Robotic Acid/Base Analyzer

Applications

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Ion analysis

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Robotic Acid/Base Analyzer

Symbols used in this document:

c (X)	Molar concentration of substance X in mol/L, often written as [X]
M (X)	Molar mass of substance or atomic mass (relative mass) of substance X in g/mol
w (X)	Mass fraction of substance X, e.g. w(NaOH) = 40%
ß (X)	Mass concentration of substance X, e.g. ß(NaCl) = 20 g/L
a (X)	Activity of substance X (only corresponds to the molar concentration in very dilute solutions; as the concentration increases, dissolved particles mutually influence each other so that their activity is lower than would be expected from the concentration).
pK_p	Autoprotolysis constant of a solvent
{ }	In this document braces such as used in the formula {AgCl} indicate solid substances (precipitates) that do not consist of single molecules (in this case AgCl), but whose ionic components form an extended ionic lattice.

tiamo methods

The methods described in this document are part of the *tiamo* installation on your PC system. To use these methods you can import them into your method groups with the built-in method manager in the *tiamo* software. Please consult the *tiamo* user manual or online-help for further instructions.

The methods can be found in the following path:

C:\Program Files\Metrohm\tiamo\examples\methods\english\855 Robotic Analyzer\Acid Base

(The *tiamo* installation path of your system may be different.)

The *tiamo* user manual (in pdf file format) can be found in the following path:

C:\Program Files\Metrohm\tiamo\doc\english

Accessories of the Robotic Acid/Base Analyzer

1.855.0020	855 Robotic Titrosampler
1.800.0010	Dosino
1.802.0010	Rod stirrer
6.0253.100	LL-Aquatrode plus OK
6.1236.020	Sleeve with SGJ 14/12 mm 2x
6.1458.040	Titration head insert 3x SGJ 14
6.1459.300	Sample beakers
6.1462.170	Robotic arm with sensor
6.1543.170	Aspiration tip M8
6.1546.030	Piston rod
6.1608.023	Bottle 1 L
6.1621.000	PE container 10 L 2x
6.1805.060	FEP tubing / M6 / 60 cm 3x
6.1805.120	FEP tubing / M6 / 100 cm
6.1805.510	PTFE tubing M8, 60 cm
6.1812.000	PTFE tubing 4/6 mm, 4m
6.1828.000	PVDF connection nipple 2x
6.1909.020	Stirring propeller 104 mm
6.2001.120	Bottle holder base
6.2041.840	Sample rack 59 x 120 mL
6.2053.000	Cable clip 10x
6.2061.010	Bottle holder
6.2104.020	Electrode cable 1 m
6.2151.000	Cable USB A - mini-DIN 8P
6.2308.050	KCl solution 3 mol/L (50 mL)
6.2323.000	Storage solution
6.2621.030	Hexagon key 4 mm
6.2621.070	Hexagon key 5 mm
6.2621.130	Hexagon key 2 mm
6.2621.140	Hexagon key 2.5 mm
6.2740.020	Spray nozzle 3x
6.2751.100	Safety shield
6.3032.220	Dosing Unit 20 mL
6.6056.112	tiamo 1.1 full version CD
T.2400.102	Ferrite cores 4x

Table of contents

1 Application Information

1.1 Introduction: titration means counting!

Together with gravimetry, titration is one of the oldest analytical methods. Both belong to a group of analytical methods that is based on chemical reaction.

In a titration one determines the volume of a standard solution (titrant) that is necessary for complete chemical reaction with the analyte. The titrant contains a known amount of a particular substance.

Since Loschmidt and Avogadro we know that one gram molecule of a substance contains a defined number of particles. A standard solution is produced by dissolving a particular weight of a substance in a solvent. Each volume fraction of this standard solution contains a defined number of particles of the dissolved substance. This means that measuring the volume of a standard solution is a method of counting particles: Titration means counting!

Despite many new, mainly physical instrumental analytical methods, titrimetry as a «wet-chemistry method» still remains a standard procedure for quantitative analysis today. This is because it has a number of specific advantages:

- Titration is one of the absolute content determination methods, i.e. the result of the analysis provides direct information about the amount of substance to be determined, without instrument or method-specific factors having to be calibrated (such as is normal in relative methods, for example HPLC, atomic spectroscopy or UV/VIS photometry).
- Titrations are easy to carry out: The equipment and the procedures to be performed are simple. They are easy to understand – the fundamentals of titrimetric methods are widely known or can be learned in a short time.
- Titrations are carried out rapidly: If the total time for setting up the workplace to obtaining the analytical result is taken into consideration, then titrimetric determinations require much less time than other methods.
- Titration is a versatile method: Numerous titration methods have been drawn up, these range from the determination of inorganic ions up to the determination of complex organic compounds. The analyte concentrations can range from 100% or virtually 100% (analysis of ultra pure substances, purity determinations) down to the ppm range. Sample amounts of a few micrograms are adequate, amounts in the gram range are also possible.
- Titration supplies highly reproducible and correct results. A typical reproducibility is <1%. In high-precision titrations values of 0.1% are demanded and also achieved. For such demands the accuracy should lie within the limits of the standard deviation.
- Titrations can be automated: Titrimetric determinations can be automated to a high degree. This means that, for example, they are suitable for analyzing the content in routine operation (e.g. active ingredient content in tablets).

1.2 Acid/Base reactions

The term acid-base has been revised several times since the 18th century in accordance with the state of knowledge:

- Acids contain oxygen (Lavoisier)
- Acids contain hydrogen that can be replaced by a metal (Liebig)
- Acids dissociate in aqueous solution to release protons and bases release hydroxide ions (Arrhenius, Ostwald)

These theories can only partly explain chemical reactions. They refer to aqueous solutions; ampholytes are not included. Examples are aqueous solutions of salts: $KHSO_4$ reacts acidic, Na_2HPO_4 alkaline.

Brønsted defined the acid-base reaction as the exchange of protons. The *acid* acts as *proton donor* and the *base* as *proton acceptor*. A deprotonated acid is called the conjugate base and a protonated base is called the conjugate acid. In this way the theory can also be applied without any problem to ampholytes, salts and prototropes of non-aqueous solvents. The equilibrium constants of the reactions allow a quantitative reactivity series of acids and bases to be drawn up (see below).

Lewis extended the Brønsted theory (Brönsted theory). A Lewis base has a free electron pair, a Lewis acid an electron **pair** gap. Lewis acid and Lewis base react to form a covalent or coordinative compound. Examples:

$$2\ CN^- + Ag^+ \longrightarrow [Ag(CN)_2]^-$$

$$2\ Cl^- + SnCl_4 \longrightarrow [SnCl_6]^{2-}$$

Typical Lewis acids are molecules with an incomplete valency shell, cations as the central atoms of complexes and molecules with multiple polar bonds (e.g. acid anhydrides). Typical Lewis bases are molecules and ions with free electron pairs, anions as complex ligands and molecules with multiple bonds. The Lewis model can also be used to describe precipitation and complex-forming reactions. As no universal reference acid or base exists, there is no practical quantitative reactivity series for Lewis acids and bases; however, the Lewis conception allows numerous chemical reactions to be systemized qualitatively.

Protolysis

Polar (prototropic, protic) solvents undergo self-dissociation, i.e. they form an acid-base pair to a slight extent.

Example water:

$$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$$

Neither free protons nor free electrons are found in a solution. For protons this means that H^+ should not be used as an expression, but rather H_3O^+ to represent the clusters of protons and water effectively present in an aqueous solution.

According to the law of mass action, the ionic product of water $\mathbf{K_w}$ is calculated as follows:

$$a(X^+) \times a(Y^-) / a^2(XY)$$

for H_2O this means:

$$a(H_3O^+) \times a(OH^-) / a^2(H_2O) = K_W = 10^{-14}$$

K is temperature-dependent. In tables it is usually given for 25 °C (the values for H_2O are 14.9 at 0 °C, 14.2 at 20 °C, 14.0 at 25 °C, 13.5 at 40 °C, etc.).

The relative «strength» of an acid or base in an aqueous solution is described by the equilibrium constants. These provide information about the extent to which an acid or base dissolved in water at equilibrium can accept or donate protons. Water is the reference base for each acid and the reference acid for each base. These acidity and basicity constants are

known as $\mathbf{K_a}$ and $\mathbf{K_b}$ respectively. We have simplified their formulation here by using the molar concentration instead of the activities of the participating species. The molar concentration of water in a mixture is regarded as being constant for diluted solutions (55.5 mol/L) and not included.

$$K_a = [H_3O^+] \times [A^-] / [HA]$$

$$K_b = [BH^+] \times [OH^-] / [B]$$

The negative common logarithms of these values are, analogous to the pH definition, known as $\mathbf{pK_a}$ and $\mathbf{pK_b}$ respectively. The higher the pK value, the weaker the acid or base.

The neutral point of a non-aqueous solvent is calculated in a similar manner to that for water. Clearly, the pH term only applies to purely aqueous solutions!

$$H_2O, neutral\ pH = -\log\sqrt{K_W} = -\log\sqrt{10^{-14.0}} = +7.0$$

The following table shows a small selection of autoprotolysis constants of prototropic solvents (at 25 °C).

Solvent	Autoprotolysis			pK_p
Ethanol	$2\ C_2H_5OH$	⇌	$C_2H_5OH_2^+ + C_2H_5O^-$	19.1
Methanol	$2\ CH_3OH$	⇌	$CH_3OH_2^+ + CH_3O^-$	16.7
Acetic acid	$2\ CH_3COOH$	⇌	$CH_3COOH_2^+ + CH_3COO^-$	14.5
Water	$2\ H_2O$	⇌	$H_3O^+ + OH^-$	14.0
Formic acid	$2\ HCOOH$	⇌	$HCOOH_2^+ + HCOO^-$	6.2
Sulfuric acid	$2\ H_2SO_4$	⇌	$H_3SO_4^+ + HSO_4^-$	3.6

Acid-base reactions with water

In aqueous solutions the protolysis reaction with water normally predominates (as an ampholyte H_2O can act as a Brønsted acid or a Brønsted base):

acidic reaction of solvent

$$HB\ (a) + H_2O\ (b) \rightleftharpoons H_3O^+ + B^-$$

basic reaction of solvent

$$B^-\ (b) + H_2O\ (a) \rightleftharpoons HB + OH^-$$

Just as with the ionic product of water, a(solvent) is set = 1 for dilute solutions. The resulting equilibrium constants are known as the *acidity constant* $\mathbf{K_a}$ and the *basicity constant* $\mathbf{K_b}$.

$$K_a \times K_b = K_w$$

$$pK_a + pK_b = pK_w = 14\ (25\ °C)$$

The stronger the acid or base, the weaker the conjugate base or acid.

At the same time the pK values of the aqueous system limit the acidic or basic strength of protolytes in aqueous solution (differentiation).

Stronger acids and bases (pK <0 or pK >14 for the conjugate protolyte) are converted to oxonium ions (H_3O^+) and hydroxide ions (OH^-) in aqueous solution. *Leveling* occurs – the separate determination of mixed very strong acids or mixed very strong bases in an aqueous solution is not possible by titration. (Only one endpoint is found in the titration of mixtures of e.g. KOH/NaOH or HCl/H_2SO_4).

The known corresponding acid-base pairs are arranged according to increasing pK_a (or decreasing pK_b value) and normally divided into the following categories:

- very strong $pK_a < 0$
- strong pK_a 0…4
- weak pK_a 4…10
- very weak pK_a 10…14
- extremely weak $pK_a > 14$

Protolytes

As a result of the leveling effect of water, differences in the protolysis constants of strong protolytes can only be determined in non-aqueous solvents. In such solvents the relationship $pK_a + pK_b = pK_{solvent}$ also applies for the conjugate acid-base pair. This means that the solvent cation (*lyonium ion*) and the solvent anion (*lyate ion*) are always the strongest acids and bases in the affected system.

Whereas acetic acid behaves in water like a weak acid, in $HClO_4$ it behaves like a base:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

$$HClO_4 + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + ClO_4^-$$

In order to be able to achieve the separate determination of the components in an aqueous solution by titration, the differences in their pK values should be approx. 5 units. In contrast, in suitable non-aqueous solvents a difference of 2 to 3 pK units is normally sufficient.

pKa values of some selected acids

Acids	pKa
Acetic acid	4.73
Acrylic acid	4.26
Benzoic acid	4.20
Boric acid	9.24
Chloroacetic acid	2.81
Hydrobromic acid	≈ –6
Hydrochloric acid	≈ –3
Hydrocyanic acid	9.40
Hydrofluoric acid	3.14
Hydrogen sulfide acid 1st stage	6.90
Hydrogen sulfide acid 2nd stage	12.9
Lactic acid	3.86
Nitric acid	1.32
Oxalic acid 1st stage	4.31
Oxalic acid 2nd stage	1.42
Perchloric acid	≈ –9
Phenol	9.95
Phosphoric acid 1st stage	1.96
Phosphoric acid 2nd stage	7.12
Phosphoric acid 3rd stage	12.36
Salicylic acid	2.98
Sulfuric acid 1st stage	≈ –3
Sulfuric acid 2nd stage	1.92

pKb values of some selected bases

Bases	pKb
2-Picoline	7.52
Acridine	9.89
Ammonia	4.75
Aniline	9.42
Benzylamine	4.62
Calcium hydroxide	1.30
Coffeine	13.39
Cyclohexylamine	3.36
Diethanolamine	5.12
Ethanolamine	4.56
Ethylamine	3.33
Imidazole	7.00
Lithium hydroxide	–0.10
Magnesium hydroxide	3.36
Naphthylamine	10.08
o-aminobenzoic acid	10.92
o-toluidine	9.61
Piperidine	2.80
Pyridine	8.81
Triethanolamine	6.23
Triethylamine	3.28
Trimethylamine	4.20
Urea	13.8

The strongest acid in the list is perchloric acid, the strongest base is lithium hydroxide.

The following empirical rules apply for the *relative acid strength* of inorganic acids:

- *Hydracids*: the acidity increases as the atomic number increases, both within the group and within the period. (This means that HI is the strongest acid.):

  $HF < HCl < HBr < HI$

- *Oxyacids* are stronger the fewer H atoms and more O atoms they contain. (The strongest mono-oxyacid is $HClO_4$).

  $HClO < HClO_2 < HClO_3 < HClO_4$

  $H_4SiO_4 < H_3PO_4 < H_2SO_4 < HClO_4$

1.3 Acid-base titrations

Acid-base reactions occur very rapidly (proton transfer takes far less then one millionth of a second).

In mixtures of acids the titration is always carried out in the sequence of the relative acid strengths. This means that the strongest acid is always titrated first, the weakest acid last.

Example:

The titration curve of a mixture of HCl and CH_3COOH shows two equivalence points/endpoints. The consumption up to EP1 corresponds to the molar concentration of HCl and the consumption for the difference EP2 – EP1 to the molar concentration of acetic acid.

Titration of strong protolytes (strong acid with strong base and vice versa)

The salts of strong acids with strong bases do not undergo protolysis with water, which means that an equivalent amount of these acids and bases react neutrally. The equivalence point in the titration of a strong acid with a strong base and vice versa is therefore identical with the neutral point (pH = 7.0 in H_2O).

The shape of the titration curve results from the fact that in order to increase the pH from 1 to 2 it is necessary to reduce the H_3O^+ concentration to 1/10 of the original value (or that 90% of the equivalent base has already been added). From pH = 2 to pH = 3 it is then 9%, from pH = 3 to pH = 4 then 0.9%, etc. With the excess base it is exactly the opposite; from pH = 7 to pH = 8 0.0009% is necessary, from pH = 8 to pH = 9 requires 0.009%, from pH = 9 to pH = 10 it is 0.09% excess base, etc.

This is why typical symmetric titration curves with a steep «jump region» are obtained, whose equivalence point (titration endpoint, corresponds to the point of inflection of the curve) lies at pH = 7.0.

Titration of a weak acid with a strong base

Before the start of the titration it can be seen that the pH is acidic, which corresponds to the weak acid not being completely dissociated in water. After the start of the titration a buffering range (10...90% of neutralization) can be observed in which the weak acid and its salt or acid anion are both present. In this buffering range the addition of the base only alters the pH slightly. The point of inflection of the buffering range corresponds to the semi-equivalence point of the titration (half reaction) and therefore, according to the Henderson-Hasselbalch equation, the pK_a value of the weak acid is given by: $pH = pK_a + \log [A^-] / [HA]$, where at half reaction the molar concentrations of acid anion and acid are equal – resulting in log 1, which is equal to 0.

In the above case the equivalence point no longer lies at pH = 7, because the added base competes with the conjugate base of the acid. At the equivalence point the *salt solution* present has an *alkaline* reaction, as the acid anions of a weak acid undergo protolysis with water (hydrolysis). The equivalence point of such a titration lies – depending on the relative strength of the acid – in the pH range 7.5...10.

The higher the concentration of acid and base in the solution, the wider the buffering range on the volume axis. The pH value achieved by adding additional base beyond the equivalence point finally approaches that of the base used as the titrant.

Titration of a weak base with a strong acid

Before the start of the titration an alkaline pH is measured that corresponds to that of the not fully dissociated weak base in water. After the start of the titration a buffering range can also be observed (10...90% of the neutralization), in which the weak base and its conjugated protonated form are both present. Addition of acid hardly alters the pH in this buffering range at all. The point of inflection of the buffering range corresponds to the semi-equivalence point of the titration (half reaction) and lies at that pH value which corresponds to the pK_b value of the base. The equivalence point is again no longer at pH = 7, because the added acid competes with the conjugate acid of the base. The corresponding salt solution is acidic as the protonated base undergoes protolysis with water (hydrolysis). The equivalence point lies – depending on the relative strength of the base – in the pH range 6.5...4.

Titration of a weak acid with a weak base

This titration is unsuitable for quantitative determinations! There is no marked jump in the titration curve, and the slope of the curve in the equivalence region does not achieve a maximum value. No suitable titration endpoint for a quantitative determination is reached. This means that, when selecting a titrant for the titration of weak acids and bases, weak bases and acids should not be chosen.

Titration curve

The following applies in general: The «jump» of a titration curve is more marked the higher the K_a or K_b values of the two reaction partners and the higher the concentrations of both species.

1.4 Calibrating the pH glass electrode

Recommended accessory

- Comb. pH glass electrode for aqueous titrations 6.0257.000 Aquatrode Plus with 6.2104.020 electrode cable

Reagents

- Buffer solutions pH = 4.00, 7.00 and 9.00, e.g. 6.2307.100, 6.2307.110 and 6.2307.120

General

Free protons (H^+ ions) occur in solutions just as little as free electrons. They combine with water to form oxonium ions:

$$H^+ + H_2O \longrightarrow H_3O^+$$

The pH value is defined as the negative logarithm of the oxonium ion activity, i.e. of the concentration of free, dissociated oxonium ions in mol/L: $pH = -\log [H_3O^+]$

Strictly speaking, the term pH only applies to purely aqueous solutions.

The pH scale ranges from 0 to 14 with the neutral point at pH = 7.0, where the H_3O^+ and OH^- ions are present in equilibrium. pH values below 7 result from an H_3O^+ excess, pH values above 7 from an OH^- ion excess. The more acidic a solution the higher its H_3O^+ ion concentration and the lower its pH value.

Weak acids, e.g. tartaric acid, do not dissociate completely. This means that only a small fraction (approx. 2...3%) of their acid ions are released. This also means that only on very rare occasions can the pH value be used as a measure of the concentration of acids or bases.

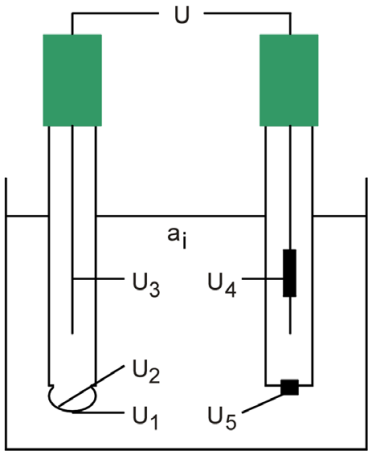
As the pH scale is logarithmic this means that small differences in pH correspond to large differences in the concentration of H_3O^+ ions. For example, at pH = 3.0 there are ten times more H_3O^+ ions present than at pH = 4.0, and at pH = 3.1 there are twice as many H_3O^+ ions present than at pH = 3.4.

The measuring setup for potentiometric measurements always consists of two electrodes – a *measuring or indicator electrode* and a *reference electrode*. For practical reasons these two electrodes are usually contained in a single *combined* electrode.

The indicator electrode (in this case the pH glass electrode) produces a potential that is dependent on the composition of the sample solution.

The reference electrode (usually Ag/AgCl) has the task of providing a potential that is as independent as possible of the sample solution (reference potential).

The potential measurement itself takes place virtually current-free by using a «voltmeter» with a high-impedance measuring input (this is necessary to avoid unwanted potential drops). The measured potential U is made up from the individual potentials produced by the indicator and reference electrodes. The following illustration shows a schematic diagram with a separate pH glass electrode (left) and a reference electrode (right):



U_1: Galvani potential between measuring electrode and measuring solution

U_2: Galvani potential between internal buffer and glass membrane

U_3: Galvani potential between internal reference electrode and internal buffer

U_4: Galvani potential of reference electrode

U_5: Diffusion potential at the diaphragm

The individual potentials U_2, U_3 and U_4 are determined by the construction of the electrodes and are therefore constant for a given electrode pair. The diffusion potential U_5 should be kept relatively constant and low by taking suitable measures. These measures include an optimal and clean diaphragm, constant stirrer speed during the measurements as well as a suitable reference electrolyte solution whose anions and cations have similar ionic mobilities – e.g. KCl. In this way the potential U_1 measured between the electrodes depends only on the sample solution. In the pH measurement this potential is again dependent on the activity a_i of the measuring ion (H_3O^+ ion / OH^- ion). This relationship is described by the *Nernst equation*:

$$U = U_0 + \frac{2.303 \times R \times T}{z_i \times F} \times \log a_i = U_0 + U_N \times \log a_i$$

where:

U	measured difference in potential between indicator and reference electrode
U_0	standard potential of the combined electrode (depends on its construction)
R	gas constant (8.31441 J / (K mol)
T	absolute temperature in K (273.15 + t / °C)
z_i	charge on the measuring ion i including its sign (+1 for H_3O^+ and –1 for OH^-)
a_i	activity of measuring ion

U_N Nernst slope (59.16 mV at 25 °C and z = 1)

2.303 conversion factor from natural to common logarithm

The Nernst slope U_N describes the theoretical electrode slope and corresponds to the change in potential produced by altering a_i by a factor of ten. It depends on the temperature and charge z of the measuring ion. **Please note: The instrument compensates the effect of temperature on U_N but not on the pH value of the solution!**

The following table shows values of U_N as a function of t / °C for z = 1:

Temperature t / °C	U / mV	Temperature t / °C	U / mV
0	54.20	40	62.14
10	56.18	50	64.12
20	58.17	60	66.10
25	59.16	70	68.09
30	60.15	80	70.07
38	61.74	90	72.06

An ideal pH glass electrode has a slope of 1 (100% of the Nernst slope) and an electrode zero point pH_{as} of 7.0, the latter corresponding to U_{as} = 0 mV.

Things are different in practice. The electrode zero point should have a value for U_{as} of ±15 mV (corresponds to pH_{as} = 6.75...7.25) and the slope should be >0.95 (>56.2 mV / pH at 25 °C).

In order to «inform» the instrument of the true electrode data it is necessary to calibrate the electrode. Buffer solutions have a defined pH value which, however, is temperature-dependent. The relevant information about the buffer solution is entered during the calibration procedure. The following table shows the pH values of Metrohm buffer solutions as a function of the temperature:

Temperature t / °C	pH = 4.00 ±0.02	pH = 7.00 ±0.02	pH = 9.00 ±0.02
10	3.99	7.06	9.13
20	3.99	7.02	9.04
25	4.00	7.00	9.00
30	4.00	6.99	8.96
38	4.02	6.98	8.91
40	4.02	6.98	8.90
50	4.04	6.97	8.84
60	4.07	6.97	8.79
70	4.11	6.98	8.74
80	4.15	7.00	8.71
90	4.20	7.01	8.68

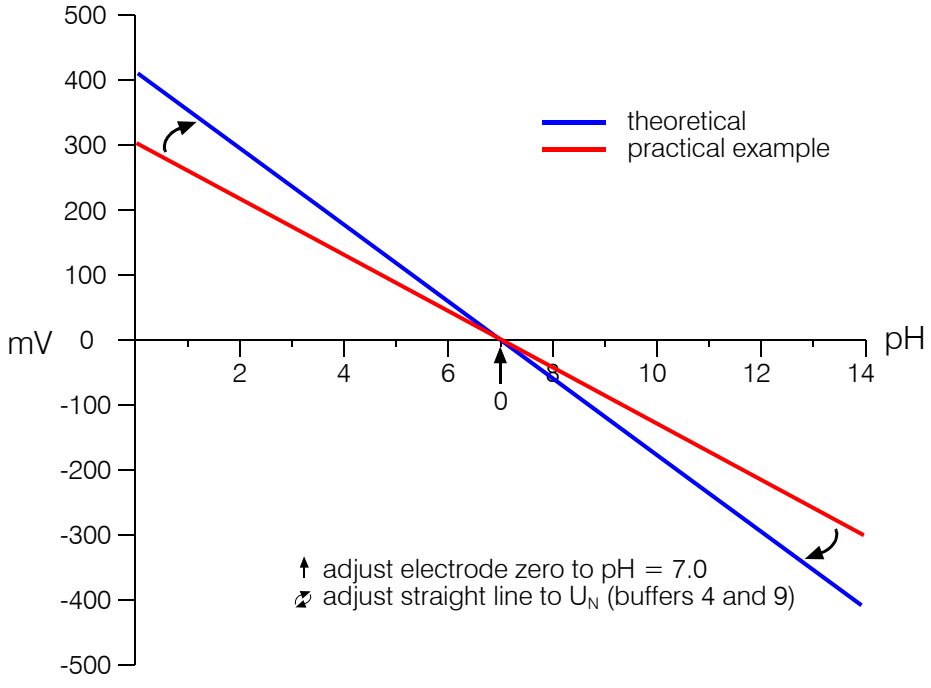
Buffer solutions are not stable!! They can be decomposed by bacteria and/or molds or – this applies to alkaline buffer solutions – alter their pH value by absorbing CO_2 from the atmosphere. This is why you should always use only fresh buffer solutions and reject them after use, i.e. not pour them back into the storage bottle.

Electrode calibration and electrode handling

We recommend the following procedure for **calibrating** a pH glass electrode:

- Remove the electrode from its storage vessel, attach a cable if necessary and connect it to the instrument.
- Open the electrolyte filling opening and, if necessary, top up the electrolyte solution.
- Rinse the electrode thoroughly with dist. H_2O and dab dry with a soft paper tissue (do not rub).
- Fill pH = 7.0 buffer solution into a beaker and add a stirrer bar.
- Immerse the electrode into the buffer solution and stir for approx. 1 min.
- On the ***tiamo*** enter the pH value of the buffer solution (at the corresponding temperature) and start the calibration with buffer 1 under stirring.
- When the measured value has been accepted, remove the electrode from the solution, rinse it thoroughly with dist. H_2O and dab dry with a soft paper tissue.
- Add pH = 4.0 or 9.0 buffer solution to a second beaker, add a stirrer bar, immerse the electrode and stir for approx. 1 min (the second buffer solution must have the same temperature as the first one).
- On the ***tiamo*** enter the pH value of the second buffer solution (at the corresponding temperature) and continue the calibration under stirring.
- After the measured value has been accepted, end the calibration. Remove the electrode from the solution, rinse the electrode thoroughly with dist. H_2O and dab dry with a soft paper tissue.

What happens in the instrument during calibration can be seen in the following plot:



Handling

Laboratory electrodes should have a long lifetime. Their characteristics (slope, response behavior, pH_{as} / U_{as}) must lie within the given criteria. In order to ensure this a few basic rules must be observed:

- After use rinse the electrode thoroughly with dist. H_2O and dab dry with a soft paper tissue. Close off the electrolyte filling opening and store the electrode by immersing it in storage solution to an adequate depth. Dry storage leads to delayed and poor response behavior. The electrolyte solution may become concentrated and pH_{as} / U_{as} could alter. Storage in dist. H_2O could result in the diaphragm being blocked by AgCl.
- If the electrode responds sluggishly and/or the slope is unsatisfactory then the electrode membrane must be etched. This is done by immersing the membrane in a 10% solution of ammonium difluoride (NH_4HF_2, use plastic beaker) for 1 min, then swirling it for approx. 10 s in c(HCl) = 5 mol/L, rinsing it thoroughly with dist. H_2O and then wiping off the silicate residue with a moist tissue. In order to build up a new gel layer the electrode is placed in c(KCl) = 3 mol/L for 24 h (or for 5 h in the same solution at 50 °C).
- If the diaphragm becomes blocked please refer to the electrode data sheet that accompanies each electrode. Removing such a blockage is complicated and time-consuming – it is better to send the electrode to your local Metrohm distributor for this.
- Contamination by fats, oils, lacquers, paints, etc.: remove the contamination with an organic solvent (acetone, petroleum benzene, toluene), rinse thoroughly with ethanol and dist. H_2O, dab dry and place in electrolyte solution.
- Contamination by proteins: immerse the electrode in a solution of 5% pepsin in c(HCl) = 0.1 mol/L for a few hours. Then rinse thoroughly with dist. H_2O, dab dry and place in electrolyte solution.

1.5 *tiamo* method: Calibrating the pH glass electrode

Application note

This is a method to calibrate a pH glass electrode. It consists of three different tracks.

In the series start track the rack is initialized and the system prepared for the measurement. Additionally the electrode is removed from the storage beaker and rinsed thoroughly.

The main track deals the calibration measurements followed by the rinsing of the electrode. After the measurements the results are calculated, a report is printed and the data saved in the previously defined database 'Robotic Acid Base Analyzer' (can be modified).

Procedure

Fill three beakers with Metrohm buffer solutions pH 4, 7 and 9. Make sure that the electrode is properly immersed in the buffer solution. The special beaker for storing the electrode has to be filled with Metrohm storage solution.

Remark

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted.

The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a sensor the head has to touch the beaker brim when moving to the work position. If this requirement can not be fulfilled no beaker will be recognized. Two special beakers have to be defined including their own work positions. Special beaker 2 is used for rinsing the electrode while special beaker 1 contains storage solution for a proper electrode treatment between the determination series.

Calibration report (example)

tiamo™ titration and more

Robotic Acid / Base Analyzer
Calibration

Programm version tiamo 1.1

2005-09-13 11:12:24 UTC+2

Results report

Determination

Method	Calibrating the pH glass electrode
Method saving date	2005-08-19 11:02:38 UTC+2
Method version	1
Method state	original
Determination ID	-4f2e45c7:105cd5e9155:-7e1c
Determination start	2005-08-19 11:05:00 UTC+2
Determination state	original
Determination version	1
Run number	3
User (full name)	Metrohm

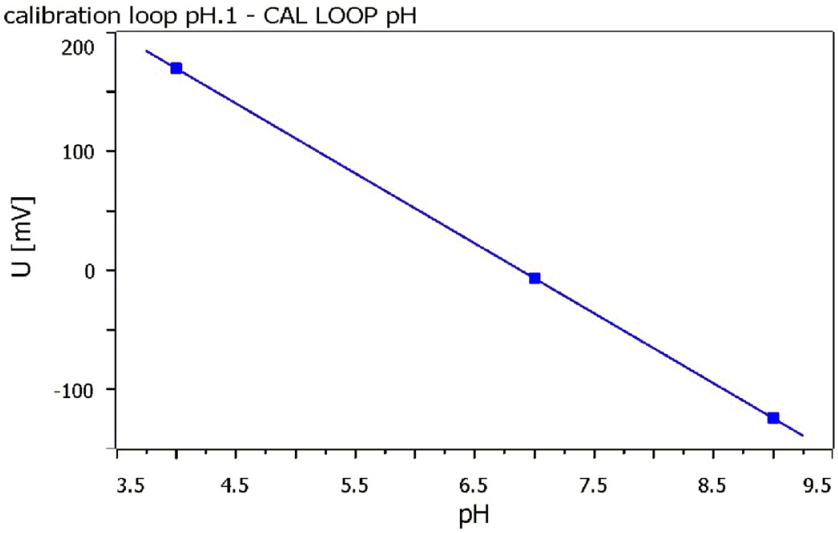
Sample data

Sample Identification 1	Calibration

Results

slope	**99.30**	**%**
zero point	**6.89**	

Calibration curve



2 Titrants

2.1 Preparing the most important alkaline and acidic titrants

General

Titrants are standard solutions, i.e. solutions that contain a defined content of a reactant. This content is given as the molar concentration *c* in mol/L. The «normality», which was frequently used previously, is no longer valid today and should therefore not be used.

Examples:

- 0.1 N HCl $\Rightarrow c(HCl) = 0.1$ mol/L
- 0.1 N H_2SO_4 $\Rightarrow c(H_2SO_4) = 0.05$ mol/L

Not all titrants have a stable titer, i.e. their concentration can vary with time.

Examples:

- Hydroxides absorb CO_2 from the atmosphere to form carbonates

This all means that the titer of the titrant may alter as time passes. In order to know the true titer concentration the titer must be determined at regular intervals.

The so-called standard titrimetric substances are used for determining the titer. Their content hardly changes, they are available with a defined degree of purity, can be dried and can be traced back directly to standard reference materials (e.g. National Institute of Standards and Technology – NIST, USA).

Such standard titrimetric substances /secondary standards are:

- For bases potassium hydrogen phthalate, M = 204.23 g/mol
- For acids tris(hydroxymethyl)-aminomethane, M = 121.14 g/mol

Most standard solutions/titrants are commercially available as ready-to-use solutions with a titer adjusted by the manufacturer at 20 °C to 1.000. We recommend that you purchase such ready-to-use solutions and do not prepare them yourselves.

In principle titer determinations should always be carried out at the same temperature at which the analyses are later to be carried out. Please note that solutions expand as their temperature increases.

For aqueous solutions a temperature difference of 5 °C for a theoretical consumption of 10.00 mL results in a difference in volume of 12.5 µL. This means that a titer of 1.0000 at 20 °C becomes a titer of 0.9988 at 25 °C – and for non-aqueous solutions this difference is even larger. In such a case a titer of 1.0000 at 20 °C becomes a titer of 0.9950 at 25 °C (possible error 0.5%)!

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer** is saved as «TITER» in the titrant list of tiamo.

** In Europe a dimensionless factor, with at least 4 decimal places (e.g. 1.0015).
In the USA already multiplied by ***c***, with at least 4 decimal places (e.g. 1.0015 mol/L).

2.2 Titer determination of alkaline titrants

Alkaline titrants do not have a stable titer. They may absorb CO_2 from the atmosphere to form carbonates, e.g.:

$$2\ NaOH + CO_2 = Na_2CO_3 + H_2O$$

This not only reduces the titer. The different strengths of the bases NaOH and Na_2CO_3 may negatively influence the titration curves and therefore the results – high-bias results are simulated, particularly for weak acids. In order to reduce CO_2 absorption as much as possible, soda lime (e.g. Merck no. 106839) is placed in the drying/absorber tube of the Exchange Unit.

– c(NaOH) = 0.1 mol/L

If possible this titrant should be bought ready for use. Otherwise dissolve 4.0 g NaOH in CO_2-free dist. H_2O, make up to 1 liter and mix.

Recommended accessories

- Comb. pH glass electrode for aqueous titrations 6.0257.000 Aquatrode Plus with 6.2104.020 electrode cable
- 20 mL Dosing Unit: 6.3032.220

Titer determination

Potassium hydrogen phthalate is dried overnight in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h.

Approx. 200 mg potassium hydrogen phthalate is weighed out into the titration beaker with an accuracy of 0.1 mg and dissolved in approx. 50 mL dist. H_2O. It is then immediately titrated to after the first endpoint with c(base) = 0.1 mol/L.

Calculation

Titer = 'MV.Sample size' * 1000 / ('DET pH.EP{1}.VOL' * 'DET pH.CONC' * 204.23)

where:

'MV.Sample size'	weight of potassium hydrogen phthalate [g]
1000	conversion factor for milliliter
'DET pH.EP{1}.VOL'	mL base up to endpoint
'DET pH.CONC'	concentration of the NaOH [mol/L]
204.23	molecular mass of potassium hydrogen phthalate [g/mol]

2.3 *tiamo* method: Titer determination of alkaline titrants

Application note

This is a method to determine the titer of an alkaline titrant. Alkaline titrants tend to absorb CO_2 from the atmosphere which results in a reduced titer value. With the titration of a primary standard the actual titer is determined. The method consists of five different tracks. In the start series track the rack is initialized and the system prepared for the measurements. The main track handles the determination followed by the rinsing of the electrode, which is done after every determination. In the exit track the results are calculated, a report is printed and the data is saved in the predefined database Robotic Acid Base Analyzer (can be modified). In the series end track the electrode is moved to a storage beaker where it is stored in Metrohm storage solution for a proper electrode treatment between the determination series. In case of an error, the error track guarantees that the electrode is moved to the storage beaker.

Sample preparation

The potassium hydrogen phthalate is dried over night in a drying oven at 105°C and allowed to cool down in a desiccator for at least 1 hour. Approximately 200 mg potassium hydrogen phthalate are weighed out in a beaker with an accuracy of 0.1 mg.

Procedure

The beakers are placed on the rack and ca. 60 mL distilled water are added automatically for dissolving. The solution is titrated with c(NaOH) = 0.1 mol/L and the titration stopped after the first endpoint. Then the solution is removed and the electrode is rinsed thoroughly before the next determination.

Remarks

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving to the work position. If this requirement can not be fulfilled no beaker will be recognized. One special beaker has to be defined including its work position. Special beaker 1 is used to ensure a proper electrode treatment between the determination series.

The value '204.23' used in the calculation formula is the molecular weight of potassium hydrogen phthalate in [g/mol].

Result report (example)

tiamo™ titration and more

Robotic Acid / Base Analyzer
Titer determination

Programm version tiamo 1.1

2005-09-13 10:49:57 UTC+2

Results report

Determination

Method	Titer determination of alkaline titrants
Method saving date	2005-08-19 13:54:25 UTC+2
Method version	1
Method state	original
Determination ID	-4f2e45c7:105cd5e9155:-7d4a
Determination start	2005-08-19 14:06:00 UTC+2
Determination state	original
Determination version	1
Run number	7
User (full name)	Metrohm

Sample data

Sample Identification 1	Titer NaOH
Sample size	154.8 mg

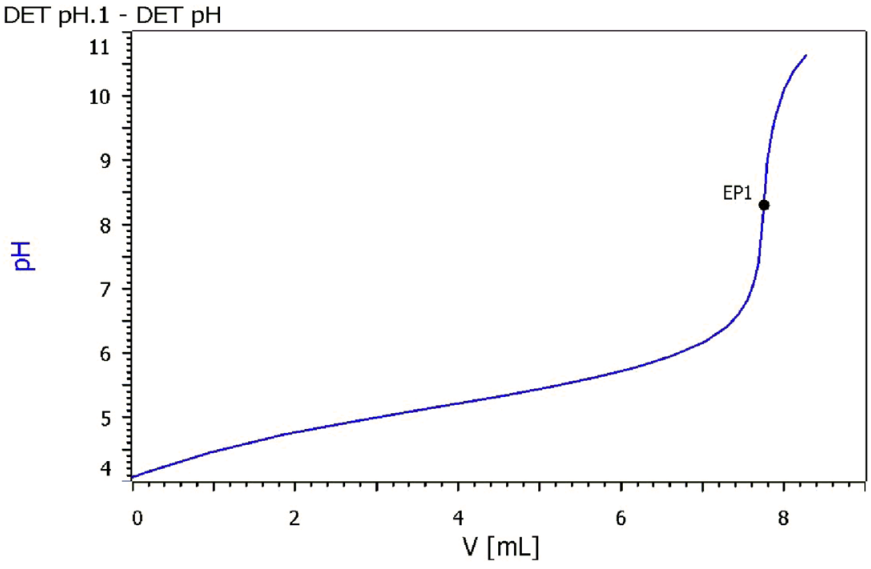
End points

DET pH **DET pH.1**

EP1	8.302	pH	7.7528	mL

Results

Titer	**0.9777**
mean value titer	**0.9776**



Statistical data (short)

Robotic Acid / Base Analyzer
Titer determination

Programm version tiamo 1.1

2005-09-13 10:49:57 UTC+2

Method . . . . . titer determination of alkaline titrants
Number of single determinations 3

Result name	n	Mean value	s +/-	s rel
Titer	3	0.9776	0.00410	0.42 %

Page 2 of 2

Statistical results (example)

Titer determination NaOH (0.1M)

Sample size [g]	Titer
0.1797	0.9735
0.2079	0.9817
0.1548	0.9777
0.2078	0.9821
0.1798	0.9728
0.1732	0.9743
0.2113	0.9772
0.1815	0.9773
0.1604	0.9787
0.1739	0.9781
Mean value	0.9773
abs. std. dev.	0.0031
rel. std. dev. %	0.32

2.4 Titer determination of acidic titrants

– c(HCl) = 0.1 mol/L in H_2O

If possible this titrant should be bought ready for use. Otherwise place approx. 800 mL dist. H_2O in a 1000 mL volumetric flask, add 9.8 mL *w*(HCl) = 32%, make up to the mark with dist. H_2O or ethanol and mix.

– c(H_2SO_4) = 0.05 mol/L

If possible this titrant should be bought ready for use. Otherwise place approx. 800 mL dist. H_2O in a 1000 mL volumetric flask and carefully add 2.7 mL *w*(H_2SO_4) = 96% while swirling the flask. Make up to the mark with dist. H_2O and mix.

Recommended accessories

- Comb. pH glass electrode for aqueous titrations 6.0257.000 Aquatrode Plus
- 20 mL Dosing Unit: 6.3032.220

Titer determination

Tris(hydroxymethyl)-aminomethane (TRIS) is dried overnight in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h. Approx. 100 mg TRIS is weighed out into the titration beaker with an accuracy of 0.1 mg and dissolved in approx. 50 mL dist. H_2O. It is then immediately titrated with HCl or H_2SO_4 to after the first endpoint.

Calculation

Titer = 'MV.Sample size' / ('DET pH.EP{1}.VOL' * 'DET pH.CONC' * 121.14)

where:

'MV.Sample size'	weight of TRIS [mg]
'DET pH.EP{1}.VOL'	mL acid up to endpoint
'DET pH.CONC'	concentration of the used acid [mol/L]
121.14	molecular weight of the TRIS [g/mol]

2.5 *tiamo* method: Titer determination of acidic titrants

Application note

This is a method to determine the titer of an acidic titrant. Once the titrant bottle is open the titer value changes. With the titration of a primary standard the actual titer is determined. The method consists of five different tracks. In the start series track the rack is initialized and the system prepared for the measurements. The main track handles the titration followed by the rinsing of the electrode, which is done after every determination. In the exit track the results are calculated, a report is printed and the data is saved in the predefined database Robotic 'Acid Base Analyzer' (can be modified). In the series end track, the electrode is moved to a storage beaker where it is stored in Metrohm storage solution for a proper electrode treatment between the determination series. In case of an error, the error track is carried out, which guarantees that the electrode is moved to the storage beaker.

Sample preparation

The tris(hydroxymethyl)-aminoethane (TRIS) is dried over night in a drying oven at 105°C and allowed to cool down in a desiccator for at leas t 1 hour. Approximately 100 mg TRIS are weighed out in a beaker with an accuracy of 0.1 mg.

Procedure

The beakers are placed on the rack and ca. 60 mL distilled water are added automatically for dissolving. The solution is then titrated with c(HCl) = 0.1 mol/L and the titration stopped after the first endpoint. Then the solution is removed and the electrode is rinsed thoroughly before the next determination.

Remarks

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving to the work position. If this requirement can not be fulfilled no beaker will be recognized. One special beaker has to be defined including its work position. Special beaker 1 is used for a proper electrode treatment between the determination series.

The value '121.14' in the calculation formula is the molecular weight of TRIS in [g/mol].

Result report (example)

tiamo™ titration and more

Robotic Acid / Base Analyzer
Titer determination

Programm version tiamo 1.1

2005-09-13 11:02:29 UTC+2

Results report

Determination

Method	Titer determination of acidic titrants
Method saving date	2005-08-24 10:35:22 UTC+2
Method version	1
Method state	original
Determination ID	6de54dcc:105e79b0d60:-7f6b
Determination start	2005-08-24 10:52:20 UTC+2
Determination state	original
Determination version	1
Run number	6
User (full name)	Metrohm

Sample data

Sample Identification 1	Titer HCl
Sample size	0.0872 g

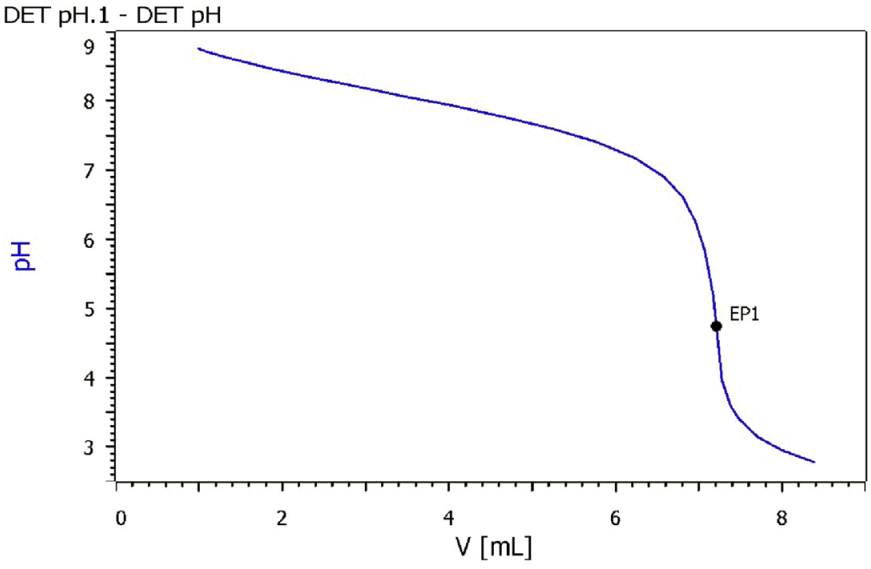
End points

DET pH **DET pH.1**

EP1	4.745	pH	7.2152	mL

Results

Titer	**0.9977**
mean value titer	**0.9986**



Statistical data (short)

tiamo™ titration and more

Robotic Acid / Base Analyzer
Titer determination

Programm version tiamo 1.1

2005-09-13 11:02:29 UTC+2

Method . . . . . Titer determination of acidic titrants
Number of single determinations 10

Result name	n	Mean value	s +/-	s rel
Titer	4	0.9986	0.00194	0.19 %

Page 2 of 2

Metrohm

Statistical results (example)

Titer determination HCl (0.1M)

Sample size [g]	Titer
0.1040	0.9970
0.1035	0.9830
0.1200	1.0140
0.0872	0.9977
0.0769	1.0021
0.0939	1.0041
0.0911	0.9988
0.0841	1.0020
0.0997	1.0002
0.1019	1.0050
Mean value	1.0007
abs. std. dev.	0.0027
rel. std. dev. %	0.27

3 Typical applications for the Robotic Acid/Base Analyzer

3.1 pH value and acid capacity in water

General

The acid capacity of a water (K_A) is the molar amount of oxonium ions that the water can accept before reaching certain predefined pH values. It is given in mmol/L.

For the acid capacity up to pH 8.2 ($K_{A\,8.2}$, previously p value) HCl is used to titrate to pH = 8.2; for the acid capacity up to pH 4.3 ($K_{A\,4.3}$, previously m value) the titration is to pH = 4.3.

Recommended accessories

- Comb. pH glass electrode for aqueous titrations 6.0257.000 Aquatrode Plus with 6.2104.020 electrode cable
- 20 mL Dosing Unit: 6.3032.220

Reagents

- Titrant: c(HCl) = 0.1 mol/L. For very soft water possibly use c(HCl) = 0.02 mol/L.

Analysis

The Aquatrode has already been calibrated.

50 mL water sample is added to the titration beakers which are placed on their positions on the sample rack. The pH value is first measured under stirring. The samples are then titrated with c(HCl) = 0.1 mol/L using pH = 3.5 as the stop criterion.

Calculations

(Results given to two decimal places)

$K_{A\,8.2}$ = 'SET pH.EP{1}.VOL' * 'SET pH.CONC' * 'SET pH.TITER' * 1000 /'MV.Sample size'

$K_{A\,4.3}$ = 'SET pH.EP{2}.VOL' * 'SET pH.CONC' * 'SET pH.TITER' * 1000 /'MV.Sample size'

where

'SET pH.EP{1}.VOL'	mL HCl until first endpoint is reached or a fixed EP at pH = 8.2
'SET pH.EP{2}.VOL'	mL HCl until second EP is reached or a fixed EP at pH = 4.3
'SET pH.CONC'	concentration of HCl solution [mol/L] (0.1 or 0.02)
'SET pH.TITER'	titer of HCl solution
1000	1000 (conversion factor for mmol/L)
'MV.Sample size'	volume of the sample [mL]

Remarks

Many waters have an initial pH value below 8.2 – $K_{A\,8.2}$ is not found and therefore cannot be calculated (only EP1 at pH = 4.3).

– Because the pH value depends on the temperature of the sample it is recommended to measure the temperature (temperature sensor 6.1110.100) during determinations

3.2 *tiamo* method: pH value and acid capacity in water

Application note

This is a method to measure the pH value and to determine the acid capacity of water samples. The acid capacity of water (KA) is the molar amount of oxonium ions that water can accept before reaching certain predefined pH values. There are existing two KA values, one at pH 8.2 and one at a pH of 4.3. Many waters have an initial pH value below 8.2. Therefore it is impossible to determine the KA at a pH of 8.2. The method consists of six different tracks. In the start series track the rack is initialized and the system is prepared for the determination runs. The main track handles the measurement of the pH and the titration of the sample. The electrode is rinsed after every determination according to the procedure in the rinsing track. In the exit track the results are calculated, a report is printed and the data is saved in the previously defined database 'Robotic Acid Base Analyzer' (can be modified). When the determination series is finished the series end track is executed in which the electrode is moved to a storage beaker where it is stored in a Metrohm storage solution for a proper treatment between the determination series. In case of an error, the error track is carried out, which guarantees that the electrode is moved to the storing beaker.

Sample preparation

50 mL water sample are filled in a titration beaker.

Procedure

The beakers are placed on the rack and the determination series started. The solution is titrated with c(HCl) = 0.1 mol/L and the titration stopped after the endpoint at ph 4.3 is reached. Then the beaker is emptied and the electrode is thoroughly rinsed before the next determination.

Remarks

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving to work position. If this requirement can not be fulfilled no beaker will be recognized. One special beaker has to be defined including its work position. Special beaker 1 is used for a proper electrode treatment between the determination series.

Result report (example)

tiamo™ titration and more

Robotic Acid / Base Analyzer
pH value and acid capacity in water

Programm version tiamo 1.1

2005-09-13 11:16:05 UTC+2

Results report

Determination

Method	pH value and acid capacity in water
Method saving date	2005-08-25 13:56:24 UTC+2
Method version	1
Method state	original
Determination ID	5ba76f4:105ec3853fe:-7d0b
Determination start	2005-08-25 14:22:23 UTC+2
Determination state	original
Determination version	1
Run number	9
User (full name)	Metrohm

Sample data

Sample Identification 1	Tab water
Sample size	50 mL

End points

MEAS pH **MEAS pH.1**

EME	7.979	pH		

SET pH **SET pH.1**

EP1	0.0000	mL	6.31	s
EP2	2.8180	mL	158.41	s

Results

pH	**7.98**	
Temperature	**25.33**	**°C**
K (s 8,2)	**0.00**	**mmol/L**
K (s 4,3)	**11.18**	**mmol/L**

Statistical results (example)

pH value and acid capacity in water

Sample size [mL]	pH value	Temperature [°C]	Acid capacity [mmol/L]
50	7.95	25.62	11.20
50	7.96	25.50	11.20
50	7.97	25.52	11.20
50	7.97	25.46	11.20
50	7.97	25.42	11.20
50	7.98	25.41	11.19
50	7.98	25.33	11.18
50	7.99	25.29	11.19
50	8.00	25.21	11.18
50	8.00	25.18	11.18
Mean value	7.98	25.39	11.19
abs. std. dev.	0.02	0.14	0.01
rel. std. dev. %	0.21	0.55	0.08

3.3 Determination of the total titratable acidity in wine

Recommended accessories

- 20 mL Dosing Unit: 6.3032.220
- Comb. pH glass electrode for aqueous titrations 6.0257.000 Aquatrode Plus with 6.2104.020 electrode cable

Reagents

- Titrant: *c*(NaOH) = 0.1 mol/L
- Possibly nitrogen from a pressure cylinder

General

The total titratable acidity is understood to be that fraction of acids contained in the must and/or wine (with the exception of carbonic acid) that are determined when the must is neutralized with NaOH to an agreed or predefined pH value. These titratable acids are mainly weak acids (tartaric acid, malic acid, etc.). Their neutral point is above pH = 7.0 (at approx. pH = 8.2). It is therefore obvious that lower values will be obtained by titrating to pH = 7.0 than when titrating to pH = 8.2. To be able to compare the analytical values it is essential that the titration is carried out to the agreed pH value. As this latter is defined differently, it is best to record the whole titration curve and to allow the titrant consumption up to the given pH value to be recalculated (by the titrator).

- CH, EU, Israel and RSA Titration to pH = 7.0
- Au and USA Titration to pH = 8.2 or to the point of inflection

General procedure

The sample is degassed by passing nitrogen through it, by briefly boiling and cooling it down rapidly or under vacuum (CO_2 removal). The given sample volume is diluted with CO_2-free dist. H_2O and titrated immediately with *c*(NaOH) = 0.1 mol/L.

Detailed procedures

A) CH, EU, Israel, RSA

Manual titration: Titrate 10 mL degassed sample plus 10 mL dist. H_2O (CO_2-free) with c(NaOH) = 0.1 mol/L up to pH = 7.0.

Automated titration: It is recommended to use 50 mL dist. H_2O (CO_2-free) to make sure that the electrode is immersed in the sample.

B) Au

Titrate 10 mL degassed sample plus 50 mL dist. H_2O (CO_2-free) with c(NaOH) = 0.1 mol/L up to pH = 8.2 or, preferably, to the inflection point of the titration curve.

C) USA

Titrate 5 mL degassed sample plus 100 mL dist. H_2O (CO_2-free) with c(NaOH) = 0.1 mol/L up to pH = 8.2 or, preferably, to the inflection point of the titration curve.

D) SA

Titrate 20 mL degassed sample with c(NaOH) = 0.1 mol/L up to pH = 7.0. Result also given in g/L H_2SO_4.

Calculation

The total titratable acidity is usually given in g/L tartaric.

total acidity at pH 7 = 'DET pH.FP{1}.VOL' * 'DET pH.TITER' * 'DET pH.CONC' * 150.1 / 'MV.Sample size'

total acidity at pH 8.2 = 'DET pH.FP{2}.VOL' * 'DET pH.TITER' * 'DET pH.CONC' * 150.1 / 'MV.Sample size'

where:

'DET pH.FP{1}.VOL'	mL NaOH up to pH = 7.0
'DET pH.FP{2}.VOL'	mL NaOH up to pH = 8.2
'DET pH.TITER'	titer of the NaOH solution
'DET pH.CONC'	concentration of NaOH solution [mol/L]
150.1	molecular weight of tartaric acid [g/mol]
'MV.Sample size'	sample volume [mL]

Remarks

The determination of the total titratable acidity is important for:

- musts, to be able to adjust the acidity and add the correct amount of SO_2;
- wines, to be able to follow the change in pH and the tartaric acid concentration.

After acid degradation the values for the **total titratable acidity** normally lie between **4.0 and 6.5 g/L** (red wines 4.0...5.5 g/L, «dry» wines 6.0...9.0 g/L).

3.4 *tiamo* method: Determination of the total titratable acidity in wine

Application note

This is a method to determine the acidity in wine. The total titratable acidity is understood to be the fraction of acids contained in the wine that are determined when the wine is neutralized with sodium hydroxide to a predefined pH value. These acids are mainly weak acids and their neutral point is above pH = 7.0. It is therefore obvious that lower values will be obtained by titrating to pH = 7.0 than when titrating to pH = 8.2. To be able to compare the analytical values it is essential that the titration is carried out to the agreed pH value. As there exist different defined values it is best to record the whole titration curve and to allow the titrant consumption up to the given pH value to be recalculated.

CH, EU, Israel and RSA:	Titration to pH = 7
Au and USA:	Titration to pH = 8.2 or to the inflection point

The method consists of six different tracks. In the start track the rack is initialized and the system prepared for the determination series. The main track handles the moving of the electrode to the sample beaker and the titration. The electrode is rinsed after every determination according to the procedure in the rinsing track. In the exit track the results are calculated, a report is printed and the data is stored in the predefined database 'Robotic Acid Base Analyzer' (can be modified). When the determination is finished the series end track is executed in which the electrode is moved to a storage beaker where it is stored in Metrohm storage solution for a proper electrode treatment between the determination series. In case of an error the error track is carried out which guarantees that the electrode is moved to the storage beaker.

Sample preparation and procedure

The sample has to be degassed before the determination either by passing nitrogen through it, by briefly boiling and cooling it down rapidly or under vacuum.

Depending on the country the sample preparation has to be adapted.

CH, EU, Israel and RSA:

Manual titration:	10 mL of the degassed sample plus 10 mL of dist. water are titrated with c(NaOH) = 0.1 mol/L up to pH = 7.0.
Automated titration:	It is recommended to use 50 mL of dist. water to make sure that the electrode is immersed in the sample.

Au:

10 mL of the degassed sample plus 50 mL of dist. water are titrated with c(NaOH) = 0.1 mol/L up to pH = 8.2 or to the inflection point of the titration curve.

USA:

5 mL of the degassed sample plus 100 mL of dist. water are titrated with c(NaOH) = 0.1 mol/L up to pH = 8.2 or to the inflection point of the titration curve.

The value 150.1 in the calculation formula is the molecular weight of tartaric acid in [g/mol]. Two values for the total acidity will be obtained, one at a pH value of 7.0 and one at 8.2.

Remark

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving down to work position. If that requirement can not be fulfilled no beaker will be recognized. One special beaker has to be defined including its own work position. Special beaker 1 is used for a proper electrode treatment between the determination series.

Result report

Robotic Acid / Base Analyzer
Total acidity of wine

Programm version tiamo 1.1

2005-09-13 10:55:05 UTC+2

Results report

Determination

Method	Total acidity in wine
Method saving date	2005-08-23 10:59:21 UTC+2
Method version	1
Method state	original
Determination ID	-1bd7dce7:105e1e3c5c4:-7d79
Determination start	2005-08-23 11:50:49 UTC+2
Determination state	original
Determination version	1
Run number	24
User (full name)	Metrohm

Sample data

Sample Identification 1	acidity in wine
Sample size	10 mL

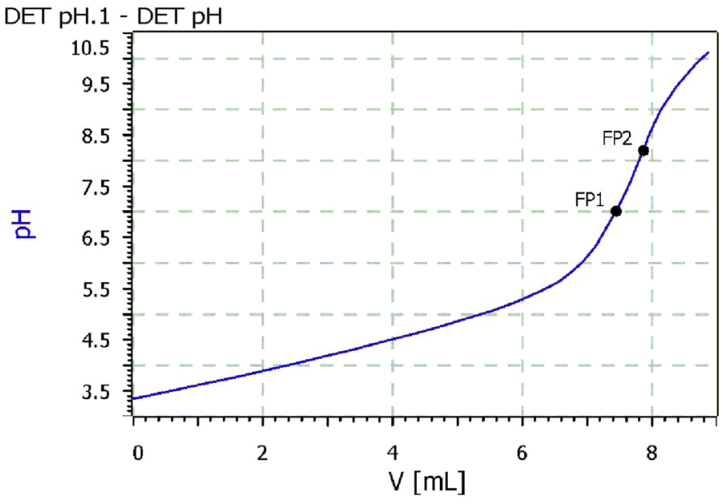
End points

DET pH **DET pH.1**

FP1	7.000	pH	7.4442	mL
FP2	8.200	pH	7.8674	mL
FP3	invalid	pH	invalid	mL

Results

total aciditiy at pH 7	**10.93**	**g/L**
total acidity at pH 8,2	**11.55**	**g/L**



Statistical results (example)

Total acidity of wine

Sample size	Content tartaric acid at pH 7	Content tartaric acid at pH 8.2
[mL]	[g/L]	[g/L]
10	10.94	11.57
10	10.91	11.52
10	10.92	11.54
10	10.90	11.53
10	10.91	11.52
10	10.93	11.55
10	10.92	11.54
10	10.91	11.54
10	10.94	11.60
10	10.91	11.56
Mean value	10.92	11.55
abs. std. dev.	0.01	0.02
rel. std. dev. %	0.13	0.21

3.5 Determination of different pharmaceutical substances

Example titration with citric acid

Recommended accessories

- 20 mL Dosing Unit: 6.3032.220
- Comb. pH glass electrode for aqueous titrations 6.0257.000 Aquatrode Plus with 6.2104.020 electrode cable

Reagents

- *c*(NaOH) = 0.1 mol/L
- *c*(NaOH) = 1.0 mol/L
- Dist. H_2O, CO_2-free (or demineralized H_2O)
- Ethanol and methanol, analytical grade
- Sorbitol

Citric acid (USP)

Weigh approx. 80 mg sample into the titration beaker and dissolve in 50 mL dist. H_2O. Titrate with *c*(NaOH) = 1 mol/L past the last endpoint.

Molecular weight ($C_6H_8O_7$) = 192.12 g/mol

Calculation

Mass fraction *w* in % = 'DET pH.EP{3}.VOL' * 'DET pH.TITER' * 'DET pH.CONC' * 192.12 * 100 / ('MV.Sample size' 3)

where:

'DET pH.EP{3}.VOL'	mL NaOH until third endpoint is reached
'DET pH.TITER'	titer of NaOH solution
'DET pH.CONC'	concentration of NaOH solution [mol/L]
192.12	molecular weight of citric acid [g/mol]
100	factor for conversion to %
'MV.Sample size'	sample weight [mg]

The following substances can also be titrated according to this method, though the calculation formula has to be adjusted:

N-Acetyltyrosine (Pharm. Europe)

Weigh approx. 0.180 g sample into the titration beaker and dissolve in 50 mL dist. H_2O. Titrate with *c*(NaOH) = 0.1 mol/L.

Molecular weight ($C_{11}H_{13}NO_4$) = 223.22 g/mol

Allantoin (Pharm. Europe)

Weigh approx. 0.120 g sample into the titration beaker and dissolve in 40 mL dist. H_2O. Titrate with *c*(NaOH) = 0.1 mol/L.

Molecular weight ($C_4H_6N_4O_3$) = 158.11 g/mol

Biotin (USP)

Weigh approx. 0.500 g (0.250 g) sample into the titration beaker, add 100 mL dist. H_2O and heat to 50 °C under stirring. Titrate slowly with c(NaOH) = 0.1 mol/L past the first endpoint (suspension).

Molecular weight ($C_{10}H_{16}N_2O_3S$) = 244.31 g/mol

Busulfan (USP)

Weigh approx. 0.160 g sample into an Erlenmeyer flask and dissolve in 50 mL dist. H_2O. Titrate with c(NaOH) = 0.1 mol/L past the first endpoint. Mount a reflux condenser and boil for 30 min. After the mixture has cooled down, titrate with c(NaOH) = 0.1 mol/L past the first endpoint. Use the total NaOH consumption for the calculation.

Molecular weight ($C_6H_{14}O_6S_2$) = 246.30 g/mol

Cilazapril (Pharm. Europe)

Weigh approx. 0.300 g sample into the titration beaker, dissolve in 25 mL ethanol, add 50 mL dist. H_2O and titrate with c(NaOH) = 0.1 mol/L.

Molecular weight ($C_{22}H_{31}N_3O_5$) = 417.50 g/mol

Enalapril maleate (Pharm. Europe)

Weigh approx. 0.100 g sample into the titration beaker and dissolve in 30 mL dist. H_2O. Titrate with c(NaOH) = 0.1 mol/L.

Molecular weight ($C_{24}H_{32}N_2O_9$) = 492.51 g/mol

Glutamic acid (Pharm. Europe)

Weigh approx. 0.130 g sample into the titration beaker and dissolve in 50 mL dist. H_2O under slight warming. Titrate with c(NaOH) = 0.1 mol/L.

Molecular weight ($C_5H_9NO_4$) = 147.13 g/mol

Histidine hydrochloride monohydrate (Pharm. Europe)

Weigh approx. 0.160 g sample into the titration beaker and dissolve in 50 mL dist. H_2O. Titrate with c(NaOH) = 0.1 mol/L.

Molecular weight ($C_6H_{10}ClN_3O_2$) = 191.61 g/mol

Lisinopril dihydrate (Pharm. Europe)

Weigh approx. 0.350 g sample into the titration beaker and dissolve in 50 mL dist. H_2O. Titrate with c(NaOH) = 0.1 mol/L.

Molecular weight ($C_{21}H_{31}N_3O_5$) = 405.48 g/mol

Mandelic acid (USP)

Weigh approx. 0.500 g (0.200 g) previously dried sample into the titration beaker and dissolve in 100 mL dist. H_2O. Titrate with c(NaOH) = 0.1 mol/L past the first endpoint.

Molecular weight ($C_8H_8O_3$) = 152.12 g/mol (C01)

Methimazole (USP)

Weigh approx. 0.250 g sample into the titration beaker and dissolve in 75 mL dist. H_2O. Under stirring add 15.00 mL c(NaOH) = 0.1 mol/L and 30 mL $AgNO_3$ solution. Titrate with c(NaOH) = 0.1 mol/L past the first endpoint. Use the total NaOH consumption for the calculation, i.e. 15 mL + mL EP1.

Molecular weight ($C_4H_6N_2S$) = 114.17 g/mol

Phenylmercuric borate (Pharm. Europe)

Weigh approx. 0.600 g sample into the titration beaker and dissolve in 25 mL dist. H_2O under slight warming. Dissolve 10 g sorbitol in the warm solution, leave to cool and titrate with c(NaOH) = 0.1 mol/L.

Molecular weight (H_3BO_3) = 61.83g/mol

Potassium hydrogen tartrate (Pharm. Europe)

Weigh approx. 0.170 g sample into the titration beaker and dissolve in 100 mL dist. H_2O. Heat and titrate the warm solution with c(NaOH) = 0.1 mol/L past the first endpoint.

Molecular weight ($C_4H_5KO_6$) = 188.17g/mol

Procarbazin hydrochloride (USP)

Weigh approx. 0.750 g (0.250 g) sample into the titration beaker and dissolve in 100 mL dist. H_2O. Titrate with c(NaOH) = 0.1 mol/L past the first endpoint.

Molecular weight = ($C_{12}H_{20}ClN_3O$) = 257.76 g/mol

Ramipril (Pharm. Europe)

Weigh approx. 0.300 g sample into the titration beaker and dissolve in 25 mL methanol. Add 25 mL dist. H_2O and titrate with c(NaOH) = 0.1 mol/L.

Molecular weight ($C_{23}H_{32}N_2O_5$) = 416.15 g/mol

Saccharin calcium (USP)

Weigh 0.500 g (0.200 g) sample into a separating funnel, add 10 mL dist. H_2O and 6 mL c(HCl) = 1 mol/L and shake/extract first with 30 mL and subsequently five times with 20 mL

chloroform/ethanol 9:1 (vol/vol). Evaporate the combined extracts to dryness and dissolve in 40 mL ethanol. Add 40 mL dist. H_2O and titrate with c(NaOH) = 0.1 mol/L past the first endpoint.

Molecular weight ($C_{14}H_8CaN_2O_6S_2$) = 404.43 g/mol

Saccharin sodium (USP)

Same sample preparation and titration as under saccharin calcium.

Molecular weight ($C_7H_4NNaO_3S$) = 205.17 g/mol

Tiaprofenic acid (Pharm. Europe)

Weigh approx. 0.500 g sample into the titration beaker and dissolve in 25 mL ethanol. Add 25 mL dist. H_2O and titrate with c(NaOH) = 0.1 mol/L.

Molecular weight ($C_{14}H_{12}O_3S$) =260.31 g/mol

3.6 *tiamo* method (example): Titration of citric acid

Application note

This is a method to determine the content of citric acid. The method consists of five different tracks. In the start series track the rack is initialized and the system prepared for the determination series. The main track handles the dissolving of the sample and the titration followed by the rinsing of the electrode, which is done after every determination. In the exit track the results are calculated, a report is printed and the data is saved in the predefined database Robotic Acid Base Analyzer (can be modified). In the series end track, the electrode is moved to a storing beaker where it is stored in Metrohm storage solution for a proper electrode treatment between the determination series. In case of an error, the error track is carried out, which guarantees that the electrode is moved to the storage beaker.

Sample preparation

Approximately 0.08 g of the sample are weighed out in a titration beaker.

Procedure

The beakers are placed on the rack and the determination series started. Approximately 60 mL dist. water are added automatically to the sample for dissolving. The addition is followed by a waiting time of 30 seconds while the solution is mixed thoroughly. In case the sample can not be dissolved completely within these 30 seconds the waiting time should be adjusted. The solution is then titrated with c(NaOH) = 0.1 mol/L and the titration stopped after 20 mL titrant have been consumed. Then the electrode is rinsed before the next determination.

The value ‘192.12’ in the calculation formula is the molecular weight of citric acid in [g/mol].

Remarks

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving to the work position. If this requirement can not be fulfilled no beaker will be recognized.

One special beaker has to be defined including its own work position. Special beaker 1 is used for a proper electrode treatment between determination series.

Result report

tiamo™ titration and more

Robotic Acid / Base Analyzer
Citric acid

Programm version tiamo 1.1

2005-08-23 16:11:31 UTC+2

Results report

Determination

Method	Titration of citric acid
Method saving date	2005-08-23 08:24:37 UTC+2
Method version	1
Method state	original
Determination ID	-1bd7dce7:105e1e3c5c4:-7f0b
Determination start	2005-08-23 08:46:24 UTC+2
Determination state	original
Determination version	1
Run number	8
User (full name)	Metrohm

Sample data

Sample Identification 1	citric acid
Sample size	0.0493 g

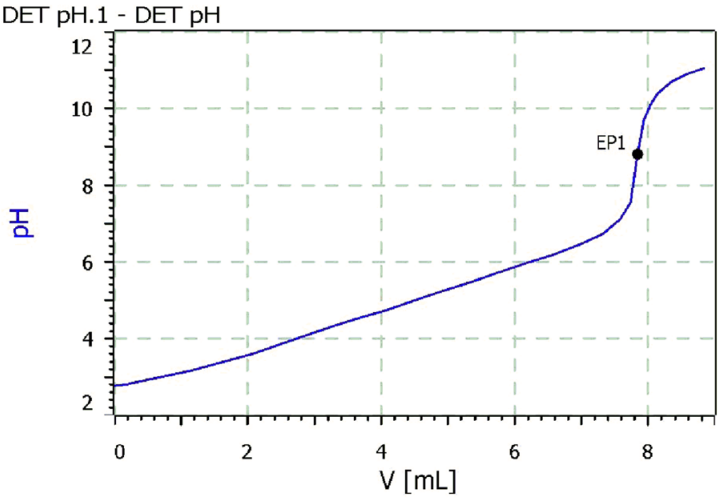
End points

DET pH **DET pH.1**

EP1	8.802	pH	7.8387	mL

Results

percent by weight	99.59	%



Statistical results (example)

Determination of citric acid

Sample size [g]	Percent by weight [%]
0.0758	99.32
0.0589	99.49
0.0554	99.58
0.0719	98.81
0.0630	99.36
0.0493	99.59
0.0580	99.13
0.0690	99.24
0.0488	99.30
0.0733	99.07
Mean value	99.29
abs. std. dev.	0.24
rel. std. dev. %	0.24

3.7 Determination of phosphoric acid in cola drinks

Recommended accessories

- Comb. pH glass electrode for aqueous titrations 6.0257.000 Aquatrode Plus with 6.2104.020 electrode cable
- 20 mL Dosing Unit: 6.3032.220

Reagents

- Titrant: *c*(NaOH) = 0.1 mol/L

Sample preparation

Cola drink is degassed in an ultrasonic bath for 5 min (degassing can also be carried out under vacuum).

Analysis

50 mL of the degassed sample solution is titrated with *c*(NaOH) = 0.1 mol/L to after the first endpoint (first phosphoric acid step at pH = approx. 4.6).

Calculations

g/L H_3PO_4 = 'DET pH.EP{1}.VOL' * 'DET pH.TITER' * 'DET pH.CONC' * 97.993 / 'MV.Sample size'

where:

'DET pH.EP{1}.VOL'	mL NaOH up to endpoint
'DET pH.TITER'	titer of NaOH solution
'DET pH.CONC'	concentration of NaOH solution [mol/L]
97.993	molecular weight of phosphoric acid [g/mol]
'MV.Sample size'	sample volume [mL]

Remarks

The determination only works in cola drinks that contain no citric acid, as the citric acid is also determined. Such samples must be analyzed according to a different method, in which the sample is ashed (after previous neutralization to pH = approx. 8 with NaOH).

The 761 SD Compact IC is an ion chromatography system that has been developed by Metrohm specially for the rapid and reliable determination of phosphoric acid (and citric acid) in these drinks. This instruments is recommended worldwide by leading manufacturers of cola drinks.

3.8 *tiamo* method: Determination of phosphoric acid in cola drinks

Application note

This is a method to determine the content of phosphoric acid in cola drinks. It only works in cola drinks that contain no citric acid, because the citric acid is also determined.

The method is built up of six different tracks. In the start track the rack is initialized and the system prepared for the measurement. The main track handles the measurement as the electrode is moved to the sample beaker and immersed in the solution. After the measurement the electrode is moved to a special beaker, where the rinsing takes place. For this step a special beaker has to be defined. The electrode is thoroughly rinsed with water after every determination. In the exit track the results are calculated, a report is printed and the data is stored in the predefined database Robotic Acid Base Analyzer. The end track contains the command to move the electrode to second special beaker (has to be defined). This beaker is filled with storing solution in order to store the electrode in an adequate way.

In case of an error the error track is carried out which guarantees that the electrode is moved to the storing beaker.

Sample preparation

The cola drink has to be degassed either in an ultrasonic bath (for 5 minutes) or under vacuum.

Procedure

50 mL of the degassed sample are titrated with c(NaOH) = 0.1 mol/ L and the titration stopped after the first endpoint.

Remark

To run this method the settings of the 855 Robotic Titrosampler have to be adjusted. The lift positions have to be defined according to the rack and beakers used. As the robotic swing arm is equipped with a beaker sensor the head has to touch the beaker brim when moving to work position. If this requirement can not be fulfilled no beaker will be recognized.

For the rinsing as well as for the storing procedure a special beaker has to be defined. Each special beaker requires an own work position.

The value '97.993' in the calculation formula is the molecular weight of phosphoric acid in [g/mol].

Result report

tiamo™ titration and more

Robotic Acid / Base Analyzer
Phosphoric acid in cola drinks

Programm version tiamo 1.1

2005-08-23 16:03:31 UTC+2

Results report

Determination

Method	Determination of phosphoric acid in cola drinks
Method saving date	2005-08-23 14:55:12 UTC+2
Method version	1
Method state	original
Determination ID	-1bd7dce7:105e1e3c5c4:-7b42
Determination start	2005-08-23 14:59:54 UTC+2
Determination state	original
Determination version	1
Run number	47
User (full name)	Metrohm

Sample data

Sample Identification 1	phosphoric acid in cola drinks
Sample size	50 mL

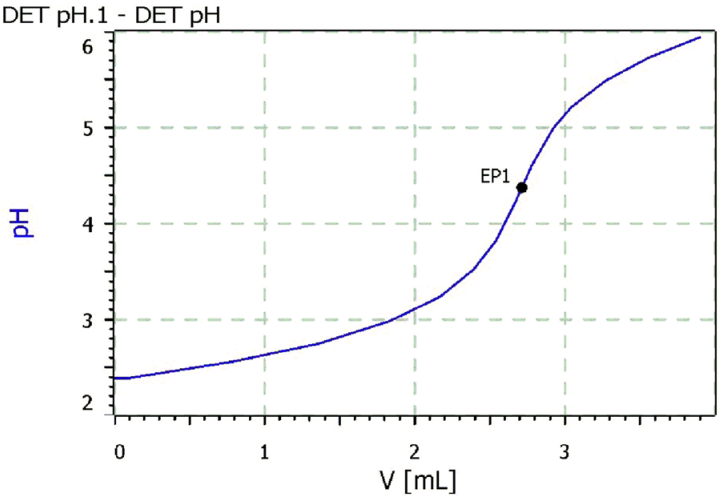
End points

DET pH **DET pH.1**

EP1	4.372	pH	2.7134	mL

Results

content phosphoric acid	0.520	g/L



Statistical results (example)

Phosphoric acid in cola drinks

Sample size [mL]	Phosphoric acid [g/L]
50	0.516
50	0.518
50	0.518
50	0.517
50	0.518
50	0.520
50	0.520
50	0.519
50	0.520
50	0.518
Mean value	0.518
abs. std. dev.	0.0013
rel. std. dev. %	0.26

4 Troubleshooting pH glass electrodes

4.1 Troubleshooting glass membrane

Source of error	Effects	Cleaning	Alternatives
HF-containing solutions	Etching and dissolution of the glass membrane ➔ corrosion potential during the measurement/short working life		Use of the Sb electrode
High pH value and high alkali content	Increased alkali error ➔ pH too low		Use of electrodes with U glass
High temperatures	Rapid rise in membrane resistance by aging ➔ increased polarizability and drift		Use of electrodes with U glass. Careful treatment with etching salt and HCl
Measurements at low temperatures	High membrane resistance ➔ polarization effects		Use of electrodes with T glass and Idrolyte as reference electrolyte
Dry storage	Zero point drift	Storage in 6.2323.000 storage solution	
Non-aqueous media	Reduced sensitivity	Store in water	T glass / non-aqueous electrolyte solution
Deposition of solids on membrane surface	Slow response, zero point shift, slope reduction	Solvent or strong acids	
Deposition of proteins on membrane surface	Slow response, zero point shift, slope reduction	5% pepsin in 0.1 mol/L HCl	

4.2 Cleaning and care of pH-electrodes with fixed-sleeve diaphragm

Diaphragm type	Type of contamination	Cleaning
General	Precipitates of silver halides and silver sulfides	Immerse diaphragm for several hours in a solution of 7% thiourea in 0.1 mol/L HCl.
	Proteins, polypeptides	Immerse diaphragm for several hours in a solution of 5% pepsin in 0.1 mol/L HCl.
	Suspensions, solids, resins, glues, oils, fats	Clean electrode with suitable solvent
Fixed ground joint	All types of contamination	Aspirate off reference electrolyte and immerse electrode in the corresponding cleaning solution.
Separable ground joint	All types of contamination	Loosen the ground-joint sleeve (using hot water if necessary) and clean according to the type of contamination.

4.3 Storage

Aquatrode Plus: Store in 6.2323.000 storage solution only! The filling plug for the bridge electrolyte must not be opened.

5 Method reports

5.1 Calibrating the pH glass electrode

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm		2005-09-13 09:17:19 UTC+2

Method parameters

Method . . . . . Calibrating the pH glass electrode
Method saving date . . . . . 2005-09-13 09:17:07 UTC+2
Method version 1
Method group . . . . . Robotic Acid Base Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view
Current view . . . . . on
Track view for live window
Live display 1 . . . . . Main track
Live display 2 . . . . . Main track
Statistics . . . . . off
Conditioning
Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on, Sample size
Value . . . . . off,
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off

Mail to	
Subject	Message from tiamo - Method 'New method 1' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample position**
Type	Number
Assignment	on. Sample position
Value	off.
Check at start	on
Comment	Sample position number
Variable monitoring	off
Lower limit	
Upper limit	
Message	
Display message	on
Record message	on
Message by e-mail	off
Mail to	
Subject	Message from tiamo - Method 'New method 1' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample size unit**
Type	Text
Assignment	on. Sample size unit
Value	off.
Check at start	on
Comment	Sample size unit

Name	**ID1**
Type	Text
Assignment	on. ID1

Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 3

CAL LOOP pH **calibration loop pH**

Buffers
- Number of buffers 3
- Buffer type . . . . . Metrohm
- Request for buffer exchange . . . . . off
- Subsequent command . . . . . calculation

MOVE **to sample**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Rack position
- Number . . . . . =0 + 'calibration loop pH.LCO'

Beaker test
- Display message . . . . . off
- Stop determination . . . . . off
- Stop determination and series . . . . . on

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

CAL MEAS pH **CAL MEAS pH**

General/Hardware

Device
- Device name . . . . . 855_1

Sensor
- Measuring input 1

Sensor . . . . . Aquatrode Plus
Temperature measurement . . . . . automatic
Stirrer
Stirrer 1
Stirring rate 8
Switch off automatically . . . . . on
Measuring parameters
Measurement with drift control
Signal drift . . . . . 2.0 mV/min
Min. waiting time . . . . . 10 s
Max. waiting time . . . . . 110 s
Measuring interval . . . . . 2.0 s
Temperature
Temperature . . . . . 25.0 °C

MOVE **to rinsing beaker**
Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 2
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

PUMP **rinse and aspirate**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 10.0 s

PUMP **aspirate**
Device
Device name . . . . . 855_1
Pumps
Tower 1

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 09:17:19 UTC+2

Pump(s) 2

Action

Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
slope	= 'calibration loop pH.SLO'	%	2	RS01	off
zero point	= 'calibration loop pH.ENP'		2	RS02	off

Result name . . . . . **slope**
Formula . . . . . = 'calibration loop pH.SLO'
Unit . . . . . %
Decimal places 2
Assignment RS01
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

Result name . . . . . **zero point**
Formula . . . . . = 'calibration loop pH.ENP'
Unit . . . . .
Decimal places 2
Assignment RS02
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

REPORT **report**

Report template

Report template . . . . . calibration

Report output

Printer . . . . . off
PDF file . . . . . on
PDF file . . . . . C:\Programme\Metrohm\tiamo\Data\Calibrating the pH Glass Electrode.pdf

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 09:17:19 UTC+2

Send e-mail . . . . . off

DATABASE **database**

Database

Robotic Acid Base Analyzer

SERIES START **Series start track**

RACK **initialize rack**

Device
Device name . . . . . 855_1
Rack test . . . . . off

MOVE **to rinse beaker**

Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 2
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

PUMP **aspirate and rinse**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 10.0 s

PUMP **empty beaker**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	09:17:19 UTC+2

Action
- Switch on . . . . . off
- Switch off . . . . . off
- Duration . . . . . on
- Time . . . . . 5 s

SERIES END **Series end track**

MOVE **to storage beaker**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Special beaker
- Number 1

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

5.2 Titer determination of alkaline titrants

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm		2005-09-13 09:26:24 UTC+2

Method parameters

Method . . . . . Titer determination of alkaline titrants
Method saving date . . . . . 2005-09-13 09:25:27 UTC+2
Method version 1
Method group . . . . . Robotic Acid Base Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view
Current view . . . . . on
Track view for live window
Live display 1 . . . . . Main track
Live display 2 . . . . . Main track
Statistics . . . . . on
Number of single determinations . . . . . not defined
Conditioning
Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample size
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on

Message by e-mail . . . . . off
Mail to . . . . .
Subject . . . . . Message from tiamo - Method 'New method 5' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample position**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample position
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample position number
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .
Subject . . . . . Message from tiamo - Method 'New method 5' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample size unit**
Type . . . . . Text
Assignment . . . . . on . . . . . Sample size unit
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size unit

Name **ID1**
Type . . . . . Text

Assignment . . . . . on. ID1
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on. ID2
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on. ID3
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample position**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Sample position

Beaker test
- Display message . . . . . off
- Stop determination . . . . . off
- Stop determination and series . . . . . on

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

PUMP **add water**

Device
- Device name . . . . . 855_1

Pumps
- Tower 1
- Pump(s) 1

Action
- Switch on . . . . . off
- Switch off . . . . . off
- Duration . . . . . on
- Time . . . . . 9 s

STIR **stirrer on**

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 09:26:24 UTC+2

Device
Device name . . . . . 855_1
Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 10
Action
Switch on . . . . . on
Switch off . . . . . off
Duration . . . . . off

WAIT **dissolving**
Wait
Stop track and waiting for [Continue] . . . . . off
Stop all tracks and waiting for [Continue] . . . . . off
Waiting time . . . . . on
Time 90
Unit . . . . . s
Message
Record message . . . . . on
Message by e-mail . . . . . off
Acoustic signal . . . . . off

DET pH **DET pH**
General/Hardware
Device
Device name . . . . . 855_1
Dosing device
Dosing device 1
Solution . . . . . NaOH
Sensor
Measuring input 1
Sensor . . . . . Aquatrode Plus
Temperature measurement . . . . . automatic
Stirrer
Stirrer . . . . . off
Start conditions
Initial measured value
Signal drift . . . . . off mV/min
Min. waiting time . . . . . 0 s
Max. waiting time . . . . . 1 s
Start volume
Start volume . . . . . 0 mL
Dosing rate . . . . . maximum mL/min
Start measured value
Start measured value pH . . . . . off
Dosing rate . . . . . 5 mL/min

Start slope
Start slope . . . . . off pH/mL
Dosing rate . . . . . 5 mL/min
Pause
Pause . . . . . 0 s

Titration parameters

Titration rate
Titration rate . . . . . user
Measured value acceptance
Signal drift . . . . . 50.0 mV/min
Min. waiting time . . . . . 0 s
Max. waiting time . . . . . 38 s
Dosing of increments
Measuring point density 4
Min. increment . . . . . 50.0 µL
Max. increment . . . . . off µL
Dosing rate . . . . . maximum mL/min
Temperature
Temperature . . . . . 25.0 °C

Stop conditions

Stop volume . . . . . 20 mL
Stop measured value pH . . . . . off
Stop EP 1
Volume after EP . . . . . 0.5 mL
Stop time . . . . . off s
Filling rate . . . . . maximum mL/min

Potentiometric evaluation

Evaluation without window . . . . . on
EP criterion 5
EP recognition . . . . . all
Evaluation with measured value window (pH) . . . . . off
Evaluation with volume window (mL) . . . . . off

Additional evaluations

Fix end point evaluation . . . . . off
pK/HNP evaluation . . . . . off
Minimum evaluation . . . . . off
Maximum evaluation . . . . . off
Break point evaluation . . . . . off

Additional measured values

Additional calculated measured values . . . . . off
Additional external measured values . . . . . off

STIR **stirrer off**

Device
Device name . . . . . 855_1
Stirrer
Stirrer 1

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 09:26:24 UTC+2

Stirrer type . . . . . unknown
Stirring rate 10
Action
Switch on . . . . . off
Switch off . . . . . on
Duration . . . . . off

PUMP **aspirate sample solution**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **rinse and aspirate**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **aspirate**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3 s

SERIES START **Series start track**

RACK **initialize rack**
Device
Device name . . . . . 855_1

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 09:26:24 UTC+2

Rack test . . . . . off

EXIT **Exit track**

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
Titer	= 'MV.Sample size' * 1000 / ('DET pH.EP{1}.VOL' * 'DET pH.CONC' * 204.23)		4	RS01	on
mean value titer	= 'RS.Titer.MNV'		4	RS02	off

Result name . . . . . **Titer**
Formula . . . . . = 'MV.Sample size' * 1000 / ('DET pH.EP{1}.VOL' * 'DET pH.CONC' * 204.23)
Unit . . . . .
Decimal places 4
Assignment RS01
Statistics . . . . . on
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . on
Solution name . . . . . NaOH

Result name . . . . . **mean value titer**
Formula . . . . . = 'RS.Titer.MNV'
Unit . . . . .
Decimal places 4
Assignment RS02
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . on
Solution name . . . . . NaOH

REPORT **report**

Report template
Report template . . . . . titer determination

Report output
Printer . . . . . off
PDF file . . . . . on
PDF file . . . . . C:\Programme\Metrohm\tiamo\Data\Titer determination of alkaline titrants.pdf
Send e-mail . . . . . off

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 09:26:24 UTC+2

DATABASE **database**

Database

Robotic Acid Base Analyzer

SERIES **Series end track**
END

MOVE **to storing beaker**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Special beaker
- Number 1

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

ERROR **Error track**

MOVE **to storage beaker**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Special beaker
- Number 1

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

5.3 Titer determination of acidic titrants

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:06:48 UTC+2

Method parameters

Method . . . . . Titer determination of acidic titrants
Method saving date . . . . . 2005-09-13 10:06:43 UTC+2
Method version 1
Method group . . . . . Robotic Acid Base Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view
Current view . . . . . on
Track view for live window
Live display 1 . . . . . Main track
Live display 2 . . . . . Main track
Statistics . . . . . on
Number of single determinations . . . . . not defined
Conditioning
Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample size
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on

Message by e-mail . . . . . off
Mail to . . . . .
Subject . . . . . Message from tiamo - Method 'New method 4' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample position**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample position
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample position number
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .
Subject . . . . . Message from tiamo - Method 'New method 4' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample size unit**
Type . . . . . Text
Assignment . . . . . on . . . . . Sample size unit
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size unit

Name **ID1**
Type . . . . . Text

Assignment . . . . . on. ID1
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on. ID2
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on. ID3
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample position**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Sample position

Beaker test
- Display message . . . . . off
- Stop determination . . . . . off
- Stop determination and series . . . . . on

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

PUMP **add water**

Device
- Device name . . . . . 855_1

Pumps
- Tower 1
- Pump(s) 1

Action
- Switch on . . . . . off
- Switch off . . . . . off
- Duration . . . . . on
- Time . . . . . 20 s

STIR **stirrer on**

Device
Device name . . . . . 855_1
Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 8
Action
Switch on . . . . . on
Switch off . . . . . off
Duration . . . . . off

WAIT **dissolving**
Wait
Stop track and waiting for [Continue] . . . . . off
Stop all tracks and waiting for [Continue] . . . . . off
Waiting time . . . . . on
Time 90
Unit . . . . . s
Message
Record message . . . . . on
Message by e-mail . . . . . off
Acoustic signal . . . . . off

DET pH **DET pH**
General/Hardware
Device
Device name . . . . . 855_1
Dosing device
Dosing device 1
Solution . . . . . HCl
Sensor
Measuring input 1
Sensor . . . . . Aquatrode Plus
Temperature measurement . . . . . automatic
Stirrer
Stirrer . . . . . off
Start conditions
Initial measured value
Signal drift . . . . . off mV/min
Min. waiting time . . . . . 0 s
Max. waiting time . . . . . 1 s
Start volume
Start volume . . . . . 1 mL
Dosing rate . . . . . maximum mL/min
Start measured value
Start measured value pH . . . . . off
Dosing rate . . . . . 5 mL/min

Start slope
Start slope . . . . . off pH/mL
Dosing rate . . . . . 5 mL/min
Pause
Pause . . . . . 5 s

Titration parameters

Titration rate
Titration rate . . . . . user
Measured value acceptance
Signal drift . . . . . 50.0 mV/min
Min. waiting time . . . . . 0 s
Max. waiting time . . . . . 26 s
Dosing of increments
Measuring point density 4
Min. increment . . . . . 100 µL
Max. increment . . . . . off µL
Dosing rate . . . . . maximum mL/min
Temperature
Temperature . . . . . 25.0 °C

Stop conditions

Stop volume . . . . . 20 mL
Stop measured value pH . . . . . off
Stop EP 1
Volume after EP . . . . . 0.5 mL
Stop time . . . . . off s
Filling rate . . . . . maximum mL/min

Potentiometric evaluation

Evaluation without window . . . . . on
EP criterion 5
EP recognition . . . . . all
Evaluation with measured value window (pH) . . . . . off
Evaluation with volume window (mL) . . . . . off

Additional evaluations

Fix end point evaluation . . . . . off
pK/HNP evaluation . . . . . off
Minimum evaluation . . . . . off
Maximum evaluation . . . . . off
Break point evaluation . . . . . off

Additional measured values

Additional calculated measured values . . . . . off
Additional external measured values . . . . . off

STIR **stirrer off**

Device
Device name . . . . . 855_1
Stirrer
Stirrer 1

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:06:48 UTC+2

Start slope
- Start slope . . . off pH/mL
- Dosing rate . . . 5 mL/min

Pause
- Pause . . . 5 s

Titration parameters

Titration rate
- Titration rate . . . user

Measured value acceptance
- Signal drift . . . 50.0 mV/min
- Min. waiting time . . . 0 s
- Max. waiting time . . . 26 s

Dosing of increments
- Measuring point density . . . 4
- Min. increment . . . 100 µL
- Max. increment . . . off µL
- Dosing rate . . . maximum mL/min

Temperature
- Temperature . . . 25.0 °C

Stop conditions
- Stop volume . . . 20 mL
- Stop measured value pH . . . off
- Stop EP . . . 1
- Volume after EP . . . 0.5 mL
- Stop time . . . off s
- Filling rate . . . maximum mL/min

Potentiometric evaluation
- Evaluation without window . . . on
- EP criterion . . . 5
- EP recognition . . . all
- Evaluation with measured value window (pH) . . . off
- Evaluation with volume window (mL) . . . off

Additional evaluations
- Fix end point evaluation . . . off
- pK/HNP evaluation . . . off
- Minimum evaluation . . . off
- Maximum evaluation . . . off
- Break point evaluation . . . off

Additional measured values
- Additional calculated measured values . . . off
- Additional external measured values . . . off

STIR **stirrer off**

Device
- Device name . . . 855_1

Stirrer
- Stirrer . . . 1

Stirrer type . . . . . unknown
Stirring rate 8
Action
Switch on . . . . . off
Switch off . . . . . on
Duration . . . . . off

PUMP **aspirate sample solution**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 7 s

PUMP **rinse and aspirate**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **aspirate**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3 s

SERIES START **Series start track**

RACK **initialize rack**
Device
Device name . . . . . 855_1

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 10:06:48 UTC+2

Rack test . . . . . off

EXIT **Exit track**

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
Titer	= 'MV.Sample size' * 1000 / ('DET pH.EP {1}.VOL' * 'DET pH.CONC' * 121.14)		4	RS01	on
mean value titer	= 'RS.Titer.MNV'		4	RS02	off

Result name . . . . . **Titer**
Formula . . . . . = 'MV.Sample size' * 1000 / ('DET pH.EP{1}.VOL' * 'DET pH.CONC' * 121.14)
Unit . . . . .
Decimal places 4
Assignment RS01
Statistics . . . . . on
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

Result name . . . . . **mean value titer**
Formula . . . . . = 'RS.Titer.MNV'
Unit . . . . .
Decimal places 4
Assignment RS02
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . on
Solution name . . . . . HCl

REPORT **report**

Report template
Report template . . . . . titer determination

Report output
Printer . . . . . off
PDF file . . . . . on
PDF file . . . . . C:\Programme\Metrohm\tiamo\Data\titer determination acid titrants.pdf
Send e-mail . . . . . off

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:06:48 UTC+2

DATABASE **database**

Database

Robotic Acid Base Analyzer

SERIES **Series end track**
END

MOVE **to storing beaker**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Special beaker
- Number 1

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

ERROR **Error track**

MOVE **to storage beaker**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Special beaker
- Number 1

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

5.4 pH value and acid capacity in water

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:11:14 UTC+2

Method parameters

Method . . . . . pH value and acid capacity in water
Method saving date . . . . . 2005-09-13 10:11:10 UTC+2
Method version 1
Method group . . . . . Robotic Acid Base Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view
Current view . . . . . on
Track view for live window
Live display 1 . . . . . Main track
Live display 2 . . . . . Main track
Statistics . . . . . off
Conditioning
Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on. . . . . Sample size
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . . .
Upper limit . . . . . .
Message . . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off

Mail to	
Subject	Message from tiamo - Method 'New method 2' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample position**
Type	Number
Assignment	on. Sample position
Value	off.
Check at start	on
Comment	Sample position number
Variable monitoring	off
Lower limit	
Upper limit	
Message	
Display message	on
Record message	on
Message by e-mail	off
Mail to	
Subject	Message from tiamo - Method 'New method 2' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample size unit**
Type	Text
Assignment	on. Sample size unit
Value	off.
Check at start	on
Comment	Sample size unit

Name	**ID1**
Type	Text
Assignment	on. ID1

Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Sample position

Beaker test
- Display message . . . . . off
- Stop determination . . . . . off
- Stop determination and series . . . . . on

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

MEAS pH **MEAS pH**

General/Hardware

Device
- Device name . . . . . 855_1

Sensor
- Measuring input 1
- Sensor . . . . . Aquatrode Plus
- Temperature measurement . . . . . automatic

Stirrer
- Stirrer 1
- Stirring rate 8
- Switch off automatically . . . . . on

Measuring parameters

Measurement

Measurement with drift control . . . . . on
Signal drift . . . . . 5 mV/min
Min. waiting time . . . . . 30 s
Max. waiting time . . . . . 120 s
Measuring interval . . . . . 1 s
Stop measured value pH . . . . . off
Measurement without drift control . . . . . off

Temperature

Temperature . . . . . 25.0 °C

Evaluations

Fix end point evaluation . . . . . off
Minimum evaluation . . . . . off
Maximum evaluation . . . . . off
Break point evaluation . . . . . off

Additional measured values

Additional calculated measured values . . . . . off
Additional external measured values . . . . . off

WAIT **wait**

Wait

Stop track and waiting for [Continue] . . . . . off
Stop all tracks and waiting for [Continue] . . . . . off
Waiting time . . . . . on
Time 2
Unit . . . . . s

Message

Record message . . . . . off
Message by e-mail . . . . . off
Acoustic signal . . . . . off

SET pH **SET pH**

General/Hardware

Device

Device name . . . . . 855_1

Dosing device

Dosing device 1
Solution . . . . . HCl

Sensor

Measuring input 1
Sensor . . . . . Aquatrode Plus
Temperature measurement . . . . . automatic

Stirrer

Stirrer 1
Stirring rate 8
Switch off automatically . . . . . on

Start conditions

Initial measured value

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:11:14 UTC+2

Signal drift	off	mV/min
Min. waiting time	0	s
Max. waiting time	1	s
Pause 1		
Pause 1	0	s
Start volume		
Start volume	0	mL
Dosing rate	maximum	mL/min
Pause 2		
Pause 2	0	s
Control parameters		
End point 1		
EP1 at pH	8.2	
Titration rate		
Titration rate	user	
Control		
Dynamics pH	2	
Max. rate	10	mL/min
Min. rate	5	µL/min
Stop criterion		
Stop criterion	drift	
Stop drift	20	µL/min
End point 2	on	
EP2 at pH	4.3	
Titration rate		
Titration rate	user	
Control		
Dynamics pH	3	
Max. rate	10.00	mL/min
Min. rate	5	µL/min
Stop criterion		
Stop criterion	drift	
Stop drift	20	µL/min
Titration parameters		
Titration direction	auto	
Extraction time	0	s
Temperature	25.0	°C
Time interval measuring point	2.0	s
Stop conditions		
Stop volume	20	mL
Stop time	off	s
Filling rate	maximum	mL/min
Conditioning		
Conditioning	off	
Additional evaluations		
Fix end point evaluation	off	

Minimum evaluation . . . . . off
Maximum evaluation . . . . . off

Additional measured values

Additional calculated measured values . . . . . off
Additional external measured values . . . . . off

PUMP **aspirate sample solution**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **rinse and aspirate**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **empty beaker**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3 s

SERIES START **Series start track**

RACK **initialize rack**

Device
Device name . . . . . 855_1
Rack test . . . . . off

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 10:11:14 UTC+2

EXIT **Exit track**

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
pH	= 'MEAS pH.LP.MEA'		2	RS01	off
Temperature	='MEAS pH.LP.TEM'	°C	2	RS02	off
K (s 8,2)	= 'SET pH.EP{1}.VOL' * 'SET pH.CONC' * 2 * 'SET pH.TITER' * 1000 / 'MV.Sample size'	mmol/L	2	RS03	off
K (s 4,3)	= 'SET pH.EP{2}.VOL' * 'SET pH.CONC' * 2 * 'SET pH.TITER' * 1000 / 'MV.Sample size'	mmol/L	2	RS04	off

Result name . . . . . **pH**
Formula . . . . . = 'MEAS pH.LP.MEA'
Unit . . . . .
Decimal places 2
Assignment RS01
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

Result name . . . . . **Temperature**
Formula . . . . . ='MEAS pH.LP.TEM'
Unit . . . . . °C
Decimal places 2
Assignment RS02
Statistics . . . . . off
Description . . . . .
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

Result name . . . . . **K (s 8,2)**
Formula . . . . . = 'SET pH.EP{1}.VOL' * 'SET pH.CONC' * 2 * 'SET pH.TITER' * 1000 / 'MV. Sample size'
Unit . . . . . mmol/L
Decimal places 2
Assignment RS03
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.

Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

Result name . . . . . **K (s 4,3)**
Formula . . . . . = 'SET pH.EP{2}.VOL' * 'SET pH.CONC' * 2 * 'SET pH.TITER' * 1000 / 'MV. Sample size'
Unit . . . . . mmol/L
Decimal places 2
Assignment RS04
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

REPORT **report**

Report template
Report template . . . . . pH value and acid capacity in water
Report output
Printer . . . . . off
PDF file . . . . . on
PDF file . . . . . C:\Programme\Metrohm\tiamo\Data\pH value and acid capacity in water.pdf
Send e-mail . . . . . off

DATABASE **database**

Database

Robotic Acid Base Analyzer

SERIES END **Series end track**

MOVE **to storing beaker**

Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off

Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

ERROR **Error track**

MOVE **to storage beaker**
Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

5.5 Determination of the total titratable acidity in wine

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:14:07 UTC+2

Method parameters

Method . . . . . Total acidity of wine
Method saving date . . . . . 2005-09-13 10:14:02 UTC+2
Method version 1
Method group . . . . . Robotic Acid Base Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view

Current view . . . . . on

Track view for live window

Live display 1 . . . . . Main track

Live display 2 . . . . . Main track

Statistics . . . . . off

Conditioning

Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample size
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .

Subject . . . . . Message from tiamo - Method 'New method 7' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample position**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample position
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample position number
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .
Subject . . . . . Message from tiamo - Method 'New method 7' - Command 'Main track'
User . . . . .
Mail from . . . . .
SMTP Server . . . . .
POP3 Server . . . . .
Acoustic signal . . . . . off
Action . . . . . off
Stop determination . . . . . on
Stop determination and series . . . . . off

Name . . . . . **Sample size unit**
Type . . . . . Text
Assignment . . . . . on . . . . . Sample size unit
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size unit

Name **ID1**
Type . . . . . Text
Assignment . . . . . on ID1
Value . . . . . off . . . . .

Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample position**

Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Sample position
Beaker test
Display message . . . . . off
Stop determination . . . . . off
Stop determination and series . . . . . on
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

DET pH **DET pH**

General/Hardware

Device
Device name . . . . . 855_1
Dosing device
Dosing device 1
Solution . . . . . NaOH
Sensor
Measuring input 1
Sensor . . . . . Aquatrode Plus
Temperature measurement . . . . . automatic
Stirrer
Stirrer 1
Stirring rate 8
Switch off automatically . . . . . on

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:14:07 UTC+2

Start conditions

Initial measured value

Signal drift	off	mV/min
Min. waiting time	0	s
Max. waiting time	1	s

Start volume

Start volume	0	mL
Dosing rate	maximum	mL/min

Start measured value

Start measured value pH	off	
Dosing rate	5	mL/min

Start slope

Start slope	off	pH/mL
Dosing rate	5	mL/min

Pause

Pause	0	s

Titration parameters

Titration rate

Titration rate	user	

Measured value acceptance

Signal drift	50.0	mV/min
Min. waiting time	0	s
Max. waiting time	26	s

Dosing of increments

Measuring point density	4	
Min. increment	10.0	µL
Max. increment	off	µL
Dosing rate	maximum	mL/min

Temperature

Temperature	25.0	°C

Stop conditions

Stop volume	20	mL
Stop measured value pH	10	
Stop EP	off	
Volume after EP	off	mL
Stop time	off	s
Filling rate	maximum	mL/min

Potentiometric evaluation

Evaluation without window	on
EP criterion	5
EP recognition	off
Evaluation with measured value window (pH)	off
Evaluation with volume window (mL)	off

Additional evaluations

Fix end point evaluation	on
Fixed quantity	Measured value

Fix EP1 at pH 7
Fix EP2 at pH 8.2
Fix EP3 at pH . . . . . off
pK/HNP evaluation . . . . . off
Minimum evaluation . . . . . off
Maximum evaluation . . . . . off
Break point evaluation . . . . . off

Additional measured values

Additional calculated measured values . . . . . off
Additional external measured values . . . . . off

PUMP **aspirate**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **rinse and aspirate**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **aspirate rinsing solution**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3 s

SERIES START **Series start track**

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 10:14:07 UTC+2

RACK **initialize rack**

Device
Device name . . . . . 855_1
Rack test . . . . . off

EXIT **Exit track**

CALC **calculations**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
total aciditiy at pH 7	= 'DET pH.FP{1}.VOL' * 'DET pH.TITER' * 'DET pH.CONC' * 150.1 / 'MV.Sample size'	g/L	2	RS01	off
total acidity at pH 8,2	= 'DET pH.FP{2}.VOL' * 'DET pH.CONC' * 'DET pH.TITER' * 150.1 / 'MV.Sample size'	g/L	2	RS02	off

Result name . . . . . **total aciditiy at pH 7**
Formula . . . . . = 'DET pH.FP{1}.VOL' * 'DET pH.TITER' * 'DET pH.CONC' * 150.1 / 'MV.Sample size'
Unit . . . . . g/L
Decimal places 2
Assignment RS01
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

Result name . . . . . **total acidity at pH 8,2**
Formula . . . . . = 'DET pH.FP{2}.VOL' * 'DET pH.CONC' * 'DET pH.TITER' * 150.1 / 'MV.Sample size'
Unit . . . . . g/L
Decimal places 2
Assignment RS02
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

REPORT **report**

Report template
Report template . . . . . report acidity of wine

Report output
- Printer . . . . . off
- PDF file . . . . . on
- PDF file . . . . . C:\Programme\Metrohm\tiamo\Data\total acidity of wine.pdf
- Send e-mail . . . . . off

DATABASE **database**

Database

Robotic Acid Base Analyzer

SERIES END **Series end track**

MOVE **to storing beaker**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Special beaker
- Number 1

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

ERROR **Error track**

MOVE **to storage beaker**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Special beaker
- Number 1

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

5.6 Titration of citric acid

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:16:25 UTC+2

Method parameters

Method . . . . . Titration of citric acid
Method saving date . . . . . 2005-09-13 10:16:21 UTC+2
Method version 1
Method group . . . . . Robotic Acid Base Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view

Current view . . . . . on

Track view for live window

Live display 1 . . . . . Main track

Live display 2 . . . . . Main track

Statistics . . . . . off

Conditioning

Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on . . . . . Sample size
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . .
Upper limit . . . . .
Message . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off
Mail to . . . . .

Subject	Message from tiamo - Method 'New method 6' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample position**
Type	Number
Assignment	on. Sample position
Value	off.
Check at start	on
Comment	Sample position number
Variable monitoring	off
Lower limit	
Upper limit	
Message	
Display message	on
Record message	on
Message by e-mail	off
Mail to	
Subject	Message from tiamo - Method 'New method 6' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample size unit**
Type	Text
Assignment	on. Sample size unit
Value	off.
Check at start	on
Comment	Sample size unit

Name	**ID1**
Type	Text
Assignment	on. ID1
Value	off.

Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off . . . . .
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample position**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Sample position

Beaker test
- Display message . . . . . off
- Stop determination . . . . . off
- Stop determination and series . . . . . on

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

PUMP **add water**

Device
- Device name . . . . . 855_1

Pumps
- Tower 1
- Pump(s) 1

Action
- Switch on . . . . . off
- Switch off . . . . . off
- Duration . . . . . on
- Time . . . . . 10.0 s

STIR **stirrer on**

Device
- Device name . . . . . 855_1

Stirrer
Stirrer 1
Stirrer type . . . . . unknown
Stirring rate 8
Action
Switch on . . . . . on
Switch off . . . . . off
Duration . . . . . off

WAIT **dissolving sample**

Wait
Stop track and waiting for [Continue] . . . . . off
Stop all tracks and waiting for [Continue] . . . . . off
Waiting time . . . . . on
Time 60
Unit . . . . . s
Message
Record message . . . . . on
Message by e-mail . . . . . off
Acoustic signal . . . . . off

DET pH **DET pH**

General/Hardware

Device
Device name . . . . . 855_1
Dosing device
Dosing device 1
Solution . . . . . NaOH
Sensor
Measuring input 1
Sensor . . . . . Aquatrode Plus
Temperature measurement . . . . . automatic
Stirrer
Stirrer . . . . . off

Start conditions

Initial measured value
Signal drift . . . . . off mV/min
Min. waiting time . . . . . 0 s
Max. waiting time . . . . . 1 s
Start volume
Start volume . . . . . 0 mL
Dosing rate . . . . . maximum mL/min
Start measured value
Start measured value pH . . . . . off
Dosing rate . . . . . 5 mL/min
Start slope
Start slope . . . . . off pH/mL

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 10:16:25 UTC+2

	Dosing rate	5	mL/min
	Pause		
	Pause	0	s
	Titration parameters		
	Titration rate		
	Titration rate	user	
	Measured value acceptance		
	Signal drift	50.0	mV/min
	Min. waiting time	0	s
	Max. waiting time	26	s
	Dosing of increments		
	Measuring point density	4	
	Min. increment	100	µL
	Max. increment	off	µL
	Dosing rate	maximum	mL/min
	Temperature		
	Temperature	25.0	°C
	Stop conditions		
	Stop volume	20	mL
	Stop measured value pH	off	
	Stop EP	1	
	Volume after EP	1	mL
	Stop time	off	s
	Filling rate	maximum	mL/min
	Potentiometric evaluation		
	Evaluation without window	on	
	EP criterion	20	
	EP recognition	all	
	Evaluation with measured value window (pH)	off	
	Evaluation with volume window (mL)	off	
	Additional evaluations		
	Fix end point evaluation	off	
	pK/HNP evaluation	off	
	Minimum evaluation	off	
	Maximum evaluation	off	
	Break point evaluation	off	
	Additional measured values		
	Additional calculated measured values	off	
	Additional external measured values	off	
STIR	**stirrer off**		
	Device		
	Device name	855_1	
	Stirrer		
	Stirrer	1	
	Stirrer type	unknown	
	Stirring rate	8	

Action
Switch on . . . . . off
Switch off . . . . . on
Duration . . . . . off

PUMP **aspirate sample solution**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **rinse and aspirate**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **aspirate**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3 s

SERIES START **Series start track**

RACK **initialize rack**
Device
Device name . . . . . 855_1
Rack test . . . . . off

SERIES END **Series end track**

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 10:16:25 UTC+2

MOVE **to storing beaker**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Special beaker
- Number 1

Beaker test
- Display message . . . . . off
- Stop determination . . . . . on
- Stop determination and series . . . . . off

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

EXIT **Exit track**

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
percent by weight	='DET pH.EP{1}.VOL' * 192.12 * 'DET pH.CONC' * 'DET pH.TITER' * 100 / ('MV.Sample size' * 3 * 1000)	%	2	RS01	off

Result name . . . . . **percent by weight**
Formula . . . . . ='DET pH.EP{1}.VOL' * 192.12 * 'DET pH.CONC' * 'DET pH.TITER' * 100 / ('MV.Sample size' * 3 * 1000)
Unit . . . . . %
Decimal places 2
Assignment RS01
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
- Name . . . . .

Save result as titer . . . . . off
- Solution name . . . . .

REPORT **report**

Report template
- Report template . . . . . citric acid

Report output
- Printer . . . . . off
- PDF file . . . . . on
- PDF file . . . . . C:\Programme\Metrohm\tiamo\Data\titration of citric acid.pdf

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:16:25 UTC+2

Send e-mail . . . . . off

DATABASE **database**

Database

Robotic Acid Base Analyzer

ERROR **Error track**

MOVE **to storage beaker**

Device

Device name . . . . . 855_1

Target

Tower 1

Move . . . . . Special beaker

Number 1

Beaker test

Display message . . . . . off

Stop determination . . . . . on

Stop determination and series . . . . . off

Parameters

Shift rate . . . . . 20 °/s

Shift direction . . . . . auto

Swing rate . . . . . 55 °/s

5.7 Determination of Phosphoric acid in cola drinks

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:20:41 UTC+2

Method parameters

Method . . . . . Determination of phosphoric acid in cola drinks
Method saving date . . . . . 2005-09-13 10:20:36 UTC+2
Method version 1
Method group . . . . . Robotic Acid Base Analyzer
Method status . . . . . original
Method saved by (full name) . . . . . Metrohm
Method saved by (short name) . . . . . Metrohm

START **Main track**

General

Workplace view
Current view . . . . . on
Track view for live window
Live display 1 . . . . . Main track
Live display 2 . . . . . Main track
Statistics . . . . . off
Conditioning
Automatic conditioning . . . . . off

Application note

See attached documents

Method variables

Name	Type	Assignment	Value	Comment	Monitoring
Sample size	Number	Sample size		Sample size	off
Sample size unit	Text	Sample size unit		Sample size unit	off
Sample position	Number	Sample position		Sample position number	off
ID1	Text	ID1		Sample identification 1	off
ID2	Text	ID2		Sample identification 2	off
ID3	Text	ID3		Sample identification 3	off

Name . . . . . **Sample size**
Type . . . . . Number
Assignment . . . . . on. . . . . Sample size
Value . . . . . off. . . . . .
Check at start . . . . . on
Comment . . . . . Sample size
Variable monitoring . . . . . off
Lower limit . . . . . .
Upper limit . . . . . .
Message . . . . . .
Display message . . . . . on
Record message . . . . . on
Message by e-mail . . . . . off

Mail to	
Subject	Message from tiamo - Method 'New method 3' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample position**
Type	Number
Assignment	on. Sample position
Value	off.
Check at start	on
Comment	Sample position number
Variable monitoring	off
Lower limit	
Upper limit	
Message	
Display message	on
Record message	on
Message by e-mail	off
Mail to	
Subject	Message from tiamo - Method 'New method 3' - Command 'Main track'
User	
Mail from	
SMTP Server	
POP3 Server	
Acoustic signal	off
Action	off
Stop determination	on
Stop determination and series	off

Name	**Sample size unit**
Type	Text
Assignment	on. Sample size unit
Value	off.
Check at start	on
Comment	Sample size unit

Name	**ID1**
Type	Text
Assignment	on. ID1

Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 1

Name **ID2**
Type . . . . . Text
Assignment . . . . . on ID2
Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 2

Name **ID3**
Type . . . . . Text
Assignment . . . . . on ID3
Value . . . . . off
Check at start . . . . . on
Comment . . . . . Sample identification 3

MOVE **to sample position**

Device
- Device name . . . . . 855_1

Target
- Tower 1
- Move . . . . . Sample position

Beaker test
- Display message . . . . . off
- Stop determination . . . . . off
- Stop determination and series . . . . . on

Parameters
- Shift rate . . . . . 20 °/s
- Shift direction . . . . . auto
- Swing rate . . . . . 55 °/s

DET pH **DET pH**

General/Hardware

Device
- Device name . . . . . 855_1

Dosing device
- Dosing device 1
- Solution . . . . . NaOH

Sensor
- Measuring input 1
- Sensor . . . . . Aquatrode Plus
- Temperature measurement . . . . . automatic

Stirrer
- Stirrer 1
- Stirring rate 8

Switch off automatically	on	
Start conditions		
Initial measured value		
Signal drift	off	mV/min
Min. waiting time	0	s
Max. waiting time	1	s
Start volume		
Start volume	0	mL
Dosing rate	maximum	mL/min
Start measured value		
Start measured value pH	off	
Dosing rate	5	mL/min
Start slope		
Start slope	off	pH/mL
Dosing rate	5	mL/min
Pause		
Pause	0	s
Titration parameters		
Titration rate		
Titration rate	user	
Measured value acceptance		
Signal drift	50.0	mV/min
Min. waiting time	0	s
Max. waiting time	26	s
Dosing of increments		
Measuring point density	4	
Min. increment	100	µL
Max. increment	off	µL
Dosing rate	maximum	mL/min
Temperature		
Temperature	25.0	°C
Stop conditions		
Stop volume	20	mL
Stop measured value pH	off	
Stop EP	1	
Volume after EP	1	mL
Stop time	off	s
Filling rate	maximum	mL/min
Potentiometric evaluation		
Evaluation without window	on	
EP criterion	5	
EP recognition	all	
Evaluation with measured value window (pH)	off	
Evaluation with volume window (mL)	off	
Additional evaluations		
Fix end point evaluation	off	

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License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 10:20:41 UTC+2

pK/HNP evaluation . . . . . off
Minimum evaluation . . . . . off
Maximum evaluation . . . . . off
Break point evaluation . . . . . off

Additional measured values

Additional calculated measured values . . . . . off
Additional external measured values . . . . . off

PUMP **aspirate sample solution**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 7 s

PUMP **rinse and aspirate**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 5 s

PUMP **aspirate**

Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 3.0 s

SERIES START **Series start track**

RACK **initialize rack**

Device

Device name . . . . . 855_1
Rack test . . . . . off

EXIT **Exit track**

CALC **calculation**

Result name	Formula	Unit	Decimal places	Assignment	Statistics
content phosphoric acid	='DET pH.EP{1}.VOL' * 97.993 * 'DET pH.TITER' * 'DET pH.CONC' / 'MV.Sample size'	g/L	3	RS01	off

Result name . . . . . **content phosphoric acid**
Formula . . . . . ='DET pH.EP{1}.VOL' * 97.993 * 'DET pH.TITER' * 'DET pH.CONC' / 'MV.Sample size'
Unit . . . . . g/L
Decimal places 3
Assignment RS01
Statistics . . . . . off
Description . . . . . RS.'Result name'[.VAL]Result value.
Result monitoring . . . . . off
Save result as common variable . . . . . off
Name . . . . .
Save result as titer . . . . . off
Solution name . . . . .

REPORT **report**

Report template
Report template . . . . . phosphoric acid in cola drinks
Report output
Printer . . . . . off
PDF file . . . . . on
PDF file . . . . . C:\Programme\Metrohm\tiamo\Data\Determination of phosphoric acid in cola drinks.pdf
Send e-mail . . . . . off

DATABASE **database**

Database

Robotic Acid Base Analyzer

SERIES END **Series end track**

MOVE **to storing beaker**

Device
Device name . . . . . 855_1
Target

tiamo™ titration and more

License ID 124049905 Program version tiamo 1.1 - 31
Client name TITRATION14
User Metrohm 2005-09-13 10:20:41 UTC+2

Tower 1
Move . . . . . Special beaker
Number 1
Beaker test
Display message . . . . . off
Stop determination . . . . . off
Stop determination and series . . . . . on
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

ERROR **Error track**

MOVE **to rinsing beaker**
Device
Device name . . . . . 855_1
Target
Tower 1
Move . . . . . Special beaker
Number 2
Beaker test
Display message . . . . . off
Stop determination . . . . . off
Stop determination and series . . . . . on
Parameters
Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s

PUMP **aspirate and rinse**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) . . . . . 1+2
Action
Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 10 s

PUMP **empty rinsing beaker**
Device
Device name . . . . . 855_1
Pumps
Tower 1
Pump(s) 2

tiamo™ titration and more

License ID	124049905	Program version	tiamo 1.1 - 31
Client name	TITRATION14		
User	Metrohm	2005-09-13	10:20:41 UTC+2

Action

Switch on . . . . . off
Switch off . . . . . off
Duration . . . . . on
Time . . . . . 10 s

MOVE **to storage beaker**

Device

Device name . . . . . 855_1

Target

Tower 1
Move . . . . . Special beaker
Number 1

Beaker test

Display message . . . . . off
Stop determination . . . . . off
Stop determination and series . . . . . on

Parameters

Shift rate . . . . . 20 °/s
Shift direction . . . . . auto
Swing rate . . . . . 55 °/s