Application Bulletin 249/2e

Determination of free and residual chlorine based on DIN EN ISO 7393-1 and APHA 4500-Cl

Branch

Water, wastewater, air, environmental protection

Keywords

Chlorine; free chlorine; residual chlorine; ion selective electrode; I^- - ISE; iodide ISE; titration; potentiometric titration; iodometric method, iodine, ammonium iron(II) sulfate; Pt-Titrode; Optrode; pH-electrode; DIN EN ISO 7393-1; APHA 4500-Cl; branch 2

Summary

Water chlorination is a worldwide-used method for water disinfection. Being highly toxic, chlorine kills pathogenic microorganisms (e.g., bacteria) but also poses a health risk to humans. The reason for this high toxicity is that chlorine reacts with organic compounds to form disinfection by-products (DBPs), such as trichloromethane and chloroacetic acid. To prevent this, regulatory authorities worldwide impose strict limit values on chlorine concentration.

This Application Bulletin describes 3 different ways to determine chlorine. The methods have been slightly modified; e.g., omitting mercury chloride for stabilization or replacing chromate with permanganate. All modifications are mentioned in the corresponding comment sections.

A fourth commonly applied method using phenyl arsine oxide as reducing agent is no longer mentioned in this document, as Metrohm does not recommend this method given the toxicity of phenyl arsine. This method involves back-titration of phenyl arsine oxide with iodine and recording the volume.

Note: We still offer support for this analysis in accordance with the relevant standards (4500-Cl C, Iodometric method; ASTM D1253, EPA 330.1 and 330.2).

Method 1 – DIN EN ISO 7393-1

Introduction

This method describes the possibility to measure free and total chlorine by iodometric titration. According to the standard the end point is detected photometrically. During this work it was observed that it doesn’t matter if the equivalence or end point, respectively, is detected with the Optrode or with the Pt-Titrode.

The species which contribute to the free chlorine are mainly elementary chlorine and hypochloric acid whereas the species contributing to the total chlorine are elementary chlorine, hypochloric acid, hypochlorites and chloramines. This method is recommended for a chlorine concentration between 0.3 and 5 mg/L.

Instruments

- Titrator with MET U mode
- 5 mL buret
- 20 mL buret

Electrodes

Pt-Titrode	6.0431.100
Optrode	6.1115.000
Unitrode with Pt 1000 (head U)	6.0258.600

Reagents

- Ammonium iron(II) sulfate hexahydrate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, ACS reagent, 99%
- Sulfuric acid, puriss p.a., 95-97 %
- N,N-diethyl-1,4-phenylene diamine sulfate (DPD), puriss p.a., >99%
- Disodium hydrogen phosphate, Na_2HPO_4, purum >= 99%
- Potassium dihydrogen phosphate, KH_2PO_4, puriss p.a., 99.5 100.5 %

- Disodium EDTA dihydrate, Na_2EDTA, Reag Ph. Eur., 99–101 %
- Potassium iodide, KI, puriss, 99.0–100.5%

Solutions

$c[(NH_4)_2Fe(SO_4)_2·6H_2O)]$ = 0.056 mol/L	22 g ammonium iron(II) sulfate hexahydrate is transferred into a 1 L volumetric flask and dissolved in approx. 250 mL deion. water. 5 mL conc. sulfuric acid is added and the solution is filled up to the mark with deion. water. The solution is kept in a brown-glass flask to prevent any decomposition caused by sunlight.
Buffer solution pH = 6.5	24 g Na_2HPO_4 and 46 g KH_2PO_4 are dissolved in approx. 500 mL deion water and 0.8 g Na_2EDTA is added. After dissolution of the Na_2EDTA the solution is filled up to the mark with deion. water
β(DPD) = 1.1 g/L	250 mL deion water, 2 mL conc. sulfuric acid and 0.2 g Na_2EDTA are transferred into a 1 L volumetric flask and 1.1 g anhydrous DPD is added. After dissolution of all compounds the solution is filled up to the mark with deion. water. The solution is kept in a brown-glass flask to prevent any decomposition caused by sunlight.
Titrant $c[(NH_4)_2Fe(SO_4)_2 · 6\ H_2O]$ = 0.0028 mol/L	50 mL of the $c[(NH_4)_2Fe(SO_4)_2·6\ H_2O]$ = 0.056 mol/L solution which titer is previously determined is transferred into a 1 L volumetric flask and filled up to the mark with deion. water. The solution is kept in a brown-glass flask to prevent any decomposition caused by sunlight.

Standard solution

$c(KMnO_4)$ = 0.02 mol/L	If possible this solution should be bought from a supplier.

Sample preparation

No sample preparation required

Analysis

Titer determination

5 mL $c(KMnO_4)$ = 0.02 mol/L is pipetted into a 150 mL beaker and approx. 80 mL deion. water is added. After addition of 5 mL conc. sulfuric acid the titration is carried out with $c[(NH_4)_2Fe(SO_4)_2·6\ H_2O]$ = 0.056 mol/L (20 mL DU) until after the equivalence point.

The titer is determined for the $c[(NH_4)_2Fe(SO_4)_2·6H_2O]$ = 0.056 mol/L solution and is used as titer for the $c[(NH_4)_2Fe(SO_4)_2·6H_2O]$ = 0.0028 mol/L solution. The titer has to be determined on a daily basis.

Sample determination

Determination of free chlorine

5 mL buffer solution pH = 6.5, 5 mL β(DPD) = 1.1 g/L and 100 mL sample are given into a 250 mL beaker. After mixing, the titration is carried out with $c[(NH_4)_2Fe(SO_4)_2·6\ H_2O]$ = 0.0028 mol/L (5 mL DU) until after the equivalence point.

For indication an Optrode or a Pt-Titrode can be used. If the Pt-Titrode is chosen, the addition of the DPD solution can be omitted.

Determination of total chlorine

5 mL buffer solution pH = 6.5, 5 mL β(DPD) = 1.1 g/L, 100 mL sample and approx. 1 g KI are given into a 250 mL beaker. After mixing and waiting for 2 minutes, the titration is carried out with $c[(NH_4)_2Fe(SO_4)_2·6\ H_2O]$ = 0.0028 mol/L (5 mL DU) until after the equivalence point.

For indication, an Optrode or a Pt-Titrode can be used. If the Pt-Titrode is chosen, the addition of the DPD solution can be omitted.

Check of chlorine in water

For all determinations, chlorine free water has to be used. This can be checked by the following procedure:

100 mL deion. water is transferred into a 250 mL beaker and 1 g KI is dissolved. After 1 minute, 5 mL buffer solution pH = 6.5 and 5 mL DPD solution are added. To a second 250 mL beaker the same procedure is applied but adding two drops of hypochlorite solution to the deion. water.

The deion. water in the first beaker should show no coloration where the solution in the second beaker should show a pinkish color.

Parameters

Titer determination

Mode	MET U
Stirring rate	12
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Volume increment	0.1 mL
Stop volume	5 mL
EP criterion	30 mV
EP recognition	greatest

Check of chlorine in water /Sample determination by potentiometric titration

Mode	MET U
Stirring rate	12
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Volume increment	0.02 mL
Stop volume	5 mL
EP criterion	30 mV
EP recognition	greatest

Check of chlorine in water /Sample determination by photometric titration

Mode	MET U
Stirring rate	12
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Volume increment	0.02 mL
Stop volume	5 mL
Break point evaluation	
EP criterion	0.3
Slope	0.9
Smoothing factor	20

Calculation

Titer

$$f = \frac{V_{Std} \times c_{Std} \times 5}{V_{EP1} \times c_{Titrant}}$$

f: Titer of the selected titrant

V_{Std}: Added volume of $c(KMnO_4) = 0.02$ mol/L in mL, here 5 mL

c_{Std}: Concentration of $KMnO_4$ solution in mol/L, here 0.02 mol/L

5: Stoichiometric factor (5 mol Fe(II) correspond to 1 mol Mn(VII).)

V_{EP1}: Used amount of titrant until the first equivalence point in mL

$c_{Titrant}$: Concentration of ferrous ammonium sulfate solution, here 0.056 mol/L

Calculation for free and total chlorine

$$\beta_{Cl2} = \frac{M_{Cl2} \times V_{EP1} \times f \times c_{titrant} \times 1000}{V_{Sample} \times 4}$$

β_{Cl2}: Mass concentration of chlorine in mg/L

M_{Cl2}: Molar mass of chlorine in g/mol, here 70.906 g/mol

V_{EP1}: Used amount of $c[(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O] = 0.0028$ mol/L until the first equivalence point in mL

f: Titer of titrant

$c_{titrant}$: Concentration of $c[(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O]$, here 0.0028 mol/L

1000: Conversion factor for g/L in mg/L

V_{Sample}: Amount of sample used for titration in mL

4: Stoichiometric factor (2 mol ClO^- correspond to 1 mol Cl_2. 1 mol Cl_2 corresponds to 2 mol Fe(II))

Example determination

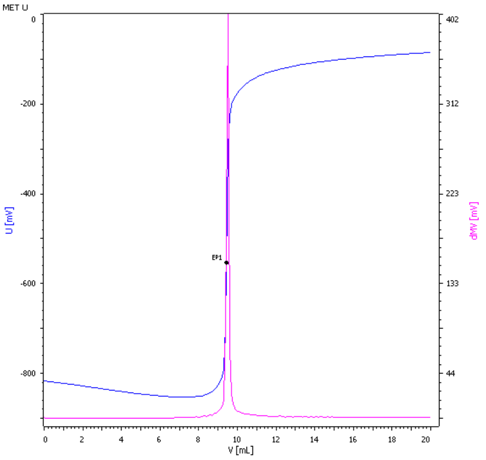

Fig. 1: Titer determination of c[$(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$] = 0.0028 mol/L with c($KMnO_4$) = 0.02 mol/L as standard

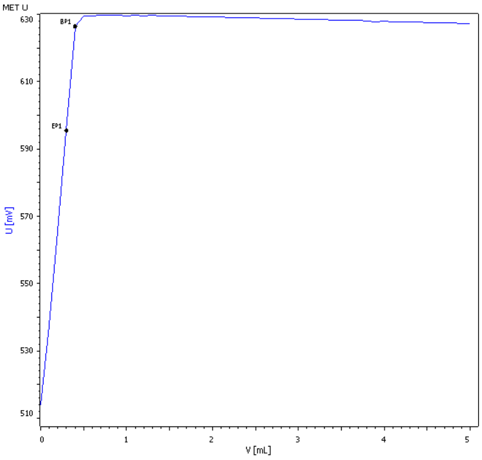

Fig. 2: Determination of free chlorine in 100 mL of a β(Ca(ClO4)$_2$) = 1.28 mg/L solution. Indication is carried out using an Optrode

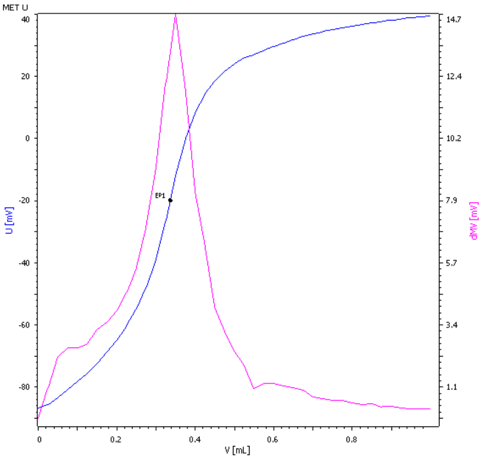

Fig. 3: Determination of free chlorine in 100 mL of a β(Ca(ClO4)$_2$) = 1.28 mg/L solution. Indication is carried out using a Pt-Titrode

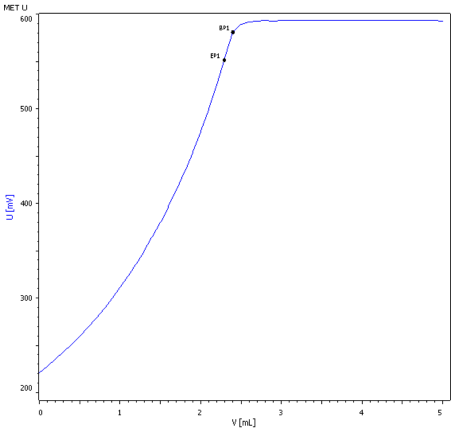

Fig. 4: Determination of total chlorine in 100 mL of a β(Ca(ClO4)$_2$) = 1.28 mg/L solution spiked with 0.3 mL of a β(monochloramine) = 1000 mg/L solution. The indication is carried out using an Optrode.

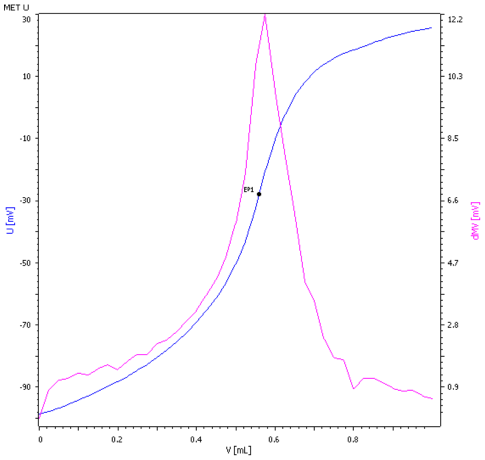

Fig. 5: Determination of total chlorine in 100 mL of a β(Ca(ClO4)$_2$) = 1.28 mg/L solution spiked with 0.3 mL of a β(monochloramine) = 1000 mg/L. The indication is carried out using a Pt-Titrode.

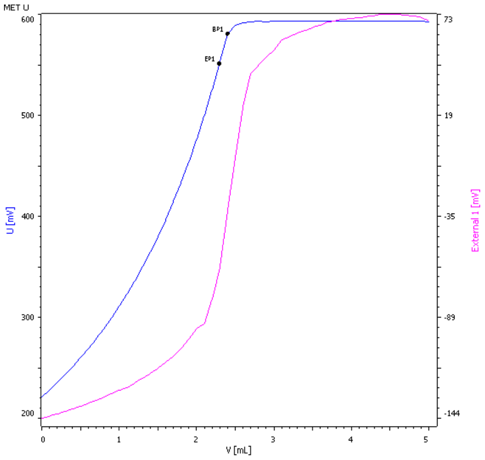

Fig. 6: The blue curve correspond to the titration curve obtained by indication with the Optrode. The pink curve corresponds to the titration curve recorded with the Pt-Titrode. Both titration curves show the equivalence or the endpoint, respectively at the approx. same volume.

Comments

- According to the norm it is recommended to add 20 mg mercury(II)chloride to the buffer pH = 6.5 to avoid mold formation and get rid of traces of iodide. As mercury(II)chloride is very toxic Metrohm AG recommends omitting this step.
- The titer determination according to the norm is carried out with potassium dichromate. As this substance is toxic as well and should be avoided, the titer determination is carried out with potassium permanganate instead.
- A comparison between the results obtained by the Optrode and the Pt-Titrode shows that it doesn't matter if the indication is carried out by the Optrode or by the Pt-Titrode. The results are the same within the uncertainty range.
- The titration of chloramine takes a little bit longer because the monochloramine liberates the chlorine active species very slowly.
- If the determination of chlorine is carried out with the Pt-Titrode it is also possible to use a DET U mode for titration.

References

- DIN EN ISO 7393-1
  Water quality - Determination of free chlorine and total chlorine - Part 1: Titrimetric method using N,N-diethyl-1,4-phenylenediamine

Method 2 – APHA 4500-Cl Method B, Iodometric Method

Introduction

Iodide is oxidized with chlorine or chlorine active species, respectively, to form iodine. The generated iodine is afterwards titrated with sodium thiosulfate. It is important that the reaction is carried out at a pH between 3 and 4 as otherwise the reaction will not be stoichiometric. Manganese and other oxidizing agents will interfere with the titration and lead to too high results.

According to the standard, the titration is carried out using starch indicator. The comparison between the indication with the Optrode and starch indicator compared to the indication with the Pt-Titrode shows that the results are comparable.

All deviations from the norm are mentioned under the section *Comments*.

Instruments

- Titrator with DET U and MET U mode
- 20 mL buret

Electrodes

Optrode	6.1115.000
Pt-Titrode	6.0431.100

Reagents

- Acetic acid, purum, >= 99%
- Potassium iodide, KI, puriss, 99.0 – 100.5%
- Potassium iodate, KIO_3, ASC reagent, 99.5%
- Sulfuric acid, puriss p.a., 95-97 %
- Starch (soluble); puriss p.a.
- $c(Na_2S_2O_3)$ = 0.1 mol/L, Titripur Reak. Ph. Eur.

Solutions

Titrant $c(Na_2S_2O_3)$ = 0.01 mol/L	This solution is prepared by transferring 100 mL of $c(Na_2S_2O_3)$ = 0.1 mol/L into a 1 L volumetric flask and filling up to the mark with deion. water.
Starch solution β(starch) = 10 g/L	1 g starch is weighed into a 100 mL beaker and approx. 70 mL deion. water is added. The solution is heated to approx. 80 °C until all the starch is dissolved. Afterwards the solution is transferred into a 100 mL volumetric flask and filled up to the mark with deion. water.

Standard solution

$\beta(KIO_3)$ = 0.3567 g/L	0.3567 g KIO_3 (previously dried at 105°C for 1 h) is weighed into a 1 L volumetric flask and filled up to the mark with deion. water.

Sample preparation

No sample preparation required

Analysis

Titer determination

10 mL of the $\beta(KIO_3)$ = 0.3567 g/L solution is transferred to a 150 mL beaker and filled up with deion. water to 100 mL. After addition of 1 mL conc. sulfuric acid the titration if carried out with $c(Na_2S_2O_3)$ = 0.01 mol/L until after the equivalence point.

Sample determination

If the chlorine concentration lies between 1 and 10 mg/L, 500 mL sample solution is transferred to a 800 mL beaker, 5 mL conc. acetic acid or enough to reduce the pH to between 3 and 4, 1 mL β(starch) = 10 g/L as well as 1 g KI is added. The titration is carried out until after the equivalence point using $c(Na_2S_2O_3)$ = 0.01 mol/L as titrant.

If the chlorine concentration is higher than 10 mg/L, the sample size is reduced accordingly.

The standard describes the photometrical titration with starch as indicator. Our investigations showed that the results obtained with the Pt-Titrode and Optrode lied in the same uncertainty range. In case the Pt-Titrode is used for indication, the addition of starch can be omitted.

Blank determination

The blank determination is carried out in the same manner as the sample determination but using 100 mL deion. water instead of sample. Two cases can be applied:

1. The obtained solution before titration shows a blue color
2. The obtained solution before titration is colorless

Depending on the observations two procedures are applied:

1. The solution is titrated with $c(Na_2S_2O_3)$ = 0.01 mol/L until after the equivalence point. The blank is negative and is subtracted from the volume for reaching the equivalence point in the sample determination.
2. As much c(iodine) = 0.005 mol/L as needed is added to observe a blue color. The added iodine is afterwards back titrated with $c(Na_2S_2O_3)$ = 0.01 mol/L until after the equivalence point. The blank is positive and has to be added to the used volume for reaching the equivalence point in the sample determination.

The standard describes the photometrical titration with starch as indicator. Our investigations showed that the results obtained with the Pt-Titrode and Optrode lied in the same uncertainty range. In case the Pt-Titrode is used, the addition of starch can be omitted.

Parameters

Titer, blank and sample determination with the Pt-Titrode

Mode	DET U
Stirring rate	8
Signal drift	10 mV/min
Min. waiting time	0 s
Max. waiting time	52 s
Min. increment	10 µL
Max. increment	Off
Stop volume	20 mL
EP criterion	5 mV
EP recognition	greatest

Titer, blank and sample determination with the Optrode

Mode	MET U
Stirring rate	6
Signal drift	5 mV/min
Min. waiting time	0 s
Max. waiting time	72 s
Volume increment	0.1 mL
Stop volume	20 mL
Break point evaluation	
EP criterion	0.6
Slope	1.2
Smoothing factor	20
Window	off

Calculation

Titer

$$f = \frac{\beta_{Std} \times V_{Std}}{V_{EP1}{}^{*} \times c_{Na2S2O3} \times M_{Std}}$$

f:	Titer of $c(Na_2S_2O_3)$ = 0.01 mol/L
β_{Std}:	Mass concentration of potassium iodate in g/L
V_{Std}:	Volume of β_{Std} added, here 10 mL
V_{EP1}:	Titrant consumption until the first equivalence point in mL
$c_{Na2S2O3}$:	Concentration of sodium thiosulfate solution, here 0.01 mol/L
M_{Std}:	Molecular weight of potassium iodate; 214.0 g/mol

Sample

$$\beta_{Cl2} = \frac{f \times (V_{EP1}{}^{*} \pm V_{blank}) \times c_{Na2S2O3} \times M_{Cl2} \times 1000}{V_{sample} \times 2}$$

β_{Cl2}:	Mass concentration of chlorine in mg Cl_2/L
f:	Titer of $c(Na_2S_2O_3)$ = 0.01 mol/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
V_{blank}:	Titrant consumption of the blank determination until the first equivalence point in mL; if procedure 1 is used the blank is negative; for procedure 2 the blank is positive.
$c_{Na2S2O3}$:	Concentration of the selected titrant in mol/L; here $c(Na_2S_2O_3)$ = 0.01 mol/L
M_{Cl2}:	Molecular weight of chlorine; here 70.9 g/mol
1000:	Conversion factor from mg/mL to mg/L
V_{sample}:	Used amount of sample; here 500 mL
2:	Stoichiometric factor

* if the determination is carried out with the Optrode, the break point is used for calculation instead of the equivalence point.

Example determination

Determinations with the Pt-Titrode

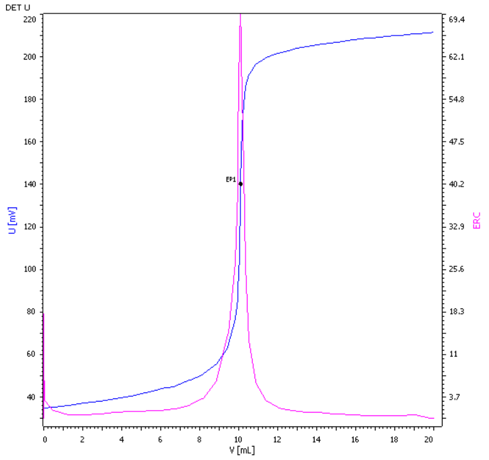

Fig. 7: Titer determination of c(Na2S2O3) = 0.01 mol/L with the Pt-Titrode

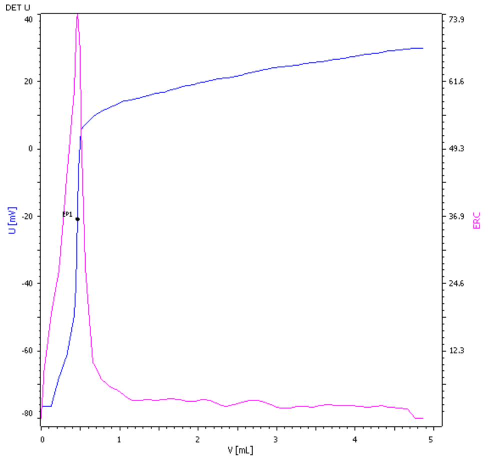

Fig. 8: Blank determination with the Pt-Titrode

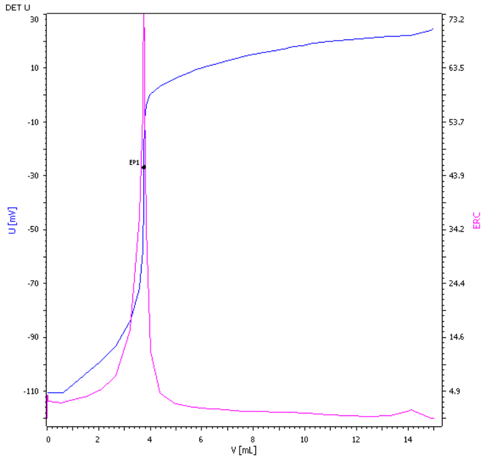

Fig. 9: Sample determination with the Pt-Titrode

Determinations with the Optrode

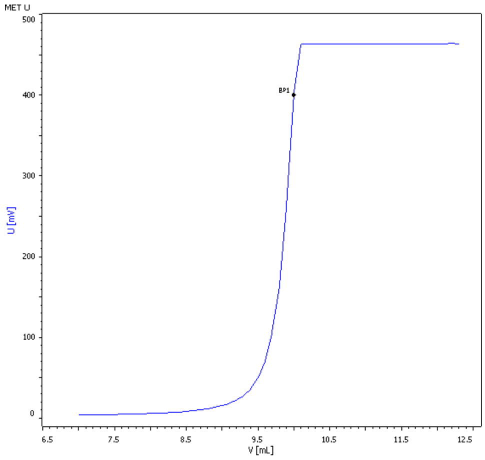

Fig. 10: Titer determination of c($Na_2S_2O_3$) = 0.01 mol/L with the Optrode and starch indicator

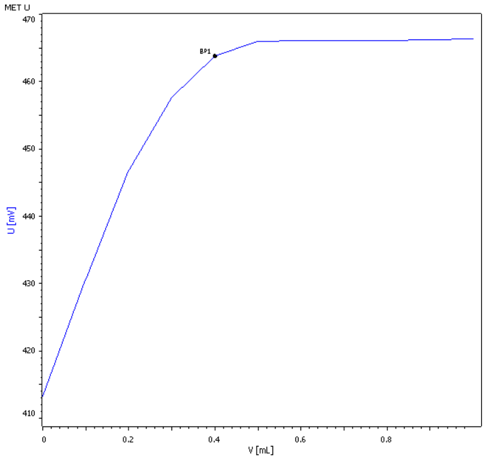

Fig. 10: Sample determination with the Optrode and starch as indicator

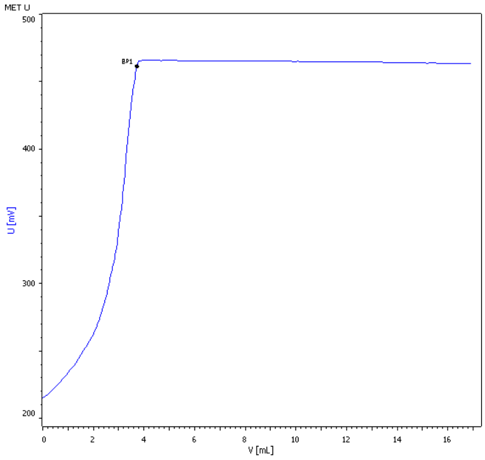

Fig. 12: Sample determination with the Optrode and starch as indicator

Comments

- No mercuric iodide was added to the c($Na_2S_2O_3$) = 0.01 mol/L solution as the use of mercuric iodide should be avoided.
- The starch indicator was not prepared as described by the standard.
- In the standard two methods are mentioned to determine the titer. The second should be avoided because potassium dichromate is used as primary standard.
- The values obtained by photometric and potentiometric titrations are the same within the uncertainty range.

References

- APHA 4500-Cl Chlorine (Residual)

Method 3 – APHA 4500-Cl Method I, Iodometric electrode technique

Introduction

Chlorine active species and the added potassium iodide react to form iodine. As the iodide ion selective electrode is only sensitive to iodide and not to iodine the iodide selective electrode is used as reference electrode. The concentration of the iodine and therefore from the chlorine active species, is determined by measuring the potential produced by the iodide/iodine pair with a Pt rod electrode.

Instruments

- Titrator or pH meter with ability to measure ion concentration

Electrodes

Shaft for separate metal-rod electrode, without cable	6.1241.040
Strand / 2 m / 2 x B	6.2106.060
Electrode rod Pt	6.1248.000
Iodide ISE	6.0502.160

Reagents

- Sodium acetate anhydrous, ReagentPlus, >= 99 %
- Acetic acid, ReagentPlus, >= 99 %
- Potassium iodide, KI, puriss, 99 – 100.5 %
- Sodium carbonate, Na_2CO_3, ReagentPlus, >=99.5 %
- Potassium iodate, KIO_3, ASC reagent, 99.5%

Solutions

Acetate buffer solution, pH 4.0	146 g anhydrous sodium acetate is transferred into a 1 L volumetric flask dissolved in approx. 400 mL deion. water. 480 g glacial acetic acid is added and the obtained solution is filled up to the mark with deion. water.
β(KI) = 84 g/L	42 g KI and 0.5 g Na_2CO_3 are given into a 500 mL volumetric flask and dissolved in about 400 mL deion. water. After dissolution the flask is filled up to the mark with deion. water. The solution is kept in a brown-glass flask to prevent any decomposition caused by sunlight.

Standard solution

Standard potassium iodate solution β(KIO_3) = 0.1002 g/L	0.1002 g $KIO_3$is transferred into a 1 L volumetric flask and dissolved in deion. water. Afterwards the flask is filled up to the mark with deion. water. Each 1.0 mL is equivalent to 1.0 mg/L Cl_2 if diluted to 100 mL with deion. water.

Sample preparation

No sample preparation required

Analysis

Calibration

0.2 mL, 1.00 mL and 5.00 mL β(KIO_3) = 0.1002 g/L are pipetted each into a 100 mL volumetric flask.

To each 100 mL volumetric flask 1 mL of acetate buffer solution pH 4.0 and 1 mL of β(KI) = 84 g/L are added. The volumetric flask is closed with a stopper, swirled, mixed and allowed to stand for 2 minutes. After these 2 minutes, each standard is filled up to the mark with deion. water and mixed thoroughly. The content is poured into a 150 mL beaker and stirred gently by the use of a magnetic stirrer without turbulence. The electrodes are immersed into the 0.2 mg/L standard and as soon as the voltage is constant, the value is recorded. The procedure is repeated for the 1 mg/L and for the 5 mg/L standards as well. A calibration curve is obtained by plotting the potential against concentration. This can be done manually or automatically.

Reagent blank

To a 100 mL volumetric flask, 1 mL of acetate buffer solution pH 4.0 and 1 mL of β(KI) = 84 g/L are added. The volumetric flask is closed with a stopper, swirled, mixed and allowed to stand for 2 minutes. After these 2 minutes, the solution is filled up to the mark with deion. water and mixed thoroughly. The content is poured into a 150 mL beaker and stirred gently by the use of a magnetic stirrer without turbulence. The electrodes are immersed and as soon as the voltage is constant, the value is recorded. From the obtained calibration curve and linear regression, the reagent blank can be determined. This can be carried out automatically.

Sample analysis

An aliquot of the sample containing not more than 0.5 mg chlorine is pipetted into a 100 mL volumetric flask. 1 mL of acetate buffer solution pH 4.0 and 1 mL of β(KI) = 84 g/L are added. The volumetric flask is closed with a stopper, swirled, mixed and allowed to stand for 2 minutes. The pH of the sample is adjusted, if necessary, to pH 4.0 by adding acetic acid. After these 2 minutes, the solution is filled up to the mark with deion. water and mixed thoroughly. The content is poured into a 150 mL beaker and stirred gently by the use of a magnetic stirrer without turbulence. The electrodes are immersed and as soon as the voltage is constant, the value is recorded. From the obtained calibration curve and linear regression, respectively, the chlorine concentration can be determined. This can be carried out automatically.

Parameters

Calibration

Mode	CAL MEAS Conc
Stirring rate	8
Signal drift	0.1 mV/min
Min. waiting time	150 s
Max. waiting time	600 s
Measuring interval	2.0 s

Reagent blank and analysis

Mode	MEAS Conc
Stirring rate	8
Signal drift	0.1 mV/min
Min. waiting time	150 s
Max. waiting time	600 s
Measuring interval	2.0 s

Calculation

The calculation is carried out automatically.

Example determination

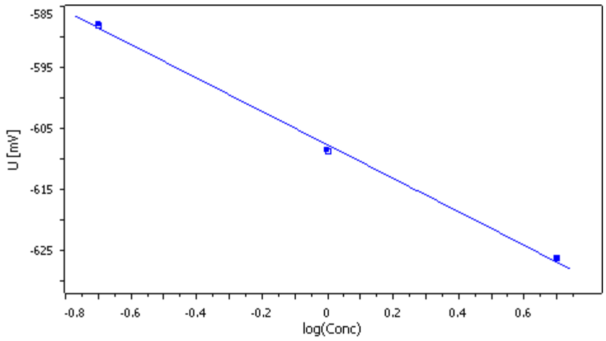

Fig. 13: Calibration carried out by using the above-mentioned standards (0.2 mg/L, 1 mg/L and 5 mg/L). The slope is about -27.4 mV, E(0) is -607.7 mV, c(blank) is 0.00 mg/L and the variance about 1.566. This corresponds to a correlation factor of 0.9978.

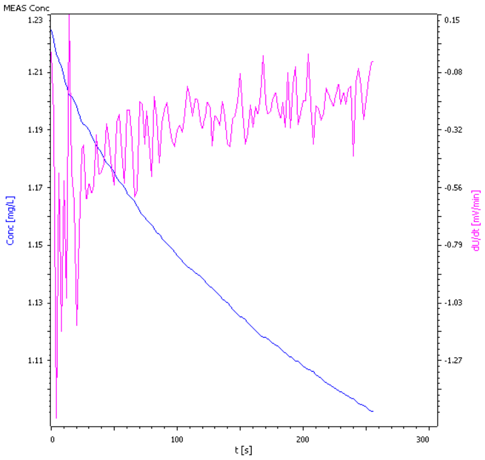

Fig. 13: Measurement of a 1 ppm chlorine standard purchased from Orion. A concentration of 1.092 ppm was measured.

Comments

- All oxidizing agents like manganese, iodate, bromate and cupric ions will interfere with this method. Silver and mercuric ions with a concentration above 10 and 20 mg/l will interfere as well.
- The iodide selective electrode is polished before use by using the polishing set 6.2802.000. Additionally the electrode is conditioned in c(KI) = 0.01 mol/L for 5 min before measurements.

References

- APHA 4500-Cl Chlorine (Residual)

Author

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