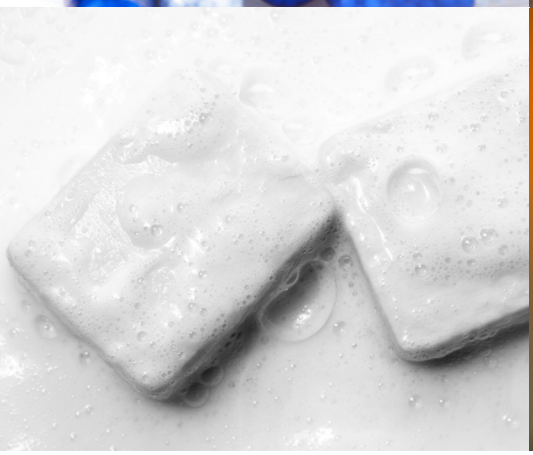
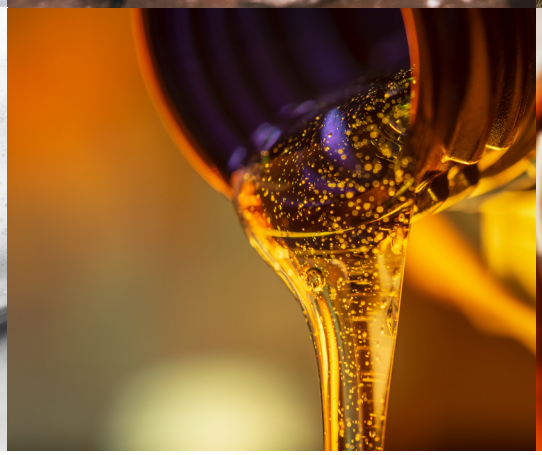
Eco Titrator




Application Booklet

Metrohm

Introduction

Congratulations for choosing the Eco Titrator, the universal instrument for nearly all kinds of potentiometric titrations. This booklet contains a collection of the most common applications in the branches Food & Beverage, Petrochemicals, Wine, Surfactants and Plating. All applications are described in detail and template methods are included on the USB memory stick provided with the Eco Titrator.

Table of content

Abbreviations for calculations

Formula	Eco Titrator
m_{Sample}	COO
V_{Sample}	COO
Blank	CVO1
V_{EP1}	EP1
V_{EP2}	EP2
V_{EP3}	EP3
$c_{Solution}$	CONC
$t_{Solution}$	TITER

Recommendations for the most common titrants

Titrant	Recommendations for storage	Recommendations for adsorbing tube	Recommendations for titrant concentration determination
Sodium ethylenediaminetetraacetic acid (Na_2EDTA)	No special recommendations	Fill with cotton to adsorb dust	Depending on the accuracy required, determine the concentration of the titrant weekly to monthly
Sodium hydroxide (NaOH)	Do not allow to stand open as otherwise CO_2 will be adsorbed. Keep in a plastic bottle.	Fill with soda lime to adsorb CO_2 from the air.	Depending on the accuracy required, determine the concentration of the titrant daily to weekly
Hydrochloric acid (HCl)	No special recommendations	Fill with cotton to adsorb dust	Depending on the accuracy required, determine the concentration of the titrant weekly to monthly
Iodine solution (I_2)	Use a brown-glass bottle and store in a dark place if not in use	No absorber material, as otherwise the material takes up the iodine (e.g., cotton gets colored)	Depending on the accuracy required, determine the concentration of the titrant daily to weekly
Silver nitrate ($AgNO_3$)	Use a brown-glass bottle and store in a dark place if not in use	Fill with cotton to adsorb dust	Depending on the accuracy required, determine the concentration of the titrant weekly to monthly
Sodium thiosulfate ($Na_2S_2O_3$)	No special recommendations	Fill with cotton to adsorb dust	Depending on the accuracy required, determine the concentration of the titrant weekly to monthly
Perchloric acid ($HClO_4$)	Store in a tightly sealed bottle, as perchloric acid is hygroscopic	Fill with molecular sieve	Depending on the accuracy required, determine the concentration of the titrant daily to weekly
Potassium hydroxide (KOH)	Don't allow to stand open as otherwise CO_2 will be adsorbed. Keep in a plastic bottle.	Fill with soda lime to adsorb CO_2 from the air.	Depending on the accuracy required, determine the concentration of the titrant daily to weekly
TEGOtrant	No special recommendations	Fill with cotton to adsorb dust	Depending on the accuracy required, determine the concentration of the titrant weekly to monthly
Sodium dodecyl sulfate (SDS)	No special recommendations	Fill with cotton to adsorb dust	Depending on the accuracy required, determine the concentration of the titrant weekly to monthly
Sodium tetraphenyl borate (STPB)	No special recommendations	Fill with cotton to adsorb dust	Depending on the accuracy required, determine the concentration of the titrant weekly to monthly
Potassium bromide (KBr)	Use a brown-glass bottle and store in a dark place as otherwise bromine might be formed.	Fill with cotton to adsorb dust	Depending on the accuracy required, determine the concentration of the titrant weekly to monthly

Recommendations for electrodes used in this Booklet

Electrode Ordering Number	Specifics	Recommendations for cleaning and storage
Solitrode 6.0220.100	For solutions not containing precipitates, proteins or sulfides	Check the filling level of c(KCl) = 3 mol/L (6.23xx.xxx) in the electrode regularly, refill if necessary and store the electrode in storage solution (6.2323.000).
Unitrode with Pt1000 6.0258.600	For universal use, even in dyes, pigments, inks, suspensions, resins and polymers For samples at high temperatures or high pH	Check the filling level of c(KCl) = 3 mol/L (6.23xxxxx) in the electrode regularly, refill if necessary and store the electrode in storage solution (6.2323.000).
Ecotrode plus 6.0262.100	For acid/base titrations in various kinds of solutions	Check the filling level of c(KCl) = 3 mol/L (623xxxx) in the electrode regularly, refill if necessary and store the electrode in storage solution (6.2323.000).
Aquatrode plus with Pt1000 6.0257.600	For measurements in ion-deficient or weakly buffered solutions	Check the filling level of c(KCl) = 3 mol/L (623xxxx) in the electrode regularly, refill if necessary and store the electrode in storage solution (6.2323.000).
Porotrode 6.0235.200	For measurements in very contaminated, protein-containing or viscous samples	Check the filling level of Porolyte (6.2318.000) in the electrode regularly, refill if necessary and store the electrode in Porolyte.
Solvotrode easy clean 6.0229.010	For determination in non-aqueous media	Check the filling level of the corresponding electrolyte in the electrode regularly, refill if necessary and store the electrode in the same solution. If titrations with alkaline titrants are carried out, use c(TEABr) = 0.4 mol/L in ethylene glycol, if the titrations are done with acidic titrants use c(LiCl) = 2 mol/L in ethanol.
Ag Titrode 6.00430.100 Optional available with AgCl, AgBr or Ag_2S coating	For precipitation reactions with $AgNO_3$ under constant pH conditions	The electrode is stored in deionized water when not in use. Electrodes **without** coatings can be polished by using the polishing set 6.2802.010 or by dipping the electrode into w(NH_3) = 1%.Make sure that the pH membrane of the electrode is not touched while polishing the ring.
Pt Titrode 6.0431.100	For redox titrations under pH constant conditions	The electrode is stored in deionized water when not in use. The Pt ring can be polished by using the polishing set 6.2802.010. Make sure the pH membrane of the electrode is not touched while polishing the ring.
Double Pt sheet electrode 6.0309.100	For titrations in I_{pol} mode	The electrode is stored dry when not in use. When using a new electrode the titration curve might be flat. The platinum is passivated in this case. 2–3 titrations with iodine showed an activation of the platinum.
Surfactrode Refill 6.0507.140	For titrations of anionic and cationic surfactants in non-aqueous medium and for two-phase titrations	The electrode is stored dry when not in use. The active part of the electrode can be refilled by using the Surfactrode refill paste (6.2319.000) and the filling tool (6.2826.010).
Ionic surfactant electrode 6.0507.120	For titrations of anionic and cationic surfactants in aqueous matrices	The electrode is stored dry when not in use. If the titration curve gets flat, regenerate the electrode by immersing it for approx. 30 min in c(SDS) = 0.004 mol/L. This electrode must not be used in organic solvents.
NIO surfactant electrode 6.0507.010	For titration of non-ionic surfactants and of pharmaceutical ingredients with sodium tetraphenylborate	The electrode is stored dry when not in use. If the titration curve gets flat, regenerate the electrode by immersing it for approx. 30 min in c(STPB) = 0.01 mol/L. The electrode should be used for titration of pharmaceutical ingredients or for NIO surfactant titrations, but not for both. This electrode must no be used in organic solvents.
LL-ISE Reference electrode 6.0750.100	Reference electrode for almost all applications	The electrode is stored in c(KCl) = 3 mol/L.

1. General – Titer determination of c(Na_2EDTA) = 0.1 mol/L

Summary

Na_2EDTA is a chelating agent and is used for the determination of metals by complexometric titration. Its titer is relatively stable and there are no special recommendations for storage.

Adsorbing material	Cotton
Frequency of titer determination	Weekly to monthly
Material of storage bottle	No special recommendations

Solutions

Titrant c(Na_2EDTA) = 0.1 mol/L	Should be bought from a supplier.
Buffer pH 10	Weigh 54 g NH_4Cl into a 1 L volumetric flask and add 350 mL w(NH_3) = 25%. After dissolution, fill up to the mark with deionized water.
c(HCl) = 5 mol/L	Weigh 492 g w(HCl) = 37% into a 1 L volumetric flask, already containing 200 mL deionized water. Then, allow to cool down and fill up to the mark with deionized water.

Standard substance

Dry calcium carbonate for at least 2 h at 105 °C and allow to cool down in a desiccator.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Combined polymer membrane electrode, Ca	6.0510.100

Sample preparation

No sample preparation is required.

System configuration

1. Load ***Method_1*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***EDTA_0.1*** to the *solution list* under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Ca-ISE*** under *System → Sensors* to the *sensor list.*
5. Prepare the sample solution as defined under ***Analysis***

Analysis

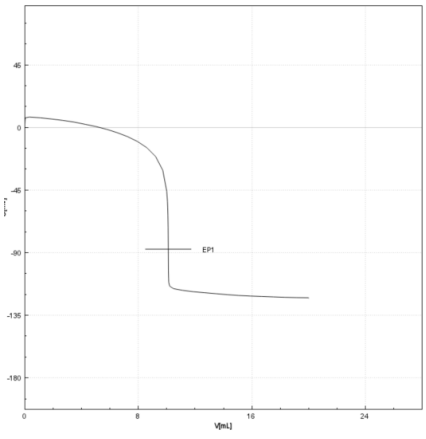
Weigh approx. 100 mg dried $CaCO_3$ into a 100 mL beaker, suspend it in approx. 20 mL deionized water and dissolve it by dropwise addition of c(HCl) = 5 mol/L. After dissolution, add 40 mL deionized water and 5 mL buffer pH 10 and start the titration by pressing the start button. Enter all requested sample data and titrate with c(Na_2EDTA) = 0.1 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method

Calculation

$$t_{EDTA} = \frac{m_{CaCO3}}{c_{EDTA} \cdot M(CaCO_3) \cdot V_{EP1}}$$

t_{EDTA}: titer of EDTA solution
m_{CaCO3}: mass of $CaCO_3$ used for analysis in mg
c_{EDTA}: concentration of EDTA solution; here: 0.1 mol/L
$M(CaCO_3)$: molar mass of calcium carbonate; 100.09 g/mol
V_{EP1}: consumption of titrant up to the first equivalence point in mL

Example curve



Results

Mean value (n = 3)	1.0027
s(abs)	0.0020
s(rel)	0.20%

Comments

- The combined Ca ISE electrode can be used out of the box without any special treatment for conditioning. It is stored dry with some residual moisture (e.g., some drops of deionized water) if not in use.
- Make sure that all calcium carbonate is dissolved before you start the titration.
- If no c(HCl) = 5 mol/L is available, also other concentrations of HCl can be used. However, the added volume has to be adjusted to ensure that the calcium carbonate fully dissolves.

2. General – Titer determination of c(NaOH) = 0.1 mol/L

Summary

NaOH is used as alkaline titrant for the titration of many different acids. Alkaline titrants do not have a stable titer and might absorb CO_2 from the atmosphere to form carbonates. Therefore, the titer has to be determined daily to weekly to know its exact concentration.

Adsorbing material	Soda lime
Frequency of titer determination	Daily to weekly
Material of storage bottle	Plastic (e.g. HD-PE) attacks glass

Solutions

Titrant c(NaOH) = 0.1 mol/L	Should be bought from a supplier

Standard substance

Dry potassium hydrogen phthalate (KHP) for at least 2 h at 105 °C and allow to cool down in a desiccator.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

e.g., Solitrode (or any other suitable combined pH electrode)	6.0220.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_2*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***NaOH_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the corresponding electrode (e.g., ***Solitrode***) to the *sensor list* under *System* → *Sensors*.
5. Choose the defined electrode under *Parameters* → *Titration parameters*
6. Prepare the sample solution as defined under ***Analysis***

Analysis

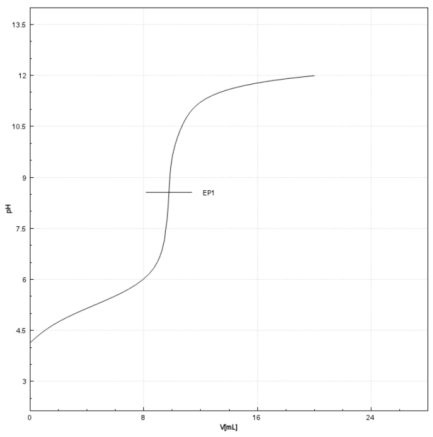
Weigh approx. 200 mg dried KHP into a 100 mL beaker and dissolve it in about 60 mL deionized water. Then start the titration by pressing the start button and enter the requested sample data. Titrate with c(NaOH) = 0.1 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$t_{NaOH} = \frac{m_{KHP}}{c_{KHP} \cdot M(KHP) \cdot V_{EP1}}$$

t_{NaOH}: titer of NaOH solution
m_{KHP}: mass of KHP used for analysis in mg
c_{NaOH}: concentration of NaOH solution; here: 0.1 mol/L
M(KHP): molar mass of KHP; 204.22 g/mol
V_{EP1}: consumption of titrant up to the first equivalence point in mL

Example curve



Results

Mean value (n = 3)	0.9254
s(abs)	0.0026
s(rel)	0.29%

Comments

- Make sure that the electrolyte filling level of the electrode is higher than the level of the sample solution as otherwise sample might diffuse into the electrode and contaminate the reference system.
- Two equivalent points might be visible because of the dissolved CO_2. The difference between the first and second equivalence point corresponds to the carbonate.
- In order to reduce CO_2 absorption as much as possible, fill soda lime into the drying/absorber tube mounted on the bottle.
- A start volume might be used to reduce the analysis time.

3. General – Titer determination of c(HCl) = 0.1 mol/L

Summary

HCl is an acidic titrant, which is used for determination of many different bases. Its titer is relatively stable and needs to be determined weekly to monthly only.

Adsorbing material	Cotton
Frequency of titer determination	Weekly to monthly
Material of storage bottle	No special recommendations

Solutions

Titrant c(HCl) = 0.1 mol/L	Should be bought from a supplier.

Standard substance

Dry TRIS (Tris(hydroxymethyl)aminomethane) for 2 h at 105 °C and allow to cool down in a desiccator.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

e.g., Solitrode (or any other suitable combined pH electrode)	6.0220.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_3*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***HCl_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the corresponding electrode (e.g., ***Solitrode***) to the sensor list under *System* → *Sensors.*
5. Change the electrode under *Parameters* → *Titration parameters.*
6. Prepare the sample solution as defined under ***Analysis***

Analysis

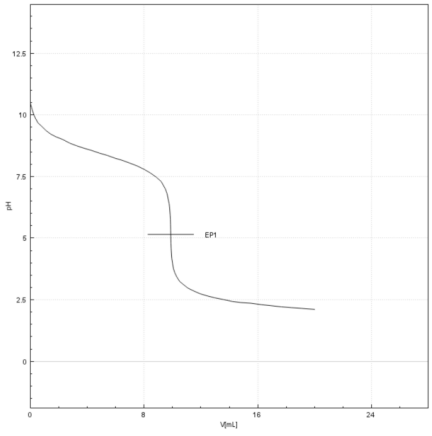
Weigh approx. 100 mg dried TRIS into a 100 mL beaker. Dissolve it in about 60 mL deionized water and press the start button. Enter all requested sample data and titrate wth c(HCl) = 0.1 mol/L until after the first equivalence point. All the other parameters and calculations are already defined within the method.

Calculation

$$t_{HCl} = \frac{m_{TRIS}}{c_{HCl} \cdot M(TRIS) \cdot V_{EP1}}$$

t_{HCl}: titer of HCl solution
m_{TRIS}: mass of TRIS used for analysis in mg
c_{HCl}: concentration of HCl solution; here: 0.1 mol/L
M(TRIS): molar mass of TRIS; 121.14 g/mol
V_{EP1}: consumption of titrant up to the first equivalence point mL

Example curve



Results

Mean value (n = 3)	1.0001
s(abs)	0.0013
s(rel)	0.13%

Comments

- Make sure that the electrolyte filling level of the electrode is higher than the level of your sample solution as otherwise solution might diffuse into the electrode and destroy the reference system.
- At the beginning of the titration curve an equivalence point is often observed. This EP can be removed from the titration curve by using a start volume.
- Make sure that the level of solution is high enough that the diaphragm is immersed into the solution.

4. General – Titer determination of $c(I_2)$ = 0.01 mol/L

Summary

Over time, the iodine concentration changes due to the volatile nature of iodine and degradation by UV light. Therefore, the titer has to be determined at least weekly.

Adsorbing material	Cotton
Frequency of titer determination	Daily to weekly
Material of storage bottle	Brown glass bottle

Store the solution in the dark when not in use as otherwise the iodine decomposes.

Solutions

Titrant $c(I_2)$ = 0.01 mol/L	Pipette 200 mL $c(I_2)$ = 0.05 mol/L (should be bought from a supplier) into a 1 L volumetric flask and fill up to the mark with deionized water.

Standard solution

$c(Na_2S_2O_3)$ = 0.1 mol/L	Should be bought from a supplier.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Pt Titrode	6.0431.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method 4*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***I2_0.01*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Pt Titrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as defined under ***Analysis***

Analysis

Pipette 1.0 mL standard solution $c(Na_2S_2O_3)$ = 0.1 mol/L into a 100 mL beaker and fill up to approx. 60 mL with deionized water. Press the start button and enter all requested sample data. Titrate afterwards with $c(I_2)$ = 0.01 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$t_{I2} = \frac{V_{Na2S2O3} \cdot 10}{V_{EP1} \cdot 2}$$

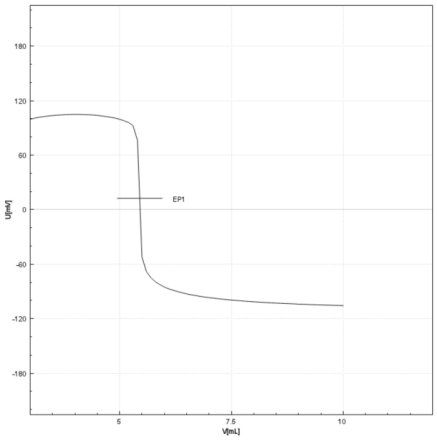
$V_{Na2S2O3}$: volume of standard solution; here 1 mL

10: conversion factor from 0.01 mol/L to 0.1 mol/L

V_{EP1}: consumption of titrant up to the first equivalence point in mL

2: stoichiometric factor

Example curve



Results

Mean value (n = 3)	1.0001
s(abs)	0.0013
s(rel)	0.13%

Comments

- The Pt Titrode is stored in deionized water to keep the glass membrane ready for use.
- Solid sodium thiosulfate can also be used as solid standard, however, it is not recommended as thiosulfate is hygroscopic and therefore more difficult to handle. If a solution is used, make sure that it is bought from a supplier and has a known concentration so that it can be used directly for standardization. Should you make the solution by yourself determine the titer by using ***Method_6***.
- Iodine is very volatile. The titer is not very stable and should be determined at least once a week.

5. General – Titer determination of $c(AgNO_3)$ = 0.1 mol/L

Summary

Silver nitrate is a common titrant for the determination of anions like chloride, bromide, sulfide and iodide. Its titer is relatively stable; however, the UV/light may degrade it. Therefore it is necessary to determine the titer frequently and store it away from UV light.

Adsorbing material	Cotton
Frequency of titer determination	Daily to weekly
Material of storage bottle	Brown glass bottle

Solutions

Titrant $c(AgNO_3)$ = 0.1 mol/L	Should be bought from a supplier.
$c(HNO_3)$ = 2 mol/L	Weigh 194 g $c(HNO_3)$ = 65% into a 1 L volumetric flask already containing 500 mL deionized water, allow to cool down and fill it up to the mark with deionized water.

Standard substance

Dry NaCl for at least 2 h at 105 °C and allow to cool down in a desiccator.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.210

Sensors

Ag Titrode	6.00430.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_5*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***AgNO3_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Ag Titrode*** to the sensor list under *System* → *Sensors*.
5. Prepare the sample solution as defined under ***Analysis***

Analysis

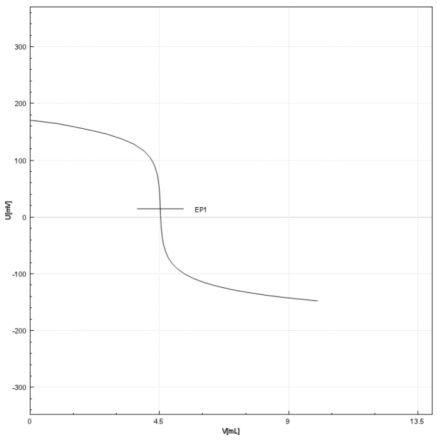
Weigh approx. 30 mg NaCl into a 100 mL beaker, dissolve it in about 60 mL deionized water, add 2 mL $c(HNO_3)$ = 2 mol/L and press the start button. Enter all requested sample data and titrate with $c(AgNO_3)$ = 0.1 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$t_{AgNO3} = \frac{m_{NaCl}}{c_{AgNO3} \cdot M(NaCl) \cdot V_{EP1}}$$

t_{AgNO3}: titer of $AgNO_3$ solution
m_{NaCl}: mass of NaCl used for analysis in mg
c_{AgNO3}: concentration of $AgNO_3$ solution; here: 0.1 mol/L
M(NaCl): molar mass of sodium chloride; 58.44 g/mol
V_{EP1}: consumption of titrant up to the first equivalence point in mL

Example curve



Results

Mean value (n = 3)	1.0015
s(abs)	0.0011
s(rel)	0.11%

Comments

- The Ag Titrode is stored in deionized water to keep the glass membrane ready for use.
- Silver nitrate can lead to black spots if it is spilled onto the skin or equipment. It can be removed by using an appropriate cleaning solution or sodium bisulfite solution.
- The remaining silver ions must be removed from the waste solution by adding e.g., sodium chloride.
- The use of the Ag ring electrode is only recommended if the pH is significantly changing during titration because a diaphragm free electrode is easier to handle in argentometric titrations.

6. General – Titer determination of $c(Na_2S_2O_3)$ = 0.1 mol/L

Summary

Sodium thiosulfate is used for redox titrations, in particular for titrations of iodine. This titrant is relatively stable and no special treatment is necessary.

Adsorbing material	Cotton
Frequency of titer determination	Weekly to monthly
Material of storage bottle	No special recommendations

Solutions

Titrant $c(Na_2S_2O_3)$ = 0.1 mol/L	Should be bought from a supplier.
$w(H_2SO_4)$ = 25%	Transfer 255 g $w(H_2SO_4)$ = 98% into a 1 L volumetric flask, already containing 400 mL deionized water. After cooling down, fill the solution up to the mark with deionized water.

Standard substance

Dry KIO_3 for at least 2 h at 105 °C and allow to cool down in a desiccator.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Pt Titrode	6.0431.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_6*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***Na2S2O3_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Pt Titrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as defined under ***Analysis.***

Analysis

Weigh approx. 50 mg KIO_3 into a 100 mL beaker, dissolve it in about 60 mL deionized water and add 1 g KI to the solution. After addition of 10 mL $w(H_2SO_4)$ = 25%, press the start button, enter all requested sample data and titrate with $c(Na_2S_2O_3)$ = 0.1 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$t_{Na2S2O3} = \frac{m_{KIO3} \cdot z^*}{c_{Na2S2O3} \cdot M(KIO3) \cdot V_{EP1}}$$

$t_{Na2S2O3}$: titer of sodium thiosulfate solution

m_{KIO3}: mass of potassium iodate used for analysis in mg

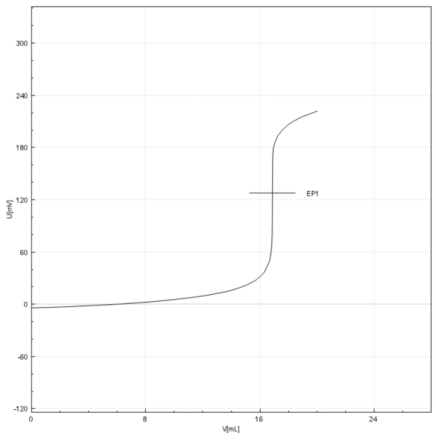
z^*: stoichiometric factor; here 6

$c_{Na2S2O3}$: concentration of sodium thiosulfate solution; here: 0.1 mol/L

$M(KIO_3)$: molar mass of KIO_3; 214.00 g/mol

V_{EP1}: consumption of titrant up to the first equivalence point mL

Example curve

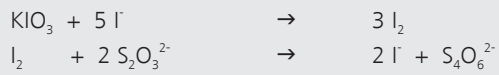


Results

Mean value (n = 3)	1.0067
s(abs)	0.0014
s(rel)	0.11%

Comments

- Store the Pt Titrode in deionized water to keep the glass membrane ready for use.
- Iodine is not used as standard as it sublimates rapidly. Instead, iodine is formed by comproportionation reaction of iodide and iodate.
- z^* has to be set to 6 due to the following reaction equation for titer determination:



7. General – Titer determination of c($HClO_4$) = 0.1 mol/L in glacial acetic acid

Summary

Perchloric acid is one of the strongest acid and used in non-aqueous titration to obtain a sharp and steep potential jump at the equivalence point. As glacial acetic acid is relatively volatile and hygroscopic, the bottle has to be tightly closed when stored.

Adsorbing material	Molecular sieve
Frequency of titer determination	Daily to weekly
Material of storage bottle	No special recommendations

Solutions

Titrant c($HClO_4$) = 0.1 mol/L in glacial acetic acid	Should be bought from a supplier.

Standard substance

Dry potassium hydrogen phthalate (KHP) for at least 2 h at 105 °C and allow to cool down in a desiccator.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Solvotrode easyClean	6.0229.010

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_7*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***HClO4_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Solvotrode*** to the sensor list under *System* → *Sensors*.
5. Prepare the sample solution as defined under ***Analysis***

Analysis

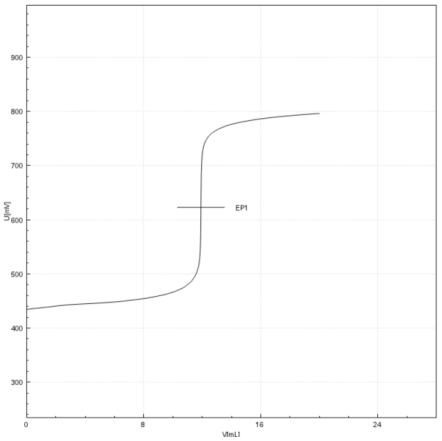
Weigh approx. 200 mg KHP into a 150 mL beaker and add 40 mL glacial acetic acid. After everything is dissolved, add 40 mL toluene, press start and enter all requested sample data. Titrate with c($HClO_4$) = 0.1 mol/L in glacial acetic acid until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$t_{HClO4} = \frac{m_{KHP}}{c_{HClO4} \cdot M(KHP) \cdot V_{EP1}}$$

t_{HClO4}: titer of HClO4 solution
m_{KHP}: mass of KHP used for analysis in mg
c_{HClO4}: concentration of HClO4 solution; here: 0.1 mol/L
M(KHP): molar mass of KHP; 204.22 g/mol
V_{EP1}: consumption of titrant up to the first equivalence point in mL

Example curve



Results

Mean value (n = 3)	0.9960
s(abs)	0.0006
s(rel)	0.064%

Comments

- Store the Solvotrode easyClean in the corresponding electrolyte (c(TEABr) = 0.4 mol/L in ethylene glycol or c(LiCl) = 2 mol/L in ethanol).
- Between measurements, regenerate the electrode by immersing the glass bulb of the electrode for 1 min into deionized water.
- Open the diaphragm from time to time by pressing the electrode head to release some electrolyte. This ensures that the diaphragm is not blocked.

Potassium hydrogen phthalate has two carboxylic functional groups, one in its acidic and the other in its alkaline form. Therefore it can be used for the titer determination of acids as well as for bases.

8. General – Titer determination of c(KOH) = 0.1 mol/L in isopropanol

Summary

Potassium hydroxide has a good solubility in ethanol and isopropanol. Therefore, it is often used for non-aqueous titrations. KOH solutions tend to absorb CO_2 from the air, therefore soda lime has to be used as adsorber filling material.

Adsorbing material	Soda lime
Frequency of titer determination	Daily to weekly
Material of storage bottle	Plastic bottle (e.g. HD-PE); KOH attacks glass

Solutions

Titrant c(KOH) = 0.1 mol/L in isopropanol	Should be bought from a supplier.

Standard substance

Dry potassium hydrogen phthalate (KHP) for at least 2 h at 105 °C and allow to cool down in a desiccator.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Solvotrode easyClean	6.0229.010

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_8*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***KOH_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Solvotrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as defined under ***Analysis***

Analysis

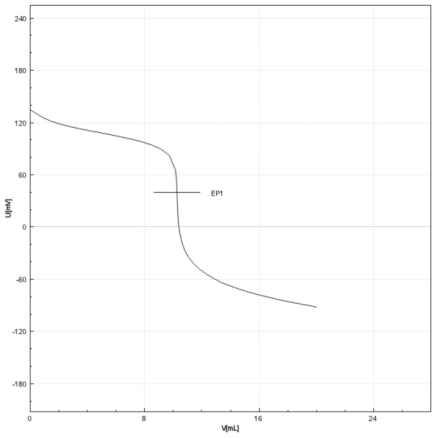
Weigh approx. 200 mg KHP into a 100 mL beaker and dissolve it in about 40 mL deionized water. After dissolution, add 20 mL isopropanol and titrate with c(KOH) = 0.1 mol/L in IPA until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$t_{KOH} = \frac{m_{KHP}}{c_{KOH} \cdot M(KHP) \cdot V_{EP1}}$$

t_{KOH}: titer of KOH solution
m_{KHP}: mass of KHP used for analysis in mg
c_{KOH}: concentration of KOH solution; here: 0.1 mol/L
M(KHP): molar mass of KHP; 204.22 g/mol
V_{EP1}: consumption of titrant up to the first equivalence point in mL

Example curve



Results

Mean value (n = 3)	0.9960
s(abs)	0.0006
s(rel)	0.064%

Comments

- Store the Solvotrode easyClean in the corresponding electrolyte (c(TEABr) = 0.4 mol/L in ethylene glycol or c(LiCl) = 2 mol/L in ethanol).
- Between measurements, regenerate the electrode by immersing the glass bulb of the electrode for 1 min into deionized water.
- Open the diaphragm from time to time by pressing the electrode head to release some electrolyte. This ensures, that the diaphragm is not blocked.
- KOH in IPA is very corrosive against glass and may attack the cylinder unit. It is recommended to empty the glass cylinder and rinse it with deionized water if the device is not in use for one week.

9. General – Titer determination of c(TEGOtrant) = 0.005 mol/L

Summary

The titer has to be determined frequently to assure that the concentration of the solution remains the same or at least to know the exact concentration of the used titrant. In case of the surfactant titer determination, the cationic surfactant is used as standard for the anionic titer determination and the other way round. Therefore, it is recommended to buy at least the standard solution from a supplier where the concentration is already determined.

Adsorbing material	Cotton
Frequency of titer determination	Weekly to monthly
Material of storage bottle	No special recommendations

Solutions

Titrant c(TEGOtrant) = 0.005 mol/L	Weigh approx. 2.2 g TEGOtrant (6.2317.030) into a 1 L volumetric flask and add 150 mL deionized water. After dissolution, fill the solution up to the mark with deionized water. Make sure that no foam is present anymore when filling the solution up to the mark with deionized water.
TEGOadd	Metrohm 6.2317.120
c(HCl) = 0.5 mol/L	Weigh 49.3 g w(HCl) = 37% into a 1 L volumetric flask containing already 500 mL deionized water. After allowing to cool down, fill the solution up to the mark with deionized water.
Solvent mixture Methyl isobutyl ketone : ethanol (1:1 (v:v))	Transfer 500 mL MIBK and 500 mL ethanol into a glass bottle and mix thoroughly.

Standard solution

c(SDS) = 0.005 mol/L	Should be bought from a supplier.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Surfactrode Refill	6.0507.140
LL ISE Reference electrode	6.0750.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_9*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***TEGO_0.005*** to the *solution list* under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Surf Refill*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as defined under ***Analysis.***

Analysis

Fill the cylinder unit on the evening before the first titration. On the next day, carry out a "PREP" before the first titration.

Pipette 10 mL c(SDS) = 0.005 mol/L into a 100 mL beaker and add 50 mL deionized water as well as 0.2 mL TEGOadd. Adjust the pH of the mixture with c(HCl) = 0.5 mol/L to pH 2. After the addition of 20 mL solvent mixture, press start and enter all requested sample data. Titrate with c(TEGOtrant) = 0.005 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

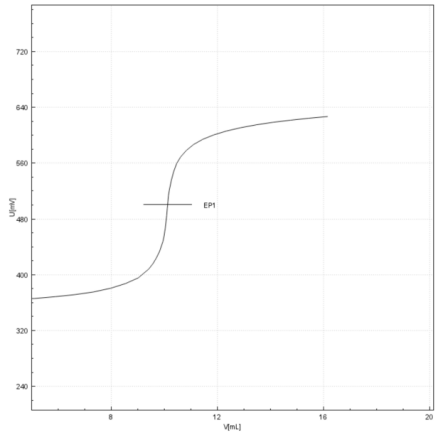
$$t_{TEGO} = \frac{V_{SDS}}{V_{EP1}}$$

T_{TEGO}: titer of TEGOtrant solution

V_{SDS}: volume sodium lauryl sulfate solution added; here 10 mL

V_{EP1}: consumption of titrant up to the first equivalence point in mL

Example curve



Results

Mean value (n = 3)	0.9892
s(abs)	0.0010
s(rel)	0.10%

Comments

- The Surfactrode Refill is stored dry when not in use.
- The active part of the electrode can be renewed with the Surfactrode refill paste 6.2319.000 and the Filling tool 6.2826.010. This guarantees almost unlimited lifetime.
- Use the first titration of a titration series for conditioning the electrode and discard the result.
- Surfactants tend to adhere to the wall of the glass and the tubes. It is therefore necessary to condition the system overnight. Before the first titration, discard the solution that is used for conditioning by using the “PREP” function of the device.

10. General – Titer determination of c(SDS) = 0.005 mol/L

Summary

The titer has to be determined frequently to assure that the concentration of the solution remains the same or at least to know the exact concentration of the used titrant. In case of the surfactant titer determination, the cationic surfactant is used as standard for the anionic titer determination and the other way round. Therefore, it is recommended to buy at least the standard solution from a supplier where the concentration is certified.

Adsorbing material	Cotton
Frequency of titer determination	Weekly to monthly
Material of storage bottle	No special recommendations

Solutions

Titrant c(SDS) = 0.005 mol/L	Dry approx. 2 g SDS at 105°C overnight and allow to cool down in a desiccator. Afterwards weigh 1.4535 g SDS into a 1 L volumetric flask and dissolve it in about 150 mL deionized water. Add 10 mL w(formaldehyde) = 35% and fill the solution up to the mark with deionized water.
TEGOadd	Metrohm 6.2317.120
c(NaOH) = 0.5 mol/L	Weigh 20 g NaOH pellets into a 1 L volumetric flask containing already 500 mL deionized water and dissolve the NaOH. After cooling down, make the solution up to the mark with deionized water.
Solvent mixture Methyl isobutyl ketone : ethanol (1:1 (v:v))	Transfer 500 mL MIBK and 500 mL Ethanol into a glass bottle and mix thoroughly.

Standard solution

c(Hyamine 1622) = 0.005 mol/L	Should be bought from a supplier

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Surfactrode Refill	6.0507.140
LL ISE Reference electrode	6.0750.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_10*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***SDS_0.005*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Surf Refill*** to the sensor list under *System* → *Sensors*.
5. Prepare the sample solution as defined under ***Analysis.***

Analysis

Fill the cylinder unit on the evening before the first titration. On the next day, carry out a "PREP" before the first titration.

Pipette 10 mL c(Hyamine 1622) = 0.005 mol/L into a 100 mL beaker and add 50 mL deionized water as well as 0.2 mL TEGOadd. Adjust the pH of the mixture with c(NaOH) = 0.5 mol/L to pH 10. After the addition of 20 mL solvent mixture, press start and enter all requested sample data. Titrate with c(SDS) = 0.005 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

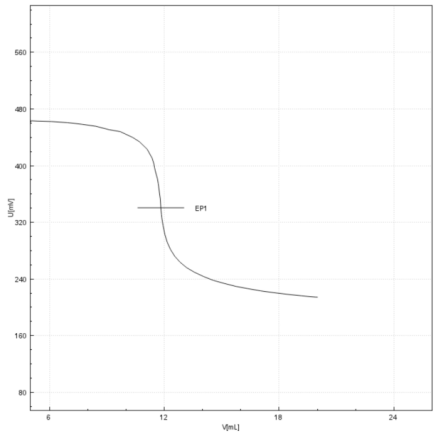
$$t_{SDS} = \frac{V_{Hyamine}}{V_{EP1}}$$

t_{SDS}: titer of SDS solution

$V_{Hyamine}$: volume hyamine solution added; here 10 mL

V_{EP1}: consumption of titrant up to the first equivalence point in mL

Example curve



Results

Mean value (n = 3)	0.8443
s(abs)	0.0034
s(rel)	0.40%

Comments

- Store the Surfactrode Refill dry when not in use.
- The active part of the electrode can be renewed with the Surfactrode refill paste 6.2319.000 and the Filling tool 6.2826.010. This guarantees almost unlimited lifetime.
- Use the first titration of a titration series for conditioning the electrode and discard the result.
- Surfactants tend to adhere to the wall of the glass and the tubes. It is therefore necessary to condition the system overnight. Before the first titration, discard the solution that is used for conditioning by using the "PREP" function of the device.

TEGOadd was developed in particular for surfactant titrations using the Solvotrode Resistant electrode. This additive has a positive influence on the whole course of titration, especially in the region of inflection and keeps the electrode clean.

11. General – Calibration factor of c(STPB) = 0.01 mol/L

Summary

The content calculation cannot be done directly because the non-ionic (NIO) surfactants are non-uniform substances and the precipitation with sodium tetraphenylborate (STPB) is not strictly stoichiometric. As with other analytical methods (e.g., HPLC) a calibration factor (f) has to be determined first. This is done either using the NIO surfactant which has to be determined or a NIO surfactant that has been defined as a standard (e.g. Triton X-100).

Adsorbing material	Cotton
Frequency of titer determination	Weekly to monthly
Material of storage bottle	No special recommendations

Solutions

Buffer pH 10	Weigh 1.24 g H_3BO_3 into a 100 mL flask and add 10 mL c(NaOH) = 1 mol/L. Fill the solution up to the mark with deionized water.
Titrant c(STPB) = 0.01 mol/L	Weigh 3.4223 g sodium tetraphenylborate (STPB) into a beaker and dissolve in about 300 mL deionized water. In a second beaker, dissolve 10 g polyvinyl alcohol (PVA) under heating in 300 mL deionized water. Allow PVA solution to cool down Afterwards transfer both solutions into a 1 L volumetric flask and add 10 mL buffer pH 10. Mix the solution well and fill up to the mark with deionized water.
Auxiliary solution c($BaCl_2$) = 0.1 mol/L	Transfer 21 g $BaCl_2$ into a 1 L volumetric flask, dissolve in deionized water and fill up to the mark with deionized water.

Standard solution

β(Triton X-100) = 1 g/L	Dissolve 100 mg Triton X-100 in about 80 mL deionized water and fill up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

NIO surfactant electrode	6.0507.010
LL ISE Reference electrode	6.0750.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_11*** from the USB Stick under *System → File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***STPB_0.01*** to the *solution list* under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***NIO Surf*** to the sensor list under *System → Sensors*.
5. Prepare the sample solution as defined under ***Analysis***

Analysis

Fill the cylinder unit on the evening before the first titration. On the next day, carry out a "PREP" before the first titration. Pipette 20 mL β(Triton X-100) = 1 g/L into a 150 mL beaker and add 60 mL deionized water as well as 10 mL c($BaCl_2$) = 0.1 mol/L. Press the start button, enter all requested sample data and titration with c(STPB) = 0.01 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

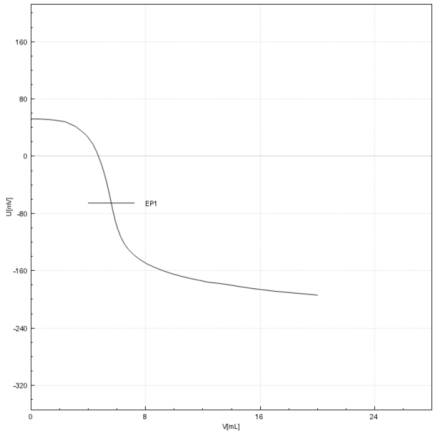
$$f_{STPB} = \frac{V_{Triton\ X-100}}{V_{EP1}}$$

f_{STPB}: factor of STPB solution

$V_{Triton\ X-100}$: volume Triton X-100 solution added; here 20 mL

V_{EP1}: consumption of titrant up to the first equivalence point in mL

Example curve



Results

Mean value (n = 3)	3.5740
s(abs)	0.0113
s(rel)	0.32%

Comments

- Store the NIO Surfactant electrode dry when not in use.
- After each 2 – 3 titrations, clean the electrode with a tissue moistened with methanol.
- Use the first 2 – 3 titrations of a titration series for conditioning the electrode and discard the results.
- If the electrode is used frequently, store the electrode in a 1% aqueous solution of PEG 1000. Conditioning the electrode is then no longer necessary.
- Barium is toxic and its waste has to be disposed according to your local regulations.

12. General – Titer determination of c(KBr) = 0.1 mol/L

Summary

Any halogenoid can be used for the determination of silver salts as all of them form precipitations. Bromide is very suitable as the solubility constant is very low and therefore the analysis can be carried out very accurate. Make sure that the solution is stored away from UV light as otherwise bromine will be formed which will cause too high results.

Adsorbing material	Cotton
Frequency of titer determination	Weekly to monthly
Material of storage bottle	Brown glass bottle

Solutions

Titrant c(KBr) = 0.1 mol/L	Weigh 11.901 g dried KBr into a 1 L volumetric flask and dissolve in distilled water. Then, fill the flask up to the mark with distilled water.
$c(HNO_3)$ = 33%	Transfer 508 g $c(HNO_3)$ = 65% into a 1 L volumetric flask already containing 300 mL distilled water. After cooling down, fill the solution up to the mark with distilled water.

Standard substance

Fine silver with purity >99.99%

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Ag Titrode with AgBr coating	6.00430.100Br

Sample preparation

Weigh 300 – 500 mg fine silver into a beaker and add 5 mL $w(HNO_3)$ = 33%. Heat the suspension slowly until no nitrous gases are formed anymore.

System configuration

1. Load the method ***Method_12*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***KBr_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Ag Titrode*** to the sensor list under *System* → *Sensors*.
5. Prepare the sample solution as defined under Analysis

Analysis

After cooling down, add deionized water to the prepared sample solution until the electrode is immersed. Press the start button, enter all requested sample data and titrate with c(KBr) = 0.1 mol/L until after the equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$t_{KBr} = \frac{m_{Sample}}{c_{KBr} \cdot V_{EP1} \cdot M_{Ag}}$$

t_{KBr}: titer of potassium bromide solution

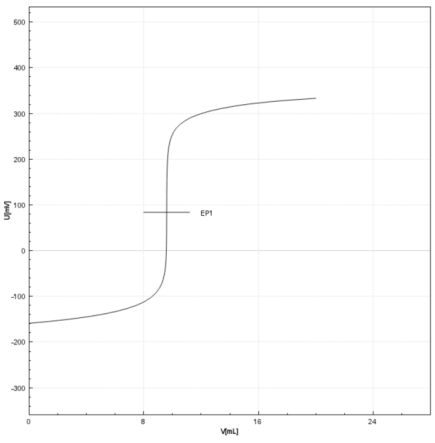
m_{Sample}: sample size of fine silver in mg

c_{KBr}: concentration of potassium bromide solution; here 0.1 mol/L

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

M_{Ag}: molar mass of silver; 107.87 g/mol

Example curve



Results

Mean value (n = 3)	0.9999
s(abs)	0.0024
s(rel)	0.24%

Comments

- The Ag Titrode is stored in deionized water to keep the glass membrane ready for use.
- The titer determination mentioned here is carried out according to EN ISO 11427.
- The titer can also be determined by buying a silver nitrate solution of known concentration or using silver nitrate in its solid form.

13. Food – Calcium and Magnesium in Water

Summary

Calcium and magnesium are essential elements for the human body to build up bones and for organ functions. Furthermore, these ions are mainly responsible for calcification. As water is a very important source for these ions, their determination in water is explained in this method.

Solutions

Titrant c(Na_2EDTA) = 0.1 mol/L	Should be bought from a supplier
Auxiliary complexing solution c(Acetylaceton) = 0.1 mol/L + c(TRIS) = 0.2 mol/L	Weigh 20.4 g TRIS into a 1 L volumetric flask and dissolve in approx. 500 mL deionized water. Add 12 mL acetylacetone and fill the solution up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Combined polymer membrane electrode, Ca	6.0510.100

Sample preparation

No sample preparation is required

System configuration

1. Load the method ***Method_13*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***EDTA_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Ca-ISE*** to the sensor list under *System* → *Sensors*.
5. Prepare the sample solution as defined under ***Analysis.***

Analysis

Pipette 100 mL sample into a 150 mL beaker and add 15 mL auxiliary solution. Press the start button, enter all requested sample data and titrate with c(Na_2EDTA) = 0.1 mol/L until after the second equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$\beta(Ca^{2+}) = \frac{V_{EP1} \cdot t_{EDTA} \cdot c_{EDTA} \cdot M(Ca^{2+}) \cdot 1000}{V_{Sample}}$$

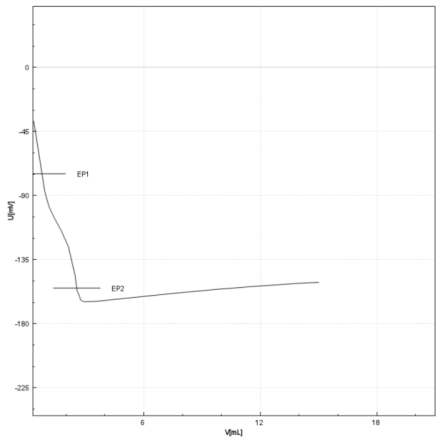
$\beta(Ca^{2+})$: concentration of calcium in mg/L
V_{EP1}: consumption of titrant up to the first equivalence point in mL
t_{EDTA}: titer of EDTA solution
c_{EDTA}: concentration of EDTA solution; here: 0.1 mol/L
$M(Ca^{2+})$: molar mass of calcium; 40.08 g/mol
1000: conversion factor from g/L to mg/L
V_{Sample}: volume of sample in mL

$$\beta(Mg^{2+}) = \frac{(V_{EP2} - V_{EP1}) \cdot t_{EDTA} \cdot c_{EDTA} \cdot M(Ca^{2+}) \cdot 1000}{V_{Sample}}$$

$\beta(Mg^{2+})$: concentration of magnesium in mg/L
V_{EP2}: consumption of titrant up to the second equivalence point in mL
V_{EP1}: consumption of titrant up to the first equivalence point in mL
t_{EDTA}: titer of EDTA solution
c_{EDTA}: concentration of EDTA solution; here: 0.1 mol/L
$M(Mg^{2+})$: molar mass of magnesium; 24.31 g/mol
1000: conversion factor from g/L to mg/L
V_{Sample}: volume of sample in mL

Example curves

Water



Results

Calcium

Mean value (n = 3)	30.48 mg/L
s(abs)	0.35 mg/L
s(rel)	1.13%

Magnesium

Mean value (n = 3)	43.19 mg/L
s(abs)	0.66 mg/L
s(rel)	1.53%

Comments

- Determine the titer according to ***Method_1.***
- The titration has to be carried out under alkaline conditions as otherwise the complex formation constants will be too low.
- Acetylacetone complexes magnesium and leads to a shift in complex formation constant. This results in a possible differentiation of calcium and magnesium in one titration.
- The auxiliary solution must not be stored for longer than 1 week as it is not stable. If the solution is stored for a longer time, the separation of magnesium and calcium is no longer possible.
- Store the electrode dry if not in use with some residual moisture (e.g., some drops of deionized water) in the electrode storage vessel. It is not necessary to condition the electrode before use.

14. Food – Calcium in Milk

Summary

Calcium is an essential element for the body as it is e.g., necessary for the stability of bones. Dairy products contain a lot of calcium, which needs to be assessed for declaration. This method describes a way to determine the calcium content in milk by complexometric titration using the Cu-ISE.

Solutions

Titrant c(EGTA) = 0.1 mol/L	Dissolve 38.04 g EGTA in 250 mL c(NaOH) = 1 mol/L, transfer it into a 1 L volumetric flask and fill up to the mark with deionized water.
Auxiliary solution c(CuEGTA) = 0.05 mol/L	Weigh 2.2 g NH_4Cl and 3.751 g $Cu(NO_3)_2$ into a 1 L volumetric flask, dissolve it and fill up to the mark with deionized water. Mix 50 mL of this solution with 50 mL c(EGTA) = 0.1 mol/L.
Buffer pH 10	Transfer 54 g NH_4Cl and 350 mL $w(NH_3)$ = 25% into a 1 L volumetric flask, dissolve it and fill up to the mark with deionized water.
c(NaOH) = 0.1 mol/L	Weigh 40 g NaOH into a 1 L volumetric flask, dissolve it and fill up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Ion selective electrode, Cu	6.0502.140
LL ISE reference electrode	6.0750.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_14*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***EGTA_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Cu-ISE*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as defined under ***Analysis***

Analysis

Titer determination

Determine the titer the same way as mentioned under General – Titer determination of $c(Na_2EDTA)$ = 0.1 mol/L (page 4). The following changes in the procedure have to be considered:

- Use the electrodes mentioned in this section for the indication.
- Add 1 mL c(CuEGTA) = 0.05 mol/L to the sample solution before the titration start.
- After the addition of the c(CuEGTA) = 0.05 mol/L, allow the solution to react for 30 s before starting the titration

Analysis

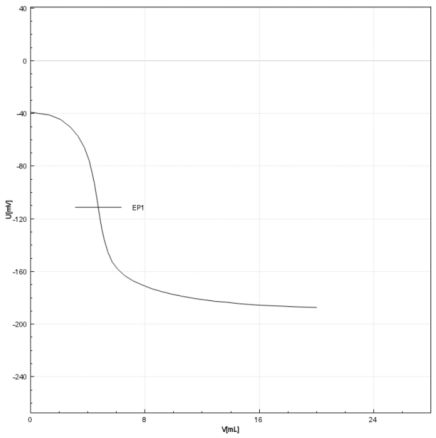
Weigh approx. 10 g sample into a 150 mL beaker and dilute with 90 mL deionized water. Afterwards, add 1 mL c(CuEGTA) = 0.05 mol/L and allow the solution to react for 30 s. After the addition of 5 mL of buffer pH 10, press the start button and enter all requested sample data. Titrate with c(EGTA) = 0.1 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$w(Ca^{2+}) = \frac{V_{EP1} \cdot t_{EGTA} \cdot c_{EGTA} \cdot M(Ca^{2+})}{m_{Sample} \cdot 10}$$

$w(Ca^{2+})$:	concentration of calcium in %
V_{EP1}:	consumption of titrant up to the first equivalence point in mL
t_{EGTA}:	titer of EGTA solution
c_{EGTA}:	concentration of EGTA solution; here: 0.1 mol/L
$M(Ca^{2+})$:	molar mass of calcium; 40.08 g/mol
m_{Sample}:	volume of sample in mL
10:	conversion factor to %

Example curve



Results

Mean value (n = 3)	1.800%
s(abs)	0.017%
s(rel)	0.96%

Comments

- Both EGTA and EDTA form complexes with calcium, but EGTA is selective for calcium only. EDTA also forms complexes with magnesium.
- If magnesium and calcium have to be determined, use EDTA as titrant in a second titration. Calculate the magnesium content from the difference between the first and second titration.
- Store the Cu-ISE dry if not in use. Polish the Cu-ISE with the polishing set for solid-state electrodes 6.2802.000 if deposits are observed on the crystal membrane surface.

15. Food – pH and Alkalinity in Water

Summary

Alkalinity is a measure for the puffer capacity of water. Should water be too acidic, it can promote corrosion. Additionally the alkalinity is used to describe temporary hardness which consists of $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$.

Solution

Titrant c(HCl) = 0.1 mol/L	Should be bought from a supplier.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Aquatrode plus with Pt1000	6.0257.600

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_15*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***HCl_0.1*** to the *solution list* under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Aquatrode*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as defined under ***Analysis.***

Analysis

Calibrate the Aquatrode Plus before measurement and titration. For this purpose, we propose a 3-point calibration with buffers pH 4, 7 and 9.

For the titration, pipette 100 mL water sample into a 150 mL beaker, press start and enter all requested sample data. Titrate with c(HCl) = 0.1 mol/L until pH 3.5 is reached. All other parameters and calculations are already defined within the method.

Calculation

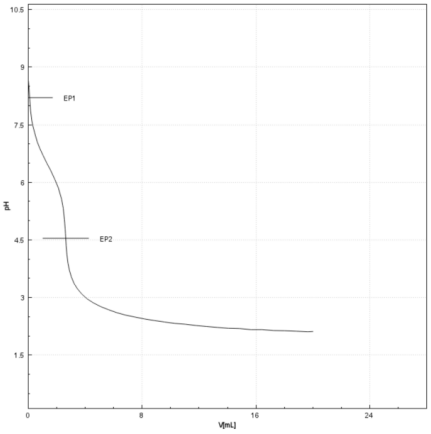
$$K_{A,\,8.2} = \frac{V_{FP,\,8.2} \cdot c_{HCl} \cdot t_{HCl}}{V_{Sample}}$$

$K_{A,\,8.2}$: acid capacity in mmol/L up to pH 8.2
$V_{FP,\,8.2}$: consumption of titrant up to pH 8.2 in mL
c_{HCl}: concentration of HCl solution; here: 0.1 mol/L
t_{HCl}: titer of HCl solution
V_{Sample}: volume of sample in L; here 0.1 L

$$K_{A,\,4.3} = \frac{V_{FP,\,4.3} \cdot c_{HCl} \cdot t_{HCl}}{V_{Sample}}$$

$K_{A,\,4.3}$: acid capacity in mmol/L up to pH 4.3
$V_{FP,\,4.3}$: consumption of titrant up to pH 4.3 in mL
c_{HCl}: concentration of HCl solution; here: 0.1 mol/L
t_{HCl}: titer of HCl solution
V_{Sample}: volume of sample in L; here 0.1 L

Example curve



Results

$K_{A,\ 8.2}$

Mean value (n = 3)	0.089 mmol/L
s(abs)	0.005 mmol/L
s(rel)	5.50%

$K_{A,\ 4.3}$

Mean value (n = 3)	2.650 mmol/L
s(abs)	0.016 mmol/L
s(rel)	0.62%

Start pH value

Mean value (n = 3)	8.50
s(abs)	0.16
s(rel)	1.89%

Comments

- Store the Aquatrode plus in storage solution. This ensures that the electrode will not get slower in response.
- The endpoint at pH 8.2 is not obtained with every water. Some water have a lower pH value and only the endpoint at 4.3 is obtained.
- The endpoint at pH 8.2 is also called p-value (phenolphthaleine value) and the endpoint at 4.3 is called m-value (methylorange value).
- The titration can also be carried out by using a SET titration with one end point at pH 8.2 and the other at pH 4.3.
- It is recommended to use the Aquatrode Plus for this titration because this electrode has specially been designed for ion-deficient matrices.
- Determine the titer according to ***Method_3***.

16. Food – pH and Acidity in Milk and Juices

Summary

The pH value and the acidity are very important parameters to determine in the food industry. The pH value has a huge impact on sterilization processes, conservation and thus on the shelf life of a product. Therefore, these parameters are determined frequently in dairy products, juices and other food.

Solutions

Titrant c(NaOH) = 0.1 mol/L	Should be bought from a supplier.
Titrant c(NaOH) = 0.25 mol/L	Should be bought from a supplier.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Milk

Porotrode	6.0235.200
Pt1000 Temperature sensor	6.1110.100

Juices

Unitrode with Pt1000	6.0258.600

Sample preparation

No sample preparation is required.

System configuration

Milk

1. Load the method ***Method_16.1*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***NaOH_0.25*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Porotrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as defined under ***Analysis Milk.***

Juices

1. Load the method ***Method_16.2*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***NaOH_0.1*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Unitrode*** to the sensor list under *System* → *Sensors.*
5. Adjust the calculations depending on the acid as which the result should be expressed (adjustment of M(acid)). The molecular weight of citric acid is predefined in the method.
6. Prepare the sample solution as defined under ***Analysis Juices.***

Analysis

Milk

Calibrate the Porotrode before measurement and titration. For this purpose, we suggest a 3-point calibration with buffers pH 4, 7 and 9.

For the titration, pipette 25 mL milk into a 50 mL beaker. Immerse the electrode into the solution, press start and enter all requested sample data. The SET titration is started with c(NaOH) = 0.25 mol/L until pH 8.3 is reached and the pH is automatically recorded from the start of titration. All other parameters and calculations are already defined within the method.

Juices

Calibrate the Unitrode before measurement and titration. For this purpose, we propose a 3-point calibration with buffers pH 4, 7 and 9.

or titration, pipette 10 mL juice and 40 mL deionized water into a 100 mL beaker. Immerse the electrode into the solution, press start and enter all requested sample data. The SET titration is started with c(NaOH) = 0.1 mol/L until pH 8.5 is reached and the pH is automatically recorded from the start of titration. All other parameters and calculations are already defined within the method.

Calculation

Milk

$$\text{Acidity} = \frac{V_{EP,\,8.3} \cdot 100 \cdot t_{NaOH}}{m_{sample}}$$

Acidity: degree of acidity, expressed as consumption of c(NaOH) = 0.25 mol/L per 100 g sample.

$V_{EP,\,8.3}$: consumption of titrant up to pH 8.3 in mL

100: conversion factor for 100 g
t_{NaOH}: titer of NaOH solution
m_{Sample}: sample size in g; here 25 g

Juices

Depending on the juice, the titratable acid content is expressed as different acids:

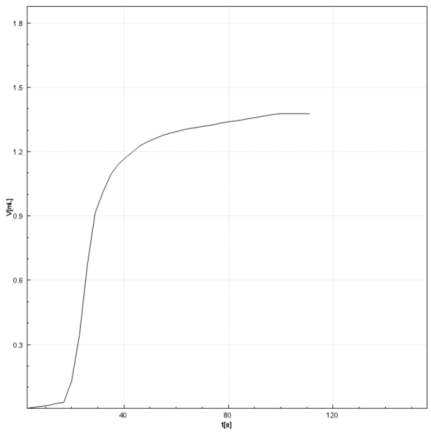
Grape juice:	tartartic acid
Apple juice:	malic acid
Pear juice:	malic acid
Stone fruit juice:	malic acid
Berries fruit juice:	citric acid
Citrus fruit juice:	citric acid

$$\beta_{Acidity} = \frac{V_{EP,\,8.5} \cdot c_{NaOH} \cdot t_{NaOH} \cdot M(acid)}{V_{sample} \cdot z^*}$$

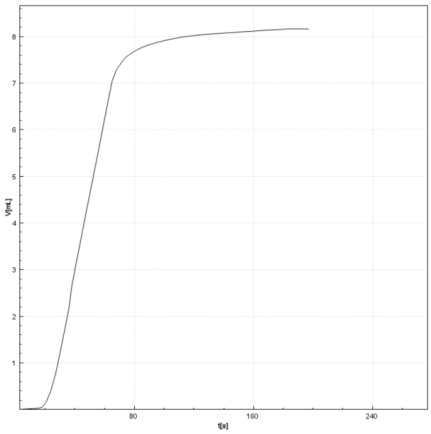
$\beta_{Acidity}$: mass concentration of acid in sample in g/L
$V_{EP,\,8.5}$: consumption of titrant up to pH 8.5 in mL
c_{NaOH}: concentration of NaOH solution; here 0.1 mol/L
t_{NaOH}: titer of NaOH solution
M(acid): tartaric acid: 150.08 g/mol
malic acid: 134.09 g/mol
citric acid: 192.12 g/mol
V_{Sample}: volume of sample in mL; here 10 mL
z^*: tartaric acid: 2
malic acid: 2
citric acid: 3

Example curve

Milk



Juices



Results

Milk

Mean value (n = 3)	13.478 g/L
s(abs)	0.167 g/L
s(rel)	1.24%

Juices

Mean value (n = 3)	4.870 g/L
s(abs)	0.022 g/L
s(rel)	0.44%

Comments

General

- Place the titration buret in such a way that the titrant is reaching the electrode as fast as possible to avoid any overtitration.
- Determine the titer according to ***Method_2***.

Juices

- Store the Unitrode in storage solution to ensure a fast response time.

Milk

- The diaphragm of the Porotrode consists of a double capillary and is therefore well suited for samples containing a high amount of proteins.
- Porolyte must be used as reference electrolyte.
- Store the Porotrode in Porolyte if not in use.
- As an accurate pH value has to be determined the temperature has to be measured as well.
- Carry out the titration as fast as possible because otherwise, the proteins are hydrolyzed and a higher acidity is obtained.

17. Food – Chloride in Water, Milk and Juices

Summary

Chloride is an essential mineral for the human body. It is one of several electrolytes and necessary for maintaining the fluid balance and with it homeostasis. Furthermore, it helps to keep a decent blood pressure. However, a too high intake can lead to diseases like high blood pressure and therefore the chloride content has to be declared for most food. This section is dedicated to its analysis in different food.

Solutions

$c(AgNO_3)$ = 0.01 mol/L	Pipette 100 mL $c(AgNO_3)$ = 0.1 mol/L into a 1 L volumetric flask and fill it up to the mark with deionized water.
$c(HNO_3)$ = 2 mol/L	Weigh 194 g $c(HNO_3)$ = 65% into a 1 L volumetric flask and fill it up to the mark with deionized water.
c(NaOH) = 2 mol/L	Weigh 80 g NaOH into a 1 L volumetric flask, dissolve it and fill the flask up to the mark with deionized water.
$w(Al_2(SO_4)_3)$ = 20%	Transfer 200 g $Al_2(SO_4)_3$ into a 1 L volumetric flask, dissolve it and fill the flask up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.210

Sensors

Ag Titrode with Ag_2S coating	6.00430.100S

Sample preparation

Juice and water do not require sample preparation.

Milk

Pipette 20 mL milk, approx. 150 mL deionized water and 5 mL c(NaOH) = 2 mol/L into a 200 mL volumetric flask and mix well. Afterwards, add 10 mL $w(Al_2(SO_4)_3)$ = 20% and fill the flask up to the mark with deionized water. Allow the suspension to settle and then filter it.

System configuration

1. Load the method ***Method_17*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***AgNO3_0.01*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Ag Titrode*** to the sensor list under *System* → *Sensors*.
5. Prepare the sample solution as defined under ***Analysis Water, Analysis Milk or Analysis Juice,*** respectively.

Analysis

Water

Pipette 100 mL water into a 150 mL beaker and add 2 mL $c(HNO_3)$ = 2 mol/L. Press start and enter all required sample data and carry out the titration with $c(AgNO_3)$ = 0.01 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Milk

Pipette 25 mL of the prepared sample into a 150 mL beaker and add 2 mL $c(HNO_3)$ = 2 mol/L. Press start and enter all required sample data and carry out the titration with $c(AgNO_3)$ = 0.01 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Juice

Pipette 25 mL into a 150 mL beaker and add 2 mL $c(HNO_3)$ = 2 mol/L. Press start and enter all required sample data and carry out the titration with $c(AgNO_3)$ = 0.01 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

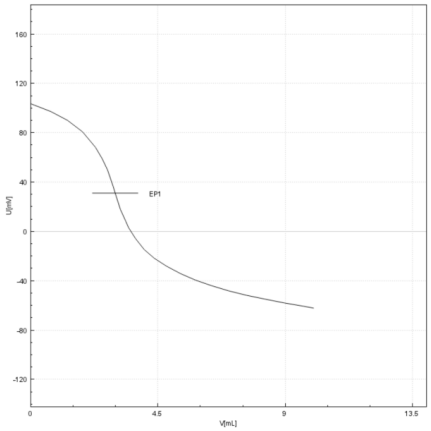
Calculation

$$\beta_{Cl} = \frac{V_{EP1} \cdot c_{AgNO3} \cdot t_{AgNO3} \cdot M_{Cl} \cdot 1000}{V_{sample}}$$

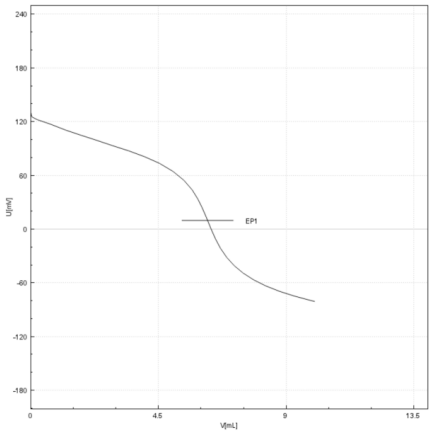
β_{Cl}: mass concentration of chloride in mg/L
V_{EP1}: consumption of titrant up to the first equivalence point in mL
c_{AgNO3}: concentration of silver nitrate in mol/L; here 0.01 mol/L
t_{AgNO3}: titer of silver nitrate solution
M_{Cl}: molar mass of chloride; 35.45 g/mol
1000: conversion factor from g/L to mg/L
V_{Sample}: sample size in mL; here 100 mL for water, 25 mL for juices and 2.5 mL for milk

Example curve

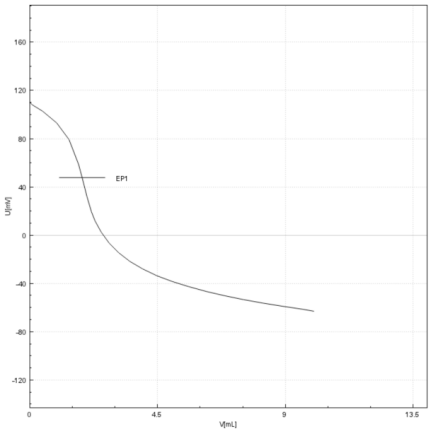
Water



Milk



Juice



Results

Water

Mean value (n = 3)	10.58 mg/L
s(abs)	0.005 mg/L
s(rel)	0.04%

Milk

Mean value (n = 3)	771.04 mg/L
s(abs)	1.47 mg/L
s(rel)	0.19%

Juice

Mean value (n = 3)	21.53 mg/L
s(abs)	0.46 mg/L
s(rel)	2.14%

Comments

- Store the Ag Titrode in deionized water if not in use. This ensures that the hydrated layer of the glass membrane remains intact and the electrode is ready to use without preparation.
- Do not clean the silver ring with abrasives if a coating is present on the silver ring because otherwise the coating might be damaged.
- The sulfide coating increases the sensitivity of the electrode and should be used when low chloride concentrations, like in water, have to be determined.
- With a sample size of 2.5 mL the dilution factor of 10 for milk is already taken into account.
- If the calculation should be done for NaCl the molar mass has of M(Cl) has to be exchanged for M(NaCl) = 58.44 g/mol.
- Determine the titer according to ***Method_5***.

18. Food – Vitamin C in Orange Juice

Summary

Ascorbic acid, known as vitamin C, belongs to the essential water-soluble vitamins. Therefore, it is only stored in limited amount in the human body and needs to be taken up by nutrition. Vitamin C is important as antioxidant, for the immune system and the nervous system. Therefore, it is often declared on food and thus the determination of its content is necessary.

Solutions

$c(I_2)$ = 0.05mol/L	Should be bought from a supplier
Titrant $c(I_2)$ = 0.01 mol/L	Transfer 200 mL $c(I_2)$ = 0.05mol/L into a 1 L volumetric flask and fill it up to the mark with deionized water.
w(glyoxal) = 40%	Adjust the pH of 200 mL w(glyoxal) = 40% with c(NaOH) = 1 mol/L to pH 7.
$w(H_2SO_4)$ = 25%	Transfer 255 g $w(H_2SO_4)$ = 98% into a 1 L volumetric flask, already containing 400 mL deionized water. After cooling down the solution, fill the flask up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Double Pt sheet electrode	6.0309.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_18*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***I2_0.01*** to the *solution list* under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Pt Sheet*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as defined under ***Analysis.***

Analysis

Pipette 50 mL orange juice into a 100 mL beaker and add 2 mL w(glyoxal) = 40%. Stir the solution for 5 min. Afterwards, add 5 mL $w(H_2SO_4)$ = 25%, press the start button and enter all requested sample data. Titrate with $c(I_2)$ = 0.01 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$\beta_{AA} = \frac{V_{EP1} \cdot c_{I2} \cdot t_{I2} \cdot M_{AA} \cdot 1000}{V_{Sample}}$$

β_{AA}: ascorbic acid content in mg/L

V_{EP1}: consumption of titrant up to first equivalence point in mL

c_{I2}: concentration of iodine solution; here: 0.01 mol/L

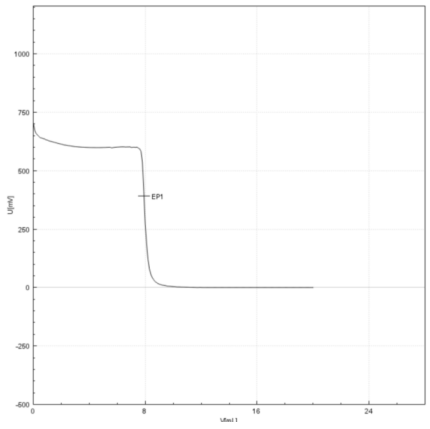
t_{I2}: titer of iodine solution

M_{AA}: molecular weight of ascorbic acid; 176.12 g/mol

1000: conversion factor to mg

V_{Sample}: volume of sample in mL; here 50 mL

Example curve



Results

Mean value (n = 3)	389.42 mg/L
s(abs)	3.23 mg/L
s(rel)	0.83%

Comments

- The platinum of new double Pt sheet electrodes might be passivated so that poor or no signal change at the equivalence point is observed. In such cases, 2 – 3 titrations with iodine can regenerate the platinum.
- Store the electrode dry when not in use.
- Connect the electrode to the «Pol» connection of the Eco titrator.
- Glyoxal is added to react with sulfite (SO2) to form the addition compound aldehyde disulfite. This compound cannot be determined titrimetrically. With this method not only Vitamin C is determined but also other reductants present in juice.
- Determine the titer according to ***Method_4***.

19. Food – Peroxide value (PV) of edible fats and oils

Summary

The peroxide value is a measure for the amount of hydroperoxide functional groups present in oils and can be used to assess the rancidity of oils.

Solutions

$c(Na_2S_2O_3)$ = 0.1mol/L	Should be bought from a supplier.
Titrant $c(Na_2S_2O_3)$ = 0.01 mol/L	Transfer 100 mL $c(Na_2S_2O_3)$ = 0.1mol/L into a 1 L volumetric flask and fill it up to the mark with deionized water.
KI sat.	Weigh approx. 130 g KI into an amber glass bottle and add 100 mL deionized water. Protect the solution against light.
Solvent Glacial acetic acid : 1-decanol (3:2), containing 15 mg iodine	Dissolve approx. 15 mg iodine in 200 mL 1-decanol and add 300 mL glacial acetic solution. Mix the solution well.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.210

Sensors

Pt Titrode	6.0431.100

Sample preparation

No sample preparation is required.

System configuration

Blank

1. Load the method ***Method_19.1*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***Na2S2O3_0.01*** to the *solution list* under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Pt Titrode*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as defined under ***Analysis Blank.***

Sample

6. Load the method ***Method_19.2*** from the USB Stick under *System → File management.*
7. Load the corresponding method in the home screen.
8. Add the solution ***Na2S2O3_0.01*** to the *solution list* under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
9. Add the electrode ***Pt Titrode*** to the sensor list under *System → Sensors.*
10. Prepare the sample solution as defined under ***Analysis Sample.***

Analysis

Blank

Pipette 10 mL solvent into a 100 mL titration beaker and add 0.2 mL KI = sat.. Mix the solution thoroughly and place it in the dark for 1 min. After the addition of 50 mL deionized water press start and enter all requested sample data. Titrate the solution with $c(Na_2S_2O_3)$ = 0.01 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method. The mean value of the blank is automatically saved as common variable CV01.

Sample

Depending on the expected peroxide number, weigh 5 or 10 g sample into a 100 mL beaker and dissolve it in 10 mL solvent. After dissolution, add 0.2 mL KI = sat. mix the solution thoroughly and allow to react for 1 min in the dark. After that, add 50 mL deionized water, press start and enter all requested sample data. Titrate the solution using $c(Na_2S_2O_3)$ = 0.01 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$PV = \frac{(V_{EP1} - CV01) \cdot t_{Na2S2O3} \cdot 10}{m_{Sample}}$$

PV: peroxide value in meq O2 / kg

V_{EP1}: consumption of titrant up to first equivalence point in mL

CV01: blank value in mL

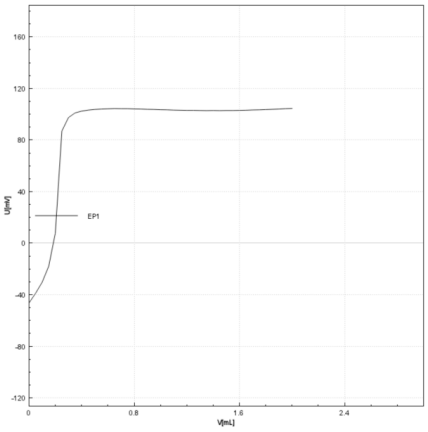
t_{Na2SO3}: titer of sodium thiosulfate solution

m_{Sample}: mass of sample in g

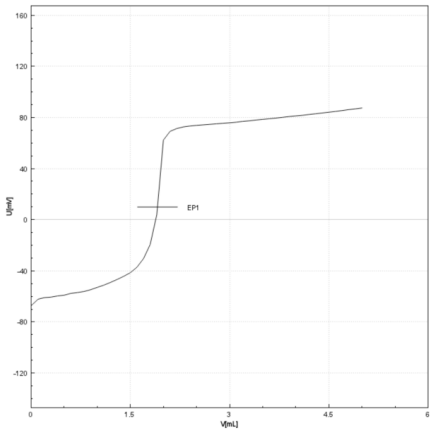
10: conversion factor from mol/L to mmol/L

Example curve

Blank



Sample



Comments

- Store the Pt Titrode in deionized water if not in use. This keeps the hydration layer of the glass membrane intact and the electrode ready to use.
- Store the KI sat. solution in a brown glass bottle and protect it from light as otherwise iodine is generated.
- Determine the titer according to ***Method_6***.
- The blank value of the pure solvent is very small. To obtain a better recognition and reproducibility of the blank value a small amount of iodine is added to the solvent. However, this entails that for the blank and the sample analysis the same amount of solvent is used.
- As the peroxide value depends on the sample size the ISO/TC 34/SC 11 has decided to fix the sample size to 5 g for PV greater than 1, and at 10 g for PV less than or equal to 1.

Results

Blank

Mean value (n = 3)	0.2078 mL
s(abs)	0.0023 mL
s(rel)	1.11%

Peroxide value

Mean value (n = 3)	1.743 meq O_2/kg
s(abs)	0.012 meq O_2/kg
s(rel)	0.72%

20. Food – Saponification number of edible fats and oils

Summary

The saponification number is used to estimate the molecular weight of the fatty acid present in the oil. The higher the saponification number the lower the molecular weight of the fatty acids.

Solutions

Titrant c(HCl) = 0.5 mol/L	Should be bought from a supplier.
Reaction solution c(KOH) = 0.5 mol/L in ethanol	Should be bought from a supplier.
Ethanol abs.	Should be bought from a supplier.

Cylinder unit

Eco Cylinder unit 50 mL	6.03002.250

Sensors

Solvotrode easyClean	6.0229.010

Sample preparation

No sample preparation is required.

System configuration

Blank

1. Load the method ***Method_20.1*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***HCl_0.5*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Solvotrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as defined under ***Analysis Blank.***

Sample

1. Load the method ***Method_20.2*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***HCl_0.5*** to the *solution list* under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Solvotrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as defined under ***Analysis Sample.***

Analysis

Blank

Pipette 25 mL c(KOH) = 0.5 mol/L in ethanol into a 100 mL Erlenmeyer flask and add a stirring bar. Attach a reflux condenser and reflux the solution 30 min. Allow the solution to cool down and dilute it with 50 mL ethanol. Press start, enter all requested sample data and titrate with c(HCl) = 0.5 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method. The mean value of the blank consumption is automatically saved as common variable CV01.

Sample

Pipette 0.5 up to 3 g sample as well as 25 mL c(KOH) = 0.5 mol/L in ethanol into a 100 mL Erlenmeyer flask and add a stirring bar. Attach a reflux condenser and reflux the solution for 30 min. Allow the solution to cool down and dilute it with 50 mL ethanol. Press start, enter all requested sample data and titrate with c(HCl) = 0.5 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

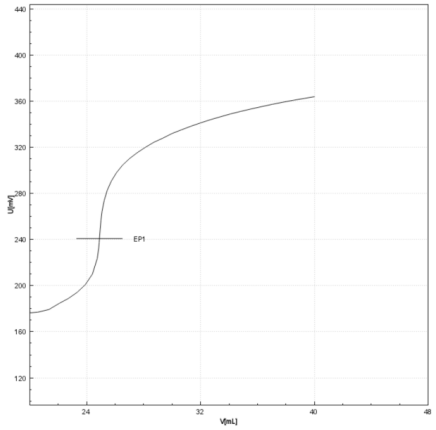
Calculation

$$SN = \frac{(CV01 - V_{EP1}) \cdot c_{HCl} \cdot t_{HCl} \cdot M_{KOH}}{m_{Sample}}$$

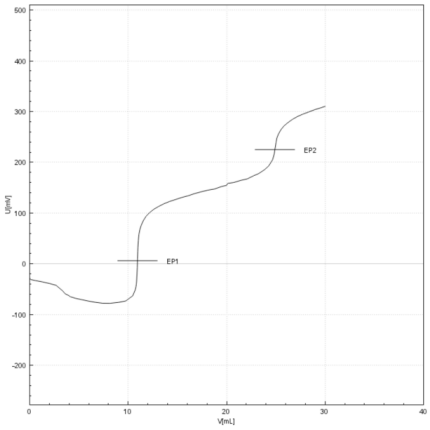
SN:	saponification number in mg KOH / g
CV01:	blank value in mL
V_{EP1}:	consumption of titrant up to first equivalence point in mL
c_{HCl}:	concentration of hydrochloric acid solution; here: 0.5 mol/L
t_{HCl}:	titer of hydrochloric acid solution
M_{KOH}:	molar mass of potassium hydroxide; 56.11 g/mol
m_{Sample}:	mass of sample in g

Example curve

Blank



Sample



Comments

- Store the Solvotrode in the corresponding reference electrolyte if not in use.
- Condition the glass membrane of the electrode (bulp) in between measurments for 1 min in deionized water.
- Make sure that the reflux time of 30 min is exactly met. Otherwise the reproducibility of your results is lower.
- The sample determination shows two equivalence points. The first corresponds to the free KOH and the second to the overall amount of base.
- Determine the titer according to ***Method_3***.

Results

Blank

Mean value (n = 3)	25.0577 mL
s(abs)	0.1807 mL
s(rel)	0.72%

Sample

Mean value (n = 3)	194.31 mg KOH/g
s(abs)	3.03 mg KOH/g
s(rel)	1.56%

21. Wine – pH and acidity

Summary

The pH value is of great importance for biological systems. In wines, it plays a larger role than the titratable total acidity. The pH influences the growth of microorganisms, the color and shade, taste, redox potential, the ratio of free to bound SO_2, the stability, the possibility of forming or preventing iron phosphate turbidity, etc. There is no direct relationship between the pH value and the content of titratable total acidity; in contrast, there is an (empirical) relationship between the pH value and the potassium hydrogen tartrate / tartaric acid ratio.

Solutions

Titrant c(NaOH) = 0.1 mol/L	Should be bought from a supplier.
Buffer solutions pH 4, 7 and 9	Metrohm 6.2307.230

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Ecotrode plus	6.0262.100
Pt1000 temperature sensor	6.1110.100

Sample preparation

The sample is degassed by using nitrogen, vacuum or by agitation.

System configuration

For CH, EU, IL, ZA and SA

1. Load the method ***Method_21.1*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***NaOH_0.1*** to the *solution list* under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Ecotrode*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as defined under ***Analysis.***

For AU and US

6. Load the method ***Method_21.2*** from the USB Stick under *System → File management.*
7. Load the corresponding method in the home screen.
8. Add the solution ***NaOH_0.1*** to the *solution list* under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
9. Add the electrode ***Ecotrode*** to the sensor list under *System → Sensors.*
10. Prepare the sample solution as defined under ***Analysis***.

Analysis

Calibrate the electrode by a 3-point calibration with buffers pH 4, 7 and 9. Afterwards, immerse the electrode in the non-degased sample and measure the pH using the manual control of the Eco Titrator.

CH, EU, IL and ZA

Pipette 10 mL degassed sample and 10 mL deionized water into a 50 mL beaker press start, enter all requested sample data and titrate with c(NaOH) = 0.1 mol/L to pH 7.0. All other parameters and calculations are already defined within the method.

SA

Pipette 20 mL degassed sample into a 50 mL beaker and press start, enter all requested sample data and titrate with c(NaOH) = 0.1 mol/L to pH 7.0. All other parameters and calculations are already defined within the method.

AU

Pipette 10 mL degassed sample and 50 mL deionized water into a 100 mL beaker press start, enter all requested sample data and titrate with c(NaOH) = 0.1 mol/L to pH 8.2. All other parameters and calculations are already defined within the method.

US

Pipette 5 mL degassed sample and 100 mL deionized water into a 150 mL beaker and press start, enter all requested sample data and titrate with c(NaOH) = 0.1 mol/L to pH 8.2. All other parameters and calculations are already defined within the method.

Calculation

$$\beta_{Acid} = \frac{V_{EP1} \cdot c_{NaOH} \cdot t_{NaOH} \cdot M_{Acid}}{V_{Sample} \cdot z^*}$$

β_{Acid}: acid content in g/L; sulfuric or tartaric acid

V_{EP1}: consumption of titrant up to first equivalence point in mL

c_{NaOH}: concentration of sodium hydroxide solution; here 0.1 mol/L

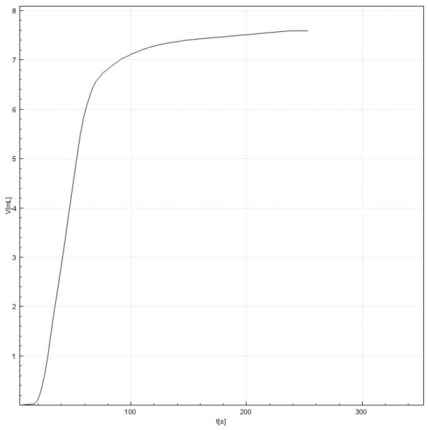
t_{NaOH}: titer of sodium hydroxide solution

M_{Acid}: molar mass of the corresponding acid;
tartaric acid: 150.09 g/mol
sulfuric acid: 98.08 g/mol

V_{Sample}: volume of sample in mL; here 10 mL, 5 mL or 20 mL

z^*: stoichiometric factor; here 2

Example curve



Results

Mean value (n = 3)	5.512 g/L
s(abs)	0.036 g/L
s(rel)	0.66%

Comments

- The pH value and the calibration of the electrode are temperature depended. For comparing different values, the calibration as well as the measurement should be performed at the same temperature. A deviation in pH value may occur if the measurement and the calibration are done at different temperatures.
- Depending on the standard, different end pH values and sample sizes are required.
- The stirring speed during titration should not be too high as otherwise CO_2 can be absorbed by the solution and a lower acidity will be measured.
- During titration, it is recommended to cover the sample solution with nitrogen to prevent uptake of CO_2.
- Purging with nitrogen, vacuum and agitation may be used for degassing the wine.
- For degassing with nitrogen the gas is bubbled approx. 5 min through the solution.
- If the agitation method is used for degassing, the magnetic stirrer is used and the direction of the stirrer is changed every 30 s. Make sure that the stirring speed is not too high as otherwise CO_2 will again be taken up by the solution.
- When using vacuum for degassing the solution is placed under vacuum for 1 min at 100 mbar.
- The programmed method expresses the acid content as tartaric acid. Should the result be expressed as sulfuric acid, the molar mass is changed under *Parameters* → *Calculation* from 150.09 g/mol to 98.08 g/mol.
- Determine the titer according to ***Method_2***.

22. Wine – Free sulfurous acid

Summary

Sulfite or sulfurous acid is present in wines in bound and free form. In its free form it is present as SO_2, HSO_3^- and SO_3^{2-}. SO_2 acts antimicrobial, HSO_3^- binds side products which are produced during fermentation and SO_3^{2-} prevents the wine from oxidation. The concentration range usually obtained for free sulfurous acid is between 5 – 70 mg/L.

Solutions

$c(I_2)$ = 0.05mol/L	Should be bought from a supplier.
Titrant 1 $c(I_2)$ = 0.01 mol/L	Transfer 200 mL $c(I_2)$ = 0.05 mol/L into a 1 L volumetric flask and fill it up to the mark with deionized water.
Titrant 2 $c(I_2)$ = 1/128 mol/L = 0.0078 mol/L	Transfer 156.25 mL $c(I_2)$ = 0.05 mol/L into a 1 L volumetric flask and fill it up to the mark with deionized water.
$w(H_2SO_4)$ = 25%	Transfer 255 g $w(H_2SO_4)$ = 98% into a 1 L volumetric flask, already containing 400 mL deionized water. After cooling down, fill up the flask to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Double Pt sheet electrode	6.0309.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_22*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***I2_0.01*** (for AU, USA, SA) or ***I2_0.007*** (CH and ZA) to the solution list under *System* → *Sensors* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Pt sheet*** to the sensor list under *System* → *Solutions.*
5. Adjust the solution under *Parameters* → *Titrations parameters.*
6. Prepare the sample solution as defined under ***Analysis***

Analysis

AU, US

Pipette 50 mL sample into a 100 mL beaker, add 5 mL $w(H_2SO_4)$ = 25% as well as 1 g $NaHCO_3$. After all the foam has disappeared, press start, enter all requested sample data and titrate the solution with $c(I_2)$ = 0.01 mol/L until after the equivalence point. All other parameters and calculations are already defined within the method.

SA

Pipette 10 mL sample and approx. 20 mL deionized water into a 100 mL beaker. Add 1 mL $w(H_2SO_4)$ = 25% as well as 0.2 g $NaHCO_3$. After all the foam has disappeared, press start, enter all requested sample data and titrate the solution with $c(I_2)$ = 0.01 mol/L until after the equivalence point. All other parameters and calculations are already defined within the method.

CH, ZA

Pipette 50 mL sample into a 100 mL beaker and add 1 g KI as well as 5 mL $w(H_2SO_4)$ = 25%. Afterwards press start, enter all requested sample data and titrate the solution with $c(I_2)$ = 0.0078 mol/L until after the equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$\beta_{SO2} = \frac{V_{EP1} \cdot c_{I2} \cdot t_{I2} \cdot M_{SO2} \cdot 1000}{V_{Sample}}$$

β_{SO2}: SO_2 content in mg/L

V_{EP1}: consumption of titrant up to first equivalence point in mL

c_{I2}: Concentration of iodine solution; here:
0.01 mol/L (AU, US, SA) or
0.0078125 mol/L (CH, ZA)

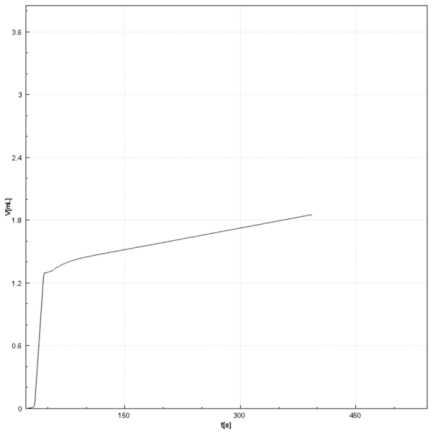
t_{I2}: titer of iodine solution

M_{SO2}: molar mass of SO_2, 64.06 g/mol

1000: conversion factor from g/L to mg/L

V_{Sample}: volume of sample in mL; here 50 mL or 10 mL

Example curve



Results

Mean value (n = 3)	45.87 mg/L
s(abs)	1.30 mg/L
s(rel)	2.83%

Comments

- Store the double Pt sheet electrode dry when not in use.
- Carry out the titer determination according to ***Method_4.***
- With this method the free SO_2 as well as other reductants like ascorbic acid are determined. The ascorbic acid has to be quantified separately and subtracted from the obtained value in this method.
- Normally the concentration of free SO_2 is between 5 – 70 mg/L.
- The official reference method consists of a distillation procedure. The SO_2 is released by adding phosphoric acid. At room temperature, nitrogen is bubbled through the solution and the SO_2 is carried over into a H_2O_2 solution. The SO_2 in combination with H_2O_2 will form H_2SO_4 which is titrated with c(NaOH) = 0.01 mol/L.
- The method is programmed for an iodine solution concentration of $c(I_2)$ = 0.01 mol/L. If a concentration of $c(I_2)$ = 0.007 mol/L is used, the right solution has to be chosen under *Parameters* → *Titration parameters.*

23. Wine – Total sulfurous acid, orienting Ripper method

Summary

Sulfite or sulfurous acid is present in wines in bound and free form. It is used for conservation. As sulfite acts antimicrobial, as a reducing agent and deactivates enzymes, the concentration of total sulfite in wine must not exceed 200 mg/L.

Solutions

c(NaOH) = 1 mol/L	Weigh 40 g NaOH into a 1 L volumetric flask, dissolve in approx. 500 mL deionized water and allow to cool down. Afterwards fill up to the mark with deionized water.
$c(I_2)$ = 0.05mol/L	Should be bought from a supplier.
Titrant 1 $c(I_2)$ = 0.01 mol/L	Transfer 200 mL $c(I_2)$ = 0.05 mol/L into a 1 L volumetric flask and fill it up to the mark with deionized water.
Titrant 2 $c(I_2)$ = 1/128 mol/L = 0.0078 mol/L	Transfer 156.25 mL $c(I_2)$ = 0.05 mol/L into a 1 L volumetric flask and fill it up to the mark with deionized water.
$w(H_2SO_4)$ = 25%	Transfer 255 g $w(H_2SO_4)$ = 98% into a 1 L volumetric flask, already containing 400 mL deionized water. After cooling down, fill up the flask to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Double Pt sheet electrode	6.0309.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_23*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***I2_0.01*** (for AU, USA, SA) or ***I2_0.007*** (CH and ZA) to the solution list under *System → Sensors* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Pt sheet*** to the sensor list under *System → Solutions.*
5. Adjust the solution under *Parameters → Titrations parameters.*
6. Prepare the sample solution as defined under ***Analysis***

Analysis

AU, US

Pipette 20 mL sample and 25 mL w(NaOH) = 1 mol/L into a 150 mL beaker and allow to react for 10 min. Afterwards, add 10 mL $w(H_2SO_4)$ = 25% as well as 1 g $NaHCO_3$. After all foam has disappeared, press start, enter all requested sample data and titrate the solution with $c(I_2)$ = 0.01 mol/L until after the equivalence point. All other parameters and calculations are already defined within the method.

SA

Pipette 25 mL sample and 25 mL w(NaOH) = 1 mol/L into a 150 mL beaker and allow to react for 10 min. Afterwards, add 10 mL $w(H_2SO_4)$ = 25% as well as 0.2 g $NaHCO_3$. After all foam has disappeared, press start, enter all requested sample data and titrate the solution with $c(I_2)$ = 0.01 mol/L until after the equivalence point. All other parameters and calculations are already defined within the method.

CH, ZA

Pipette 50 mL sample and 25 mL w(NaOH) = 1 mol/L into a 150 mL beaker and allow to react for 10 min. Afterwards, add 10 mL $w(H_2SO_4)$ = 25% as well as 1 g KI. Then press start, enter all requested sample data and titrate the solution with $c(I_2)$ = 1/128 mol/L until after the equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$\beta_{SO2} = \frac{V_{EP1} \cdot c_{I2} \cdot t_{I2} \cdot M_{SO2} \cdot 1000}{V_{Sample}}$$

β_{SO2}: SO_2 content in mg/L

V_{EP1}: consumption of titrant up to first equivalence point in mL

c_{I2}: concentration of iodine solution; here: 0.01 mol/L or 0.0078125 mol/L

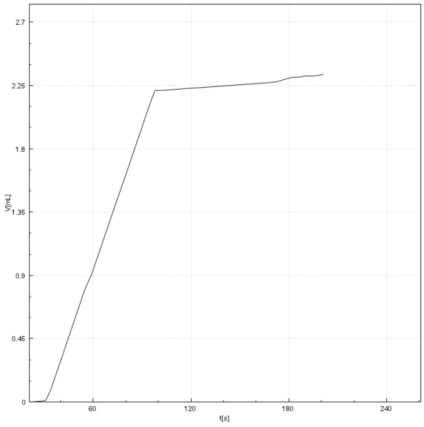
t_{I2}: titer of iodine solution

M_{SO2}: molar mass of SO_2; 64.06 g/mol

1000: conversion factor from g/L to mg/L

V_{Sample}: volume of sample in mL; here 20 mL, 25 mL or 50 mL

Example curve



Results

Mean value (n = 3)	69.57 mg/L
s(abs)	1.68 mg/L
s(rel)	2.42%

Comments

- Store the double Pt sheet electrode dry when not in use.
- Carry out the titer determination according to ***Method_4.***
- With this method the total SO_2 as well as other reductants like ascorbic acid are determined. The ascorbic acid has to be determined separately and subtracted from the obtained value in this method.
- Normally the concentration of total SO_2 lie in between 40 – 300 mg/L.
- The official reference method consists of a distillation procedure. The SO_2 is released by adding phosphoric acid to the solution and boiling the corresponding solution. While boiling the nitrogen is bubbled through the solution and the SO_2 is carried over into a H_2O_2 solution. The SO_2 in combination with H_2O_2 will form H_2SO_4 which is titrated with c(NaOH) = 0.01 mol/L.
- The method is programmed for an iodine solution concentration of $c(I_2)$ = 0.01 mol/L. If a concentration of $c(I_2)$ = 0.007 mol/L is used, the right solution has to be chosen under *Parameters* → *Titration parameters.*

24. Wine – Determination of ascorbic acid

Summary

The ascorbic acid content of grapes ranges from 5 to 150 mg/L. After fermentation, usually only approx. 2 mg/L remain. In some cases, ascorbic acid is added to the produced wine because of its reductive properties. The addition of ascorbic acid can reduce the content of total SO_2. However, this addition is limited to 150 mg/L.

Solutions

$c(I_2)$ = 0.05 mol/L	Should be bought from a supplier.
Titrant $c(I_2)$ = 0.01 mol/L	Transfer 200 mL $c(I_2)$ = 0.05 mol/L into a 1 L volumetric flask and fill it up to the mark with deionized water.
w(glyoxal) = 40%	Adjust the pH of 200 mL w(glyoxal) = 40% with c(NaOH) = 1 mol/L to pH 7.
$w(H_2SO_4)$ = 25%	Transfer 255 g $w(H_2SO_4)$ = 98% into a 1 L volumetric flask, already containing 400 mL deionized water. After cooling down, fill the flask up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Double Pt sheet electrode	6.0309.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_24*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***I2_0.01*** to the solution list under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Pt sheet*** to the sensor list under *System* → *Sensors*.
5. Prepare the solutions as described under ***Analysis.***

Analysis

Pipette 50 mL wine into a 100 mL beaker and add 2 mL w(glyoxal) = 40%. Stir the solution for 5 min. Afterwards, add 5 mL $w(H_2SO_4)$ = 25%, press start, enter all requested sample data and titrate with $c(I_2)$ = 0.01 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$\beta_{AA} = \frac{V_{EP1} \cdot c_{I2} \cdot t_{I2} \cdot M_{AA} \cdot 1000}{V_{Sample}}$$

β_{AA}: ascorbic acid content in g/L

V_{EP1}: consumption of titrant up to first equivalence point in mL

c_{I2}: concentration of iodine solution; here: 0.01 mol/L

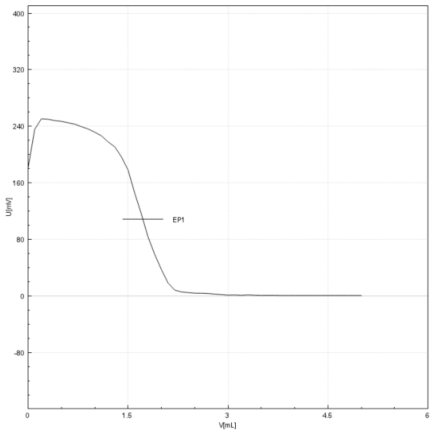
t_{I2}: titer of iodine solution

M_{AA}: molecular mass of ascorbic acid, 176.12 mol/L

1000: conversion factor from g to mg

V_{Sample}: volume of sample in mL; here 50 mL

Example curve



Results

Mean value (n = 3)	95.07 mg/L
s(abs)	1.03 mg/L
s(rel)	1.08%

Comments

- Store the double Pt sheet electrode dry when not in use.
- Use the same titrant for the determination of free and total SO_2. With the addition of glyoxal the free SO_2 is bound and no longer determined. This allows to obtain the ascorbic acid content only.
- The ascorbic acid content in wine ranges normally from 1 – 10 mg/L.
- Other procedures mention Dichlorophenolindophenol (DPIP) as titrant. This may also be applied here, however, iodine solution is proposed as it is also used for the SO_2 determination.
- Determine the titer according to ***Method_4***.

25. Wine – Determination of calcium and magnesium

Summary

The Ca and Mg contents of wines vary greatly. Their concentrations depend on the composition of the soil and can therefore, depending on the location and country, vary between 40 and 300 mg/L for calcium and between 20 and 250 mg/L for magnesium. By treating the must with $CaSO_4$ or $CaCO_3$ or by adding bentonite, Ca and Mg may also be introduced into wine.

A too high Ca content can lead to unwanted precipitation, which, however, usually occurs after the wine has been bottled. Mg influences the stability of the tartrate and the «acid taste» of the wine. The Ca content is reduced during fermentation and the Mg/Ca ratio increases.

Both ions can be determined simultaneously by complexometric titration.

Solutions

Titrant c(Na_2EDTA) = 0.1 mol/L	Should be bought from a supplier.
Auxiliary complexing solution c(Acetylacetone) = 0.1 mol/L + c(TRIS) = 0.2 mol/L	Weigh 20.4 g TRIS into a 1 L volumetric flask and dissolve it in approx. 500 mL deionized water. Add 12 mL acetylacetone and fill the solution up to the mark with deionized water.
w(HCl) = 20%	Weigh 540 g w(HCl) = 37% into a 1 L volumetric flask, already containing 200 mL deionized water. Then, allow to cool down and fill up to the mark with deionized water.
w(NaOH) = 20%	Weigh 200 g NaOH into a 1 L volumetric flask, already containing 500 mL deionized water and fill up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Combined polymer membrane electrode, Ca	6.0510.100

Sample preparation

Pipette 75 mL sample into a platinum or quartz crucible and heat it at 600 °C in a muffle furnace until only a pure white ash remains. After cooling down, add 2 mL w(HCl) = 20% to dissolve the ash (possibly under warming). Then transfer the solution quantitatively to the titration beaker with deionized water.

System configuration

1. Load the method ***Method_25*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***EDTA_0.1*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Ca-ISE*** to the sensor list under *System → Sensors.*
5. Prepare the solutions as described under ***Analysis.***

Analysis

Transfer the sample quantitatively into a 150 mL beaker and neutralize the solution to pH 6 to 6.5 with w(NaOH) = 20%. Add 20 mL auxiliary solution, press the start button and enter all requested sample data. Titrate afterwards with c(Na_2EDTA) = 0.1 mol/L until after the second equivalence point. All other parameters and calculations are already defined within the method.

Calculation

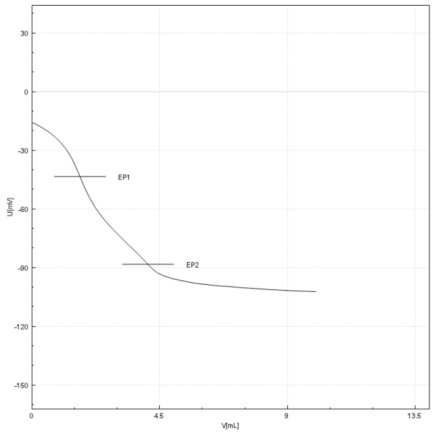
$$\beta(Ca^{2+}) = \frac{V_{EP1} \cdot t_{EDTA} \cdot c_{EDTA} \cdot M(Ca^{2+}) \cdot 1000}{V_{Sample}}$$

$\beta(Ca^{2+})$:	concentration of calcium in mg/L
V_{EP1}:	consumption of titrant up to the first equivalence point in mL
t_{EDTA}:	titer of EDTA solution
c_{EDTA}:	concentration of EDTA solution; here: 0.1 mol/L
$M(Ca^{2+})$:	molar mass of calcium; 40.08 g/mol
1000:	conversion factor from g/L to mg/L
V_{Sample}:	volume of sample in mL

$$\beta(Mg^{2+}) = \frac{(V_{EP2} - V_{EP1}) \cdot t_{EDTA} \cdot c_{EDTA} \cdot M(Ca^{2+}) \cdot 1000}{V_{Sample}}$$

$\beta(Mg^{2+})$:	concentration of magnesium in mg/L
V_{EP2}:	consumption of titrant up to the second equivalence point in mL
V_{EP1}:	consumption of titrant up to the first equivalence point in mL
t_{EDTA}:	titer of EDTA solution
c_{EDTA}:	concentration of EDTA solution; here: 0.1 mol/L
$M(Mg^{2+})$:	molar mass of magnesium; 24.31 g/mol
1000:	conversion factor from g/L to mg/L
V_{Sample}:	volume of sample in mL

Example curve



Results

Calcium

Mean value (n = 3)	92.26 mg/L
s(abs)	1.25 mg/L
s(rel)	1.35%

Magnesium

Mean value (n = 3)	77.03 mg/L
s(abs)	0.63 mg/L
s(rel)	0.82%

Comments

- Store the combined Ca-ISE dry when not in use containing some residual moisture (e.g., some drops of deionized water) in the electrode vessel.
- Use ***Method_1*** for the determination of the titer.
- Do not store the auxiliary solution longer than a week. The separation of calcium and magnesium will become worse.

26. Wine – Determination of chloride

Summary

The chloride content of wine lie normally between 50 – 200 mg/L. Contents of to 600 mg/L have been found in wines from vineyards near the sea. In Switzerland and the European Union, wines with a content of >500 mg/L chloride are not allowed to be sold. The USA and AU do not have any regulation regarding the chloride content in wine.

Solutions

Titrant 1 $c(AgNO_3) = 0.1$ mol/L	Should be bought from a supplier.
Titrant 2 $c(AgNO_3) = 0.01$ mol/L	Pipette 100 mL $c(AgNO_3) = 0.1$ mol/L into a 1 L volumetric flask and fill it up to the mark with deionized water.
$c(HNO_3) = 2$ mol/L	Weigh 194 g $c(HNO_3) = 65\%$ into a 1 L volumetric flask and fill it up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Ag Titrode with Ag_2S coating	6.00430.100S

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_26*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***AgNO3_0.01*** to the solution list under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Ag Titrode*** to the sensor list under *System* → *Sensors*.
5. Prepare the solution as described under ***Analysis***

Analysis

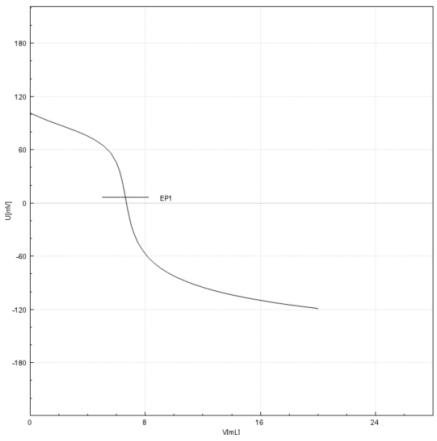
Pipette 50 mL sample into a 100 mL beaker. Add 1 mL $c(HNO_3) = 2$ mol/L, press start and enter all requested sample data. Titrate with $c(AgNO_3) = 0.01$ mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$\beta_{Cl} = \frac{V_{EP1} \cdot c_{AgNO3} \cdot t_{AgNO3} \cdot M_{Cl}}{V_{sample}}$$

β_{Cl}:	mass concentration of chloride in g/L
V_{EP1}:	consumption of titrant in mL
c_{AgNO3}:	concentration of silver nitrate in mol/L; here 0.05 mol/L
t_{AgNO3}:	titer of silver nitrate solution
M_{Cl}:	molar mass of chloride; 35.45 g/mol
V_{sample}:	sample size in mL; here 50 mL

Example curve



Results

Mean value (n = 3)	46.86 mg/L
s(abs)	0.20 mg/L
s(rel)	0.43%

Comments

- Store the electrode in deionized water if not in use. The hydration layer of the glass membrane remains intact and the electrode is ready for use.
- A coated silver ring must not be polished as otherwise the coating is removed.
- Instead of an Ag Titrode also an Ag ring electrode can be used.
- Depending on the chloride concentration the sample size has to be decreased.
- Determine the titer according to ***Method_5***.

27. Oil – Determination of total base number

Summary

Components in oil products that exhibit an alkaline reaction are determined as a cumulative total under the base number. These are chiefly primary organic and inorganic amino compounds, but the salts of weak acids and alkaline salts of polycarboxylic acids, as well as some heavy metal salts and detergents, are also determined. The determination is used to assess relative alterations during the working life of the product.

Solutions

Titrant $c(HClO_4)$ = 0.1 mol/L in glacial acetic acid	Should be bought from a supplier.
Solvent Toluene : glacial acetic acid : acetone (6:3:1 (v:v:v))	Transfer 600 mL toluene, 300 mL glacial acetic acid and 100 mL acetone into a glass bottle and mix thoroughly.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Solvotrode easyClean	6.0229.010

Sample preparation

No sample preparation is required.

System configuration

Blank

1. Load the method ***Method_27.1*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***HClO4_0.1*** to the solution list under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Solvotrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as described under ***Analysis Blank***

Sample

1. Load the method ***Method_27.2*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***HClO4_0.1*** to the solution list under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Solvotrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as described under ***Analysis Sample***

Analysis

Blank

Pipette 50 mL solvent into a 100 mL titration beaker, press start and enter all requested sample data. Titrate with $c(HClO_4)$ = 0.1 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method. The mean value of the blank is saved as CV01

Sample

Weigh an appropriate amount of sample (see table below) into a 100 mL beaker and dissolve it in 50 mL solvent. Press start, enter all requested sample data and carry out the titration with $c(HClO_4)$ = 0.1 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

expected TBN / (mg KOH / g sample)	Sample weight / g	Weighing accuracy / mg
3 – 15	2.00	1
15 – 30	1.00	1
30 – 45	0.25	0.1

Calculation

$$TBN = \frac{(V_{EP1} - CV01) \cdot c_{HClO4} \cdot t_{HClO4} \cdot M_{KOH}}{m_{Sample}}$$

TBN: total base number in mg KOH / g sample

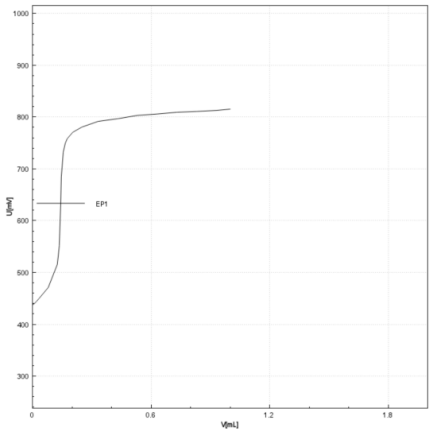
V_{EP1}: consumption of titrant up to first equivalence point in mL

CV01: blank value in mL

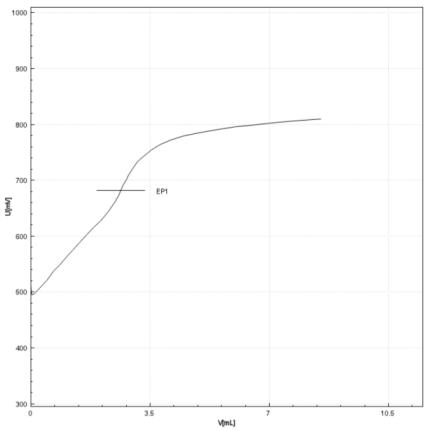
c_{HClO4}: concentration of perchloric acid solution
here: 0.1 mol/L
t_{HClO4}: titer of perchloric acid solution
M_{KOH}: molar mass of potassium hydroxide; 56.11 g/mol
m_{Sample}: mass of sample in g

Example curve

Blank



Sample



Results

Blank

Mean value (n = 3)	0.1465 mL
s(abs)	0.0035 mL
s(rel)	2.38%

Sample

Mean value (n = 3)	6.8 mg KOH/g
s(abs)	0.2 mg KOH/g
s(rel)	2.90%

Comments

- Fill the electrode with c(LiCl) = 2 mol/L as reference electrolyte.
- Store the electrode in the corresponding reference electrolyte if not in use.
- From time to time, open the sleeve of the ground-joint diaphragm and release some electrolyte.
- The condition of the electrode can be tested by immersing the electrode in buffer pH 4 and buffer pH 7 and measuring the voltage difference. The difference should be at least 162 mV. If this is not the case, release some electrolyte and repeat the measurement.
- In between measurements, the glass membrane (bulp) of the electrode is immersed for 1 min in deionized water.
- The TBN analysis might show more than one equivalence point. In such a case the last equivalence point is used for calculation.
- Determine the titer according to ***Method_7***.

28. Oil – Determination of total acid number

Summary

TAN is an important parameter for determining the quality of e.g., petroleum products. It gives its acidity and is determined by the amount of potassium hydroxide, which is necessary for its neutralization. This value is usually determined to monitor the oxidation of petrochemical products which may lead to failure of machinery due to corrosion.

Solutions

Titrant c(KOH) = 0.1 mol/L in isopropanol	Should be bought from a supplier.
Solvent Toluene : isopropanol; deionized water (1:0.99:0.01)	Transfer 500 mL toluene, 495 mL isopropanol and 5 mL deionized water into a glass bottler and mix thoroughly.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Solvotrode easyClean	6.0229.010

Sample preparation

No sample preparation is required.

System configuration

Blank

1. Load the method ***Method_28.1*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***KOH_0.1*** to the solution list under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Solvotrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as described under ***Analysis Blank***

Sample

1. Load the method ***Method_28.2*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***KOH_0.1*** to the solution list under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Solvotrode*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as described under ***Analysis Sample***

Analysis

Blank

Pipette 60 mL solvent into a 100 mL titration beaker, press start, enter all requested sample data and titrate with c(KOH) = 0.1 mol/L in isopropanol until after the first equivalence point. All other parameters and calculations are already defined within the method. The mean value of the blank is saved as common variable CV01.

Sample

Weigh an appropriate amount of sample (see table below) into a 100 mL beaker and dissolve it in 60 mL solvent. Press start, enter the requested sample data and carry out the titration with c(KOH) = 0.1 mol/L in isopropanol until after the first equivalence point. All other parameters and calculations are already defined within the method.

expected TAN / (mg KOH / g sample)	Sample weight / g
0.05 – <1.0	10.0 ± 2.0
1.0 – <5.0	5.0 ± 0.5
5 – <20	1.0 ± 0.1
20 – <100	0.25 ± 0.02
100 – <260	0.1 ± 0.01

Calculation

$$TAN = \frac{(V_{EP1} - CV01) \cdot c_{KOH} \cdot t_{KOH} \cdot M_{KOH}}{m_{Sample}}$$

TAN: total acid number in mg KOH / g sample

V_{EP1}: consumption of titrant up to first equivalence point in mL

CV01: blank value in mL

c_{KOH}: concentration of potassium hydroxide solution here: 0.1 mol/L

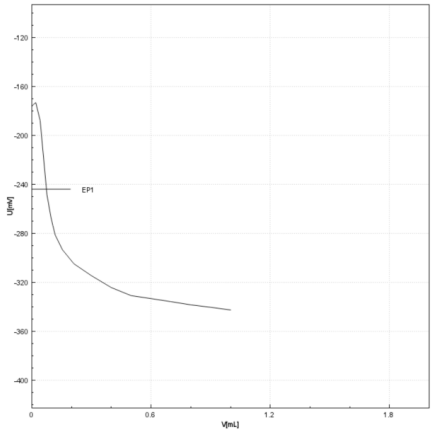
t_{KOH}: titer of potassium hydroxide solution

M_{KOH}: molar mass of potassium hydroxide; 56.11 g/mol

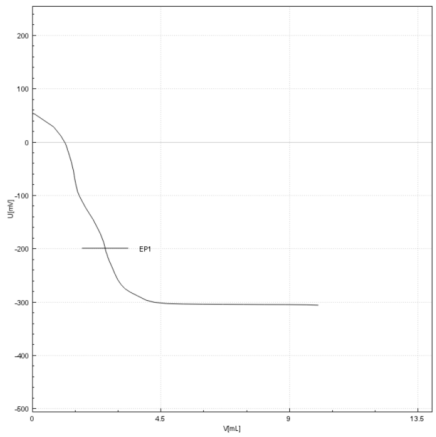
m_{Sample}: mass of sample in g

Example curve

Blank



Sample



Results

Blank

Mean value (n = 3)	0.0748 mL
s(abs)	0.0009 mL
s(rel)	1.22%

Sample

Mean value (n = 3)	1.27 mg KOH/g
s(abs)	0.01 mg KOH/g
s(rel)	0.67%

Comments

- Fill the electrode with c(TEABr) = 0.4 mol/L in ethylene glycol.
- Store the electrode in the corresponding electrolyte if not in use.
- From time to time, open the flexible ground-joint diaphragm and release some electrolyte.
- The condition of the electrode can be tested by immersing the electrode in buffer pH 4 and buffer pH 7 and measuring the voltage difference. The difference should be at least 162 mV. If the difference is smaller, release some electrolyte and repeat the measurement.
- In between measurements the glass membrane (bulp) of the electrode is immersed for 1 min in deionized water.
- The TAN analysis might show more than one equivalence point. In such a case the last equivalence point is used for calculation.
- Determine the titer according to ***Method_8***.

29. Oil – Determination of sulfur compounds in petrochemical products

Summary

Sulfur compounds contained in petrochemicals do not only have an unpleasant odor, they also cause environmental problems and have a corrosive effect. This method describes the determination of hydrogen sulfide and mercaptans in liquid hydrocarbons (gasoline, petrol), kerosene, naphtha and similar distillates. The sulfur compounds are titrated with silver nitrate solution, whereby silver sulfide and silver mercaptides are formed.

Two well-defined potential jumps are obtained. The first endpoint corresponds to the hydrogen sulfide; the second to the mercaptans. The Ag Titrode with Ag_2S coating is used as indicator electrode.

Solutions

$c(AgNO_3)$ = 0.1 mol/L	Should be bought from a supplier.
Titrant $c(AgNO_3)$ = 0.01 mol/L in isopropanol (IPA)	Transfer 100 mL $c(AgNO_3)$ = 0.1 mol/L and 80 mL deionized water into a 1 L volumetric flask. Afterwards fill the solution up to the mark with isopropanol.
Acidic solvent for high-molecular mercaptans	Dissolve 2.7 g sodium acetate trihydrate in 25 mL deionized water and add 4.6 mL glacial acetic acid. Transfer the solution with IPA quantitatively into a 1 L volumetric flask and fill it up to the mark with IPA.
Alkaline solvent for low-molecular mercaptans	Dissolve 2.7 g sodium acetate trihydrate in 25 mL deionized water and add 10 mL $w(NH_3)$ = 25%. Transfer the solution with IPA quantitatively into a 1 L volumetric flask and fill it up to the mark with IPA.

Cylinder unit

Eco Cylinder unit 10 mL	6.03002.210

Sensors

Ag Titrode with Ag_2S coating	6.00430.100S

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_29*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***AgNO3_0.01*** to the solution list under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the electrode ***Ag Titrode*** to the sensor list under *System* → *Sensors*.
5. Prepare the sample solution as described under ***Analysis***

Analysis

Place 100 mL solvent solution – acidic or alkaline solvent depending on the kind of mercaptan – into a titration vessel and purge 5 min with nitrogen. Afterwards, cover the sample solution with nitrogen while adding the corresponding amount of sample (see table below). Press the start button, enter all requested sample data and titrate the mixture with $c(AgNO_3)$ = 0.01 mol/L in isopropanol. All other parameters and calculations are already defined within the method.

ppm mercaptan S expected	Sample size / mL
1 – <50	50
50 – <100	25
100 – <300	10
300 – 500	5

Calculation

If only hydrogen sulfide or only mercaptan are present, one equivalence point will be obtained.

If both are present, two equivalence points will be obtained, whereof EP1 corresponds to H_2S and EP2 to the mercaptans.

Should sulfur be present (sulfur can form disulfide) a third flat potential jump between EP1 and EP2 will be visible which corresponds to sulfur.

In case only mercaptans are present:

$$\beta_{mer} = \frac{V_{EP1} \cdot c_{AgNO3} \cdot t_{AgNO3} \cdot M_S \cdot 1000}{m_{Sample}}$$

β_{mer}: mass concentration of mercaptanic sulfur in mg/kg
V_{EP1}: consumption of titrant up to first equivalence point in mL
c_{AgNO3}: concentration of silver nitrate solution here: 0.01 mol/L
t_{AgNO3}: titer of silver nitrate solution
M_S: molecular mass of sulfur; 32.06 g/mol
1000: conversion factor to mg/kg
m_{Sample}: mass of sample in g

If both hydrogen sulfide and mercaptans are present: Hydrogen sulfide

$$\beta_{H2S} = \frac{V_{EP1} \cdot c_{AgNO3} \cdot t_{AgNO3} \cdot M_S \cdot 1000}{m_{Sample} \cdot z^*}$$

β_{H2S}: mass concentration of hydrogen sulfide in mg/kg
V_{EP1}: consumption of titrant up to first equivalence point in mL
c_{AgNO3}: concentration of silver nitrate solution here: 0.01 mol/L
t_{AgNO3}: titer of silver nitrate solution
M_S: molecular mass of sulfur; 32.06 g/mol
1000: conversion factor to mg/kg
m_{Sample}: mass of sample in g
z^*: stoichiometric factor; here 2

Mercaptans

$$\beta_{mer} = \frac{(V_{EP2} - V_{EP1}) \cdot c_{AgNO3} \cdot t_{AgNO3} \cdot M_S \cdot 1000}{m_{Sample}}$$

β_{mer}: mass concentration of mercaptanic sulfur in mg/kg
V_{EP2}: consumption of titrant up to second equivalence point in mL
V_{EP1}: consumption of titrant up to first equivalence point in mL
c_{AgNO3}: concentration of silver nitrate solution here: 0.01 mol/L
t_{AgNO3}: titer of silver nitrate solution
M_S: molecular mass of sulfur; 32.06 g/mol
1000: conversion factor to mg/kg
m_{Sample}: mass of sample in g

If hydrogen sulfide, mercaptans and sulfur are present: Hydrogen sulfide

$$\beta_{H2S} = \frac{V_{EP1} \cdot c_{AgNO3} \cdot t_{AgNO3} \cdot M_S \cdot 1000}{m_{Sample} \cdot z^*}$$

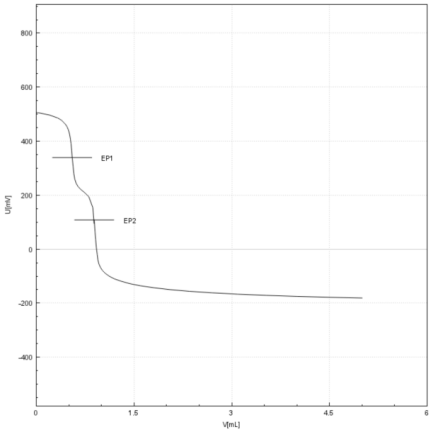
β_{H2S}: mass concentration of hydrogen sulfide in mg/kg
V_{EP1}: consumption of titrant up to first equivalence point in mL
c_{AgNO3}: concentration of silver nitrate solution here: 0.01 mol/L
t_{AgNO3}: titer of silver nitrate solution
M_S: molecular mass of sulfur; 32.06 g/mol
1000: conversion factor to mg/kg
m_{Sample}: mass of sample in g
z^*: stoichiometric factor; here 2

Mercaptans

$$\beta_{mer} = \frac{(V_{EP3} - V_{EP1}) \cdot c_{AgNO3} \cdot t_{AgNO3} \cdot M_S \cdot 1000}{m_{Sample}}$$

β_{mer}: mass concentration of mercaptanic sulfur in mg/kg
V_{EP3}: consumption of titrant up to third equivalence point in mL
V_{EP1}: consumption of titrant up to first equivalence point in mL
c_{AgNO3}: concentration of silver nitrate solution here: 0.01 mol/L
t_{AgNO3}: titer of silver nitrate solution
M_S: molecular mass of sulfur; 32.06 g/mol
1000: conversion factor to mg/kg
m_{Sample}: mass of sample in g

Example curve



Results

Hydrogen sulfide

Mean value (n = 3)	2.37 mg/kg
s(abs)	0.05 mg/kg
s(rel)	1.89%

Mercaptans

Mean value (n = 3)	3.01 mg/kg
s(abs)	0.03 mg/kg
s(rel)	1.02%

Comments

- Because the concentration of sulfide is very low it is mandatory to use an Ag Titrode with Ag_2S coating as its sensitivity is higher.
- H_2S and mercaptans are easily oxidized by atmospheric oxygen. Therefore, the samples need to be covered with nitrogen during titration.
- Store the Ag Titrode in deionized water if not in use. This ensures a well hydrated glass membrane and therefore the electrode remains ready to use.
- You must not polish the silver ring when it is coated. This would remove the coating.
- IPA is added instead of water to sharpen the potential change at the equivalence point.
- The method is suitable for titrations where two EPs are obtained. Should a third EP be observed, the calculation has to be adapted under *Parameters* → *Calculation* accordingly.
- Low molecular weight mercaptans are usually found in gasoline, where high molecular weight mercaptans are found in kerosines, aviation turbine fuels and distillate fuels. Normally, argentometric titrations take place in an acidic medium. This is not possible with low molecular mercaptanes as they would get lost easily. Therefore for this type of mercaptanes the alkaline titration solvent is used.
- Determine the titer according to ***Method_5***.

30. Surf – Anionic surfactants and soaps in washing powder by potentiometric two-phase titration

Summary

Soaps lose their surfactant properties under acidic conditions and cannot be determined anymore. In contrast, anionic surfactants can be titrated under both acidic and alkaline conditions. Thus, two titrations are required to determine both soaps and anionic surfactants of a sample:

- In a first titration at pH = 2.0 only the anionic surfactants are determined.
- In a second titration at pH = 11.5 the total of anionic surfactants and soaps is determined.

Solutions

Titrant c(TEGOtrant) = 0.005 mol/L	Weigh approx. 2.2 g TEGOtrant into a 1 L volumetric flask and add 150 mL deionized water. After dissolution (make sure no foam is present), fill up the solution to the mark with deionized water.
TEGOadd	Metrohm article number 6.2317.120
c(HCl) = 0.5 mol/L	Weigh 49.3 g w(HCl) = 37% into a 1 L volumetric flask containing already 500 mL deionized water. Allow to cool down and afterwards make up the solution to the mark with deionized water.
c(NaOH) = 0.5 mol/L	Weigh 20 g NaOH into a 1 L volumetric flask containing already 500 mL deionized water and dissolve it. Allow to cool down, then make up the solution to the mark with deionized water.
Solvent mixture Methyl isobutyl ketone : ethanol (1:1 (v:v))	Transfer 500 mL MIBK and 500 mL Ethanol into a glass bottle and mix thoroughly.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Surfactrode Refill	6.0507.140
LL ISE Reference electrode	6.0750.100

Sample preparation

No sample preparation is required.

System configuration

Anionic Surfactants

1. Load the method ***Method_30.1*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***TEGO_0.005*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***Surf Refill*** to the sensor list under *System → Sensors*.
5. Prepare the sample solution as described under ***Analysis***

Anionic Surfactants and soaps

1. Load the method ***Method_30.2*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***TEGO_0.005*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***Surf Refill*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as described under ***Analysis***

Analysis

Anionic Surfactants

Weigh an appropriate amount of sample sothat a consumption of approx. 10 mL titrant is obtained, into a closed titration beaker with a volume of approx. 100 mL (e.g., 6.01406.220). Add 70 mL deionized water and 0.2 mL TEGOadd. Adjust the pH of the solution with c(HCl) = 0.5 mol/L to pH 2 and afterwards add 20 mL solvent mixture. Press start, enter all requested sample data and carry out the titration with c(TEGOtrant) = 0.005 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method. The value obtained from the calculation is additionally saved as CV01.

Anionic Surfactants and soaps

Weigh an appropriate amount of sample so that a consumption of approx. 10 mL titrant is obtained, into a closed titration beaker with a volume of approx. 100 mL (e.g., 6.01406.220). Add 70 mL deionized water and 0.2 mL TEGOadd. Adjust the pH of the solution with c(NaOH) = 0.5 mol/L to pH 11.5 and afterwards add 20 mL solvent mixture. Press start, enter all requested sample data and carry out the titration with c(TEGOtrant) = 0.005 mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

Anionic Surfactants

$$b_{A\text{-}Surf} = \frac{V_{EP1} \cdot c_{TEGO} \cdot 100 \cdot t_{TEGO}}{m_{Sample}}$$

$b_{A\text{-}Surf}$: molality of anionic surfactants in mmol/100 g
V_{EP1}: consumption of titrant up to the first equivalence point in mL
c_{TEGO}: concentration of TEGOtrant solution; here 0.005 mol/L
100: conversion factor for 100 g
t_{TEGO}: titer of TEGOtrant solution
m_{Sample}: sample size in g

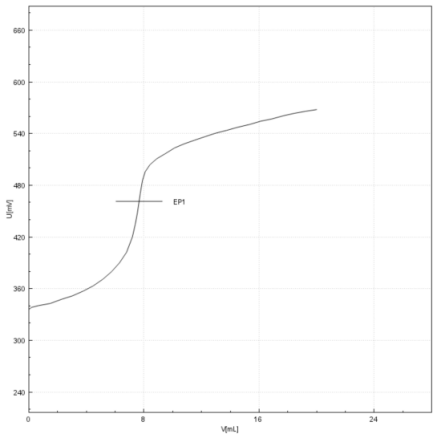
Soaps

$$b_{total} = \frac{V_{EP1} \cdot c_{TEGO} \cdot 100 \cdot t_{TEGO}}{m_{Sample}} - CV01$$

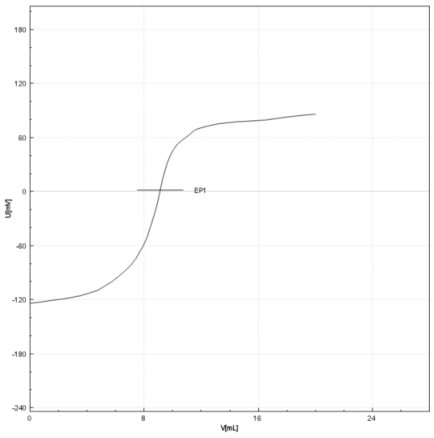
b_{total}: molality of anionic surfactants and soaps in mmol/100 g
V_{EP1}: consumption of titrant up to the first equivalence point in mL.
c_{TEGO}: concentration of TEGOtrant solution; here 0.005 mol/L
100: conversion factor for 100 g
t_{TEGO}: titer of TEGOtrant solution
m_{Sample}: sample size in g
CV01: value obtained from calculation Anionic surfactants

Example curve

Anionic Surfactants



Anionic Surfactants and Soaps



Results

Anionic Surfactants

Mean value (n = 3)	19.00 mmol/g
s(abs)	0.33 mmol/g
s(rel)	1.71%

Soaps

Mean value (n = 3)	4.44 mmol/g
s(abs)	0.06 mmol/g
s(rel)	1.24%

Comments

- Store the Surfactrode Refill dry when not in use.
- Should the titration curve flatten, refilling of the indicator electrode with the Surfactrode refill paste 6.2319.000 and the Filling tool 6.2826.010 is recommended. This guarantees almost unlimited lifetime.
- The titrant consumption should be about 10 mL to increase the precision of your results.
- It is recommended to work in a fume hood or to work with a closed titration vessel, to avoid odour nuisance by MIBK.
- The stirrer has to be set to a very high stirring rate. Otherwise, the two phases will not be mixed thoroughly.
- Determine the titer according to ***Method_9***.
- Do not use higher concentrations of TEGOtrant because then the stoichiometry of 1:1 is no longer given.
- For adjusting the pH value a pH meter, a pH paper or the manual control of the Eco Titrator can be used. Make sure the electrode is calibrated before use.
- TEGOadd was developed in particular for surfactant titrations using the Solvotrode Resistant electrode. This additive has a positive influence on the whole course of titration, especially in the region of inflection and keeps the electrode clean.

31. Surf – Anionic surfactants in dishwashing con centrates by potentiometric aqueous titration

Summary

Synthetic soaps and dishwashing concentrates often contain betains; Betains behave like cationic surfactants if the solution is acidified too much. This means that they partially cancel out the anionic surfactants and low-bias results are obtained.

Solutions

Titrant c(TEGOtrant) = 0.005 mol/L	Weigh approx. 2.2 g TEGOtrant into a 1 L volumetric flask and add 150 mL deionized water. After dissolution, fill the solution up to the mark with deionized water. Make sure that no foam is present anymore.
Buffer pH 3	Should be bought from a supplier.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Ionic Surfactant electrode	6.0507.120
LL ISE Reference electrode	6.0750.100

Sample preparation

Depending on the concentration of anionic surfactants, weigh 0.5 – 1 g sample into a 100 mL volumetric flask and fill it up to the mark with deionized water. Make sure, that the solution does not contain any foam.

System configuration

1. Load the method ***Method_31*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***TEGO_0.005*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***Ionic Surf*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as described under ***Analysis***

Analysis

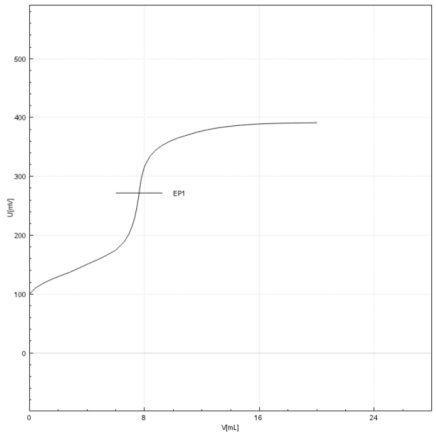
Pipette 10 mL of the prepared solution into a 100 mL beaker and add 10 mL buffer pH = 3, 40 mL deionized water and 10 mL methanol. Press start, enter all requested sample data and carry out the titration with c(TEGOtrant) = 0.005 mol/ until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$b_{A\text{-}Surf} = \frac{V_{EP1} \cdot c_{TEGO} \cdot 100 \cdot t_{TEGO}}{m_{Sample}}$$

$b_{A\text{-}Surf}$:	molality of anionic surfactants in mmol/100 g
V_{EP1}:	consumption of titrant up to the first equivalence point in mL
c_{TEGO}:	concentration of TEGOtrant solution; here 0.005 mol/L
100:	conversion factor for 100 g
t_{TEGO}:	titer of TEGOtrant solution
m_{Sample}:	sample size in g

Example curve



Results

Mean value (n = 3)	36.96 mmol/100 g
s(abs)	0.11 mmol/100 g
s(rel)	0.11%

Comments

- Store the Ionic Surfactant electrode dry when not in use.
- The titrant consumption should be about 10 mL to increase the precision of your results.
- Products analyzed here often contain α-olefin sulfates or secondary alkane sulfonates which lead to higher results. If such surfactants are present, it is recommended to use the two-phase titration method.
- The Ionic Surfactant electrode is not solvent resistant. Chloroform, hydrocarbons, acetone, MIBK, tetrahydrofuran, etc. destroy the electrode. High proportions of methanol (30 – 40%) or ethanol (20%) in the solvent shorten the lifetime of the electrode.
- To condition the electrode, carry out 2 – 3 sample titration, discarding the obtained results.
- Remove adherent deposits with a soft paper towel, moistened in methanol.
- Determine the titer according to ***Method_9***.
- Methanol is added to prevent foam formation.

32. Surf – Cationic surfactants in mouth rinses by potentiometric aqueous titration

Summary

In mouthwashes and gargling solutions, cetylpyridinium chloride monohydrate is mostly used as cationic surfactant and disinfectant (approx. 20 – 50 mg/100 mL). Further possible ingredients are ethanol (10 – 20%), methyl salicylate, menthol, polysorbate, peppermint oil, saccharin and sodium benzoate, just to mention a few. The titration curves obtained by this type of titration are flat in most cases and difficult to evaluate.

Solutions

Titrant c(SDS) = 0.005 mol/L	Dry approx. 2 g SDS at 105°C overnight and allow to cool down in a desiccator. Afterwards, weigh 1.4535 g SDS into a 1 L volumetric flask and dissolve it in about 150 mL deionized water. Add 10 mL w(form-aldehyde) = 35% and fill the solution to the mark with deionized water.
Buffer pH 3	Should be bought from a supplier.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Ionic Surfactant electrode	6.0507.120
LL ISE Reference electrode	6.0750.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_32*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***SDS_0.005*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***Ionic Surf*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as described under ***Analysis***

Analysis

Prepare the cylinder unit after allowing the solution to stand overnight. Pipette 40 mL sample into a 150 mL beaker and add 10 mL methanol, 10 mL buffer pH 3 and 40 mL deionized water. Press start, enter all requested sample data and titrate with c(SDS) = 0.005 mol/ until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$\beta_{CPC} = \frac{V_{EP1} \cdot c_{SDS} \cdot 100 \cdot t_{SDS} \cdot M_{CPC}}{V_{Sample}}$$

β_{CPC}: mass concentration of cetylpyridinium chloride in mg/100 mL

V_{EP1}: consumption of titrant up to the first equivalence point in mL

c_{SDS}: concentration of sodium lauryl sulfate solution; here 0.005 mol/L

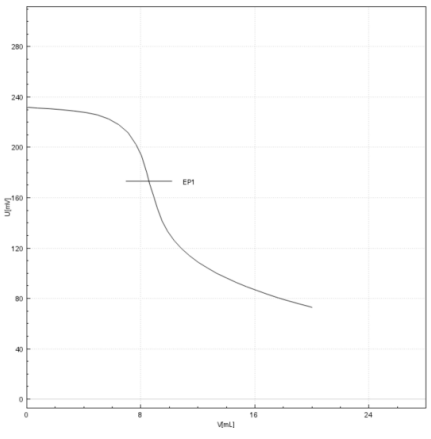
100: conversion factor for 100 mL

t_{SDS}: titer of sodium lauryl sulfate solution

M_{CPC}: molar mass of cetylpyridinium chloride monohydrate; 358.01 g/mol

V_{Sample}: sample size in mL

Example curve



Results

Mean value (n = 3)	31.58 mg/100 mL
s(abs)	0.59 mg/100 mL
s(rel)	1.88%

Comments

- Store the Ionic Surfactant electrode dry when not in use.
- To obtain more precise results, it is recommended to have a titrant consumption of about 10 mL.
- The Ionic Surfactant electrode is not solvent resistant. Chloroform, hydrocarbons, acetone, MIBK, tetrahydrofuran, etc. destroy the electrode. High proportions of methanol (30 – 40%) or ethanol (20%) in the solvent shorten the lifetime of the electrode.
- To condition the electrode, carry out 2 – 3 sample titration, discarding the obtained results.
- Remove adherent deposits with a soft paper towel, moistened in methanol.
- Determine the titer according to ***Method_10***.

33. Surf – Cationic surfactants in hair conditioners by potentiometric two-phase titration

Summary

Hair conditioner often contains relatively large amounts of higher fatty alcohols (cetyl and stearyl alcohol) and cellulose derivatives. The cationic surfactants are partially adsorbed on these compounds and are difficult to titrate in aqueous solution as it results in very long titration times. For this reason potentiometric two-phase titration is to be preferred.

Solutions

Titrant c(SDS) = 0.005 mol/L	Dry approx. 2 g SDS at 105°C overnight and allow to cool down in a desiccator. Afterwards, weigh 1.4535 g SDS into a 1 L volumetric flask and dissolve it in about 150 mL deionized water. Add 10 mL w(formaldehyde) = 35% and fill the solution to the mark with deionized water.
TEGOadd	Metrohm article no. 6.2317.120
c(HCl) = 0.5 mol/L	Weigh 49.3 g w(HCl) = 37% into a 1 L volumetric flask containing already 500 mL deionized water. Allow to cool down, then make up the solution to the mark with deionized water.
Solvent mixture Methyl isobutyl ketone : ethanol (1:1 (v:v))	Transfer 500 mL MIBK and 500 mL ethanol into a glass bottle and mix thoroughly.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Surfactrode Refill electrode	6.0507.140
LL ISE Reference electrode	6.0750.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_33*** from the USB Stick under *System* → *File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***SDS_0.005*** to the solution list under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***Surf Refill*** to the sensor list under *System* → *Sensors.*
5. Prepare the sample solution as described under ***Analysis***

Analysis

Prepare the cylinder unit after allowing the solution to stand overnight. Weigh approx. 1 g sample into a 100 mL closed titration beaker (e.g., 6.01406.220) and add 20 mL solvent mixture and 70 mL deionized water. Adjust the pH with c(HCl) = 0.5 mol/L to pH 3 and then add 0.2 mL TEGOadd. Press start, enter all requested sample data and titrate with c(SDS) = 0.005 mol/ until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$b_{C\text{-}Surf} = \frac{V_{EP1} \cdot c_{SDS} \cdot 100 \cdot t_{SDS}}{m_{Sample}}$$

$b_{C\text{-}Surf}$: molality of cationic surfactants in mmol/100 g

V_{EP1}: consumption of titrant up to the first equivalence point in mL

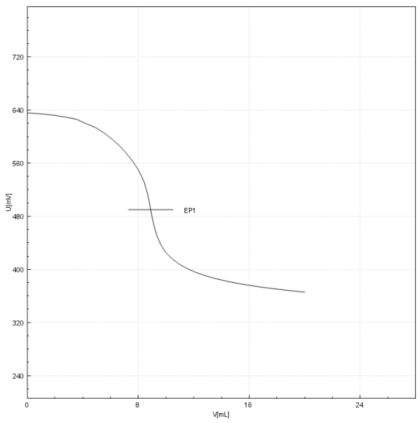
c_{SDS}: concentration of sodium lauryl sulfate solution; here 0.005 mol/L

100: conversion factor for 100 g

t_{SDS}: titer of sodium lauryl sulfate solution

m_{Sample}: sample size in g

Example curve



Results

Mean value (n = 3)	7.0000 mmol/g
s(abs)	0.0730 mmol/g
s(rel)	1.04%

Comments

- Store the Surfactrode Refill dry when not in use.
- Should the titration curve flatten, it is recommended to freshly fill the Surfactrode Refill with Refill paste 6.2319.000 using the Filling tool 6.2826.010. This guarantees almost unlimited lifetime.
- To obtain more precise results, it is recommended to have a titrant consumption of about 10 mL.
- The concentration is given in mmol/g. If the kind of surfactant and therefore, its molar mass is known content can also be calculated in %.
- For adjusting the pH value a pH meter, a pH paper or the manual control of the Eco Titrator may be used. Make sure the electrode is calibrated before use.
- Determine the titer according to ***Method_10***.

34. Surf – Nonionic surfactants in wool shampoo

Summary

Wool shampoos are mild liquid washing agents for wool and silk. They normally contain up to 5% non-ionic surfactant. Other additives are primarily amphoteric surfactants (up to 5%) and anionic surfactants (10 – 30%). Sodium lauryl sulfates do not interfere. However, if lauryl ether sulfates with an average of more than 3 polyoxyethylene (POE) units are used in these formulations then the interferences increase as the number of POE units increases. Such anionic surfactants are also titrated and feint an increased nonionic surfactant content. As the total amount is determined, the only possibility to determine the NIO content is the anionic surfactants separately and to subtract the anionic content from the content determined during this analysis.

Solutions

Titrant c(STPB) = 0.01 mol/L	Weigh 3.4223 g sodium tetraphenyl borate into a beaker and dissolve it in about 300 mL deionized water. Prepare a second beaker where 10 g polyvinyl alcohol (PVA) is dissolved under heating in 300 mL deionized water. Allow the PVA solution to cool down. Afterwards, transfer both solutions into a 1 L volumetric flask and add 10 mL buffer pH 10. Mix the solution well and fill it up to the mark with deionized water
Auxiliary solution c($BaCl_2$) = 0.1 mol/L	Transfer 21 g $BaCl_2$ into a 1 L volumetric flask, dissolve it and fill it up to the mark with deionized water.
c(CH_3COOH) = 2 mol/L	Transfer 120.1 g glacial acetic acid into a 1 L volumetric flask and fill it up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

NIO Surfactant electrode	6.0507.010
LL ISE Reference electrode	6.0750.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_34*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***STPB_0.01*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***NIO Surf*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as described under ***Analysis***

Analysis

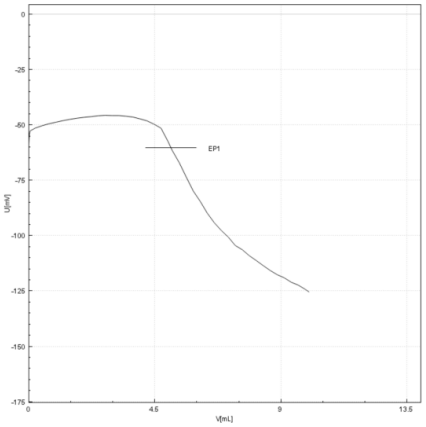
Prepare the cylinder unit after allowing the solution to stand overnight. Weigh approx. 1 g sample into a 150 mL beaker and dissolve it in about 80 mL deionized water. Adjust the pH with c(CH_3COOH) = 2 mol/L to approx. pH 4 and add 10 mL c($BaCl_2$) = 0.1 mol/L. Press start, enter all requested sample data and titrate with c(STPB) = 0.01 mol/ until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$b_{NIO\text{-}Surf} = \frac{V_{EP1} \cdot c_{STPB} \cdot 100 \cdot t_{STPB}}{m_{Sample}}$$

$b_{NIO\text{-}Surf}$:	molality of nonionic surfactants in mmol/100 g
V_{EP1}:	consumption of titrant up to the first equivalence point in mL
c_{STPB}:	concentration of STPB solution; here 0.005 mol/L
100:	conversion factor for 100 mmol/100 g
t_{STPB}:	titer calibration factor of STPB solution
m_{Sample}:	sample size in g

Example curve



Results

Mean value (n = 3)	18.47 mmol/100g
s(abs)	0.25 mmol/100g
s(rel)	1.35%

Comments

- Store the NIO Surfactant electrode dry when not in use.
- Barium is toxic. Dispose barium waste according to your local regulations.
- After each 2 – 3 titrations wipe the electrode with a tissue moistened with methanol.
- After dry storage, use the first 2 – 3 titrations for conditioning and discard the result.
- If NIO titrations are carried out frequently, store the electrode in w(Polyethylene glycol 1000, PEG) = 1% and the electrode is directly ready to use.
- For adjusting the pH value a pH meter, a pH paper or the manual control of the Eco Titrator may be used. Make sure the electrode is calibrated before use.
- Determine the calibration factor according to ***Method_11***.

35. Plate – Determination of the silver content in pure silver

Summary

The knowledge of the purity of silver used for jewelry is very important to ensure its quality. Therefore, the determination procedure is regulated internationally and nationally. A common approach is the titration with potassium bromide after an acidic digestion of the silver using a silver electrode for indication.

Solutions

Titrant c(KBr) = 0.1 mol/L	Weigh 11.901 g dried KBr into a 1 L volumetric flask and dissolve it in deionized water. Fill the flask up to the mark with deionized water.
$c(HNO_3)$ = 33%	Transfer 508 g $c(HNO_3)$ = 65% into a 1 L volumetric flask already containing 300 mL deionized water. Allow to cool down, and fill up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Ag Titrode with AgBr coating	6.00430.100Br

Sample preparation

Weigh 300 up to 500 mg silver into a 100 mL titration beaker and add 5 mL $w(HNO_3)$ = 33%. Heat the suspension slowly until the evolution of nitrous gases disappears.

System configuration

1. Load the method ***Method_35*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***KBr_0.1*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***Ag Titrode*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as described under ***Analysis***

Analysis

After allowing to cool down, add as much deionized water as needed to immerse the electrode to the prepared sample solution press start and enter all requested sample data. Titrate with c(KBr) = 0.1 mol/ until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$w_{Ag} = \frac{V_{EP1} \cdot c_{KBr} \cdot 100 \cdot t_{KBr}}{m_{Sample}}$$

w_{Ag}: Purity of silver in %

V_{EP1}: consumption of titrant up to the first equivalence point in mL

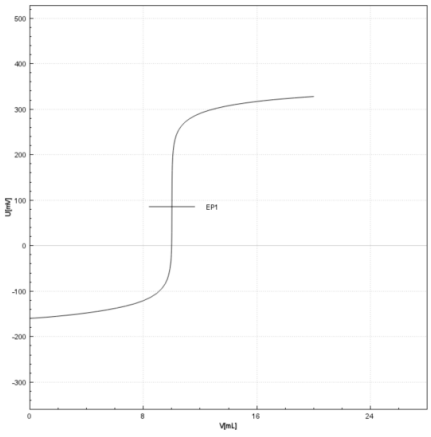
c_{KBr}: concentration of potassium bromide solution; here 0.1 mol/L

100: conversion factor for %

t_{KBr}: titer of potassium bromide solution

m_{Sample}: sample size in mg

Example curve



Results

Mean value (n = 3)	99.91%
s(abs)	0.16%
s(rel)	0.16%

Comments

- Store the Ag Titrode in deionized water to ensure that the hydration layer of the glass membrane stays intact and the electrode is ready to use.
- You must not polish the silver ring with abrasives if the ring is coated, as otherwise the coating will be removed.
- This procedure follows the standard EN ISO 11427.
- Heat the solution in a fume hood. Nitrous gases are toxic and should not be inhaled. These gases can also be absorbed by using a gas wash flask filled with water or sodium hydroxide solution.
- Determine the titer according to ***Method_12***.

36. Plate – Potentiometric determination of copper in copper bath

Summary

Copper baths are used to copper various items. They are present in an alkaline and acidic form. For the alkaline bath, normally cyanide is added whereas sulfuric acid is present when the bath is acidic. To analyze alkaline bathes the sample has to be acidified. This may result in a release of HCN, which must not be inhaled. Therefore, it is mandatory that the titration is carried out in a fume hood.

Solutions

Titrant $c(Na_2S_2O_3)$ = 0.1 mol/L	Should be bought from a supplier.
$c(H_2SO_4)$ = 2 mol/L	Transfer 200 g $c(H_2SO_4)$ = 98% into a 1 L volumetric flask already containing 500 mL deionized water. Allow to cool down, then fill the solution up to the mark with deionized water.
Auxiliary solution w(KI) = 10% + w(KSCN) = 20%	Weigh 10 g KI and 20 g KSCN into a 100 mL volumetric flask, dissolve it and fill it up to the mark with deionized water. Protect the solution from light.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Pt Titrode	6.0431.100

Sample preparation

No sample preparation is required.

System configuration

1. Load the method ***Method_36*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***Na2S2O3_0.1*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***Pt Titrode*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as described under ***Analysis***

Analysis

Pipette 1 mL bath sample into a 150 mL beaker and dilute it with 60 mL deionized water. Add 10 mL of the auxiliary solution and 10 mL of $c(H_2SO_4)$ = 2 mol/L. Press start, enter all requested sample data and titrate the generated iodine with $c(Na_2S_2O_3)$ = 0.1 mol/L until after the first equivalent point. All other parameters and calculations are already defined within the method.

Calculation

$$\beta_{Cu} = \frac{V_{EP1} \cdot c_{Na2S2O3} \cdot t_{Na2S2O3} \cdot M_{Cu}}{V_{Sample}}$$

β_{Cu}: mass concentration of copper in g/L

V_{EP1}: consumption of titrant up to the first equivalence point in mL

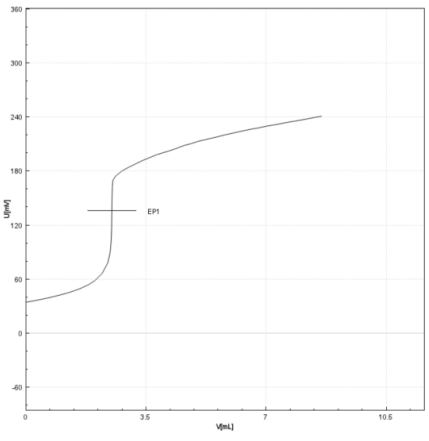
$c_{Na2S2O3}$: concentration of sodium thiosulfate solution; here 0.1 mol/L

$t_{Na2S2O3}$: titer of sodium thiosulfate solution

M_{Cu}: molar mass of copper; 63.55 g/mol

V_{Sample}: sample size in mL

Example curve



Results

Mean value (n = 3)	15.98 g/L
s(abs)	0.034 g/L
s(rel)	0.21%

Comments

- Store the Pt Titrode in deionized water to ensure that the hydration layer of the glass membrane stays intact and the electrode is ready to use.
- Copper can also be determined by a complexometric titration using EDTA as titrant.
- Determine the titer according to ***Method_6***.

37. Plate – Photometric determination of the zinc content

Summary

In alkaline cyanide baths zinc is present as a mixture of $Na_2Zn(CN)_4$ and Na_2ZnO_2 complexes and it is not amenable to direct potentiometric titration. Sulfuric acid destroys these complexes and converts them to $ZnSO_4$ – after this, titration can be performed with Na_2EDTA

Solutions

Titrant $c(Na_2EDTA) = 0.1$ mol/L	Should be bought from a supplier.
$c(H_2SO_4) = 25\%$	Transfer 255 g $w(H_2SO_4) = 98\%$ into a 1 L volumetric flask, already containing 400 mL deionized water. Allow to cool down, then fill the solution up to the mark with deionized water.
c(NaOH) = 2 mol/L	Dissolve 80 g NaOH pellets in approx. 500 mL deionized water, allow to cool to room temperature and fill it up to the mark with deionized water.
Buffer pH 10	Transfer 54 g NH_4Cl and 350 mL $w(NH_3) = 25\%$ into a 1 L volumetric flask, dissolve it and filled to the mark with deionized water.
Indicator solution: Eriochrome black T	Weigh 100 mg Eriochrome black T and 100 mg ascorbic acid into a 100 mL volumetric flask and fill it up to the mark with deionized water.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

Optrode	6.1115.000

Sample preparation

Pipette 10 mL bath sample into a 100 mL Erlenmeyer flask and add 20 mL $w(H_2SO_4) = 25\%$. Heat the solution and boil it for 3 – 5 min. Allow to cool down, then transfer the solution into a 100 mL volumetric flask and fill it up to the mark with deionized water.

System configuration

1. Load the method ***Method_37*** from the USB Stick under *System* → *File management*.
2. Load the corresponding method in the home screen.
3. Add the solution ***EDTA_0.1*** to the solution list under *System* → *Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***Optrode*** to the sensor list under *System* → *Sensors*.
5. Prepare the sample solution as described under ***Analysis***

Analysis

Pipette 10 mL of the prepared sample solution into the beaker and add approx. 30 mL deionized water. Adjust to pH 4 with c(NaOH) = 2 mol/L, then add 0.5 mL indicator solution and 10 mL buffer pH 10. Press start, enter all requested sample data and titrate the solution with $c(NA_2EDTA) = 0.1$ mol/L until after the first equivalence point. All other parameters and calculations are already defined within the method.

Calculation

$$\beta_{Zn} = \frac{V_{EP1} \cdot c_{EDTA} \cdot t_{EDTA} \cdot M_{Zn}}{V_{Sample}}$$

β_{Zn}: mass concentration of zinc in g/L

V_{EP1}: consumption of titrant up to the first equivalence point

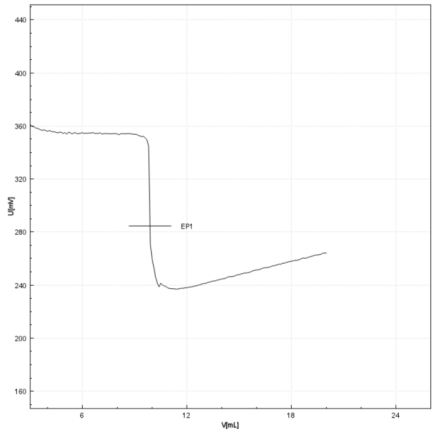
c_{EDTA}: concentration of EDTA solution; here 0.1 mol/L

t_{EDTA}: titer of EDTA solution

M_{Zn}: molar mass of copper; 65.38 g/mol

V_{Sample}: sample size in mL; here 1 mL

Example curve



Results

Mean value (n = 3)	6.489 g/L
s(abs)	0.007
s(rel)	0.11%

Comments

- The Optrode is used to indicate a change of color of the solution, but it can only be use for clear solutions.
- If the samples are turbid, they can be filtered before the analysis.
- Eriochrome Black T can be used as a solution or as a solid mixed with NaCl (1:100). In case the solid form is used, a small amount (tip of a spatula) of the mixture is added to solution prior to analysis.
- Zinc is often present in complexes. They can be destroyed by boiling the solution with sulfuric acid.
- Determine the titer according to ***Method_1***. Use calconcarbonic acid as indicator.

38. Plate – Simultaneous determination of HNO_3, H_3PO_4 and CH_3COOH

Summary

In the electroplating industry, the galvanization has to take place under certain conditions. One of these parameters is the right acid or base content of the bathes. In this example the determination of nitric acid, phosphoric adic and acetic acid is shown, where the nitric acid content is very low compared to the other two.

Solutions

Titrant c(NaOH) = 1 mol/L	Should be bought from a supplier.
c(TBAOH) = 0.1 mol/L in methanol	Should be bought from a supplier.

Cylinder unit

Eco Cylinder unit 20 mL	6.03002.220

Sensors

LL Solvotrode easyClean	6.0229.010
Ecotrode plus	6.0262.100

Sample preparation

No sample preparation is required.

System configuration

Non-aqueous titration

1. Load the method ***Method_38.1*** from the USB Stick under *System → File management.*
2. Load the corresponding method in the home screen.
3. Add the solution ***TBAOH_0.1*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
4. Add the ***Solvotrode*** to the sensor list under *System → Sensors.*
5. Prepare the sample solution as described under ***Analysis***

Aqueous titration

1. Load the method ***Method_38.2*** from the USB Stick under *System → File management.*
2. Add the solution ***NaOH_1.0*** to the solution list under *System → Solutions* and enter all necessary solution data like concentration and cylinder unit volume.
3. Add the ***Ecotrode*** to the sensor list under *System → Sensors.*
4. Add under ***System → Common Variables*** the ***titer*** of the TBAOH_0.1 solution to ***CV02*** and the ***concentration*** of the TBAOH_0.1 solution to ***CV03***.
5. Prepare the sample solution as described under ***Analysis***

Analysis

Non-aqueous titration

Pipette 1 mL sample solution into the 100 mL titration beaker and dilute it with 60 mL methanol. Press start, enter all requested sample data and titrate the solution with c(TBAOH) = 0.1 mol/L in methanol until after the first equivalence point. All other parameters and calculations are already defined within the method. The mean value is automatically saved as CV01.

Aqueous titration

Pipette 0.5 mL of the sample into the 100 mL titration beaker and add 60 mL deionized water. Press start, enter all requested sample data and titrate the solution with c(NaOH) = 0.1 mol/L until after the third equivalence point. All other parameters and calculations are already defined within the method.

Calculation

Nitric acid

$$\beta_{HNO3} = \frac{V_{EP1,\,naq} \cdot c_{TBAOH} \cdot t_{TBAOH} \cdot M_{HNO3}}{V_{Sample}}$$

β_{HNO3}: mass concentration of nitric acid in g/L

$V_{EP1,\,naq}$: consumption of titrant up to the first equivalence point from non-aqueous titration in mL

c_{TBAOH}: concentration of TBAOH solution; here 0.1 mol/L

t_{TBAOH}: titer of TBAOH solution

M_{HNO3}: molar mass of nitric acid; 63.01 g/mol

V_{Sample}: sample size in mL; here 1 mL

Phosphoric acid

$$n_{H3PO4} = (V_{EP1,aq} \cdot c_{NaOH} \cdot t_{NaOH} - CV01 \cdot CV02 \cdot CV03)$$

n_{H3PO4}: amount of phosphoric acid in mmol
$V_{EP1,aq}$: consumption of titrant up to the first equivalence point of the aqueous titration in mL
c_{NaOH}: concentration of sodium hydroxide solution; here 1 mol/L
t_{NaOH}: titer of sodium hydroxide solution
CV01: mean consumption of titrant up to the first equivalence point of the non-aqueous titration in mL
CV02: concentration of TBAOH solution; here 0.1 mol/L
CV03: titer of TBAOH solution

$$\beta_{H3PO4} = \frac{n_{H3PO4} \cdot M_{H3PO4}}{V_{Sample}}$$

β_{H3PO4}: mass concentration of phosphoric acid in g/L
n_{H3PO4}: amount of phosphoric acid in mmol
M_{H3PO4}: molar mass of phosphoric acid; 97.99 g/mol
V_{Sample}: sample size in mL; here 0.5 mL

Acetic acid

$$n_{HAc} = (V_{EP3,aq} \cdot c_{NaOH} \cdot t_{NaOH} - 2 \cdot V_{EP1,aq} \cdot t_{NaOH} \cdot c_{NaOH} - CV01 \cdot CV02 \cdot CV03)$$

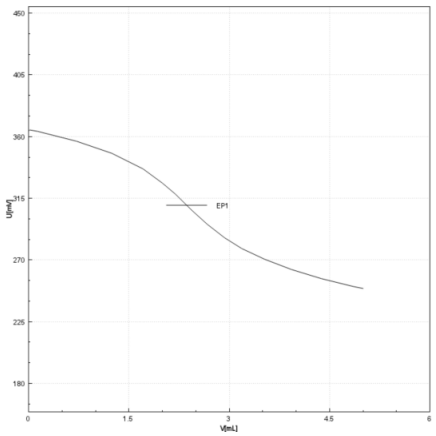
n_{HAc}: amount of acetic acid in mmol
$V_{EP3,aq}$: consumption of titrant up to the third equivalence point of the aqueous titration in mL
c_{NaOH}: concentration of sodium hydroxide solution; here 1 mol/L
t_{NaOH}: titer of sodium hydroxide solution
2: stoichiometric factor
$V_{EP1,aq}$: consumption of titrant of the aqueous titration in mL
c_{NaOH}: concentration of sodium hydroxide solution; here 1 mol/L
t_{NaOH}: titer of sodium hydroxide solution
CV01: titrant consumption of the non-aqueous titration in mL
CV02: concentration of TBAOH solution; here 0.1 mol/L
CV03: titer of TBAOH solution

$$\beta_{HAc} = \frac{n_{HAc} \cdot M_{H3PO4}}{V_{Sample}}$$

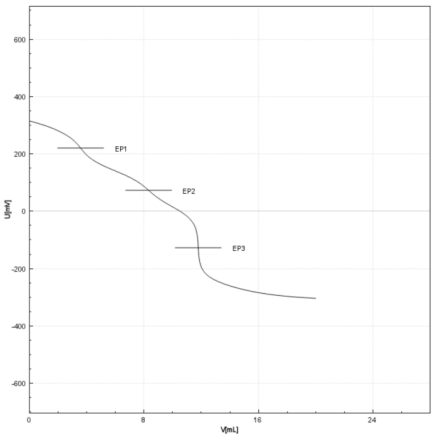
β_{HAc}: mass concentration of acetic acid in g/L
n_{HAc}: amount of actic acid in mmol
M_{H3PO4}: molar mass of actic acid 60.05 g/mol
V_{Sample}: sample size in mL; here 0.5 mL

Example curve

Non-aqueous titration



Aqueous titration



Results

Nitric acid

Mean value (n = 3)	14.80 g/L
s(abs)	0.09 g/L
s(rel)	0.62%

Phosphoric acid

Mean value (n = 3)	647.73 g/L
s(abs)	5.35 g/L
s(rel)	0.82%

Acetic acid

Mean value (n = 3)	526.63 g/L
s(abs)	3.02 g/L
s(rel)	0.57%

Comments

- This determination works only if the nitric acid concentration is much lower as the concentration of the other two acids. In the example determination the concentrations were as follows:
  $\beta(HNO_3)$ = 14.1 g/L
  $\beta(H_3PO_4)$ = 650 g/L
  $\beta(CH_3COOH)$ = 525 g/L
- The third equivalence point is used for evaluation as the potential jump is steeper as for the second equivalence point.
- Store the Solvotrode easyClean in the corresponding electrolyte if not in use.
- Store the Ecotrode plus in 6.2323.000 Storage solution to ensure a fast response time.
- Determine the titer of the TBAOH solution according to ***Method_8***.
- Determine the titer of the NaOH solution according to ***Method_2***.

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Subject to change
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