th>
<th>Ingredients according to EU recommendation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Great Britain</td>
<td>&lt;5% nonionic surfactants &lt;5% phosphates &lt;5% cationic surfactants Preservatives</td>
</tr>
</tbody>
</table>

The anionic or cationic surfactant content in the above-mentioned or similarly made-up household cleaner formulations can be determined simply and without any problems with the Surfactrode Resistant as described in section 18.2.2. Relative standard deviations of <0.5% are achieved. An interfering or limiting influence from the phosphate content in the formulations could not be recognised for any cleaner. The titration curves and the titration behaviour were identical to similarly made-up phosphate-free formulations. In other cleaner formulations that were specially made up for our experiments by our surfactant application technology group, with and without the addition of phosphate, no influence by the phosphate could be recognised.

### 8.2.7 Household cleaner (concentrate)

<table>
<thead>
<tr>
<th>Origin</th>
<th>Ingredients according to EU recommendation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>&lt;5% nonionic surfactants</td>
</tr>
</tbody>
</table>

**Multi-Purpose Cleaner**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;5% nonionic surfactants</td>
<td>&lt;5% anionic surfactants</td>
</tr>
<tr>
<td>&lt;5% phosphates</td>
<td>&lt;5% tetrapotassium pyrophosphate</td>
</tr>
</tbody>
</table>
8.2.8 Special soap-based cleaners

A special cleaner for wood from the North American market with no declaration was analysed by us. According to our analysis it contained approx. 15% soaps, chiefly C_{14/16}. It did not contain any classical anionic surfactants.

A potentiometric titration of this special soap-based cleaner is only possible and sensible with TEGO trant A100 as titrant. The most suitable method for determining the soaps in such a formulation is potentiometric two-phase titration at pH = 10, with detection by the Metrosensor Surfactrode Resistant. The best, steepest potential jumps with the lowest relative standard deviation of <0.5% were obtained by potentiometric two-phase titration, when chloroform was used as the water-immiscible phase. In this way all soaps with a C-chain length ≥ 12 are determined quantitatively. The use of methyl isobutyl ketone as the water-immiscible phase is also possible.

In the potentiometric two-phase titration of special soap-based cleaners with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

The addition of 200 µL TEGO add is recommended.

8.2.9 Liquid soft soap

Origin: Germany

Liquid soft soaps certainly belong to the first generation of household cleaners that our grandmothers used for cleaning purposes. Even today liquid soft soaps still have a fixed place among the household cleaners for special applications, in particular for cleaning floors made of PVC, artificial or natural stone, marble or parquet. The high «fat content» of the liquid soft soaps is particularly valued.

Potentiometric two-phase titration for the determination of the soaps in liquid soft soap can be carried out without problems. The titration is performed under the standard conditions described in section 18.2.1 using the Surfactrode Resistant as indicator electrode. As is usual for soaps, the determination is carried out at pH = 10 with 0.004 mol/L TEGO trant A100 solution as titrant. The titration curves are easy to evaluate and relative standard deviations of approx. 0.6% are obtained by the potentiometric two-phase titration.

8.2.10 Cleaners with natural oils

8.2.10.1 Cleaners with pine oil (soap-based)

Origin North America

• Pine oil 5%
• Soap 12.5%
• Inert ingredients 82.5%

This is a much-loved type of cleaner in the USA containing soaps and pine oil. These cleaners are normally alkaline. The titration of the fatty acid salts (soaps) is only possible with the Metrosensor Surfactrode Resistant. The high proportion of pine oil leads to the destruction of the PVC membrane of normal surfactant electrodes, as we have experimentally confirmed.

The determination of the soaps in the above-mentioned cleaners by potentiometric two-phase titration is easily possible. It is well-known that the ability to titrate soaps depends on the chain length of the fatty acids. Only fatty acid salts (soaps) with at least 12 carbon atoms, i.e. from lauric acid upwards, can be titrated. We have used HPLC to investigate the fatty acid distribution in the cleaners with pine oil that we have examined. In most cleaners only fatty acid salts of lauric acid or higher were present, so that these could be titrated without any problem. In one of the cleaner formulations examined the fatty acid distribution corresponded approximately to that of a coconut oil fatty acid. This means that it contains appreciable amounts of caprylic and capric acids which are not determined. In this case the soaps can only be determined by the use of a standard, in which a calibration titration is carried out with the fatty raw material employed and then this calibration titration is used to determine the fatty acids in the cleaner. As a result of this calibration titration the short-chain fatty acids that cannot be determined are nevertheless included in the calculation.

The titration is carried out after the cleaner has been directly weighed into the titration beaker at pH = 10 under the standard conditions described in section 18.2.1. Only TEGO trant A100 c = 0.004 mol/L should be used as titrant.

In the formulations we investigated, typical relative standard deviations of about 0.5% were obtained.
In the potentiometric two-phase titration of soaps in pine-oil-based cleaners with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

8.2.10.2 Cleaners with pine oil (cationic)

**Origin** North America

- Pine oil 9.0%
- N-alkyl (50% C\(_{14}\), 40% C\(_{12}\), 10% C\(_{16}\)) 0.8%
- Dimethyl benzyl ammonium chloride 0.25%
- Octyl decyl dimethyl ammonium chloride 0.125%
- Dioctyl dimethyl ammonium chloride 0.125%
- Inert ingredients 89.7%

**Titration in aqueous media**

Because of the high pine-oil content titration with a surfactant electrode based on a plasticised PVC membrane should not be attempted. The pine oil dissolves the plasticiser from the membrane, thus destroying the membrane. In a deliberate test in our laboratory the surfactant electrode was destroyed after four titrations.

**Potentiometric two-phase titrations**

The determination of cationic surfactants in the above-mentioned formulation is possible without any problems by potentiometric two-phase titration using the Surfactrode Resistant as indicator electrode. The various quaternary ammonium compounds could not be differentiated in the titration. The determination gives the total of the cationic surfactants. The titration is carried out according to the standard method either at pH = 3 or at pH = 10, with dodecyl sulphate sodium salt c = 0.004 mol/L as titrant. The relative standard deviation is 0.7%.

In the potentiometric two-phase titration of household cleaners with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

8.2.10.3 Cleaners with pine oil (anionic)

«Sanitary Clean, Deodorises»

«Kitchen and Bathroom Cleaner, Deodorises»

The determination of the anionic surfactant content in these and similar formulations is again only possible by potentiometric two-phase titration using the Metro sensor Surfactrode Resistant\(^{16}\). The pine oil in the formulations would dissolve the plasticiser in the membrane of a normal PVC-based surfactant electrode and very quickly destroy the electrode.

In the potentiometric two-phase titration no problems are to be expected and none occurred in our tests. The acids contained in a sanitary cleaner or kitchen and bathroom cleaner do not interfere with or influence the titration of the anionic surfactants. This means that the titration can be carried out at pH = 3 under the standard conditions described in section 18.2.1. TEGO trant A100 c = 0.004 mol/L is used as titrant. The titration should be carried out with the addition of TEGO add. Typical relative standard deviations of <0.5% are achieved.

8.2.10.4 Cleaners with orange oil (anionic)

**Origin** Germany

**Declaration according to EU recommendation:**

- 5-15% anionic surfactants
- Pearl gloss agent
- Cosmetic colourants
- Fragrant oil
- below 5% amphoteric surfactants
- Preservatives
- Orange oil

**Titration in aqueous media**

The orange oil or rather the orange terpenes have similar properties to pine oil; see section 8.2.10.2

**Potentiometric two-phase titrations**

The determination of cationic surfactants in the above-mentioned formulation is possible without any problems by potentiometric two-phase titration with the Surfactrode Resistant as indicator electrode. The titration is carried out according to the standard method with TEGO trant A100 c = 0.02 mol/L or c = 0.004 mol/L as titrant. The relative standard deviation is 0.42%.
8.2.11 Glass cleaners

Origin: Germany
Ingredients according to the EU recommendation:
- Organic solvents
- <5% anionic surfactants
- Fragrance

Origin: North America
Ingredients:
- Isopropanol
- Butoxypropanol
- Cleaning agent
- Perfume

Titrations in aqueous media

Glass cleaners only contain very low surfactant concentrations, usually between 0.1 and 0.2%. In the majority of formulations dioctyl sulphosuccinate is used as the surfactant. However, there are also formulations that contain sodium laureth sulphate. For the surfactant titration it does not matter which of these two raw materials is present as both can be very easily titrated. The alcohol content of the glass cleaner, which can be between 2 and 20%, also does not interfere with the titration. In order to achieve an acceptable titrant consumption the weight of the glass cleaner sample must be relatively high; in most cases 10 to 25 g is required.

8.2.12 Cleaners for glass and frames

Origin: Germany
Ingredients according to EU recommendation:
- <5% anionic surfactants
- 5-15% nonionic surfactants
- Preservatives
- Surfactants
- Fragrance
- Alcohol
- Polymers
- Cellulose derivates

Potentiometric two-phase titrations

The titrations can be carried out without any problems as described in section 18.2.1. The relative standard deviations are 0.4%.

North American formulation
Contains:
- Surfactants
- Fragrance

It was not possible for us to determine the surfactant content of this product; all our attempts failed. The declaration given allows few conclusions to be made about the surfactant used. The tests were abandoned.

8.2.13 Scouring milk

Origin: Germany
Ingredients according to EU recommendation:
- <5% anionic surfactants
- <5% nonionic surfactants
- Fragrances
- Colourants
- Preservatives
- Mineral scouring agents
- Auxiliaries

A so-called scouring milk contains insoluble polishing agents, usually from a natural source such as finely ground marble powder or similar. The particle size distribution is uniform and is <100 μm. In combination with specially selected and matched surfactants this enables the abrasive cleaning of tenacious dirt on smooth, hard surfaces, e.g. pots, pans, tiles, wash-basins, baths, sinks, etc. By matching the surfactants and the mineral abrasives the dirt is not scratched away, but is carefully rubbed off without causing scratches or damaging the surface.

If the Ionic Surfactant Electrode is used for determining the anionic surfactants in a scouring milk it is no longer necessary to prepare an ethanol-soluble fraction before the determination itself. This allows a large amount of time and therefore money to be saved in the determination. It is true that the abrasives in a scouring milk have a negative effect on the working life of the electrode, but the costs of acquiring a new electrode amount to only a fraction of those which are saved by being able to titrate the substance directly, i.e. without any sample preparation.

The abrasives cause the PVC-membrane to become opaque. However, this is only an optical effect that does not have any influence on the quality of the titration or the usefulness of the electrode.

Fig. 171: Titration of a scouring milk
The surfactants that are normally used in such scouring milks, such as linear alkyl benzene sulphonate or similar, can be very easily potentiometrically titrated. However, it is important to carry out the titration more slowly than normal in order to give the titrant the possibility of desorbing the anionic surfactants substantively attached to the abrasives and allow the ion associate to precipitate out.

The titration curve clearly has a smaller slope than would be expected from pure surfactants. Nevertheless, as shown in Fig. 171, the potential difference is sufficient for the titration endpoint to be recognised unambiguously by the titrator algorithm and evaluated.

Depending on the anionic surfactant content 1 to 2 g of the scouring milk are weighed out directly into the titration beaker and then 10 mL methanol are added. The titration beaker is gently moved about so that the scouring milk is finely distributed in the methanol. Only when this has been achieved are 80 mL water and 10 mL pH = 5 buffer added and then titrated against 0.004 mol/L TEGO trant A100 solution.

Titration with the Surfactrode Resistant is also possible. In this case only chloroform is suitable as the solvent.

In this case 1 to 2 g of the scouring milk are weighed out directly into the titration beaker and suspended with 50 mL water. The pH is adjusted to pH = 3 with hydrochloric acid c(HCl) = 0.1 mol/L; 10 mL ethanol, 10 mL chloroform and 200 µL TEGO add are added and the total volume made up to 100 mL with water.

In both methods titration curves that can be evaluated are obtained; it is not possible to recommend one of the methods as being better than the other.

8.2.14 Oven and grill cleaners
Ingredients according to EU recommendation:
- <5% nonionic surfactants
- 2-aminoethanol
- Water-soluble solvent
- Anionic surfactant

Potentiometric two-phase titration
The surfactant determination is carried out by two-phase titration detected with the Metrosensor Surfactrode Resistant. The anionic surfactants are titrated as usual at pH = 3. The product has a strongly alkaline reaction. The pH adjustment is carried out with sulphuric acid c = 0.05 mol/L. The resulting titration curves are flatter than normal, but can still be easily evaluated by the titrator.

TEGO trant A100 c = 0.02 mol/L was used as the titrant. The relative standard deviation for the titration at pH = 3 was 0.6%.

No attempt was made to determine the soap content of this formulation.

8.2.15 WC cleaners
Ingredients according to EU recommendation:
- <5% anionic surfactants
- Citric acid
- Formic acid
- Colourants
- Auxiliaries

The surfactant content of WC cleaners is not particularly high. In most cases the surfactant concentration is 1% or less. On the other hand WC cleaners contain high concentrations of acids. In modern formulations these are chiefly formic acid and citric acid. A further important component in the formulation is the gelatinising agent, which increases the viscosity of the formulation and therefore the contact time of the acids on the ceramic surface for sufficient time for the acids to remove lime and urine deposits. For the potentiometric surfactant titration of the anionic surfactants between 1 and 5 g (depending on the expected content) of the WC cleaner are weighed out directly into the titration beaker and 90 mL water are added followed by 5 mL methanol and then sufficient sodium hydroxide solution is added drop by drop until the pH value is approximately 3. Exact pH adjustment is not necessary in this case. Titration against a cationic titrant, e.g. TEGO trant A100, can be carried out directly.

8.2.16 WC cistern tablets
Ingredients according to EU recommendation:
- >30% anionic surfactants
- Inorganic and organic builders
- Colourants
- Fragrances

The determination of anionic surfactants in WC cistern tablets is relatively free from problems. However, to obtain reproducible results it is necessary to use a stock solution from which aliquots are taken for the determination. If the outer layer has dried out or if a white sodium sulphate layer has formed then this must be removed before weighing out the sample. Depending on the content about 12 to 16 g are weighed out into a 500 mL volumetric flask. Approx. 250 mL water are then added and the sample is dissolved completely by stirring and gentle heating. Under no circumstances should the sample be heated to the boiling point. The solution is allowed to cool down to room temperature and, after the magnetic stirrer bar has been removed, filled up to the mark and thoroughly mixed. In order to prevent too much foam from being produced, mixing should be carried out with a magnetic stirrer bar on a magnetic stirrer plate. Exactly 10.0 mL of this stock solution are pipetted into a titration beaker and the anionic surfactants are determined as described in section 18.2.
8.2.17 WC perfume blocks

Origin: Germany

Ingredients according to EU recommendation:
- 15-30% anionic surfactants
- Builders
- Colourants
- Fragrances

The determination of anionic surfactants in WC perfume blocks is relatively free from problems. However, to obtain reproducible results it is necessary to use a stock solution from which aliquots are taken for the determination. If the outer layer has dried out or if a white sodium sulphate layer has formed then this must be removed before weighing out the sample. Depending on the content about 15 to 25 g are weighed out into a 500 mL volumetric flask. Approx. 250 mL water are then added and the sample is dissolved completely by stirring and gentle heating. Under no circumstances should the sample be heated to the boiling point. The solution is allowed to cool down to room temperature and, after the magnetic stirrer bar has been removed, filled up to the mark and thoroughly mixed. In order to prevent too much foam from being produced, mixing should be carried out with a magnetic stirrer bar on a magnetic stirrer plate. Exactly 10.0 mL of this stock solution are pipetted into a titration beaker and the anion-active surfactants are determined as described in section 18.2.2.

8.2.18 Vinegar cleaners

Formulation 1

Origin: Germany

Ingredients according to EU recommendation:
- <5% anionic surfactants
- Vinegar
- Cosmetic colourant

Formulation 2

Ingredients according to EU recommendation:
- <5% anionic surfactants
- Vinegar

Formulation 3

Ingredients according to EU recommendation:
- Pearl gloss agent
- Cosmetic colourant
- Perfume oil

Titrations in aqueous media

Among others, sec. alkane sulphonates are used as the basic surfactants in such vinegar cleaners; their determination is not free from problems (see section 7.2.5).

Acceptable values which correlate with those obtained by two-phase titration are obtained if the following instructions are adhered to:

Approx. 500 to 600 mg of the vinegar cleaner are weighed out directly into the titration beaker, diluted with 90 mL water and then 10 mL of 1 mol/L sulphuric acid solution are added. After addition of 5 mL methanol the titration is carried out against 0.004 mol/L TEGO trant A100 solution.

Potentiometric two-phase titrations

Potentiometric two-phase titration detected with the Surfactrode Resistant can also be carried out on vinegar cleaners easily and without any problems. It provides results that correlate with those obtained by two-phase titration. The titration is carried out as described in sections 18.2.1 or 18.2.2 at pH = 3. The addition of 200 µL TEGO add is necessary. TEGO trant A100 c = 0.02 or c = 0.004 mol/L should be used as the titrant. The achievable relative standard deviations are below 0.5%.

8.2.19 Neutral cleaners

Origin: Germany

Ingredients according to EU recommendation:
- 5 to 15% anionic surfactants
- <5% amphoteric surfactants
- <5% nonionic surfactants
- Fragrances
- Auxiliaries

Titration of such a formulation causes no problems. The anionic surfactants used in such neutral cleaners also usually cause no problems, so that an error-free and interference-free titration can be expected. To eliminate possible interference from betains it is important to maintain a pH of preferably 3 during the titration.
**9 Cosmetics**

This section was produced in cooperation with Peter Bruttel, Head Application Laboratory, Metrohm Ltd., CH-9101 Herisau, Switzerland

**9.1 Rinse-off formulations for personal hygiene**

***9.1.1 Titrant concentration***

Titrants for the determination of ionic surfactants with a concentration of 0.004 mol/L have been successfully used in practice. This concentration is also found in very old publications. In all the titrations carried out in the author’s laboratory, which form the basis of this monograph, a titration solution concentration of 0.004 mol/L was used.

In parallel to this other laboratories have established a titrant concentration of 0.005 mol/L for the determination of ionic surfactants. All the applications mentioned in this monograph can also be carried out with a 0.005 mol/L titrant solution. The sample weight must be adjusted accordingly.

The titration should not be carried out with more dilute solutions because then the influence of the special physicochemical properties of the surfactants becomes even greater and linearity between the sample weight and titrant consumption cannot be achieved.

Higher titrant concentrations up to 0.05 mol/L are possible. They produce steeper titration curves, but the results are no better. This is why this technique cannot be recommended for routine daily use where titrations are always carried out in aqueous solution. Only in cases where the use of 0.004 mol/L solutions results in flat titration curves that cannot be evaluated should more concentrated solutions be used. Another reason for the use of more concentrated solutions is a wide distribution of the alkyl chains of the surfactants as may be found, e.g., in surfactants based on natural coconut oil. Thus, the quantitative determination of sodium cocoyl isethionates is only possible with 0.04 or 0.05 mol/L TEGO trant A100 solution.

During the development and test phase of the Metrosensor Surfactrode Resistant it could be seen that it made more sense to titrate with a 0.02 mol/L solution for most cosmetic formulations as well as for cleaning agents and detergents. This applies to both anionic and cationic titrants. In this way better, smoother and more «typical» titration curves can be obtained. In this case «typical» means that the titration curves approach the ideal S-shape and therefore the titrator algorithms can evaluate them better. By carrying out an extremely large number of titrations in our laboratory we were able to prove that better standard deviations could be achieved for the formulations mentioned above. In addition, the higher titrant concentration allowed a single method to be used for almost all formulations without the need for having a lot of background knowledge of the products to be analysed. This has considerable advantages, particularly when competitors’ products are being analysed. This is the reason for my recommendation of a titrant concentration of 0.02 mol/L in such cases.

In many cases the question of which titrant concentration is the optimal one or just the most suitable one cannot be answered simply and sometimes it is a good idea to carry out the titration with different titrant concentrations. This will show which titrant concentration produces the better titration curves.

In this monograph a titrant concentration of 0.02 mol/L is often recommended for the formulations sector. Of course, every rule has its exceptions. This became very clear to us when we investigated formulations found on the North American market. In the cosmetics sector new tendencies became apparent in rinse-off formulations. As an example we list hair & body shampoo and body shampoo formulations.

**Hair & Body Shampoo**

- Water
- PEG-80 sorbitan laurate
- Cocamidopropyl betain
- Sodium trideceth sulphate
- Glycerin
- Disodium lauroamphodiacetate
- PEG-150 distearate
- Sodium laureth-13 carboxylate
- Fragrance
- Polyquaternium-10
- Tetrasodium EDTA
- Quaternium-15
- Guar hydroxypropyltrimonium chloride
- Sodium hydroxide
- Butylated hydroxytoluene (BHT)
- Methylchloroisothiazolinone
- Methylisothiazolinone
- Benzophenone-4
- Chamomile Oil

**Body Shampoo**

- Water
- Cocamidopropyl betain
- Dimethicone
- Sodium laureth sulphate
- Ammonium sulphate
- Fragrance
- Laureth-4
- Laureth-23
- Carbomer
- Mica
- Titanium dioxide

In both formulations it can be recognised that nonionic surfactants are the basic surfactants used, e.g. those based on POE sorbitan fatty acid esters or betains. The anionic surfactants to be titrated are listed in the CTFA or INCI declarations in the third place or even later. For these formulations better titration curves can be achieved with a 0.004 mol/L TEGO trant A100 solution as titrant. The reason for this is quite simple. The low titrant concentration results in a
However, if the formulations also contain surfactants such as cocoyl isethionate or lauroyl sarcosinate then the titration must naturally be carried out with a correspondingly higher titrant concentration, because a quantitative determination is only possible in this way.

In classical formulations, as represented by the body shampoo and hair shampoo formulations given below, the 0.02 mol/L TEGO trant A100 solution has proved its value as the titrant.

**Body Shampoo**
- Water
- Ammonium lauryl sulphate
- Ammonium laureth sulphate
- Lauramide DEA
- Citric acid
- Hydroxypropyl methylcellulose
- Tetrasodium EDTA
- Ammonium chloride
- Benzophenone-4
- Methylchloroisothiazolinone
- Methylisothiazolinone
- DMDM hydantoin
- Ammonium xylenesulphonate
- PEG-40 hydrogenated castor oil
- Propylene glycol
- Citric acid
- Sodium chloride
- Sodium benzoate
- Sodium salicylate
- Fragrance
- D & C Red No. 33
- D & C Orange No. 4

**Hair Shampoo**
- Aqua
- Sodium laureth sulphate
- PEG-7 glycercylo cocoate
- Disodium cocoamphodiacetate
- Cocamidopropyl betain
- Laureth-2
- Perfume
- Glycol distearate
- Laureth-4
- Allantoin

In these formulations the anionic surfactant to be titrated is the first mentioned in the CTFA or INCI declaration and is therefore the primary surfactant in the formulation. These and similar formulations can be titrated better with a 0.02 mol/L TEGO trant A100 solution.

For the preparation of the titration solutions only the purest chemicals available on the market should be used. Many of the substances that are required here can be found in the catalogues of the well-known laboratory chemical companies. Merck in Darmstadt, Germany, offers chemicals with the qualification «for surfactant tests (für T ensiduntersuchungen)» as a speciality.

TEGO trant A100 is a research product of Th. Goldschmidt AG in Essen, Germany, and was specially developed for the titration of anionic surfactants. It shows its strengths particularly when used with the Ionic Surfactant Electrode and also the Surfactrode Resistant. TEGO trant A100 is marketed worldwide exclusively by Metrohm Ltd. and the Metrohm agencies. This special titrant allows the range of potentiometric surfactant titration applications to be significantly extended.

### 9.1.2 Shower gels and foam baths – European standard formulations

#### Titration in aqueous media

In many laboratories that carry out the quality control of rinse-off products it is the daily practice not to determine the actual content of anionic components, but only to carry out an empirical two-phase titration against a standard product. The reason for this is the interfering betain content in such formulations.

In contrast, in potentiometric surfactant titration with the Ionic Surfactant Electrode, which can be used throughout a wide pH range, a pH value can be selected at which the betain is present in its «amphoteric» structure and does not act as a cationic surfactant. Under these conditions the anionic surfactant to be determined can be titrated without any interference.

As such formulations are often very complex the qualitative composition of the sample must be known. The determination of the active content of anionic surfactants by potentiometric titration indicated with surfactant electrodes can already be used as a standard today, e.g. DGK Method AO11.1.
In our application laboratory seven formulations were prepared; these are listed in Table 38. For each of the ionic surfactants used here the active content was first determined by classical two-phase titration and by potentiometric surfactant titration. The concentration of anionics was then calculated from the total formulation. As the formulations sometimes contain mixtures of anionic surfactants with very different molar masses, it made sense to calculate the concentration of anionic surfactants in mmol/100 g. The formulations were not prepared according to normal criteria, i.e. the viscosity or technical application properties of the end product played no role; it was more important that all co-surfactants or formulation ingredients were added at realistic concentrations to allow statements about the quantitative determination of these formulations to be made.

<table>
<thead>
<tr>
<th>Table 38 Composition of model formulations (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Product</strong></td>
</tr>
<tr>
<td>Sodium laureth-2.5 sulphate</td>
</tr>
<tr>
<td>PEG-7 glyceryl cocoate</td>
</tr>
<tr>
<td>Cocamidopropyl betain</td>
</tr>
<tr>
<td>Polyquaternium 10</td>
</tr>
<tr>
<td>Disodium laureth sulphasuccinate</td>
</tr>
<tr>
<td>POE-40 hydrogenated castor oil</td>
</tr>
<tr>
<td>POE-20 sorbitan monostearate</td>
</tr>
<tr>
<td>Sodium C14-C16 olefin sulphonate and glycol distearate and cocamidopropyl betain and sorbitan laurate</td>
</tr>
<tr>
<td>Sodium cocoyl isethionate</td>
</tr>
<tr>
<td>Water</td>
</tr>
</tbody>
</table>

**Titration conditions**

For the quantitative determination of the anionic surfactants 200 to 250 mg of the rinse-off formulation are weighed out directly into the titration beaker. The sample weight is selected so that a consumption of between 10 and 18 mL 0.004 mol/L TEGO tran A100 solution can be expected. Then 5 mL methanol and 10 mL buffer solution are added to the sample. Most samples dissolve very well in this mixture. If the products contain pearl lustre agent then the glycol distearate this contains is finely distributed without interfering with the titration. After the addition of 85 mL water the titration can be carried out directly.

The titrator and the titrator settings are of the utmost importance in surfactant titrations. In many titrations we have found that dynamic titration, in which the change of the electrode signal determines the size of the titrant increment, is the most suitable mode. This titration mode ensures that sufficient measuring points are present in the region of the inflection point for a good and reproducible evaluation to be achieved. In this way it is possible to adjust to the peculiarities of all surfactant titrations. When selecting the parameters the fact that the reaction rate in a surfactant titration is slower than that of an acid-base titration must be taken into account. Good titration parameters are:

### 726 Titroprocessor

**Titration parameters**

- **Meas.pt.density**: 2
- **Signal drift**: 15 mV/min
- **Min.increment**: 50 µl
- **Equilibr.time**: auto s
- **Dos. rate**: 30 mL/min

The formulations A to E contain cocamidopropyl betain and anionic surfactants that can be titrated well at pH = 5.0. At this pH the betain is present in its internally balanced molecular form similar to a nonionic surfactant. It therefore cannot interfere with the determination.

**Table 39 Results of surfactant titrations in synthetic formulations**

<table>
<thead>
<tr>
<th><strong>Anionic surfactant (theoretical) in mmol/100 g</strong></th>
<th><strong>A</strong></th>
<th><strong>B</strong></th>
<th><strong>C</strong></th>
<th><strong>D</strong></th>
<th><strong>E</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anionic surfactant (actual) in mmol/100 g</strong></td>
<td>24.8</td>
<td>31.7</td>
<td>26.2</td>
<td>24.7</td>
<td>24.9</td>
</tr>
<tr>
<td><strong>Deviation from theoretical content in mmol/100 g</strong></td>
<td>+0.5</td>
<td>+0.2</td>
<td>+0.7</td>
<td>+0.4</td>
<td>+0.6</td>
</tr>
<tr>
<td><strong>Standard deviation (absolute)</strong></td>
<td>0.40</td>
<td>0.27</td>
<td>0.35</td>
<td>0.34</td>
<td>0.75</td>
</tr>
<tr>
<td><strong>Standard deviation (relative, %)</strong></td>
<td>1.60</td>
<td>0.86</td>
<td>1.35</td>
<td>1.36</td>
<td>3.02</td>
</tr>
</tbody>
</table>
reactive. Therefore, in this pH range 2 mol cationic surfactant are consumed in the titration per mol sulphonesuccinate. This means that in the following table there are differing theoretical and actual contents, which depend on the pH, for an identical formulation. However, this fact allows the differentiation of a mixture of classical anionics and sulphonesuccinate monoesters. Sulphonesuccinates should under no circumstances be titrated at pH = 5.0 like the previous 5 compounds, because flat titration curves that cannot be evaluated will be obtained for the disodium laureth sulphonesuccinate. The results are shown in Table 40.

Table 40 Titration results obtained at different pH values of formulations containing sulphonesuccinates

<table>
<thead>
<tr>
<th></th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 3</td>
<td></td>
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</tr>
<tr>
<td>Anionic surfactant (theoretical) in mmol/100 g</td>
<td>29.8</td>
<td>29.8</td>
</tr>
<tr>
<td>Anionic surfactant (actual) in mmol/100 g</td>
<td>30.2</td>
<td>30.2</td>
</tr>
<tr>
<td>Deviation from theoretical content in mmol/100 g</td>
<td>+0.4</td>
<td>+0.4</td>
</tr>
<tr>
<td>Standard deviation (absolute)</td>
<td>0.26</td>
<td>0.21</td>
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<tr>
<td>Standard deviation (relative, %)</td>
<td>0.85</td>
<td>0.71</td>
</tr>
<tr>
<td>pH = 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anionic surfactant (theoretical) in mmol/100 g</td>
<td>34.9</td>
<td>34.9</td>
</tr>
<tr>
<td>Anionic surfactant (actual) in mmol/100 g</td>
<td>36.6</td>
<td>36.2</td>
</tr>
<tr>
<td>Deviation from theoretical content in mmol/100 g</td>
<td>+1.7</td>
<td>+1.3</td>
</tr>
<tr>
<td>Standard deviation (absolute)</td>
<td>0.62</td>
<td>0.34</td>
</tr>
<tr>
<td>Standard deviation (relative, %)</td>
<td>1.67</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Sulphonesuccinates certainly belong to those surfactants that cannot be titrated very easily. This applies both to potentialmetric titration and classical two-phase titration. In formulations prepared using them the disadvantages of Hyamine 1622 as a titrant are very plainly seen. The titration curves were sometimes so flat that evaluation of the point of inflection was impossible. In addition the standard deviations obtained with Hyamine 1622 are generally worse than those with TEGO trant A100. The Polyquaternium 10 contained in formulation F is indeed a quaternary ammonium compound, but has no surfactant properties and does not interfere with the titration. This was additionally confirmed by a test titration on pure Polyquaternium 10.

Table 41 again shows the analytical results, obtained with Hyamine 1622 and TEGO trant A100, for two formulations.

Table 41 Dependence of the titration results on the titrant used

<table>
<thead>
<tr>
<th></th>
<th>TEGO trant A100</th>
<th>Hyamine 1622</th>
<th>TEGO trant A100</th>
<th>Hyamine 1622</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 3</td>
<td>24.3</td>
<td>24.3</td>
<td>24.3</td>
<td>24.3</td>
</tr>
<tr>
<td>pH = 10</td>
<td>24.8</td>
<td>25.1</td>
<td>24.9</td>
<td>23.5</td>
</tr>
<tr>
<td>Deviation from theoretical content in mmol/100 g</td>
<td>+0.5</td>
<td>+0.8</td>
<td>+0.6</td>
<td>-0.8</td>
</tr>
<tr>
<td>Standard deviation (abs.)</td>
<td>0.40</td>
<td>0.41</td>
<td>0.75</td>
<td>0.63</td>
</tr>
<tr>
<td>Standard deviation (rel.)</td>
<td>1.60</td>
<td>1.63</td>
<td>3.02</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Figs. 172 and 173 provide a comparison of the titration curves and results for these formulations.

Fig. 172: Comparison of the titration results of a 3-component model formulation using TEGO trant A100 and Hyamine 1622
Titrimetric determination of surfactants and pharmaceuticals

Titration of commercial products

The surfactant content of a total of 67 different commercial products was investigated by potentiometric surfactant titration indicated with surfactant electrodes. The rinse-off products came from Germany, Great Britain, North America and Switzerland. The complete price range from no-name products up to famous brands was included. The products were obtained from stores, supermarkets, chemists, perfume shops and druggists. A third of the formulation were two-in-one products.

The titration parameters were selected according to the CTFA or INCI declarations. After carrying out a sample titration a sixfold determination was carried out with optimised sample weight and the quality of the titration curve was assessed together with the calculated standard deviation. All the titration curves obtained could be evaluated by the titrator algorithm. The relative standard deviations were between 0.4 and 2.6%.

This allows the conclusion to be drawn that the test method suggested here can be used for most of the formulations found on the market.

Potentiometric two-phase titrations

European formulations

The investigations mentioned in the previous section were carried out in 1993. In the meantime the formulations have changed significantly. The formulations have become milder as a result of the use of

- various sugar surfactants such as lauryl glucoside, lauryl polyglucose, PEG-120 methyl glucose dioleate and others,
- but also higher concentrations of cocamidopropylamines, cocoamphoacetates or specially mild classical nonionic surfactants based on POE adducts such as
  - PEG-6 caprylic/capric glycerides, PEG-7 glyceryl cokoate, PEG-40 hydrogenated castor oil, PEG-10 olive glycerides or PEG-120 methyl glucose dioleate.

However, milder does not only mean that these shower gels are suitable for use on sensitive skin. A surfactant analyst can see that the above-mentioned particularly mild surfactants are those that impair titrations in aqueous media. All the above-mentioned surfactants have a solubilising effect on the insoluble ion associate produced by the anionic analyte and the cationic titrant during the titration in an aqueous medium.

In order to be able to include all formulations in a single table the INCI or CTFA rules, according to which the declaration should be made in order of decreasing concentration, have not been observed. This is why sorbitol is found at the bottom of the table. Nevertheless some of these formulations have a sorbitol concentration of more than 10%. Formulation ingredients that have no relevance for the titration have been omitted. These include perfume oils, preservatives and herbal, plant or root extracts. Only 8 of the 20 sensitive shower gels listed in Table 42 could be titrated in an aqueous medium.
### Table 42 Formulations for «sensitive» shower gels

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
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<td>x</td>
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<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
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<tr>
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<td></td>
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<td>PEG-6 caprylic/capric glycerides</td>
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<td>x</td>
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<tr>
<td>PEG-7 glyceryl cocoate</td>
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<td>x</td>
<td>x</td>
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<td>Polyquaternium-10</td>
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<td>Polyquaternium-7</td>
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<td>Potassium cocoyl hydrolysed collagen</td>
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<tr>
<td>Sorbitol</td>
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</tr>
</tbody>
</table>

In potentiometric titration in two-phase media less problems are encountered. All the above-mentioned formulations could be titrated. All these shower gels could also be titrated with a single method. In order to prevent interference from betains the titrations were carried out at pH = 3. For many years this pH has proved to be the optimal value for the titration of anionic surfactants in rinse-off formulations.

The titration is carried out according to the conditions described in section 18.2.2. TEGO trant A100 c=0.02 mol/L was used as the titrant. Although all the analysed products contained nonionic surfactants the titrations should nevertheless be carried out with the addition of 100 to 200 µL TEGO add. The relative standard deviations for all 15 formulations were between 0.5 and 1.0%.

Use of a 0.02 mol/L Hyamine 1622 solution sometimes produced low-bias results, depending on the formulation, of up to 8%.

Titration of the shower gel formulations at pH = 10 was not carried out.

In the potentiometric two-phase titration of shower gels with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.
9.1.3 Shower gels and foam baths – European «natural cosmetics»

A = Shower peeling Germany
B = Coconut shower gel Germany
C = Liquid Niehm soap Germany
D = Protein shampoo Germany
E = Herbal shampoo Germany
F = Shower and bath gel Great Britain

The numbers given in Table 43 indicate the position of the raw material in the INCI declaration.

Table 43 Composition of some «natural cosmetic» shower gels

<table>
<thead>
<tr>
<th>Formulation</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium laureth sulphate</td>
<td>7</td>
<td>7</td>
<td>1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>MIPA-laureth sulphate</td>
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<td>1</td>
<td>2</td>
<td>2</td>
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<tr>
<td>Disodium PEG-10 laurylctrate sulphosuccinate</td>
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<td></td>
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<tr>
<td>Disodium PEG-5 laurylctrate sulphosuccinate</td>
<td>4</td>
<td>4</td>
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<tr>
<td>Cocamidoproyl betain</td>
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<td>1</td>
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<td></td>
</tr>
<tr>
<td>Decyl polyglucose</td>
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<td>3</td>
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<td>2</td>
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<td></td>
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<td>PEG-7 glyceryl cocoate</td>
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<td>4</td>
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</tr>
<tr>
<td>Citric acid</td>
<td>10</td>
<td>6</td>
<td>11</td>
<td>11</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Sucrose cocoate</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lauryldimonium hydroxypropyl Hydrolysed wheat protein</td>
<td>8</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrolysed wheat protein</td>
<td>9</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lauramide DEA</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trisodium HEDTA</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Formulation ingredients that are not relevant for surfactant titration and are normally only present at low concentrations, e.g. preservatives, colourants or herbal extracts, have been omitted from the CTFA or INCI declaration. The sequence of the other ingredients has been left so that it corresponds to the original declaration.

The potentiometric two-phase titration of formulation F could be carried out as described in section 18.2.2. The declared formulation can be classified as a standard formulation. A relative standard deviation of 0.3% was achieved.

Despite great efforts it was not possible to determine the anionic surfactant content of formulations A to E. This content is very low with a very high proportion of surfactants that normally are used as co-surfactants in classical formulations. Even carrying out the titration at widely varying pH values or exchanging the solvent used in the titration brought no significant improvement.

Even with the classical Epton two-phase titration it is not possible to determine the anionic surfactant content of formulations A to E.

We have titrated the two sulphosuccinates, disodium PEG-10 laurylcitrte sulphosuccinate and disodium PEG-5 laurylcitrte sulphosuccinate, as raw materials. Both can be classified as being extremely problematical to titrate. To determine the pH-dependence, surfactant titrations were carried out throughout the relevant range. Evaluable titration curves were only obtained at pH = 3. The derivative curves have very broad peaks and the reproducibility is poor. A relative standard deviation of approx. 2% must be expected. We also could not determine model mixtures containing the two sulphosuccinates mentioned.
9.1.4 Shower gels and foam baths on the North American market

Formulations on the North American market differ from European formulations both in the surfactant composition and in the surfactants used.

Table 44 North American body wash and liquid soap formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<th>6</th>
<th>7</th>
<th>8</th>
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<tbody>
<tr>
<td>Sodium laureth sulphate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Decyl polyglycosce</td>
<td>X</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cocamidopropyl betain</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triclosan</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Polyquaternium-7</td>
<td>X</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>PEG-7 glyceryl cocoate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG-120 methyl glucose dioleate</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
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</tr>
<tr>
<td>Sodium C14-16 olefin sulphonate</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Lauramide DEA</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
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<tr>
<td>Silk peptide</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Hydrolysed silk protein</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium cocoamphoacetate</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Sodium myreth sulphate</td>
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<tr>
<td>Glycol stearate</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cocamide MEA</td>
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<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Potassium C9-15 alkylyphosphate</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyceryl laurate</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyquaternium-10</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral oil</td>
<td></td>
<td>X</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Soybean oil</td>
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<td>X</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sucrose octaacetate</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium cocoyl isethionate</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethicone</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laureth-4</td>
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<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laureth-23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the potentiometric two-phase titrations of the formulations listed in the table practically no problems were encountered. For formulations containing sodium cocoyl isethionate the additional explanations given in section 9.1.6.4 apply.

9.1.5 Shower gels and foam baths on the Asian/Pacific market*

The formulations on the Asian/Pacific markets are similar to those on the North American market. See section 9.1.4 for the titration conditions. If the formulations contain soaps then see also section 9.1.6.6, «Soap-based shower creams».

9.1.6 Shower gels and foam baths with special surfactants

9.1.6.1 Formulations with lauroyl sarcosinates

With their soap-like structure, sarcosinates cause similar problems to those encountered in the titration of soaps. TEGO trant A100 is the only titrant that can be used. Titration curves with Hyamine 1622 are so flat that they cannot be evaluated. Even if TEGO trant A100 is used as titrant the conditions described in section 18.2.2 must be altered because otherwise significantly too high results are obtained. However, if TEGO trant A100 c = 0.05 mol/L solution is used then correct results are obtained with a good reproducibility. The titration is carried out at pH = 10. Relative standard deviations of 0.7% can be achieved.

On the North American market in particular sarcosinates are used as co-surfactants in many different cosmetic formulations.

In the potentiometric two-phase titration of shower gels containing lauroyl sarcosinates with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

* Hong Kong, Taiwan, Singapore, Malaysia, Japan, Indonesia, China, Philippines, Australia, New Zealand
**Body Washes**

Formulation A
- Ammonium laureth sulphate
- Ammonium lauryl sulphate
- Sodium lauroyl sarcosinate
- Glycol distearate
- Polyquaternium 10

Formulation B
- Sodium laureth sulphate
- Cocamidopropyl betain
- Sodium lauroyl sarcosinate

Classical anionic surfactants in a body wash formulation are titrated as usual at pH = 3. A second titration is then carried out at pH = 10. In this titration the sum of the anionic surfactants and lauroyl sarcosinates is determined. These titrations should be carried out with c = 0.05 mol/L TEGO trant A100 solution.

**Potentiometric two-phase titrations**

The potentiometric two-phase titration of formulations containing lauroyl sarcosinates is carried out using the Surfactrode Resistant. If TEGO trant A100 c = 0.02 mol/L is used as the titrant the titration produces curves that are easy to evaluate and correct results.

The titrations are carried out at pH = 10 as described in section 18.2.2. The addition of 200 µL TEGO add is recommended.

In the potentiometric two-phase titration of body wash formulations containing lauroyl sarcosinates with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

9.1.6.2 Formulations containing fatty alcohol ether carboxylic acids

**Titrations in aqueous media**

In the titration of shower gels, shampoos and similar formulations that contain fatty alcohol ether carboxylic acids these are not determined. This applies to surfactant titration under both acidic and alkaline conditions. A titration in aqueous media of formulations that contain laureth-11 carboxylic acid cannot be recommended for determining the surfactant concentration. The laureth-11 carboxylic acid has a levelling effect on the titration curve of the anionic surfactants.

**Potentiometric two-phase titrations**

Apart from the co-surfactant cocamidopropyl betain, shower gel formulations may contain so-called ether carboxylic acids such as laureth-11 carboxylic acid as an additional co-surfactant. Naturally a wide range of different products is possible in the ether carboxylic acids both in terms of the number of POE units and of different starter alcohols. While in the raw materials (see section 7.3.4) a wide range of different ether carboxylic acids was analysed, the systematic investigation into shower gel preparations was limited to laureth-11 carboxylic acid. The commercial products listed in Table 45 were also titrated.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium laureth sulphate</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Cocamidopropyl betain</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Laureth-11 carboxylic acid</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Glycol distearate</td>
<td>x</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>PEG-7 glyceryl cocaate</td>
<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Polysorbate 20</td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>PEG-55 propylene glycol oleate</td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Sodium cocoamphoacetate</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>PEG-120 methyl glucose dioleate</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

While most raw materials based on ether carboxylic acids, e.g. laureth-11 carboxylic acid, can be titrated very well in a two-phase medium, this is not possible for shower gel or shampoo formulations.

**Titrations at pH = 3**

At pH = 3 the anionic surfactants in such rinse-off formulations as described in section 18.2.2 can be determined without interference from laureth-11 carboxylic acid. The laureth-11 carboxylic acid is, as expected, not determined at this pH.

**Titrations at pH = 10**

According to theory, at pH = 10 the sum of anionic surfactants plus laureth-11 carboxylic acid should be titrated. In practice no titration curves that could be evaluated were obtained with formulations containing ether carboxylic acids.
This means that the titrimetric determination of ether carboxylic acids, using laureth-11 carboxylic acid as an example, is also impossible by potentiometric two-phase titration.

In the potentiometric two-phase titration of ether carboxylic acids with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

9.1.6.3 Formulations with monoalkylphosphate (MAP)

Monoalkylphosphate (MAP) is a mild non-soap cleaning agent that is mainly used in body shampoos, etc., of the North American and Pacific markets. It is manufactured by KAO and is chiefly used in the KAO group’s formulations.

Example of a formulation of a body shampoo containing MAP

- Potassium C9-C15 alkyl phosphate
- Sodium laureth sulphate
- Lauric acid sodium cocoamphoacetate
- Glycol distearate
- Cocamide MEA
- Glyceryl laurate
- Polyquaternium 10

Titration in aqueous media

All attempts to titrate the anionic surfactants contained in this formulation in an aqueous medium were unsuccessful. Titrations were carried out between pH = 3 and pH = 10. In no case did potentiometric titrations produce titration curves that could be evaluated.

Potentiometric two-phase titrations

The potentiometric two-phase titration was also not successful. None of the selected and widely varying conditions produced titration curves that could be evaluated.

9.1.6.4 Formulations containing sodium cocoyl isethionate

As already described for isethionates in the chapter on raw materials (see section 7.2.7), the titration of this class of compounds is not free from problems. Using TEGO trant A100 c = 0.05 mol/L as the titrant it is only possible to determine the lower chain lengths such as sodium octyl isethionate or sodium decyl isethionate quantitatively. The use of the Metrosensor Surfactrode Resistant has no advantages in this case, so that it is recommended to carry out the titration using the Ionic Surfactant Electrode. Under all circumstances pH = 5.0 must be maintained for these formulations. However, as the titration of sulphosuccinates such as disodium laureth sulphosuccinate is not possible at pH = 5, sodium cocoyl isethionate and disodium laureth sulphosuccinate must not be present in the same formulation if the surfactant titration is to be carried out.

The use of TEGO trant A100 solution c = 0.05 mol/L is absolutely necessary. For the determination of the anionic surfactants in such a formulation relative standard deviations of 0.5% can be achieved.

9.1.6.5 Formulations with sulphosuccinates

Whether sulphosuccinates such as disodium laureth sulphosuccinate should still be numbered among the special surfactants in shower gel formulations is a debatable point – these surfactants have established themselves on a broad front, particularly in Europe. In any case we analysts regard the representatives of this group as being special surfactants. The selection of the correct pH is extremely important for the titration of the sulphosuccinates. This is why we can only recommend that section 9.1.2 be studied with great care.

9.1.6.6 Soap-based shower creams

Soap-based shower creams certainly only form a small market segment seen from a global point of view. However, regionally these classical soap formulations may have a crucial market share.

Ingredients:

Water, distilled palm kernel fatty acids, potassium hydroxide, propane 1-2-3 triol, ethylene glycol stearate, fragrance, hydroxyethylcellulose, citric acid, sodium lactate, tetrasodium EDTA, formaldehyde, butylated hydroxytoluene (BHT)

Whether these soap-based shower creams can be titrated depends entirely on the alkyl chain distribution of the fat used in the manufacture of the soap. The palm kernel oil used here contains small amounts of C<sub>8</sub> and C<sub>10</sub> fatty acids. In potentiometric soap titration these are not determined. This is why the titration should be carried out against a standard. For calibration purposes a pure palm kernel oil fatty acid is titrated. Potentiometric titration of these soap-based shower creams is only possible and sensible with TEGO trant A100 as titrant. The most suitable method for determining the soaps in such a formulation is potentiometric two-phase titration at pH = 10 with detection by the Metrosensor Surfactrode Resistant. The best and steepest potential jumps with the smallest relative standard deviation of <0.5% are obtained by potentiometric two-phase titration when chloroform is used as the water-immiscible phase. In this way all soaps with a C-chain length of ≥12 are quantitatively determined. The use of methyl isobutyl ketone as the water-immiscible phase is also possible.

In the potentiometric two-phase titration of soap-based shower creams with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by
adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8. The addition of 200 µL TEGO add is recommended.

9.1.7 Medical products for skin cleansing

**Formulation A**

Special washing fluid for extremely dry skin
- Sodium laureth sulphate
- Sodium cocoamphoacetate
- Cocamidopropyl betain
- PEG-7 glycerylcoocotate
- Dead Sea salt
- Disodium undecyleneamido MEA sulphosuccinate
- PEG 40 hydrogenated castor oil
- Cocamide DEA
- Cocamide MEA
- Glycol stearate

**Formulation B**

Mineral washing lotion for sensitive to problematic skin
- MIPA laureth sulphate
- Linolamide DEA
- Cocamidopropyl betain
- Disodium laureth sulphosuccinate

**Formulation C**

Basic therapy for skin diseases and dermatomycosis
- Dodecylbenzenesulphonic acid nitritolriethanol salt
- POE oleic acid amide
- Ammonium dodecylsulphate
- Hexylaurate
- Lecithin

**Formulation D**

Washing lotion with panthenol
- Sodium laureth sulphate
- Sodium cocoamphoacetate
- Cocamidopropyl betain
- Panthenol
- PEG-7 glycerylcoococate
- Glycol stearate

**Formulation E**

Medical washing gel
- Sodium laureth sulphate
- Disodium laureth sulphosuccinate
- Cocamidopropyl betain
- PEG-6 caprylic/capric glycerides
- Laureth-3
- PEG-3 distearate
- Allantoin

**Formulation F**

Washing fluid for fatty, acne-affected skin
- MIPA laureth sulphate
- MIPA lauryl sulphate
- Disodium laureth sulphosuccinate
- Lactic acid
- Cocamidopropyl betain
- Laureth 12
- Lecithin
- PEG-75 lanolin
- Disodium cocodiamphodiacetate
- Milk serum

All the preparations mentioned above can be titrated as described in section 18.2.2 easily and without problems. The relative standard deviations achieved in the titrations were 0.3 to 0.6%. For formulation G the limitations regarding the ability to titrate lauroyl sarcosinates apply (see section 9.1.6.1).

9.1.8 Shower peeling
All the shower peeling preparations tested by us could be titrated potentiometrically in a two-phase medium using the Surfactrode Resistant. The titration is carried out as described in section 18.2.2 with standard parameters. Whether the addition of TEGO add is necessary must be tested in each individual case.

### 9.1.9 Shower milks

Shower milks are shower formulations in the form of an emulsion. Apart from the wash-active substances themselves, these formulations also contain naturally-based and synthetically-based skin care oils. As can be seen below, these products often have very complex formulations.

**Origin Germany**

**Ingredients:**
- Sodium laureth sulphate
- Cocamide DEA
- Glycine soya
- Glyceryl stearate
- PEG-30 stearate
- Cocamidopropyl betain
- Disodium lauroamphodiacetate
- Sodium lauryl sulphate
- Isopropyl palmitate
- Microcrystalline wax
- Lanolin alcohol
- Polyglycerin-3-caprate
- Cetearyl alcohol
- Hexylene glycol
- Glycol distearate
- PEG 40 hydrogenated castor oil
- Liquid paraffin

Nevertheless the anionic surfactants content in such a shower milk formulation can be potentiometrically titrated in a two-phase medium. This is done by weighing out sufficient sample directly into a titration beaker so that a titrant consumption of at least 10 mL 0.02 mol/L TEGO trant A100 solution can be expected. The titration is carried out at pH = 3 with the addition of ethanol and methyl isobutyl ketone. The addition of 200 µL TEGO add is an absolute necessity.

### 9.1.10 Bath oils and shower oils

**Potentiometric two-phase titrations**

Both bath oils and shower oils contain a relatively high proportion of natural oils and fats in their formulations. In most cases the oil amounts to approx. 50%; however, contents of up to 70% are also known. The oils are mostly triglycerides such as soybean oil, castor oil, etc. In addition, they also contain large amounts of polyvalent alcohols such as glycerol or propylene glycol. The anionic surfactants are often fatty alcohol sulphates or fatty alcohol ether sulphates. However, these do not have the normal counter ions found in aqueous formulations such as sodium or magnesium, but the salts used here are monoisopropanolamine, monoethanolamine or diethanolamine salts.

Typically a bath oil could be made up or declared as follows:

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPA laureth sulphate</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIPA laureth sulphate</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Magnesium laureth sulphate</td>
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<td>X</td>
</tr>
<tr>
<td>Cetearyl octanoate</td>
<td>X</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cocamide DEA</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Glycine soya</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isohexadecane</td>
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<td>X</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Isopropyl myristate</td>
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<tr>
<td>Lanolin alcohol</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Laureth-4</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Octyldodecanol</td>
<td>X</td>
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<tr>
<td>Lecithin</td>
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<td></td>
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<tr>
<td>Liquid paraffin</td>
<td></td>
<td>X</td>
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<td></td>
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<tr>
<td>Poloxamer 101</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Pentylene glycol</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene glycol</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ricinus communis</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Castor oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Soybean oil</td>
<td></td>
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<td>X</td>
</tr>
</tbody>
</table>
The natural ester oils used in these formulations, such as soybean oil or castor oil, in many cases have an apolarity similar to the plasticisers used in the membranes of surfactant electrodes. We have often found that the natural oils contained in the formulations are miscible at any ratio with the plasticiser. This means that the oils in the samples to be analysed will remove the plasticiser from the membrane. This will rapidly lead to destruction of the electrode membrane.

This is the reason why only the Metrosensor Surfactrode Resistant can be used as the indicator electrode for determining the anionic surfactant content in bath oils and shower oils. In our laboratory the best results were obtained using 0.02 mol/L TEGO trant A100 solution as the titrant. The sample weights required were usually several hundred mg, so that intermediate dilution steps are not required and the sample can be weighed out immediately into the titration beaker.

Surfactant titrations in such systems can be carried out without any problems. The best solvent has again turned out to be methyl isobutyl ketone (MIBK). Typical relative standard deviations obtained in these titrations were 1% or less. The titration is carried out as described in section 18.2.2 with standard parameters.

Bath oil formulations that contain no anionic surfactants but only nonionic surfactants also exist. These cannot be titrated.

9.1.11 Syndet soaps

Table 47 Typical formulations of some syndet soaps

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
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</thead>
<tbody>
<tr>
<td>Sodium cocoyl isethionate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Disodium lauryl sulphosuccinate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Sodium lauryl sulphate</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium lauroamphoacetate</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene glycol 200</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Coceth-20</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Cetearyl alcohol</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Glyceryl stearate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Glyceryl distearate</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Cetyl palmitate</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>PEG-6 caprylic/capric glycerides</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paraffin</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Corn starch</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Hydrolysed milk protein</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic acid</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lecithin</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Petrolatum</td>
<td>X</td>
<td></td>
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</tr>
</tbody>
</table>

The composition of syndet soaps is extremely complex. In most cases they contain sodium cocoyl isethionate as the basic surfactant. The quantitative determination of sodium cocoyl isethionate is not completely without problems (see also section 7.2.7). For this reason the potentiometric determination of the anionic surfactants in syndet soaps cannot be recommended. This applies to titration in aqueous media as well as for potentiometric two-phase titration.

9.1.12 Soap-based liquid soaps

Many products are called liquid soaps, but the dispensers only contain a true soap-based liquid soap on rare occasions. Globally seen, this group of products represents a small share of the market, but in some regions classical soap formulations may have an important share of the market.

Ingredients:
Water, distilled palm kernel fatty acids, potassium hydroxide, propane 1-2-3 triol, ethylene glycol stearate, fragrance, hydroxyethylcellulose, citric acid, sodium lactate, tetra sodium EDTA, formaldehyde, butylated hydroxytoluene (BHT)

Details about the titration of soaps can be found in section 9.1.6.6 «Soap-based shower creams».

In the potentiometric two-phase titration of soap-based liquid soaps with the Surfactrode Resistant it is absolutely necessary to observe the limits to which this electrode can be used in alkaline media. The pH should only be set by adding a buffer solution and pH = 10 must not be exceeded as otherwise the electrode may be destroyed. See also section 4.5.8.

The addition of 200 µL TEGO acid is recommended.
9.1.13 Surfactant-based liquid soaps

The name «liquid soap» does not necessarily mean that the product in question is a formulation based on soap, i.e. the alkaline salts of fatty acids. In by far the most cases «liquid soap» only means that these formulations can be used in the same manner for daily hand washing purposes as ordinary bar soap.

Very often formulations based on sodium laureth sulphate and cocamidopropyl betain as the wash-active substances are used. This class of compounds is very similar to classical shower gels or body wash formulations.

Details about the titration of these products can be found in the sections on shower gels, 9.1.2 to 9.1.7.

9.2 Hair care products

9.2.1 Shampoos

Potentiometric two-phase titrations

The titration for the determination of the ionic surfactants in shampoos with the Metrosensor Surfactrode Resistant is considerably simpler than a titration in an aqueous medium. As described elsewhere, far less information about the composition of the sample is required for the titration in a two-phase medium with the Metrosensor Surfactrode Resistant. This means that much less attention must be given to the special features of a sample, which also means that less manpower resources are required. Moreover, the titrations can be carried out by less qualified personnel.

Even a higher content of nonionic surfactants, based on POE adducts or on APG has, in the order of magnitude in which these are used in shampoo formulations, practically no influence on the titration. The possible negative influence of amphoteric surfactants such as betains or amphoglycinates is so small that these require practically no consideration in the titration of the anionic surfactants in shampoo. A precondition is that the pH of the titration solution is selected so that interferences from the cation-activity of the protonated betains are excluded. See also section 5.15 «Influence of betains».

Some shampoo formulations also contain nonionic silicone or siloxane compounds, sometimes also emulsified silicone oil. All these nonionic compounds in shampoo formulations have no influence on the titration of the anionic compounds in a two-phase medium with the Metrosensor Surfactrode Resistant. A current trend in the formulation of more expensive shampoos is the inclusion of fruit acids or alphahydroxy acids (AHA). The influence of these additives has been tested, also at concentrations considerably above the normal formulation concentration. No influence on the potentiometric two-phase titration could be recognised.

The potentiometric determination of the anionic surfactants in shampoo formulations should be carried out with 0.02 mol/L TEGO trant A100 solution.

Table 48 Formulations of some European hair shampoos

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
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</thead>
<tbody>
<tr>
<td>Sodium C_{14-16} olefin sulphonate</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
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<td>X</td>
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<td>X</td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>X</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Cocamidopropyl betain</td>
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<td>X</td>
<td></td>
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<td>X</td>
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<td></td>
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<td>Decyl glucoside</td>
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<td></td>
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<td>X</td>
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<td>Glycol distearate</td>
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<td>Isolauryl thioether</td>
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<td>Cetyl alcohol</td>
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</tr>
<tr>
<td>Lauryl hydroxysultain</td>
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<tr>
<td>PEG-18 glyceryl oleate/cocoate</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
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<td>X</td>
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<tr>
<td>Potassium abietoyl hydrolysed collagen</td>
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<td></td>
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Table 48 Formulations of some European hair shampoos (continued)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
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<th>3</th>
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<th>6</th>
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<tr>
<td>Sodium isostearoyl lactylate</td>
<td>X</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sodium PEG-4 lauramide carboxylate</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sucrose cocoate</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Trideceth-8</td>
<td>X</td>
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<td></td>
<td></td>
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</tbody>
</table>

The determination of the anionic surfactants by potentiometric two-phase titration using the Metrosensor Surfactrode Resistant could be carried out on all the formulations listed above and a large number of other formulations. Modification of the standard method was not necessary for any of the given formulations. All titrations were carried out at pH = 3. At this pH, formulation components such as cocamidopropyl betain and lauramine oxide do not interfere. TEGO trant A100 c = 0.02 mol/L was used as the titrant. Relative standard deviations of 0.3 to 0.46% can be achieved.

9.2.1.1 North American formulations

Table 49 North American hair shampoo formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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</thead>
<tbody>
<tr>
<td>Sodium C14-16 olefin sulphonate</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cocamidopropyl betain</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lauramide DEA</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium laureth sulphate</td>
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<td>Ammonium lauryl sulphate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium laureth sulphate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium lauroyl sarcosinate</td>
<td>X</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cocamidopropyl hydroxysultain</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Cocoamphodiacetate</td>
<td>X</td>
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<td>PEG-80 glyceryl cocoate</td>
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<tr>
<td>Cocamide DEA</td>
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</tr>
<tr>
<td>Glycol stearate</td>
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<td>Ammonium xylenesulphonate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethicone copolyol</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethicone</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycol distearate</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cocamide MEA</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tricetylammonium chloride</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyquaternium-10</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The potentiometric two-phase titration for the determination of the anionic surfactants could be carried out on all the formulations listed above and a large number of other formulations. Modification of the standard method was not required for any of the given formulations. The titrations were all carried out at pH = 3. At this pH, formulation components such as cocamidopropyl betain and cocamidopropyl hydroxysultain do not interfere. As a hydrotropic substance, ammonium xylenesulphonate has no surfactant properties. This means that it is not determined, but neither does it interfere with the determination of the anionic surfactants. One of the formulations listed above contains tricetylammonium chloride. This is a cationic surfactant. It is only natural that this cationic surfactant neutralises an equimolar amount of the anionic surfactant by forming an ion associate. The analytical results obtained from this titration will be too low by this amount. This interference cannot be compensated or avoided. In a quality assurance context it is only possible to compensate the analytical result mathematically by the corresponding amount of cationic surfactant. The quaternary cellulose, Polyquaternium-10, contained in a further formulation has no surfactant properties and therefore does not interfere with the determination of the anionic surfactants in the formulation.

TEGO trant A100 c = 0.02 mol/L was used as the titrant. Relative standard deviations of 0.3 to 0.46% were achieved.
9.2.1.2 Formulations on the Asian/Pacific markets*

Table 50 Typical shampoo formulations on the Asian/Pacific markets (in %)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium laureth sulphate</td>
<td></td>
<td>1</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Sodium lauryl ether sulphate</td>
<td>1</td>
<td></td>
<td>1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Disodium laureth sulphonate</td>
<td></td>
<td>4</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Cocoomido propybetain</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>PEG-3 diestrate and sodium laureth sulphate and glycol diestrate</td>
<td>3</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphoteric methacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Polygonum multiflorum thunb</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polygonatum sibiricum reducte</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Angelica sinensis</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Camellia oleifera abel</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycol diestrate</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethicone</td>
<td>4</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td></td>
<td></td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Octyl methoxycinnamate</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium glutamate</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guar hydroxypropyl trimmonium alkyl chloride</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Panthenol</td>
<td>10</td>
<td></td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Glyoxyllic acid</td>
<td>9</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxy propyl chitosan trimonium chloride</td>
<td></td>
<td></td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyquaternium 10</td>
<td></td>
<td></td>
<td>11</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

Formulation ingredients that are not relevant for surfactant titration and are normally only present at low concentrations, e.g. preservatives, colourants or herbal extracts, have been omitted from the CTFA or INCI declaration. The sequence of the other ingredients has been left so that it corresponds to the original declaration.

These formulations do not differ significantly from those of European and American shampoo formulations. It is noticeable that only very small amounts of APG and other sugar surfactants are incorporated in the formulations. All formulations given in the table could be titrated by potentiometric two-phase titration. TEGO trant A100 c = 0.02 mol/L was used as the titrant. Typical relative standard deviations of 0.5% or less were achieved.

9.2.2 Hair conditioners

Hair conditioners are used after the hair has been washed. They contain cationic compounds as the effective components, mostly monomeric or polymeric quaternary ammonium compounds that behave substantively towards the keratin structure of the hair.

Titrations in aqueous media

The representative formulations listed in Table 51 were investigated:

Table 51 Formulations of some hair conditioners

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetrimonium bromide</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Cetrimonium chloride</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steatrimonium chloride</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tallowtrimonium chloride</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distearylidimonium chloride</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Dimethicone</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetylalcohol</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Glyceril stearate</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxyethylcellulose</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

The potentiometric titration of the quaternary ammonium compounds as raw materials such as distearyldimonium chloride; steatrimonium chloride, cetrimonium bromide, or tallowtrimonium chloride can be carried out without any problems. If 0.004 mol/L dodecylsulphate sodium salt solution is used as titrant then standard deviations of approx. 1% can be achieved.

* Hong Kong, Taiwan, Singapore, Malaysia, Japan, Indonesia, China, Philippines, Australia, New Zealand
All four formulations listed above contain relatively little of the quaternary ammonium compounds and a relatively large amount of water-insoluble compounds such as higher fatty alcohols or cellulose derivates. The strongly substantive quaternary ammonium compounds are attached to the surfaces of these substances and are difficult to determine quantitatively. The determination of the quats in all four formulations was possible in the end. The relative standard deviations were between 3 and 5%.

0.004 mol/L dodecylsulphate sodium salt solution should be used as the titrant. The methanol content is very important with these formulations and the amount required depends on the concentration of water-insoluble substances. Cellulose derivates in particular require a methanol content in the titration solution of approx. 25%. Sometimes exchanging methanol for propanol-2 helps. In this case the concentration should be halved; more than 15% should not be used. The analyst must also select the optimal pH. For each formulation a test should be carried out to find the pH at which the best titration curves are obtained. Take into account that at pH values of more than 7 only the quaternary ammonium will be determined whereas at pH values below 5 other surfactant-like amine compounds such as dequaternised quats will additionally be determined.

The TEA-dodecylbenzenesulphonate contained in formulation 1 neutralises an equimolar amount of the quaternary ammonium compound. This leads to results that are too low and cannot be compensated. The evaluation of these analytical results should be carried out with extreme caution.

Quaternary cellulose derivates, e.g. Polyquaternium 10, are not determined in this titration as they are not surfactants.

**Potentiometric two-phase titrations**

The titration for the determination of the quaternary ammonium compounds in hair conditioners or other hair cures with the Metrosensor Surfactrode Resistant is considerably simpler than a titration in an aqueous medium. As described elsewhere, far less information about the composition of the sample is required for the titration in a two-phase medium with the Metrosensor Surfactrode Resistant. This means that much less attention must be given to the special features of a sample, which also means that less manpower resources are required. Moreover, the titrations can be carried out by less qualified personnel.

Hair conditioners or hair cures often contain large amounts of higher fatty alcohols such as cetyl or stearyl alcohol. These are not soluble in water. As a result of the solvent present in potentiometric two-phase titration these have no influence on the titration. The same applies for cellulose derivates or similar substances in the formulations. In a titration in an aqueous medium the quaternary ammonium compounds could be attached substantively to these water-insoluble substances. This would mean longer titration times because the quaternary ammonium compounds would only be released slowly from the cellulose during the titration. In a two-phase titration with the Surfactrode Resistant the cellulose does not represent a limiting factor. The same also applies to nonionic silicone or siloxane compounds in such formulations.

It must again be pointed out here that cationic polymers, e.g. those based on cellulose such as Polyquaternium 10, are not determined in the titration. As these have no surfactant properties they do not interfere in the determination of the QACs in these hair care products.

Our application department prepared some typical formulations for us. In all cases we were able to determine the quaternary ammonium compounds content correctly. The same applies to numerous market products for which we compared our results with those of some of the manufacturers.

**Table 52 Typical formulations of some hair cures from the European, North American and Asian/Pacific markets (in %)**

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dicethyldimonium chloride</td>
<td></td>
<td>3</td>
<td>6</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>DI-C 12-15 alkyl dimonium chloride</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steartrimonium chloride</td>
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<td>9</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxyl propyl guar hydroxypropyltrimonium chloride</td>
<td>8</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ditallowdimonium chloride</td>
<td>3</td>
<td>3</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Behentrimonium chloride</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetearyl alcohol</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cetyl alcohol</td>
<td>2</td>
<td>2</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearyl alcohol</td>
<td></td>
<td>5</td>
<td>4</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetostearyl alcohol</td>
<td>1</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coco-caprylate/caprate</td>
<td></td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Dioctyldecyl lauryl glutamate</td>
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<tr>
<td>Ethoxydiglycol</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyceril stearate</td>
<td>3</td>
<td>11</td>
<td>10</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxyethylcellulose</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl myristate</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isostearyl glyceril pentaerythryl ether</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isostearyl pentaerythyl glycylether</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearamidopropyl dimethylamine</td>
<td>4</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Panthenol</td>
<td></td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Table 52 Typical formulations of some hair cures from the European, North American and Asian/Pacific markets (continued)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steareth-5 stearate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclomethicone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td>1</td>
<td></td>
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</tr>
<tr>
<td>Dimethicone</td>
<td></td>
<td></td>
<td>6</td>
<td>4</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polywax</td>
<td></td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paraffin wax</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Octyl methoxycinnamate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Formulation ingredients that are not relevant for surfactant titration and are normally only present at low concentrations, e.g. preservatives, colourants or herbal extracts, have been omitted from the CTFA or INCI declaration. The sequence of the other ingredients has been left so that it corresponds to the original declaration.

The potentiometric two-phase titration for the determination of the cationic surfactants using the Metrohm Surfactrode Resistant could be carried out on all the formulations listed above as well as on a large number of other formulations. Modification of the standard method was not required for any of the given formulations. The titrations can be carried out at pH = 3 or also at pH = 10. If the titration is carried out at pH = 10 then only the amount of intact quaternary ammonium compounds will be determined. In contrast, titration at pH = 3 additionally determines the non-quaternised starter amine or ammonium compounds that have already been dequaternised. This means that in the context of a stability investigation it may make sense to carry out titrations at both pH = 10 and pH = 3.

The titrations are carried out as described in section 18.2.4; dodecylsulphate sodium salt c = 0.02 mol/L is used as titrant. Relative standard deviations of 0.35 to 0.58% can be achieved.

9.2.3 Styling products

Many styling products, whether gels, waxes, foams or others contain quaternary ammonium compounds.

Ingredients:
- Sorbitol
- Liquid paraffin
- Oleth-5, oleth-3, phosphate
- Butylene glycol
- Panthenol
- Glycerin
- Tetrahydroxypropyl ethylenediamine
- Ceteareth-20
- Octyl methoxycinnamate
- Cetrimonium chloride

In the above formulation the small quaternary ammonium compound content could be determined by potentiometric two-phase titration. The titration was carried out using standard parameters and with dodecylsulphate sodium salt c = 0.004 mol/L as the titrant. However, a determination is not possible in every case; if the quaternary ammonium compound content in the formulation is below 0.5% then determination by potentiometric two-phase titration is rarely possible.

9.2.4 Hair colours

**Formulation 1**

Ingredients: water, cetearyl alcohol, stearamide MEA, cocamide MEA, sodium cetearyl sulphate, oleic acid, hops extract, horse chestnut extract, hydrolysed wheat protein, propylene glycol, PEG-5 cocamide, sodium lauryl sulphate, hydroxyethylcellulose, sodium sulphite, ammonium chloride, tetrasodium EDTA, ascorbic acid, toluene-2,5-diamine, 2,5,6-triamino-4-pyrimidinol sulphate, resorcinol, M-aminophenol, picramic acid, P-aminophenol, 4-amino-2-hydroxytoluene, HC yellow no. 5, manganese oxide, fragrance

**Formulation 2**

Ingredients: water, cetearyl alcohol, isobutane, propane, stearamide MEA, cocamide MEA, sodium cetearyl sulphate, oleic acid, sodium hydroxide, PEG-5 cocamide, sodium lauryl sulphate, hydroxyethylcellulose, butane, sodium sulphite, ammonium chloride, tetrasodium EDTA, perfume, ascorbic acid, hydrolysed wheat protein, manganese oxide, Humulus lupulus, Aesculus hippocastanum, potassium iodide, toluene-2,5-diamine sulphate, resorcinol, m-aminophenol, sodium picramate, 4-amino-2-hydroxytoluene, 2,5,6-triamino-4-pyrimidinol sulphate, HC yellow No. 5

**Formulation 3**

Ingredients: water, cetearyl alcohol, isobutane, propane, stearamide MEA, cocamide MEA, sodium cetearyl sulphate, oleic acid, sodium hydroxide, PEG-5 cocamide, sodium lauryl sulphate, hydroxyethylcellulose, butane, sodium sulphite, ammonium chloride, tetrasodium EDTA, perfume, ascorbic acid, hydrolysed wheat protein, manganese oxide, Humulus lupulus, Aesculus hippocastanum, potassium iodide, toluene-2,5-diamine sulphate, resorcinol, 2-amino-3-hydroxypyridine, 2,5,6-triamino-4-pyrimidinol sulphate, 4-amino-M-cresol, HC red No. 3, HC yellow No. 5
Potentiometric two-phase titrations

In the above-mentioned and some other hair colour formulations the anionic surfactant content could be determined. The titrations are carried out as described in section 18.2.2. The relative standard deviations were between 0.45 and 0.6%.

A further hair colour preparation with the following declared composition

- Cetearyl alcohol
- Stearamide MEA
- Cocamide MEA
- Sodium cetearyl sulphate
- Oleic acid, sodium hydrosolate
- Ammonium chloride
- Tetrasodium EDTA

only produced very poor titration curves on potentiometric two-phase titration. Attempts to titrate this formulation in an aqueous medium with the Ionic Surfactant Electrode were very positive and resulted in titration curves that could be evaluated easily.

The achievable relative standard deviation is 0.9%.

9.2.5 Hydrogen peroxide solutions

A hydrogen peroxide solution is used in combination with hair colours for bleaching the hair.

**Ingredients:**

- Water
- Phosphoric acid
- Sodium lauryl sulphate
- Salicylic acid
- Dimethicone

The hydrogen peroxide content in such a solution is typically 6%. In contrast, the content of anionic surfactants, e.g. sodium lauryl sulphate, is very low. This means that, depending on the manufacturer, a hydrogen peroxide sample weight of between 5 and 10 g is required. This means that 300 to 500 mg H$_2$O$_2$ are introduced into the titration solution. Despite this high amount of active oxidant a potentiometric two-phase titration for the determination of the ionic surfactant content indicated by the Surfactrode Resistant can be carried out successfully.

The titration is performed applying the standard conditions described in section 18.2.1, with 0.004 mol/L TEGO trant A100 as the titrant. The determination is carried out at pH = 3. In this titration relative standard deviations of approx. 0.4% can be achieved.

9.2.6 Developer solution

**Ingredients:**

- Water

In this solution the anionic surfactants content can also be determined by potentiometric two-phase titration using the Metrosensor Surfactrode Resistant.

The titration is carried out under standard conditions as described in section 18.2.1, with 0.004 mol/L TEGO trant A100 as the titrant. The determination is carried out at pH = 3. In this titration relative standard deviations of approx. 0.7% can be achieved.
9.3 Rinse-off formulations for baby care

Formulations for cleansing baby skin such as baby bath oil, baby bath, baby washing lotions or baby shampoos differ significantly from formulations intended for the skin of adults. This applies particularly when these formulations are examined from the viewpoint of a surfactant analyst. Cleansing products are formulated so that low-irritant basic surfactants are used to obtain final products that are as irritant-free as possible. Whereas standard shower gels, shampoos, etc. contain sodium laureth sulphate as the standard surfactant, in cleansing formulations for baby skin betains or amphoglycinates take over the role of the basic surfactant. Because of their good skin compatibility the nonionic surfactant content is also higher than normal. Ethoxylated glycerol partial esters such as POE 20 glycerinmono-di-laurate, ethoxylated sorbitan fatty acid esters such as POE 80 sorbitan laurate or even APG or sucroseoctoates are used. The anionic surfactants to be analysed such as sodium laureth sulphosuccinate or sodium laureth sulphate are only found in the middle of the INCI or CTFA declaration. There are also some formulations on the market that contain no anionic surfactants at all.

Table 53 Formulations of some baby bath products

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<td>Sodium lauryl sulphate</td>
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<td></td>
</tr>
<tr>
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</tr>
<tr>
<td>MIPA C 12-15 pareth sulphate</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Cocamidopropyl betain</td>
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<td>6</td>
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<td>Disodium lauroamphodiacetate</td>
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<td>X</td>
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</tr>
<tr>
<td>Lauroamphoglycinat</td>
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<td></td>
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</tr>
<tr>
<td>Lauroamphocarboxyglycinat</td>
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<td></td>
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<tr>
<td>Glycol distearate</td>
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<td></td>
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<td>Glycol stearat</td>
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<td>X</td>
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<td>Linoleamide DEA</td>
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<td></td>
<td></td>
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<tr>
<td>PEG-15 glycerol isostearate</td>
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<tr>
<td>PEG-150 distearate</td>
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<tr>
<td>PEG-200 glycerol tallowate</td>
<td>X</td>
<td>X</td>
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<td></td>
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<td>PEG-7 glycerol cocoate</td>
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<td>PEG-80 sorbitan laurate</td>
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<td>Polysquaternium-10</td>
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<tr>
<td>Polysorbate 20</td>
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<tr>
<td>Sodium laureth-13 carboxylate</td>
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<td></td>
</tr>
<tr>
<td>Sodium trideceth sulphate</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Sorbitol</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td></td>
<td></td>
<td></td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

Titrations in aqueous media

The relatively low anionic surfactants content in the formulations combined with a high content of betains and highly ethoxylated fatty acid partial esters means that there seems to be little chance of carrying out a titrimetric determination of the anionic surfactants in an aqueous medium. In our laboratory we only obtained an evaluable titration curve on very rare occasions.

Potentiometric two-phase titrations

As a result of the completely different detection method, the determination of the anionic surfactant content can be carried out with the Metrosensor Surfactrode Resistant. Titration in the two-phase medium usually produces titration curves that are easy to evaluate.

The relative standard deviations were about 1%, but somewhat higher if the anionic surfactant content was very low. Apart from the high proportion of nonionic surfactants and sugar surfactants, cleansing products for baby skin often contain amphoteric surfactants, the so-called amphoacetates. These amphoacetates such as cocoamphoacetate or lauroamphoacetate, amphodiacetates such as cocoamphodiacetate or lauroamphodiacetate, can even be used as the primary surfactant or in combinations with cocamidopropyl betain. If the anionic surfactant to be titrated only appears in fifth position in the INCI declaration or even lower, then the potentiometric two-phase titration also reaches its limits.
In many formulations for cleansing baby skin which contain amphoacetates and amphodiacetates better titration curves are obtained when the titration is carried out at pH = 5. This technique can only be used if disodium laureth sulphosuccinate is not also present as a further ingredient in the formulation.

If both amphoacetates and disodium laureth sulphosuccinate are present then the potentiometric two-phase titration method for the determination of the anionic surfactants content should not be used.

As for all potentiometric surfactant titrations, even those with the Surfactrode Resistant, the sample weight should be selected so that a minimum titrant consumption of 10 mL is obtained. This is the only way to obtain correct results.

### 9.4 Oral hygiene

#### 9.4.1 Toothpaste

**9.4.1.1 Toothpastes with anionic surfactants**

Toothpastes can contain the following surfactants:

- Cocamidopropyl betain
- Alkylpolyglucoside
- Anionic surfactants such as sodium lauryl sulphate

Of this group the only two anionic surfactants that can be detected and therefore determined by the Ionic Surfactant Electrode are sodium lauryl sulphate and amine fluoride.

Because of their soap-like structure lauroyl sarcosinates cause similar problems to those encountered in the titration of soaps. On the North American market in particular sarcosinates are used as well as dodecyl sulphate as a co-surfactant in toothpastes. The low amount of lauroyl sarcosinate in toothpaste samples cannot be determined by a potentiometric surfactant titration, neither in an aqueous medium nor in potentiometric two-phase titration.

Toothpastes also contain various abrasive materials based on different sources.

For our investigations into the group of products containing anionic surfactants the three following representative formulations were used.

**Formulation A**

- Sorbitol
- Glycerin
- Potassium nitrate
- Carbowax 400
- Sylodent 15
- Sylodent 704
- Flavour
- Methylparaben
- Sodium saccharin
- Sodium lauryl sulphate
- Titanium dioxide
- Sodium fluoride
- Carboxymethylcellulose
- Flavour
- Methylparaben
- Sodium saccharin

**Formulation B**

- Calcium pyrophosphate
- Sorbitol
- Zinc chloride
- Flavour
- Methylparaben
- Sodium saccharin
- Sodium lauryl sulphate
- Stannous fluoride
- Hydrated silica
- Sorbitol
- Glycerin
- Cellulose gum

**Formulation C**

- Sodium lauryl sulphate
- Sodium monofluorophosphate
- Titanium dioxide
- Flavour
- Methylparaben
- Sodium saccharin

A uniform analytical method can be used for formulations A, B and C. The sodium lauryl sulphate content can be determined easily. If a known amount of sodium lauryl sulphate is added to these samples then the added amount is determined quantitatively in all three formulations. Just as with all titrations involving sodium lauryl sulphate, care should be taken that the toothpaste sample weight is selected so that the consumption of 0.004 mol/L TEGO trantr A100 solution is more than 10 mL. Problems caused by the water-insoluble abrasives do not occur during the titration. The methanol content in the titration solution should be increased to 15% from the normal 5%, as this reduces the substantivity to the abrasives and the reaction with the TEGO trantr A100 titrant can take place more rapidly.
9.4.1.2 Toothpastes with amine fluorides

Table 54 Typical formulations for toothpastes on the Asian/Pacific and North American markets (in %)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<td>5</td>
<td>13</td>
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<tr>
<td>Sodium lauroyl sarcosinate</td>
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<td></td>
<td>5</td>
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<tr>
<td>Cocoyl taurate</td>
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<td></td>
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<td>Xanthan gum</td>
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<tr>
<td>Flavour</td>
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<td>13</td>
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<td>8</td>
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<td>Glycerine</td>
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<td>Carrageenan</td>
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<tr>
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<td>Sodium fluoride</td>
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<tr>
<td>Titanium dioxide</td>
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<tr>
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<td>Guar gum</td>
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<tr>
<td>Cellulose gum</td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

Formulation ingredients that are not relevant for surfactant titration and are normally only present at low concentrations, e.g. preservatives, colourants or herbal extracts, have been omitted from the CTFA or INCI declaration. The sequence of the other ingredients has been left so that it corresponds to the original declaration.

Toothpaste formulations from the Asian/Pacific region differ only slightly from those on the European and North American markets. They can be titrated in the same way. This applies at least to the sodium lauryl sulphate contained in most formulations. Formulation 4 contains the anionic surfactant cocoyl taurate. The quantitative determination of cocoyl taurate in this formulation by potentiometric titration is not possible.

9.4.2 Mouth rinses

This group of products also contains various subgroups containing different surfactant ingredients.

1. Gargling solutions with antibacterial substances, mostly benzalkonium chloride.
2. Plaque prophylaxis solutions containing cetlypyridinium chloride
3. Tooth rinsing solutions against plaque, often with sodium laureth sulphate
4. Mouth rinses based on amine fluorides.

9.4.2.1 Gargling solutions with antibacterial substances

Apart from quaternary benzalkonium chloride (alkyl-dimethylbenzylammonium chloride) and flavour correctives, gargling solutions often only contain water or some alcohol. They are usually marketed as concentrates with approx. 5% active substance content. These gargling solutions can be titrated with the Ionic Surfactant Electrode. 0.004 mol/L solutions such as dodecylsulphate sodium salt or dioctylsulphosuccinate sodium salt (DOS = bis-2-ethylhexylsulphosuccinate) are suitable as titrants. The sample weight of the gargling solution should be selected so that a titrant consumption of between 12 and 18 mL can be expected.
9.4.2.2 Mouth rinsing solutions for plaque prophylaxis

The typical composition of a mouth rinsing solution for plaque prophylaxis could be as follows.

- Glycerin
- Alcohol
- Cetylpyridinium chloride
- Sodium fluoride
- Flavours

In this formulation cetylpyridinium chloride is the active and surfactant-like component. In this case the determination is also free from problems; nothing else could be expected as cetylpyridinium chloride can even be used as the titrant for the determination of anionic surfactants. No influence on the titration is to be expected from the other ingredients. For model formulations prepared in our laboratory the potentiometric titration with the Ionic Surfactant Electrode produced correct results with a relative standard deviation of 0.8%.

9.4.2.3 Tooth rinsing solutions against plaque

Tooth rinsing solutions against plaque normally contain anionic surfactants in combination with other active and auxiliary ingredients to achieve a pretreatment or preliminary cleaning of the teeth before the teeth cleaning process itself.

A typical tooth rinsing solution against plaque could, for example, have the following ingredients:

- Sodium laureth sulphate
- Polysorbate-20
- Sodium salicylate
- Citric acid
- Sodium saccharin
- Colourants
- Ethanol 2 to 10%
- Sodium fluoride or tin fluoride

The sodium laureth sulphate content is between 0.1 and 0.5%, depending on the formulation. As a nonionic surfactant based on the POE adducts of a sorbitan fatty acid ester, Polysorbate-20 has, like all nonionic surfactants, a negative influence on the surfactant titration but in the mixture ratios found here this influence is not significant. The titration curves have the typical shape for sodium laureth sulphate and the results are correct provided that the sample weight has been calculated so that a titrant consumption of 10 to 18 mL results. The relative standard deviation of such a determination is less than 1%.

9.4.2.4 Mouth rinses based on amine fluorides

Mouth rinses based on amine fluorides are often used for fluorinating the teeth in between teeth cleaning processes. One of the most often used amine fluorides is N’-octadecyltrimethylenediamine-N,N,N’-tris-(2-ethanol)-dihydrogen fluoride, see also Fig. 175. Because of the hydrophobic octadeyl group this substance has marked surfactant properties. On the other hand, the three hydroxyethyl groups have a negative influence on the titration. Nevertheless a titration can be carried out on the above-mentioned formulation.

A typical mouth rinse based on amine fluorides could, for example, have the following ingredients:

- N’-octadecyltrimethylenediamine-N,N,N’-tris-(2-ethanol)-dihydrogen fluoride
- Ethanol 2 to 10%
- Sodium fluoride or tin fluoride

The relative standard deviation of a sixfold determination was 1.6%. The derivative curve of the titration curve had a broad peak. This is linked to the relatively polar hydroxyethyl groups. The other components of the above-mentioned formulation do not interfere. Although the formulation already contains alcohol, the normal 5% methanol should still be added to the titration solution. The titration is carried out at pH = 3.
9.5 Miscellaneous

9.5.1 Soap-based shaving creams, shaving foams or shaving gels

<table>
<thead>
<tr>
<th>Shaving gel</th>
<th>Shaving foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>• No declaration</td>
<td>• TEA-stearate</td>
</tr>
<tr>
<td></td>
<td>• Laureth-23</td>
</tr>
<tr>
<td></td>
<td>• Stearic acid</td>
</tr>
<tr>
<td></td>
<td>• Sodium laureth sulphate</td>
</tr>
</tbody>
</table>

The potentiometric two-phase titration for determining the soaps in a shaving gel, shaving foam or a shaving cream can be carried out successfully. As in this case only long-chain fatty acids such as stearic acid and similar are used, this good result could be expected.

The titration is carried out under standard conditions (see section 18.2.1) with the Surfactrode Resistant. The determination is carried out at the usual pH value of 10 for soap titrations with 0.004 mol/L TEGO trant A100 solution as titrant. The titration curves can easily be evaluated and relative standard deviations of approx. 0.6% can be obtained from the potentiometric two-phase titration.

In formulations such as shaving foam that, apart from soaps, also contain anionic surfactants such as fatty alcohol sulphates or fatty alcohol ether sulphates, titration at pH = 10 determines the sum of classical anionic surfactants and soaps. In this case it makes sense to carry out a second potentiometric two-phase titration at pH = 3. This second titration should be carried out under comparable conditions with only the pH being altered. It is absolutely necessary that the pH adjustment for titration at pH = 3 is made with a dilute solution of hydrochloric or sulphuric acid.
10 Surfactants in pharmaceuticals and related products

10.1 Benzalkonium chloride in gargling solutions

Benzalkonium-based gargling solutions are usually concentrates with a benzalkonium content between 3 and 5%. The ready-to-use mouth-rinsing solutions are prepared by diluting these solutions with water. As already described in section 7.5.3, benzalkonium chlorides can be easily titrated. In the concentrates that we investigated, all of which were only available on prescription, no other ingredients were declared. It must therefore be assumed that the products contain a large amount of water, possibly with the addition of higher alcohols such as 1,2- or 1,3-propylene glycol. These alcohols are not expected to cause any interference. It is only necessary to weigh out part of the sample directly into the titration beaker. Then 10 mL methanol, 10 mL buffer solution pH = 10 and 75 mL water are added and the solution is titrated against 0.004 mol/L dodecyl sulphate sodium salt solution. The mean molar mass of the benzalkonium chloride used must be known for the calculation. As an approximation 350 g/mol can be used. In this case the sample weight should be selected so that a consumption of 10 mL 0.004 mol/L dodecyl sulphate sodium salt solution is achieved.

10.2 Cetylpyridinium chloride in gargling solutions

Mouth-rinsing and pharyngal therapeutic solutions containing cetylpyridinium chloride as the active substance are available on the market from different manufacturers. Some formulations contain only cetylpyridinium chloride as the active substance, usually in a concentration of 50 mg cetylpyridinium chloride x H$_2$O in 100 mL solution, while other formulations additionally contain a local anaesthetic, e.g. benzocaine or lidocaine, in concentrations of 100 to 500 mg/100 mL solution. Other ingredients in such solutions could be:

- Sodium chloride EDTA
- Methyl salicylate
- Peppermint oil
- Menthol
- Ethanol
- Benzyl alcohol
- Colourants

The volume concentration of ethanol in these solutions lies between 10 and 20%.

None of the secondary ingredients mentioned above, including benzocaine or lidocaine, interferes with the potentiometric determination of cetylpyridinium chloride, i.e. the active substance, which can be easily titrated potentiometrically. Cetylpyridinium chloride is also used as a titrant for the determination of anionic surfactants.

For the determination 40 mL gargling solution are placed in a titration beaker and a further 10 mL methanol are added. After the addition of 40 mL water and 10 mL pH = 3 buffer solution the titration is carried out against dodecyl sulphate sodium salt solution as described in section 18.1.2.

The calculation is carried out using the molar mass of the cetylpyridinium chloride x H$_2$O, i.e. 358.01 g/mol (see also section 9.4.2.2.).

10.3 Benzalkonium chloride in lozenges

Many of the lozenges that are used for infections of the oral cavity or the throat contain the quaternary ammonium compound benzalkonium chloride as the antibacterial ingredient. The declared concentration of benzalkonium chloride ranges from 1 up to 2.5 mg per tablet. The tablet weight varies between 500 and 1000 mg. Other declared tablet ingredients, for example, could be:

- Benzocaine = ethyl-4-aminobenzoate
- Talcum
- Calcium stearate
- Starch
- Sodium cyclamate
- Aspartame
- Sodium saccharin
- Sugar substitutes such as maltose or sorbite
- Gelatin
- Dimethicone
- Poly(1-vinyl-2-pyrrolidone)
- Sodium carboxymethylcellulose
- Stearic acid triglyceride

All the auxiliary substances listed above have been investigated separately. Most of them show no interference at all. They do not react with the titrant, nor do they cause any low-bias or high-bias results. Only with magnesium stearate is caution necessary. Magnesium stearate is regarded as being water-insoluble; however, there is a potential possibility that fatty acids, e.g. when buffered to approx. pH = 10, could form soluble soaps that could then neutralise part of the benzalkonium chloride in the lozenge itself by the formation of an ion associate. This would inevitably lead to too little benzalkonium chloride being found in the lozenge. This is the reason why a titration of the quaternary ammonium compounds in a mixture containing magnesium stearate should only be carried out under acidic conditions. In this special case it is advantageous if the pH adjustment for the titration is not carried out in the normal manner by adding a buffer solution but by adding dilute hydrochloric acid to adjust the pH value to 2 ... 3. With an active substance content of only 1 mg benzalkonium chloride in one gram of tablet the potentiometric surfactant ti...
Titration is not free from problems as a result of the extremely low content. If only one of these lozenges is used then only 1 mg benzalkonium chloride is available; this corresponds to a consumption of 0.7 mL 0.004 mol/L dodecyl sulphate sodium salt solution.

As can be seen from Figs. 176 and 177, the error-free determination of a benzalkonium concentration of only 1 mg is not possible with either titrant. Bis-2-ethylhexylsulphosuccinate is clearly the more suitable titrant and should therefore be used for the determination. It makes more sense when this titration is not evaluated stoichiometrically as usual, but titrated against a self-made standard. In this case a stock solution with a known concentration of benzalkonium chloride is prepared, preferably in a methanolic solution or a methanol/water mixture. Then an aliquot of this solution is taken which exactly corresponds to 1.0 mg benzalkonium chloride. Methanol is added to this standard and it is then adjusted to a pH value between 2 and 3 with dilute hydrochloric acid. The titration is then carried out against bis-2-ethylhexylsulphosuccinate solution.

The tablets to be analysed are placed in the titration beaker in their normal state. Approx. 20 mL water are added and the mixture is allowed to stand for approx. 15 minutes at room temperature. In this time the carboxymethylcellulose swells up and the tablets break down. In order to complete this process the beakers are then placed, for a further 15 minutes, on a hotplate which is at 100 °C. The titration beaker should be gently swirled about from time to time. Then 10 mL methanol and 65 mL water are added and adjusted to a pH value between 2 and 3 with dilute hydrochloric acid. The titration is now carried out against bis-2-ethylhexylsulphosuccinate solution. Care must be taken that a low titration speed is selected because the expected titrant consumption is below 1 mL and the sample also contains several insoluble compounds such as talcum and magnesium stearate. It is to be expected that the benzalkonium chloride to be analysed will be substantively attracted to these particles. With a slow titration under the given conditions the complete benzalkonium chloride in the sample solution can be titrated. See also the titration curves in Fig. 178, obtained during an investigation of the linearity.

The calculation of the benzalkonium chloride content in the throat tablets is carried out against the previously titrated standard of 1 mg benzalkonium chloride according to the rule of three. With this method a standard deviation of approx. 2% can be achieved (n = 10).

10.4 Benzalkonium chloride in eye drops and nose drops

Many nose drops or nasal sprays contain the anti-swelling agent xylometazolin hydrochloride in a concentration of 1 mg/mL in a buffered aqueous solution based on citric acid and sodium citrate. Apart from glycerol or other polyvalent alcohols these preparations contain benzalkonium chloride as a preservative, usually at a concentration of 0.2 mg/mL. The normal pack size for this type of medicine is 10 mL.

The determination of the preservative benzalkonium chloride in this formulation is quite possible. The active ingredient or the other chemicals used as auxiliaries do not interfere. The only problem is the somewhat low concentration in the solution. This is why the whole contents of a bottle, i.e. 10 mL, should be used for a single titration. This then contains 2 mg benzalkonium chloride, which corresponds to a titrant consumption of approx. 1.5 mL (see also Fig. 179).

Bis-2-ethylhexyl sulphosuccinate should again be used as the titrant; the titration can again be carried out as described in section 18.1.2. There are two possibilities for calculating the benzalkonium chloride content:

1. From the stoichiometric reaction using the mean molar mass of the benzalkonium chloride. It should be remembered that, at a titrant consumption of approx. 1.5 mL, we are not quite in the linear range of the titration. However, the possible errors which may arise from this are very small.

2. A titration can again be carried out against a standard, similar to the method used for benzalkonium chloride in lozenges. An aliquot containing exactly 2.0 mg benzalkonium chloride is taken from a specially prepared methanolic benzalkonium chloride solution. The calculation, based on the rule of three, is carried out using the consumption for the sample solution and the consumption for the 2 mg standard benzalkonium chloride.

The method described here is similar to that used for the determination of benzalkonium chloride in eye drops.
10.5 Surface disinfectants

Surface disinfectants may be declared according to the EU recommendations; however, there are those which are approved according to the laws relating to the manufacture and distribution of pharmaceuticals and which therefore have a more detailed declaration. Surface disinfectants are usually concentrates that are used at a dilution of between 1 : 100 and 1 : 500. These surface disinfectants are used to wash down corridors and operating theatres in hospitals. They are also used to maintain operational hygiene in food processing companies or large kitchens, where surfaces or floors also have to be cleaned and disinfected in a single working process.

Accordingly, surface disinfectants usually contain a combination of aldehydes, quaternary ammonium compounds and nonionic surfactants. The main aldehyde components used are formaldehyde, glutaraldehyde or glyoxal. The commonest quaternary ammonium compound is benzenesulphonium chloride, followed by alkyl(dimethyl) ammonium chloride, or even a dialkyl(dimethyl) ammonium chloride, usually dodecyl(dimethyl) ammonium chloride. The nonionic surfactants contained in the formulations are there to provide better surface wetting properties and have a surface-cleaning effect at the same time. While in early days alkylphenolethoxylates were used for this purpose, for a long time now these have been replaced by fatty alcohol ethoxylates or other products with a better degradability. The aldehydes content normally amounts to between 5 and 12.5%, the quaternary ammonium compounds content lies between 3 and 6%. It is the quaternary ammonium compounds which can be analysed by potentiometric surfactant titration. With the relatively high quaternary ammonium compounds content and the ease with which the ammonium compounds used can be titrated there are no problems in carrying out the titration. The aldehydes have no influence on the titration and the nonionic surfactants are present at a concentration that does not exert any large interfering influence. Although a slight widening of the volume scale in the region of the end point can be noticed this does not affect the evaluation by the titrators. It is best to titrate with dodecyl sulphate sodium salt at pH = 10.

Surface disinfectants that are based on amphoteric surfactants can also be found on the market. These disinfectants cannot be determined by this method.

10.6 Hand disinfectants

Hand disinfectants are used after normal hand cleaning with soap and water in order to reduce the number of microorganisms on the skin. As disinfecting agents hand disinfectants contain alcohols such as ethanol or 2-propanol at concentrations of between 50 and 70% as well as quaternary ammonium compounds or disinfectants based on amphoteric surfactants as the microbicidal active substance. Further ingredients could be benzyl alcohol or propanediol.

The microbicidal substance content normally lies in the range from 100 to 200 mg/100 mL solution. With the titration method described here only the quaternary ammonium compounds can be determined but not the amphoteric surfactants. The relatively high content of alcohols such as ethanol or 2-propanol has no interfering influence on the titration. Depending on the expected quaternary ammonium content 10 to 25 g sample are weighed out into a titration beaker. The sample weight should be calculated so that a titrant consumption of approx. 10 to 15 mL is to be expected. Following the addition of approximately 50 to 75 mL water, 10 mL buffer solution pH = 10 are added and the titration is carried out. The titration curves can still be evaluated easily; as is to be expected, the titration curves can still be evaluated easily; they are nevertheless flatter in the endpoint region than is the case with other cationic substances.

10.7 Amine fluoride in toothpaste

A toothpaste containing amine fluoride could have the following composition:
- Octadecyltrimethylenediamine-N,N,N’-tris-(2-ethanol)-dihydrogenfluoride
- Sorbitol
- Hydroxyethylcellulose
- Silica
- Titanium dioxide

The chemical structure of amine fluoride shown in Fig. 180 allows the recognition of several special features which are important for the surfactant analyst who has to titrate this class of substances. Apart from hydrophilic groups which provide the surfactant properties of the molecule, there are three further ethanol groups in the molecule, each with a terminally placed primary OH group, which give the molecule an additional strong hydrophilicity. This is to some extent held in check by the fact that the octadecyl group causes the oleophilic properties to be strongly developed and in this way the negative properties of the three ethanol groups in the molecule are partly compensated. As is to be expected, the titration curves can still be evaluated easily; they are nevertheless flatter in the endpoint region than is the case with other cationic substances.

The amine fluoride content can be determined according to the same procedure as given for the determination of anionics in toothpaste, see section 9.4.1. However, the titrant must be replaced. For the titration of amine fluorides 0.004 mol/L dodecyl sulphate sodium solution has proved itself in practice. The relative standard deviation that can be achieved for the determination of amine fluorides in toothpaste is 2.8% (n = 10).
10.8 Amine fluorides in prophylactic gels

These products are used once per week after the teeth have been cleaned for intensive fluoridation of the teeth. Their fluoride content is correspondingly high and therefore also the surfactant content of such products. They contain one or more amine fluorides as the surfactant compound.

A typical formulation could appear as follows.
- N’-octadecyltrimethyleneamine-N,N,N’-tris-(2-ethanol)-dihydrogenfluoride
- 9-octadecenylamine-hydrofluoride
- Sodium fluoride
- Gel base

In this case the potentiometric titration is possible if the general information given about amine fluorides in the previous section is taken into consideration. The gel base also presents no problems, as can be seen from Fig. 181.

Amine-fluoride-based prophylactic gel against caries

- Sample weight: 100 to 500 mg
- Buffer: 10 mL pH = 3
- Methanol: 5 mL
- Preparation: none
- Titrant: 0.004 mol/L dodecylsulphate sodium salt solution
- Min. consumption: 10 mL

Parameter setting: method for flat titration curves

Fig. 181: Titration of an amine-fluoride-based toothpaste

10.9 Tooth and mouth washes

Tooth washes based on amine fluoride are often used for fluorinating the teeth between teeth cleaning sessions. One of the often-used amine fluorides is N’-octadecyltrimethyleneamine-N, N, N’-tris-(2-ethanol)-dihydrogenfluoride, see Fig. 175. The hydrophobic octadecyl group gives it marked surfactant properties. In contrast, the three hydroxyethyl groups have a negative effect on the ability to carry out the titration. However, a titration of the above formulation is still possible.

A typical formulation could appear as follows:
- Octadecyltrimethyleneamine-N, N, N’-tris-(2-ethanol)-dihydrogenfluoride
- Ethanol 2 to 10%
- Sodium fluoride or tin fluoride

The relative standard deviation on a sixfold determination was 1.6%. The derivative curve of the titration curve shows a wide transition interval around the point of inflection. This is caused by the relatively polar hydroxyethyl groups. The other ingredients in the above-mentioned formulation do not interfere. Although the formulation already contains alcohol, the usual 5% methanol should still be added to the titration solution. The titration is carried out at pH = 3.
11 Cooling lubricants

11.1 General

According to their definition, cooling lubricants are mixtures that are used for cooling and lubricating the workpieces and tools when metals are being machined or formed.

In the previous century vegetable oils and animal fats were already being used as cooling lubricants in industry. In recent times only synthetic substances have been used as cooling lubricants, as in this way special properties can be achieved. The cooling lubricant consumption in Germany is enormous. In 1994* no less than 28'416 t water-miscible and an additional 47'076 t of water-immiscible cooling lubricants were produced and used.

Terms such as drilling emulsion, drilling milk, coolant, grinding water, grinding oil or reaming oil are still often used today by operators. The classification and identification of cooling lubricants is regulated today in Germany by DIN 51 385 No.1, see Table 55.

Table 55 Cooling lubricant designation and classification

<table>
<thead>
<tr>
<th>No.</th>
<th>Designation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Cooling lubricant</td>
<td>Substance used for cooling and lubrication in machining and sometimes in the forming of workpieces.</td>
</tr>
<tr>
<td>1</td>
<td>Water-immiscible cooling lubricant</td>
<td>Cooling lubricant that is not mixed with water during use.</td>
</tr>
<tr>
<td>2</td>
<td>Water-miscible cooling lubricant</td>
<td>Cooling lubricants that is mixed with water before use.</td>
</tr>
<tr>
<td>2.1</td>
<td>Emulsifiable cooling lubricant</td>
<td>Water-miscible cooling lubricant that can form the discontinuous phase of an oil-in-water emulsion.</td>
</tr>
<tr>
<td>2.2</td>
<td>Emulsifying cooling lubricant</td>
<td>Water-miscible cooling lubricant that can form the continuous phase of a water-in-oil emulsion.</td>
</tr>
<tr>
<td>2.3</td>
<td>Water-soluble cooling lubricant</td>
<td>Cooling lubricant that gives mixed solutions with water. Apart from real solutions, these also include solutions of the associate colloids, e.g. «soap solutions».</td>
</tr>
<tr>
<td>3</td>
<td>Water-mixed cooling lubricant</td>
<td>Cooling lubricant mixed with water (water-miscible cooling lubricant in the state of use).</td>
</tr>
<tr>
<td>3.1</td>
<td>Cooling lubricant emulsion</td>
<td>Emulsifiable cooling lubricant mixed with water (ready-to-use mixture).</td>
</tr>
<tr>
<td>3.2</td>
<td>Cooling lubricant emulsion</td>
<td>Emulsifying cooling lubricant mixed with water (ready-to-use mixture).</td>
</tr>
<tr>
<td>3.3</td>
<td>Cooling lubricant solutions</td>
<td>Water-soluble cooling lubricant mixed with water (ready-to-use mixture).</td>
</tr>
</tbody>
</table>

Since 1\textsuperscript{st} January 1990 the new Law on the Biodegradability of Detergents has been in effect in Germany. It contains minimum requirements regarding the biodegradability of surfactants contained in aqueous cleaning agents, washing agents and detergents.

According to the Council Directive of the EC dated 23\textsuperscript{rd} November 1973, only those detergents that are eliminated from wastewater to 90% within 28 days may be offered for sale.

Water-mixed types of cooling lubricant currently used:

Coarsely dispersed emulsions

Coarsely dispersed emulsions are frequently used in forming work in which tribology is the main concern.

Coarsely dispersed emulsions may have an oil content or rather a lipophilic phase content of up to 85%. The dispersity sometimes goes so far that free oil can be seen on the surface if allowed to stand for some time.

Semi-synthetic or finely dispersed emulsions

This type of emulsion is preferably used in the metal working industry for metal cutting, the principal material being steel.

Synthetic, mineral-oil-free cutting fluids

Synthetic, mineral-oil-free cutting fluids are used for grinding, for light to medium metal cutting and in a few special cases, e.g. as hydraulic liquid, for rolling work, etc.

* Figures from the Federal Office of Economics, Germany (Bundesamt für Wirtschaft, BAW)
Cooling lubricants must meet the following requirements:

- good processing performance
- long working life
- stable pH
- good corrosion protection
- good rinsing and washing activity
- easy to filter
- high cooling performance
- good skin compatibility
- easy disposal

Differences in composition to amine-containing products:

The concentrates based on primary amines which are offered today by many manufacturers are fairly similar in their composition. The most important characteristic is the buffer system which is present in the form of a condensation product and which consists of boric acid, primary alkanolamines (in excess) and usually vegetable or perhaps synthetic fatty acids.

In amine-free products this boron/amine buffer system set to a fixed pH value is completely missing. These concentrates have mainly anionic-based emulsifiers which, for example, may be present in the form of carboxylic acid salts and as salts of organic sulphonates. The non-ionogenic portion of the emulsifier of these products is mostly of the polyglycol ether type.

Analysis

As is clearly shown in this general part, cooling lubricants have fairly complicated compositions and also have to fulfil complicated tasks in the metal-working sector. The surfactants which are to be determined in the different cooling lubricants primarily function as emulsifiers. This is the reason why it is doubtful whether the determination of the emulsifier in a system with such tasks is actually an important criterion for the usability of such a cooling lubricant system. This can only be answered individually from case to case by the analysts.

11.2 Titration in aqueous media

The determination of ionic surfactants in cooling lubricants using, e.g., the Ionic Surfactant Electrode, is not possible in all cases. This technique has so many weaknesses that it cannot be generally recommended. In addition, very contradictory experiences have been made with the Ionic Surfactant Electrode regarding its working life. On the one hand reports of a very short working life have been made; on the other hand periods of use of more than one year have also been reported. Under worst-case conditions it should be expected that the fats and oils to be found in such cooling lubricants will attack the electrode membrane and that the oleophilic constituents of the cooling lubricant are able to dissolve the plasticisers or ion carriers, thus destroying the electrode. As a rule of thumb it can be said that the cooling lubricant concentrates are easy to titrate with the Ionic Surfactant Electrode, but that the dilutions used in practice are more likely to cause problems. If these have already been used for some time then a titration is often no longer possible.

To summarise it can be said that the titration of ionic surfactants in cooling lubricants only then can or should be carried out with an Ionic Surfactant Electrode if, as a result of experimental studies that have previously been carried out, the operator is convinced that this method is suitable for solving the existing analytical problem. Raulf, Buschmann and Sommer have reported about a method in which the oil is first separated off on silica gel with the aid of a solid phase extraction cartridge (SPE) and subsequently eluted with solvents of increasing polarity. The last eluate, methanol : ammonia at a ratio of 8 : 1, then contains the anionic surfactants. These are then titrated with Hyamine 1622 with indication by a surfactant electrode. The authors report a relative standard deviation of 2.4%.

11.3 Potentiometric two-phase titration

As already mentioned in section 4.5, an electrode has been developed that is resistant to organic solvents. This allows anionic surfactants in cooling lubricants to be determined by potentiometric surfactant titration. The titration can be carried out directly in the cooling lubricant solution, which has been weighed in previously and diluted with water or methanol. Even better and more reproducible results are obtained if the potentiometric surfactant titration is carried out in a two-phase medium. Chloroform would be possible as a second phase here; however, because of its toxicity and other problems described elsewhere, it should not be used. Replacement solvents such as methyl isobutyl ketone, hexane or even cyclohexane are extremely suitable for use in this titration as the second, water-immiscible phase. All cooling lubricants that have been made available up to now can be titrated with this technique; this includes both concentrates as well as ready-to-use solutions, whether new or after long periods of use.

Surfactants such as linear alkyl benzene sulphonates or similar are almost always used in the so-called water-soluble cooling lubricants; their titration yields excellent potential jumps. With this technique the titration of anionic surfactants in cooling lubricants is just as simple and easy as the titration of an anionic raw material using the Ionic Surfactant Electrode. A similar amount of time is also required for the titration; with well-optimised titration conditions between 5 and 10 minutes are needed for one titration.

It must again be pointed out here that this special electrode places great demands on the titrator which is used to carry out the titration. The optimisation of the titrator settings, the stirrer speed and other critical factors must be taken into account for this titration. For titrations in two-phase media the stirrer speed must be increased so much that the two immiscible phases form an emulsion. This requires the use of a propeller-type stirrer as this is the only way to obtain
optimal mixing without vortex formation. Relative standard deviations in the range from 0.5 to 1% (n = 10) can be achieved under optimised conditions.

A typical titration curve can be seen in Fig. 182.

### 11.4 Titration with the RI sensor

Cooling lubricants represent the main application of the RI sensor as the indicator system for surfactant titration. Naturally the RI sensor is only suitable for use as the indicator for the determination of ionic surfactants in water-soluble cooling lubricants.

The determination of surfactants in cooling lubricants is carried out according to the following instructions.

#### Chemicals

Hyamine 1622 (Merck)

#### Instrument parameters

<table>
<thead>
<tr>
<th>Titrino</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>titration mode</td>
<td>MET</td>
</tr>
<tr>
<td>V step</td>
<td>0.1 ml</td>
</tr>
<tr>
<td>tr.rate</td>
<td>25 ml/min</td>
</tr>
<tr>
<td>signal drift</td>
<td>100 mV/min</td>
</tr>
<tr>
<td>pause</td>
<td>10 s</td>
</tr>
</tbody>
</table>

#### Procedure

**Determination of the factor**

A 5% fresh water-miscible emulsion is prepared from the concentrate.

10 mL fresh emulsion is placed in a 150 mL beaker (tall form) and diluted to 100 mL with boiled-out distilled water.

The RI sensor is immersed in the centre to the 60 mL mark.

Adjustment is made with the stirrer switched off.

The stirrer is switched on and the titration carried out.

The glass tip is cleaned with methanol after each run.

**Sample**

10 mL sample emulsion is placed in a 150 mL beaker (tall form) and diluted to 100 mL with boiled-out distilled water.

The RI sensor is immersed in the centre to the 60 mL mark.

Adjustment is made with the stirrer switched off.

The stirrer is switched on and the titration carried out.

The glass tip is cleaned with methanol after each run.

**Evaluation**

The peak maximum or the point of inflection of the downward jump is evaluated.

Factor = concentrate content / consumption of Hyamine 1622

cooling lubricant content = consumption x factor

The titration of concentrates can be carried out without any problems, as can be seen from Figs. 183 and 184.

Titration of samples that have already been used as cooling lubricants for some time give very different curves. Jumps cannot be recognised clearly. Some appear to depend on the concentration while other different cooling lubricants with different compositions give differently shaped curves, as can be seen from Figs. 185 and 186.

The determination of anionic surfactants in original cooling lubricants was possible in all the samples analysed.

For cooling lubricant emulsions, i.e. the samples that had already been used for some time, no generally valid statement could be made. The number of samples which produced evaluable titration curves was approx. 50 to 60%. The shapes of the titration curves obtained from cooling lubricants from different manufacturers differ markedly. Sometimes
when the titration curve could not be evaluated an improvement could be obtained by either increasing or decreasing the sample weight. A uniform statement about the applicability of this method cannot be made in this case.

The evaluation is often deceptive and most titrators do not have the appropriate special evaluation algorithm. This means that evaluation can only be carried out by external programs or graphically.

11.5 Titration with the light-guide photometer

As during the determination of ionic surfactants in cooling lubricants the titration is carried out with a oppositely-charged surfactant to the analyte a turbidity occurs when the cooling lubricant concentrate or sample is titrated. This means that the course of the titration can also be monitored with a light-guide photometer, as shown in Figs. 187 and 188. At the start of the titration the sample is not clear but turbid; this is compensated by the electronics of the light-guide photometer.

The very different compositions of the various cooling lubricants and the differing turbidity behaviour make it impossible for all cooling lubricants to be determined with a single method; see Figs. 189 and 190.

The photometrically indicated titration for the determination of ionic surfactants in cooling lubricants also does not cover the whole range of cooling lubricants. The situation is similar to that of the RI sensor. The cooling lubricant concentrates can be titrated better than samples that have been in use for some time. However, the surfactant determination is certainly more interesting in such cases than on an unused concentrate. In some cases it is a great advantage if the...
samples that have already been in use for some time are previously dewatered on a rotary evaporator. However, this means that considerably more time must be spent, time which in many cases is not available.

Photometric turbidity detection can also only be applied if the solution is clear or only slightly turbid at the start of the titration, if it slowly becomes more turbid as the titrant is added and if the maximum turbidity occurs at the equivalence point. This must be newly tested for each cooling lubricant.

The endpoint of a turbidity titration corresponds to the maximum turbidity. Unfortunately, not all current titrators are able to detect this maximum automatically. This again means that the endpoint evaluation can only be carried out with external software or graphically. See also section 4.6.2.

11.6 Comparison between RI sensor, photometer and Ionic Surfactant Electrode

This topic is treated in section 4.9.

It is important to repeat again that the comparison of these different detector types was not carried out on a cooling lubricant, but on an aqueous surfactant solution. A transfer to the cooling lubricant model can only be made with the greatest caution; it may not even be possible as the clear favourite, the Ionic Surfactant Electrode does not possess the chemical stability required for its use as an indicator electrode.

In this case the Metrosensor Surfactrode Resistant can be regarded as being the equal of the Ionic Surfactant Electrode. Comparative measurements have not yet been carried out with it.

At this point the author would like to thank Markus Steinke* for his cooperation on sections 11.4, 11.5 and 11.6.

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* Product Manager with Metrohm Ltd., CH-9101 Herisau, Switzerland
12 Electroplating baths

Up to now the author has received little information concerning surfactant determination in electroplating baths. However, from time to time problems are reported that are caused by the special composition of electroplating baths, i.e. their high salt content and sometimes high sulphuric acid concentration.

In comparison, only small concentrations of surfactants are added to electroplating baths. These additives are to ensure a uniform deposition of the metals on the surface to be electroplated. During the electroplating process the surfactants become depleted. The surfactant concentration must be determined to establish the amount of surfactants to be added.

Surfactant additives in electroplating baths can be of completely different types:

- Nonionic surfactants, e.g. based on ethoxylated o xoalcohols or ethoxylated alkyl phenols
- Polyethylene glycols (PEG) with molar masses from 1000 to 10000
- Fatty amines, fatty amine ethoxylates or alkanolamides
- Anionic surfactants
- All the above-mentioned surfactants can also be partially fluorinated.

The problems arising during surfactant determination have two main causes:

- The surfactant concentration in electroplating baths is very low.
- Electroplating baths have a very high salt content.

It is well known that a very high salt content, including metal salts such as nickel salts or chromium salts which are used in electroplating baths, renders the surfactant titration more difficult.

In most cases the surfactants enter the electroplating baths via so-called wetting agents. Which surfactants this additive contains is very often one of the manufacturer’s well-guarded secrets. This is why in most cases a direct calculation of the surfactant content is not possible; it is also not necessary. A calibration is carried out against the surfactant-containing additive. In this way when a titration has been carried out on the electroplating bath solution it is easy to calculate whether and how much of the additive must be added.

The thio compounds contained in the brightener additives such as thiourea, etc., do not interfere with the titration of either ionic or nonionic surfactants.

12.1 Ionic surfactants

Surfactants are primarily used in electroplating as wetting agents. During the electroplating process these wetting agents become depleted. This is why it is necessary to determine the wetting agent content in the electroplating bath so that these can be added as necessary. This is also why it is not so important to determine the surfactant content to the highest degree of accuracy; in most cases a relative error of approx. 10% is acceptable. The calculation of the surfactant is not normally carried out as the surfactant substance itself but as the wetting agent used in the form in which it is supplied by the manufacturer. This is why calibration titrations are first carried out on the wetting agent used. On this basis it is then possible to make up the wetting agent as required.

As a relatively large error can be accepted in this application it is also possible to work with a lower titrant consumption. If this is also taken into account in the calibration titrations then the resulting error is very small.

The analytical results must be obtained in as short a time as possible.

The determination of ionic surfactants can be carried out according to two different titration methods. Which of the two methods is better must be tried out in practice. To date it has not been possible to work out a specific guideline.

1. Potentiometric titration in an aqueous medium, i.e. directly on the original sample without sample preparation, with the Ionic Surfactant Electrode.

2. Potentiometric titration in a two-phase medium with the Surfactrode Resistant after the extraction of the ionic surfactants.

12.1.1 Titration in aqueous media

Surfactants are salted out by high salt concentrations. Even well below the saturation limit of sodium chloride in water most surfactants are no longer present in a dissolved, dissociated form. They have become insoluble in this concentrated brine; as the name says, they have been salted out. As the surfactant concentration in electroplating baths is usually very small a further dilution cannot be used for the titration. This would lower the salt concentration and therefore automatically improve the titrability but, at the same time, the surfactant concentration would be lowered even further. The undissociated, partially salted-out surfactant cannot be detected by the surfactant electrode as it is not present in ionic form. Such samples can nevertheless be titrated. To do this it is necessary to change from the dynamic mode which is normally used for the titration of ionic surfactants. Monotonic titration, in which each volume increment is of the same size, offers better possibilities in this case. Much more time must be allowed for the reaction because only the dissociated surfactants can react with the titrant. This is why it takes a certain time for the equilibrium to be reached. For the same reason a drift-controlled titration should not be carried out under any circumstances. Only the acquisition of the measured value after a preset delay period can be recommended here. In this case the delay period should be at least 30 seconds. This means that the time required for a titration is increased by some orders of magnitude. A titration time of half an hour must be allowed for such a sample having a high salt content. In this single exception, in which the titration takes a very long time anyway, preliminary addition of titrant can also be justified. Titration times of approx. 20 minutes must be reckoned with if results with a relative standard deviation of around 2% are to be achieved.

Under no circumstances should a reference electrode with a platinum diaphragm be used in such a titration, e.g. in a nickel bath, as considerable interference can be caused by redox potentials. In this case a reference electrode with an inert ceramic diaphragm can be recommended.
In this way we were able to determine in a chromium bath and also in a nickel bath the concentrations of an anionic and in other samples that of a cationic surfactant. The concentrations of these two surfactants were between 100 and 200 mg/L. Sample volumes of approx. 30 mL were used and the methanol concentration in the titration solution was 5%. Partially fluorinated surfactants cause no further problems in potentiometric surfactant titration. In these electroplating baths they can be determined just as well or just as badly as pure hydrocarbon surfactants.

Summarising it can be said that correct titrations can be carried out even in electrolyte-rich solutions but that somewhat poorer standard deviations must be reckoned with. In systems with a very high electrolyte content a special technique in the form of an additional method which has been especially adapted for this purpose must be used.

12.1.2 Potentiometric two-phase titration

Direct titration of ionic surfactants in electroplating baths with the Surfactrode Resistant is not possible and should also not be attempted. The Surfactrode Resistant is simply not suitable for use in samples having a high salt content, as is the case with electroplating baths. A further technique has been successfully applied. The high salt content in electroplating baths has the effect that surfactants can be very easily extracted by apolar solvents such as chloroform. For example, 100 mL of the electroplating bath sample can be extracted with 2 x 10 mL chloroform. The chloroform phases are combined and 10 mL ethanol and 70 mL water are added. After addition of 100 µL TEGO add and adjustment to the corresponding pH for the surfactant (see chapter 5, Figs. 71 and 72), the titration can be carried out immediately. An addition of 200 µL TEGO add can be recommended.

In this way both the anionic surfactants as well as the seldom-occurring cationic surfactants can be determined. The analysis time for a single determination including the extraction is approx. 10 minutes. The relative standard deviations for this method are approx. 1% and thus better than those for titrations in aqueous media.

The extraction step causes the surfactant to become more concentrated. This is why this technique should always be used when low surfactant concentrations are to be titrated in electroplating baths.

12.2 Nonionic surfactants

We have also gained some experience with the titration of nonionic surfactants in electroplating baths. In numerous samples which we have examined the concentration of a POE oxo-fatty alcohol or other nonionic surfactants based on POE adducts or also of polyethylene glycols could be determined. Whether the determination of nonionic surfactants in an electroplating bath is possible depends on two factors:

1. The surfactant concentration must be sufficiently high.
2. The sulphuric acid content of the bath must not be too high.

The sulphuric acid in the sample precipitates the barium ions added for the formation of the pseudo-cationic complex. This is why it is absolutely necessary to ensure that the barium ion content in the solution is sufficient for the pseudo-cationic complex to be formed with the nonionic surfactant.

Whether the nonionic surfactant can still be titrated now depends on the amount of precipitated barium sulphate. If a good titration curve with a typical potential difference is obtained in the subsequent titration with sodium tetraphenylborate then it can be assumed that the results found are correct. If this is not the case the results should not be used. Filtering off or centrifuging off the barium sulphate formed when the barium is added cannot be recommended. In most cases this leads to no improvement in the titration curves or the results.

If the nonionic surfactants in the electroplating bath cannot be determined in the way described here then in virtually all cases this is possible after extraction with an apolar solvent. In samples containing large amounts of sulphuric acid this acidity should be reduced by the addition of sodium hydroxide. However, the sample should remain sufficiently acidic so that the metal ions it contains do not precipitate out as hydroxides. Titration of the nonionic surfactants is then only possible when the solvent has been evaporated off.

CAUTION!

Electroplating baths or electroplating bath additives can contain cyanides. This represents a serious poisoning hazard! Alkaline electroplating baths in particular should only be acidified if one is absolutely sure that these samples do not contain any cyanide.

Summarising it can be said that surfactants in electroplating baths can be determined in many cases. However, there is still no general procedure applicable to these cases so that one has to depend on trial and error. A further difficulty resides in the fact that the composition of the additives is normally not declared by the manufacturers. The Surfactrode Resistant is only of little importance for the direct potentiometric surfactant titration in electrolytic plating baths. It should only be used after the extraction of the surfactants, i.e. after separation from the salt-containing bath.
13 Titration of nonionic surfactants

13.1 General

Recently a further surfactant electrode for the titration of nonionic (NIO) surfactants based on polyoxyethylene (POE) adducts has been introduced (see section 4.3). Carrying out the nonionics titration is extremely simple and is comparable with the titration of ionic surfactants as regards expenditure and handling. The outstanding features of this new electrode are its rapid response and good reproducibility\(^{118}\). With a typical nonionic surfactant such as a fatty alcohol, a fatty acid or an alkyl phenol with 10 to 50 POE in the molecule, standard deviations of better than 0.5\% can be achieved (Fig. 45 shows an example of a titration curve). This means that this titration method is able to replace the unpopular BIAS (bismuth-active substance)\(^{119}\) method throughout a wide range. This analysis method requires an extremely large expenditure on time and the handling of aggressive chemicals such as concentrated acetic acid. The range of surfactants that can be determined with the new surfactant electrode is practically the same as for the BIAS determination, which means that the same cross sensitivities to polyethylene glycols (PEG) exist. This must be taken into account, for example in the determination of nonionic surfactants in wastewater as in this case the determination of the non-surfactant PEG is not permitted. Today’s «trend-setters» in surfactant chemistry, the APGs (alkyl polyglucosides) and other sugar surfactants cannot be analysed by this method.

13.1.1 Structural formulae of important nonionic surfactants

The structural formulae given here of the most important nonionic surfactants and surfactant groups are intended to help those who only come into occasional contact with surfactants or surfactant analysis to find their way through the following pages of this monograph.

![Ethylene oxide](image1)

**Fig. 191:** Ethylene oxide, the monomer for the preparation of POE addition products or of polyethylene glycols

![Polyethylene glycol](image2)

**Fig. 192:** Polyethylene glycol, homopolymer of ethylene oxide

![Propylene oxide](image3)

**Fig. 193:** Propylene oxide, the monomer for the preparation of POP addition products or of polypropylene glycols

![Polypropylene glycol](image4)

**Fig. 194:** Polypropylene glycol, homopolymer of propylene oxide

The fatty alcohol POE shown in Fig. 195 is an addition product of POE (polyoxyethylene) on the fatty alcohol starter molecule. The fatty alcohol can have a natural source, recognisable from the even-numbered C chains such as C\(_{12}\) or C\(_{14}\), but may also be based on synthetic fatty alcohols (oxoalcohols), recognisable from the odd-numbered C chains such as C\(_{11}\) or C\(_{13}\).

![Fatty alcohol POE](image5)

**Fig. 195:** Fatty alcohol POE

The fatty acid POE shown in Fig. 196 is an addition product of POE on a fatty acid starter molecule. The fatty acids used normally have a natural source, recognisable from the even-numbered C chains such as C\(_{12}\) or C\(_{14}\).

![Fatty acid POE](image6)

**Fig. 196:** Fatty acid POE

![Alkyl phenol POE](image7)

**Fig. 197:** Alkyl phenol POE, addition product of POE on an alkyl phenol starter molecule (often an octyl or nonyl phenol)
The fatty amine POE shown in Fig. 198 is an addition product of POE on a fatty amine starter molecule. This could be a primary fatty amine to which 2 POE chains can be added, or a secondary amine to which a single POE chain can be added.

The alkyl POE-POP block polymer shown in Fig. 199 is a reaction product from the block addition of ethylene oxide and propylene oxide on monovalent or polyvalent starter alcohols such as butanol, butanediol, glycols, glycerol or even sugar alcohols such as sorbite, etc.

In the esterification of sorbit with fatty acids, sorbitan fatty acid esters are formed (Fig. 201) with water separation and ring closure in the sugar component. The remaining OH groups are subsequently reacted with ethylene oxide.

Fig. 202 shows an addition product of POE on a glycerol partial ester starter molecule. Glycerol partial ester means that it is a mono- or di-fatty acid ester or a mixture of both. Examples are glycerol monolaurate or glycerol dilaurate. The remaining OH groups in the ester molecule are subsequently reacted with ethylene oxide.

![Fig. 198: Fatty amine POE](image)

![Fig. 199: Alkyl POE-POP block polymer](image)

![Fig. 200: Fatty acid alkylolamide POE](image)

![Fig. 201: POE sorbitan fatty acid ester](image)

![Fig. 202: POE part. glycerol fatty acid ester](image)

![Fig. 203: POE glycerol fatty acid ester. In this surfactant type the glycerol is first reacted with ethylene oxide and then esterified with fatty acids.](image)

![Fig. 204: Silicone polyether type Si-C](image)

![Fig. 205: Silicone polyether type Si-O-C](image)
13.1.2 Reaction mechanism of nonionic surfactant titration

The most important subgroup of the nonionic surfactants with by far the greatest share of the production is formed by the alkylpropylene oxide derivatives. These are addition products of ethylene oxide (POE) and propylene oxide (POP) on hydrophobic starter molecules such as fatty alcohols, fatty acids or fatty acid partial esters of polyvalent alcohols such as glycerol, etc.

If a nonionic surfactant is called, for example, stearyl alcohol-20 POE then it cannot be assumed that this is a uniform chemical compound of stearyl alcohol with 20 POE units in the molecule. It is rather to be assumed that the oleophilic starter alcohol has an alkyl chain distribution as shown in Fig. 206, that the number of POE units mentioned is only the statistical mean value and that it is quite possible to encounter distributions in a range from at least POE-10 up to POE-30.

The titration method suggested here only applies to nonionic surfactants based on POE addition products\textsuperscript{119}. This group has the ability to form complexes with divalent cations. In the complex the cation is surrounded by the POE chain in a similar manner to a crown ether. This is why the POE adducts are also derisively called the «crown ethers for poor chemists». X-ray structural analyses have shown that the POE adducts have a helical configuration with 3.5 oxyethylene units per turn\textsuperscript{121, 122}. Molecular models show that this structure is suitable for the inclusion of central atoms of metals and is able to bind with strong dipole interactions between the free electron pairs of the oxygen atoms and the positive charges of the divalent metal ions. As a result of the essentially higher mobility of the helix structure compared to a crown ether the inclusion of metal central atoms is considerably less specific. A steric hindrance, which can arise from the hydrophobic part of the molecule or may also be caused by several polyethylene oxide chains in a molecule, makes the inclusion of the metal ions in the polyether chains more difficult. As a result of this, distinct variations in the stoichiometric factors also occur. This is probably also the reason why, for example, POE glycerol partial esters or other ethoxylates of polyvalent starters can only be titrated so poorly. As in an aqueous medium additional interactions to the dipoles of the water molecules exist, the helical structure of the POE chains is not unambiguously evident. The bond between the POE adduct and the divalent cation therefore is based on a dipole interaction. The barium ion has turned out to be particularly suitable in this case. As the most optimal complex formation takes place between the barium and the POE-nonionic surfactant\textsuperscript{123}, this method is used almost exclusively for complex formation. As a result of this complex formation the nonionic surfactant gains a pseudo-cationic activity. In this form the complex can be precipitated out by large voluminous anions\textsuperscript{124}. The precipitating agent is, almost without exception, sodium tetraphenylborate.

As Fig. 207 shows, the formation of the pseudo-cationic compound from the nonionic surfactant and the barium is not based on a stoichiometric relationship. This is why direct stoichiometric calculation from the titration data, which is otherwise standard in the titration sector, is not possible in nonionic surfactant titration. Calibration steps must be carried out first in a similar manner to other analytical methods such as HPLC. This is done by carrying out calibration titrations with the nonionic surfactant to be determined; the calculation of the subsequent titrations is based on these results. The stoichiometric factor of the titration fundamentally depends on the complex formation between the barium and the POE-nonionic surfactant, with an average of 11 POE units per barium inclusion, while in the subsequent titration with sodium tetraphenylborate (NaTPB) two TPB\textsuperscript{--} are required per complex formed by Ba\textsuperscript{2+} and the nonionic surfactant.

The general formula is: 
\[ \text{[R-(CH}_2\text{-CH}_2\text{O)}_{11}\text{-H-Ba]}(\text{TPB})_{2x} \]
where R could stand for an alkyl phenol, fatty alcohol, fatty acid, polyethylene glycol or fatty amine, etc.
Cross\(^{19}\) characterises the situation very aptly as follows: «If anything characterises ethoxylated compounds then it is the complete absence of an evaluable chemical reaction in which these participate in a selective and stoichiometric manner».

If polyoxyethylene/polyoxypropylene mixed polymers or polyoxyethylene/polyoxypropylene block polymers are concerned (see section 13.2.5) then only the polyoxyethylene part forms the pseudo-cationic complex with the barium. The polyoxypropylene part in the compound remains inert. Why this is so has not yet been explained. In order not to make any mistakes in the analysis of such substances it is important that the calibration is carried out against the identical mixed polymer.

If the nonionic surfactant is unknown, e.g. in the examination of wastewater, then a calibration must be carried out with the standard surfactant nonylphenol-10 POE (Fig. 208), just as in the determination of the bismuth-active substance (BIAS), where the nonylphenol-10 POE does not act as a classical standard but only represents a quantity for reference and calculation.

### 13.1.3 Reagent solutions

Sodium tetraphenylborate \(c = 0.01 \text{ mol/L}\) with addition of protective colloids.

Auxiliary solution \(c(\text{BaCl}_2) = 0.1 \text{ mol/L}\)

More details about the preparation and titre setting of the solutions can be found in section 6.4 and Metrohm Application Bulletin No. 230\(^{19}\).

Apart from normal sodium tetraphenylborate, there may sometimes be an advantage in using modified sodium tetraphenylborates. Some fluoro-substituted derivatives in particular have a very interesting profile. Complexes of the barium-nonionic associate with this fluoro-substituted sodium tetraphenylborate are more stable than with standard sodium tetraphenylborate. This also results in advantages in the titration of nonionic surfactants at lower concentrations. This substituted sodium tetraphenylborate also has some advantages in the titration of betains. The greatest disadvantage of this fluorine-substituted sodium tetraphenylborate is, however, its very high price which can be as much as US$ 1000 for 1 L titration solution. Price reductions seem possible if demand increases, so that this development should be closely observed.

During the titration the complexes formed with the fluoro-substituted sodium tetraphenylborate increase in stability as the degree of substitution increases. However, higher fluoro-substituted sodium tetraphenylborates are less water-soluble, which further reduces their applications.

### 13.1.4 Nonionic surfactant titration

The titration curves obtained during the nonionic surfactant titration do not always correspond to the ideal S-shape. In the endpoint region in particular the curves often differ from the accustomed shape. This is why a titrator with good dynamic control and optimal endpoint recognition is particularly important for the titration of nonionic surfactants. The 670 and 726 Titroprocessors and the Titrino family perform these tasks outstandingly well. The optimal and correct titrator settings play a prominent role in nonionic surfactant titration.

#### Analysis

1. 25 to 50 mg sample are weighed out into a titration beaker.
2. 10 mL 0.1 mol/L BaCl\(_2\) solution are added and the sample dissolved by swirling.
3. 90 mL water are added and the titration carried out with the Titroprocessor or Titrino against the 0.01 mol/L NaTPB standard solution.
4. After every third or fourth titration the electrode must be rinsed with methanol or wiped off with a methanol-moistened tissue.

### 13.2 Possibilities and limits of the method

The potentiometric nonionic surfactant titration method allows a rapid determination of nonionic surfactants based on POE adducts. As this is not an absolute method, a calibration must be carried out against known concentrations of the surfactant to be determined. This means the method is limited to certain application areas. Cross-sensitivities and interferences must be taken into account. The titration of unknown nonionic surfactants in an unknown matrix is not possible.

As the titration result of a nonionic surfactant titration also depends on the number of POE units in the molecule, attempts have been made to use the nonionic surfactant titration as an alternative method for the determination of the
cloud point. This would be an interesting method for quality assurance and also for controlling the ethoxylation reaction in a production process. However, it still requires a considerable effort to correlate the results obtained by the two methods. Whether these attempts will prove successful cannot be assessed at the moment\textsuperscript{125, 126}.

### 13.2.1 The nonionic surfactant

Only nonionic surfactants based on polyoxyethylene (POE) adducts can be determined by the method described here. This means that an oleophilic starter with an alkyl chain length of C\textsubscript{12} and at least 4 POE units in a molecule must be present. In the literature\textsuperscript{127} it is mentioned that a nonionic surfactant molecule must have at least 5 POE units for it to be titratable. Our practice-oriented investigations have demonstrated that most technical products with statistically only 4 mol POE in the surfactant molecule can already be easily titrated. The share of higher ethoxylated components in the product is certainly responsible for this, as has already been shown by several MALDI-TOF spectra. Of course, at the boundary between titratable and non-titratable the stoichiometric factors differ significantly from those in the highly ethoxylated range. Gallegos\textsuperscript{128} found that only nonionic surfactants with 9 POE units and more in the molecule exhibited constant stoichiometric factors. As the following section 13.2.2 about polyethylene glycols shows, a dependence on the oleophilic starter also exists. The starter certainly assumes some share of the responsibility in determining from which POE chain length onwards the complex formed between the barium ion and sodium tetraphenylborate can be precipitated out.

It is also certain that ethoxylated fatty alcohols with approx. 2 POE units in the molecule, which are often used in the washing powder sector, cannot be determined with this method.

In nonionic surfactant titration there is a linear dependency between the sample weight and the titrant consumption. In contrast to ionic surfactants there is no minimum nonionic surfactant concentration necessary to achieve a linear relationship vs. the titrant consumption. This means that it is both possible and permissible to carry out titrations when a titrant consumption of only approx. 1 mL can be expected, e.g. in wastewater investigations.

#### 13.2.2 Polyethylene glycols

Polyethylene glycols (PEG) can also be determined with this analytical method\textsuperscript{119}. However, in this case approx. 11 to 12 POE units are necessary; this corresponds to a mean molar mass of about 500 g/mol. According to the investigations by Vytras, Dvorakova and Zeman\textsuperscript{129, 172} it must be possible to carry out a titration from 5 POE units upwards. It is to be expected that the pseudo-cationic complex is formed, but that it cannot be precipitated out with sodium tetraphenylborate; however, this is a precondition for carrying out a potentiometric determination that belongs to the group of precipitation titrations.

If nonionic surfactants based on PEG are present in addition to PEGs then a sum will be determined without the separation. However, this is a precondition for carrying out a potentiometric determination that belongs to the group of precipitation titrations. Our practice-oriented investigations have demonstrated that most technical products with statistically only 4 POE units in the molecule can already be easily titrated. The share of higher ethoxylated components in the product is certainly responsible for this, as has already been shown by several MALDI-TOF spectra. Of course, at the boundary between titratable and non-titratable the stoichiometric factors differ significantly from those in the highly ethoxylated range. Gallegos\textsuperscript{128} found that only nonionic surfactants with 9 POE units and more in the molecule exhibited constant stoichiometric factors. As the following section 13.2.2 about polyethylene glycols shows, a dependence on the oleophilic starter also exists. The starter certainly assumes some share of the responsibility in determining from which POE chain length onwards the complex formed between the barium ion and sodium tetraphenylborate can be precipitated out.

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1. For those cases which only concern the determination of the separately present PEGs a simple determination method is available. The titration curves are very well formed and can easily be evaluated by the titrator.
2. If nonionic surfactants and PEGs are present together and if, for example, these are to be used to determine the concentration of a fatty alcohol-POE adduct in a formulation then this can also be carried out.
3. If nonionic surfactants and PEGs are present together and if only the surfactant is to be determined, as is the case, e.g., in the determination of nonionic surfactants in wastewater, then a separating step must first be carried out. The POE addition products on multifunctional starter molecules

These include the fatty alcohols, but also the fatty acids, fatty amines, alkyl phenols, etc., if the minimum number of POE groups in the molecule is achieved (see section 13.2.1) this group is ideally suited for determination by a potentiometric titration. All the groups listed here can be equally well titrated and the titration curves obtained can easily be evaluated by the current titrators. The standard deviations which can be achieved with this group are <0.5.

#### 13.2.3 POE addition products on multifunctional starter molecules

The primary members of this group are the fatty acid partial esters of polyvalent alcohols such as:

- glycerol
- diglycerol
- triglycerol
- polyglycerol
- pentaerytritol
- sorbitol (sorbitanes) etc.

The resulting titration curves are very flat. A region is quickly reached where evaluation by the titrator algorithm is no longer possible. The higher the titrant consumption, the poorer and flatter the titration curves. As in nonionic surfactant titrations there is a linear relationship between the sample weight and titrant consumption. This advantage should be used and the sample weight calculated so that a consumption of 4 mL 0.01 mol/L sodium tetraphenylborate is not exceeded.

The standard deviation which can be achieved with this group is only approx. 4 to 5%.

* Trademark of 3M
We have also found some compounds that cannot be titrated with this method. These are the esters of ethoxylated polyvalent alcohols that only have short POE chains in their molecules. Glycerol POE-7 cocoate is mentioned as an example, a nonionic surfactant that is found as a re-greasing component in many shower gel formulations.

13.2.5 POE-POP mixed polymers

This group of products is generally also known as the polyethers. These are usually short starter alcohols, e.g. butanol, etc., to which ethylene oxide or propylene oxide has been added, either in blocks as so-called block polymers or mixed as mixed polymers. Both subgroups can be determined by potentiometric titration. Fig. 211 shows an example.

In order for polyethers to be determined titrimetrically the following preconditions must be fulfilled.

1. The solubility of the polyether in water must be at least 50 mg/100 mL.
2. The ratio of POE in the polyether portion must be at least 25%.

It is also important to remember that only the POE portion in a polyether undergoes the reaction with the barium to form the pseudo-cationic complex. It is this complex which can then be precipitated out with the voluminous sodium tetraphenylborate anion. From a stoichiometric point of view the POP portion in such a polyether is inert.

13.2.6 Other nonionic surfactants that do not contain POE

Practically all other nonionic surfactants that are not addition products of POE on oleophilic starter molecules cannot be determined by this method. These include the following product groups:

- glycerol fatty acid partial esters
- di-, tri- or polyglycerol fatty acid partial esters
- alkyl polyglucosides and other sugar surfactants
- sorbitan fatty acid partial esters
- glycol fatty acid partial esters

13.2.7 Polyether siloxanes

In very many cases polyether siloxanes can also be determined titrimetrically by this method. It does not matter whether these are Si-C- or Si-O-C-bound polyether siloxanes. In the vast majority of cases the polyether portion of these products consists of POE/POP mixed polymers (see section 13.2.5). In order for polyether siloxanes to be determined titrimetrically the following preconditions must be fulfilled.

1. The solubility of the polyether siloxane in water must be at least 50 mg/100 mL.
2. The ratio of POE in the polyether portion must be at least 25%.

It is also important to remember that only the POE portion in a polyether siloxane undergoes the reaction with the barium to form the pseudo-cationic complex. It is this complex which can then be precipitated out with the voluminous sodium tetraphenylborate anion. From a stoichiometric point of view the POP portion in such a polyether siloxane is inert.

13.2.8 Reference electrode

The reference electrode has a great influence on the quality of the titration, but opinions differ as to which reference electrode is the right one. Some authors recommend a double junction electrode for all surfactant titrations. They use c(KCl) = 3 mol/L as the inner and c(NaCl) = 3 mol/L as the outer electrolyte. In our laboratory, when performing titrations of nonionic surfactants, we prefer a silver/silver chloride standard reference electrode, either with a ceramic or platinum diaphragm. In addition we exchange the normal internal electrolyte solution of 3 mol/L potassium chloride for a sodium chloride solution of the same concentration. We always store the electrode in this solution when it is not in use.

13.3 Influences

If the factors that influence the nonionic surfactant titration are known and taken into account then such a titration can be carried out successfully. However, the following section should be studied carefully as the influences described in it should be taken into account when analysing samples.

13.3.1 Alcohols

Methanol or other alcohols have an important function to fulfil in the potentiometric titration of ionic surfactants. In the titration of nonionic surfactants things are different. In this case methanol or, even worse, ethanol or 2-propanol have a negative effect on the titration result because the reaction product formed during the titration from the pseudo-cationic nonionic surfactant and the sodium tetraphenylborate is soluble in the alcohols. This is the reason why no alcohol should be added to the sample solution.

An alcohol content of approx. 2 to 3% methanol or ethanol has, however, no measurable influence on the titration result. If the nonionic surfactant content is to be determined on samples that have a high alcohol content then this must be taken into account when the calibration factor is being determined.

13.3.2 Anionic surfactants

Whether anionic surfactants interfere in a nonionic surfactant titration depends on the structure of the anionic surfactant.

1. Anionic surfactants based on sulphates, such as fatty alcohol sulphates or fatty alcohol ether sulphates, do not interfere with the determination. This may be because they are precipitated out by the barium chloride present. If the content of sulphate-based anionic surfactants in the sample is high then it may be necessary to add more barium chloride so that sufficient barium ions are available for forming the complex with the POE chains.

2. Anionic surfactants based on sulphonates interfere with the determination of the nonionic surfactants but only to a slight extent, see Fig. 209. The interference already begins at a low sulphonate-based anionic surfactant concentration.
tion. However, the disturbing influence hardly increases as the sulphonate-based anionic surfactant concentration increases.

3. In each individual case a check should be made to find out whether this error can be disregarded. On the other hand, because the disturbing influence is fairly independent of the sulphonate-based anionic surfactant concentration, it is also possible to add this substance as well when the calibration factor is being determined.

13.3.3 POE-containing anionic surfactants

Anionic surfactants based on POE adducts, e.g. fatty alcohol ether sulphates or fatty alcohol ether sulphonates are determined in the titration in the range where they fulfill the conditions for the titrability of nonionic surfactants, i.e. from 4 mol POE in the molecule. In the often-used products laureth-2.5 sulphate or laureth-3 sulphonate it must always be expected that they will contain a higher ethoxylated portion that will also be determined in the nonionic surfactant titration and therefore simulate high-bias results. The longer the average POE chain in the POE-containing anionic surfactant, the greater the disturbing influence that can be expected. The degree of interference of these two surfactants also depends on the concentration. For this reason the determination of nonionic surfactants should not be carried out in this matrix.

13.3.4 Cationic surfactants

Cationic surfactants are determined in this titration because they also form insoluble compounds with sodium tetraphenylborate. The reaction between cationic surfactants and sodium tetraphenylborate takes place stoichiometrically. In this case a differentiation can be carried out as follows:

1. A titration is carried out without BaCl$_2$ addition. In this titration only the cationic surfactants are determined.
2. A titration is carried out with BaCl$_2$ addition. In this titration the joint total of cationic and nonionic surfactants is determined.

13.3.5 APG-based nonionic surfactants

The influence of alkyl polyglucosides (APG) on the titration of nonionic surfactants is comparable to the influence of sulphonate-based anionic surfactants, and can therefore be described as being slight (see Fig. 210).

The interference already begins at a low APG concentration. However, the disturbing influence hardly increases as the APG concentration increases. In each individual case a check should be made to find out whether this error can be disregarded. On the other hand, because the disturbing influence is fairly independent of the APG concentration, it is also possible to add this substance as well when the calibration factor is being determined.

13.3.6 pH adjustment

The pH is very important in the titration of ionic surfactants, particularly in the differentiation of surfactant mixtures. In the potentiometric determination of nonionic surfactants this is not the case, which is why a special pH adjustment in nonionic surfactant titrations is not necessary. A titration around the neutral point is recommended, but a determination can also be carried out without any problems between pH = 2 and pH = 10. At higher pH values the sparingly soluble barium hydroxide may precipitate out. According to current experience this has no negative influence on the titration; enough barium ions still seem to be present.

13.3.7 Complexing agents

The formation of the pseudo-cationic complex from barium and the polyoxyethylene chain of the nonionic surfactants forms the basis for carrying out the potentiometric nonionic surfactant titration. All those chemical reactions that are likely to compete with the above-described primary reaction are potentially able to interfere with the desired complex formation reaction. This is why the influences of complexing agents such as

- ethylenedinitrilotetraacetic acid disodium salt dihydrate (EDTA)
- nitrilotriacetic acid
- ethylenedinitrilotetraacetic acid

are

- 1,2-cyclohexylenedinitrilotriacetic acid monohydrate
- (N-(2-hydroxyethyl)-ethylenediamine-N,N',N'-triacetic acid trisodium salt
- (bis-(aminoethyl)-glycolether-N,N,N',N'-tetraacetic acid
- diethylenetriaminepentaacetic acid

Fig. 209: Interference by sulphonates with a sec. alkane sulpho-nate (SAS) as an example

Fig. 210: Interference by APG with C$_{7-10}$ APG as an example
• triethylenetetraminehexaacetic acid
• citric acid, etc.

have been thoroughly investigated because, with the exception of citric acid, they all form stable complexes with metals. In addition, these complexing agents are ingredients of very many cleaning agents and detergents.

The tests concerning complexing agent interference were carried out on two model substances, a fatty alcohol-10 POE and a polyethylene glycol 2000. Initially a sample weight of 40 mg of the two test substances was titrated according to the standard specifications, then 5 mg, 10 mg, 20 mg, 30 mg and 40 mg of the individual complexing agents were added. In the extreme case the ratio of surfactant to complexing agent was 1 to 1, i.e. an order of magnitude that does not occur in practice. Even at this extreme concentration the titration results were not affected.

13.3.8 Potassium or ammonium ions

Potassium, ammonium and other ions also form insoluble salts with sodium tetraphenylborate. Against all expectations the experimental experience shows that no interference occurs at all, or that any interference that does occur is negligibly small.

However, if in a special case interference is observed then the following technique is recommended:

1. A titration is carried out without BaCl₂ addition. In this titration only the interfering ions are determined.
2. A titration is carried out with BaCl₂ addition. In this titration the sum of interfering ions and nonionic surfactant is determined.

13.4 Calibration factor

Calculation

The calculation of the nonionic surfactant content cannot be carried out directly. A calibration factor must first be determined using the nonionic surfactant that is to be analysed or a nonionic surfactant that has been defined as the standard.

This is carried out by weighing the corresponding nonionic surfactant out into the titration beaker and dissolving it in 10 mL 0.1 mol/L BaCl₂ solution. Then 90 mL water are added and the titration carried out against 0.01 mol/L NaTPB standard solution.

\[
f = \frac{E \times 1000}{V}
\]

sample weight and the consumption of 0.01 mol/L NaTPB standard solution into account.

where

\( f \) calibration factor in mg/mL

\[
\text{NIO surfactant in } \% = \frac{V \times f}{10 \times E}
\]

Equation 18

Once the calibration factor has been determined the nonionic surfactant content can be calculated after the sample titration as follows:

\[
\text{V consumption of 0.01 mol/L NaTPB standard solution in mL}
\]

\[
\text{f calibration factor in mg/mL}
\]

\[
\text{E sample weight in g (referred to 100% nonionic surfactant)}
\]

\[
\text{V consumption of 0.01 mol/L NaTPB standard solution in mL}
\]

If the sample solution to be investigated contains further ingredients that could interfere with the potentiometric titration of nonionic surfactants, e.g. higher alcohol concentrations, alkyl polyglucosides or sulphonate-based anionic surfactants then this interference can be compensated by adding the potential interfering substance when the calibration factor is being determined.

The interference caused by anionic surfactants that also contain POE groups in the molecule cannot be corrected by this technique as the interference depends strongly on the concentration of the interfering surfactant.

Fig. 211: Titration curve and first derivative obtained during the determination of the calibration factor of a POE-POP polyether (65 POE/35 POP)
14 Determination of nonionic surfactants in formulations

14.1 Determination of nonionic surfactants in cleaning agents and detergents

14.1.1 Determination of nonionic surfactants in all-purpose cleaners
Ingredients according to EU recommendation:
- <5% soaps
- 5 to 15% anionic surfactants
- 15 to 30% nonionic surfactants
- Citric acid
- Fragrances

In the calibration titration for the nonionic surfactant titration of such a formulation the anionic surfactant can be added.

The standard deviation which can be achieved is about 1%.

14.1.2 Determination of nonionic surfactants in a clear rinsing agent for dishwashers
Clear rinsing agents are automatically added to the last rinsing water in dishwashers; the citric acid they contain removes lime deposits and the nonionic surfactants ensure a uniform brilliance. The declaration of such a clear rinsing agent could be as follows:
Ingredients according to EU recommendation:
- 5 to 15% nonionic surfactants
- Citric acid
- Solubiliser

No problems are to be expected with such a formulation which, apart from the nonionic surfactant to be analysed, only contains water, some alcohol and citric acid. The analytical determination is possible without any problems. As in all nonionic surfactant titrations, the nonionic surfactant used must be available to carry out the calibration titration 119.

14.1.3 Determination of nonionic surfactants in a household cleaner (concentrate)
Ingredients according to EU recommendation:
- <5 % nonionic surfactants
- 5 to 15% anionic surfactants
- 5 to 15% amphoteric surfactants
- Preservative

The determination of the nonionic surfactant content in such a formulation can be carried out easily in the quality control sector. As is usual in nonionic surfactant titration, the calibration is carried out with the nonionic surfactant concerned, moreover, it is recommended that 10% of a cocamidopropylbetain and the anionic surfactant involved are added. Standard deviations of approx. 1% can be achieved with this method.

14.1.4 Determination of nonionic surfactants in washing powders
Nonionic surfactants based on polyoxyethylene fatty alcohols are chiefly used in washing powders and these contain two or three polyoxyethylene groups. These low-ethoxylated fatty alcohols cannot be determined by a nonionic surfactant titration as, because of their short polyoxyethylene chain, they cannot form a pseudo-cationic complex with the barium ions.

14.1.5 Liquid cleaning agents for coloured fabrics
The nonionic surfactant content in this formulation can be determined by potentiometric titration. This determination should be limited to the quality assurance sector. The anionic surfactant used should be added for the calibration titration. This method is not suitable for the determination of nonionic surfactants in unknown liquid cleaning agents for coloured fabrics that have a similar declaration.

Ingredients according to EU recommendation:
- <5% polycarboxylates
- 5 to 15% anionic surfactants
- 5 to 15% soaps
- Fragrances
- Glycerin
- Sodium citrate
- 15 to 30% nonionic surfactants
- Enzymes
- Colour transfer inhibitors
- Borax

This method cannot be used for washing powders for coloured fabrics as the nonionic surfactants used, which in many cases are fatty alcohol 2-3-POE, cannot be determined with this analytical method. 119
14.1.6 Wool shampoos

Wool shampoos, as the name suggests, contain fibre-protecting surfactants which treat the sensitive wool fibres gently and are particularly mild to the skin. This is why these products are suitable for washing sensitive textiles made of silk, angora, cashmere or mohair. The anionic surfactants used are, for example, sodium laureth sulfate or sodium lauryl sulfate. These wool shampoos often also contain cocamidopropylbetaines which, together with the anionic surfactants mentioned above, are particularly mild. The nonionic surfactants can be determined in this matrix. The pH value of the titration solution must always be above 3. Below this value there would be interferences caused by the betains, and these would also be partially determined.

Ingredients according to EU recommendation, formulation 1:
- 5 to 15% anionic surfactants
- 15 to 30% nonionic surfactants
- Alcohol
- Fragrances

Ingredients according to EU recommendation, formulation 2:
- 15 to 30% nonionic surfactants
- Auxiliaries
- Fragrances

Ingredients according to EU recommendation, formulation 3:
- 5 to 15% nonionic surfactants
- Re-greasing agents
- Alcohol
- Fragrances

The calculation of the nonionic surfactant content in the wool shampoo can only be carried out by calibration using the nonionic surfactant involved.

14.1.7 Pre-wash gel

Origin: North America

Ingredients:
- Surfactant
- Polymer
- Enzymes
- Fragrance

The pre-wash contains fatty alcohol-POE as the surfactant. The titration can be carried out and evaluated by the titrator. The \( s_{\text{net}} \) that can be achieved is <0.5%.

14.2 Determination of nonionic surfactants in other formulations

14.2.1 Determination of nonionic surfactants in tooth washes

Tooth washes normally contain a combination of anionic surfactants and nonionic surfactants together with other active substances and auxiliaries intended to pre-clean or pre-treat the teeth before the teeth cleaning process itself. In this case the anionic surfactants carry out the cleaning function while the nonionic surfactants only function as co-cleaners; their primary effect is as a solubiliser.

A tooth wash against plaque could have the following declared ingredients:
- Sodium laureth sulfate
- Polysorbate-20
- Sodium salicylate
- Citric acid
- Colourants
- Sodium benzoate
- Alcohol 6
- Flavour
- Methyl paraben
- Sodium saccharin

Polysorbate-20, like all surfactants based on polyoxyethylene sorbitan fatty acid esters, belongs to the group of nonionic surfactants that are not so easy to titrate (see section 13.2.4). Nevertheless the determination of these nonionic surfactants in the tooth wash is possible. In this case it is important that the amount of sample solution is selected so that the consumption of an 0.01 mol/L sodium tetraphenylborate solution does not exceed 4 mL. The calibration can be carried out against a pure Polysorbate-20. The other ingredients contained in this formulation have no negative influence and do not need to be added during the calibration. The standard deviation achieved was 4.5% \( (n = 10) \).
14.2.2 Determination of nonionic surfactants in wastewater samples\textsuperscript{130}

A 0.002 mol/L sodium tetraphenylborate solution is used for the determination of nonionic surfactants in wastewater samples\textsuperscript{119} (see section 6.4.4).

100 mL of the unfiltered wastewater sample is placed in the titration beaker and 10 mL barium chloride solution are added to it. The titration is then carried out using 0.002 mol/L sodium tetraphenylborate solution.

In this titration the sum total of nonionic surfactants and polyethylene glycols is determined. If the determination of this total content is not required then the nonionic surfactant must first be separated from the non-surfactant polyethylene glycols. This can be carried out, for example, using the so-called blow-out method according to Wickbold\textsuperscript{131, 132}. As the chemical structure of the nonionic surfactant contained in the wastewater is very often not known, the calculation must be carried out against the standard surfactant nonylphenol POE-10 in a manner similar to the determination of the bismuth-active substance. If in a particular case the nonionic surfactant in the wastewater is known then the calibration can also be carried out against it (see section 13.4).

14.2.3 Determination of nonionic fabric conditioners on polyester fibres

Polyester fibres are often finished with nonionic surfactants or POE/POP polyethers (scrooping, Avivage). The content of these nonionic surfactant compounds can be potentiometrically determined if both the type of fabric conditioner is known and the fabric conditioner itself is available for carrying out a calibration titration.

The fabric conditioner does not first need to be extracted from the fibres, which is otherwise the normal procedure. The fibres must be cut into pieces that are so small that they do not become firmly wrapped around either the stirrer blade or the electrodes.

Even in the lower range of titrant consumption the nonionic surfactant titration shows a linear relationship between sample weight and titrant consumption. This is why the weight of sample fibres should be maximum 1 g. With higher sample weights problems occur because the fibres make the thorough mixing of the titration solution more difficult. The acquisition of the measured value in this titration must always be time-controlled in order to achieve the quantitative removal of the fabric conditioner from the fibres. This is easily carried out because the insoluble reaction product formed during the titration from the nonionic surfactant or the polyether/barium complex with sodium tetraphenylborate represents the energetically more favourable form.
15 Titration of ionic dyes

Dyes are colourants that are soluble in solvents or water whereas pigments are insoluble. While about 100 pure pigments are known, there are many tens of thousands of dyes of which only a few thousand are produced in important quantities; only five hundred are used technically. The first differentiation is between natural and synthetic dyes. The best-known natural dye is surely indigo, which is used for dying jeans fabrics. Most natural dyes are flower or vegetable dyes. Synthetic dyes are used more often; well-known representatives are:

- Aniline blue
- Aniline black
- Ciba blue
- Fuchsin
- Congo red
- Crystal violet
- Orange IV
- etc.

Most synthetic dyes are of an aromatic or heterocyclic nature and either ionic (e.g. all water-soluble dyes) or nonionic compounds (e.g. dispersed dyes). In the ionic dyes a difference is made between anionic and cationic dyes. The anionic dyes have a negatively charged dye ion, cationic dyes have a positively charged one, which is why previously the differentiation was generally made between acidic and basic dyes. The admissibility of using individual dyes, e.g. for colouring foodstuffs, is governed by corresponding regulations, e.g. by the food additive regulations. These contain lists of permitted dyes and dyes that are only permitted for external use. In 1993 well over 200 000 t of dyes were produced in Germany.

The analytical method suggested here only applies to ionic dyes. Nonionic dyes or coloured pigments remain inert during this determination method. They are not determined and usually have no negative influence on the determination.

The ionic dyes are not surfactants but they are large voluminous anions or cations and thus potentially belong to those ions that can be detected by a so-called surfactant electrode and therefore analytically determined (titrated). Normally anionic dyes are titrated with a cationic titrant, very often this is TEGO trant A100, whereas cationic dyes are titrated with the anionic surfactant dodecyl sulphate sodium salt. The special feature of the potentiometric surfactant titration of dyes is the fact that this is a direct method. This is different from measurements of dyes by light absorption, so-called photometric measurements, in which dyes of known concentration must always be used to carry out a calibration. Dyes with a defined purity that are really suitable for the calibration of spectrometric measurements are extremely rare.

This is why the determination of the dye content simply from stoichiometric equations and from a titration is much easier and causes far fewer problems. The molar mass of the dye to be analysed is required for this, but this either generally known, can be calculated or is available from literature references. Knittel and Schollmeyer have reported about a special membrane electrode for the determination of ionic dyes. However, such a special electrode is not necessary as a normal surfactant electrode such as the Ionic Surfactant Electrode can detect a very large number of dyes. Whether a dye can be titrated or not depends solely on the solubility product of the dye-titrant associate. The more insoluble the ion associate formed during the titration, the better the dye can be quantitatively determined. This principle is always valid, no matter whether a normal surfactant electrode is used or a special dye electrode. The applicability of the dye titration cannot be extended by the use of a special electrode.

However, by far not all dyes can be analytically determined in this manner; the possibilities and limits are again set solely by the degree to which the dye can be precipitated out with an oppositely charged titrant. Without this precipitation there is no evaluable titration.

In contrast to surfactant titration, the quality of a dye titration can be easily recognised visually as soon as the titration has finished. As the dye is precipitated out by the titrant, the solution is either colourless or almost colourless when the titration is finished and the ion associate produced has been allowed to settle out, filtered off or centrifuged off. This was the case for most of the dye titrations carried out, in particular for anionic dyes when TEGO trant A100 was used as the titrant.

The addition of methanol or other alcohols is not necessary for the titration of dyes. In most cases pH adjustment or correction is also not required. In their free acid or free base forms some dyes are not soluble in water or only sparingly soluble. This means that it is necessary to add a few drops of dilute sodium hydroxide to the anionic dyes or a few drops of dilute hydrochloric or sulphuric acid to the cationic dyes in order to convert these to a water-soluble form.

![Fig. 214: Structural formula of bromophenol blue](image-url)
Dyes that have been titrated

Bromophenol blue
The titration of the anionic dye bromophenol blue is possible with the Ionic Surfactant Electrode and TEGO trant A100 as titrant without any problems; see Fig. 215.

Titration conditions
Determination of bromophenol blue
Sample form commercial dye powder
Sample weight approx. 30 to 40 mg (possibly via an intermediate dilution)
Additive a few drops dilute NaOH
Sample preparation none
Water up to 100 mL
Electrode Ionic Surfactant Electrode
Calculation stoichiometric
Molar mass 669.99 g/mol
Achievable standard deviation <1%

Orange II
Orange II is an anionic dye that can also be easily titrated with the ionic titrant TEGO trant A100. The indicator electrode is again the Ionic Surfactant Electrode.

Titration conditions
Determination of Orange II
Sample form commercial dye powder
Sample weight approx. 20 to 25 mg (possibly via an intermediate dilution)
Additive not required
Sample preparation none
Water up to 100 mL
Electrode Ionic Surfactant Electrode
Calculation stoichiometric
Molar mass 350.33 g/mol
Achievable standard deviation <1%

With the Orange II dye the dependency of the reagent consumption on the sample weight was also investigated, see Fig. 216. As can be seen the resulting graph is a straight line through the origin. This means that the dye can be correctly determined by potentiometric titration even at low concentrations.

Methylene blue
Methylene blue is a cationic dye that can be titrated with bis-2-ethylhexylsulphosuccinate or with dodecyl sulphate sodium salt. As in all dye titrations, the indicator electrode is the Ionic Surfactant Electrode.

Titration conditions
Determination of methylene blue
Sample form commercial dye powder
Sample weight approx. 20 to 25 mg (possibly via an intermediate dilution)
Additive not required
Sample preparation none
Water up to 100 mL
Electrode Ionic Surfactant Electrode
Calculation stoichiometric
Molar mass 319.00 g/mol
16 Titration of pharmaceuticals

16.1 Description of the method

This section deals with the determination of pharmaceuticals, both in raw materials and in preparations. All the pharmaceuticals mentioned here have no surfactant properties. That they can nevertheless be determined with a surfactant electrode is a further proof that this is a surfactant-sensitive, but not a surfactant-selective electrode. It is well-known that this electrode responds to large voluminous ions and the pharmaceuticals which are titrated here belong exclusively to this type of ion. Most pharmaceuticals are cationic.

In the titration of cationic pharmaceuticals with perchloric acid the basicity is used for the determination. In this case it is necessary for the pharmaceutical to be present as a free base or as the salt of a weak acid. For galenic reasons pharmaceuticals are often used in the form of their hydrochlorides. Amine hydrochlorides cannot be analysed with perchloric acid because the difference between the pKₐ values of the hydrochloric acid and the perchloric acid is too small according to the rules laid down for the detection. This is the reason why the exchange of hydrochloride by perchlorate cannot be detected with an evaluable potential jump. This means that the hydrochloride must be absorbed by mercury acetate or other suitable means. In this way the free amines or amine acetates are again formed; these can be titrated with perchloric acid in a non-aqueous medium.

In the analytical method described below the presence of hydrochloric acid, i.e. the presence of the pharmaceuticals as hydrochlorides, causes no problems at all. The titration with sodium tetraphenylborate is, like most other titration methods described in this monograph, a precipitation titration. This means that during the titration of the pharmaceutical — whether in the form of a free base, hydrochloride or other salt — with sodium tetraphenylborate solution, the insoluble pharmaceutical-tetraphenylborate salt is formed.

The Metrohm NIO Surfactant Electrode is used for the titration of these pharmaceuticals; see section 13.2.8 for the reference electrode. The same sodium tetraphenylborate solution is used as for the nonionic surfactant titration and the titre determination is also carried out using papaverine.

Reports have also been made in the literature about the titration of pharmaceuticals with sodium tetraphenylborate as titrant. However, the literature references are concerned with the titration of surfactant-like pharmaceuticals, e.g. cetyltrimethylammonium bromide or cetyltrimethylammonium chloride. Pinzauti, Papeschi and La Porta describe the titration of pharmaceuticals using a silver/silver sulphide electrode with various titrants. Christopoulos, Diamandis and Hadjioannou describe the titration of non-surfactant-like pharmaceuticals with sodium tetraphenylborate. In this work a "real liquid membrane electrode" was used and the titration of pharmaceutically-relevant alkaloids is also described.

Preconditions for being able to titrate the pharmaceutical:
- The pharmaceutical must have a water solubility of at least 50 mg/100 mL water.
- The titration solution can also be made acidic or alkaline to improve the solubility. In this case acidification usually provides a better solubility. In most cases the addition of dilute acetic acid had the desired effect.
- The pharmaceutical must have a cationic group in the molecule so that it can be titrated with sodium tetraphenylborate.
- Pharmaceuticals that contain an anionic group can also be titrated; however, in this case, the Ionic Surfactant Electrode should be used together with the cationic titrant TEGO trant A100.
- The pharmaceutical must form an insoluble ion associate with the oppositely-charged titrant. This is why a qualitative test should be carried out before the titration of a pharmaceutical compound is attempted. In this test an oppositely-charged titrant is added to an aqueous solution of the pharmaceutical. If an insoluble precipitate is not formed spontaneously then a titration should not be attempted at all.

As the pharmaceutical compounds that are described here are not surfactants, no surfactant-specific problems occur during the titration. This means that pharmaceuticals show a linear relationship between sample weight and titrant consumption over a very wide range so that, depending on the requirements, titrations can also be carried out when only a titrant consumption of 1 mL 0.01 mol/L sodium tetraphenylborate solution is to be expected. On the other hand, titrations with a titrant consumption of approx. 30 mL are also possible. All the pharmaceutical titrations presented here follow the normal stoichiometric conditions and can therefore be easily calculated if the molar mass of the pharmaceutical is taken into account. Calibration titrations are not necessary in this sector.

In the pharmaceutical titration the electrode responds to both the analyte and the titrant. This results in good S-shaped titration curves that can easily be evaluated by the algorithms of modern titrators. However, it is always necessary to adjust these titrators to the special features of pharmaceutical titration. Parameters such as acquisition of the measured value, measuring point density and others must be optimised and checked by suitable test procedures before such a titration method is stored permanently and released for routine operation. Further details can be found from section 5.6 onwards.
17 Titration of pharmaceutical raw materials and formulations

17.1 Chlorhexidines

From a chemical point of view, chlorhexidines belong to the diguanide group: 1,6-di-(N-p-chlorophenyldiguanide). Three salts are of particular pharmacological interest:
1. Chlorhexidine digluconate with a water solubility of more than 70 g/L.
2. Chlorhexidine diacetate with a water solubility of 1.8 g/L.
3. Chlorhexidine with a water solubility of 0.06 g/L.

In contrast, the free base of the chlorhexidine has a water solubility of only 0.008 g/L.

Chlorhexidine salts are broad-spectrum antibacterial agents. The minimum inhibitory concentration can be characterised as being $1 \times 10^{-6}$ g/mL. Its pharmaceutical uses can be split into two groups:
1. As the active substance in throat disinfectant solutions or in lozenges.
2. Preservative for aqueous pharmaceutical preparations, e.g. eye washing solutions or eye drops.

Table 56 shows some important areas of use of chlorhexidine digluconate (if not mentioned otherwise) with the corresponding application concentrations.

<table>
<thead>
<tr>
<th>Area of use</th>
<th>Concentration</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eyes</td>
<td>0.01%</td>
<td>BPC eye drop preservative (acetate)</td>
</tr>
<tr>
<td></td>
<td>0.05%</td>
<td>Eye rinse solutions</td>
</tr>
<tr>
<td></td>
<td>0.2%</td>
<td>Highest tolerable gluconate concentration in the eye</td>
</tr>
<tr>
<td>Mucous membranes</td>
<td>0.02%</td>
<td>Rinsing the bladder, pleura and peritoneum, etc.</td>
</tr>
<tr>
<td>Injured skin up to</td>
<td>1.0%</td>
<td>Wounds and burns</td>
</tr>
<tr>
<td>Healthy skin up to</td>
<td>0.5%</td>
<td>in 70% ethanol</td>
</tr>
<tr>
<td>up to</td>
<td>4.0%</td>
<td>1. Skin disinfection before operation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Disinfection of surgeon’s hands before putting on gloves</td>
</tr>
<tr>
<td>Tablets</td>
<td>5 mg</td>
<td>Contained in ICI «Hibiscrub» for hand disinfection and cleaning</td>
</tr>
<tr>
<td>Powder, creams and ointments</td>
<td>0.1-1.0%</td>
<td>All three salts</td>
</tr>
<tr>
<td>Surgical preparations (dry)</td>
<td>0.07-0.13%</td>
<td></td>
</tr>
<tr>
<td>Liquid preparations</td>
<td>up to 2%</td>
<td>For infected wounds</td>
</tr>
<tr>
<td>Gargling solutions</td>
<td>0.1-0.25%</td>
<td></td>
</tr>
</tbody>
</table>

Chlorhexidine salts are also used in the cosmetics sector, e.g. as preservatives for oil-in-water (O/W) emulsions or as the active substance in deodorants. Chlorhexidines belong to a group of products that cause problems during HPLC analysis, which probably can be traced back to their tendency to undergo polymerisation. In HPLC analysis chlorhexidine salts exhibit strong tailing and this means that their quantitative evaluation yields poorly reproducible results. This applies to both chlorhexidine salt raw material and to the determination of chlorhexidine salts in formulations.

17.1.1 Raw materials

The two raw materials chlorhexidine digluconate and chlorhexidine dihydrochloride can be titrated without any problems. It is best to add 1 mL 5% acetic acid to the solution to be titrated. In this way it is ensured that the insoluble free bases cannot be formed; these would otherwise lead to incorrect results.

17.1.1.1 Chlorhexidine digluconate

Chlorhexidine digluconate is normally available as a 20% aqueous solution. For the analysis approx. 0.25 to 0.3 g is weighed out directly into the titration beaker and 100 mL water and 1 mL 5% acetic acid are added to it. The titration is carried out according to the standard instructions given in section 18.5. The evaluation of the titration is performed according to the stoichiometric reaction conditions, i.e. 1 mol chlorhexidine digluconate requires 2 mol sodium tetraphenylborate. The molar mass of chlorhexidine digluconate is 897.77 g/mol.
17.1.1.2 Chlorhexidine dihydrochloride

Chlorhexidine dihydrochloride is supplied in powder form as the pure substance. For the titration 25 to 30 mg are weighed out on a balance which, if possible, should have a display accurate to 0.01 mg. The preparation of a concentrated stock solution is not recommended because the total solubility is only 60 mg/100 mL and chlorhexidine dihydrochloride is not stable in aqueous solution. Its tendency to decompose is considerably favoured by an increased solution temperature or by a pH value above neutral. The sample is slowly dissolved in 100 mL water plus 1 mL 5% acetic acid under careful and slight warming. The titration is again carried out according to the standard instructions given in section 18.5 and the titration is evaluated according to the stoichiometric reaction conditions, i.e. 1 mol chlorhexidine dihydrochloride requires 2 mol sodium tetraphenylborate for salt formation. The molar mass of chlorhexidine dihydrochloride is 578.37 g/mol.

17.1.2 Chlorhexidine in formulations

17.1.2.1 Laryngeal therapeutic agents / throat sprays

Such a formulation could be declared as follows:

1 mL contains:
- 1.1 mg chlorhexidine digluconate
- 5.0 mg aluminium acetate

**Titration conditions:**
- Determination of: chlorhexidine digluconate
- In formulation: throat spray
- Declared concentration: 1.1 mg chlorhexidine digluconate/mL
- Sample weight: 30 to 40 g
- Additive: 1 mL 5% acetic acid
- Sample preparation: none
- Water: up to 100 mL
- Test method: standard instructions, section 18.5
- Electrode: NIO Surfactant Electrode
- Calculation: stoichiometric
- Molar mass: 897.77 g/mol
- Achievable standard deviation: 1%

1 mol chlorhexidine digluconate consumes 2 mol sodium tetraphenylborate

17.1.2.2 Gargling solution

Such a formulation could be declared as follows:

1 mL contains:
- 1.1 mg chlorhexidine digluconate
- Aluminium lactate
- Glycerol
- Ethanol
- Water
- Methanol
- Flavour
- Colourant
- Sodium chloride
- Sodium sulphate

In the determination of chlorhexidine digluconate in a gargling solution no problems have been encountered. The other ingredients in the formulation that are listed here do not interfere with the determination.

**Titration conditions:**
- Determination of: chlorhexidine digluconate
- In formulation: gargling solution
- Declared concentration: 1.1 mg chlorhexidine digluconate/mL
- Sample weight: 40 g
- Additive: 5 mL 5% acetic acid
- Sample preparation: none
- Water: up to 100 mL
- Test method: standard instructions, section 18.5
- Electrode: NIO Surfactant Electrode
- Calculation: stoichiometric
- Molar mass: 897.77 g/mol
- Achievable standard deviation: 1%

1 mol chlorhexidine digluconate consumes 2 mol sodium tetraphenylborate
17.1.2.3 Lozenges

Formulation A

Such a formulation could be declared as follows:

One tablet contains:

- 5 mg chlorhexidine dihydrochloride
- 1.5 mg benzocain
- Auxiliaries
  - Flavours
  - Aspartam
  - Isomalt as sugar substitute

In this tablet formulation based on sugar substitutes the chlorhexidine dihydrochloride content can be titrated without any problems. In this formulation it is important that the sample is heated carefully because of the sensitivity of the chlorhexidine dihydrochloride to decomposition and also that the sample is acidified before the warming process is started.

**Titration conditions:**

Determination of: chlorhexidine dihydrochloride

In formulation: lozenges

Declared concentration: 5 mg chlorhexidine dihydrochloride/tablet

Sample weight: 1 tablet

Additive: 5 mL 5% acetic acid

Sample preparation: standard instructions, section 18.5, paragraph 1. «Tablets»

Water: up to 100 mL

Test method: standard instructions, section 18.5

Electrode: NIO Surfactant Electrode

Calculation: stoichiometric

Molar mass: 578.37 g/mol

Achievable standard deviation: see Table 57

1 mol chlorhexidine dihydrochloride consumes 2 mol sodium tetraphenylborate

**Table 57: Standard deviations obtained in the titration of lozenges based on chlorhexidine dihydrochloride**

<table>
<thead>
<tr>
<th>Number of data</th>
<th>Minimum consumption</th>
<th>Maximum consumption</th>
<th>Mean consumption</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.82 mL</td>
<td>1.97 mL</td>
<td>1.89 mL</td>
<td>0.044 mL</td>
</tr>
</tbody>
</table>

Relative standard deviation: 2.35%

For statistical certainty P 95%

Scatter range ±0.10 mL

Confidence range ±0.03 mL

Reproducibility ±0.14 mL

* Depending on the nonionic surfactant content of the preparation the standard deviation may be worse.

A linearity check was also carried out on these chlorhexidine dihydrochloride-based lozenges. To check the linearity 1, 2, 3, 4, 5 or 6 tablets were placed in a titration beaker, dissolved and then titrated according to the conditions given in section 18.5 (see Figs. 219 and 220). Fig. 220 demonstrates the excellent linearity of this determination method.

**Formulation B**

- Sorbitol
- Talcum
- Dimeticon
- Poly-(1-vinyl-2-pyrrolidone)

Such a formulation could be declared as follows:

One tablet contains:

- 5.0 mg chlorhexidine dihydrochloride
- 2.0 mg benzocain
• Stearic acid triglyceride
• Magnesium stearate

In this lozenge formulation based on talcum, glycerides and magnesium stearate the determination is somewhat more difficult. The reason is probably an interaction between chlorhexidine and one of the auxiliaries in the tablet formulation. However, a reliable determination is possible if the pH value is reduced before the titration; buffering with a pH = 1 buffer allows the quantitative titration of the chlorhexidine dihydrochloride contained in the tablets.

**Titration conditions:**

- **Determination of:** chlorhexidine dihydrochloride
- **In formulation:** lozenges
- **Declared concentration:** 5 mg chlorhexidine dihydrochloride/tablet
- **Sample weight:** 1 tablet
- **Additive:** 10 mL buffer solution pH = 1
- **Sample preparation:** standard instructions, section 18.5, paragraph 1 «Tablets»
- **Water:** up to 100 mL
- **Test method:** standard instructions, section 18.5
- **Electrode:** NIO Surfactant Electrode
- **Calculation:** stoichiometric
- **Molar mass:** 578.37 g/mol
- **Achievable standard deviation:** approx. 2.5%

A reliable determination is possible if the pH value is reduced before the titration; buffering with a pH = 1 buffer allows the quantitative titration of the chlorhexidine dihydrochloride contained in the tablets.

**Such a formulation could be declared as follows:**

100 g contain:

- 32.251 g 1-propanol
- 20.985 g 2-propanol
- 4.2 g 20% chlorhexidine digluconate solution
- 1-tetradecanol
- Macrogol 4000
- Nonoxynol-12
- Macrogol isooctanoate-220
- Colourant
- Flavours
- Purified water

The titration of this alcoholic hand disinfectant functions extremely well, with very easily evaluable titration curves and good standard deviations (Fig. 221).

**Titration conditions:**

- **Determination of:** chlorhexidine digluconate
- **In formulation:** alcoholic hand disinfectant
- **Declared concentration:** 0.84 g chlorhexidine digluconate/100 g
- **Sample weight:** 5 to 6 g
- **Additive:** 1 mL 5% acetic acid
- **Sample preparation:** none
- **Water:** up to 100 mL
- **Test method:** standard instructions, section 18.5
- **Electrode:** NIO Surfactant Electrode
- **Calculation:** stoichiometric
- **Molar mass:** 897.77 g/mol
- **Achievable standard deviation:** <1%

1 mol chlorhexidine digluconate consumes 2 mol sodium tetraphenylborate.

**17.2 Hexetidines**

Hexetidine is the international non-proprietary name for the antiseptic/disinfectant 5-amino-1,3-bis(2-ethylhexyl)hexahydro-5-methylpyrimidine. It is used alone or combined with other quaternary ammonium compounds.
The titration of the active ingredient is easy to carry out. Under the given titration conditions the auxiliaries do not interfere.

**Titration conditions:**

<table>
<thead>
<tr>
<th>Determination of:</th>
<th>hexetidine</th>
</tr>
</thead>
<tbody>
<tr>
<td>In formulation:</td>
<td>gargling solution</td>
</tr>
<tr>
<td>Declared concentration:</td>
<td>1 mg hexetidine/mL</td>
</tr>
<tr>
<td>Sample weight:</td>
<td>40 mL</td>
</tr>
<tr>
<td>Additive:</td>
<td>1 mL 5% acetic acid</td>
</tr>
<tr>
<td>Sample preparation:</td>
<td>none</td>
</tr>
<tr>
<td>Water:</td>
<td>up to 100 mL</td>
</tr>
<tr>
<td>Test method:</td>
<td>standard instructions, section 18.5</td>
</tr>
<tr>
<td>Electrode:</td>
<td>NIO Surfactant Electrode</td>
</tr>
<tr>
<td>Calculation:</td>
<td>stoichiometric</td>
</tr>
<tr>
<td>Molar mass:</td>
<td>339.59 g/mol</td>
</tr>
<tr>
<td>Achievable standard deviation:</td>
<td>see Table 58</td>
</tr>
<tr>
<td>Reproducibility:</td>
<td>±0.72%</td>
</tr>
</tbody>
</table>

1 mol hexetidine consumes 1 mol sodium tetraphenylborate.

<table>
<thead>
<tr>
<th>Number of data</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>99.1%</td>
</tr>
<tr>
<td>Maximum</td>
<td>99.7%</td>
</tr>
<tr>
<td>Mean</td>
<td>99.4%</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.223%</td>
</tr>
<tr>
<td>Relative standard deviation</td>
<td>0.225%</td>
</tr>
<tr>
<td>For statistical certainty P</td>
<td>95%</td>
</tr>
<tr>
<td>Scatter range</td>
<td>±0.51%</td>
</tr>
<tr>
<td>Confidence range</td>
<td>±0.16%</td>
</tr>
</tbody>
</table>

Table 58: Standard deviation for the titration of a gargling solution based on hexetidine

In the quality control sector it is also possible to determine the sum of hexetidine and the nonionic surfactant Polysorbate 80 in addition to the hexetidine content.

**Titration conditions:**

<table>
<thead>
<tr>
<th>Determination of:</th>
<th>sum of hexetidine and Polysorbate 80</th>
</tr>
</thead>
<tbody>
<tr>
<td>In formulation:</td>
<td>gargling solution</td>
</tr>
<tr>
<td>Declared concentration:</td>
<td>hexetidine 1 mg/mL</td>
</tr>
<tr>
<td>Polysorbate 80</td>
<td>not declared</td>
</tr>
<tr>
<td>Sample volume:</td>
<td>2.5 mL</td>
</tr>
<tr>
<td>Additives:</td>
<td>1 mL 5% acetic acid</td>
</tr>
<tr>
<td>10 mL 0.1 mol/L barium chloride solution</td>
<td></td>
</tr>
<tr>
<td>Sample preparation:</td>
<td>none</td>
</tr>
<tr>
<td>Water:</td>
<td>up to 100 mL</td>
</tr>
<tr>
<td>Test method:</td>
<td>standard instructions, section 18.5</td>
</tr>
<tr>
<td>Electrode:</td>
<td>NIO Surfactant Electrode</td>
</tr>
<tr>
<td>Calculation:</td>
<td>hexetidine stoichiometric</td>
</tr>
<tr>
<td>Polysorbate 80</td>
<td>after calibration</td>
</tr>
<tr>
<td>Molar mass:</td>
<td>hexetidine: 339.61 g/mol</td>
</tr>
<tr>
<td>Achievable standard deviation:</td>
<td>1 to 2%</td>
</tr>
</tbody>
</table>

Apart from hexetidine, various antiseptic mouth and throat formulations contain other microbicidal substances such as cetylpyridinium chloride or benzalkonium chloride.

**Formulation B**

Such a formulation could be declared as follows:

100 mL solution contain:

- Hexetidine 100 mg/100 mL
- Cetylpyridinium chloride
- Sodium saccharin
- POE-glycerol monooleate
- Colourants
- Flavours
In such a solution the following titrations can be carried out:

- Determination of the surfactant cetylpyridinium chloride by titration with dodecyl sulphate sodium salt solution; indication by Ionic Surfactant Electrode.
- Joint determination of cetylpyridinium chloride and hexetidine by titration with sodium tetraphenylborate solution; indicator electrode NIO Surfactant Electrode
- Joint determination of cetylpyridinium chloride, hexetidine and POE-glycerol monooleate by titration with sodium tetraphenylborate after previous addition of 10 mL 0.1 mol/L barium chloride solution. Indicator electrode NIO Surfactant Electrode

17.3 Cough medicine

![Ambroxol structural formula]

Raw materials used in cough medicine and the finished preparations containing various active substances were investigated. Cough treatment therapy is approached from different angles.

- Bromhexine as secretion loosener (expectorant)
- Ambroxol as secretion loosener (expectorant)
- Clobutinol as coughing urge suppressor (antitussive)
- Codeine as coughing urge suppressor (antitussive)
- Dihydrocodeine as coughing urge suppressor (antitussive)

17.3.1 Ambroxol

Fig. 223: Structural formula of ambroxol

International non-proprietary name for the expectorant trans-(2-amino-3,5-dibromobenzylamino)-cyclohexanol. An effervescent tablet with ambroxol as active substance could be declared as follows:

1 tablet contains:
- 60 mg ambroxol hydrochloride
- Sodium hydrogen carbonate
- Sodium saccharin
- Sodium benzoate
- Flavours

**Titration conditions:**

<table>
<thead>
<tr>
<th>Determination of:</th>
<th>ambroxol</th>
</tr>
</thead>
</table>

Calculation: stoichiometric
Molar mass: 378.1 g/mol
Achievable standard deviation: not determined

1 mol ambroxol consumes 1 mol sodium tetraphenylborate.

Note: The titration of ambroxol is only possible with 0.1 mol/L sodium tetraphenylborate solution.

17.3.2 Bromhexine

Fig. 224: Structural formula of bromhexine

Bromhexine is international non-proprietary name for the broncholytically active substance 2-amino-3,5-dibromo-N-cyclohexyl-N-methylbenzylamine.

Cough drops

Cough drops based on bromhexine could be declared as follows:

4 mL contain:
- Bromhexine hydrochloride 8 mg
- Methylhydroxybenzoate 4 mg
- Tartaric acid

**Titration conditions:**

<table>
<thead>
<tr>
<th>Determination of:</th>
<th>bromhexine</th>
</tr>
</thead>
</table>

In formulation: cough drops
Declared concentration: 2 mg bromhexine hydrochloride/mL
Sample weight: 25 g
Additive: 1 mL 5% acetic acid
Sample preparation: none
Tables
Cough tablets based on bromhexine could be declared as follows:
1 tablet contains:
- 8 mg bromhexine hydrochloride
- Lactose
- Corn starch
- Magnesium stearate

Titration conditions:
<table>
<thead>
<tr>
<th>Determination of</th>
<th>bromhexine</th>
</tr>
</thead>
<tbody>
<tr>
<td>In formulation</td>
<td>tablets</td>
</tr>
<tr>
<td>Declared concentration</td>
<td>8 mg bromhexine hydrochloride/tablet</td>
</tr>
<tr>
<td>Sample weight</td>
<td>1 tablet</td>
</tr>
<tr>
<td>Additive</td>
<td>1 mL 5% acetic acid</td>
</tr>
<tr>
<td>Sample preparation</td>
<td>standard instructions, section 18.5, paragraph 1. «Tablets»</td>
</tr>
<tr>
<td>Water</td>
<td>up to 100 mL</td>
</tr>
<tr>
<td>Test method</td>
<td>standard instructions, section 18.5</td>
</tr>
<tr>
<td>Electrode</td>
<td>NIO Surfactant Electrode</td>
</tr>
<tr>
<td>Calculation</td>
<td>stoichiometric</td>
</tr>
<tr>
<td>Molar mass</td>
<td>367.14 g/mol (free base)</td>
</tr>
<tr>
<td>Achievable standard deviation</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

1 mol bromhexine consumes 1 mol sodium tetraphenylborate.

Cough mixture
A cough mixture with bromhexine as active substance could be declared as follows:
5 mL solution contain:
- Bromhexine hydrochloride 4 mg
- Benzoic acid 10 mg
- Ethanol 200 mg
- Propylene glycol 300 mg
- Sorbite 2000 mg
- Ammonium chloride
- Hydrated oligosaccharides
- Tartaric acid
- Flavours
- Colourant
- Glycerol
- Hydroxypropylmethylcellulose
- Menthol
- Sodium cyclamate

Titration conditions:
<table>
<thead>
<tr>
<th>Determination of</th>
<th>bromhexine</th>
</tr>
</thead>
<tbody>
<tr>
<td>In formulation</td>
<td>cough mixture</td>
</tr>
<tr>
<td>Declared concentration</td>
<td>0.8 mg bromhexine hydrochloride/mL</td>
</tr>
<tr>
<td>Sample weight</td>
<td>40 g</td>
</tr>
<tr>
<td>Additive</td>
<td>1 mL 5% acetic acid</td>
</tr>
<tr>
<td>Sample preparation</td>
<td>none</td>
</tr>
<tr>
<td>Water</td>
<td>up to 100 mL</td>
</tr>
<tr>
<td>Test method</td>
<td>standard instructions, section 18.5</td>
</tr>
<tr>
<td>Electrode</td>
<td>NIO Surfactant Electrode</td>
</tr>
<tr>
<td>Calculation</td>
<td>stoichiometric</td>
</tr>
<tr>
<td>Molar mass</td>
<td>367.14 g/mol (free base)</td>
</tr>
<tr>
<td>Achievable standard deviation</td>
<td>not determined</td>
</tr>
</tbody>
</table>

1 mol bromhexine consumes 1 mol sodium tetraphenylborate.

17.3.3 Clobutinol
International non-proprietary name for the antitussive 1-(4-chlorophenyl)-4-dimethylamino-2,3-dimethyl-2-butanol.

Drops
Drops against dry coughs could be declared as follows:
20 drops = 0.67 mL solution contain:
- Clobutinol hydrochloride 40 mg
- Benzoic acid 1.34 mg
- Ethanol 12% (volume fraction)
• Sodium saccharin
• Glycerol
• Aniseed oil
• Menthol

**Titration conditions:**

Determination of: clobutinol

In formulation: cough drops

Declared concentration: 59.7 mg clobutinol hydrochloride/mL

Sample weight: 0.5 g

Additive: 1 mL 5% acetic acid

Sample preparation: none

Water: up to 100 mL

Test method: standard instructions, section 18.5

Molar mass: 255.79 g/mol (free base)

Achievable standard deviation: <1%

1 mol clobutinol consumes 1 mol sodium tetraphenylborate.

**Coated cough tablets**

In coated cough tablets based on clobutinol it was not possible to determine the active substance. The cause of this was clearly the poor solubility of the coated tablet.

**17.3.4 Codeine**

**Fig. 226: Structural formula of codeine**

Methyl morphine belongs to the opium alkaloids (from the Greek kodeia = poppy head). Codeine salts are used in antitussives because of their ability to dampen the coughing centre.

Cough drops based on codeine could be declared as follows:

1 g solution = 20 drops contain:

- Codeine phosphate x 1/2 H₂O 10.5 mg equivalent to 8.2 mg codeine
- Phenyltoloxamine dihydrogen citrate 4 mg
- Ethanol 6.3% (volume fraction)
- Parabens
- Citric acid
- Sodium monohydrogen phosphate
- Sodium saccharin

**Titration conditions:**

Determination of: codeine

In formulation: cough drops

Declared concentration: 8.2 mg codeine/g

Sample weight: 15 g = contents of one pack

Additive: 1 mL 5% acetic acid

Sample preparation: none

Water: up to 100 mL

Test method: standard instructions, section 18.5

Electrode: NIO Surfactant Electrode

Calculation: stoichiometric

Molar mass: 299.36 g/mol (free base)

Achievable standard deviation: not determined

1 mol codeine consumes 1 mol sodium tetraphenylborate.

**Note:** The titration of codeine is only possible with 0.1 mol/L sodium tetraphenylborate solution.
A cough stilling solution based on dihydrocodeine could be declared as follows:

1 g solution = 20 drops contain:
- Dihydrocodeine thiocyanate 10 mg
- Flavours
- Benzoic acid
- Glycerol 85
- Sodium saccharin

**Titration conditions:**
- Determination of: dihydrocodeine
- In formulation: drops
- Declared concentration: 10 mg dihydrocodeine thiocyanate/g
- Sample weight: 10 g = contents of one pack
- Additive: 1 mL 5% acetic acid
- Sample preparation: none
- Water: up to 100 mL
- Test method: standard instructions, section 18.5
- Electrode: NIO Surfactant Electrode
- Calculation: stoichiometric
- Molar mass: 301.37 g/mol (free base)
- Achievable standard deviation: not determined

1 mol dihydrocodeine consumes 1 mol sodium tetraphenylborate.

**Note:** The titration of dihydrocodeine is only possible with 0.1 mol/L sodium tetraphenylborate solution.

### 17.4 Anti-allergens

#### 17.4.1 Bamipin

Fig. 228: Structural formula of bamipin

Non-proprietary international name for the antihistamine 4-(N-benzylanilino)-1-methylpiperidine

An anti-allergic gel against sunburn, insect bites, jellyfish stings and itching could be declared as follows:

1 g gel contains:
- 20 mg bamipin lactate
- Methylhydroxy propylcellulose
- POE-6 glycerol caprylate, -caprinate

**Titration conditions:**
- Determination of: bamipin
- In formulation: gel
- Declared concentration: 20 mg bamipin lactate/g
- Sample weight: 2.5 g
- Additive: 1 mL 5% acetic acid
- Sample preparation: none
- Water: up to 100 mL
- Test method: standard instructions, section 18.5
- Electrode: NIO Surfactant Electrode
- Calculation: stoichiometric
- Molar mass: 280.40 g/mol
- Achievable standard deviation: not determined

1 mol bamipin consumes 1 mol sodium tetraphenylborate.

#### 17.4.2 Chlorphenoxamine

Fig. 229: Structural formula of chlorphenoxamine

International non-proprietary name for the anti-allergic agent N-[2-(4-chloro-α-methylbenzylhydroxy)-ethyl]-N,N-dimethylamine

A cream formulation could be declared as follows:

1 g cream, oil-in water (O/W) base contains:
- 15 mg chlorphenoxamine hydrochloride
- Methyl-4-hydroxybenzoate
- Propyl-4-hydroxybenzoate
**Titration conditions:**

<table>
<thead>
<tr>
<th>Determination of:</th>
<th>chlorophenoxamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>In formulation:</td>
<td>cream</td>
</tr>
<tr>
<td>Declared concentration:</td>
<td>15 mg chlorophenoxamine hydrochloride/g</td>
</tr>
<tr>
<td>Sample weight:</td>
<td>1.5 to 2 g</td>
</tr>
<tr>
<td>Additive:</td>
<td>1 mL 5% acetic acid</td>
</tr>
<tr>
<td>Sample preparation:</td>
<td>standard instructions, section 18.5</td>
</tr>
<tr>
<td>Water:</td>
<td>up to 100 mL</td>
</tr>
<tr>
<td>Test method:</td>
<td>standard instructions, section 18.5, paragraph 4. «Cream-based pharmaceuticals»</td>
</tr>
<tr>
<td>Electrode:</td>
<td>NIO Surfactant Electrode</td>
</tr>
<tr>
<td>Calculation:</td>
<td>stoichiometric</td>
</tr>
<tr>
<td>Molar mass:</td>
<td>303.84 g/mol (free base)</td>
</tr>
<tr>
<td>Achievable standard deviation:</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

1 mol pharmaceutical preparation consumes 1 mol sodium tetraphenylborate.

### Gels

A gel formulation could be declared as follows.

1 g fat-free gel base contains:
- 15 mg chlorophenoxamine hydrochloride
- Methyl-4-hydroxybenzoate
- Propyl-4-hydroxybenzoate

**Titration conditions:**

<table>
<thead>
<tr>
<th>Determination of:</th>
<th>chlorophenoxamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>In formulation:</td>
<td>cream</td>
</tr>
<tr>
<td>Declared concentration:</td>
<td>15 mg chlorophenoxamine hydrochloride/g</td>
</tr>
<tr>
<td>Sample weight:</td>
<td>1.5 to 2 g</td>
</tr>
<tr>
<td>Additive:</td>
<td>1 mL 5% acetic acid</td>
</tr>
<tr>
<td>Sample preparation:</td>
<td>standard instructions, section 18.5</td>
</tr>
<tr>
<td>Water:</td>
<td>up to 100 mL</td>
</tr>
<tr>
<td>Test method:</td>
<td>standard instructions, section 18.5, paragraph 4. «Cream-based pharmaceuticals»</td>
</tr>
<tr>
<td>Electrode:</td>
<td>NIO Surfactant Electrode</td>
</tr>
<tr>
<td>Calculation:</td>
<td>stoichiometric</td>
</tr>
<tr>
<td>Molar mass:</td>
<td>303.84 g/mol (free base)</td>
</tr>
<tr>
<td>Achievable standard deviation:</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

1 mol pharmaceutical preparation consumes 1 mol sodium tetraphenylborate.

### 17.5 Antimalaria drugs

#### 17.5.1 Cloroquin

**Fig. 230: Structural formula of cloroquin**

This is one of the original drugs for malaria prophylaxis and against malaria, well known under the brand name Rechorchin. It is the international non-proprietary name for 7-chloro-4-(4-diethylamino-1-methylbutylamino)-quino-line which is effective against amoebas and plasmodia (malaria).

An antimalaria drug based on cloroquin could be declared as follows.

- Cloroquin phosphate

**Titration conditions:**

<table>
<thead>
<tr>
<th>Determination of:</th>
<th>cloroquin</th>
</tr>
</thead>
<tbody>
<tr>
<td>In formulation:</td>
<td>tablets</td>
</tr>
<tr>
<td>Declared concentration:</td>
<td>¼ tablet</td>
</tr>
<tr>
<td>Sample weight:</td>
<td>1 mL 5% acetic acid</td>
</tr>
<tr>
<td>Additive:</td>
<td>standard instructions, section 18.5, paragraph 1. «Tablets»</td>
</tr>
<tr>
<td>Sample preparation:</td>
<td>up to 100 mL</td>
</tr>
<tr>
<td>Water:</td>
<td>standard instructions, section 18.5</td>
</tr>
<tr>
<td>Test method:</td>
<td>NIO Surfactant Electrode</td>
</tr>
<tr>
<td>Electrode:</td>
<td>stoichiometric</td>
</tr>
<tr>
<td>Calculation:</td>
<td>319.89 g/mol</td>
</tr>
<tr>
<td>Molar mass:</td>
<td>not determined</td>
</tr>
<tr>
<td>Achievable standard deviation:</td>
<td>not determined</td>
</tr>
</tbody>
</table>

1 mol cloroquin consumes 1 mol sodium tetraphenylborate.
17.6 Pharmaceuticals for the stomach

17.6.1 Metoclopramid

![Structural formula of metoclopramid](image)

International non-proprietary name for the anti-emetic 4-amino-5-chloro-N-[2-(diethylamino)-2-methoxybenzamide.

A solution could be declared as follows.

1 mL solution = 17 drops contains:

5.97 mg metoclopramid hydrochloride monohydrate = 5.67 mg metoclopramid hydrochloride

**Titration conditions:**

**Determination of:** metoclopramid

**In formulation:** drops

**Declared concentration:** 5.97 mg metoclopramid hydrochloride monohydrate/mL

**Sample volume:** 4 mL

**Additive:** 1 mL 5% acetic acid

**Sample preparation:** none

**Water:** up to 100 mL

**Test method:** standard instructions, section 18.5

**Electrode:** NIO Surfactant Electrode

**Calculation:** stoichiometric

**Molar mass:** 299.81 (free base)

**Achievable standard deviation:** <0.5%

1 mol metoclopramid consumes 1 mol sodium tetraphenylborate.

17.7 Antimycotics

17.7.1 Clotrimazol

International non-proprietary name for the antimycotic 1-[[2-chlorophenyl]-diphenylmethyl]-1-H-imidazol.

**Cream**

A cream against dermatomycosis could be declared as follows:

1 g cream contains in an oil-in-water (O/W) base:

- 10 mg clotrimazol
- 2-octyldodecanol
- Benzyl alcohol
- Polysorbate 60
- Cetyl palmitate
- Sorbitan stearate
- Cetearyl alcohol

**Titration conditions:**

**Determination of:** clotrimazol

**In formulation:** O/W cream

**Declared concentration:** 10 mg clotrimazol/g

**Sample weight:** 3 g

**Additive:** 1 mL 5% acetic acid standard instructions, section 18.5, paragraph 4. «Cream-based pharmaceuticals»

**Sample preparation:** standard instructions, section 18.5, paragraph 4. «Cream-based pharmaceuticals»

**Water:** up to 100 mL

**Test method:** standard instructions, section 18.5

**Electrode:** NIO Surfactant Electrode

**Calculation:** stoichiometric

**Molar mass:** 344.84 g/mol

**Achievable standard deviation:** <1%

1 mol clotrimazol consumes 1 mol sodium tetraphenylborate.

**Solution**

A solution for treatment of fungal skin diseases could be declared as follows:

1 mL solution contains:

- 10 mg clotrimazol
- 2-propanol
- Macrogol 400
- Propylene glycol

**Titration conditions:**

**Determination of:** clotrimazol

**In formulation:** solution

**Declared concentration:** 10 mg clotrimazol/mL

**Sample weight:** 3 g (conversion to volume necessary)

**Additive:** 1 mL 5% acetic acid

**Sample preparation:** none

**Water:** up to 100 mL

**Test method:** standard instructions, section 18.5

**Electrode:** NIO Surfactant Electrode

**Calculation:** stoichiometric

**Molar mass:** 344.84 g/mol

**Achievable standard deviation:** <0.5%

1 mol clotrimazol consumes 1 mol sodium tetraphenylborate.

![Structural formula of clotrimazol](image)
17.8 Miscellaneous

17.8.1 Papaverine

Fig. 233: Structural formula of papaverine

\[
\text{Papaverine} = 1-\text{OCH}_3-6,7-\text{dimethoxyisoquinoline}-6,7-\text{dimethoxy-1-veratrylisoquinoline}
\]

17.8.2 Lidocaine

Fig. 234: Structural formula of lidocaine

International non-proprietary name for the local anaesthetic and anti-arrhythmic agent \(2'-\text{diethylamino-2',6'-dimethylacetanilide}\). An injection solution for local anaesthesia (as used by a dentist on his patients) could be declared as follows:

1 mL injection solution contains:
• Lidocaine hydrochloride 50.0 mg
• Glucose monohydrate 75 mg

17.8.3 Propafenone

Fig. 23: Structural formula of propafenone

International non-proprietary name for the active agent against cardiac arrhythmia \((RS)-2'-\text{2-hydroxy-3-propylaminopropoxy)-3-phenylpropionphenone}\). Drops against cardiac arrhythmia
Some linearity investigations have been carried out on propafenone. The linearity was excellent both at high and low sample weights.

![Fig. 236: Linearity investigation on propafenone, titration curves](image1)

![Fig. 237: Linearity investigation on propafenone](image2)

**Table 59: Pharmaceuticals that can be titrated**

<table>
<thead>
<tr>
<th>Active agent</th>
<th>Form</th>
<th>Concentration</th>
<th>Titration possible?</th>
<th>Additional information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambroxol hydrochloride</td>
<td>Drops</td>
<td>0.75%</td>
<td>Yes</td>
<td>0.1 mol/L TPB</td>
</tr>
<tr>
<td>Bromhexine hydrochloride</td>
<td>Drops</td>
<td>0.2%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Bromhexine hydrochloride</td>
<td>Tablets</td>
<td>8 mg/tabl.</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Bromhexine hydrochloride</td>
<td>Juice</td>
<td>0.08%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Chlorhexidine gluconate</td>
<td>Solution</td>
<td>4.2%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Chlorhexidine gluconate</td>
<td>Solution</td>
<td>20%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Chlorhexidine gluconate</td>
<td>Solution</td>
<td>0.11%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Chlorhexidine gluconate</td>
<td>Solution</td>
<td>0.1%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Chlorhexidine dihydrochloride</td>
<td>Powder</td>
<td>100%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Chlorhexidine dihydrochloride</td>
<td>Tablets</td>
<td>5 mg/tabl.</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Chlorhexidine dihydrochloride</td>
<td>Tablets</td>
<td>5 mg/tabl.</td>
<td>Yes</td>
<td>pH = 3</td>
</tr>
<tr>
<td>Chlorhexidine dihydrochloride</td>
<td>Solution</td>
<td>1%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Chlorhexidine dihydrochloride</td>
<td>Cream</td>
<td>1%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Chlorhexidine dihydrochloride</td>
<td>Drops</td>
<td>0.05%</td>
<td>Yes</td>
<td>0.1 mol/L TPB</td>
</tr>
<tr>
<td>Phenyltoloxamine dihydrogen citrate</td>
<td>Drops</td>
<td>0.40%</td>
<td>Yes</td>
<td>pH = 3 0.01 mol/L TPB</td>
</tr>
<tr>
<td>Dihydrocodeine thiocyanate</td>
<td>Drops</td>
<td>1.0%</td>
<td>Yes</td>
<td>0.1 mol/L TPB or pH = 3 0.01 mol/L TPB</td>
</tr>
<tr>
<td>Ethacridine lactate</td>
<td>Powder</td>
<td>100%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Ethacridine lactate</td>
<td>Solution</td>
<td>0.1%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Ipratropium bromide</td>
<td>Solution</td>
<td>0.025%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Metoclopramide hydrochloride</td>
<td>Drops</td>
<td>0.50%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Octenidin dihydrochloride</td>
<td>Solution</td>
<td>0.1%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Salbutamol sulphate</td>
<td>Solution</td>
<td>0.5%</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Verapamil hydrochloride</td>
<td>Blister tablets</td>
<td>80 mg/tabl.</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>
Table 60: Pharmaceuticals that cannot be titrated

<table>
<thead>
<tr>
<th>Active agent</th>
<th>Form</th>
<th>Concentration</th>
<th>Titration possible?</th>
<th>Additional information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl cysteine</td>
<td>Effervescent tablets</td>
<td>200 mg/tabl.</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Acetylsalicylic acid</td>
<td>Tablets</td>
<td>500 mg/tabl.</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Bromhexine hydrochloride + sulphonamide</td>
<td>Coated tablets</td>
<td>4 mg/tabl.</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Quinolinol sulphate potassium sulphate</td>
<td>Powder</td>
<td></td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Clobutinol</td>
<td>Coated tablets</td>
<td>40 mg/tabl.</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>Powder</td>
<td></td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Diazepam</td>
<td>Tablets</td>
<td>5 mg/tabl.</td>
<td>No</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Doxycycline hydrochloride</td>
<td>Tablets</td>
<td>230 mg/tabl.</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Etilefrin hydrochloride</td>
<td>Capsules</td>
<td>25 mg/cap.</td>
<td>No</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Etilefrin hydrochloride</td>
<td>Solution</td>
<td>0.75%</td>
<td>No</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>Tablets</td>
<td>200 mg/tabl.</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Methylprednisolone</td>
<td>Tablets</td>
<td>40 mg/tabl.</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Sodium picosulphate</td>
<td>Drops</td>
<td></td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Paracetamol</td>
<td>Tablets</td>
<td>500 mg/tabl.</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Piretanid</td>
<td>Tablets</td>
<td>6 mg/tabl.</td>
<td>No</td>
<td></td>
</tr>
</tbody>
</table>
18.6 Potentiometric determination of betains with sodium tetr phenylborate

Materials and reagents

NIO surfactant electrode (Metrohm 6.0507.01O)
6.0726.100 Ag/AgCl double-junction reference electrode with sleeve diaphragm (inner electrolyte 3 mol/L KCl, outer electrolyte 3 mol/L NaCl)
Automatic titrator with peripherals (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736 or 751 Titrino)
20 mL Exchange Unit with amber glass bottle and light protection (Metrohm 6.3012.223)
100 mL Beaker

Hydrochloric acid c = 0.1 mol/L (e.g. prepared from concentrated HCl or from Merck Titrisol)
Gum arabic (e.g. SIGMA G-9752)
0.1 mol/L sodium tetr phenylborate solution

Preparation of the gum arabic solution

In order to prepare 1 L gum arabic solution, 50 g gum arabic powder are weighed out. Gum arabic is a very fine white powder (SIGMA). 1 L distilled water is heated in a suitable beaker almost to boiling point. The gum arabic powder is added under vigorous stirring. The powder immediately clumps but slowly dissolves under vigorous stirring. The solution is then allowed to cool down and preserved with 10 mL 30% formaldehyde solution (Merck). Preservation is necessary to achieve a longer working life for the solution. In this concentration formaldehyde does not interfere with the titration. The finished solution has a slight yellowish colour. A brown precipitate appears at the bottom of the beaker after standing overnight. This is removed by decanting off, but does not interfere with the titration. The solution is now ready for use.

Titration parameters

Titration parameters for the Metrohm 670 and 726 Titroprocessor and 716, 736 and 751 Titrino are given below. If a different titrator is used then the parameters should be adapted accordingly.

**670 Titroprocessor**
- Meas 1
- Quantity: U
- Drift/min: off mV
- M.Delay: 32 s
- DynT 1
- meas.pt.density: 4
- Dos.Rate/min: 30.000 ml
- f.VResol: 0.10
- TStop
- N.EPs: 8
- Volume: 15.000 ml
- M.Value: Off

**726 Titroprocessor**
- Meas 1
- Quantity: U
- Drift/min: off mV
- M.Delay: 32 s
- DynT 1
- meas.pt.density: 4
- Dos.Rate/min: 30.000 ml
- f.VResol: 0.10
- TStop
- N.EPs: 8
- Volume: 15.000 ml
- M.Value: Off

**716, 736, 751 Titrino**
- Meas 1
- Quantity: U
- Drift/min: off mV
- M.Delay: 32 s
- DynT 1
- meas.pt.density: 4
- Dos.Rate/min: 30.000 ml
- f.VResol: 0.10
- TStop
- N.EPs: 8
- Volume: 15.000 ml
- M.Value: Off

Sample weight

The sample weight should be selected so that the titrant consumption is between 5 and 8 mL. If the titrant consumption lies outside this range then the sample weight should be corrected and the titration repeated. If the betain content is not known then it is a good idea to carry out a trial titration in order to determine the required sample weight.

Carrying out the betain determination

A suitable amount of the homogeneous sample is weighed out exactly to 0.1 mg into a titration beaker. The sample is dissolved in 90 mL 0.1 mol/L hydrochloric acid and then 10 mL gum arabic solution are added. The titration is now carried out by the titrator against 0.1 mol/L sodium tetr phenylborate solution using the electrode combination and the titration parameters mentioned above.

Calculation

The betain content is calculating using the mean molar mass of the betain to be determined in the sample.

\[
\% \text{betain} = \frac{V \times c \times M}{E \times 10}
\]

Equation 41

where

- \( V \) consumption of 0.1 mol/L sodium tetr phenylborate solution in mL
- \( c \) concentration of sodium tetr phenylborate solution (0.1 mol/L)
- \( M \) mean molar mass of the betain to be determined in g/mol

\( E \) sample weight in g

The calculation formula given above must be converted into the form used by the titrator.

Presentation of the result
The betain content is given to one decimal place. The molar mass on which the calculation is based should also be mentioned. A typical alkylamidopropylbetain based on hardened coconut oil has a molar mass of approx. 350 g/mol.

18.7 Potentiometric determination of the betain content with perchloric acid

**Materials and reagents**

- Automatic titrator (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736 or 751 Titrino)
- Motor-driven piston burette (Metrohm 665 Dosimat)
- 20 mL Exchange Unit (Metrohm 6.3012.220)
- pH glass electrode (e.g. Metrohm 6.0104.100)
- 6.0726.100 Ag/AgCl double-junction reference electrode with sleeve diaphragm (inner electrolyte 3 mol/L KCl, outer electrolyte LiCl sat. in Ethanol)
- 1 L Volumetric flask, class A
- 1,4-dioxan, analytical grade (e.g. Riedel-de Haen 33147)
- Methyl glycol, analytical grade (e.g. Riedel-de Haen 33457)
- Fixanal 0.1 mol/L perchloric acid (e.g. Riedel-de Haen 38330)
- Methanol, analytical grade (e.g. Riedel-de Haen 32213)
- Fixanal 1 mol/L sodium hydroxide (e.g. Riedel-de Haen 38215)
- Sodium acetate + 3 H₂O (e.g. Riedel-de Haen 32318)

**Preparation of the 0.1 mol/L perchloric acid solution**

Approx. 150 mL 1,4-dioxan are placed in a 1 L volumetric flask made of amber glass. The Fixanal ampoule is placed on the neck, opened according to the instructions and the contents quantitatively transferred into the flask with 1,4-dioxan. The solution must now be mixed immediately in order to achieve rapid dilution of the perchloric acid. The flask is then filled up to the mark with 1,4-dioxan and mixed thoroughly again.

**Preparation of the sodium hydroxide/sodium acetate solution**

80 g sodium acetate are dissolved in approx. 300 mL water and transferred to a 1 L volumetric flask. The contents of a Fixanal ampoule of 1 mol/L sodium hydroxide are added and the flask filled up to the mark with water. NaOH pellets can also be used as an alternative to a Fixanal ampoule. In this case 40 g NaOH pellets are weighed out into a beaker and dissolved in approx. 300 mL water. This solution is cooled down and transferred to the volumetric flask containing the sodium acetate. The flask is then filled up to the mark with water and mixed thoroughly. If NaOH pellets are used then a smaller amount of the solution can be prepared; this is done simply by adjusting the amounts of sodium acetate and NaOH given above.

**Titrator settings**

The titration parameters for the Metrohm 670 and 726 Titroprocessor and 716, 736 and 751 Titrino are given below. If a titrator from a different manufacturer is used then the parameters should be adapted accordingly.

**670 Titroprocessor**

- Meas 1: 30 s
- Quantity: U
- Drift/min: 50 mV
- M.Delay: 26 s
- V.Inrem: 6 ml
- equilibr.time: 30 s
- pause: 30 s

**726 Titroprocessor**

- Pause: 30 s
- Meas.pt.density: 4
- Min.increment: 10.0 µl
- Titr. rate: 30 mL/min
- Signal drift: off
- Equilibr.time: 30

**716, 736 or 751 Titrino**

**Evaluation**

The sodium hydroxide/sodium acetate solution is added and allowed to react for 5 to 10 minutes at room temperature. A few drops of 0.1% ethanolic phenolphthalein solution can be added to check whether the sample has become alkaline after the addition of sodium hydroxide. When the reaction time has elapsed, 20 mL methanol and 60 mL methyl glycol are added and the titration is carried out against 0.1 mol/L perchloric acid in dioxan using the titration parameters given above. A list of possible errors is given in Table 17 (section 7.6.1).

Equation 42

\[ \% \text{betain} = \frac{V(EP2 - EP1) \times M(\text{betain}) \times c(\text{HClO}_4)}{m \times 10} \]
18.1.2 The determination of cationic substances with the Ionic Surfactant Electrode

Materials and reagents

0.004 mol/L dodecyl sulphate sodium salt solution (instead of the 0.004 mol/L solution a \( c = 0.005 \) mol/L solution can also be used – in calculating the sample weight and the results the concentration must always be taken into account).

The preparation and titre determination of this solution is described in section 6.3.2.

Buffer solution pH = 10 (e.g. prepared form Titrisol, Merck 9890)

Methanol, analytical grade (e.g. Riedel-de Haén 32213)

Analytical balance, e.g. Sartorius A 200 S

Automatic titrator with peripherals (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736 or 751 Titrino)

Surfactant electrode (Metrosensor Ionic Surfactant Electrode 6.0507.120)

Ag/AgCl reference electrode with sleeve diaphragm: Metrohm 6.0726.100 double-junction reference electrode, 3 mol/L KCl as inner and outer electrolyte

Titrination beakers (matched to sample changer, if present)

Measuring cylinder 100 mL

Measuring cylinder 25 mL

Procedure

The titration should be carried out with a titrator that allows dynamic titrant addition, i.e. a titrator that adapts the volume increments to the change of the electrode potential.

The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be recognised.

Titration parameters

In selecting the suitable titration parameters the slope of the titration curve in the region of the point of inflection is decisive. Three basic methods are normally sufficient, one method each for steep, intermediate and flat titration curves. A list of parameters for use with the Metrohm 670 Titroprocessor and the 716, 736 or 751 Titrino is given below for each of these three methods. If a different titrator is used then the parameters should be adapted accordingly.

<table>
<thead>
<tr>
<th>Steep titration curve</th>
<th>Intermediate titration curve</th>
<th>Flat titration curve</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>670 Titroprocessor</strong></td>
<td><strong>670 Titroprocessor</strong></td>
<td><strong>670 Titroprocessor</strong></td>
</tr>
<tr>
<td>Meas 1</td>
<td>Meas 1</td>
<td>Meas 1</td>
</tr>
<tr>
<td>Quantity</td>
<td>Quantity</td>
<td>Quantity</td>
</tr>
<tr>
<td>Drift/min</td>
<td>Drift/min</td>
<td>Drift/min</td>
</tr>
<tr>
<td>M.Delay</td>
<td>M.Delay</td>
<td>M.Delay</td>
</tr>
<tr>
<td>DynT 1</td>
<td>DynT 1</td>
<td>DynT 1</td>
</tr>
<tr>
<td>MPT:Density</td>
<td>MPT:Density</td>
<td>MPT:Density</td>
</tr>
<tr>
<td>Dos.Rate/min</td>
<td>Dos.Rate/min</td>
<td>Dos.Rate/min</td>
</tr>
<tr>
<td>t:VResol</td>
<td>t:VResol</td>
<td>t:VResol</td>
</tr>
<tr>
<td>TStop</td>
<td>TStop</td>
<td>TStop</td>
</tr>
<tr>
<td>N.EPs</td>
<td>N.EPs</td>
<td>N.EPs</td>
</tr>
<tr>
<td>Volume</td>
<td>Volume</td>
<td>Volume</td>
</tr>
<tr>
<td>M.Value</td>
<td>M.Value</td>
<td>M.Value</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>716, 736 or 751 Titrino</strong></td>
<td><strong>716, 736 or 751 Titrino</strong></td>
<td><strong>716, 736 or 751 Titrino</strong></td>
</tr>
<tr>
<td>titration parameters</td>
<td>titration parameters</td>
<td>titration parameters</td>
</tr>
<tr>
<td>meas.pt.density</td>
<td>meas.pt.density</td>
<td>meas.pt.density</td>
</tr>
<tr>
<td>min.incr.</td>
<td>min.incr.</td>
<td>min.incr.</td>
</tr>
<tr>
<td>titr.rate</td>
<td>titr.rate</td>
<td>titr.rate</td>
</tr>
<tr>
<td>signal drift</td>
<td>signal drift</td>
<td>signal drift</td>
</tr>
<tr>
<td>equilibr.time</td>
<td>equilibr.time</td>
<td>equilibr.time</td>
</tr>
<tr>
<td>pause</td>
<td>pause</td>
<td>pause</td>
</tr>
<tr>
<td>stop conditions</td>
<td>stop conditions</td>
<td>stop conditions</td>
</tr>
<tr>
<td>stop V:</td>
<td>stop V:</td>
<td>stop V:</td>
</tr>
<tr>
<td>stop V</td>
<td>stop V</td>
<td>stop V</td>
</tr>
<tr>
<td>evaluation</td>
<td>evaluation</td>
<td>evaluation</td>
</tr>
</tbody>
</table>

726 Titroprocessor

Pause 30 s

Meas.pt.density 5

Min.increment 10 µl

Titr. rate max

Signal drift 15 mV/min

Equilibr.time auto

202

Titrimetric determination of surfactants and pharmaceuticals
The delay of 30 seconds before the start of the titration is necessary so that the electrodes can adapt themselves to the titration solution.

We recommend that the original curve and the first derivative curve are printed out for each titration and that the results and the raw data are stored on a computer.

**Sample weights**

The sample weight should be calculated so that a consumption of 0.004 mol/L (or 0.005 mol/L) titrant solution between 10 and 15 mL is obtained. If the consumption in the titration is outside this range then the results should not be used and the titration should be repeated with a corrected sample weight. If the consumption is below 10 mL then, depending on the surfactant being analysed, too low results must be expected.

With most raw materials or very high surfactant content it is not a good idea to weigh out the sample directly for the titration because the amount of substance is so small that this would result in an error of 1% or even more. In such cases an intermediate dilution should be made in a volumetric flask and an aliquot of this taken with a pipette. The substantivity, i.e. the tendency of the surfactant to be attracted to surfaces, is particularly noticeable with cationic surfactants. In order to eliminate or minimise surfactant properties methanol should be selected for making the dilutions. The easiest way is to select the aliquot so that the volume concentration of methanol in the subsequent sample solution is 5%.

**Procedure**

A suitable amount of the homogeneous sample is weighed out exactly to 0.1 mg into the titration beaker or the aliquot of a stock solution is pipetted into the titration beaker. If the sample has been weighed in directly then it is dissolved in 5 mL methanol; if a stock solution is used this dissolution step is not necessary. 10 mL of the pH = 10 buffer solution are now added and the solution made up to a total volume of 100 mL with water.

The titration is now carried out by the titrator using the above-mentioned electrodes with the appropriate parameters. It may be necessary to carry out a trial titration before the determination itself in order to select the suitable parameters.

During the titration the mixing of the sample is particularly important. The use of a magnetic stirrer with stirrer bar should be avoided if possible, as an adequate mixing of the solution is not possible without the entrainment of air bubbles (vortex formation). Good mixing without air bubble entrainment is best achieved with a propeller stirrer such as is used in the Metrohm 730 and 760 Sample Changers and also in the 727 Titration Stand with 722 Rod Stirrer. As the stirrer parameters are extremely important for surfactant titration, a mark should be made on the rod stirrer to enable a setting which has been optimised to be reproduced later.

**Evaluation**

The calculation of the cationic surfactants content can be carried out in various ways. If the molar mass of the surfactant to be determined is known and if a mixture of different cationic surfactants is not involved then the content of the corresponding surfactant can be calculated directly. If several cationic surfactants with different molar masses are present then a total content is determined and can only be calculated as surfactant N (nitrogen) or e.g. in mmol cationics/100 g.

**Calculation as surfactant N:**

\[
\text{% surfact} - N = \frac{V \times t \times c \times M}{10 \times E}
\]

*Equation 22*

\[
\text{mmol cationics / 100 g subst.} = \frac{V \times t \times c \times 100}{E}
\]

Calculation in mmol cationics/100 g substance:

\[
\text{% cationics} = \frac{V \times t \times c \times M}{10 \times E}
\]

Calculation as cationic surfactant of known molar mass:

\[
\text{M} \quad \text{molar mass of the surfactant to be determined}
\]

\[
\text{E} \quad \text{sample weight in g}
\]

The calculation formulae given above must be converted into the forms used by the titrator.

A Metrohm Application Bulletin has been published on this topic.¹³
18.2. Potentiometric two-phase titration

18.2.1 Titration of anionic surfactants with 0.004 mol/L (or 0.005 mol/L) TEGO trant A100 solution using the Surfactrode Resistant

Materials and reagents
0.004 mol/L TEGO trant A100 solution (instead of the 0.004 mol/L solution a c = 0.005 mol/L solution can also be used – in calculating the sample weight and the results the concentration must always be taken into account).
The preparation and titre determination of this solution is described in section 6.2.2.
Aqueous sulphuric acid c(H$_2$SO$_4$) = 0.05 mol/L
Ethanol, denatured
Methyl isobutyl ketone (MIBK)
Solvent mixture ethanol : MIBK (1 : 1)
TEGO add

Analytical balance, e.g. Sartorius A 200 S
Automatic titrator with peripherals (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736 or 751 Titrino)
pH electrode, Metrohm 6.0233.100
Surfactrode Resistant electrode, Metrohm 6.0507.130)Ag/AgCl reference electrode with sleeve diaphragm: Metrohm 6.0726.100 double-junction reference electrode, 3 mol/L KCl as inner and outer electrolyte
Titration beakers (matched to sample changer, if present)
Measuring cylinder 100 mL
Measuring cylinder 25 mL

Procedure
Parameters to be generally observed
In potentiometric two-phase titration the influence of salts must be taken into account. This influence is described in detail in section 5.11.
Sample mixing is very important, particularly in potentiometric two-phase titration. See also section 5.8.
The titration should be carried out with a titrator that allows dynamic titrant addition, i.e. a titrator that adapts the volume increments to the change of the electrode potential.
The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be recognised.

Titration parameters
The titration parameters for the 726 Titroprocessor and the 716, 736 or 751 Titrino are given below.

<table>
<thead>
<tr>
<th>726 Titroprocessor</th>
<th>716, 736 or 751 Titrino</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pause</td>
<td>30 s</td>
</tr>
<tr>
<td>Meas.pt.density</td>
<td>0</td>
</tr>
<tr>
<td>Min.increment</td>
<td>150 µl</td>
</tr>
<tr>
<td>Titr. rate</td>
<td>max</td>
</tr>
<tr>
<td>Signal drift</td>
<td>off</td>
</tr>
<tr>
<td>Equilibr.time</td>
<td>30 s</td>
</tr>
<tr>
<td>titration parameters</td>
<td></td>
</tr>
<tr>
<td>meas.pt.density</td>
<td>0</td>
</tr>
<tr>
<td>min.incr.</td>
<td>150 µl</td>
</tr>
<tr>
<td>titr.rate</td>
<td>max</td>
</tr>
<tr>
<td>signal drift</td>
<td>off</td>
</tr>
<tr>
<td>equilibr.time</td>
<td>30 s</td>
</tr>
<tr>
<td>pause</td>
<td>30 s</td>
</tr>
<tr>
<td>stop conditions</td>
<td></td>
</tr>
<tr>
<td>stop V:</td>
<td>abs.</td>
</tr>
<tr>
<td>stop V</td>
<td>20 mL</td>
</tr>
<tr>
<td>evaluation</td>
<td></td>
</tr>
<tr>
<td>EP recognition</td>
<td>all</td>
</tr>
</tbody>
</table>

We recommend that the original curve and the first derivative curve are printed out for each titration and that the results and the raw data are stored on a computer.

Sample weight
The sample weight should be calculated so that a consumption of 0.004 mol/L (or 0.005 mol/L) titrant solution between 10 and 15 mL is obtained. If the consumption in the titration is outside this range then the results should not be used and the titration should be repeated with a corrected sample weight. If the consumption is below 10 mL then, depending on the surfactant being analysed, too low results must be expected.
With most raw materials or very high surfactant content it is not a good idea to weight out the sample directly for the titration because the amount of substance is so small that this would result in an error of 1% or even more. In such cases an intermediate dilution should be made in a volumetric flask and an aliquot of this taken with a pipette. With water-insoluble raw materials the intermediate dilution can be carried out using ethanol. The amount of ethanol in the aliquot must then be taken into account. It is easiest to prepare the stock solution so that an aliquot of 10 mL can be taken.

Procedure
The procedure depends on the sample preparation method:

a) Sample weighed in directly
A suitable amount of the homogeneous sample is weighed out exactly to 0.1 mg into the titration beaker. The sample is dissolved in approx. 80 mL water. The pH of the solution is adjusted to pH = 3 with 0.05 mol/L H$_2$SO$_4$ solution. 20 mL of the ethanol : MIBK mixture are added followed by 200 µL TEGO add.

b) Aliquot of an aqueous stock solution
The aliquot of an aqueous stock solution is pipetted into a titration beaker and made up to approx. 80 mL with water. The pH of the solution is adjusted to pH = 3 with aqueous H₂SO₄ solution. 20 mL of the ethanol : MIBK mixture are added followed by 200 µL TEGO add.

c) **Aliquot of an ethanolic stock solution**

If an ethanolic stock solution has been prepared then the amount of ethanol in the aliquot must be taken into account. The volume concentration of ethanol in the titration solution should not exceed 10%. Water is added up to approx. 80 mL and the pH of the solution is adjusted to pH = 3 with aqueous H₂SO₄ solution. 10 mL MIBK are added followed by 200 µL TEGO add.

The titration is now carried out by the titrator using the above-mentioned electrodes with the appropriate parameters.

Sample mixing during the titration is particularly important. The two phases must be so thoroughly mixed that they form a stable emulsion in which as little air as possible is entrained.

The use of a magnetic stirrer with stirrer bar is absolutely unsuitable for this purpose as adequate mixing of the solution without the entrainment of air bubbles is not possible (vortex formation). Good mixing without air bubble entrainment is best achieved with a propeller stirrer such as is used in the Metrohm 730 and 760 Sample Changers and also in the 727 Titation Stand with 722 Rod Stirrer. As the stirrer parameters are extremely important for surfactant titration, a mark should be made on the rod stirrer to enable a setting which has been optimised to be reproduced later.

If the MIBK is replaced by chloroform for the titration then the stirrer speed should be increased accordingly.

**Evaluation**

The calculation of the anionic surfactants content can be carried out in various ways. If the molar mass of the surfactant to be determined is known and if a mixture of different anionic surfactants is not involved then the content of the corresponding surfactant can be calculated directly. If several anionic surfactants with different molar masses are present then a total content is determined and can only be calculated as surfactant S (sulphur) or e.g. in mmol anionics/100 g.

**Calculation as surfactant S:**

\[
\% \text{ surfact } S = \frac{V \cdot t \cdot c \cdot M}{10 \cdot E}
\]

**Equation 25**

where

- $V$ consumption of 0.004 mol/L (or 0.005 mol/L) TEGO trant A100 solution in mL
- $t$ titre of TEGO trant A100 solution
- $c$ molar concentration of TEGO trant A100 solution (0.004 mol/L (or 0.005 mol/L))
- $M$ molar mass of sulphur (32.06 g/mol)

**Calculation in mmol anionics/100 g substance:**

\[
\text{mmol anionics } / 100 \text{g subst.} = \frac{V \cdot t \cdot c \cdot 100}{E}
\]

**Equation 26**

where

- $V$ consumption of 0.004 mol/L (or 0.005 mol/L) TEGO trant A100 solution in mL
- $t$ titre of TEGO trant A100 solution
- $c$ molar concentration of TEGO trant A100 solution (0.004 mol/L (or 0.005 mol/L))
- $E$ sample weight in g

**Calculation as anionic surfactant of known molar mass:**

\[
\% \text{ anionics } = \frac{V \cdot t \cdot c \cdot M}{10 \cdot E}
\]

**Equation 27**

where

- $V$ consumption of 0.004 mol/L (or 0.005 mol/L) TEGO trant A100 solution in mL
- $t$ titre of TEGO trant A100 solution
- $c$ molar concentration of TEGO trant A100 solution (0.004 mol/L (or 0.005 mol/L))
- $M$ molar mass of the surfactant to be determined
- $E$ sample weight in g

The calculation formulae given above must be converted into the forms used by the titrator.

**Materials and reagents**

- 0.02 mol/L TEGO trant A100 solution
- Water
- Aqueous sulphuric acid c(H₂SO₄) = 0.05 mol/L
- Ethanol, denatured
- Methyl isobutyl ketone (MIBK)
- Solvent mixture of ethanol : MIBK (1:1)
- TEGO add

**18.2.2 Titration of anionic surfactants with 0.02 mol/L TEGO trant A100 solution and the Surfactrode Resistant**

Analytical balance, e.g. Sartorius A 200 S
Automatic titrator with peripherals (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736 or 751 Titris)
Fundamentals

Procedure

Parameters which must be generally observed

In potentiometric two-phase titration the influence of salts must be taken into account. This influence is described in detail in section 5.11.

Sample mixing is very important, particularly in potentiometric two-phase titration. See also section 5.8.

The titration should be carried out with a titrator that allows dynamic titrant addition, i.e. a titrator that adapts the volume increments to the change of the electrode potential.

The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be recognised.

Titration parameters

The titration parameters for the Titroprocessor 726 and the DMS 716/736 Titrino are given below.

<table>
<thead>
<tr>
<th>726 Titroprocessor</th>
<th>716, 736 or 751 Titrino</th>
<th>We recommend that the original curve and the first derivative curve are printed out for each titration and that the results and the raw data are stored on a connected computer.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pause</td>
<td>30 s</td>
<td>titration parameters</td>
</tr>
<tr>
<td>Meas.pt.density</td>
<td>0</td>
<td>meas.pt.density 0</td>
</tr>
<tr>
<td>Min.increment</td>
<td>150 µl</td>
<td>min.incr. 150 µl</td>
</tr>
<tr>
<td>Titr. rate</td>
<td>max</td>
<td>ttitr.rate max</td>
</tr>
<tr>
<td>Signal drift</td>
<td>off</td>
<td>signal drift off</td>
</tr>
<tr>
<td>Equilibr.time</td>
<td>30 s</td>
<td>equilibr.time 30 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pause 30 s</td>
</tr>
<tr>
<td>stop conditions</td>
<td></td>
<td>stop V: abs.</td>
</tr>
<tr>
<td>evaluation</td>
<td></td>
<td>stop V 20 ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP recognition all</td>
</tr>
</tbody>
</table>

Sample weight

The sample weight should be calculated so that a consumption of 0.02 mol/L titrant solution between 10 and 15 mL is obtained. If the titrant consumption is outside this range then the results should not be used and the titration should be repeated with a corrected sample weight. If the consumption is below 10 mL then, depending on the surfactant being analysed, too low results must be expected.

With most raw materials or very high surfactant content it is not a good idea to weigh out the sample directly for the titration because the amount of substance is so small that this would result in an error of 1% or even more. In such cases an intermediate dilution should be made in a volumetric flask and an aliquot of this taken with a pipette. With water-insoluble raw materials the intermediate dilution can be carried out using ethanol. The amount of ethanol in the aliquot must then be taken into account. It is easiest to prepare the stock solution so that an aliquot of 10 mL can be taken.

Procedure

The procedure depends on the sample preparation method:

a) Sample weighed in directly

A suitable amount of the homogeneous sample is weighed out exactly to 0.1 mg into the titration beaker. The sample is dissolved in approx. 80 mL water. The pH of the solution is adjusted to pH = 3 with 0.05 mol/L H₂SO₄ solution. 20 mL of the ethanol : MIBK mixture are added followed by 200 µL TEGO add.

b) Aliquot of an aqueous stock solution

The aliquot of an aqueous stock solution is pipetted into a titration beaker and made up to approx. 80 mL with water. The pH of the solution is adjusted to pH = 3 with aqueous H₂SO₄ solution. 20 mL of the ethanol : MIBK mixture are added followed by 200 µL TEGO add.

c) Aliquot of an ethanolic stock solution

If an ethanolic stock solution has been prepared then the amount of ethanol in the aliquot must be taken into account. The volume concentration of ethanol in the titration solution should not exceed 10%. Water is added up to approx. 80 mL and the pH of the solution is adjusted to pH = 3 with aqueous H₂SO₄ solution. 10 mL MIBK are added followed by 200 µL TEGO add.

The titration is now carried out by the titrator using the above-mentioned electrodes with the appropriate parameters.

Sample mixing during the titration is particularly important. The two phases must be so thoroughly mixed that they form a stable emulsion in which as little air as possible is entrained.

The use of a magnetic stirrer with stirrer bar is absolutely unsuitable for this purpose as adequate mixing of the solution without the entrainment of air bubbles is not possible (vortex formation). Good mixing without air bubble entrainment is best achieved with a propeller stirrer such as is used in the Metrohm 730 and 760 Sample Changers and also in the 727 Titration Stand with 722 Rod Stirrer. As the stirrer parameters are extremely important for surfactant titration, a mark should be made on the rod stirrer to enable a setting which has been optimised to be reproduced later.
If the MIBK is replaced by chloroform for the titration then the stirrer speed should be increased accordingly.

**Evaluation**

The calculation of the anionic surfactants content can be carried out in various ways. If the molar mass of the surfactant to be determined is known and if a mixture of different anionic surfactants is not involved then the content of the corresponding surfactant can be calculated directly. If several anionic surfactants with different molar masses are present then a total content is determined and can only be calculated as surfactant S or e.g. in mmol anionics/100 g.

Calculation as surfactant S:

\[
\% \text{ surfactant } = \frac{V \times t \times c \times M}{10 \times E}
\]

Calculation in mmol anionics/100 g substance:

\[
\frac{\text{mmol anionics}}{100 \text{ g subst.}} = \frac{V \times t \times c \times 100}{E}
\]

Calculation as % anionic surfactant of known molar mass:

\[
\% \text{ anionics} = \frac{V \times t \times c \times M}{10 \times E}
\]

The calculation formulae given above must be converted into the forms used by the titrator.

18.2.3 Titration of cationic surfactants with 0.004 mol/L (or 0.005 mol/L) dodecyl sulphate sodium salt solution and the Surfactrode Resistant

**Materials and reagents**

- 0.004 mol/L dodecyl sulphate sodium salt solution (instead of the 0.004 mol/L solution a c = 0.005 mol/L solution can also be used – in calculating the sample weight and the results the concentration must always be taken into account).
- Solvent mixture of ethanol : MIBK (1 : 1)
- TEGO add
- Analytical balance, e.g. Sartorius A 200 S
- Automatic titrator with peripherals (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736 or 751 Titrino)
- pH electrode, Metrohm 6.0233.100
- Surfactrode Resistant electrode, Metrohm 6.0507.130
- Ag/AgCl reference electrode with sleeve diaphragm: Metrohm 6.0726.100 double-junction reference electrode, 3 mol/L KCl as inner and outer electrolyte
- Titration beakers (matched to sample changer, if present)
- Measuring cylinder 100 mL
- Measuring cylinder 25 mL

**Procedure**

**Parameters which must be generally observed**

In potentiometric two-phase titration the influence of salts must be taken into account. This influence is described in detail in section 5.11.

The titration should be carried out with a titrator that allows dynamic titrant addition, i.e. a titrator that adapts the volume increments to the change of the electrode potential.

The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be recognised.
**Fundamentals**

**Titration parameters**

The titration parameters for the Titroprocessor 726 and the 716, 736 and 751 Titrino are given below.

### 726 Titroprocessor

- **Pause**: 30 s
- **Meas.pt. density**: 0
- **Min.increment**: 150 µl
- **Titr. rate max**:
- **Signal drift**: off
- **Equilibr.time**: 30 s

### 716, 736 or 751 Titrino

- **titration parameters**

<table>
<thead>
<tr>
<th>Meas.pt. density</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.increment</td>
<td>150 µl</td>
</tr>
<tr>
<td>Titr. rate max</td>
<td></td>
</tr>
<tr>
<td>Signal drift</td>
<td>off</td>
</tr>
<tr>
<td>Equilibr.time</td>
<td>30 s</td>
</tr>
<tr>
<td>Pause</td>
<td></td>
</tr>
<tr>
<td>stop conditions</td>
<td></td>
</tr>
<tr>
<td>stop V: abs.</td>
<td></td>
</tr>
<tr>
<td>stop V: 20 ml</td>
<td></td>
</tr>
<tr>
<td>evaluation</td>
<td></td>
</tr>
<tr>
<td>EP recognition</td>
<td>all</td>
</tr>
</tbody>
</table>

The delay of 30 seconds before the start of the titration is necessary so that the electrodes can adapt themselves to the titration solution.

We recommend that the original curve and the first derivative curve are printed out for each titration and that the results and the raw data are stored on a computer.

**Sample weight**

The sample weight should be calculated so that a consumption of 0.004 mol/L (or 0.005 mol/L) titrant solution between 10 and 15 mL is obtained. If the consumption in the titration is outside this range then the results should not be used and the titration should be repeated with a corrected sample weight. If the consumption is below 10 mL then, depending on the surfactant being analysed, too low results must be expected.

With most raw materials or very high surfactant content it is not a good idea to weigh out the sample directly for the titration because the amount of substance is so small that this would result in an error of 1% or even more. In such cases an intermediate dilution should be made in a volumetric flask and an aliquot of this taken with a pipette. With water-insoluble raw materials the intermediate dilution can be carried out using ethanol. The amount of ethanol in the aliquot must then be taken into account. It is easiest to prepare the stock solution so that an aliquot of 10 mL can be taken.

**Procedure**

The procedure depends on the sample preparation method:

a) **Sample weighed in directly**

A suitable amount of the homogeneous sample is weighed out exactly to 0.1 mg into the titration beaker. The sample is dissolved in approx. 70 mL water. 10 mL of the pH = 10 buffer are then added followed by 20 mL ethanol : MIBK mixture and possibly 200 µL TEGO add.

b) **Aliquot of an aqueous stock solution**

The aliquot of an aqueous stock solution is pipetted into a titration beaker and made up to approx. 70 mL with water. 10 mL of the pH = 10 buffer are then added followed by 20 mL ethanol : MIBK mixture and possibly 200 µL TEGO add.

c) **Aliquot of an ethanolic stock solution**

If an ethanolic stock solution has been prepared then the amount of ethanol in the aliquot must be taken into account. The volume concentration of ethanol in the titration solution should not exceed 10%. Water is added up to approx. 70 mL followed by 10 mL pH = 10 buffer. Then 20 mL ethanol : MIBK mixture are added and possibly 200 µL TEGO add.

The titration is now carried out using the titrator using the above-mentioned electrodes with the appropriate parameters.

Sample mixing during the titration is particularly important. The two phases must be so thoroughly mixed that they form a stable emulsion in which as little air as possible is entrained.

The use of a magnetic stirrer with stirrer bar is absolutely unsuitable for this purpose as adequate mixing of the solution without the entrainment of air bubbles is not possible (vortex formation). Good mixing without air bubble entrainment is best achieved with a propeller stirrer such as is used in the Metrohm 730 and 760 Sample Changers and also in the 727 Titration Stand with 722 Rod Stirrer. As the stirrer parameters are extremely important for surfactant titration, a mark should be made on the rod stirrer to enable a setting which has been optimised to be reproduced later. See also section 5.8. If the MIBK is replaced by chloroform for the titration then the stirrer speed should be increased accordingly.

In potentiometric two-phase titrations with the Metrosensor Surfactrode Resistant the limit at which this electrode can be used in alkaline media must always be observed. The pH should only be set with a buffer solution and the pH value must not exceed 10 as otherwise the electrode may be destroyed. See also section 4.5.8.

**Evaluation**

The calculation of the cationic surfactants content can be carried out in various ways. If the molar mass of the surfactant to be determined is known and if a mixture of different cationic surfactants is not involved then the content of the corresponding surfactant can be calculated directly. If several cationic surfactants with different molar masses are present then a total content is determined and can only be calculated as surfactant N (nitrogen) or e.g. in mmol cationics/100 g.

**Calculation as surfactant N:**

\[
\% \text{ surfact} = \frac{V \times t \times c \times M}{10 \times E}
\]

where

- **V** consumption of 0.004 mol/L (or 0.005 mol/L) dodecyl sulphate sodium salt solution in mL
- **t** titre of dodecyl sulphate sodium salt solution

The calculation of the corresponding surfactant N (nitrogen) or e.g. in mmol cationics/100 g.
Titrimetric determination of surfactants and pharmaceuticals

Fundamentals

**Titrimetric determination of surfactants and pharmaceuticals**

- **Calculation in mmol cationics/100 g substance:**
  \[ \text{mmol cationics / 100 g subst.} = \frac{V \times t \times c \times 100}{E} \]
  where:
  - \( V \) consumption of 0.004 mol/L (or 0.005 mol/L) dodecyl sulphate sodium salt solution in mL
  - \( t \) titre of dodecyl sulphate sodium salt solution
  - \( c \) molar concentration of dodecyl sulphate sodium salt solution (0.004 mol/L (or 0.005 mol/L))
  - \( E \) sample weight in g

- **Calculation as % cationic surfactant of known molar mass:**
  \[ \% \text{ cationics} = \frac{V \times t \times c \times M}{10 \times E} \]
  where:
  - \( V \) consumption of 0.004 mol/L (or 0.005 mol/L) dodecyl sulphate sodium salt solution in mL
  - \( t \) titre of dodecyl sulphate sodium salt solution
  - \( c \) molar concentration of dodecyl sulphate sodium salt solution (0.004 mol/L (or 0.005 mol/L))
  - \( M \) molar mass of the surfactant to be determined
  - \( E \) sample weight in g

The calculation formulae given above must be converted into the forms used by the titrator.

### 18.2.4 Titration of cationic surfactants with 0.02 mol/L dodecyl sulphate sodium salt solution and the Surfactrode Resistant

**Materials and reagents**
- 0.02 mol/L dodecyl sulphate sodium salt solution
- Buffer pH = 10
- Ag/AgCl reference electrode with sleeve diaphragm: Metrohm 6.0726.100 double-junction reference electrode, 3 mol/L KCl as inner and outer electrolyte
- Titration beakers (matched to sample changer, if present)
- Measuring cylinder 100 mL
- Measuring cylinder 25 mL

**Procedure**

**Parameters which must be generally observed**

In potentiometric two-phase titration the influence of salts must be taken into account. This influence is described in detail in section 5.11.

Sample mixing is very important, particularly in potentiometric two-phase titration. See also section 5.8.

The titration should be carried out with a titrator that allows dynamic titrant addition, i.e. a titrator that adapts the volume increments to the change of the electrode potential.

The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be recognised.

**Titration parameters**

The titration parameters for the Titroprocessor 726 and the DMS 716/736 Titrino are given below.

### 726 Titroprocessor

- **Pause:** 30 s
- **Meas.pt.density:** 0
- **Min.increment:** 150 µl
- **Titr. rate:** max
- **Signal drift:** off
- **Equilibr.time:** 30 s

**716, 736 or 751 Titrino**

- **titation parameters**
  - **meas.pt.density:** 0
  - **min.incr.:** 150 µl
  - **titr. rate:** max
  - **signal drift:** off
  - **equilibr.time:** 30 s
  - **pause:** 30 s
  - **stop conditions:**
    - **stop V:** abs.
    - **stop V:** 20 ml
  - **evaluation:**
    - **EP recognition:** all

The delay of 30 seconds before the start of the titration is necessary so that the electrodes can adapt themselves to the titration solution.
Sample weight

The sample weight should be calculated so that a consumption of 0.02 mol/L titrant solution between 10 and 15 mL is obtained. If the consumption in the titration is outside this range then the results should not be used and the titration should be repeated with a corrected sample weight. If the consumption is below 10 mL then, depending on the surfactant being analysed, too low results must be expected.

With most raw materials or very high surfactant content it is not a good idea to weigh out the sample directly for the titration because the amount of substance is so small that this would result in an error of 1% or even more. In such cases an intermediate dilution should be made in a volumetric flask and an aliquot of this taken with a pipette. With water-insoluble raw materials the intermediate dilution can be carried out using ethanol. The amount of ethanol in the aliquot must then be taken into account. It is easiest to prepare the stock solution so that an aliquot of 10 mL can be taken.

Procedure

The procedure depends on the sample preparation method:

a) **Sample weighed in directly**
   A suitable amount of the homogeneous sample is weighed out exactly to 0.1 mg into the titration beaker. The sample is dissolved in approx. 70 mL water. 10 mL of the pH = 10 buffer are then added followed by 20 mL ethanol : MIBK mixture and possibly 200 µL TEGO add.

b) **Aliquot of an aqueous stock solution**
   The aliquot of an aqueous stock solution is pipetted into a titration beaker and made up to approx. 70 mL with water. 10 mL of the pH = 10 buffer are then added followed by 20 mL ethanol : MIBK mixture and possibly 200 µL TEGO add.

c) **Aliquot of an ethanolic stock solution**
   If an ethanolic stock solution has been prepared then the amount of ethanol in the aliquot must be taken into account. The volume concentration of ethanol in the titration solution should not exceed 10%. Water is added up to approx. 70 mL followed by 10 mL pH = 10 buffer. Then 20 mL ethanol : MIBK mixture are added and possibly 200 µL TEGO add. The titration is now carried out by the titrator using the above-mentioned electrodes with the appropriate parameters.

Sample mixing during the titration is particularly important. The two phases must be so thoroughly mixed that they form a stable emulsion in which as little air as possible is entrained.

The use of a magnetic stirrer with stirrer bar is absolutely unsuitable for this purpose as adequate mixing of the solution without the entrainment of air bubbles is not possible (vortex formation). Good mixing without air bubble entrainment is best achieved with a propeller stirrer such as is used in the Metrohm 730 and 760 Sample Changers and also in the 727 Titration Stand with 722 Rod Stirrer. As the stirrer parameters are extremely important for surfactant titration, a mark should be made on the rod stirrer to enable a setting which has been optimised to be reproduced later. See also section 5.8.

If the MIBK is replaced by chloroform for the titration then the stirrer speed should be increased accordingly.

In potentiometric two-phase titrations with the Metrosensor Surfactrode Resistant the limit at which this electrode can be used in alkaline media must always be observed. The pH should only be set with a buffer solution and the pH must not exceed 10 as otherwise the electrode may be destroyed. See also section 4.5.8.

Evaluation

The calculation of the cationic surfactants content can be carried out in various ways. If the molar mass of the surfactant to be determined is known and if a mixture of different cationic surfactants is not involved then the content of the corresponding surfactant can be calculated directly. If several cationic surfactants with different molar masses are present then a total content is determined and can only be calculated as surfactant N:

\[
% \text{ surfact} - N = \frac{V \times t \times c \times M}{10 \times E}
\]

or e.g. in mmol

\[
\text{mmol cationics} / 100 \text{ g subst.} = \frac{V \times t \times c \times 100}{E}
\]

where

- \(V\) consumption of 0.02 mol/L dodecyl sulphate sodium salt solution in mL
- \(t\) titre of dodecyl sulphate sodium salt solution
- \(c\) molar concentration of dodecyl sulphate sodium
- \(M\) molar mass of nitrogen (14.01 g/mol)
- \(E\) sample weight in g

Calculation as surfactant N:

Equation 34

\[
\text{Calculation in mmol cationics/100 g substance:}
\]

Equation 35

\[
\text{where}
\]

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Titrimetric determination of surfactants and pharmaceuticals
\[
\% \text{ cationics} = \frac{V \times t \times c \times M}{10 \times E}
\]

where

- **V** consumption of 0.02 mol/L dodecyl sulphate sodium salt solution in mL
- **t** titre of dodecyl sulphate sodium salt solution
- **c** molar concentration dodecyl sulphate sodium salt solution (0.02 mol/L)
- **M** molar mass of the surfactant to be determined
- **E** sample weight in g

Calculation as % cationic surfactant of known molar mass:

**Equation 36**

**18.3 Validation of potentiometric surfactant titrations**

Section 18.3 has been written by Joachim Thiede, Schülke & Mayr GmbH, Zentrale Analytik, D-22840 Norderstedt, Germany

**18.3.1 Scope of the validation of potentiometric surfactant titrations**

The central topic of these observations is the analytical or testing method which is used for potentiometric surfactant determination in raw materials or finished products. The method is not just a means to its own ends, but is used to solve a clearly defined analytical problem which demands the determination of content values with an appropriate confidence level (reliability). This reliability is, for example, necessary to make statements about surfactant content values and their position within a certain tolerance range, to establish determination limits, to define the working range of the method (linearity) and to assess the effect of interferences (ruggedness).

**18.3.2 Definition of the validation parameters**

- **Precision:** The precision of the method indicates the agreement between individual determinations when a sample is analysed several times under identical conditions.
- **Accuracy:** The accuracy of an analytical method describes the agreement between the results obtained and the nominal value.
- **Linearity:** Linearity describes the ability of a method to provide results that are proportional to the concentration of the analyte within a given range.
- **Selectivity:** Selectivity is defined as the ability of a measuring procedure to differentiate the analyte from other sample constituents, transformation products or decomposition products.
- **Ruggedness:** Influences from the apparatus used and from the surroundings are investigated to determine the ruggedness of the method.
- **Limit of determination:** The limit of determination is the smallest amount of analyte that can still be determined with an adequate precision.
- **Limit of detection:** The limit of detection is the smallest amount of analyte that produces a detectable change in the measured value.

The relevant parameters must be selected from those listed above in order to prove the suitability of a surfactant determination method for a particular analytical problem.

**18.3.3 Three-step model for the validation of potentiometric surfactant titrations**

**Step 1**

The first step involves the working out of a method and the determination of suitable parameters for the automatic titrator. Attention should be given to the following points:

**Selection of the optimal pH value for the titration**

The selection of the pH value can have a decisive influence on the recovery rate, e.g. in the determination of quaternary ammonium compounds if special amines are present. Under acidic conditions amines are protonated and are then also determined as «quaternary ammonium compounds», see Table 61.

**Table 61 Determination of quaternary ammonium compounds in the presence of special amines**

<table>
<thead>
<tr>
<th>Measured values (nominal value = 10%)</th>
<th>pH = 10</th>
<th>pH = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10.1%</td>
<td>11.1%</td>
</tr>
<tr>
<td></td>
<td>10.0%</td>
<td>11.2%</td>
</tr>
<tr>
<td></td>
<td>10.1%</td>
<td>11.0%</td>
</tr>
<tr>
<td></td>
<td>10.1%</td>
<td>11.1%</td>
</tr>
</tbody>
</table>
Selection of the best titrant

Broad peaks of the derivative curve yield worse precision and accuracy than sharp peaks. Fig. 238 shows the first derivative curve obtained in the determination of a quaternary ammonium compound with sodium dodecyl sulphate (0.004 mol/L) as titrant in the presence of amines. This curve shows a broad peak in the region of the equivalence point. This affects the precision and accuracy of the method.

In Fig. 239 the same quaternary ammonium compound is determined with sodium tetraphenylborate (0.01 mol/L) as titrant in the presence of amines. The precision and accuracy of the method are noticeably improved when compared with the titration with sodium dodecyl sulphate. The cause is the sharp peak of the first derivative curve at the equivalence point.

![Fig. 238 Titration of a quaternary ammonium compound with sodium dodecyl sulphate](image1)

![Fig. 239 Titration of a quaternary ammonium compound with sodium tetraphenylborate](image2)

Optimisation of the sample size

Too small sample weights may produce too low results, e.g. with certain anionic surfactants. On the other hand, too large sample weights lead to an increase of the matrix effect, which may be accompanied by «noisy» and/or too flat titration curves that are difficult to evaluate.

Evaluation of the correct endpoint

In the context of working out the method it must be guaranteed that the correct equivalence point is used for the quantitative evaluation. In the example shown in Fig. 240 the determination was initially stopped after the first equivalence point (A), which resulted in too low contents. A renewed verification of the titration and the titration curve produced the second equivalence point (B) with a considerably higher ERC value compared to equivalence point (A). This second equivalence point, however, could not be achieved initially because of the automatic switch-off after the first equivalence point. Calculation of the content based on this new endpoint (B) produced recovery rates that were close to 100%.

Optimisation of the titration parameters of the automatic titrator

This involves the following variables:
- Equilibration time before the titration
- Stirring intensity (vigorous stirring)
- Dosing rate
- Time- or drift-controlled acquisition of the measured value

Step 2

In the second step the «raw method» worked out in step 1 is subjected to a suitability test for a particular analytical problem. A sensible selection must be made from the vast validation repertoire of parameters such as precision, accuracy, selectivity, linearity, determination and detection limits and ruggedness for the particular problem (thus, e.g., the determination of a limit of determination and detection for a raw material check with a theoretical value for the content and tolerances can only be regarded as «nice to have» activity). When determining the content of surfactants in products the surfactant raw materials used should also be subjected to the determination of their content by potentiometric surfactant determinations. This can have a positive effect on the accuracy parameter by eliminating differences between a two-phase determination of the content and potentiometric surfactant determination.

Step 3

The third phase is concerned with checking the existing method performance data against the required performance data. These required performance data can result from (just a small selection is shown):
- Legal requirements (licenses, regulations, etc.)
- Quality assurance systems (ISO 900X etc.)
- Customer requirements
- Safety requirements of the manufacturer
- Product and process properties
This means that no generally valid information about precision, accuracy, linearity, ruggedness, etc. can be made. However, in the use of automatic titrators in the routine sector, values for the accuracy with relative variations of <1% and linearity in the range of $r^2 \geq 0.995$ can be used for orientation.

**Precision:**
With the aid of a statistical data model a maximum permissible RSD (Relative Standard Deviation) can be stipulated via the required determination tolerance and the number of analyses carried out per determination. This maximum permissible RSD is then the assessment criterion for the relative standard deviation obtained from the determinations of the precision.

**Accuracy:**
The accuracy of the analysis is assessed from the relative deviation of the series of measurements for the precision data from the nominal value. The tolerance range for this deviation is again dependent on the analytical problem.

**Linearity:**
The determined equivalence point volumes are checked against the nominal content (at constant sample weight) throughout the linearity range that is to be checked for the method (e.g. 80%, 100% and 120% of an active substance in a product) for a linear relationship by means of a linear regression analysis. This regression analysis also provides an instrument for the recognition of systematic errors (variation of the Y-axis intercept).

**Selectivity:**
Checking the product sample without the surfactant that is to be analysed. If the method is selective then no equivalence point should be found within the relevant potential range.

**Ruggedness:**
Checking the influences on the method from the apparatus used and from the surroundings, e.g.:
- Different instruments
- Different operators
- Different analysis times
- Laboratory conditions
- Different electrodes
- Solvents and titrants

The selection from this wide range must be made in accordance with the analytical problem.

**Determination limit:**
The determination limit, not so often required in the routine sector, is given as the smallest amount of analyte that can still be determined with an adequate precision. The determination of an «adequate precision» (the assessment quantity is again the relative standard deviation, RSD) is made according to the analytical problem to be solved.

### 18.3.4 Example of the validation of a potentiometric surfactant titration

The determination of the cationic surfactant content in a product is to be validated with the following basic information (bulk goods release analysis):

- Nominal content: 10.0%
- Release tolerance: ±5% of nominal value, i.e. 10.5% to 9.5%
- Number of determinations per analysis: 2
- Maximum permissible RSD for precision: 1.38%
- Influencing quantities in this case are the nominal content, release tolerance and the number of determinations per analysis.
- Accuracy: up to maximum ±3% (relative) of the nominal content
- Linearity (80%, 100%, 120% range): $R^2 > 0.994$
- Ruggedness (1) «instruments»: covered by qualification
- Ruggedness (2) «operators»: standard deviation for 2nd person within the 2.571-fold standard deviation of the 1st person
- Error probability: 5%

### Further conditions

- **Sensor**: Metrosensor «High Sense» surfactant electrode
- **Titrant**: 0.01 mol/L sodium tetraphenylborate
- **Titration system**: TiNet 2.X

### Explanation of some of the basic validation data

**Precision**
The maximum permissible precision-related RSD (relative standard deviation) was obtained from the following equation:

$$RSD = \frac{(u-o) \cdot 100 \cdot n^{1/2}}{4 \cdot G \cdot 2.571}$$

*Equation 37*

where
- $o =$ upper tolerance value for the determination of the content (10.5%)
- $u =$ lower tolerance value for the determination of the content (9.5%)
- $n =$ number of analyses per determination (2)
Within the context of determining the precision, six determinations for validation were carried out. In practical release analysis, double determinations should be carried out \( n = 2 \).

Using the above equation 37, one obtains a maximum permissible precision \( \text{RSD} \) of 1.38\% for this example of a determination method.

**Ruggedness (person)**

The 2.571-fold standard deviation of the 1st person also resulted from the t-distribution value for the error probability of 5\% and the number of 6 determinations.

**Ruggedness (instrument)**

The instrument ruggedness could be covered in advance within the context of test equipment qualification. This was done by carrying out comparative measurements on different instruments with selected meaningful methods. The measurement uncertainties between these systems were therefore known.

**Linearity**

The degree of certainty \( R^2 \) should be better than 0.994 \( [ \text{maximum value: 1}] \) in the range 80\% to 120\% (here: cationic surfactant). In our example the cationic surfactant content range between 8\% and 12\% was examined.

<table>
<thead>
<tr>
<th>Validation parameter</th>
<th>Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precision</td>
<td>1st person</td>
</tr>
<tr>
<td></td>
<td>2nd person</td>
</tr>
<tr>
<td>Accuracy</td>
<td>accuracy range: 10.3% - 9.7% measurement: 10.1% ✓</td>
</tr>
<tr>
<td>«Selectivity»</td>
<td>no potential jump in sample without cationic surfactant ✓</td>
</tr>
<tr>
<td>Linearity</td>
<td>degree of certainty ( [R^2]: &gt;0.994 ) ( R^2 : 0.9997 ) ✓</td>
</tr>
</tbody>
</table>

**Conclusion:** The method is suitable for the analytical problem!

**Concluding observations**

No generally valid parameters and guide values can be given for the validation of potentiometric surfactant titrations. The example given here only provides a possible approach to the validation problem, based on proving the suitability of the method.

One of the most important tasks within the context of validation activities is to be found in the preliminary steps. The validation parameters must be selected in a sensible manner by asking oneself: «Are precision and accuracy without ruggedness, determination limit and linearity adequate for solving our problem?» Moreover, the corresponding statistical guide values must be appropriate to the purpose of the analysis. An excessive exactness for all the methods is usually only possible to achieve with a very high expenditure on personnel and instruments. These high costs then often stand in no relationship to the decision that can be made about a particular analytical method. Sometimes a «lean» validation with a somewhat larger method tolerance is completely adequate for solving the analytical problem of the internal or external «customer».

**18.4 Titrimetric determination of nonionic surfactants based on polyoxyethylene adducts**

**Instruments and accessories**

The titration curves resulting from the titration of nonionic surfactants do not always correspond to the ideal S-shape. In particular, the area before the endpoint is often different from that seen in most titrations. This is why a titrator with good dynamic control and optimal endpoint recognition is particularly important for the titration of nonionic surfactants. The 726 and 670 Titroprocessors and the Titrino family fulfil this task excellently. The optimal and correct setting of the titrator assumes an inordinately large role in nonionic surfactant titration.

- 702 SET/MET Titrino, 716 DMS Titrino 736 GP Titrino or 751 GPD Titrino
- 726 or 670 Titroprocessor
- 2.722.0010 Propeller rod stirrer
- 6.3013.223 Exchange Unit
- 6.0507.010 NIO Surfactant Electrode with 6.2104.020 electrode cable
- 6.0726.100 Ag/AgCl double-junction reference electrode with sleeve diaphragm (inner electrolyte 3 mol/L KCl, outer electrolyte 3 mol/L NaCl), requires 6.2106.020 electrode cable

**Reagents**

- 0.01 mol/L sodium tetraphenylborate
  The preparation and titre determination of this solution is described in a separate section.
Fundamentals

Titrimetric determination of surfactants and pharmaceuticals

• Auxiliary solution c(BaCl₂) = 0.1 mol/L
  21 g BaCl₂ or 25 g BaCl₂·2H₂O are dissolved in approx. 200 mL distilled water, transferred to a 1 L volumetric flask with distilled water and made up to the mark.

Preparation, maintenance and storage of the NIO Surfactant Electrode

• The electrode is conditioned by carrying out 2 to 3 titrations whose measurements are discarded. It is further advisable to include a delay period of 30 s before each titration during which the electrode can adapt itself to the particular sample matrix.

• The electrode must be rinsed with methanol or wiped off with a tissue moistened with methanol after every three to four titrations.

• When the determinations are finished the electrode is wiped off with a tissue moistened with methanol and then stored in a dry condition again.

• As an alternative the electrode can also be stored in 1% aqueous PEG 1000 solution. This type of storage is always recommended when nonionic surfactant titrations are carried out frequently. An electrode stored in this manner can be used immediately, i.e. the preliminary titrations mentioned above are not necessary in this case.

Analysis

General

• The titration should be carried out with a titrator that allows dynamic titrant addition, i.e. a titrator that adapts the volume increments to the change of the electrode potential.

• The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be recognised.

• The dynamic control must be optimally adjusted because the titration curve is sometimes not S-shaped, and so that overdosing is completely ruled out.

• With the Titrino family, the acquisition of the measured value in nonionic surfactant titration must not be drift-controlled, but occur after a fixed delay period.

• Sample mixing during the titration also plays an outstanding role. In this case it is important that the solution is well mixed throughout the titration without the formation of a vortex or entrainment of air bubbles. For this reason a magnetic stirrer is not suitable for carrying out surfactant titrations. The best mixing effect with the smallest possible vortex and air bubble formation can be achieved with a propeller stirrer, e.g. that in the 727 Titration Stand (722 Propeller Stirrer).

• If these nonionic surfactant titrations are carried out with the help of sample changers then we can unambiguously recommend Metrohm’s 730 Sample Changer. With this model a rinsing cycle with methanol or methanol/water or first methanol and then water in a separate beaker can be programmed to be carried out after each titration or after every third titration, for example.

Sample weight

The sample weight for a nonionic surfactant titration should be selected so that the consumption of 0.01 mol/L sodium tetraphenylborate solution is between 8 and 10 mL. If the expected nonionic surfactant content is not known then a trial titration should be carried out to determine the sample weight required for the ideal titrant consumption of 8 to 10 mL.

Determination of the calibration factor

The determination of nonionic surfactants is not an absolute method. This is why a calibration factor must be determined in order to be able to subsequently calculate the content. This is done by using either the nonionic surfactant that is to be determined in the sample or by using a standard nonionic surfactant as the calibration standard, with whose factor the calculation of the content is then carried out. The content in the sample is then given as nonionic surfactant.

\[ f = \frac{E \times 1000}{V} \]

To determine the calibration factor, 15 to 25 mg of the nonionic surfactant are weighed out exactly to 0.1 mg into the titration beaker. 10 mL 0.1 mol/L barium chloride solution are then added and the sample dissolved by swirling. The solution is made up to a total volume of 100 mL with water. The titration is carried out against 0.01 mol/L sodium tetraphenylborate solution using the parameters and electrode combination given below.

Calculation of the calibration factor

The factor is calculated from the sample weight and consumption of 0.01 mol/L sodium tetraphenylborate standard solution.

Equation 38

where

\[ f \text{ calibration factor in mg/mL} \]

\[ E \text{ sample weight in g (referred to 100% nonionic surfactant)} \]

\[ V \text{ consumption of 0.01 mol/L sodium tetraphenylborate standard solution in mL} \]

Determination of the sample

• In the sample titration the consumption of 0.01 mol/L sodium tetraphenylborate solution should also be between 8 and 10 mL. A corresponding sample weight is weighed out exactly to 0.1 mg into the titration beaker and dissolved in 10 mL.
Fundamentals

Calculation:
The nonionic surfactant content is calculated from the consumption of 0.01 mol/L sodium tetraphenylborate solution, the
calibration factor and sample weight:

\[ \text{NIO – surfactant in \%} = \frac{V \times f}{10 \times E} \]

where

- \( V \): consumption of 0.01 mol/L sodium
tetraphenylborate solution in mL
- \( f \): calibration factor in mg/mL
- \( E \): sample weight in g

The calculation formulae given above must be converted into the forms used by the titrator.

Titration parameters

The parameters used for the 670 and
726 Titroprocessor and the 716, 736
and 751 Titrino are given below; they
apply to both the determination of the
calibration factor and the sample titra-
tion.

**670 Titroprocessor**

- Meas 1: 30 s
- Quantity: U
- Drift/min: off mV
- M.Delay: 30 s
- DynT 1: 30 s
- TStop: meas.pt.density 2
- Dos.Rate/min: 30.000 ml
- I.VResol: 1.00
- N.EPs: 8
- Volume: 20.000 ml
- M.Value: Off
- Signal drift: off
- Equilibr.time: 32
- Pause: 30 s

**726 Titroprocessor**

- Pause: 30 s
- Meas.pt.density: 2
- Min.increment: 200 µl
- Titr. rate: 30 ml/min
- Signal drift: off
- Equilibr.time: 32

**716, 736 or 751 Titrino**

- titration parameters
- meas.pt.density: 2
- min.incr.: 200 µl
- titr.rate: 30 ml/min
- signal drift: off
- equilibr.time: 32
- pause: 30 s
- stop conditions
- stop V: abs.
- stop V 20 ml
- evaluation
- EP recognition: all

A Metrohm Application Bulletin has been published on this topic.

**18.5 Titrimetric determination of non-surfactant active substances in pharmaceuticals with
the NIO surfactant electrode**

**Instruments and accessories**

- 702 SET/MET Titrino or 716 DMS Titrino, 736 GP Titrino or 751 GPD Titrino
- 2.722.0010 Propeller rod stirrer
- 6.3013.223 Exchange Unit
- 6.0507.010 NIO surfactant electrode with 6.2104.020 electrode cable
- 6.0726.100 Ag/AgCl double-junction reference electrode with sleeve diaphragm (inner electrolyte 3 mol/L KCl, outer
electrolyte 3 mol/L NaCl), requires 6.2106.020 electrode cable

**Reagent**

- Sodium tetraphenylborate solution 0.01 mol/L

The preparation and titre determination of this solution is described in section 6.4.2.

**Preparation, maintenance and storage of the NIO surfactant electrode**

- Sometimes it may be necessary to condition the electrode by carrying out a titration whose measurements are
discarded. It is further advisable to include a delay period of 30 s before each titration during which the electrode can adapt itself to the particular sample matrix.
- The measuring and reference electrodes should be rinsed with methanol or wiped off with a tissue moistened with
methanol after every 10 to 12 titrations. After briefly rinsing with water the electrode is again ready for immediate use.
- At the end of a titration or series of titrations the electrode is wiped off with a tissue moistened with methanol and then
stored in a dry condition again.

**Analysis**

**Sample preparation**

It is very often necessary to add some acetic acid to the sample to achieve a better solubility of the active substance.
Fundamentals

1. Tablets
Tablets must be dissolved before the titration. This is done by placing the required number of tablets in the titration beaker and adding about 50 mL water. If the tablet is not soluble at room temperature or if the dissolution step takes too long than the solution can be carefully warmed. Before the titration the solution should again be allowed to cool down to room temperature.

2. Powder-form pharmaceuticals
The powder-form pharmaceutical is weighed out into the titration beaker and dissolved in approx. 50 mL water. If the active substance is not soluble in water then it can be dissolved in up to 5 mL methanol before the addition of water.

3. Liquid-form pharmaceuticals
Pharmaceuticals in liquid form, e.g. cough drops, are directly weighed out into the titration beaker and dissolved in water.

4. Pharmaceuticals with cream, gel or ointment bases
A corresponding amount of the cream, gel or ointment is weighed out directly into the titration beaker. Then approx. 5 mL methanol are added and the mixture carefully warmed until the formulation has dissolved, when approx. 90 mL water are added.

5. Raw material investigations
When raw materials are being investigated a stock solution should always be made up and an aliquot used for the determination. Water, a water/methanol mixture or methanol can be used as the solvent. Care must be taken that the aliquot does not contain more than 5 mL methanol.

As a rule of thumb a sample weight of approx. 25 to 50 mg, referred to the active substance, has proved most suitable. Depending on the molar mass this results in a titrant consumption of 5 to 15 mL.

Titration parameters
- The titration should be carried out with a titrator that allows dynamic titrant addition, i.e. a titrator that adapts the volume increments to the change of the electrode potential.
- The dynamic control parameters of the titrator should be set so that sufficient measuring points are available for an automated evaluation and so that the titration curve as well as the derivative curve, which is always used for assessing a titration, have a smooth shape and no significant spikes can be recognised.
- The titration curves obtained in the determination of pharmaceuticals with sodium tetraphenylborate have an ideal S-shape and can therefore be easily and reliably evaluated by the titrator algorithm. The rate of the reaction between the analyte and the titrant is slower than in classical precipitation titrations such as a chloride determination with silver nitrate. This should be taken into account when the parameters are being set.

Titration parameters for the Metrohm 670 and 726 Titroprocessor and 716, 736 and 751 Titrino are given below. If a different titrator is used then the parameters should be adapted accordingly.

670 Titroprocessor
<table>
<thead>
<tr>
<th>Meas 1</th>
<th>30 s</th>
<th>Quantity</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drift/min</td>
<td>off mV</td>
<td>1</td>
<td>30 s</td>
</tr>
<tr>
<td>M.Delay</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>DynT 1</td>
<td>meas.pt.density</td>
<td>1</td>
<td>30 s</td>
</tr>
<tr>
<td>Dos.Rate/min</td>
<td>30.000 ml</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>f.VResol</td>
<td>0.10</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>TStop</td>
<td>N.EPs</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Volume</td>
<td>20.000 ml</td>
<td></td>
</tr>
<tr>
<td></td>
<td>M.Value</td>
<td>Off</td>
<td></td>
</tr>
</tbody>
</table>

726 Titroprocessor
| Meas pt.density | 2 |
| Min.increment | 200 µl |
| Titr. rate | 30 ml/min |
| Signal drift | off |
| Equilibr.time | 30 s |

% act. subs. = \( \frac{V \times c \times M}{10 \times E} \)

716, 736 or 751 Titrino
| stop V | 20 ml |
| evaluation EP recognition | all |

If the titration takes too long then in many cases the parameter «equilibrium time» can be reduced to 20 or even 15 s.

Analytical procedure
Titrimetric determination of surfactants and pharmaceuticals

217
18.6 Potentiometric determination of betains with sodium tetr phenylborate

Materials and reagents

NIO surfactant electrode (Metrohm 6.0507.010)
6.0726.100 Ag/AgCl double-junction reference electrode with sleeve diaphragm (inner electrolyte 3 mol/L KCl, outer electrolyte 3 mol/L NaCl)
Automatic titrator with peripherals (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736 or 751 Titrino)
20 mL Exchange Unit with amber glass bottle and light protection (Metrohm 6.3012.223)
100 mL Beaker

Hydrochloric acid c = 0.1 mol/L (e.g. prepared from concentrated HCl or from Merck Titrisol)
Gum arabic (e.g. SIGMA G-9752)
0.1 mol/L sodium tetr phenylborate solution

The preparation and titre determination of the solution is described in a separate section.

Procedure

Preparation of the gum arabic solution

In order to prepare 1 L gum arabic solution, 50 g gum arabic powder are weighed out. Gum arabic is a very fine white powder (SIGMA). 1 L distilled water is heated in a suitable beaker almost to boiling point. The gum arabic powder is added under vigorous stirring. The powder immediately clumps but slowly dissolves under vigorous stirring. The solution is then allowed to cool down and preserved with 10 mL 30% formaldehyde solution (Merck). Preservation is necessary to achieve a longer working life for the solution. In this concentration formaldehyde does not interfere with the titration. The finished solution has a slight yellowish colour. A brown precipitate appears at the bottom of the beaker after standing overnight. This is removed by decanting off, but does not interfere with the titration. The solution is now ready for use.

Titration parameters

Titration parameters for the Metrohm 670 and 726 Titroprocessor and 716, 736 and 751 Titrino are given below. If a different titrator is used then the parameters should be adapted accordingly.

<table>
<thead>
<tr>
<th>670 Titroprocessor</th>
<th>726 Titroprocessor</th>
<th>716, 736, 751 Titrino</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meas 1 30 s</td>
<td>Meas.pt.density 4</td>
<td>4</td>
</tr>
<tr>
<td>Quantity U</td>
<td>Min.increment 10.0 µl</td>
<td>min.incr. 10.0 µl</td>
</tr>
<tr>
<td>Drift/min 32 s</td>
<td>Titr. rate 30 ml/min</td>
<td>titr.rate 30 ml/min</td>
</tr>
<tr>
<td>M.Delay 32 s</td>
<td>Signal drift off</td>
<td>equilibr.time 32 s</td>
</tr>
<tr>
<td>DynT 1 30 s</td>
<td>Equilibr.time 32 s</td>
<td>pause 30 s</td>
</tr>
<tr>
<td>meas.pt.density 4</td>
<td></td>
<td>stop conditions</td>
</tr>
<tr>
<td>Dos.Rate/min 30,000 ml</td>
<td></td>
<td>stop V: abs.</td>
</tr>
<tr>
<td>f.VResol 0.10</td>
<td></td>
<td>stop V 15 ml</td>
</tr>
<tr>
<td>TStop N.EPs 8</td>
<td></td>
<td>evaluation</td>
</tr>
<tr>
<td>Volume 15,000 ml</td>
<td></td>
<td>EP recognition all</td>
</tr>
<tr>
<td>M.Value Off</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sample weight

The sample weight should be selected so that the titrant consumption is between 5 and 8 mL. If the titrant consumption lies outside this range then the sample weight should be corrected and the titration repeated. If the betain content is not known then it is a good idea to carry out a trial titration in order to determine the required sample weight.

Carrying out the betain determination

A suitable amount of the homogeneous sample is weighed out exactly to 0.1 mg into a titration beaker. The sample is dissolved in 90 mL 0.1 mol/L hydrochloric acid and then 10 mL gum arabic solution are added. The titration is now carried out by the titrator against 0.1 mol/L sodium tetr phenylborate solution using the electrode combination and the titration parameters mentioned above.

Calculation

The betain content is calculating using the mean molar mass of the betain to be determined in the sample.

\[ \% \text{ betain} = \frac{V \times c \times M}{E \times 10} \]

where

- \( V \) consumption of 0.1 mol/L sodium tetr phenylborate solution in mL
- \( c \) concentration of sodium tetr phenylborate solution (0.1 mol/L)
- \( M \) mean molar mass of the betain to be determined in g/mol
- \( E \) sample weight in g

The calculation formula given above must be converted into the form used by the titrator.

Presentation of the result
The betain content is given to one decimal place. The molar mass on which the calculation is based should also be mentioned. A typical alkylamidopropylbetain based on hardened coconut oil has a molar mass of approx. 350 g/mol.

18.7 Potentiometric determination of the betain content with perchloric acid

Materials and reagents

Automatic titrator (e.g. Metrohm 726 or 670 Titroprocessor or 716, 736 or 751 Titrino)
Motor-driven piston burette (Metrohm 665 Dosimat)
20 mL Exchange Unit (Metrohm 6.3012.220)
pH glass electrode (e.g. Metrohm 6.0104.100)
6.0726.100 Ag/AgCl double-junction reference electrode with sleeve diaphragm (inner electrolyte 3 mol/L KCl, outer electrolyte LiCl sat. in Ethanol)
1 L Volumetric flask, class A
1,4-dioxan, analytical grade (e.g. Riedel-de Haén 33147)
Methyl glycol, analytical grade (e.g. Riedel-de Haén 33457)
Fixanal 0.1 mol/L perchloric acid (e.g. Riedel-de Haén 38330)
Methanol, analytical grade (e.g. Riedel-de Haén 32213)
Fixanal 1 mol/L sodium hydroxide (e.g. Riedel-de Haén 38215)
Sodium acetate * 3 H₂O (e.g. Riedel-de Haén 32318)

Preparation of the 0.1 mol/L perchloric acid solution

Approx. 150 mL 1,4-dioxan are placed in a 1 L volumetric flask made of amber glass. The Fixanal ampoule is placed on the neck, opened according to the instructions and the contents quantitatively transferred into the flask with 1,4-dioxan. The solution must now be mixed immediately in order to achieve rapid dilution of the perchloric acid. The flask is then filled up to the mark with 1,4-dioxan and mixed thoroughly again.

Preparation of the sodium hydroxide/sodium acetate solution

80 g sodium acetate are dissolved in approx. 300 mL water and transferred to a 1 L volumetric flask. The contents of a Fixanal ampoule of 1 mol/L sodium hydroxide are added and the flask filled up to the mark with water. NaOH pellets can also be used as an alternative to a Fixanal ampoule. In this case 40 g NaOH pellets are weighed out into a beaker and dissolved in approx. 300 mL water. This solution is cooled down and transferred to the volumetric flask containing the sodium acetate. The flask is then filled up to the mark with water and mixed thoroughly. If NaOH pellets are used then a smaller amount of the solution can be prepared; this is done simply by adjusting the amounts of sodium acetate and NaOH given above.

Titrator settings

The titration parameters for the Metrohm 670 and 726 Titroprocessor and 716, 736 and 751 Titrino are given below. If a titrator from a different manufacturer is used then the parameters should be adapted accordingly.

670 Titroprocessor

Meas 1
Quantity U
Drift/min 50 mV
M.Delay 26 s
Add 1
V.Inrem 6 ml
equilibr.time 30 s
pause 30 s
stop conditions stop V: abs. stop V 15 ml
evaluation EPC 20 EP recognition all

726 Titroprocessor

Dos.Rate max 10 s
meas.pt.density 4
Dos.Rate/min max 0.15
TStop
N.EPs 8
Volume 25.000 ml

716, 736 or 751 Titrino

titrator parameters
meas.pt.density 4
min.incr. 10.0 µl
titr.rate 30 mL/min
signal drift off

equilibr.time 30 s
pause 30 s
stop conditions stop V: abs. stop V 15 ml

Carrying out the determination

Equation 42

% betain = \( \frac{V (EP2 - EP1) \times M (betain) \times c (HClO_4)}{m \times 10} \)

the sodium hydroxide/sodium acetate solution is added and allowed to react for 5 to 10 minutes at room temperature. A few drops of 0.1% ethanolic phenolphthalein solution can be added to check whether the sample has become alkaline after the addition of sodium hydroxide. When the reaction time has elapsed, 20 mL methanol and 60 mL methyl glycol are added and the titration is carried out against 0.1 mol/L perchloric acid in dioxan using the titration parameters given above. A list of possible errors is given in Table 17 (section 7.6.1).
The content is given as a mass fraction in percent to one decimal place.
The molar mass of the betain must be known; if it is not then a typical molar mass should be assumed. A typical alkylamidopropylbetain based on hardened coconut oil has a molar mass of approx. 350 g/mol.
The molar mass on which the calculation is based must always be mentioned when the results are presented.
The calculation formula given above must be converted into the form used by the titrator.

18.8 Calculation of surfactant content

The titration of ionic surfactants, no matter whether in aqueous or non-aqueous media, always takes place according to stoichiometric principles. 1 mol of titrant is used for each mol of the functional group of the analyte which is to be titrated. This means that there is no problem in calculating the content ... provided that the molar mass of the analyte is known. This statement also applies to each surfactant titration, no matter whether it is carried out as a classical two-phase titration, a potentiometric titration or even a photometrically detected surfactant titration.
The only time that a surfactant analyst is actually in possession of a uniform substance where the molar mass can be calculated from the chemical formula is probably during the titre determination or in the case of the reagents used to prepare the titrant.
Practically no surfactant raw material consists of a single substance from whose formula a molar mass could be derived for the calculation of the titration results. This is why it is necessary, for example for the manufacturer and purchaser of a surfactant raw material, to agree about a molar mass that can be used for the calculation of the content.
In quality assurance and in other cases where the components of a formulation and their molar masses are exactly known, the calculation of the content presents no problem.
In many laboratories molar masses used for the calculation of many ionic surfactants have become firmly established. Even when these are not always correct the results still allow very good comparisons to be made between them.
Table 63 gives the molar masses as used by several raw material manufacturers for the calculation.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molar mass (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear alkylbenzene sulphonate</td>
<td>345</td>
</tr>
<tr>
<td>Fatty alcohol sulphate C₁₂</td>
<td>288</td>
</tr>
<tr>
<td>Fatty alcohol ether sulphate</td>
<td>382</td>
</tr>
<tr>
<td>Sec. alkane sulphonate</td>
<td>325</td>
</tr>
<tr>
<td>Benzalkonium chloride</td>
<td>344</td>
</tr>
</tbody>
</table>

We must repeat that with these molar masses we are not talking about absolute numbers, e.g. as are used in complexometry or in the titration of acids or alkalis. It would be more correct to speak about titration equivalents. In these titration equivalents it is also taken into account that, for example, sec. alkane sulphonates or alpha olefin sulphonates contain a portion of multiple sulphonated units.

In surfactants with a wide range of alkyl chain distribution, e.g. when the surfactant has a natural raw material basis such as coconut oil, an average molar mass is provided by the titration equivalent.
The reaction in the potentiometric surfactant titration can, particularly in surfactants with multiple functional groups in a molecule or those with a wide range of alkyl chain distribution, proceed in a different manner from that in a classical two-phase titration. As a result it may be possible to derive other, method-specific titration equivalents.
Problems can and will occur if the potentiometric titration of a sec. alkane sulphonate with a content of 8 to 10% di- and polysulphonates is calculated with the molar mass as used in a two-phase titration. Clearly too low results will be obtained from this titration in comparison to those obtained in a two-phase titration. If a different method-specific titration equivalent is used then the results obtained by different laboratories correlate with each other as well as with the results of the two-phase titration.
If a mixture of different surfactants is present then it is extremely difficult to carry out a stoichiometric calculation. Within a quality assurance context it is certainly possible to lay down a titration equivalent for a given mixture.
It often simply makes more sense to calculate the titration result in mmol/100 g.

**General equation for calculating in mmol/100 g**

\[
mmol / 100 \ g = \frac{V \times t \times c \times 100}{E}
\]

*Equation 43*

where
- \(V\) consumption of titrant in mL
- \(t\) titre of the titrant solution
- \(c\) molar concentration of the titrant solution in mol/L
- \(E\) sample weight in g

For anionic surfactants the presentation of the result in % surfactant S (sulphur), or in % surfactant N (nitrogen) for cationic surfactants can often make good sense.
General equation for calculating anionic surfactants

\[ \% \text{ anionics} = \frac{V \cdot t \cdot c \cdot M}{10 \cdot E} \]

Equation 44

where
- \(V\) consumption of TEGO trant A100 solution in mL
- \(t\) titre of the TEGO trant A100 solution
- \(c\) molar concentration of the TEGO trant A100 solution in mol/L
- \(M\) molar mass of the surfactant species to be determined (for % surfactant S: 32.06 g/mol)
- \(E\) sample weight in g

General equation for calculating cationic surfactants

\[ \% \text{ cationics} = \frac{V \cdot t \cdot c \cdot M}{10 \cdot E} \]

Equation 45

where
- \(V\) consumption of dodecyl sulphate sodium salt solution in mL
- \(t\) titre of dodecyl sulphate sodium salt solution
- \(c\) molar concentration of dodecyl sulphate sodium salt solution in mol/L
- \(M\) molar mass of the surfactant species to be determined (for % surfactant N: 14.01 g/mol)
- \(E\) sample weight in g

These equations make particular sense when surfactant titrations are to be carried out on a single product at different pH values.

Example

The degree of quaternisation of a quaternary ammonium compound is to be determined by titrations at pH = 3 and pH = 10. At pH = 10 only the quaternary ammonium compound is determined. In contrast, in the titration at pH = 3 the total content of the quaternary ammonium compound and the surfactant starter amine is determined. A consequence of this is that the results at different pH values must be calculated with different molar masses or different titration equivalents. The calculation of the surfactant equivalents in mmol/100 g or in % surfactant N results in a simpler evaluation of the results and also, in the example given, a simpler calculation of the degree of quaternisation.
19 Companies concerned with surfactant titration

19.1 Chemicals

There is a great demand for all types of highly pure surfactants having uniform chain lengths. These are indispensable for the preparation of solutions or for titre determination. This necessity has apparently not yet been recognised by any manufacturer. How else can it be understood that until now a search for such substances in the catalogues of the chemical manufacturers has been in vain? It is certain that such standard substances would be very expensive as the preparation and purification of surfactants is extremely complicated and expensive.

For example, on the reagent market there is currently no dodecyl sulphate sodium salt, also known as lauryl sulphate, available with a declared dodecyl sulphate content. The only information provided is >98 or >99%. This information does not help the analyst any further when, for example, the titre of a cationic titrant is to be determined. This means that one has to rely on the information about the content of a particular dodecyl sulphate passed on from mouth to mouth. The only other way is to determine the content of the secondary components oneself. Using dodecyl sulphate as an example, this involves the following determinations:

- free dodecyl alcohol by GC analysis
- inorganic sulphate (Na₂SO₄), e.g. by photometric titration
- water by KF titration

It is unreasonable to expect the operator to do all this. Will the reagent manufacturers accept the challenge?

19.1.1 Merck

Merck is marketing some surfactants and reagents under the name «for surfactant tests». The number of these substances has not increased in recent times. These reagents do not fulfil the particular requirements of surfactant titration with surfactant electrodes because, for example, suitable standards for anionic or cationic surfactants with certified purity are missing. Such substances are required in a particularly high degree of purity and with certification for the preparation of titrants and also for titre determination.

An extract from the list of reagents «for surfactant tests»:

<table>
<thead>
<tr>
<th>Order no.</th>
<th>Product designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>112123</td>
<td>Decyl sodium sulphate for surfactant tests</td>
</tr>
<tr>
<td>113861</td>
<td>Dihexyl sodium sulphonate for surfactant tests</td>
</tr>
<tr>
<td>112146</td>
<td>Sodium 1-dodecanesulphonate for surfactant tests</td>
</tr>
<tr>
<td>112533</td>
<td>Dodecyl sulphate sodium salt for biochemistry and for surfactant tests</td>
</tr>
<tr>
<td>112058</td>
<td>Hyamine 1622 for surfactant tests</td>
</tr>
<tr>
<td>115480</td>
<td>Hyamine 1622 solution 0.004 mol/L for the determination of anionic surfactants</td>
</tr>
<tr>
<td>112148</td>
<td>Methyl dodecylbenzene sulphonate for surfactant tests</td>
</tr>
<tr>
<td>112292</td>
<td>Sodium 1-octanesulphonate for surfactant tests</td>
</tr>
<tr>
<td>820546</td>
<td>N-dodecylpyridinium chloride</td>
</tr>
<tr>
<td>114243</td>
<td>Lithium dodecyl sulphate</td>
</tr>
<tr>
<td>112288</td>
<td>Octyl sulphate sodium salt</td>
</tr>
</tbody>
</table>

19.1.2 Metrohm

Metrohm offers the cationic titrant TEGO trant A100 for the determination of anionic surfactants and anionic dyes.

TEGO add is a special additive based on a nonionic surfactant and is added in many potentiometric titrations in two-phase media. The addition of 200 µL TEGO add per titration (100 mL) is recommended.

TEGO trant A100 and TEGO add are research products from Th. Goldschmidt AG, Zentrale Analytik, D-45127 Essen, Germany

<table>
<thead>
<tr>
<th>Order no.</th>
<th>Product designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2317.000</td>
<td>TEGO trant A100, 6 g</td>
</tr>
<tr>
<td>6.2317.010</td>
<td>TEGO trant A100, 60 g</td>
</tr>
<tr>
<td>6.2317.020</td>
<td>TEGO trant A100, 500 g</td>
</tr>
<tr>
<td>6.2317.100</td>
<td>TEGO add, bottle with 50 mL</td>
</tr>
<tr>
<td>6.2317.110</td>
<td>TEGO add, bottle with 500 mL</td>
</tr>
</tbody>
</table>
19.2 General information about titrators and surfactant electrodes

All the microprocessor-controlled automatic titrators on the market today were in the development departments of the manufacturers when the subject of potentiometric surfactant titration was still in its infancy. But this is the titration, no matter whether of ionic surfactants or of nonionic surfactants, that places the greatest demands on a titrator. When a surfactant titration is carried out under critical observation it will uncover each weak point in such an instrument. Only manufacturers who have proved that they can manufacture instruments that satisfy the requirements of demanding titration methods in hard daily laboratory use have a chance here.

It is to be hoped that the manufacturers of titrators are aware of what the market and analysts expect from them and will incorporate the corresponding features in the next generations of instruments. A good example of this is the 730 Sample Changer from Metrohm. This is designed so that it has fulfilled all the author’s expectations on the subject of surfactant titration. It can even be programmed so that during nonionic surfactant titrations, in which the electrodes very easily tend to become soiled, these are rinsed so well in normal operation that the titration can be carried out unattended. This is a promising development. Good titrations can be carried out using modern instruments but a lot of improvements could still be made, and not just in details.

If a titrator is to be purchased for surfactant titration then it is wrong to look only at the price. Take a look at the concept and what is being offered round and about the titrator. This does not just include the peripherals, but also the know-how relating to the subject of surfactants which is present in the central offices, among the field workers and, above all, in the application laboratories.

19.3 Metrohm sensors and instruments for surfactant titration

For endpoint recognition in surfactant titrations the Metrosensor range comprises all the sensors needed:

- the 6.0507.120 Ionic Surfactant Electrode for ionic surfactants and dyes (see also section 4.2)
- the 6.0504.150 High Sense Surfactant Electrode (see also section 4.2)
- the 6.0507.010 NIO Surfactant Electrode for nonionic surfactants and pharmaceutical compounds (see also section 4.3)
- the 6.0507.130 Surfactrode Resistant for two-phase surfactant titrations (see also section 4.5)
- the 6.0507.140 Surfactrode Refill for two-phase surfactant titrations (see also section 4.5.10)
- the powerful light-guide photometer with variable wavelength settings
- the Spectrodes – sensors for photometric titrations (turbidity titrations) with a fixed wavelength (525 or 610 nm) and shaped like an electrode

Metrohm titrators

- 726 Titroprocessor
- 716 DMS Titrino
- 736 GP Titrino
- 751 GPD Titrino

These Metrohm titrators are all equally well suited to surfactant titration. The decisive instrument criteria for the success of surfactant titrations, such as the algorithms for the titration control and the endpoint recognition, correspond to a high standard, as do the hardware components.

Metrodata titration software TiNet 2.2

TiNet 2.2 supports both the simple routine workplace and complex titration systems with a high degree of automation. Among other features, TiNet offers the subsequent graphical evaluation of titration curves and the possibility of directly comparing different titration curves with one another by placing them one on top of another. Data records can be freely selected and filtered, sorted, modified and arranged in accordance with GLP.

730, 717, 760 Sample Changers

These Metrohm sample changers open up new possibilities in the automation of surfactant titrations, above all with regard to the rinsing and conditioning of sensors. An efficient mixing process during the titration, which is an absolute necessity for surfactant titrations, is achieved by means of special stirrers with specific control.

19.4 Metrohm Application Bulletins covering surfactant titration

All the Application Bulletins mentioned are available in English, French and German.

Application Bulletin 230

Titrimetric/potentiometric determination of nonionic surfactants based on polyoxymethylene adducts using the NIO Surfactant Electrode

8 pages, including theory and several applications

Application Bulletin 233

Titrimetric/potentiometric determination of anionic and cationic surfactants with the «High Sense» electrode.

15 pages, including theory and more than 25 applications
**Application Bulletin 263**
Titrimetric determination of pharmaceutical compounds with the NIO electrode
11 pages, with many examples

**Application Bulletin 264**
Titrimetric methods for the determination of betains
10 pages, theory, titration with sodium tetraphenylborate or with perchloric acid, examples, assessment of the two methods

**Application Bulletin 268**
Potentiometric titration of surfactants and pharmaceutical compounds – Which surfactant electrode and which titrant for which product?
14 pages, overview of the numerous surfactants and pharmaceutical compounds that can be determined by potentiometric titration

**Application Bulletin 269**
Titrimetric/potentiometric determination of ionic surfactants by two-phase titration using the Surfactrode Resistant
18 pages, theory, numerous examples

**Metrohm Monograph**
Determination of ionic surfactants in cosmetic products, by Reiner Schulz
60 pages, treats fundamentals, surfactant determination in raw materials and formulations, giving a very large number of examples

**19.5 Contacts**
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Fax: (+41) 71 353 89 01
E-Mail:sales@metrohm.ch

Homepage:  www.metrohm.ch

The Metrohm Homepage contains a wealth of information including the addresses, telephone and fax numbers and, where applicable, the E-Mail and Homepage contacts of approximately 80 Metrohm suppliers all over the world.
20 Glossary

20.1 Definitions

Abscissa
axis of a coordinate system

Absolute method
Analytical method in which the analysis result can be calculated directly from a measurement and the chemical reaction and no further calibration is required. An example is gravimetry, where the concentration of the substance being analysed can be calculated directly from the original and final sample weights and the chemical reaction.

Additives
Retain the crystallisability of the ingredients in powder-form cleaning agents, ensure good trickling behaviour and prevent clumping. Sodium sulphate is an example of an additive.

Adducts
Addition products, generally molecular compounds.

Adsorption
Deposition of one or more components at a boundary surface (lat.: adsorbere = draw in)

Agglomeration
Accumulation, clumping together.

Algorithm
Mathematical process that proceeds according to a particular repetitive scheme. The process is so precisely formulated that it can be carried out by an instrument which functions mechanically or electronically.

Algorithm, evaluation
Mathematical process used for the recognition of a titration endpoint and the evaluation of a titration.

Algorithm, titrator
Mathematical process used for controlling a titrator.

Aliquot
Latin = some, a pair. In analytical chemistry the name for the known fraction of a whole that forms the sample to be analysed. From the content of the aliquot part the content of the whole analytical sample can be calculated by simple multiplication.

Alkalis
Substances whose aqueous solutions exhibit a basic reaction, i.e., have a pH value between 7 and 14. Common alkalis are the hydroxides of sodium and potassium.

Amine fluoride
In this case a special compound consisting of an amine having surfactant properties with fluoride as the counterion. Has a substantive effect and is used in the fluoridation of the teeth by toothpastes and mouthwashes.

Amphiphilic
Simultaneous presence of hydrophilic and hydrophobic properties in a single molecule.

Ampholytic
Properties of compounds that possess both acidic and basic groups and that may react either as an acid or an alkali depending on the test conditions.

Analyte
The substance or the sample to be analysed.

Anisotropic
Having physical properties that are different along different axes or directions, e.g. elasticity, cleavability, hardness, electrical and thermal conductivity and light refraction in numerous crystals.

Apolar
Adjective that is used, e.g. in surfactants, and is to be understood as being the opposite to polar and in the same sense as unpolar in a combination of terms such as apolar compound or apolar residue. Compounds that neither can be broken down electrolytically nor have a permanent electrical dipole moment are numbered among the apolar compounds.

Associate
Loose, salt-like low-energy association of several similar molecules or ions.

Associate, dye-surfactant
Salt-like compound formed from an ionic dye and an oppositely charged surfactant.

Associate, surfactant-surfactant
Salt-like compound formed from a cationic surfactant and an oppositely charged anionic surfactant.

Autotitrator
Modern titrators are microprocessor-controlled instruments for carrying out various types of titration automatically.

Auxiliary products industry
Here: industrial branch concerned with the production of the chemicals that are needed for processing textiles, leather, skins and paper.

Betains
Group name for chemical compounds containing quaternary ammonium and carboxyl groups in their molecules in a way similar to betain; they form internal salts and have zwitterionic properties.
**Builders**

Name for cleaning agent constituents. Their function in the washing process mainly consists of eliminating calcium and magnesium ions from the detergent solution and increasing the effect of the surfactants.

**Calibration**

In measuring technique the determination of the relationship between input and output quantities (calibration curve), e.g. the pH value of buffer solutions and the corresponding potentials measured with a pH meter.

**Calibration factor**

Numerical value obtained from a calibration operation.

**Carboxylates**

Soaps, salts of fatty acids.

**Carcinogenic**

Causing cancer.

**Cetyl alcohol**

Fatty alcohol: \( \text{C}_{16}\text{H}_{33}\text{OH} \)

**Coated wire electrode**

In this type of electrode a conductive rod, usually made of a special graphite, is coated with an ion-sensitive PVC membrane.

**Co-builder**

Auxiliary agents which, particularly in phosphate-free cleaning agents, support the effects of ion exchangers.

**Coconut oil, hardened**

The unsaturated fats of natural coconut oil are converted to saturated fats, i.e. hardened, by hydrogenation in the presence of a catalyst.

**Coconut oil, unhardened**

Natural coconut oil. The coconut palm has been cultivated in India for about 4000 years.

**Complexing agents**

Compounds that are able to form complexes (complexing and masking of metals). The name «complexing agent» is often used as a synonym for chelating agent.

**Conditioning**

The electrode is prepared for measuring by conditioning.

**Conditioning titrations**

Titrations that are used for conditioning the electrode. The results of conditioning titrations must not be used for the calculation of results.

**Co-surfactant**

Surfactant which, because of its special properties, is used to support or extend the function of the base surfactant, often synergistically.

**Cross sensitivity**

A qualitative expression for the incomplete selectivity of a measuring electrode or also a complete determination method.

**Decantation**

Procedure for separating liquids from solid components (deposits) by pouring off the supernatant liquid.

**Decyl alcohol**

Fatty alcohol: \( \text{C}_{10}\text{H}_{21}\text{OH} \)

**Deionised water**

Water from which all salts have been removed.

**Demulsifiers (splitters)**

Substances that alter the charging condition and the interfacial tension of the emulsified particles. Mixtures containing sulphonic acid sodium salts, starch, sodium oleate or even sulphobetains of higher fatty acids are often used.

**Demulsifying**

The de-mixing of emulsions by physical or chemical methods. This is done by using mechanical, electrical or thermal forces or chemical additives (demulsifiers) to oppose the stabilising emulsifiers. Important in de-mixing oil-water mixtures in oil deposits.

**Derivative curve, first**

The first derivative curve is obtained from the original titration curve using the differential quotients \( DU/DV \).

**Detergent regulations**

German regulations which controlled the use of surfactants and required their degradability. Replaced today by the Washing and Cleaning Agents Law (German Wasch- und Reinigungsmittelgesetz – WRMG).

**Detergents**


**DGF standard methods**


**DIN methods**

Standard analytical methods of Deutsches Institut für Normung e.V.

**Dipole**

In general any arrangement of two similarly sized electrical charges (electrical dipole) or magnetic poles (magnetic dipole) of opposite polarity that have a certain distance from each other.

**Direct potentiometry**

Analytical technique using ion-sensitive electrodes where the activity of an ion in solution is measured directly in mV. The evaluation is carried out either using a calibration curve or according to the so-called spiking or standard addition method, in which a known amount of the ion to be analysed is added to the sample. Modern microprocessor-controlled ion meters have special functions for single or multiple addition and for establishing a calibration curve.

**Dispersion**
Distribution of solid, liquid or gaseous particles in a continuous phase of a different composition. A suspension is a dispersion of solid particles in a liquid, an emulsion a distribution of drops of a liquid in a different liquid. A foam is a dispersion of a gas in a liquid or in a solid. Dispersions are metastable. By reducing their large interfaces and thus their high surface energy they attempt to achieve a more stable condition. Finely-dispersed systems become coarsely dispersed, emulsion droplets coalesce, foams collapse (Latin: dispersio = distribute).

**Dissociation**
Cleavage of molecules to form smaller molecules, radicals, ions or atoms.

**Dodecyl alcohol**
Fatty alcohol: C_{12}H_{25}OH
Also known as lauryl alcohol.

**Dosing step**
Titrant volume increment added during a titration.

**Double junction reference electrode**
Reference electrode with a second electrolyte chamber. This second electrolyte (bridge electrolyte) is in contact with both the reference electrode, e.g. via a ceramic diaphragm, and with the sample via a second diaphragm, e.g. a sleeve diaphragm.

**Dye salt**
Salt-like reaction product formed by an ionic dye and an oppositely charged surfactant.

**Dye-surfactant associate**
Salt-like compound formed from an ionic dye and an oppositely charged surfactant.

**Electrolyte**
Any substance that undergoes electrolytic dissociation and whose solution is electrically conductive, e.g. salts, acids, bases.

**Electroplating**
Formation of metal coatings by electrolysis, e.g. silver plating, nickel plating.

**Empore disks**
Extraction disks based on chemically modified silica gel particles that are incorporated into a chemically inert fabric made of PTFE. Empore is a trademark of 3M. Supplied, e.g., by ICT, D-61352 Bad Homburg, Germany.

**Emulsifiers**
Auxiliary agents for the preparation and stabilisation of emulsions. Their effect may be based on increasing the viscosity, protective colloid functions or the reduction of interfacial tension between the different phases of the emulsion.

**EN 45000**
European standard for the accreditation of testing laboratories.

**Enzymes**
Proteins that are involved as catalysts in almost all chemical reactions, i.e. metabolic processes, in the organism. They make the reaction possible or accelerate it.

**Epton titration**
Another name for two-phase titration. Named after the author of the first publication (1947) in which two-phase titration was described.

**Equalising, levelling**
Uniform deposition, e.g. of a dye.

**ERC**
Endpoint Recognition Criterion. Relative, Metrohm-specific factor for the definition of the 1st derivative. Without unit.

**Evaluation algorithm**
Mathematical process used for the recognition of a titration endpoint and the evaluation of a titration.

**Exchanger resin**
Ion exchangers: inorganic or organic solids that are usually present in the form of grains and take up positive or negative ions from an electrolyte solution, releasing an equivalent amount of likewise charged ions; accordingly, there are both cation and anion exchangers. Used in water softening plants, for example.

**Factor**
Correction factor for the titration solution determined with a titrimetric standard substance. It gives the relationship between the nominal and effective concentration of the standard solution:

\[
\text{effective concentration} = \text{factor} \times \text{nominal concentration}
\]

**First derivative curve**
The first derivative curve is obtained from the original titration curve using the differential quotients DU/DV.

«for surfactant tests»
Special reagent quality from Merck KGaA, Darmstadt, Germany.

**Gum arabic**
Gum resin obtained from acacias and mimosas; water-soluble, insoluble in alcohol; used as an adhesive, binding agent and thickening agent.

**Helmholtz layer**
Electrochemical double layer. Name for an electrically charged zone formed by charge transfer at the boundary between two phases; it is a few atom or molecule layers thick. The Helmholtz layer is dependent on the presence of charge carriers such as ions, electrons or oriented dipoles.

**Heterogeneous**
Non-uniform.

**HLB system**
Hydrophilic-Lipophilic Balance. A measure for the water or oil-solubility of mainly nonionic emulsifiers. The arbitrary scale (HLB value) ranges from 1 to 20, where 1 would be purely lipophilic and 20 purely oleophilic. These limiting values cannot be reached. The HLB value is also used to divide the nonionic surfactants into subgroups.

**Homogenisation**
In process technology the preparation of a uniform mixture from different components. In milk, for example, cream...
Hydrolysis, sensitive to
Sensitive to hydrolytic cleavage. The cleavage of a molecule by reaction with water, often with the aid of catalysts.

Hydrophilic
Attracting water, water-loving.
(Greek: hydro = water, philos = friend)

Hydrophilicity
Tendency of a material, e.g. a fabric, to take up water.

Hydrophobic
Water-avoiding, water-repelling.
(Greek: hydro = water, phobos = fear)

Indicator
Collective term for substances that can be used to monitor the course of a chemical reaction; e.g., pH indicators change their colour depending on the pH value of the solution, examples being litmus, methyl orange and phenolphthalein.

Indicator electrode
Also known as measuring electrode. Ideally it should only be sensitive to the ion to be measured.

Inflection point
Inflection point of the first derivative curve, also known as the endpoint or equivalence point.

Inhibitor
Substance which inhibits or delays a reaction.

Inner electrolyte
Inner filling solution for the reference electrode, normally 3 mol/L KCl.

Ion carrier
See ionophore.

Ion exchanger
Water-insoluble substances, inorganic or organic, in which atom groups are incorporated whose ions can be exchanged for other ions (anion or cation exchangers), e.g. in water softening Ca²⁺ ions are exchanged for 2 Na⁺ ions.

Ionophore
Electroactive component in an ion-selective or ion-sensitive electrode. Tailor-made lipophilic organic molecules that are able to interact with the ions to be analysed. The more selective the interaction, the more selective the resulting surfactant electrode.

ISO 900X
ISO standards concerned with quality management.

Isoelectric point
Amino acids and carboxylic acids contain one or more amino groups (–NH₂) in their molecule. The pH value at which the basic amino groups and the acidic carboxylate groups are exactly internally balanced is known as the isoelectric point, an important quantity for amino acids or betains.

Lauryl alcohol
See dodecyl alcohol.

Lecithin
Lecithins: fat-like substances in which two hydroxyl groups of the glycerin are esterified with long-chain fatty acids, e.g. oleic acid, palmitic acid and the third hydroxyl group is esterified with choline, a strong organic base, via phosphoric acid. Lecithins are important constituents of human, animal and plant cells, particularly of biological membranes.

Levelling, equalising
Uniform deposition, e.g. of a dye.

Lime soap
Non-foaming and non-cleaning reaction product from soap solutions and «hard water». Forms greasy rings in wash-basins and leaves marks on textiles. Contributes largely to the aging of fibers and textile dyes.

LIMS
Laboratory Information Management System. Computer program based on a special database for documentation and management of analytical data and results. Produces analysis certificates, etc. and is an important quality management instrument in an analytical laboratory.

Lipid
Collective term for fats and fat-like substances (lipoids).

MALDI TOF
Matrix Assisted Laser Desorption Ionisation Time Of Flight (mass spectroscopy).

Micelle
Surfactant molecules or ions in aqueous solution aggregate in the simplest case to form spherical structures or – in special surfactant structures, at higher surfactant concentrations or electrolyte concentrations – to form anisometrically arranged structures, the micelles. These are not static, but are permanently being broken down and re-formed.
(Latin: mica = grain)

Myristyl alcohol
Fatty alcohol: C₁₄H₃₀OH

Nernst behaviour
The behaviour of an ion to be measured or of an electrode in direct potentiometry according to the Nernst equation.

Nernst equation
Derived by Nernst in 1889; in the meantime the equation has been modified many times to explain the solution pressure of metals, redox potentials, pH value, the theory of electrolysis, the emf of galvanic elements, etc.

For redox systems the Nernst equation is:

\[ E = E_0 + \frac{RT}{zF} \ln \frac{c_{ox}}{c_{red}} \]

Equation 24

where \( E \) = electromotive force (emf in volt), \( E_0 \) = normal potential, \( R \) = gas constant, \( T \) = absolute temperature, \( F \) =
Faraday constant, \( c = \text{concentration (or activity \( a \)}, \text{and} \ z = \text{charge equivalent (positive integer for cations, negative integer for anions)}; \text{the factor RT} / (2F) \text{is often called the Nernst factor or Nernst potential. For} T = 293 \text{K (20 °C)} \text{we obtain}

\[
E = E_0 + \frac{0.058}{z} \log \frac{c_{\text{ox}}}{c_{\text{red}}}
\]

Equation 25

by inserting the values of the constants. By measuring the normal potentials the Nernst equation can be used to determine chemical equilibria and their Gibbs energies. If in a measuring setup the charge carrier has to pass through a diaphragm (e.g. the membranes of glass and ion-selective electrodes), then the transport numbers must also be included in the Nernst equation for the calculation.

**Neutral oil**

Non-converted starting substance still present in an anionic surfactant after the sulphonation or sulphation reaction, e.g. alkyl benzene in alkyl benzene sulphonate.

**Oxalcohydrolysis**

Organic compounds that convert invisible ultraviolet (UV) radiation into visible light and in this way cause garments, paper, etc. to have a higher degree of whiteness. Are added to cleaning agents in small amounts (0.1 to 0.3%).

**Pigment**

According to DIN an inorganic or organic dye that is practically insoluble in the medium of application.

**Potentiometry**

Electrochemical technique for monitoring a titration reaction and for endpoint determination using an electrode combination consisting of a measuring electrode (glass, redox, ISE, surfactant electrode) and a reference electrode.

**Protonated**

If a proton (\( H^+ \)) is added to a chemical compound then this latter is said to be protonated.

**Quaternary ammonium compound**

Salt of a positively charged compound of the quadrivalent, quaternary nitrogen, where each substituent on the nitrogen must be \( >H \).

**Quaternisation degree**

The quaternisation degree is a measure of how much of the starter amine used has been converted to a quaternary ammonium compound by the alkylation process.

**Polyethylene glycols**

Homopolymers of ethylene oxide. Contain two primary terminal OH groups.

**Polymerisation**

Chemical process in which many small molecules of one or several substances (monomers) join together to form larger molecules (macromolecules). The new molecular association has different properties from the starting compounds. Polymers are mainly used in the plastics industry.

**Potential**

In general something which is possible as opposed to actual. In physics a scalar quantity equal to the work done in moving a body from a standard reference point to a given point in a field of force; the potential difference between two points \( P_x \) and \( P_y \) is a measure of the work required to move a body from \( P_x \) to \( P_y \). Such potentials are described mathematically by the potential functions. An example is the electrical potential, whose difference between two points in space is the electrical voltage prevailing between these two points.

**Potential jump**

Significant potential alteration within a titration curve.

**Potentiometric indication**

Determination of a point in a field of force; the potential difference between two electrodes immersed in an electrolyte solution.

**Polydata**

x, y data pairs, e.g. mL and mV values that belong together and are accepted by the automatic titrator according to predetermined criteria during the titration. From these raw data the titrator algorithm calculates the endpoint of the titration and produces the required titration curves such as the original curve and the first derivative curve. The raw data passed on by the titrator to a PC can also be processed with different software programs.

**Reference electrode**

In contrast to the measuring electrode the reference electrode should not be affected by chemical alterations to the sample and should maintain a constant potential during the whole titration.

**Reproducibility**

Also called repeatability.
**Rheological**

Adjective referring to the phenomena that occur in the flow of liquid colloidal systems under the influence of external forces.

**Rinse-off formulations (antonym: leave-on)**

Cosmetic formulations which after application to the skin or hair are washed off again with water. Typical rinse-off formulations are shower gels, hair tonics or shampoos.

**Salting-out**

Precipitation of a substance from a solution or dispersion as a result of the salt effect.

**Scattering range**

The distribution of the individual values of a statistical series around the mean value.

**Sensors**

That part of a measuring or recording device that is directly exposed to the sample and transmits the quantity to be measured or recorded to a measuring device or recorder.

**Silicone surfactant**

Name for compounds based on silicones which enrich themselves very strongly at the solution interfaces and thus reduce the interfacial tension.

**Solubilisation**

Dissolution of water-insoluble substances in aqueous solutions with the aid of surfactants. The water-insoluble substances are surrounded by surfactant molecules and are thus no longer in direct contact with the water.

**Spikes**

Electronic voltage peaks caused by an interference which has no connection with the analysis being carried out.

**Standard operating procedure (SOP)**

Step-by-step instructions that describe, e.g., how an analysis is to be carried out. Important part of a quality management system in an analytical laboratory.

**Starter alcohol**

Original alcohol, mono or bivalent, for the addition of ethylene oxide or propylene oxide.

**Starter amine, non-quaternised**

Tertiary amine that is converted to a quaternary ammonium compound by reaction with an alkylating agent.

**Statistics**

**Accuracy**

The accuracy of an analytical method is a measure of the degree of agreement between the results obtained and the accepted (=true=) value.

**Arithmetic mean (average)**

\[
\bar{X} = \frac{1}{N} \sum_{i=1}^{N} X_i
\]

The mean value \( \bar{X} \) is equal to the sum of the independent values \( X_i \) (of a measuring series) divided by their number \( N \).

Calculation equation:

\[
\bar{X} = \frac{1}{N} \sum_{i=1}^{N} X_i
\]

**Coefficient of variation (relative standard deviation)**

The coefficient of variation \( VK \) or the relative standard deviation of a series of measurements \( X_i \) is the quotient of the standard deviation \( s \) and the mean \( \bar{X} \).

**Determination limit**

The determination limit is given as the smallest amount of analyte which can still be determined with an adequate precision.

**Linearity**

The linearity of a method is the ability of the method to produce measuring signals which are proportional to the concentration of the substance to be determined within a given range.

**Precision**

The precision of a method indicates the degree of agreement between individual determinations when a sample is repeatedly analysed under identical conditions.

**Ruggedness**

To determine the ruggedness of the method the influences of the apparatus and the surroundings on the analytical method are investigated.

**Selectivity**

The selectivity is the ability of a measuring technique to differentiate the analyte from the other components in the sample and from transformation and decomposition products.

**Standard deviation**

The standard deviation \( s \) of a series of measurements (individual values \( X_i \)) is the positive root of the squared standard deviation \( s^2 \).

Calculation equation:

\[
s = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (X_i - \bar{X})^2}
\]

It is a measure of the scatter of the individual values \( X_i \) about the mean value \( \bar{X} \):

\[
s = \sqrt{\sum_{i=1}^{N} (X_i - \bar{X})^2}\]

**Standard deviation between series**

The estimated value of the standard deviation between the series \( s_w \) is calculated from:

\[
s_w = \sqrt{(s_f)^2 + (s_b)^2}
\]

**Standard deviation in a series**

The estimated value of the standard deviation in the series \( s_f \) is determined by several individual determinations on one and the same series (e.g. on a single day).

**Total standard deviation**
The estimated value of the standard deviation for an analysis result in any series of analyses represents the total standard deviation $s_t$.
Calculation equation:

**Variance**
The variance $s^2$ of a series of measurements is the sum of the squares of the deviations of the $N$ individual values $x_i$ from the arithmetic mean $x$ divided by the number of degrees of freedom $f$ ($f = N-1$).
Calculation equation:

**Stoichiometry**
The branch of chemistry dealing with the relationships of combining elements and the quantities of chemical elements or compounds involved in chemical reactions.

**Substantivity**
Attractive behaviour of an ionic compound to a «charged» surface, e.g. of a cationic fabric conditioner to a cotton fibre.

**Surface activity**
The boundary between a liquid and a gaseous phase (water-air) is the surface. Surfactants (surface-active substances) reduce the surface tension. See Surfactants.

**Surface tension**
A material constant. The phenomenon of surface tension is based on the fact that liquid molecules attract each other. Inside the liquid these forces cancel each other out; at the surface they are directed inwards and endeavour to keep the surface as small as possible (this is why drops are spherical).

**Surfactant matchstick**
Model for representation of a surfactant
Surfactant symbol: the «surfactant matchstick»

**Surfactants**
Surface-active substances. Name for compounds that strongly enrich themselves from their solutions at boundaries and thus reduce the surface tension. In a narrower sense boundaries are understood to be the separating surfaces between condensed phases (liquid/solid, liquid/liquid, solid/solid).
By reduction of the surface tension immiscible liquids become mixable, liquid contaminants and solid dirt particles can be emulsified or dispersed.
Structure: elongated, asymmetrical polar molecules with a hydrophobic and a hydrophilic group in the molecule.

**Surfactant-surfactant associate**
Salt-like compound formed from a cationic surfactant and an oppositely charged anionic surfactant.

**Suspension**
A state in which small solid particles are mixed with a liquid but remain undissolved.

**Synergistic concept**
Concept in which components are particularly matched to each other to produce a total effect which is greater than the sum of the individual effects.

**Synergy**
The combined action of substances or factors which support each other.

**Synthetic surfactants**
Surfactants based on synthetic raw materials.

**Titrant**
Also known as titrating agent. The solution that is added to the sample solution and enters into a chemical reaction with it.

**Titration, drift-controlled**
Titration method in which, after the addition of the volume increment, the measured value is accepted after the drift has fallen below a fixed and preset value.

**Titration, dynamic**
In a dynamic titration the volume increments in the flat part of the curve are large, i.e. the titration is rapid, while in the steep part of the curve only small volume increments are added. This titration method ensures that sufficient measuring data are available in the region of the equivalence point.

**Titration, endpoint**
In endpoint titration the titration is carried out until a preset endpoint is reached. The endpoint is set in mV or as a pH value.

**Titration, monotonic**
Also known as linear titration.
In monotonic titration constant volume increments are added, independent of the slope of the curve.

**Titration, time-controlled**
Titration method in which the measured value is accepted after a fixed and preset time has elapsed after the addition of the volume increment.

**Titrator**
Modern titrators are microprocessor-controlled instruments for carrying out various types of titration automatically.

**Titrator algorithm**
Mathematical process used for controlling a titrator.

**Titre**
Is better described as factor today.
Correction factor for the titration solution. See Factor.

**Titrimetry**
See volumetric analysis.

**Turbidity titration**
**Viscosity**
The property of a liquid or gaseous medium (fluid), which on deformation causes the appearance of frictional stress in addition to the thermodynamic pressure, and which opposes the displacement of liquid or gas particles relative to one another.

**Voltage**
Difference in potential between two measuring points.

**Volume increment**
Volume dispensed in a dosing step.

**Volumetric analysis (titrimetry, volumetry)**
Important method widely used in quantitative chemical analysis. To a measured amount of a solution whose concentration is unknown a reagent solution (standard solution, titrant) of known concentration is added until the endpoint (equivalence point) of the reaction (neutralisation, reduction, oxidation, complex formation, precipitation, etc.) can be evaluated.

**Washing and Cleaning Agent Law**
This German law (WRMG) has been in force since 1\(\text{st}\) January 1990. It places well-defined demands on the biodegradability of surfactants contained in aqueous cleaning agents.

According to the Directive of the Council of the EC dated 23\(\text{rd}\) November 1973 only those detergents may be brought onto the market in which the average degradability of the surfactant components is over 90%.

**Wetting**
The spreading out of a liquid on a solid or liquid surface.

**Wetting agents**
Substances that reduce the surface tension of water or other liquids so that these can penetrate the surfaces of solid objects (e.g. textile fibers) and thoroughly wet and soak them, thus displacing the air.

**Worst-case model**
In the worst possible case, under the most unfavourable conditions. Model for working out safety device requirements.

**Zwitterions**
Substances that have both positive and negative charges in one molecule; these charges cannot be separated from each other by dissociation. Examples are betains or amino acid amphoglycinates, etc.

### 20.2 Abbreviations of general terms

**AOCS Official Method**
Standard methods of the American Oil Chemists’ Society.

**ASTM**
American Society for Testing and Materials

**BIAS**
Bismuth (Bi) Active Substance.

**CESIO**
The European Surfactants and Chemical Intermediates Organization (Comité Européen des Agents de Surface et leurs Intermédiaires Organiques)

**CMC**
Critical Micelle Concentration

**COLIPA**
Umbrella organisation of the European Body-Care Products Industry.

**CTFA**
Cosmetics, Toiletry and Fragrance Association in Washington DC.

**DGF**
German Association for Fat Sciences (Deutsche Gesellschaft für Fettwissenschaft e.V., Münster)

**DGK**
German Association for Scientific and Applied Cosmetology (Deutsche Gesellschaft für wissenschaftliche und angewandte Kosmetologie)

**EP**
Endpoint

**ERC**
Endpoint Recognition Criterion. Relative, Metrohm-specific factor for definition of the 1\(\text{st}\) derivative. No units.

**GAT**
Cooperative Committee on Surfactants (Gemeinschafts-Ausschuss Tenside)

**GLP**
Good Laboratory Practice

**GMP**
Good Manufacturing Practice

**HLB**
Hydrophilic-Lipophilic Balance

**IKW**
Industrial Association of Toiletries and Cleaning Agents (Industrieverband Körperpflege- und Waschmittel e.V., Frankfurt, Germany)

**INCI**
International Nomenclature of Cosmetic Ingredients

**ISO**
International Organisation of Standardisation
Fundamentals

**JAOCSS**
Journal of the American Oil Chemists’ Society

**LIMS**
Laboratory Information Management System

**NIO**
Nonionic surfactant

**O/W**
Oil-in-water emulsion

**PVC**
Polyvinyl chloride

**HS**
High Sense Surfactant Electrode

**IS**
Ionic Surfactant Electrode

**NIO**
Nonionic surfactant Electrode

**SR**
Surfactrode Resistant

**SOP**
Standard Operating Procedure

**SPE**
Solid Phase Extraction

**TEGEWA**
Association of the Textile, Leather, Tannery and Cleaning Agent Raw Material Auxiliaries Industry (Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoff-Industrie e.V., Frankfurt, Germany)

**W/O**
Water-in-oil emulsion

**WAS**
Wash-active substance

**WRMG**
Washing and Cleaning Agent Law, Germany (Wasch- und Reinigungsmittel-Gesetz)

### 20.3 Common abbreviations for the most important surfactants or surfactant groups and chemicals

**ABS**
Alkylbenzene sulphonate

**APE**
Alkylphenol ethoxylate

**APG**
Alkyl polyglucoside

**BHT**
Butylated hydroxytoluene

**CPC**
Cetylpyridinium chloride

**CTAB**
Cetyltrimethylammonium bromide

**DOS**
Dioctylsulphosuccinate

**DSDMAC**
Distearyldimethylammonium chloride

**EO**
Ethylene oxide, see also POE

**FAES**
Fatty alcohol ether sulphate

**FAS**
Fatty alcohol sulphate

**HPC**
Hexadecylpyridinium chloride

**LAS**
Linear alkylbenzene sulphonate

**MAP**
Mono alkyl phosphate

**NaTPB**
Sodium tetraphenylborate

**PEG**
Polyethylene glycol

**PO**
Propylene oxide, see also POP

**POE**
Polyoxyethylene

**POP**
Polyoxypropylene

**QAC**
Quaternary ammonium compound

**Quat**
Quaternary ammonium compound

**SAS**
Secondary alkane sulphonate
20.4 Registered brandnames® or trademarks™

**Aerosil**
Highly disperse silicic acid
™ Degussa

**Empore Disks**
RP18-modified silica gel in PTFE fibres
™ 3M Company USA

**High Sense Surfactant Electrode**
Surfactant-sensitive electrode for determination of ionic surfactants.
™ Metrohm Ltd.

**Hyamine 1622**
Cationic surfactant, titrant
N-Benzyl-[N,N-dimethyl-N-[4-(1,1,3,3-tetramethylbutyl)-phenoxyethoxyethyl]-ammonium chloride.
™ Rohm & Haas USA

**Ionic Surfactant Electrode**
Surfactant-sensitive electrode for determination of ionic surfactants.
™ Metrohm Ltd.

**Metrodata**
Software from Metrohm.
™ Metrohm Ltd.

**Metrosensor**
Metrohm electrodes.
™ Metrohm Ltd.

**SIGMA**
Sigma Aldrich
Internet: www.sigma.sial.com/

**Spectrode**
Photometric detector shaped like an electrode.
™ Metrohm Ltd.

**Surfactrode Resistant, Surfactrode Refill**
Surfactant-sensitive electrodes for indicating potentiometric surfactant titrations.
™Th. Goldschmidt AG, D-45127 Essen, Germany. Marketed by Metrohm Ltd.

**Surfactrode Silicon**
Surfactant-sensitive electrode for indicating potentiometric surfactant titrations.
™Th. Goldschmidt AG, D-45127 Essen, Germany.

**TEGO**
™ Th. Goldschmidt AG, D-45127 Essen, Germany

**TEGO Betain L7**
Cocamidopropyl betain
™ Th. Goldschmidt AG, D-45127 Essen, Germany

**TEGO add**
Special additive for potentiometric two-phase titration using the Surfactrode Resistant.
™Th. Goldschmidt AG, D-45127 Essen, Germany. Marketed by Metrohm Ltd,

**TEGO trantr A100**
1,3-didecyl-2-methylimidazolium chloride
Titrant for determining anionic surfactants or anionic dyes.
™ Th. Goldschmidt AG, D-45127 Essen, Germany. Marketed by Metrohm Ltd.

**TiNet**
Titration Network, Metrodata software package.
™ Metrohm Ltd.

**Titrino**: 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino
Microprocessor-controlled automatic titrators for various titration modes.
™ Metrohm Ltd.

**726, 670 Titroprocessor**
Microprocessor-controlled automatic titrators for high-performance titrimetry.
™ Metrohm Ltd.

**Triton X 100**
Octylphenolpolyethylene glycol ether n = 10.
Octylphenol 10 POE
™ Rohm & Haas USA

**VESUV**
Metrodata software.
™ Metrohm Ltd.


## 21 Appendix A

**Which electrode and which titrant for which product?**

### 21.1 General

The question of which electrode is the correct one for a given titration problem is not easy to answer in the field of surfactant titration. The same applies to the optimal titrant concentration. The table given here reflects the experience gained in the author’s laboratory in the course of several years. However, it sometimes makes very good sense to experiment with the titrant concentrations and with the surfactant electrodes: changing the electrode often opens up new prospects, but the stability of the different electrodes must be taken into account.

### 21.2 Optimal titrant

In many cases the question of which titrant concentration is the optimal one or even the most suitable one cannot be answered simply and sometimes it is a good idea to carry out the titration with different titrant concentrations. An assessment should then be made of which titrant concentration produces the better titration curves.

In this monograph a titrant concentration of 0.02 mol/L is often recommended for the formulations sector. Of course, every rule has its exceptions. This became very clear to us when we investigated formulations found on the North American market. In the cosmetics sector new tendencies have become apparent in rinse-off formulations. As an example we list hair & body shampoo and body shampoo formulations.

### Hair & body shampoo
- Water
- PEG-80 Sorbitan laurate
- Cocamidopropyl betain
- Sodium trideceth sulphate
- Glycerin
- Disodium lauroamphodiacetate
- PEG-150 distearate
- Sodium laureth-13 carboxylate
- Fragancem
- Polysquaternium-10
- Tetrasodium EDTA
- Quaternium-15
- Benzophenone-4
- Chamomile oil
- D & C yellow no. 10
- D & C green no. 5

### Body Shampoo
- Water
- Cocamidopropyl betain
- Dimethicone
- Sodium laureth sulphate
- Guar hydroxypropytrimonium chloride
- Sodium hydroxide
- Butylated hydroxytoluene (BHT)
- Methylchloroisothiazolinone
- Methylisothiazolinone
- Ammonium sulphate
- Fragrance
- Laureth-4
- Laurath-23
- Carbomer
- Mica
- Titanium dioxide

In both formulations it can be recognised that nonionic surfactants are the basic surfactants used, e.g. those based on POE sorbitan fatty acid esters or betains. The anionic surfactants to be titrated are listed in the CTFA or INCI declarations only in the third place or even later. For these formulations better titration curves can be achieved with a 0.004 mol/L TEGO trant A100 solution as titrant. The reason for this is quite simple. The low titrant concentration results in a low sample weight. This means that smaller amounts of surfactants which have a negative influence on the titration curve are found in the titration solution.

However, if the formulations also contain surfactants such as cocoyl isethionate or lauryl sarcosinate then the titration must naturally be carried out with a correspondingly higher titrant concentration, because a quantitative determination is only possible in this way.

In classical formulations, as shown for example in these body shampoo and hair shampoo formulations, the 0.02 mol/L TEGO trant A100 solution was used successfully as the titrant.

### Body Shampoo
- Water
- Ammonium lauryl sulphate
- Ammonium laureth sulphate
- Lauramide DEA
- Citric acid
- Hydroxypropyl methylcellulose
- Tetrasodium EDTA
- Ammonium chloride
- Benzophenone-4
- Methylchloroisothiazolinone
- Methylisothiazolinone
- DMDM Hydantoin
- Ammonium xylene sulphonate
- Fragrance

### Hair Shampoo
- Water
- Sodium laureth sulphate
- PEG-7 glyceryl cocoate
- Disodium cocoamphodiacetate
- Cocamidopropyl betain
# 21.3 Surfactants that can be titrated

**Table 66 List of surfactants that can be titrated**

<table>
<thead>
<tr>
<th>Abbreviations used</th>
<th>Product</th>
<th>Electrode</th>
<th>Titrant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SR</strong> Surfactrode Resistant</td>
<td>Alkane sulphonates, sec.</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td><strong>NIO</strong> Nonionic Surfactant Electrode</td>
<td>Alkyl polyglycosides (APG)</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td><strong>IS</strong> Ionic Surfactant Electrode</td>
<td>Alkyl polyglycosides</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td><strong>HS</strong> High Sense Surfactant Electrode</td>
<td>Alkylbenzene sulphonates</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td><strong>STPB</strong> Sodium tetraphenylborate</td>
<td>Alkylphenol POE adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
</tr>
<tr>
<td></td>
<td>Alkytrimethylammonium halides</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>All-purpose cleaner with orange terpenes</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
</tr>
<tr>
<td></td>
<td>Alpha-olefin sulphonates</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Amine fluorides</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Amine oxide in formulations</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Amine oxide in raw materials</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anionic dyes</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Anionic pharmaceutical agents</td>
<td>NIO</td>
<td>TEGO trant A100 c=0.01 mol/L</td>
</tr>
<tr>
<td></td>
<td>Baby care bath products (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
</tr>
<tr>
<td></td>
<td>Balsam cure for wet hair (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Balsam formulations (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Bath cleaner (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Bath cleaner with pine oil (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Benzalkonium halides</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Betains in formulations</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Betains in raw materials</td>
<td>See section 7.6.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bis 2-ethylhexyl sulphosuccinate</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Bis 2-ethylhexyl sulphosuccinic acid esters</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Bleaching agent for hair (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Car shampoo (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
</tr>
<tr>
<td></td>
<td>Carprolylplaxia gels</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Castor oil POE adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
</tr>
<tr>
<td></td>
<td>Cationic dyes</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Cetylpyridinium halides</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Cleaners for glass and frames (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
</tr>
<tr>
<td></td>
<td>Clinical body cleaning agents (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
</tr>
<tr>
<td></td>
<td>Clinical cleaning additives (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
</tr>
<tr>
<td></td>
<td>Cocoyl isethionate</td>
<td>IS</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
</tr>
<tr>
<td></td>
<td>Cocoyl polyglycosides</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Conditioners for hair (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.02 mol/L</td>
</tr>
<tr>
<td></td>
<td>Cooling lubricants (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Cooling lubricants (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Cooling lubricants (soaps)</td>
<td>SR</td>
<td>determination limited TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Cumol sulphonates</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Decyl phosphate in shower gels, liquid soaps, shampoos, etc.</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Decyl polyglycosides</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Dialkyldimethylammonium halides</td>
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<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Dioctylsulphosuccinate</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Dioctylsulphosuccinate (DOS)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td></td>
<td>Dioctylsulphosuccinic acid esters</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td>Product</td>
<td>Electrode</td>
<td>Titrant</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>Disinfectant cleaners (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Disinfectant cleaners (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Disinfectants (quats)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Distearyldimethylammonium chloride (DSDMAC)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Dodecyl benzene sulphonate</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Dodecyl phosphate in shower gels, liquid soaps, shampoos, etc.</td>
<td>cannot be determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecyl polyglucosides</td>
<td>cannot be determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electroplating baths (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Electroplating baths (cationics)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Electroplating baths (NIO)</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl$_2$</td>
<td></td>
</tr>
<tr>
<td>Electroplating baths (PEG)</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl$_2$</td>
<td></td>
</tr>
<tr>
<td>Esterquats</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Ether carboxylic acids</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Eye drops (quats)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fabric conditioners (cationics)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fabric conditioning cloths for the washing drier (cationics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fat-containing formulations (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fat-containing formulations (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty acid POE adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl$_2$</td>
<td></td>
</tr>
<tr>
<td>Fatty acid salts &lt;C12</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Fatty acid salts &gt;=C12</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty acid salts &gt;=C12</td>
<td>NIO</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty acid salts C$_{10}$</td>
<td>cannot be determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fatty acid salts C$_{8}$</td>
<td>cannot be determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol ether carboxylic acids</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol ether sulphonates (FAES)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol ether-2 sulphates</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol ether-2.5 sulphates</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol ether-3 sulphates</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol ether-3 sulphisuccinates</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol ether-4 sulphisuccinates</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol POE adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl$_2$</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol sulphates</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty amine POE 1 to 4 adducts</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Fatty amine POE adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl$_2$</td>
<td></td>
</tr>
<tr>
<td>Fatty amines</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Foam baths (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Foam baths with fatty alcohol PEG sulphonates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Foam baths with fatty alcohol PEG sulphonates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Foam baths with high betain content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Foam baths with high nonionic surfactant content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Foam baths with sodium cocoyl isethionates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Formulations containing scouring agents (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Formulations containing scouring agents (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Formulations containing solvents (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Formulations containing solvents (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>Electrode</td>
<td>Titrant</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>-----------</td>
<td>-------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Gargling solution (quats)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Glass and frame cleaners (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Glass cleaners (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Grill cleaning gel (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>H₂O₂ for bleaching (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Hair colourants (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Hair colourants (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Hair conditioner (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Hair cures (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Hand disinfectants (quats)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Household cleaners (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Household cleaners (cationics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Household cleaners with high nonionic surfactant content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Household cleaners with orange terpenes (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Hydrogen peroxide for hair bleaching (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Hydrotropes</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Ionic Si surfactants (anionics)</td>
<td>HS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Ionic Si surfactants (cationics)</td>
<td>HS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Lauroyl sarcosinates</td>
<td>IS</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Lauroyl sarcosinates in body washes</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Lauroyl sarcosinates in toothpaste</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Lauryl phosphate in shower gels, liquid soaps, shampoos, etc.</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Lauryl polyglycosides</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Linear alkylbenzene sulphonates (LAS)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Liquid soap, surfactant base</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Liquid soap, traditional soap base</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L pH = 10</td>
<td></td>
</tr>
<tr>
<td>Liquid soaps with fatty alcohol PEG &gt;3 sulphates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Liquid soaps with fatty alcohol PEG sulphonates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Liquid soaps with high betain content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Liquid soaps with high nonionic surfactant content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Liquid soaps with sodium cocoyl isethionates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Liquid soft soap</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Liquid washing agents (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Lozenges (benzalkonium chloride)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Lozenges (cetylpyridinium chloride)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>MAP (monoaikyl phosphate) in shower gels, liquid soaps, shampoos, etc.</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Metallic soaps</td>
<td>NIO</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Methyl taurides</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Methyl taurides</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Monodecyl phosphate in shower gels, liquid soaps, shampoos, etc.</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Monolauryl phosphates in shower gels, liquid soaps, shampoos, etc.</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Mouth washes (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Mouth washes (cationics)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Mouth washes (quats)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Neutral cleaners</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>Electrode</td>
<td>Titrant</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>-----------</td>
<td>----------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Neutral cleaners with high betain or nonionic surfactant content</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactant POE &lt;4</td>
<td>NIO</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactant POE &gt;4</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>Nose drops (quats)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Oil baths (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Oil shower gels (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Oil-containing formulations (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Oil-containing formulations (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Olefin sulphonates</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Orange oil universal cleaner</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Oven cleaning gel (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Paraffin sulphonates</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>PE siloxanes</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>Peeling shower gel (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>PEG, MG &lt;500</td>
<td>NIO</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>PEG, MG &gt;500</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>Permanent wave preparations (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Phosphoric acid esters, surfactant-like</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Phosphoric surfactants</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Pine oil cleaners</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Pine oil cleaners based on anionic surfactants</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Pine oil cleaners based on cationic surfactants</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Pine oil cleaners based on soap</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Pine-oil-containing cleaners (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Pine-oil-containing cleaners (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>POE adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE alkyl phenol adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE castor oil</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE fatty acid adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE fatty alcohol adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE fatty amine adducts</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE glucose esters</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE glycerin fatty acid partial esters</td>
<td>NIO</td>
<td>determination limited STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE polyethers</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE polyglycerin fatty acid partial esters</td>
<td>NIO</td>
<td>determination limited STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE sorbitan fatty acid partial esters</td>
<td>NIO</td>
<td>determination limited STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE/POP mixed polyethers</td>
<td>NIO</td>
<td>determination limited STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POE-POP polymers</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>Polyether siloxanes</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>Polyethers</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>Polyethylene glycols</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L + BaCl₂</td>
<td></td>
</tr>
<tr>
<td>POP adducts</td>
<td>NIO</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>POP polyethers</td>
<td>NIO</td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Quaternary ammonium compounds</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Quaternary imidazoline compounds</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Quaternary imidazolium compounds</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Rinsing agents (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Rinsing agents with high nonionic surfactant content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Sample containing metal particles due to abrasion (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Samples containing active chlorine (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Samples containing active chlorine (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Samples containing active oxygen (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>Electrode</td>
<td>Titrant</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------------------------------------</td>
<td>-----------</td>
<td>----------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Samples containing active oxygen (cationics)</td>
<td>SR</td>
<td>dodecy1 sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Samples containing metal particles due to abrasion (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Sarcosinates</td>
<td>SR</td>
<td>TEGO trant A100 c=0.005 mol/L</td>
<td></td>
</tr>
<tr>
<td>Sarcosinates in body washes</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Sarcosinates in toothpaste</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Scouring milk (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Scouring milk (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Scouring powder (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Scouring powder (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Sec. alkane sulphonates (SAS)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Secondary alkane sulphonates (SAS)</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Sensitive formulations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>shower gels, foam baths, liquid soaps, rinsing agents (manual), household cleaners (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with cocoyl isethionate (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with fatty alcohol PEG &gt;3 sulphates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with fatty alcohol PEG &gt;3 sulphates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with fatty alcohol PEG sulphosuccinates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with fatty alcohol PEG sulphosuccinates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with high betain content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with high betain content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with high nonionic surfactant content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with high nonionic surfactant content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shampoos with sodium cocoyl isethionates (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shower cream 2 in 1 (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shower creams, soap-based (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L pH = 10</td>
<td></td>
</tr>
<tr>
<td>Shower gel formulations with lauryl sarcosinates</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shower gels</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shower gels with fatty alcohol ether carboxylic acids (anionics)</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Shower gels with fatty alcohol ether carboxylic acids, pH = 10</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shower gels with fatty alcohol PEG &gt;3 sulphates</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shower gels with fatty alcohol PEG sulphosuccinates</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shower gels with high betain content</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shower gels with high nonionic surfactant content</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Shower gels with MAP</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Shower gels with sodium cocoyl isethionate</td>
<td>SR</td>
<td>TEGO trant A100 c=0.05 mol/L</td>
<td></td>
</tr>
<tr>
<td>Skin disinfectants (quats)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Soaps (syndets) (anionics)</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Soaps &lt;C&lt;sub&gt;12&lt;/sub&gt;</td>
<td></td>
<td>cannot be determined</td>
<td></td>
</tr>
<tr>
<td>Soaps &gt;C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Soaps C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>NIO</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Soaps cannot be determined</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>Electrode</td>
<td>Titrant</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>-----------</td>
<td>----------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Soaps C₈</td>
<td>cannot be determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soft soap</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Special soap-based cleaners</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Stain removers (anionic surfactant)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Styling gels (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Styling gels (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Styling products (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Styling products (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Sulphosuccinate diesters</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Sulphosuccinate monoesters</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Syndet soaps (anionics)</td>
<td>cannot be determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taurides</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Toluene sulphonates</td>
<td>cannot be determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toothpaste (amine fluoride)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Toothpaste (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Toothpaste (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Toothpaste (lauroyl sarcosinates)</td>
<td>cannot be determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toothpaste (lauryl sulphates)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Toothpaste (taurides)</td>
<td>determination limited</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Universal cleaner (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Universal cleaner with high nonionics content (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Universal cleaner with orange oil (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Universal cleaner with pine oil (cationics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Universal cleaners, soap-based</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Universal cleaners, soap-based</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Washing powders (anionics and soaps)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Washing powders (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>WC cistern tablets (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>WC cleaners (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>WC cleaners (cationics)</td>
<td>SR</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>WC cleaners with pine oil (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>WC perfume blocks (anionics)</td>
<td>SR</td>
<td>TEGO trant A100 c=0.02 mol/L</td>
<td></td>
</tr>
<tr>
<td>Window cleaners (anionics)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
<td></td>
</tr>
<tr>
<td>Xylene sulphonates</td>
<td>cannot be determined</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### 21.4 Pharmaceuticals that can be titrated

**Table 67 List of pharmaceuticals that can be titrated**

<table>
<thead>
<tr>
<th>Product</th>
<th>Electrode</th>
<th>Titrant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambroxol hydrochloride</td>
<td>NIO</td>
<td>STPB c=0.1 mol/L</td>
</tr>
<tr>
<td>Anionic pharmaceutical agents</td>
<td>NIO</td>
<td>TEGO trant A100 c=0.01 mol/L</td>
</tr>
<tr>
<td>Bromhexine hydrochloride</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Cationic pharmaceutical agents</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Chlorhexidine dihexylurate</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Chlorhexidine dichloride</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Chlorhexidine dichloride</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Clobutinol</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Clotrimazol</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Codeine phosphate</td>
<td>NIO</td>
<td>STPB c=0.1 mol/L (determination limited)</td>
</tr>
<tr>
<td>Dihydrocodeine thiocyanate</td>
<td>NIO</td>
<td>STPB c=0.1 mol/L (determination limited)</td>
</tr>
<tr>
<td>Ethacridine lactate</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Gargling solution (chlorhexidine dihexylurate)</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Hand disinfectant (chlorhexidine dihexylurate)</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Hand disinfectant (hexetidine)</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Hexetidine</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Ipratropium bromide</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Lidocaine</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Lozenges (benzalkonium chloride)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td>Lozenges (cetylpyridinium chloride)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td>Lozenges (chlorhexidine dihexylurate)</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Metoclopramide hydrochloride</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Mouth rinsing solution (anions)</td>
<td>IS</td>
<td>TEGO trant A100 c=0.004 mol/L</td>
</tr>
<tr>
<td>Mouth rinsing solution (cations)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td>Mouth rinsing solution (quats)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td>Nose drops (quats)</td>
<td>IS</td>
<td>dodecyl sulphate sodium salt c=0.004 mol/L</td>
</tr>
<tr>
<td>Octenidine dihydrochloride</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Papaverine</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Phenytoinolate dihydrogen citrate</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Propafenone</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Salbutamol sulphate</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Skin disinfectant (chlorhexidine dihexylurate)</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Skin disinfectant (hexetidine)</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
<tr>
<td>Verapamil hydrochloride</td>
<td>NIO</td>
<td>STPB c=0.01 mol/L</td>
</tr>
</tbody>
</table>

The list of titratable pharmaceuticals is not exhaustive by any means. It is based on tests that were carried out with several pharmaceutical raw materials and finished pharmaceutical products selected at random.

### 21.5 Incompatibilities between electrodes and a number of selected sample matrices

**Table 68 Electrode incompatibility with selected sample matrices**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Incompatible with</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS, NIO</td>
<td>Samples with high oil and solvent content, e.g. cooling lubricants, oil-containing formulations, etc.</td>
</tr>
<tr>
<td>IS, NIO</td>
<td>Samples containing metal particles (due to abrasion) and aggressive scouring agents</td>
</tr>
<tr>
<td>IS, NIO</td>
<td>Added solvents</td>
</tr>
<tr>
<td>IS, NIO</td>
<td>Alcohols above the recommended concentration</td>
</tr>
<tr>
<td>SR</td>
<td>Samples with a high salt load, e.g. electroplating baths, etc.</td>
</tr>
</tbody>
</table>

The above table is not complete. Substances that are not listed here may still destroy the electrodes or make them unusable in other ways.
22 Appendix B

The author would like to thank ...

The author would like to express his particular thanks to the colleagues of his working group: Christian Götz, Ms. Regina Unthan, Ms. Andrea van Baal, Holger Bast, Patrick Winter for the help which they have provided in many different ways. As a result of their committed active and passive help in carrying out many thousand titrations, in preparing graphs and proofreading they have contributed to the fact that writing this monograph has always been enjoyable and a source of pleasure.

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