Monograph

Practical Titration

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Metrohm

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Training Manual for Titrimetric Volumetric Analysis

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Preface

Recently a college lecturer was told that in the Geological Institute of a University the determinations of content were basically to be carried out by instrumental methods alone, for example atomic spectroscopy. The «old-fashioned» wet chemistry was no longer to be used. How good it is that students with experience in industrial laboratories can inform their teachers during their courses about all the applications in which the «old-fashioned» but still young titration method is being used in practice today.

This small book is based on the many years of experience gained by Metrohm in the development of instruments and applications. Peter Bruttel and Marcus von Kloeden have worked out the applications and collected them. The Europa Fachhochschule Fresenius (EFF) Idstein, Germany, previously the Chemieschule Fresenius Wiesbaden, can look back on more than 150 years of practice-oriented teaching. Students of the EFF have tried out the practical examples. Since 1981 Leo Gros has taught analytical techniques at the EFF. Marcus von Kloeden was one of his students and became acquainted with Metrohm during a practical course abroad. The authors would like to thank Jan Volker Geil, Vice President, Metrohm Ltd., and himself a graduate of the EFF, for the many different ways in which he supported this project, as well as the EFF students Kevin Müller and Volker Beenders, who carried out the titrations. The authors would like to thank Heinz Gorbauch, their collegue of the Fresenius Institute and graduate of the EFF for his critical reading and additional remarks.

This «Tutorial» is primarily intended for training purposes but can also, of course, be used to advantage in any laboratory. It is intended to explain the theory in a simple manner and, by using practical examples, demonstrate just how versatile and accurate titrimetric analyses are. The individual methods and procedures also provide the reader with many useful tips and explanations. This book is a practical manual – not a detailed textbook – and cannot and will not replace textbooks (see list of literature references in the Appendix)! Nevertheless, in order to be able to understand the practical applications better, some of the theory concerning types of reaction, substances and methods is briefly presented.

The titrations can be carried out with any Metrohm titrator (Titrando, Titrino, Titroprocessor) as a matter of course.

Safety aspects

Please note that this manual contains no information about the dangers related to the toxicity of the chemicals used nor about their disposal and handling. Please obtain the necessary knowledge from other sources. The chemicals used can be obtained from any qualified supplier. Any mention of manufacturers in the practical part is just meant to indicate with which chemicals the experiments were carried out.

We hope that you will have a lot of pleasure and success with your work,

Your Metrohm Ltd. and Europa Fachhochschule Fresenius (EFF)

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I. 1 Introduction: titration means counting!

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

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

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

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

- Titration is one of the absolute content determination methods, i.e. the result of the analysis provides direct information about the amount of substance to be determined, without instrument or method-specific factors having to be calibrated (such as is normal in relative methods, for example HPLC, atomic spectroscopy or UV/VIS photometry).
- Titrations are easy to carry out: The equipment and the procedures to be performed are simple. They are easy to understand – the fundamentals of titrimetric methods are widely known or can be learned in a short time.
- Titrations are carried out rapidly: If the total time for setting up the workplace to obtaining the analytical result is taken into consideration, then titrimetric determinations require much less time than other methods.
- Titration is a versatile method: Numerous titration methods have been drawn up, these range from the determination of inorganic ions up to the determination of complex organic compounds. The analyte concentrations can range from 100% or virtually 100% (analysis of ultrapure substances, purity determinations) down to the ppm range. Sample amounts of a few micrograms are adequate, amounts in the gram range are also possible.
- Titration supplies highly reproducible and correct results. A typical reproducibility is <1%. In high-precision titrations values of 0.1% are demanded and also achieved. For such demands the accuracy should lie within the limits of the standard deviation.
- Titrations can be automated: Titrimetric determinations can be automated to a high degree. This means that, for example, they are suitable for analyzing the content in routine operation (e.g. active ingredient content in tablets).
- Titrations are economical: Compared with other analytical methods, the costs are favorable – the price/performance ratio is excellent. An example: pH and total acidity in fruit juice; 20 titrations per day (or 4500 p.a.); Titrino complete with accessories, approx. Euro 4200. Investment costs per titration with one year pay-back time for the purchase = approx. 95 cts.

Important symbols used in the methods:

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

I. 2 Titration reactions

I.2.1 Acid-base reactions

The term acid-base has been revised several times since the18th century in accordance with the state of knowledge:

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

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

- Brønstedt defined the acid-base reaction as the exchange of protons. The acid acts as proton donor and the base as proton acceptor. A deprotonated acid is called the conjugate base and a protonated base is called the conjugate acid. In this way the theory can also be applied without any problem to ampholytes, salts and prototropes of non-aqueous solvents. The equilibrium constants of the reactions allow a quantitative reactivity series of acids and bases to be drawn up (see below).
- Lewis extended the Brønstedt theory. A Lewis base has a free electron pair, a Lewis acid an electron pair gap. Lewis acid and Lewis base react to form a covalent or coordinative compound. Examples:

$$2\ CN^- + Ag^+ \rightarrow [Ag(CN)_2]^-$$
$$2\ Cl^- + SnCl_4 \rightarrow [SnCl_6]^{2-}$$

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

Protolysis

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

Example water: $2\ H_2O \rightleftharpoons H_3O^+ + OH^-$

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

According to the law of mass action, the ionic product of water K_w is calculated as follows:

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

for H_2O this means:

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

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

The relative «strength» of an acid or base in an aqueous solution are described by the equilibrium constants. These provide information about the extent to which an acid or base dissolved in water at equilibrium can accept or donate protons. Water is the reference base for each acid and the reference acid for each base. These acidity and basicity constants are known as $\mathbf{K_a}$ and $\mathbf{K_b}$ respectively. We have simplified their formulation here by using the molar concentration instead of the activities of the participating species. The molar concentration of water in a mixture is regarded as being constant for dilute solutions (55.5 mol/L) and not included.

$$K_s = [H_3O^+] \bullet [S^-] / [HS]$$

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

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

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

$$H_2O,\ \text{neutral pH} = -\log \sqrt{K_W} = -\log \sqrt{10^{-14}}$$

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

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

Acid-base reactions with water

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

acidic reaction of solvent $\quad HB\ (s) + H_2O\ (b) \rightleftharpoons H_3O^+ + B^-$

basic reaction of solvent $\quad B^-\ (b) + H_2O\ (s) \rightleftharpoons HB + OH^-$

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

$$K_s \cdot K_b = K_w$$

$$pK_s + pK_b = pK_w = 14\ (25\ ^0C)$$

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

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

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

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

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

Protolytes

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

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

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

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

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

pK_a values of some selected acids		pK_b values of some selected bases	
Acids	**pK_a**	**Bases**	**pK_b**
Acetic acid	4.73	Acridine	9.89
Acrylic acid	4.26	Ammonia	4.75
Benzoic acid	4.20	Aniline	9.42
Boric acid	9.24	Benzylamine	4.62
Chloroacetic acid	2.81	Calcium hydroxide	1.30
Hydrobromic acid	approx. –6	Coffeine	13.39
Hydrochloric acid	approx. –3	Cyclohexylamine	3.36
Hydrocyanic acid	9.40	Diethanolamine	5.12
Hydrofluoric acid	3.14	Ethanolamine	4.56
Hydrogen sulfide acid 1st stage	6.90	Ethylamine	3.33
Hydrogen sulfide acid 2nd stage	12.9	Imidazole	7.00
Lactic acid	3.86	Lithium hydroxide	–0.10
Nitric acid	1.32	Magnesium hydroxide	3.36
Oxalic acid 1st stage	4.31	Naphthylamine	10.08
Oxalic acid 2nd stage	1.42	o-aminobenzoic acid	10.92
Perchloric acid	approx. –9	o-toluidine	9.61
Phenol	9.95	2-Picoline	7.52
Phosphoric acid 1st stage	1.96	Piperidine	2.80
Phosphoric acid 2nd stage	7.12	Pyridine	8.81
Phosphoric acid 3rd stage	12.36	Triethanolamine	6.23
Salicylic acid	2.98	Triethylamine	3.28
Sulfuric acid 1st stage	approx. –3	Trimethylamine	4.20
Sulfuric acid 2nd stage	1.92	Urea	13.8

Source: see literature reference 8.

The strongest acid in the list is $HClO_4$, the strongest base is lithium hydroxide.

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

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

$$HF < HCl < HBr < HI$$

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

$$HClO < HClO_2 < HClO_3 < HClO_4$$

$$H_2SiO_4 < H_3PO_4 < H_2SO_4 < HClO_4$$

Acid-base titrations

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

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

Example:

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

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

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

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

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

b) Titration of a weak acid with a strong base

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

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

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

c) Titration of a weak base with a strong acid

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

d) Titration of a weak acid with a weak base

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

e) Titration curve

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

I. 2.2 Precipitation reactions

Solubility and solubility product

The solubility of a dissociated sparingly soluble compound is determined by the maximum ionic product or solubility product K_L. This means that the product of the molar concentrations of the dissolved ions of a salt cannot be larger than the value K_L. In equilibrium this value becomes established when so much of the sparingly soluble compound is added to water that a precipitate is formed. This value is not exceeded even when the amount of precipitate is increased!

The solubility L is understood to be the total concentration of the substance in its saturated solution. For a binary hardly soluble salt the following applies:

$\{ A^+ B^- \} \rightleftharpoons A^+ + B^-$ and, approximately,

$c(A^+) \cdot c(B^-) = K_L$ (for the stoichiometric solubility product)

$L = c(AB)_{\text{dissolved}} = c(A^+) = c(B^-)$

$L = \sqrt{K_L}$

With AgCl as an example: $K_L = 10^{-10}$ mol²/L², $L = 10^{-5}$ mol/L

Precipitation only begins when the product of the molar concentrations of the dissolved ions A and B, the ionic product $c(A^+) \cdot c(B^-) > K_L$. Tables of solubility products show that the known K_L values of salts differ by many factors of ten and in aqueous solution for 1:1 electrolytes values between approx. 10^2 (e.g. NaOH) and 10^{-52} (e.g. HgS) are achieved. (For HgS this would mean that only 10^{-26} mol/L Hg should dissolve. However, the actual solubility is consid-

erably higher – precipitate aging, complex formation and other effects also play a role. Strictly speaking, the molar concentrations should also be replaced by the activities.)

The equations mentioned above only apply when the dissolved ions A^+ and B^- are in equilibrium with the precipitate. If one of the partners occurs in excess (isoionic addition), then the solubility depends on the ion with the lower concentration. With isoionic addition the solubility decreases – the solubility product is never exceeded. (This is why in gravimetry an excess of the precipitation reagent is always used.)

If foreign ions are added (foreign ion addition) the opposite takes place – the solubility increases. (In this case the coefficients of activity of all the ions present in solution – the total ionic strength – play a role.)

The determination limit for precipitation titrations depends very strongly on the solubility product. Concentrations below the solubility (the precipitation) can no longer be titrated. In some cases the solubility product can be reduced by the addition of an organic solvent (e.g. acetone or ethanol); this also results in a lower determination limit. (For chloride titration with $AgNO_3$ the determination limit in H_2O is approx. 3.5 mg/L; in glacial acetic acid, for example AOX determination, it is a few μg/L.)

Many precipitates formed during the titration are voluminous and inclusions could occur (sample ion and/or titrant). A more finely distributed precipitate, almost free from inclusions, is obtained by the addition of protective colloids (e.g. polyvinyl alcohol) or organic solvents (e.g. acetone or ethanol).

For $AgNO_3$ titrations Ag electrodes (Ag Titrode) are usually used for indication of the titrations, with ISEs usually being used for the determination of other ions.

In this monograph we are only concerned with substances that form sparingly soluble precipitates and can therefore be determined titrimetrically.

a) Inorganic compounds

Ion (analyte)	Titrant	Precipitation product
Ag^+	KBr	AgBr
Ba^{2+}	Na_2SO_4	$BaSO_4$
Bromide	$AgNO_3$	AgBr
Chloride	$AgNO_3$	AgCl
Cyanide	$AgNO_3$	AgCN
Fluoride	$La(NO_3)_3$	LaF_3
Iodide	$AgNO_3$	AgI
Sulfate	$BaCl_2$	$BaSO_4$
Sulfide	$AgNO_3$	Ag_2S
Thiocyanate	$AgNO_3$	AgSCN

In order to be able to titrate quantitatively the various ions present in a mixture, the differences between their solubility products must be at least three factors of ten. This means that the determination of bromide/chloride mixtures is only possible at a ratio of 1:1. If this ratio changes then problems occur or the ions can no longer be determined quantitatively in the mixture. (In contrast, chloride and iodide mixtures can be separated titrimetrically without any problems.)

The formation of precipitates from mixtures depends strictly on the solubility products of the individual components. The most sparingly soluble product is always titrated first, e.g. in the titration of halides with $AgNO_3$ the sequence is always iodide – bromide – chloride.

Solubility products of some selected substances at 25 °C *

Substance	K_L
$BaCO_3$	8.1×10^{-9} mol²/L²
$BaSO_4$	1.08×10^{-19} mol²/L²
CaF_2	3.95×10^{-11} mol³/L³
$CaC_2O_4 \times H_2O$	2.57×10^{-9} mol²/L²
$PbCrO_4$	1.77×10^{-14} mol²/L²
$PbSO_4$	1.06×10^{-8} mol²/L²
PbS	3.4×10^{-28} mol²/L²
AgBr	7.7×10^{-13} mol²/L²
Ag_2CO_3	6.15×10^{-12} mol³/L³
AgCl	1.56×10^{-10} mol²/L²
Ag_2CrO_4	9×10^{-12} mol³/L³
AgI	1.5×10^{-16} mol²/L²
AgSCN	1.16×10^{-12} mol²/L²
AgCN	2.2×10^{-12} mol²/L²
Ag_2S	1.6×10^{-49} mol³/L³
HgS	1×10^{-52} mol²/L²
Hg_2S	1×10^{-45} mol³/L³

Source: see literature reference 9.

* With most substances the solubility product increases as the temperature increases (more of the substance dissolves).

If a sensor (electrode) is used for the titration that responds to both the cation and the anion (ISE) then the titration curve is similar to that obtained for the titration of a strong acid with a strong base (pH electrode). This means that when the concentration changes by a factor of ten the electrode potential changes by approx. 59 mV (29 mV for z = 2). z corresponds to the valency, e.g. +2 for Ca. This also means that for the first 59 mV difference 90% of the ions to be determined have been titrated, for the second 59 mV difference 99% of the ions have already been titrated, etc.

The resulting titration curves are symmetrical, and the point of inflection of the curve corresponds to the equivalence point/titration endpoint.

Self-dissociation/solubility product and dilution must be taken into account in order to obtain the true endpoint. In most cases, however, the resulting systematic error is so small that it hardly affects the result. (The modern evaluation software of the Metrohm titrators at least takes the «dilution error» into account.)

b) Titration of surfactants

Surfactants – or surface-active substances – are compounds that consist of a long-chain hydrophobic group («tail») and a hydrophilic head group. In sufficient concentration in water they form aggregates (micelles), in whose hydrophobic «interior» lipophilic substances are

solubilized. Their effectiveness as detergents is based upon this fact, among others. Until about 1995 surfactants were titrated «manually» by the classical Epton method. This is an extraction titration (two-phase titration) with visual endpoint recognition. A chloroform/ethanol mixture is added to dissolve the sample, the pH adjusted to a particular value (usually with a buffer solution) and the titrant is added step by step. After each addition of titrant the solution is vigorously shaken and the ion associate formed (sample surfactant-titrant) is extracted in the organic phase. As soon as the titration endpoint has been reached, the added colored indicator also changes to the organic phase and the titration is finished. From this brief description of the titration it is not difficult to recognize that automation would be both very difficult and, if at all possible, unsatisfactory.

In the last few years Metrohm has concerned itself with this problem and can today offer complete solutions for anionic, cationic and nonionic surfactants. The solution to the problem is the use of ion-selective electrodes (ISEs) for the potentiometric indication of these titrations. It almost goes without saying that a single electrode is not sufficient to cover all the different possibilities and requirements. This is why Metrohm offers five different surfactant ISEs. This means that the customers can find «custom-made» solutions to their specific problems. The methods can be automated and – ever more important – also be validated.

As will be seen later, in surfactants only the active group is titrated. This means that the titrimetric separation of different surfactants of the same class (e.g. those with different chain lengths, such as are present in technical surfactants as a mixture of species of a homologous series) is not possible. It is always the total amount of surfactant of a class in the sample solution that is determined.

Techniques such as TLC and liquid chromatography must be used for the detection and determination of individual surfactants or for the analysis of mixtures of surfactants in detergents and hygiene products.

The main surfactant groups

a) Anionic surfactants and soaps (this is the largest and most frequently used of the main groups).

- Alkylbenzene sulfonates (LAS)
- Fatty alcohol sulfates (FAS)
- Fatty alcohol ether sulfates (FAES)
- Secondary alkane sulfonates
- α-Olefin sulfonates
- Isethionates
- Sulfosuccinates (mono- and di-esters)
- Taurides
- Soaps (fatty acid salts), lauroyl sarcosinates, ether carboxylic acids

b) Cationic surfactants

- ialkyldimethyl ammonium halides *
- Benzalkonium halides *
- Imidazolium quats **
- Esterquats **
- Fatty amines
- Fatty amine ethoxylates

* usually chlorides or bromides
** quat = quaternary ammonium compound

c) Amphoteric surfactants

Amphoteric surfactants have both an anionic and a cationic functional group. Depending on the pH value, one or the other becomes active. Amphoteric surfactants cannot be titrated – at least in formulations.

- Betaines
- Amphoglycinates
- Lauryl aminopropionic acid

d) Nonionic surfactants

- Alcohol ethoxylates
- Fatty alcohol ethoxylates
- Alkylphenol ethoxylates
- Fatty acid polyglycol esters
- Fatty acid alkanolamines
- Fatty amine ethoxylates
- Fatty acid glycerides (cannot be titrated)
- Sorbitan esters (cannot be titrated)
- Alkylpolyglycosides – sugar surfactants (cannot be titrated)

1. Ionic surfactants (anionic/cationic)

Anionic surfactants and cationic surfactants (and vice versa) form ion associates that are sparingly soluble in aqueous solution and precipitate. The worse the solubility of these associates, the more pronounced and steeper the titration curve. This is why the choice of titrant is very important. The pH of the solution to be titrated is also important as the surfactant-active head groups are protonated or deprotonated; this influences their hydrophilicity.

The choice of the correct electrode is also crucial. Further information is provided below.

1.1 Anionic surfactants and soaps

In this case the titrant is a cationic surfactant. The best-known one for this purpose is Hyamine 1622 – [N-benzyl-N,N-dimethyl-N-[4-(1,1,3,3-tetramethylbutyl)-phenoxy-ethoxyethyl] ammonium chloride. It is relatively cheap, but has the disadvantage that certain anionic surfactants either cannot be titrated or the titration is not sufficiently accurate. (Chain lengths <C12, several ether side-chain ether groups result in flat titration curves.) However, we can recommend the use of TEGOtrant A100 (Metrohm no. 6.2317.0X0) – 1,3-didecyl-2-methyl-imidazolium chloride. It is slightly more expensive than Hyamine 1622, but its use is worthwhile whenever more accurate results are required or special surfactants have to be titrated.

The titrant is usually used at a concentration of c = 0.005 mol/L. With cationic surfactants it must be remembered that they are strongly substantive – i.e. they are attracted to surfaces (Lenor-effect in fabric conditioners). This means that after the titrant has been filled into the Exchange Unit it must be conditioned (preferably overnight) before its titer is determined.

The precipitating ion associates formed are 1:1 compounds (one anionic reacts with one cationic surfactant group).

For the aqueous titration of anionic surfactants we recommend the Ionic Surfactant Electrode (6.0507.120), for the two-phase titration of anionic surfactants and soaps the 6.0507.140 Surfactrode Refill. (The 6.0726.107 Ag/AgCl electrode should be used as the reference electrode.)

Optimal pH ranges for the titration of anionic surfactants:

- Sulfates and sulfonates pH = 2…4
- Carboxylates and soaps pH = 10.5…12
- Sulfosuccinates for the anionic sulfone group pH = 1…3
- Sulfosuccinates for the anionic sulfone group and the carboxyl group, which is also anionic pH = 8…10

1.2 Cationic surfactants

The titrant is an anionic surfactant. Sodium dodecylsulfate (sodium lauryl sulfate, SDS) is usually used at a concentration of c = 0.005 mol/L. The precipitating ion associates formed are 1:1 compounds (one cationic reacts with one anionic surfactant group).

For the aqueous titration of cationic surfactants we recommend the Cationic Surfactant Electrode (6.0507.150), for the two-phase titration of cationic surfactants 6.0507.130 Surfactrode Resistant. (The 6.0726.100 Ag/AgCl electrode should be used as the reference electrode with 6.2320.000 electrolyte and 3.421.3720 ground glass diaphragm.).

Optimal pH ranges for the titration of cationic surfactants:

- Quats pH = 9.5…10.5
- Esterquats pH = 1…2
- Fatty amines pH = 3…4
- Fatty amine ethoxylates pH = 3…4

2. Nonionic surfactants (NIO surfactants)

As their name says, nonionic surfactants have no reactive surfactant groups – they therefore neither react with anionic nor cationic surfactants. In order to still be able to titrate them we must use a trick.

Nonionic surfactants based on polyoxyethylene (POE) adducts (these contain [R-CH_2-CH_2-O-] groups) are converted to a pseudo-ionic form by the addition of barium ions that can be titrated with Na tetraphenylborate. (The barium ions are inserted into a helix structure – complex-like «supramolecular» compounds are formed in which the oxygen atoms in the helix coordinately bond with the barium ions to form a «guest-host complex» with the surfactant acting as the host and the barium ions as the guest.) The following points must be observed:

- Complex formation depends largely on the chain length of the starter molecule. Short EO chains are not able to bind the barium ions. Rule of thumb: in order to be able to be determined titrimetrically, at least 4 EO groups are required for ethylene oxide addition products based on lipophilic starter molecules; for polyethylene glycols at least 11 to 12 POE groups are required.
- Experience has shown that approx. 11 EO groups form a barium complex with a double positive charge. In order to precipitate this complex, two Na tetraphenylborate molecules are required (this means that 1 consumed Na TPB particle corresponds to approx. 5.5 EO groups).
- If a NIO surfactant (as a technical product) is known, for example, by the name POE-(20)-stearyl alcohol, it cannot be assumed that this is a uniform product consisting exclusively of stearyl alcohol with 20 POE groups. The number 20 rather represents a statistical mean value, with POE distributions normally being encountered in the range between at least POE 10 to POE 30.

For the above-mentioned reasons NIO surfactants do not react stoichiometrically on titration. As in other analytical methods (e.g. HPLC) a calibration factor is determined for the titrant instead of a titer. Whenever possible, this determination of the calibration factor should be carried out with the NIO surfactant that is to be determined. Should this not be possible, or if a mixture of NIO surfactants is to be analyzed then, for example, a mean molar mass can be used for the calculation, or Triton X-100 or polyethylene glycol 1000 can be used for determining the calibration factor.

Nonionic surfactants cannot be determined with a two-phase titration.

For the titration of nonionic surfactants we recommend the 6.0507.010 NIO Surfactant Electrode with 6.0726.107 Ag/AgCl reference electrode (outer electrolyte NaCl, c = 1 mol/L, as KCl is precipitated with NaTPB – «Kalignost»; inner electrolyte KCl, c = 3 mol/L).

I.2.3 Redox reactions

In addition to acid-base reactions, redox processes form a further important group of exchange processes. In oxidation electrons are donated, in reduction electrons are accepted. This means that an oxidizing agent is an electron acceptor and a reducing agent is an electron donor.

$$Ox + z\,e^- \rightarrow Red \quad // \quad Red - z\,e^- \rightarrow Ox$$

Just like positive protons, negative electrons are also elementary particles but with a negative charge and, because of their high reaction potential (small particle radius), only exist very briefly in concentrated materials (half-life value approx. 1 ms). Free electrons act as very strong reducing agents and, for example, spontaneously decompose H_2O:

$$H_2O + e^- \rightarrow \tfrac{1}{2}\,H_2 + OH^-$$

Many redox processes are inhibited, i.e., no conversion takes place even though it would be thermodynamically possible. Example:

$$Fe^{3+} + \tfrac{1}{2}\,H_2 \rightarrow Fe^{2+} + H^+$$

In practice it is important that, in contrast to protons, in aqueous solution electrons cannot «migrate» via water molecules. For example, they migrate via «electron bridges» – using complex-forming partners such as chloride. This means that in some cases considerable activation enthalpies are necessary. Such reactions take place relatively slowly (e.g. Fe(III)/Sn(II)). The same applies if the number of electrons accepted by the oxidizing agent is not the same as the number donated by the reducing agent (e.g. permanganate/oxalate and dichromate/iron(II) – in this case a series of three single-electron steps is required to transfer chromium to oxidation state III).

The time taken for complete conversion after mixing can amount to several seconds. Both catalysts and heating can accelerate the reaction.

Oxidation and reduction of chemical compounds can also be described as an alteration in the oxidation state. (Oxidation increases while reduction reduces the oxidation state.)

In a similar manner to the acid-base reaction, oxidation and reduction can only occur together (redox reaction). Most redox titrations are carried out under acidic conditions (excess protons).

Some examples of titrations:

Iodine – Thiosulfate

$$I_2 + 2\,S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\,I^-$$

Sulfite – Iodine

$$SO_3^{2-} + I_2 + 3\,H_2O \rightarrow SO_4^{2-} + 2\,H_3O^+ + 2\,I^-$$

Arsenite – Bromate

$$3\,As^{3+} + BrO_3^- + 6\,H_3O^+ \rightarrow Br^- + 3\,As^{5+} + 9\,H_2O$$

Hydroxylamine – Bromate

$$NH_2OH + BrO_3^- \rightarrow NO_3^- + Br^- + H_3O^+$$

Bromate as titrant

$$BrO_3^- + 5\,Br^- + 6\,H_3O^+ \rightarrow 9\,H_2O + 3\,Br_2$$

Bromine number

$$-HC=CH- + Br_2 \rightarrow -HBrC-CBrH-$$

electrophilic addition of bromine at the double bond)

Nitrite – Cerium(IV)

$$NO_2^- + 2\,Ce^{4+} + 3\,H_2O \rightarrow NO_3^- + 2\,Ce^{3+} + 2\,H_3O^+$$

Dichromate – Iron(II)

$$Cr_2O_7^{2-} + 6\,Fe^{2+} + 14\,H_3O^+ \rightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 21\,H_2O$$

Permanganate – Oxalate

$$2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H_3O^+ \rightarrow 2\,Mn^{2+} + 10\,CO_2 + 24\,H_2O$$

Permanganate – hydrogen peroxide

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H_3O^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 14\,H_2O$$

Noble metal electrodes are used to indicate redox titrations. They are usually made of platinum; gold electrodes are used less frequently. We recommend the use of combined electrodes.

The redox potential is measured. The general formulation of the Nernst equation for the equilibrium $Ox + z\,e^- \rightleftharpoons Red$ is

$$E = E^0 + (0.059 / z) \times \log a_{ox} / a_{red} \quad \text{(at 25 °C)}$$

Example:

$$Sn^{4+} + 2\,e^- \rightleftharpoons Sn^{2+}$$

$$E = E^0 + (0.059 / 2) \times \log a\,(Sn^{4+}) / a\,(Sn^{2+})$$

Example of a pH-dependent redox reaction for which the ion activities H^+ or OH^- are used directly in the Nernst equation:

$$MnO_4^- + 8\,H_3O^+ + 5\,e^- \quad Mn^{2+} + 12\,H_2O$$

$$E = E^0 + (0.059 / 5) \times \log [a\,(MnO_4^-) \times a^8\,(H_3O^+)] / a\,(Mn^{2+})$$

From this equation it can be clearly seen that the redox potential E is very pH-dependent.

Titration curve

In this case the electrode potential also represents a logarithmic function of the concentration, just as in the other donor-acceptor reaction, the acid-base reaction. This means that the (potentiometric) curve appears similar to an (acid-base) neutralization curve. The height of the potential jump is determined by the potential difference of the two redox systems and their concentration in the solution. The further apart the two redox potentials (sample/titrant) and the higher their concentration, the greater and steeper the potential jump.

At the point of inflection of the curve (the endpoint) a redox equilibrium exists, whereas before or after the endpoint one or the other component is present in excess. For a combined Pt electrode the curve runs as follows:

– titrant is oxidized → to «plus»

– titrant is reduced → to «minus»

(For the Pt Titrode the reverse is true, as the glass electrode as reference electrode is connected to the high-impedance «plus pole».)

Many reducing agents are sensitive to oxygen. This means that they are oxidized by atmospheric oxygen and are not determined (low-bias results). In this case we recommend that the titration is carried out under an inert gas (N_2 or CO_2). In some cases the sample solution is treated with an excess of the oxidizing or reducing agent and, after the conversion, the remaining fraction is back-titrated with a reducing or oxidizing agent. However, back-titrations are more time-consuming than direct titrations and require two titers.

I.2.4 Complexometry / chelometry

All particles made up of individual ions or molecules and with the form $[ML_n]^{+/-z}$ are known as complexes. In the stricter sense complexes are compounds that can easily be broken up into simpler ions and molecules, e.g. dicyanoargentate: $[Ag(CN)_2]^- \quad Ag^+ + 2\ CN^-$(cyanide is the ligand).

The coordination number of the central ion gives the number of monodentate ligands that are bonded. In aqueous solutions cations are mostly present as aquacomplexes of the form $[M(OH_2)_4]^{z+}$ or $M(OH_2)_6]^{z+}$.

«Dentation» is understood to be the number of possible or actually occupied coordination sites of the ligand. Complexes with multi-dentate ligands are known as **chelates.**

Thermodynamic and kinetic factors determine the stability of complexes. A measure of the thermodynamic stability is the complex formation constant K_B, or the dissociation constant $\mathbf{K} = 1/K_B$.

Derivatives of aminopolycarboxylic acids have proven to be best for titration. In addition to their chemical names, protected brand names are often used, e.g.. «Komplexon» (Chemische Fabrik Uetikon, Switzerland), «Titriplex» (Merck), «Idranal» (Riedel-de Haën) etc.

For example, the stability of the metal complexes is given by the following simplified equation (in this case using EDTA, ethylenediamine tetraacetic acid as the complexone):

$$K_B = [MeEDTA^{2-}] \times [\ H_3O^+\ ]^2 / [Me^{2+}] \times [H_2EDTA^{2-}]$$

The complex formation constant is usually given as log K_B in tables. The larger that K_B the more stable the complex.

The effective complex formation constants are generally lowered by protons (acids), as these react in competition to the metal ions with the complexing agent – they protonate e.g. the carboxyl groups of the titrand. The following can be used as rule of thumb:

Metals with complex formation constants <10 are titrated under alkaline conditions, metals with complex formation constant >15 under slightly acidic conditions (Fe^{3+} and Bi^{3+} can even be titrated at pH = 2). The solutions are usually buffered (see below).

The table below lists some selected complex formation constants log K_B for two common titrants (EDTA = ethylenediamine tetraacetic acid, NTA = nitrilotriacetic acid):

Metal ion	log K_B EDTA	log K_B NTA
Al(III)	16.1	–
Ba(II)	7.8	4.8
Bi(III)	27.9	–
Ca(II)	10.7	6.4
Cd(II)	16.5	9.8
Co(II)	16.3	10.4
Cu(II)	18.8	13.0
Fe(II)	14.3	8.8
Fe(III)	25.1	15.9
Hg(II)	21.8	–
Mg(II)	8.7	5.4
Mn(II)	13.8	7.4
Ni(II)	18.6	6.5
Pb(II)	18.0	11.4
Sr(II)	8.6	5.0
Zn(II)	16.5	10.7

Source: Metrohm Application Bulletin no. 101

From the above table the following conclusions can be drawn:

- EDTA forms more stable complexes than NTA (ligand has more «teeth»).
- Metal ions with a triple positive charge form more stable complexes than those with a double positive charge.
- The most stable complex is formed by Bi(III) with EDTA, the least stable by Ba(II) with NTA.

Titration curve

The curves of complex forming titrations are similar to those obtained with acids and bases or in redox titrations as a logarithmic function of the titration. The jump is more marked the larger the complex formation constant K_B and the higher the concentrations of titrant and analyte.

Titration methods

As EDTA forms 1:1 complexes with all metal ions (their «valency» does not matter), the titrant is usually used at a concentration of c = 0.1 mol/L. EDTA is practically insoluble in water, the solution normally used is that of the disodium salt Na_2EDTA (more correctly Na_2H_2EDTA).

Direct titration is possible if complexing takes place quickly and completely. Otherwise *indirect titration* (in this case *back-titration*) is used (an excess of EDTA is added, heated if necessary and back-titrated with Mg(II) or Zn(II)).

The separate determination of mixtures of different metal ions present in the same solution is normally not possible by titration. For example, titration must be carried out at different pH values, by recomplexing, by the addition of masking agents or by the use of a more selective complexing agent (see also under 5.).

It is important to chose a suitable pH range for the titration. If the pH is too low then the carboxyl groups of the EDTA will be wholly or partially present as undissociated carboxylic acids and cannot complex the metal ion. If the pH is too high then the metal could precipitate as a hydroxide.

Titration is almost always carried out in a buffered solution as during complex formation protons are released and – as we have seen – the complex formation constant is pH-dependent. Examples:

$$Ca^{2+} + Na_2H_2EDTA + 2\,H_2O \rightleftharpoons Na_2CaEDTA + 2\,H_3O^+$$

$$Al^{3+} + Na_2H_2EDTA + 2\,H_2O \rightleftharpoons NaAlEDTA + 2\,H_3O^+ + Na^+$$

The oxonium ions produced during the titration are neutralized by the buffer, which displaces the equilibrium to the right.

I.3 Indication methods

General

The equivalence point is reached when titrant and analyte have reacted completely with each other in the corresponding stoichiometric ratio. If titration is regarded as being «counting molecules or ions», then this point must be detected as accurately as possible. This is done by using the properties of the solution or an added indicator which, at the equivalence point, changes as abruptly as possible and in a well-defined manner. The volume of titrant consumed up to the point that this change occurs is the endpoint volume. The endpoint should be as close as possible to or identical with the equivalence point. This means that the indication method is very important. In addition to the accuracy of the titrant addition it makes an important contribution to the reproducibility and, above all, the correctness of the results. Details of the three most important indication methods are given in the following subsections (less important ones such as conductometry/conductivity and calorimetry are not considered here). These are:

– Visual or photometric indication
– Potentiometric indication
– Indication with polarized electrodes (bivoltametry/biamperometry)

I.3.1 Visual or photometric indication

Visual indication with colored indicators is certainly the oldest method for recognizing the endpoint of the titration; it is still frequently used today. It can be realized without any complicated instrumentation and at a low cost.

Colored indicators react

- with the analyte: a small amount of indicator is added at the start of the titration and, together with the analyte, forms a species A. When the analyte has almost completely reacted with the titrant the titrant displaces the indicator from species A which releases the indicator. This takes place with a change of color (in acid-base titrations phenolphthalein reacts with protons to give a colorless substance. Under alkaline conditions the proton is split off and the color changes to red-violet).
- with the titrant: a small amount of indicator is added at the start of the titration. It does not react with the analyte, and the color remains unchanged until the first excess titrant is present. The titrant then combines with the indicator. This takes place with a change in color (e.g. chloride determination by MOHR's method, see below).

If the correct colored indicator is chosen then good results are obtained. The chief disadvantage of this method is that it cannot be automated and can hardly be validated. (The color sensitivity differs from person to person and also depends on the lighting conditions. In addition, difficulties occur with colored and/or turbid solutions.)

Photometric indication can bring an improvement. The (individual) human eye is replaced by a (neutral) sensor. The method can be automated and validated – provided that the correct colored indicator is chosen and that the solutions are not too turbid or no intense turbidity occurs during the titration.

In addition to added colored indicators, cases of self-indication also occur. An example of this is the pink-violet colored $KMnO_4$, which in redox titrations is converted into Mn(II), the latter being colorless in dilute solutions.

Colored indicators do not have a transition *point* – they have a transition range. This fact can considerably influence the correctness of the results of titrations with visual endpoint recognition. An empirical rule is that the human eye recognizes a change in color when the concentration ratio of the two indicator species changes from a ratio of e.g. 1/10 to 10/1. For pH indicators this means that the pH must have altered by two units.

The size of the error that occurs (particularly with flat titration curves) must be known exactly. It is often better to use mixed indicators with a smaller transition range.

The table shows a selection of frequently used colored indicators for **aqueous acid-base titrations:**

Indicator	Volume concentration in solvent	Range of color change (pH)	Color change*
Thymol blue, 1st change	0.04% in water	1.2...2.8	red – yellow
M Cresol purple, 1st change	0.04% in water	1.2...2.8	red – yellow
Bromophenol blue	0.05% in ethanol	3.0...4.6	yellow – violet
Methyl orange	0.04% in water	3.1...4.4	red – yellow orange
Bromocresol green	0.1% in 20% ethanol	3.8...5.4	yellow – blue
Methyl red	0.1% in ethanol	4.4...6.2	red – yellow
Litmus	0.2% in ethanol	5.0...8.0	red – blue
Bromophenol red	0.1% in 20% ethanol	5.2...6.8	yellow – crimson
Bromothymol blue	0.1% in 20% ethanol	6.0...7.6	yellow – blue
Thymol blue, 2nd change	0.04% in water	8.0...9.6	yellow – blue
Phenolphthalein	0.1% in ethanol	8.2...9.8	colorless – reddish violet
Alizarin yellow R	0.1% in water	10.0...12.1	light yellow – reddish brown
Epsilon blue	0.1% in water	12.0...13.0	orange – violet

* First color mentioned refers to more acidic condition.

Source: see literature reference 9.

Titration example H_3PO_4 with c(NaOH) = 0.1 mol/L:

– Methyl orange $H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$ (1st step)
1 mL c(NaOH) = 0.1 mol/L corresponds to 9.7995 mg H_3PO_4

– Phenolphthalein $H_3PO_4 + 2\ NaOH \rightarrow Na_2HPO_4 + 2\ H_2O$ (2nd step)
1 mL c(NaOH) = 0.1 mol/L corresponds to 4.8998 mg H_3PO_4

If both colored indicators are added then the solution will first change from red to yellow – 1st step – and then from yellow to red-violet – 2nd step.

In **precipitation titrations** adsorption indicators can be used. They take their name from the fact that they are adsorbed onto the surface of the precipitate. Precipitate surfaces carry charges. This means that you must remember that the behavior of adsorption indicators greatly depends on the pH of the solution and that, in the presence of larger amounts of electrolytes, interference could occur as a result of flocculation (strong precipitate formation). In such cases a protective colloid should be added in order to obtain a fine precipitate.

Examples of adsorption indicators are:

– with excess silver ions.

– Eosin for bromide and iodide; pink with excess halide, deep-pink with excess silver ions.

For special precipitation titrations two methods have been established for many years:

Chloride determination according to Mohr

For this determination potassium chromate is used as the indicator. The endpoint is obtained when a slight excess of silver ions leads to the precipitation of brown-red silver chromate:

$$2\ Ag^{+} + CrO_4^{2-} \rightleftarrows \{Ag_2CrO_4\}$$

The pH must be between 6.5 and 9. Dichromate is formed under too acidic conditions which does not form a sufficiently sparingly soluble silver precipitate. Under too alkaline conditions silver hydroxide is formed which precipitates.

All determinations (including that of the titer) must be carried out under conditions that are as identical as possible with respect to the halide and chromate ion concentrations so that the silver ion excess necessary for the recognition of the brown-red color is always the same.

Silver determination according to Volhard

In this case the silver ions are titrated with thiocyanate. Excess thiocyanate ions are recognized with the aid of Fe(III) ions (red coloration). The simplified reaction equation is:

$$Fe^{3+} + 3\ SCN^{-} \rightleftarrows Fe(SCN)_3$$

The titration is carried out in a solution of nitric acid (approx. c = 0.4 mol/L). The indicator is a saturated solution of $(NH_4)Fe(SO_4)_2 \times 12\ H_2O$ in water, which is treated with boiled nitric acid until the brown coloration disappears. Acidification suppresses the hydrolysis of the iron(II)-hexaquo complex according to $[Fe(H_2O)_6]^{3+} + 3\ H_2O \rightleftarrows \{Fe(H_2O)_3(OH)_3\} + 3\ H_3O^{+}$ with the formation of iron hydroxide precipitates.

Nitrous acid must be absent as it forms red nitrosyl thiocyanate (NOSCN) with thiocyanate.

Redox indicators are compounds whose reduced and oxidized forms differ in color. This means that during a titration their color adapts itself in accordance with the prevailing redox potential. Please note that the redox potential of the colored indicator is higher than that of the corresponding titrant if an oxidizing titrant is used and lower than that of the corresponding titrant if a reducing titrant is used.

Redox titrations are usually carried out in strongly acidic solutions. The following table gives a short overview of some redox indicators:

Indicator	Potential in V*	Color change**
Safranine O	0.24	blue violet – colorless
Methylene blue	0.53	blue – colorless
2,6-Dichlorophenolindophenol	0.67	red – colorless
Variamine B blue	0.71	blue – colorless
Diphenylamine	0.76	violet – colorless
Diphenylamine-4-sulfonic acid	0.85	crimson – colorless

* At pH = 0

** Oxidized / reduced form

It has been the development of **colored indicators for complexometric/chelometric titrations** that has made such titrations possible at all. Together with the metal ion to be determined these indicators form a colored complex whose color changes abruptly when all the metal ions have been (re)complexed or titrated by the titrant. The following table contains a small selection of colored indicators used for such titrations:

Indicator	Suitable for	Color change*
Pyrocatechol violet	Bi, Cd, Co, In, Mn, Ni, Zn	blue – yellow
Dithizone	Zn	red – green violet
Eriochrome T black	Ca, Cd, Hg, Mg, Pb, Zn	red – blue
HHSNN**	Ca as well as Mg (pH = 12)	red – blue
Murexide	Co, Cu, Ni	yellow – violet
Phthalein purple	Ba, Ca, Sr	purple – colorless
Tiron	Fe(III)	blue – yellow
Xylenol orange	Al, Bi, La, Sc, Th, Zr	red – yellow

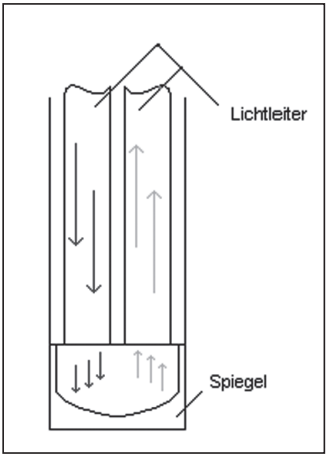
* Metal – excess EDTA
** 2-Hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid

Light guide sensors for photometric titrations

These consist of a light source, two glass fiber (light) guides, a concave mirror and an amplifier.

Monochromatic light from the first light guide passes through the solution where it is partially absorbed by the color of the sample: it reaches the concave mirror where it is reflected to the second light guide, again with part of the light being absorbed by the sample solution. A potential signal is finally produced in the amplifier and transmitted to the titrator via the electrode input.

The light path through the solution to the mirror and back from it determines the path length (l). For example, if the mirror is mounted at a distance of 0.5 cm then l = 1 cm.



Schematic of light guide sensor

Curve shapes of photometrically indicated titrations

Photometrically indicated titration curves can have different shapes; these depend on:

– the type of indication: self-indication or external indication (indicator)

– the stability constant of the indicator with the educt or product of the titration reaction (with externally indicated titrations).

Externally indicated titrations produce three basic structures whose titration curves (or their endpoint) can be evaluated in different ways:

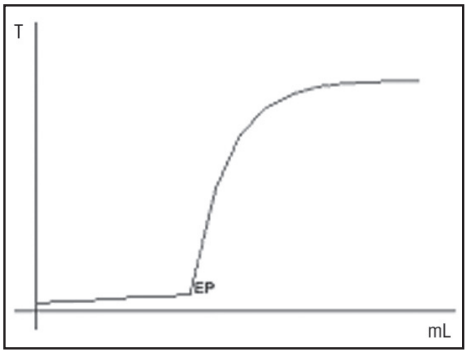


Fig. 1 – The indicator only changes its color after the endpoint of the titration → break-point evaluation

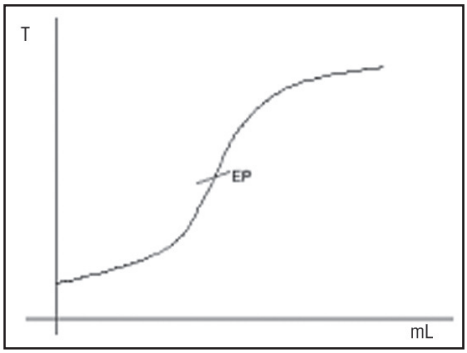


Fig. 2 – The indicator changes its color in the region of the endpoint of the titration reaction → «potentiometric» inflection point evaluation.

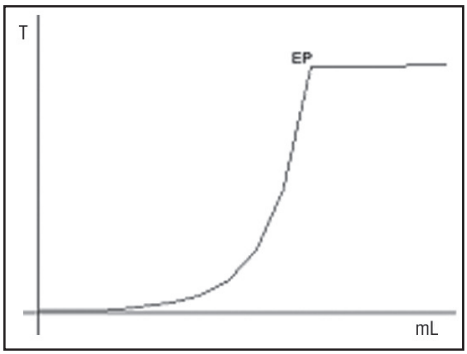


Fig. 3 – The indicator stops changing its color after the endpoint of the titration reaction → break-point evaluation.

For the type of curve shown in Fig. 2 a potentiometric inflection point / endpoint evaluation is advisable and correct. This evaluation is preprogrammed in the Titrino as standard.

The curve types shown in Figs. 1 and 3 must be evaluated by the break-point method, e.g. with Metrodata VESUV or TiNet (preprogrammed) or in the Metrohm Titrando.

I.3.2 Potentiometric indication

General

In addition to visual/photometric methods, potentiometry is one of the most frequently used methods for the endpoint indication of titrimetric analyses. Numerous sensors are available (some of which have been specially developed for a particular application). They cover the whole wide range of titrations – aqueous and non-aqueous acid-base titrations, redox titrations, precipitation titrations and chelometric/complexometric titrations.

The principle of potentiometric measurements

The measuring arrangement for potentiometric measurements always consists of two electrodes – an indicator electrode and a reference electrode. The quantities measured are not potentials (also known as Galvani potentials), but differences in potential (voltages).

The indicator electrode (e.g. pH, ISE, redox, Ag) provides an electrode potential that depends upon the composition of the solution.

The reference electrode (e.g. Ag/AgCl, Hg/Hg_2Cl_2) has the job of supplying an electrode potential that is as independent as possible of the solution to be measured (reference potential).

The potential is measured practically current-free with a «voltmeter» (e.g. Titrino) having a high-impedance measuring input. This is important as any potential drops should be avoided.

The measured potential U is made up of the individual potentials given by the indicator and reference electrodes. Fig. 1 shows a schematic setup with a separate pH glass electrode (left) and a reference electrode (right).

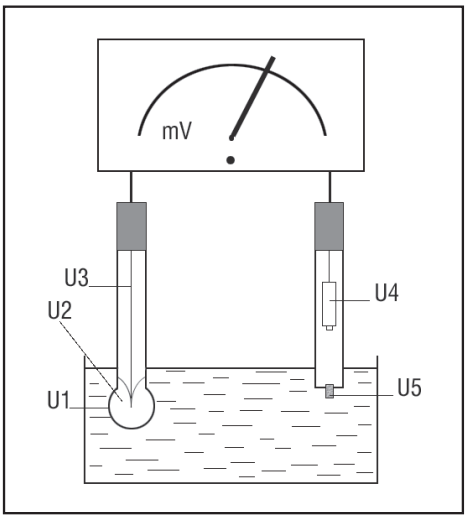


Fig. 1

U_1: Galvani potential between measuring electrode and solution

U_2: Galvani potential between inner buffer and glass membrane

U_3: Galvani potential between inner bleeder electrode and inner buffer

U_4: Galvani potential of reference electrode

U_5: Diffusion potential at diaphragm

The individual potentials U_2, U_3 and U_4 are determined by the construction of the electrode; they are therefore constant for a particular electrode pair. The diffusion potential U_5 should be kept relatively constant and small by taking suitable measures (optimal and clean diaphragm, constant stirring speed during the measurements, suitable reference electrolyte solution whose anions and cations have similar ionic mobilities – e.g. KCl). In this way the potential U_1 measured between the two electrodes depends on the measuring solution alone. This potential is again dependent on the activity a_i of the measuring ion (only active, dissociated ions are measured). For pH and ISE measurements this relationship is described by the Nernst equation:

$$1)\ U = U_0 + \frac{2.303 \times RT}{z_i \times F} \times \log a\ ; = U_0 + U_N \times \log a\ ;$$

U: measured potential between indicator and reference electrodes
U_0: standard potential of the electrode (depends on its construction)
R: gas constant (8.31441 J/K/mol)
T: absolute temperature in K (273.15 + t °C)
z_i: charge of measuring ion i including its sign (e.g. +1 for H_3O^+, –2 for S^{2-})
F: Faraday constant (96484.56 C/mol)
a_i: activity of measuring ion
U_N: Nernst slope (59.16 mV at 25 °C and z = 1, or 29.58 mV at 25 °C and z = 2)
2.303 conversion factor from natural to common logarithm

The Nernst slope U_N gives the theoretical electrode slope and corresponds to the change in potential that results when a_i changes by a factor of 10. It depends on the temperature and the charge z of the measuring ion. U_N and not the pH value of the solution is temperature-compensated by the instrument! In the following table these values are summarized (U_N versus t in °C for z = 1):

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

For redox potential measurements – for which inert noble metal electrodes (e.g. Pt or Au) are used – the following applies:

$$2)\quad U = U_o + U_N \cdot \log \frac{a_{ox}}{a_{red}}$$

U_0: standard potential
U_N: Nernst slope
a_{ox}: activity of oxidized form
a_{red}: activity of reduced form (of the redox pair)

Redox reactions are pH-dependent. They often occur with the participation of hydrogen ions, as can be seen in the following example. The equation indicates that the pH must be taken into account in redox titrations. In extreme cases, for example, an alkaline pH value for the below reaction could lead to the manganese only being reduced to Mn(VI) or Mn(V), or being precipitated as manganese hydroxide.

$$MnO_4^- + 8\,H_3O^+ + 5\,e^- \rightarrow Mn^{2+} + 12\,H_2O$$

The associated Peters equation describes the pH dependency of the potential U and is:

$$3)\ U = U_0 + U_N \times \log \frac{a\,MnO_4^-}{a\,Mn^{2+}} - U_N \times 8 \times pH$$

with a Nernst slope of U_N = 1/5 x 59.16 mV = 11.83 at 25 °C.

Electrodes for potentiometry

As mentioned earlier in this section, potentiometric electrodes always consist of two electrodes – an indicator electrode and a reference electrode. In such a combined electrode the indicator and reference electrodes are constructed together to form a so-called single-rod electrode. This has the advantage that measurements can be simplified and can also be made in small volumes. Combined electrodes are primarily used for pH and redox measurements and precipitation titrations.

The measuring electrode depends upon the ion or species to be measured and the titrant (e.g. pH glass electrode, ISE, Pt electrode, Ag electrode).

With reference electrodes the type of electrolyte filling plays a large role. This electrolyte should have an adequate conductivity and must not take part in the reaction, nor should it interfere with the determination. The following table shows some applications:

Titration	Electrolyte solution
Acid-base, aqueous	3 mol/L KCl in water
Acid-base, non-aqueous, alkaline titrant	0.4 mol/L TEABr in ethylene glycol
Acid-base, non-aqueous, more acid titrant	1...2 mol/L LiCl in ethanol
Redox, general	3 mol/L KCl in water
Redox. very acid, hot	sat. K_2SO_4 in water
Precipitations with Ag	sat. KNO_3 in water
Precipitations of surfactants, general	3 mol/L KCl in water
Precipitations of surfactants, with STPB	1 mol/L NaCl in water

TEABr tetraethylammonium bromide
STPB sodium tetraphenylborate
sat. saturated

When recording the whole titration curve the electrodes do not need to be calibrated in order to determine the content. However, the situation is different when an endpoint titration has to be carried out to a particular pH value. In this case it is essential to calibrate the electrodes used. A two-point calibration is normally carried out – with buffer solution pH = 7 for the electrode zero point and buffer solution pH = 4 (EP on the acidic side) or buffer solution pH = 9 (EP on the alkaline side) in order to correct the electrode slope.

A theoretical pH glass electrode has a slope of 1 (100% of the Nernst slope, 59.16 mV per 1 pH at 25 °C) and an electrode zero point pH_{as} / pH(0) of 7.0 or U_{as} of 0 mV. In practice the situation is different. The electrode zero point U_{as} should be within ±15 mV (pH_{as} 6.75...7.25) and the slope >0.95 (>56.2 mV per 1 pH at 25 °C).

pH_{as} and U_{as} are used to describe the real values by which the variations/asymmetries of the pH glass electrode differ from the theoretical values – pH_{as} = 7.00 and U_{as} = 0.0 mV. As the two sides of the glass electrode are never fully identical, a small potential – known as the asymmetry potential – occurs across the glass membrane.

In order to «inform» the instrument about the real electrode data the electrode has to be calibrated. Buffer solutions have a defined pH value that is temperature-dependent. The temperature profile of the buffer solution can be compensated on the instrument! The appropriate data for the buffer solutions is entered during calibration or, as with Metrohm pH meters / Titrandos, is already stored in the instrument. The temperature profile of the measuring solution cannot be compensated. This means that the instrument shows the correct value for the actual measuring temperature. The following table shows the temperature-dependent values for Metrohm buffer solutions:

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

Buffer solutions are not stable. They can be decomposed by bacteria and/or molds, while the pH of alkaline buffer solutions can change as a result of CO_2 absorption from the atmosphere. This is why you should always use fresh buffer solutions and never pour used buffers back into the storage bottle!

I.3.3 Indication with polarized electrodes

General

These methods are primarily used for redox titrations in dilute solutions or if dilute titrants are used, as in such cases potentiometric indication is not longer satisfactory (titration curves are too flat – loss in precision).

Terminology:

Amperometry: potential polarization/current measurement with one polarizable electrode – $\mathbf{U_{pol}}$

Biamperometry: potential polarization/current measurement with two polarizable electrodes – $\mathbf{U_{pol}}$

Voltametry: current polarization/potential measurement with one polarizable electrode – $\mathbf{I_{pol}}$

Bivoltametry: current polarization/potential measurement with two polarizable electrodes – $\mathbf{I_{pol}}$

$\mathbf{U_{pol}}$ and I_{pol} are included in the Titrino as so-called polarizers and can be set throughout a wide range. Never connect pH glass electrodes and ISEs to a polarizer – they will be destroyed!

Amperometric indication

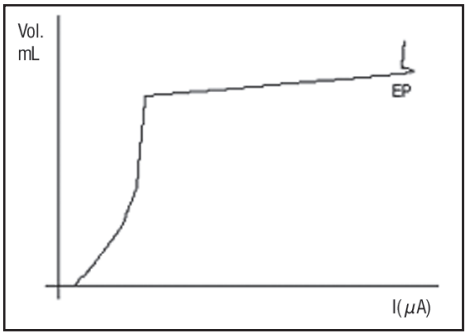
The use of amperometric indication (as well as polarimetric indication) for titration originated in polarography. A dropping mercury electrode (DME) is used as the indicator electrode (switched as the cathode) and an Ag/AgCl electrode as the reference electrode. A constant potential is applied between the two electrodes that is so high that at least one of the reaction partners (sample ion or titrant) is reduced at the cathode. This causes a diffusion current, which is evaluated. The method is very sensitive and can be used for concentrations down to $c = 10^{-6}$ mol/L. However, this method has never been able to become properly established because of the indicator electrode (DME). The resulting titration curves are T-shaped (one active reaction partner) or V-shaped (both reaction partners active).

Biamperometric (dead-stop) indication

In this case both the electrodes (usually double-Pt electrodes) are polarizable. A constant potential is also applied to the electrodes, but this is considerably lower (max. 250 mV) than in amperometric indication. This method is chiefly used for iodometric determinations. The following reactions occur at the electrodes:

Cathode: $I_2 + 2\,e^- \rightarrow 2\,I^-$ (reduction)
Anode: $2\,I^- - 2\,e^- \rightarrow I_2$ (oxidation)

This means that a current flows for as long as iodine is present. When the iodine has been consumed (e.g. by titration with thiosulfate) the current drops to zero (dead-stop); the resistance between the electrodes increases greatly and the electrodes are again polarized.



Example of a biamperometric titration curve

Voltametric indication

As in amperometry, only one electrode (the indicator electrode) is polarizable. In contrast to amperometry the current polarization takes place with only a few μA, i.e. 1...5 μA. If I_{pol} has the correct sign («plus» for oxidizing titrants, «minus» for reducing titrants) then the resulting titration curves are similar to those for potentiometric indication. However, the curves are steeper and cover a larger potential range. An example of the use of this method is the titration of free chlorine in drinking water with $c(As_2O_3)$ = 0.005 mol/L using a combined Pt electrode, I_{pol} = 1 μA.

Bivoltametric indication

Again two electrodes (usually double-Pt electrodes) are polarized by applying a small DC or AC current (AC is considerably more sensitive than DC) between the electrodes and measuring the resulting potential. The titration curves obtained are similar to those found in biamperometry, but are usually more pronounced and larger. If both the sample and titrant are electrochemically active then peak-shaped titration curves are produced (Fig. 1). If only one partner is electrochemically active then L-shaped curves are produced (Fig. 2).

Examples:

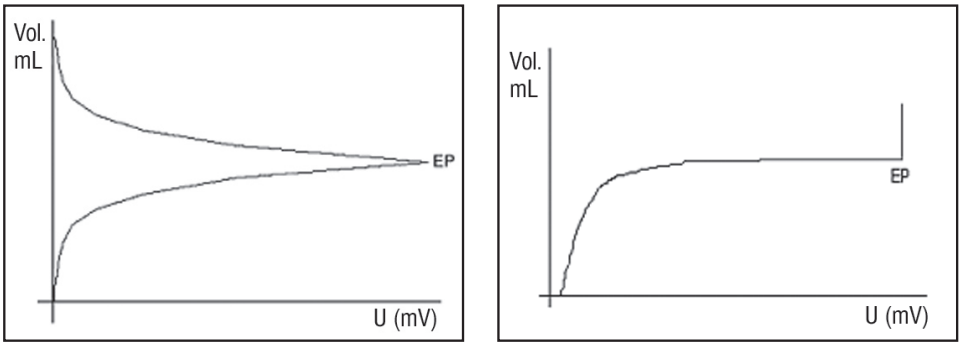


Fig. 1

This indication method is used very frequently in the Karl Fischer titration for water determination. The resulting potentials for iodine or excess water are, of course, dependent on the applied current (I_{pol}). Three examples (separate double Pt-sheet electrode):

I_{pol} = 50 μA, U approx. 100 mV for excess iodine, approx. 680 mV for excess water
I_{pol} = 10 μA, U approx. 5 mV for excess iodine, approx. 580 mV for excess water
I_{pol} = 1 μA, U approx. 0 mV for excess iodine, approx. 350 mV for excess water

I. 4 Electrodes

General

One of the most important criteria for volumetric analysis is to find the equivalence point (the point in the titration at which it is indicated that the species of the sample has been completely titrated – stoichiometrically converted – and at which there is not yet an excess of titrant). The associated value for the volume or endpoint shown by the instrument must be as close as possible to the equivalence point. Even the most modern analytical instruments, with their high resolution on the volume axis (of the titrant), are of little use if unsuitable sensors are used or if they have a poor response. In Section I.3 «Indication methods» the theory behind the various possibilities has already been mentioned. In this section we are concerned with providing details of the most important electrodes for the methods described in the practical section and passing on information and recommendations to the users.

1. Acid-base titrations, aqueous

The choice of electrode depends mainly on the matrix (type of sample) in which the titration is to be carried out. The sample solution could influence both the glass membrane and the diaphragm and therefore affect the reference electrode. Combined electrodes are normally used – measuring electrode and reference electrode (possibly with an additional temperature sensor) are contained in a single «electrode».

1.1 For general use

Contents of uncontaminated acids and bases are best deermined with the 6.0232.100 Ecotrode – LL combined pH glass electrode with ceramic pin diaphragm.

1.2 For beverages (fruit or vegetable juice, wine, beer) and pharmaceutical ingredients according to USP and Pharm. Europe and for solutions containing phosphates

Recommended electrode: 6.0259.100 LL Unitrode. This electrode has a fixed ground-joint diaphragm that is not easily blocked and ensures a stable, rapid response.

1.3 Water and ion-deficient solutions

Recommended electrode: 6.0253.100 LL Aquatrode Plus. It has been developed specially for such applications and has a fixed ground-joint diaphragm, which ensures that the total resistance remains low. A special glass combining a low membrane resistance with the greatest possible robustness is also used for this electrode.

1.4 Products containing proteins (dairy products, nutrient solutions)

Recommended electrode: 6.0235.100 LL Porotrode. It has special diaphragms (two capillaries) and a special electrolyte that prevents proteins from being precipitated at or on the diaphragm and negatively affecting the electrode response.

1.5 Acidic solutions containing fluoride

Recommended electrode: 6.0421.100 combined Sb electrode. No pH glass electrode can be used in such solutions as glass is attacked by hydrofluoric acid – the electrode would only respond slowly and would lose its «slope».

1.6 Electroplating baths, dye baths, Bayer caustic solution (strongly alkaline digestion mixtures used in aluminum production from bauxite), amine-containing absorption solutions, dispersions, liquid manure, wastewater containing sulfides

Recommended electrode: 6.0255.100 LL combined pH glass electrode with ground-joint diaphragm, double junction. In order to prevent sample solution or sample constituents from entering the reference electrolyte (this would destroy the Ag/AgCl reference system and make the electrode unusable) an electrode with a double electrolyte chamber (double junction) is used. The outer electrode chamber can be filled with any electrolyte solution, which can be easily exchanged. The electrode has a separable ground-joint glass diaphragm that is almost impossible to block.

2. Acid-base titrations, non-aqueous

General

The choice of electrode system depends primarily upon the solvent (mixture) that is to be titrated and the titrant used. In principle, a differentiation can be made between more or less polar and completely nonpolar solvents. Nonpolar solvents (e.g. pure hydrocarbons or chlorinated hydrocarbons) have a very high electrical resistance. Although they are easily able to dissolve oils and fats (as well as paraffins), ionic compounds are only poorly soluble. If the total resistance (solvent plus sample) is too high then potentiometric indication of the titration is no longer possible. Massive interference occurs as a result of electrostatic charges – in such cases the titration curve can no longer be evaluated.

2.1 In solvents with a moderate electrical resistance

Recommended electrode: 6.0229.100 LL Solvotrode. This electrode has been specially developed for titrations in non-aqueous solvents and has the following advantages:

- Large membrane glass surface with comparatively low resistance and good response
- Electric shielding of the whole electrode up to the connection plug
- Separable ground-joint diaphragm with good electrolyte flow – almost never becomes blocked
- Single-rod (combined) electrode
- Easy to exchange the electrolyte solution

We recommend the use of the following electrolyte solutions:

a) Titrant is an acid

c(LiCl) = approx. 2 mol/L in ethanol. Dilute saturated solution of LiCl (Metrohm no. 6.2312.000) 1:1 with ethanol.

b) Titrant is an base

c(TEABr) = 0.4 mol/L in ethylene glycol (Metrohm no. 6.2320.000)

TAEBr = tetraethylammonium bromide

2.2 In solutions with a relatively high electrical resistance

Recommended electrodes: 6.0431.100 Pt Titrode plus 6.0729.100 Ag/AgCl reference electrode, shielded, with double junction and ground-joint diaphragm. Electrolyte filling differs depending on whether the titrant is acidic or basic. See also remarks under a) and b) in 2.1.

The higher the electrical resistance of the solution to be titrated, the greater the interference by electrostatic charges. If this interference is so large that the Solvotrode can no longer be used then work must be carried out with the so-called **three-electrode technique** and the **differential amplifier** input (diff) of the Titrino. The specially shielded Ag/AgCl electrode is used as the reference electrode, the pH glass membrane of the Pt Titrode as the measuring electrode and the platinum ring of the Pt Titrode as auxiliary/bleeder electrode.

If this electrode combination does not help (too strong interference is still present) then the titration cannot be indicated potentiometrically. In such cases we recommend the use of a different solvent or the addition of approx. 5...10% V/V acetone or IPA (isopropanol) to the solution. (In pure aprotic solvents it is often only possible to titrate photometrically using a colored indicator.)

3. Precipitation titrations

General

By far the most frequent titrations of this type are precipitations with silver nitrate. Many anions produce sparingly soluble silver compounds that can be used for the determination of these anions. In mixtures it is always the most sparingly soluble compound that is titrated (smallest solubility product). In order to achieve a good separation the solubility products must differ sufficiently from each other. The following are titrated with silver nitrate: chloride, bromide, iodide, cyanide, sulfide, mercaptans and thiocyanate (the anions of other sparingly soluble Ag compounds – e.g. chromate or thiosulfate – are determined better by redox titrations).

Further precipitation titrations are, for example, sulfate determination (with barium chloride or acetate or perchlorate), fluoride determination (with lanthanum nitrate) and naturally the determination of the purity of silver (with potassium bromide).

In recent years the potentiometric titration of surfactants has greatly increased and is replacing more and more the complicated visual Epton titration, which is either difficult to automate or cannot be automated at all. More details about electrodes for surfactant titrations are given under 3.2.

3.1 Titrations with $AgNO_3$

Recommended electrodes: **6.0430.100** Ag Titrode and/or **6.0450.100** combined Ag-ring electrode.

Bright silver electrodes do not always stabilize quickly (independent of the construction). This applies in particular whenever titrations are carried out in dilute solutions or solutions with a high ionic strength (examples are traces of chloride in drinking water, in salts, or in NaOH or Na_2CO_3 after neutralization). The electrode does not remain «bright», as the corresponding Ag salt is formed little by little on its surface. For this reason we recommend giving the electrode an **Ag_2S coating** right from the start. This provides it with a rapid response with usually large potential jumps; the reproducibility of the results is also improved. The electrode behaves like an ion-selective electrode (ISE), i.e. it responds both to Ag^+ and the corresponding anion.

However, the Ag Titrode should be preferred. Its glass membrane acts as a reference electrode and hardly alters its potential at all if the titration is carried out in buffered solutions (acidic or alkaline). As this glass electrode is connected to the high-impedance input of the Titrino (measuring electrode input), the titration curves are produced in the opposite (and unusual) direction compared with a titration with a combined Ag electrode. The Ag Titrode has the advantage that no diaphragm is present (and therefore cannot be blocked) and no elec-

trolyte solution needs to be refilled. It can be stored in dist. H_2O. With combined Ag electrodes it is, of course, not possible to use electrolyte solutions containing chloride (formation of AgCl which influences the result and blocks the diaphragm). KNO_3 solutions are normally used.

In acidic solution (pH <4, in order to avoid possible precipitation of Ag_2CO_3) the following are titrated: chloride, bromide, iodide and thiocyanate

In alkaline solution (pH >11) the following are titrated: cyanide, sulfide and (usually) mercaptans.

3.2 Surfactant titrations

General

Surfactants are divided into the following classes (see also I.2.):

- Anionic (anion-active) surfactants and soaps
- Cationic (cation-active) surfactants
- Amphoteric surfactants (can be either anionic or cationic depending on the pH)
- Nonionic surfactants (NIOs)

The anionic, cationic and the largest group of nonionic surfactants – the polyoxyethylene (POE) adducts – can be titrated potentiometrically.

Anionic surfactants react with cationic surfactants and vice versa. In aqueous solutions the corresponding ion association is precipitated (in the two-phase titration it is extracted into the organic phase).

As their name says, nonionic surfactants have no groups that can react and therefore cannot be titrated directly. Barium ions are added to their solutions. A Ba pseudo-complex is formed that can be precipitated and thus titrated with sodium tetraphenylborate.

Single-rod electrodes (combined electrodes) are difficult to handle in surfactant analysis. Changes in the diffusion potential occur at the diaphragm during the titration; these may falsify the titration curve and therefore produce incorrect results. This is why Metrohm in principle uses only separate electrodes: on one side is the measuring electrode (surfactant ISE), on the other side is the Ag/AgCl reference electrode with double junction and a ground-joint diaphragm.

Recommended reference electrode: **6.0726.107** (electrolyte solution for ionic surfactants is KCl, c = 3 mol/L, for nonionic surfactants NaCl, c = 1 mol/L – at least in the outer electrolyte vessel). We recommend the use of the 3.421.3720 ground-joint glass sleeve for cationic surfactants.

3.2.1 Anionic surfactants, aqueous

Recommended electrode: **6.0507.120** Ionic Surfactant Electrode

3.2.2 Cationic surfactants, aqueous

Recommended electrode: **6.0507.150** Cationic Surfactant Electrode

3.2.3 Nonionic surfactants (aqueous only)

Recommended electrode: **6.0507.010** NIO Surfactant Electrode

3.2.4 Two-phase titration, anionic and cationic surfactants, pH <10, organic medium chloroform or MIBK

Recommended electrode: **6.0507.130** Surfactrode Resistant

3.2.5 Two-phase titration, anionic surfactants and soaps, cationic surfactants, pH >10, organic medium MIBK

Recommended electrode: **6.0507.140** Surfactrode Refill

The surfactant ISEs for aqueous titrations are polymer membrane (PVC) ISEs and are either not resistant to solvents or have a limited resistance. Metrohm (in contrast to other suppliers) offers five different surfactant electrodes. Among them you will find the optimal electrode for your application and do not have to try to solve all your problems (usually unsatisfactorily) with a single electrode.

4. Redox titrations

General

Probably the most frequently carried out redox titrations are iodometric titrations using iodine as the titrant (in the form of the water-soluble triiodide, KI_3) and thiosulfate. Other titrants are $KMnO_4$, Ce(IV), $KBrO_3$, Fe(II) and As(III), which latter, because of its toxicity, is relatively seldom used.

Noble metal electrodes must be used for indicating these titrations. Silver is unsuitable, as it oxidizes rapidly or forms silver halide or silver sulfide coatings. These damage the electrode – the potential stabilization takes longer. Gold is only used for a few special applications. Platinum electrodes are normally used.

But even the surfaces of platinum electrodes are not immune to oxidation. Oxidized Pt electrodes only become stabilized very slowly, the titration curves are flat and the potential jumps are small. In order to obtain a perfectly functioning and «quick» electrode it must be regenerated. This is best carried out by electrolytic hydrogen evolution on its surface:

The Pt electrode to be treated is connected to the minus pole (cathode) of a DC source of 4.5...6 V (e.g. a battery). A further platinum (wire) electrode or an iron nail is connected to the plus pole (anode). Do not use copper as anode as this would copper-plate the Pt!

Both electrodes are immersed in a stirred solution of $c(H_2SO_4)$ = approx. 2 mol/L under voltage. Hydrogen should be produced at the cathode (and accordingly oxygen at the anode) – this can be recognized by the formation of bubbles. After approx. 5 min the electrodes – still under voltage – are removed from the solution and rinsed thoroughly with dist. H_2O.

4. 1 Potentiometric indication

Recommended electrodes: **6.0431.100** Pt Titrode and/or 6.0451.100 LL combined Pt-ring electrode.

The Pt Titrode is to be preferred. Its glass membrane acts as the reference electrode and hardly changes its potential at all if the titration is carried out in buffered solutions (usually acidic). As the glass electrode is connected to the high-impedance input of the Titrino (measuring electrode input) the titration curves are produced in the opposite (and unusual) direction compared with a titration with a combined Pt electrode. The Titrode has the advantage that no diaphragm is present (and therefore cannot be blocked) and no electrolyte solution needs to be refilled. It can be stored in dist. H_2O.

4.2 Bivoltametric and/or biamperometric (dead stop) indication

Recommended electrodes: **6.0341.100** double Pt-wire electrode or 6.0309.100 double Pt-sheet electrode.

The double-wire electrode is suitable for general applications (e.g. iodometry); the double-sheet electrode is mainly used with dilute titrants (examples are SO_2 in wine or vitamin C with dichlorophenolindophenol).

5. Complexometric / chelometric titrations

General

Apart from acid-base titrations, complexometric titrations are probably the most frequently used volumetric titrations throughout the world. In more than 90% of the cases the disodium salt of ethylenediamine tetraacetic acid (EDTA) is used. In earlier days nitrilotriacetic acid (NTA) was frequently used – today its use is no longer so important. For special, more selective titrations the sodium salts of the following complexing agents are still used:

- DCTA trans-diaminocyclohexane tetraacetic acid
- DIGITA bis-(aminoethyl)-glycol ether tetraacetic acid
- DTPA diethylenetriamine pentaacetic acid
- EGTA ethylene glycol-bis-(2-aminoethyl)-tetraacetic acid

One thing that all of these have in common is that they form 1:1 complexes with metal ions, no matter whether the metal ions have a double or triple positive charge. This means that, for example, 1 mL $c(Na_2EDTA)$ = 0.1 mol/L corresponds to 4.008 mg Ca, 2.431 mg Mg, 2.698 mg Al, 5.585 mg Fe(II) or Fe(III), etc. Using Na_2EDTA as an example this appears as follows:

$$Ca^{2+} + Na_2H_2EDTA + 2\,H_2O \rightleftharpoons Na_2CaEDTA + 2\,H_3O^+$$

$$Al^{3+} + Na_2H_2EDTA + 2\,H_2O \rightleftharpoons NaAlEDTA + 2\,H_3O^+ + Na^+$$

The acids of the complexing agents are hardly soluble in water. For this reason their sodium salts are generally used.

The separate determination of mixtures of different metal ions present in the same solution is normally not possible by titration. For example, titration must be carried out at different pH values, by recomplexing or by the addition of masking agents. Examples:

Ca/Mg mixtures:	addition of acetylacetone (recomplexing)
Ca/Al mixtures:	titrate Ca alkaline, titrate Al acidic
KCN addition:	masks Ag, Cd, Co, Cu, Hg, Ni and Zn
Triethanolamine addition:	masks Al and Fe

5.1 Titrations with photometric indication

Recommended electrodes: **6.1109.110** Spectrosense 610 nm or 6.1109.100 Spectrosense 523 nm.

The oldest and still the most widespread method for endpoint recognition in complexometric titrations is the use of suitable colored indicators. Together with the metal ion to be determined these form a colored complex, whose structure and color changes abruptly when all the metal ions have been (re)complexed or titrated, e.g. by EDTA. Here is a small selection of frequently used colored indicators (the metals whose ions are determined are shown in brackets):

- Eriochrome black T (Mg, Zn, Cd, Pb, Hg)
- Murexide (Co, Ni, Cu)
- Tiron (Fe)
- Phthalein purple (Ca, Sr, Ba)
- Pyrocatechol violet (Bi, Co, Ni, Mn, In, Zn, Cd)
- Xylenol orange (Al, La, Th, Bi, Sc, Zn)
- HHSNN (Ca in the presence of a large amount of Mg at pH = approx. 12) HHSNN is 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid

Colored indicators for complexometric titrations are also complexing agents. However, their complex formation constants must be smaller than those of the titrants. In addition, the indicator complex must also have a different color from that of the free indicator and have a more intensive color than that of the titrant complex. As these colored indicators are usually multivalent acids, it must be remembered that their color-change range is pH-dependent. As already mentioned in Section I.2., the titration is carried out in a buffered solution.

At the start of the titration the color of the solution is determined by the metal-indicator complex. The titrant reacts first with the free metal ions and towards the end of the titration it also extracts the metal ion from the weaker indicator complex. The endpoint/point of inflection is reached when 50% of the indicator has been released (mixed color). A sharper color change can often be achieved if an organic solvent (e.g. acetone or ethanol) is added to the solution.

Of course, titrations can also be carried out with visual endpoint recognition. However, these methods cannot be automated and, above all, are virtually impossible to validate as each analyst sees the color change differently – depending on the lighting conditions. This is the reason behind the use of photometric sensors, such as are built into the Spectrosense 523 nm and 610 nm.

5.2 Indication with the Cu ISE

Recommended electrode: **6.0502.140** Cu ISE (do not forget the reference electrode, e.g. Metrohm 6.0726.107).

The Cu ISE is a crystal membrane electrode.

The Cu ISE responds (only) to Cu(II) ions (otherwise it would not be an ion-selective electrode). In order to be able to indicate the titration of other metal ions a trick has to be used. Some CuEDTA is added to the solution to be titrated. CuEDTA is a very stable complex and only releases a very small amount of Cu(II) ions. However, in alkaline solution and in the presence of e.g. Ca(II) ions all the Cu(II) ions are released and the Ca-EDTA complex is formed. This means that during the titration the concentration of Cu(II) ions is continuously reduced until at the endpoint the very small initial value is again reached. A typical potentiometric titration curve is obtained. The following equations symbolize the three steps:

$$\text{CuEDTA} \leftarrow \text{Cu(II)} + \text{EDTA}$$

$$\text{CuEDTA} + \text{Ca(II)} \rightarrow \text{CaEDTA} + \text{Cu(II)}$$

$$\text{Cu(II)} + \text{EDTA} \rightarrow \text{CuEDTA}$$

5.3 Indication with the Ca ISE

Recommended electrode: **6.0508.110** Ca ISE (do not forget the reference electrode, e.g. Metrohm 6.0726.107).

The Ca ISE is a polymer membrane electrode.

This electrode is used especially for the complexometric titration of calcium. In many cases the Mg(II) content of the sample is also to be determined at the same time as the Ca(II) content. A typical and frequently used example is the titration of water hardness. This is also done by using a trick. An auxiliary complexing agent (acetylacetone in Tris buffer) is added to the solution.

If the titration is now carried out with EDTA the Ca(II) reacts first. If Ca(II) is no longer present the auxiliary complexing agent enters the picture. Mg(II) reacts with CaEDTA to form MgEDTA, the corresponding amount of Ca(II) is again released and can be titrated again with EDTA. A potentiometric titration curve with two endpoints is obtained. EP1 (flat) corresponds to Ca(II) and EP2 – EP1 to the Mg(II).

I. 5 Titrants: preparation and titer determination

General

Titrants are standard solutions, i.e. solutions that contain a defined content of a reactant. This content is given as the molar concentration *c* in mol/L. The term «normality» (mol/L divided by the valency), which was frequently used in earlier days, is no longer valid and should therefore no longer be used. Examples:

0.1 N HCl $\Rightarrow$ $c(HCl)$ = 0.1 mol/L
0.1 N H_2SO_4 $\Rightarrow$ $c(H_2SO_4)$ = 0.05 mol/L
0.1 N iodine solution $\Rightarrow$ $c(I_2)$ = 0.05 mol/L
0.1 N $KMnO_4$ $\Rightarrow$ $c(KMnO_4)$ = 0.02 mol/L

Not all titrants have a stable titer, i.e. the molar concentration of the dissolved reactant can change with time. Examples:

- Bases absorb CO_2 from the atmosphere, the pH drops
- Iodine solutions release iodine
- Arsenite solutions are oxidized to arsenates by atmospheric oxygen
- Thiosulfate solutions decompose as a result of CO_2 absorption with the deposition of sulfur
- Potassium permanganate solutions in the presence of organic substances (e.g. dust particles) deposit MnO_2 (permanganate oxidizes such foreign bodies and is itself reduced).
- Titrants in organic solvents can be concentrated by evaporation.

This means that the titer of such a solution is constantly changing. Titer determinations are carried out in order to know the correct molar concentration so that correct calculations can be carried out.

The titer is determined by comparison with so-called standard titrimetric substances. These hardly change in content, are available at a defined degree of purity, can be dried and are directly traceable to standard reference materials (e.g. National Institute of Standards and Technology – NIST, USA).

Such **standard titrimetric substances or secondary standards** are:

For bases	potassium hydrogen phthalate	M = 204.23 g/mol
For acids	tris(hydroxymethyl)-aminomethane	M = 121.14 g/mol
For iodine solution	arsenic trioxide	M = 197.841 g/mol
For thiosulfate	potassium iodate	M = 214.001 g/mol
For cerium(IV):	disodium oxalate	M = 133.999 g/mol
For $KMnO_4$	disodium oxalate	M = 133.999 g/mol
For silver nitrate	sodium chloride	M = 58.443 g/mol
For Na_2EDTA	calcium carbonate	M = 100.09 g/mol
For potassium dichromate	this is itself a standard titrimetric substance; its solutions have a stable titer	M = 294.184
For potassium bromate	this is itself a standard titrimetric substance; its solutions have a stable titer	M = 167.001

Most standard solutions and titrants are commercially available in the form of ready-to-use solutions or concentrates; their titer has been adjusted by the manufacturer to 1.000 at 20 °C.

However, we nevertheless strongly urge you to carry out a titer determination! This provides you with more security, and it could mean that you avoid serious errors.

In principle titer determinations should always be carried out at the same temperature as that used for the subsequent titrations. As the temperature increases the titrants expand – aqueous solutions not as much as non-aqueous ones.

Thus, for a temperature difference of 5 °C and a theoretical consumption of 10.00 mL, the consumption will be higher by 12.5 µL for aqueous and about 50 µL for non-aqueous titrants. Accordingly, a titer of 1.000 at 20 °C becomes 0.9988 and 0.9950 at 25 °C, respectively.

Examples

I.5.1 c(NaOH) = 0.1 mol/L

NaOH solutions do not have a stable titer. They can absorb CO_2 from the atmosphere to form sodium carbonate:

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

This means that not only the titer decreases. As NaOH and Na_2CO_3 have different base strengths this will affect the titration curve and therefore the results. In order to largely avoid CO_2 absorption from the atmosphere the drying or absorber tube of the Exchange Unit is filled with soda lime (CO_2 absorber). As strong bases attack glass the Exchange Unit should be provided with a plastic storage bottle.

Preparation

Approx. 4.4 g NaOH pellets are weighed out into a beaker, treated with a little dist. H_2O and swirled briefly in order to dissolve any Na_2CO_3 present on the surfaces. This solution is rejected and the remaining NaOH is dissolved in CO_2-free dist. H_2O, transferred to a 1000 mL volumetric flask, made up to the mark and mixed. Carbon dioxide is removed from the dist. H_2O by boiling or by passing a stream of e.g. nitrogen through it.

Titer determination

Potassium hydrogen phthalate is dried overnight in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the titrator as a «common variable».

Approx. 200 mg potassium hydrogen phthalate is accurately weighed out into the titration beaker to the nearest 0.1 mg and dissolved in approx. 50 mL CO_2-free dist. H_2O. It is immediately titrated with *c*(NaOH) = 0.1 mol/L to after the first endpoint (combined pH glass electrode).

Calculating the titer

1 mL *c*(NaOH) = 0.1 mol/L corresponds to 20.423 mg KH phtalate

Titer = C00 / C01 / EP1 (formula entered in the Titrino)

EP1 = mL NaOH up to endpoint
C00 = weight of KH phthalate in mg
C01 = 20.423
Result to be given to four decimal places.

I.5.2 c(HCl) = 0.1 mol/L

Preparation

Approx. 800 mL dist. H_2O is placed in a 1000 mL volumetric flask. 9.8 mL hydrochloric acid, w(HCl) = 32% is added, made up to the mark with dist. H_2O and mixed.

Titer determination

Tris(hydroxymethyl)-aminomethane (Tris) is dried overnight in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the Titrino as a «common variable».

Approx. 100 mg Tris is accurately weighed out into the titration beaker to the nearest 0.1 mg and dissolved in approx. 50 mL CO_2-free dist. H_2O. It is immediately titrated with c(HCl) = 0.1 mol/L to after the first endpoint (combined pH glass electrode).

Calculating the titer

1 mL c(HCl) = 0.1 mol/L corresponds to 12.114 mg Tris

Titer = C00 / C01 / EP1

EP1 = mL HCl up to endpoint
C00 = weight of Tris in mg
C01 = 12.114
Result to be given to four decimal places.

I.5.3 c(I_2) = 0.05 mol/L

Iodine solutions do not have a stable titer. Iodine escapes from the solution by sublimation – the molar concentration decreases.

Preparation

25 g pure, iodate-free potassium iodide is weighed out into a 1000 mL volumetric flask and dissolved in 40 mL dist. H_2O. 12.8 g iodine is added and the flask is sealed and then shaken until all the iodine has dissolved (as KI_3). It is then made up to the mark with dist. H_2O and mixed. Do not dilute with dist. H_2O too soon as otherwise the iodine will no longer dissolve.

Titer determination

Arsenic trioxide is dried overnight in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the Titrino as a «common variable».

Approx. 60 mg As_2O_3 is accurately weighed out into the titration beaker to the nearest 0.1 mg and quickly dissolved in approx. 10 mL c(NaOH) = 0.1 mol/L. 12 mL c(HCl) = 0.1 mol/L is added immediately followed by approx. 2 g $NaHCO_3$ and then diluted to approx. 80 mL with dist. H_2O (the solutions used should be free from oxygen). Titrate with $c(I_2)$ = 0.05 mol/L to after the first endpoint (Pt Titrode or combined Pt-ring electrode).

$$Na_3AsO_3 + I_2 + H_2O \rightleftharpoons Na_3AsO_4 + 2\,HI$$

Calculating the titer

1 mL $c(I_2)$ = 0.05 mol/L corresponds to 4.946 mg As_2O_3

Titer = C00 / C01 / EP1

EP1 = mL iodine solution up to endpoint
C00 = weight of As_2O_3 in mg
C01 = 4.946
Result to be given to four decimal places.

I.5.4 c($Na_2S_2O_3$) = 0.1 mol/L

Thiosulfate solutions do not always have a stable titer. They can be decomposed due to catalysis by traces of heavy metals, be oxidized by microorganisms or undergo CO_2 absorption. This reduces the molar concentration. It is best to use boiled ultrapure water to prepare the solution.

Preparation

25 g $Na_2S_2O_3$ x 5 H_2O is weighed out into a 1000 mL volumetric flask, dissolved in CO_2-free dist. H_2O, made up to the mark and mixed.

Titer determination

Potassium iodate is dried overnight in a drying oven at 180 °C and allowed to cool down in a desiccator for at least 2 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the Titrino as a «common variable».

Approx. 50 mg KIO_3 is accurately weighed out into the titration beaker to the nearest 0.1 mg and dissolved in approx. 100 mL dist. H_2O. Approx. 1 g potassium iodide and 10 mL sulfuric acid $w(H_2SO_4)$ = 25% are added and immediately titrated with $c(Na_2S_2O_3)$ = 0.1 mol/L to after the first endpoint (Pt Titrode or combined Pt-ring electrode).

$$KIO_3 + 5\ KI + 3\ H_2SO_4 \rightarrow 3\ I_2 + 3\ K_2SO_4 + 3\ H_2O$$

$$2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6\ (\text{Na tetrathionate}) + 2\ NaI$$

Calculating the titer

1 mL $c(Na_2S_2O_3)$ = 0.1 mol/L corresponds to 3.567 mg KIO_3

Titer = C00 / C01 / EP1

EP1 = mL thiosulfate solution up to endpoint
C00 = weight of KIO_3 in mg
C01 = 3.567
Result to be given to four decimal places.

I.5.5 c(Na_2EDTA) = 0.1 mol/L

EDTA solutions have a stable titer. They always form 1:1 complexes with metal ions, irrespective of their charge number:

$$Me^{2+} + Na_2H_2EDTA + 2\ H_2O \rightleftharpoons Na_2MeEDTA + 2\ H_3O^+$$

$$Me^{3+} + Na_2H_2EDTA + 2\ H_2O \rightleftharpoons NaMeEDTA + 2\ H_3O^+ + Na^+$$

The separate determination of mixtures of different metal ions present in the same solution is normally not possible by titration. For example, titration must be carried out at different pH values or after the addition of masking agents.

The endpoint of the titration can be indicated in different ways. The oldest and still the most widespread method is the use of suitable colored indicators (photometric titration). For potentiometric indication ion-selective electrodes are usually used (e.g. Cu ISE, Ca ISE). Explanations are given for the individual determinations in Section II.5.

Preparation

37.224 g Na_2EDTA x 2 H_2O is weighed out into a 1000 mL volumetric flask, dissolved in dist. H_2O, made up to the mark and mixed.

Additional reagents

- Buffer solution pH = 10: 54 g NH_4Cl and 350 mL ammonia solution, w(NH_3) = 25%, are dissolved in dist. H_2O and made up to 1 liter.
- Auxiliary solution: $Cu(NH_4)_2EDTA$, c = 0.1 mol/L (e.g. Merck no. 105217)

Titer determination

Calcium carbonate is dried overnight in a drying oven at 140 °C and allowed to cool down in a desiccator for at least 2 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the Titrino as a «common variable».

Approx. 100 mg $CaCO_3$ is accurately weighed out into the titration beaker to the nearest 0.1 mg and suspended in approx. 20 mL dist. H_2O. Hydrochloric acid c(HCl) = 5 mol/L is added drop by drop under stirring until everything has dissolved (as $CaCl_2$). After the addition of approx. 30 mL dist. H_2O, 5 mL buffer solution pH = 10 and 0.5 mL auxiliary solution it is titrated with c(Na_2EDTA) = 0.1 mol/L to after the first endpoint (Cu ISE/reference electrode).

Calculating the titer

1 mL c(Na_2EDTA) = 0.1 mol/L corresponds to 10.009 mg $CaCO_3$

Titer = C00 / C01 / EP1

EP1 = mL Na_2EDTA solution up to endpoint
C00 = weight of $CaCO_3$ in mg
C01 = 10.009
Result to be given to four decimal places.

I.5.6 c($AgNO_3$) = 0.1 mol/L

Silver nitrate solutions are sensitive to light. After they have been placed in the Exchange Unit they are automatically protected against light.

Precipitation titrations with silver nitrate are normally carried out in acidified solutions (with the exception of cyanide) in order to prevent the formation of interfering AgOH or Ag_2CO_3. For potentiometric indication we recommend the use of an Ag electrode with an Ag_2S coating. In comparison to a «bright» Ag electrode it has a more stable potential and a quicker response. Metrohm Application Bulletin no. 25 describes the preparation of the coating on Ag electrodes.

Preparation

16.99 g $AgNO_3$ is weighed out into a 1000 mL volumetric flask and dissolved in approx. 200 mL dist. H_2O. After the addition of 0.1 mL nitric acid, c(HNO_3) = 2 mol/L, it is made up to the mark with dist. H_2O and mixed.

Titer determination

Sodium chloride is dried overnight in a drying oven at 140 °C and allowed to cool down in a desiccator for at least 2 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the Titrino as a «common variable».

Approx. 60 mg NaCl is accurately weighed out into the titration beaker to the nearest 0.1 mg and dissolved in approx. 50 mL dist. H_2O. After the addition of 1 mL $c(HNO_3)$ = 2 mol/L it is titrated with $c(AgNO_3)$ = 0.1 mol/L to after the first endpoint (Ag Titrode with Ag_2S coating).

Calculating the titer

1 mL $c(AgNO_3)$ = 0.1 mol/L corresponds to 5.844 mg NaCl

Titer = C00 / C01 / EP1

EP1 = mL $AgNO_3$ solution up to endpoint
C00 = weight of NaCl in mg
C01 = 5.844
Result to be given to four decimal places.

I.5.7 c($KMnO_4$) = 0.02 mol/L

Permanganate solutions have – if pretreated correctly and stored protected against light – a relatively stable titer. However, traces of ammonium salts and organic substances (e.g. dust particles) have the effect of reducing $KMnO_4$ to MnO_2. If this is not removed from the solution it acts as a catalyst and the titer continuously decreases:

$$MnO_4^- + 4\,H_3O^+ + 3\,e^- \rightarrow \{MnO_2\} + 6\,H_2O$$

Preparation

3.2 g $KMnO_4$ is weighed out into a beaker and dissolved in approx. 950 mL dist. H_2O. The solution is heated to boiling and kept boiling for approx. 15 min. After cooling down it is filtered through a glass filter crucible (not a paper filter! – permanganate oxidizes paper constituents and is reduced to MnO_2!) into a thoroughly cleaned 1000 mL volumetric flask, made up to the mark with dist. H_2O and mixed. (If the solution is prepared directly without heating then the MnO_2 formed must be filtered off after approx. 2 weeks.)

Titer determination

Disodium oxalate is dried overnight in a drying oven at 240 °C and allowed to cool down in a desiccator for at least 2 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the Titrino as a «common variable».

Approx. 70 mg $Na_2C_2O_4$ is accurately weighed out into the titration beaker to the nearest 0.1 mg and dissolved in approx. 50 mL dist. H_2O. It is treated with 0.5 to 1 g $MnSO_4$*, 5 mL sulfuric acid $w(H_2SO_4)$ = 25% is added and then titrated with $c(KMnO_4)$ = 0.02 mol/L to after the first endpoint (Pt Titrode or combined Pt-ring electrode).

* Manganese sulfate acts as a catalyst and accelerates the oxidation of the oxalate so that the titration does not have to be carried out in a hot solution.

$$2\,KMnO_4 + 5\,Na_2C_2O_4 + 8\,H_2SO_4 \rightarrow 2\,MnSO_4 + 5\,Na_2SO_4 + K_2SO_4 + 10\,CO_2 + 8\,H_2O$$

Calculating the titer

1 mL $c(KMnO_4)$ = 0.02 mol/L corresponds to 6.700 mg $Na_2C_2O_4$

Titer = C00 / C01 / EP1

EP1 = mL $KMnO_4$ solution up to endpoint
C00 = weight of $Na_2C_2O_4$ in mg
C01 = 6.7
Result to be given to four decimal places.

I.5.8 Cer(IV), c = 0.1 mol/L

Cerium(IV) solutions are strong oxidizing agents with a stable titer; titrations with them are only carried out under strongly acidic conditions. In comparison to $KMnO_4$ they have the advantage that titrations can also be carried out in solutions containing chlorides (chloride ions interfere with the $KMnO_4$ titration – $KMnO_4$ oxidizes them to chlorine / chlorine dioxide).

Preparation

41 g $Ce(SO_4)_2$ x 4 H_2O is weighed out into a beaker and dissolved in approx. 500 mL sulfuric acid, $c(H_2SO_4)$ = 1 mol/L under moderate heat. After cooling down the solution is transferred to a 1000 mL volumetric flask using dist. H_2O, made up to the mark and mixed.

Titer determination

Disodium oxalate is dried overnight in a drying oven at 240 °C and allowed to cool down in a desiccator for at least 2 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the Titrino as a «common variable».

Approx. 70 mg $Na_2C_2O_4$ is accurately weighed out into the titration beaker to the nearest 0.1 mg and dissolved in approx. 50 mL dist. H_2O. After the addition of 10 mL sulfuric acid, $w(H_2SO_4)$ = 25%, the solution is heated to approx. 40 to 50 °C and titrated with Ce(IV), c = 0.1 mol/L to after the first endpoint (Pt Titrode or combined Pt-ring electrode). The reaction can be described by the following simplified equation:

$$2\ Ce(IV) + C_2O_4^{2-} \rightarrow 2\ Ce(III) + 2\ CO_2$$

Calculating the titer

1 mL Ce(IV), c = 0.1 mol/L corresponds to 6.700 mg $Na_2C_2O_4$

Titer = C00 / C01 / EP1

EP1 = mL cerium(IV) solution up to endpoint
C00 = weight of $Na_2C_2O_4$ in mg
C01 = 6.7
Result to be given to four decimal places.

I.5.9 Alcoholic solution c(KOH) = 0.1 mol/L

KOH solutions do not have a stable titer. They can absorb CO_2 from the air to form potassium carbonate. This means that not only the titer becomes reduced. As KOH and K_2CO_3 have different base strengths this will affect the titration curve and therefore the results. In order to largely avoid CO_2 absorption from the atmosphere the drying or absorber tube of the Exchange Unit is filled with soda lime (CO_2 absorber). As strong bases attack glass the Exchange Unit should be provided with a plastic storage bottle.

Please also note that non-aqueous titrants have a coefficient of expansion that is higher than that of water by a factor of 4!

Preparation

6 g KOH is weighed out into a beaker, treated with a little dist. H_2O and swirled about briefly in order to dissolve any K_2CO_3 on the surface. This solution is rejected. 20 mL CO_2-free dist. H_2O is added and the KOH is completely dissolved. The solution is transferred to a 1000 mL volumetric flask using CO_2-free ethanol or isopropanol (isopropyl alcohol, IPA), made up to the mark with this solvent and mixed.

Titer determination

Benzoic acid is dried overnight in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the Titrino as a «common variable».

Approx. 120 mg benzoic acid is accurately weighed out into the titration beaker to the nearest 0.1 mg and dissolved in approx. 50 mL ethanol. It is immediately titrated with alcoholic c(KOH) = 0.1 mol/L to after the first endpoint (Solvotrode).

Calculating the titer

1 mL alcoholic potassium hydroxide, c(KOH) = 0.1 mol/L corresponds to 12.212 mg benzoic acid ($C_7H_6O_2$)

Titer = C00 / C01 / EP1

EP1 = mL alcoholic KOH up to endpoint
C00 = weight of benzoic acid in mg
C01 = 12.212
Result to be given to four decimal places.

I.5.10 c(HClO$_4$) = 0.1 mol/L in glacial acetic acid

The strongest acid for non-aqueous media is $HClO_4$ in glacial acetic acid (concentrated acetic acid). It is particularly suitable for the titration of weak bases that can no longer be titrated in purely aqueous solution.

Please also note that non-aqueous titrants have a coefficient of expansion that is higher than that of water by a factor of 4!

Preparation

8.5 mL perchloric acid, w($HClO_4$) = 70% (1.68 g/mL), is measured out into a 1000 mL volumetric flask, made up to the mark with concentrated acetic acid (w = 96...100%) and mixed.

Titer determination

Potassium hydrogen phthalate is dried overnight in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h. Care must be taken that the titrations are carried out at a constant temperature.

Normally the titer determination is carried out three times and the mean value is used. The mean value of the titer can be stored in the Titrino as a «common variable».

Approx. 200 mg KH phthalate is accurately weighed out into the titration beaker to the nearest 0.1 mg. It is treated with 50 mL glacial acetic acid and stirred at room temperature until

everything has dissolved (5 to 10 min). It is then titrated with perchloric acid, $c(HClO_4)$ = 0.1 mol/L, to after the first endpoint (Solvotrode).

Calculating the titer

1 mL perchloric acid $c(HClO_4)$ = 0.1 mol/L corresponds to 20.423 mg KH phthalate

Titer = C00 / C01 / EP1

EP1 = mL $HClO_4$ solution up to endpoint
C00 = weight of KH phthalate in mg
C01 = 20.423
Result to be given to four decimal places.

II. Practical part

Preliminary remarks

What must a modern titrator be able to do in order to meet market demands?

This is a question that Metrohm always has to face, no matter whether for new developments or the further development of existing instruments.

The basis can be assumed to be the knowledge about titrations that has been acquired by a qualified laboratory technician, i.e. the correct working procedure for each type of titration. This includes the titration speed (as fast as possible – but always waiting for the equilibrium to be established), as accurate as possible (volume increments that are as small as possible toward the end of the titration) and recognition of the true titration endpoint.

In addition there are such matter-of-course things as PC and balance connections, flexible calculation possibilities, automation possibilities, compliance with regulations, etc.

Titration endpoint

The simplest way of finding the endpoint of an S-shaped potentiometric titration curve (U/mL) is the differentiation **ΔU/ΔmL**. Peak-shaped curves are produced whose peak maximum contains two pieces of information:

- on the volume axis (mL) the titration endpoint **(EP)**
- on the potential axis (U) the shape of the curve (steep, flat, symmetrical, asymmetrical) and, with Metrohm, an endpoint criterion **(EPC)** with whose help endpoints can be selected deliberately (e.g. filter functions).

However, this possibility for evaluation only applies to ideal and symmetrical single curves. For mixtures (several endpoints) or with asymmetrical curves Metrohm has developed its own algorithm (polynomial of the n^{th} degree), with which these possibilities can also be taken into account.

Further information about ***the titration modes used by Metrohm***:

SET (**S**et **E**ndpoint **T**itration)

Titration to a predefined endpoint. For quick, quantitative determinations when the EP does not become displaced during a series of determinations or for titrations in which an excess of titrant has to be avoided. In this mode there is no point in printing out titration curves (they contain no useful information).

MET (**M**onotonic **E**quivalence point **T**itration)

Constant volume increment dosing, not dependent on the slope of the curve. Measured value acceptance can be either drift-controlled (equilibrium titration) and/or after a predefined waiting period. For slow titration reactions (e.g. diazotization, bromination) and/or slowly responding sensors (electrodes).

DET (**D**ynamic **E**quivalence point **T**itration)

Reagent (titrant) dosing with variable volume increments, depending on the slope of the titration curve (large in the flat parts and small in the steep parts of the curve). Measured value acceptance can also be either drift-controlled and/or after a predefined waiting period. Suitable for most titrations. This method recognizes jumps that are close together or relatively flat.

TIP (**Ti**tration **P**rocedure)

Combination of different commands to give a titration sequence. This is a first step toward automation, e.g. different additions (auxiliary reagents), measurements and titrations can be linked together and printed out as a results block.

II.1 Acid-base titrations and methods, aqueous

II.1.1 Electrode calibration and electrode handling

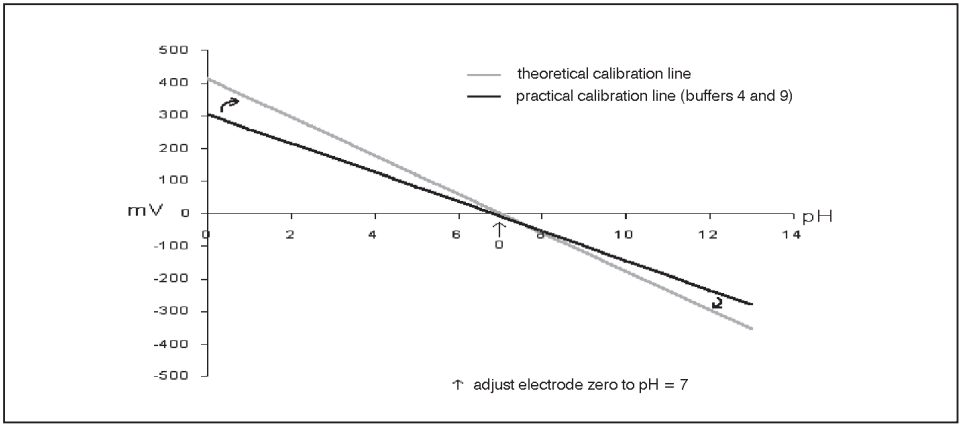
As mentioned in «Electrodes for potentiometry», the pH of the buffer and sample solutions is temperature-dependent and cannot be compensated by the instrument.

We would also like to remind you again that buffer solutions are not stable and should always be disposed of after use.

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

- Remove the electrode from its storage vessel, attach the cable and connect it to the instrument.
- Open the filling opening (electrolyte), top up the electrolyte solution if necessary.
- Thoroughly rinse the electrode with dist. H_2O and dab dry with a soft paper tissue (do not rub).
- Fill buffer solution pH = 7.0 into a beaker and add a magnetic stirrer bar.
- Immerse the electrode in the buffer solution and stir for approx. 1 min. Measure the buffer solution temperature and enter it in the instrument (a Pt 1000 temperature sensor can also be connected).
- Enter the pH value (for the corresponding temperature) and start the calibration with buffer 1 under stirring.
- As soon as the measurement has been accepted, remove the electrode from the solution, thoroughly rinse it with dist. H_2O and dab dry with a soft paper tissue.
- Fill buffer solution pH = 4.0 or pH = 9.0 into a second beaker, add a magnetic stirrer bar, immerse the electrode and stir for 1 min (the second buffer solution must be at the same temperature as the first buffer solution).
- Enter the pH value of the second buffer solution (for the corresponding temperature) and continue the calibration under stirring.
- When the measurement has been accepted, end the calibration, rinse the electrode with dist. H_2O and dab dry with a soft paper tissue.

What takes place in the instrument during calibration can be seen in the following diagram:



Handling the combined pH glass electrode

The working life of electrodes used in the laboratory should be as long as possible. Their characteristic data must lie within the given criteria (slope, pH_{as} and U_{as}) and they should have a rapid response behavior. In order to ensure that these targets are met, a few basic rules must be observed.

A) Purchase and use of the correct electrode

This is the first decisive step that you can take. Selecting the correct electrode will save you a lot of trouble. Information is provided in the Metrohm catalogue «Metrosensor Electrodes» under chapter «Which electrode for which application?».

In which samples will my electrode be used? What influence do these samples have on my electrode? These questions primarily concern the diaphragm, the electrolyte solution and the Ag/AgCl reference system.

In «older» Ag/AgCl reference electrodes the electrolyte solution becomes saturated with complexed silver ions. AgCl can precipitate in the diaphragm as AgCl or, in the presence of sulfide ions, as Ag_2S and block the diaphragm – this mainly affects ceramic diaphragms.

With LL electrodes this occurs less frequently as only traces of AgCl can enter the electrolyte solution. The glass membrane is also affected less frequently (drying out, abrasion or aging of the gel layer).

B) Electrode storage and maintenance

After use rinse the electrode thoroughly with dist. H_2O and dab it dry with a soft paper tissue. Close the filling opening (electrolyte) and store the electrode by immersing it to a sufficient depth in the electrolyte solution – usually c(KCl) = 3 mol/L.

Caution: Dry storage leads to a delayed and poor response. The electrolyte could become more concentrated and pH_{as}/U_{as} could change. Storage in dist. H_2O could block the diaphragm.

C) Troubleshooting

- For blocked diaphragms please consult the electrode data sheet that accompanies each electrode. Remedying a blocked diaphragm is complicated; it is better to send the electrode to your local Metrohm agency for repair.
- Contamination by fats, paints, lacquers, etc.: Remove the contamination with an organic solvent (acetone, benzine, toluene), then rinse it thoroughly with ethanol and dist. H_2O and immerse the electrode in electrolyte solution.
- Contamination by proteins: Immerse the electrode for several hours in a solution of 5% pepsin in hydrochloric acid, c(HCl) = 0.1 mol/L. Then rinse thoroughly with dist. H_2O.
- If the measured value is slow to stabilize and/or the slope is unsatisfactory then the electrode requires etching. This is done by immersing the electrode for 10 s in a solution of ammonium difluoride (NH_4HF_2, w = 10%, plastic beaker), then swirling it in hydrochloric acid, c(HCl) = 5 mol/L, for approx. 10 s, rinsing it with dist. H_2O, removing silicate residues with a moist tissue and immersing the electrode in c(KCl) = 3 mol/L for 24 h (or 5 h at 50 °C).

II.1.2 Titer determination of hydrochloric acid, *c*(HCl) = 0.1 mol/L with Tris

Learning topics

- Use of standard titrimetric substances.
- Clean working practices.
- Titration of a weak base with a strong acid.
- Titration curve and position of endpoint.

Titer determination of HCl

Principles

As a dilute HCl standard solution frequently is not adjusted exactly to a particular concentration, but only has an approximate concentration of e.g. 0.1 mol/L, its accurate concentration must be determined by using a standard titrimetric substance. The titer of HCl is determined by using tris(hydroxymethyl)-aminomethane (Tris) as the standard titrimetric substance. As Tris is a weak base, the equivalence point of the titration is at approx. pH 5.2, i.e. on the acidic side. The broad plateau that lies before it demonstrates the buffering properties of the Tris/Tris hydrochloride mixture formed during the titration. The true concentration of the HCl is obtained from the product of the approximate concentration and the titer.

Reaction equation

$(CH_2OH)_3CNH_2 + HCl \rightarrow$

$(CH_2OH)_3CNH \times HCl$

Materials and apparatus

Analytical balance 5-digit	Sartorius 1702
Exchange Unit	20 mL
Ecotrode	6.0232.100

Reagents and chemicals

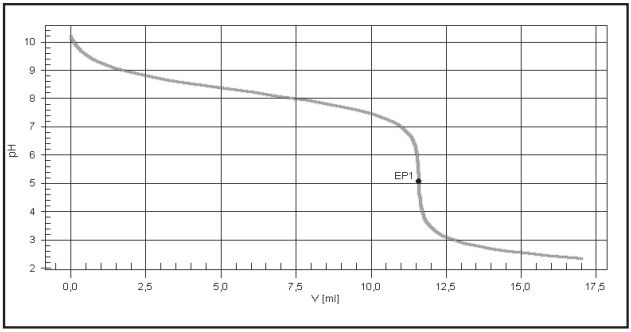
HCl_{aq} c = 0.1 mol/L	Riedel-de Haën 35335
Tris	Fluka 93350

Procedure

Tris is placed in a weighing bottle and dried in a drying oven at 105 °C for 2 h, then cooled down and stored in a desiccator. 10 samples between 100 and 150 mg are then weighed out with an accuracy of 0.1 mg and each is placed in a 100 mL beaker. 60 mL dist. H_2O is added and the titration is carried out with the following parameters:

```
DET  pH
>titration parameters
  meas.pt.density          4
  min.incr.             10.0 µl
  titr.rate             max. ml/min
  signal drift            50 mV/min
  equilibr.time           26 s
  start V:              abs.
  start V                  0 ml
  dos.rate              max. ml/min
  pause                    0 s
  meas.input:              1
  temperature           25.0 °C
>stop conditions
  stop V:                abs.
  stop V                  20 ml
  stop pH                OFF
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                  ON
  mean              n=     10
  res.tab:          original
>evaluation
  EPC                      5
  EP recognition:        all
  fix EP1 at pH          OFF
  pK/HNP:                OFF
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
          ------------
```

Example of a titration curve



Calculation

In order to obtain the titer of hydrochloric acid the following formula must be entered in the instrument:

Titer = C00 x C01 /C02 / EP1;4;

The individual variables are:

EP1 = added volume up to first equivalence point [mL]

C00 = weight of standard titrimetric substance [g]

C01 = correction factor (c = 0.1 mol/L ➔ 10'000 mL/mol)

C02 = molar mass of Tris (121.17 g/mol)

The titer has no unit and should be given to 4 decimal places.

Measured values and statistics

Measured value	Sample size Tris (g)	Consumption of HCl (mL)	Titer
1	0.08973	7.422	0.9980
2	0.11924	9.867	0.9976
3	0.09025	7.454	0.9995
4	0.08714	7.216	0.9969
5	0.08699	7.205	0.9967
6	0.07515	6.213	0.9985
7	0.09383	7.763	0.9978
8	0.07066	5.850	0.9971
9	0.79730	6.591	0.9986
10	0.11616	9.596	0.9993
$\bar{\chi}$			**0.9980**
S ±			**0.0001**
S_{rel} ±%			**0.1**

II.1.3 Titer determination of hydrochloric acid, *c*(HCl) = 0.1 mol/L and validation of the titrator

Learning topics

- Temperature coefficient of the titrant. Systematic errors and their correction.
- Achievable precision. Validation of the titrator as a complete system and not as individual components.
- For texts and calculations please refer to Application Bulletin no. 252.

Principles: see II.1.2.

Work is carried out with different sample weights so that between 20% and 80% of the cylinder volume is consumed up to the endpoint. Procedure otherwise as under 1.2.

Possible sources of error

The greatest source of error lies in weighing out the standard titrimetric substance. It is important that the balance and standard titrimetric substance have the same temperature, and that the balance is not exposed to drafts. If the weights are not accurate enough the accuracy can be improved by making a relative measurement. The weighing boat is tared and then reweighed after the standard titrimetric substance has been added. This allows the weight of added substance to be read off directly and very accurately. Before the start of the titration it is essential that the standard titrimetric substance has been completely dissolved, as only solvated and, if applicable, dissociated molecules can take part in the reaction.

II.1.4 Titration of NaOH

Learning topics

- Titration of a strong base with a strong acid.
- Titration curve and position of the endpoint.

Titer adjustment can be avoided by using a ready-to-use standard solution. If the titer is to be determined then Tris is used; this must have been dried for approx. 2 h at 105 °C.

Reaction equations

1. $NaOH \rightarrow Na^+ + OH^-$ dissociation of base
2. $OH^- + H_3O^+ \rightarrow 2\,H_2O$ neutralization

Materials and apparatus

Exchange Unit	20 mL
Ecotrode	6.0232.100

Reagents and chemicals

c(HCl) = 0.1 mol/L	Riedel-de Haën 35335
c(NaOH) = 0.1 mol/L	CO_2-free

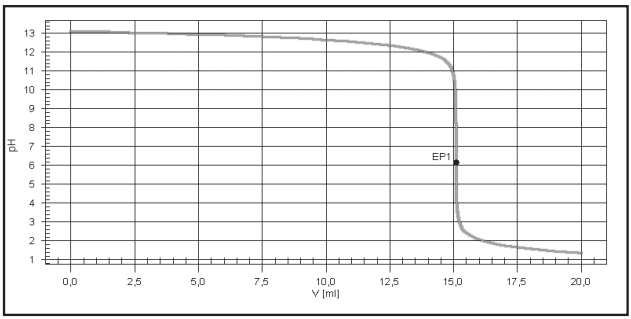
Procedure

15 mL c(NaOH) = 0.1 mol/L is pipetted into 10 beakers (100 mL) and made up to 60 mL with dist. H_2O. It is essential that the NaOH is carbonate-free, as otherwise 2 equivalence points will be found, one the equivalence point of NaOH and the other the equivalence point of the carbonate. In order to achieve results that are as good as possible we recommend that only that beaker is prepared which is to be titrated immediately. In this way the carbonate error is kept as small as possible.

The titration is carried out with the following parameters:

```
DET  pH
>titration parameters
  meas.pt.density          4
  min.incr.             10.0 µl
  titr.rate             max. ml/min
  signal drift            50 mV/min
  equilibr.time           26 s
  start V:              abs.
  start V                  0 ml
  dos.rate              max. ml/min
  pause                    0 s
  meas.input:              1
  temperature           25.0 °C
>stop conditions
  stop V:                abs.
  stop V                  20 ml
  stop pH                OFF
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                  ON
  mean                n=    10
  res.tab:            original
>evaluation
  EPC                      8
  EP recognition:        all
  fix EP1 at pH         OFF
  pK/HNP:                OFF
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
          ------------
```

Example of a titration curve



Measured values and statistics

Measured value	Sample size NaOH (mL)	Consumption of HCl (mL)	*c* (NaOH) in mol/L
1	15.000	15.115	1.0098
2	15.000	15.055	1.0058
3	15.000	15.101	1.0088
4	15.000	15.082	1.0076
5	15.000	15.124	1.0103
6	15.000	15.055	1.0058
7	15.000	15.089	1.0081
8	15.000	15.059	1.0060
9	15.000	15.049	1.0054
10	15.000	15.097	1.0086
$\overline{\chi}$			**1.0076**
S ±			**0.0018**
S_{rel} ±%			**0.18**

Possible sources of error

Possible sources of error in the titration could be, for example, pipetting errors, or an HCl solution with an inaccurate titer. We recommend that pipetting is carried out with great care and that the titer of the standard solution is checked.

If two equivalence points are found in the titration the possible cause could be dissolved CO_2. In this case freshly-made NaOH should provide help.

Calculation

In order to obtain the titer of the NaOH solution, the following formula must be entered in the instrument:

c(NaOH) = EP1 x C01 x C02 / C00;3;mol/L

The individual variables are:

EP1 = added volume up to first equivalence point [mL]

C00 = volume of NaOH solution [mL]

C01 = concentration of HCl solution (1) [mol/L]

C02 = titer (1.0021) [–]

This results in *c*(NaOH) having the unit [mol/L]; the concentration of the base should be given to 4 decimal places.

II.1.5 Titration of NaOH containing a small amount of Na_2CO_3

Learning topics

- Absorption of CO_2 from the air.
- Titration curve and position / displacement of the endpoints.
- Titration sequence according to base strength.
- Calculating the CO_2 content.

Principles

The sodium hydroxide solution containing the carbonate is titrated against a strong acid of known concentration. The sodium hydroxide is titrated first, followed by the carbonate. The titration curve has 2 equivalence points; the first equivalence point is produced by NaOH, the second by the carbonate.

Titer adjustment can be avoided by using a ready-to-use standard solution. If the titer is to be determined then Tris is used; this must have been dried for approx. 2 h at 105 °C.

Reaction equations

1. $NaOH \rightarrow Na^+ + OH^-$
   dissociation of base
2. $OH^- + H_3O^+ \rightarrow 2\ H_2O$
   titration of NaOH
3. $CO_3^{2-} + 2\ H_3O^+ \rightarrow CO_2 + 3\ H_2O$
   titration of carbonate

Materials and apparatus

Exchange Unit	20 mL
Ecotrode	6.0232.100

Reagents and chemicals

HCl_{aq} c = 0.1 mol/L
Riedel-de Haën 35335

$NaOH_{aq}$ c = 0.1 mol/L

Procedure

15 mL c(NaOH) = 0.1 mol/L is pipetted into 10 beakers (100 mL) and made up to 60 mL with dist. H_2O. In order to achieve results that are as good as possible we recommend that only that beaker is prepared which is to be titrated immediately.

The titration is carried out with the following parameters:

```
DET  pH
>titration parameters
  meas.pt.density          4
  min.incr.             10.0 µl
  titr.rate             max. ml/min
  signal drift            50 mV/min
  equilibr.time           26 s
  start V:              abs.
  start V                 0.0 ml
  dos.rate              max. ml/min
  pause                    0 s
  meas.input:              1
  temperature           25.0 °C
>stop conditions
  stop V:                abs.
  stop V                  20 ml
  stop pH                OFF
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                  ON
  mean                n=    10
  res.tab:            original
>evaluation
  EPC                      10
  EP recognition:         all
  fix EP1 at pH          OFF
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
          ------------
```

Example of a titration curve

Calculation

Two formulas are entered in the instrument:

1. To obtain the concentration of the NaOH solution:

   c(NaOH) = EP1 x C01 x C02 / C00;3;mol/L

2. To obtain the carbonat concentration of the solution:

   c(carb.) = (EP2 – EP1) x C01 x C02 / C00=;3;mol/L

The individual variables are:

EP1 = added volume up to first equivalence point [mL]

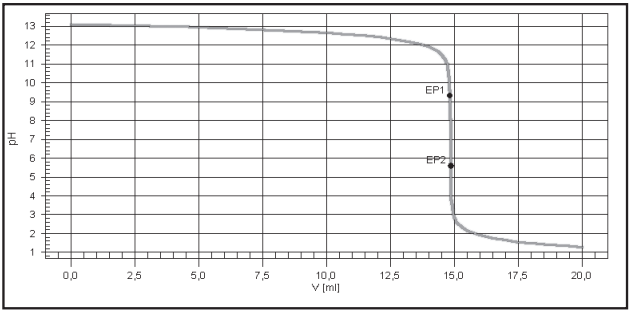
EP2 = added volume up to second equivalence point [mL]

C00 = volume of NaOH solution [mL]

C01 = concentration of HCl solution (0.1) [mol/L]

C02 = titer (1.0021) [–]

This results in c(NaOH) and c(carb.) having the unit [mol/L]. The concentrations should be given to three decimal places.



Measured values and statistics

Measured value	Sample size NaOH (mL)	mL HCl EP1	mL HCl EP2	c(NaOH) in mol/L	$c(CO_3^{2-})$ in mol/L
1	15.000	14.841	14.880	0.0991	0.0003
2	15.000	14.832	14.873	0.0990	0.0003
3	15.000	14.832	14.874	0.0991	0.0003
4	15.000	14.824	14.869	0.0990	0.0003
5	15.000	14.851	14.890	0.0992	0.0003
6	15.000	14.827	14.865	0.0991	0.0003
7	15.000	14.853	14.893	0.0992	0.0003
8	15.000	14.831	14.873	0.0991	0.0003
9	15.000	14.821	14.865	0.0990	0.0003
10	15.000	14.831	14.872	0.0991	0.0003
$\bar{\chi}$				**0.0991**	**0.0003**
S ±				**0.0001**	**0**
S_{rel} ±%				**0.1**	**0**

Possible sources of error

Possible sources of error in the titration could be, for example, pipetting errors, or an HCl solution with an inaccurate titer. We recommend that pipetting is carried out with great care and that the titer of the standard solution is checked.

II.1.6 Titration of sulfuric acid H_2SO_4

Learning topics

- Titration of a strong acid with a strong base.
- Titration curve and position of the endpoint.
- Leveling (of acids, i.e. the two dissociation steps of sulfuric acid) in aqueous solution.

With purchased and fresh ready-to-use standard solution the titer determination can be avoided. However, the titer has to be determined in regular time intervals with self-made or used standard solutions.

Reaction equations

1. $H_2SO_4 + 2\ H_2O \rightarrow 2\ H_3O^+ + SO_4^{2-}$ dissociation of acid
2. $H_3O^+ + OH^- \rightarrow 2\ H_2O$ neutralization

Materials and apparatus

Exchange Unit 20 mL
Ecotrode 6.0232.100
Nitrogen from the cylinder
Buret tip as gas inlet

Reagents and chemicals

$NaOH_{aq}$ c = 0.1 mol/L accurate titer
Riedel-de Haën 35263

$c(H_2SO_4)$ = ca. 0.1 mol/L

Procedure

8 mL of the H_2SO_4 is pipetted into 10 beakers (100 mL) and made up to approx. 60 mL with distilled water.

During the titration, nitrogen is continuously passed through the analyte solution to remove any dissolved CO_2 that could interfere with the titration. By setting a waiting period of 35 seconds before the titration, the CO_2 contained in the water is also displaced.

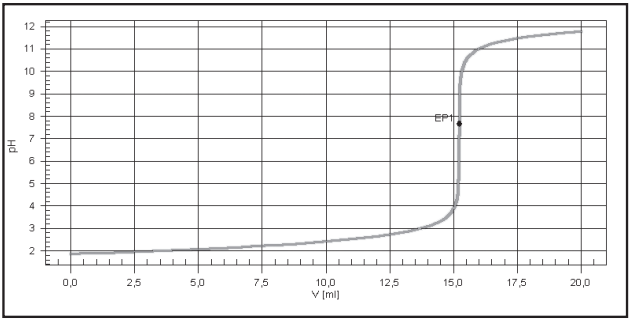
The titration is carried out using the following parameters:

```
DET  pH
>titration parameters
  meas.pt.density          4
  min.incr.             10.0 µl
  titr.rate             max. ml/min
  signal drift            50 mV/min
  equilibr.time           26 s
  start V:               OFF
  pause                   35 s
  meas.input:              1
  temperature           25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                   20 ml
  stop pH                OFF
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                  ON
  mean               n=    10
  res.tab:           original
>evaluation
  EPC                      10
  EP recognition:         all
  fix EP1 at pH          OFF
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
          ------------
```

Remark

[1] Ready-to-use standard solutions are commercially available standard solutions whose titer has been adjusted to 1.000 at 20 °C. We recommend the purchase of such ready-to-use solutions in preference to preparing them yourself. Alkaline titrants in particular do not have a stable titer (see titration of NaOH).

Example of a titration curve



Calculation

In order to obtain the concentration of the H_2SO_4 solution the following formula must be entered in the instrument:

$c(H_2SO_4)$ = EP1 x CO1 x C02 / C03 / C00;3;mol/L

The individual variables are:

EP1 = added volume up to the first equivalence point [mL]

C00 = volume of H_2SO_4 solution [mL]

C01 = concentration of NaOH solution (0.1) [mol/L]

C02 = titer (1.0000 for volumetric standard solution) [–]

C03 = valency of the acid (2) [–]

This results in $c(H_2SO_4)$ having the unit [mol/L]; the concentration of the acid should be given to three decimal places.

Measured values and statistics

Measured value	Sample size H_2SO_4 (mL)	Consumption of NaOH (mL)	$c(H_2SO_4)$ in mol/L
1	8.000	15.169	0.0948
2	8.000	15.211	0.0951
3	8.000	15.187	0.0949
4	8.000	15.195	0.0950
5	8.000	15.214	0.0951
6	8.000	15.183	0.0949
7	8.000	15.194	0.0949
8	8.000	15.182	0.0949
9	8.000	15.213	0.0951
10	8.000	15.240	0.0953
$\bar{\chi}$			**0.0950**
S ±			**0.0001**
S_{rel} ±%			**0.16**

Possible sources of error

Possible sources of error in the titration could be, for example, pipetting errors, or an NaOH solution with an inaccurate titer. We recommend that pipetting is carried out with great care and that the titer of the standard solution is checked.

If two equivalence points are found in the titration the possible cause could be dissolved CO_2. In this case a higher nitrogen throughput and/or a freshly made NaOH solution should provide help. Small amounts of carbonate in NaOH solution can change the value of the EP to a pH value of >7.0.

II.1.7 Titration of acetic acid, DET and endpoint titration (SET)

Learning topics

- Titration of a weak acid with a strong base.
- Titration curve and position of the endpoint.
- Determining the titration endpoint and SET titration; buffering range.

Principles

The equivalence point of the titration curve lies on the alkaline side as a weak acid is titrated with a strong base. In order to reduce the titration time for routine measurements a SET titration can be carried out to the true endpoint. This endpoint/equivalence point is first determined in a DET titration. A precondition is that the electrode is first calibrated using buffer solutions. In our example the EP is at pH = 8.16.

Reaction equations

1. $CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$
2. $H_3O^+ + OH^- \rightarrow 2\,H_2O$
3. $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Materials and apparatus

Exchange Unit 20 mL

Ecotrode 6.0232.100

Reagents and chemicals

Titrant c(NaOH) = 0.1 mol/L

«Sample» c(CH_3COOH) = approx. 0.1 mol/L. 5.75 mL glacial acetic acid is made up to 1 liter with dist. H_2O

Procedure

5.00 mL c(CH_3COOH) = 0.1 mol/L is diluted to approx. 50 mL with dist. H_2O in a beaker and then titrated with c(NaOH) = 0.1 mol/L.

Calculation

In order to obtain the concentration of the acetic acid solution the following formula must be entered in the Titrino:

mol/L acetic acid = EP1 x C01 x C30 / C00

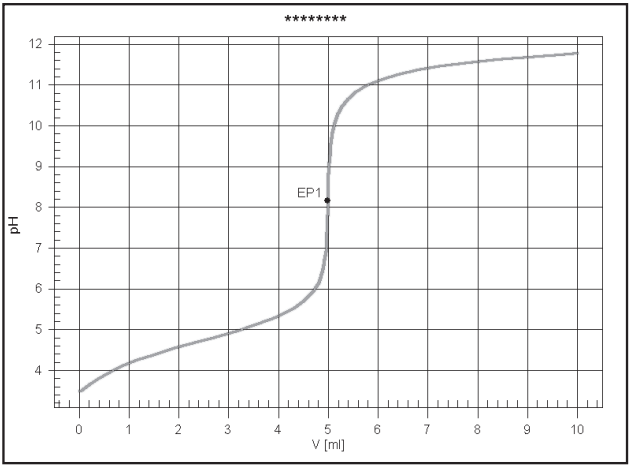
EP1 = mL NaOH up to endpoint [mL]
C00 = sample volume in mL
C01 = 0.1 (concentration of NaOH in mol/L)
C30 = titer of NaOH

The following parameters are entered in the Titrino:

```
DET titration
794 Titrino            OE2/239   794.0010
date 2002-04-19     time  10:42         2
pH(init)       3.47     DET pH         HAC
smpl size         5 ml     id#1          1
id#2              1        id#3          1
EP1            5.156 ml               8.16
c(VINEGAR)    0.103 mol/l
manual stop
no new com.var.
          ------------
 'pa
794 Titrino            OE2/239   794.0010
Date 2002-04-19     time  10:42         2
DET  pH                      HAC
parameters
>titration parameters
  meas.pt.density              4
  min.incr.                 10.0 µl
  titr.rate                 max. ml/min
  signal drift                50 mV/min
  equilibr.time               26 s
  start V:                  abs.
  start V                     0.0 ml
  dos.rate                  max. ml/min
  pause                        0 s
  meas.input:                  1
  temperature               25.0 °C
>stop conditions
  stop V:                   abs.
  stop V                      10 ml
  stop pH                   OFF
  stop EP                     9
  filling rate              max. ml/min
>statistics
  status:                   OFF
>evaluation
  E
>preselections
  req.ident:                OFF
  req.smpl size:            OFF
  activate pulse:           OFF
          ------------
```

Example of a titration curve (DET titration)

Measured values and statistics



Measured values and statistics

Sample size	CH_3COOH (mL)	Consumption of NaOH (mL)	*c* in mol/L
1	5.00	5.156	0.1031
2	5.00	5.145	0.1029
3	5.00	5.145	0.1029
4	5.00	5.189	0.1038
5	5.00	5.186	0.1037
6	5.00	5.194	0.1039
7	5.00	5.193	0.1039
8	5.00	5.222	0.1044
9	5.00	5.189	0.1038
10	5.00	5.208	0.1042
$\overline{\chi}$			**0.1037**
S ±			**0.0005**
S_{rel} ± %			**0.50**

SET titration

```
794 Titrino           OE2/239   794.0010
date 2002-04-19     time  13:19       34
pH(init)     3.48     SET pH        HAC2
smpl size           5 ml    id#1       1
id#2              1       id#3         1
EP1          5.239 ml                8.45
ACETIC AC    0.105 mol/l
          ------------

 'pa
794 Titrino           OE2/239   794.0010
Date 2002-04-19     time  13:19       34
SET  pH               HAC2
parameters
>SET1
  EP at pH              8.16
  dynamics               OFF
  max.rate             20.0 ml/min
  min.rate             25.0 µl/min
  stop crit:          drift
  stop drift             20 µl/min
>SET2
  EP at pH               OFF
>titration parameters
  titr.direction:       auto
  start V:              abs.
  start V              4.50 ml
  dos.rate             max. ml/min
  pause                   0 s
  meas.input:             1
  temperature          25.0 °C
>stop conditions
  stop V:               abs.
  stop V                 10 ml
  filling rate         max. ml/min
>statistics
  status:                OFF
>preselections
  conditioning:          OFF
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
          ------------
```

Measured values and statistics

Measured value	Sample size CH_3COOH (mL)	Consumption of NaOH (mL)	*c* in mol/L
1	5.00	5.239	0.1048
2	5.00	5.233	0.1047
3	5.00	5.243	0.1049
4	5.00	5.242	0.1048
5	5.00	5.241	0.1048
6	5.00	5.226	0.1045
7	5.00	5.230	0.1046
8	5.00	5.248	0.1050
9	5.00	5.249	0.1050
10	5.00	5.241	0.1048
			0.1048
S ±			**0.0002**
S_{rel} ±%			**0.15**

II.1.8 Titration of phosphoric acid (H_3PO_4), DET and MET

Learning topics

- Titration of a mixture of acids with a strong base.
- Titration curve and position of the endpoints.
- Titration sequence according to acid strength.
- Difference between dynamic / monotonic titration and its influence on the results.

Principles

Phosphoric acid is said to be a «tribasic acid», it corresponds theoretically to a mixture of three acids with the pK_a values 1.96, 7.12 and 12.32. The first proton corresponds to a strong acid, the second to a weak one and the third to a very weak acid. The strongest acid in a mixture is always titrated first. In aqueous solution only the first two acid groups have an endpoint, while the third acid group (as it is too weak) is not detected (leveling).

If it is assumed that the titration is carried out with a carbonate-free base then the NaOH consumption up to the second endpoint will be exactly twice the NaOH consumption up to the first endpoint. However, if the NaOH contains carbonate then more than double the amount will be required for EP2 than that for EP1 (the more, the greater the amount of carbonate in the base), as the amount of carbonate is also determined at EP2. As the carbonate/CO_2 equilibrium is not achieved very quickly, the titration up to EP2 must be carried out slowly. The difference is demonstrated by using a DET (quick) and a MET (slow) titration. For routine measurements we recommend titrating only up to EP1 (so that the carbonate error is eliminated).

Reaction equations

1. $H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$ (EP1 at pH = approx. 4.7)
2. $NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$ (EP2 at pH = approx. 9.3)
3. $Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$ (no EP)

$H_3PO_4 + 3\ NaOH \rightarrow Na_3PO_4 + 3\ H_2O$

Materials and apparatus

Exchange Unit 20 mL

Ecotrode 6.0232.100

Reagents and chemicals

Titrant c(NaOH) = 0.1 mol/L

«Sample» $c(H_3PO_4)$ = approx. 0.1 mol/L. Approx. 7 mL w(H_3PO_4) = 85% is made up to 1 liter with dist H_2O

Procedure

5.00 mL $c(H_3PO_4)$ = 0.1 mol/L is diluted with dist. H_2O to approx. 50 mL in a beaker and titrated with c(NaOH) = 0.1 mol/L to after the second endpoint.

Calculation

The following formulas must be entered into the Titrino in order to obtain the concentration of the phosphoric acid:

mol/L H_3PO_4 = EP1 x C01 x C30 / C00

or

(EP2 – EP1) x C01 x C30 / C00

or

EP2 x C01 x C30 / C02 / C00

EP1 = mL NaOH up to first endpoint
EP2 = mL NaOH up to second endpoint
C00 = sample volume in mL (5)
C01 = 0.1 (concentration of NaOH in mol/L)
C02 = 2 (double consumption up to EP2)
C30 = titer of NaOH

DET titration

Parameters

```
'pa
794 Titrino           OE2/239   794.0010
date 2002-05-03     time  09:47       14
DET  pH            PHOSPH 1
parameters
>titration parameters
  meas.pt.density              4
  min.incr.                10.0 µl
  titr.rate                max. ml/min
  signal drift               50 mV/min
  equilibr.time              26 s
  start V:                   OFF
  pause                       0 s
  meas.input:                 1
  temperature              25.0 °C
>stop conditions
  stop V:                    abs.
  stop V                     20 ml
  stop pH                    OFF
  stop EP                     9
  filling rate             max. ml/min
>statistics
  status:                    OFF
>evaluation
  EPC                         5
  EP recognition:           all
  fix EP1 at pH             OFF
  pK/HNP:                   OFF
>preselections
  req.ident:                OFF
  req.smpl size:            OFF
  activate pulse:           OFF
          ------------
```

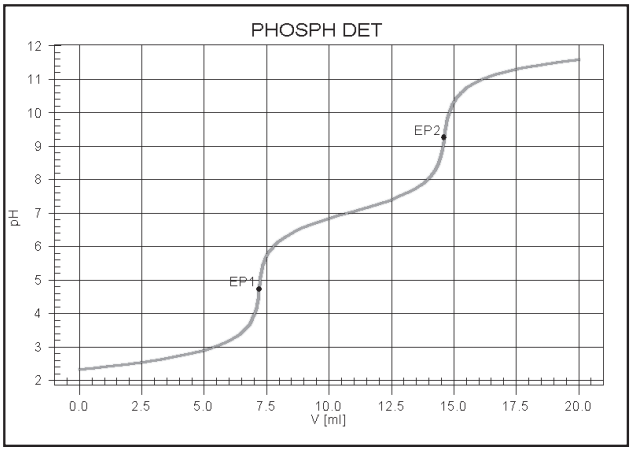
Measured values and statistics

Measured value	Sample size H_3PO_4 (mL)	Consumption of NaOH EP1 (mL)	*c* in mol/L	Consumption of NaOH EP2 (mL)	*c* in mol/L
1	5.00	7.205	0.1441	14.613	0.1461
2	5.00	7.203	0.1441	14.648	0.1465
3	5.00	7.216	0.1443	14.658	0.1466
4	5.00	7.205	0.1441	14.643	0.1464
5	5.00	7.224	0.1445	14.651	0.1465
6	5.00	7.207	0.1441	14.644	0.1464
7	5.00	7.230	0.1446	14.669	0.1467
8	5.00	7.252	0.1450	14.737	0.1474
9	5.00	7.219	0.1444	14.678	0.1468
10	5.00	7.216	0.1443	14.697	0.1470
$\overline{\chi}$			0.1444		**0.1466**
S ±			0.0003		**0.0004**
S_{rel} ±%			0.20		**0.25**

Calculation of carbonate portion with DET titration:

0.1466 mol/L – 0.1444 mol/L = 0.0022 mol/L

Example of a titration curve



MET titration

Parameters

```
'pa
794 Titrino            OE2/239    794.0010
date 2002-05-03     time  12:49         28
MET  pH             PHOSPH 2
parameters
>titration parameters
  V step                    0.10 ml
  titr.rate                 max. ml/min
  signal drift                50 mV/min
  equilibr.time               26 s
  start V:                   OFF
  pause                        0 s
  meas.input:                  1
  temperature               25.0 °C
>stop conditions
  stop V:                   abs.
  stop V                      20 ml
  stop pH                    OFF
  stop EP                      9
  filling rate              max. ml/min
>statistics
  status:                    OFF
>evaluation
  EPC                       0.50
  EP recognition:            all
  fix EP1 at pH             OFF
  pK/HNP:                    OFF
>preselections
  req.ident:                 OFF
  req.smpl size:             OFF
  activate pulse:            OFF
          ------------
```

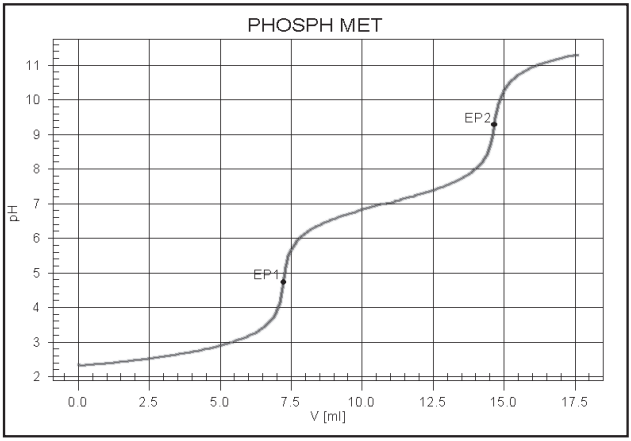
Measured values and statistics

Measured value	Sample size H_3PO_4 (mL)	Consumption of NaOH EP1 (mL)	*c* in mol/L	Consumption of NaOH EP2 (mL)	*c* in mol/L
1	5.00	7.217	0.1443	14.642	0.1464
2	5.00	7.227	0.1445	14.642	0.1464
3	5.00	7.227	0.1445	14.635	0.1464
4	5.00	7.232	0.1446	14.678	0.1468
5	5.00	7.225	0.1445	14.666	0.1467
6	5.00	7.241	0.1448	14.690	0.1469
7	5.00	7.258	0.1452	14.699	0.1470
8	5.00	7.226	0.1445	14.670	0.1467
9	5.00	7.260	0.1452	14.724	0.1472
10	5.00	7.230	0.1446	14.660	0.1466
$\bar{\chi}$			**0.1447**		**0.1467**
S ±			**0.0003**		**0.0003**
S_{rel} ±%			**0.21**		**0.19**

Calculation of carbonate concentration with MET titration:

0.1467 mol/L – 0.1447 mol/L = 0.0020 mol/L. With this small carbonate content, the difference between the DET and MET mode is irrelevant.

Example of a titration curve



II.1.9 Titration of boric acid (H_3BO_3) with and without addition of mannitol

Learning topics

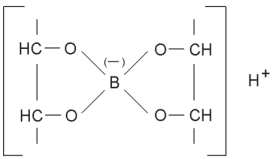
- Titration of a weak acid with a strong base.
- Titration curve and position of the endpoint.
- Buffering range.
- Increasing the acid strength by complex formation with the release of a proton.

Principles

The equivalence point of the titration curve lies on the alkaline side as a weak acid is titrated with a strong base.

Boric acid is a weak acid (pK 9.24) and, in aqueous solution, only shows a weakly pronounced, flat titration curve. However, its titration is no problem for modern titrators. Formerly this was not the case. This is why a chemical reaction between boric acid and a polyalcohol was used to obtain a steeper titration curve that was easier to evaluate.

With polyvalent alcohols, which must have at least three neighboring alcohol groups, boric acid forms an ester. As boron always attempts to achieve a coordination number of 4, this means that a further bond is formed to the oxygen atom of a neighboring alcohol group. This weakens its bond to hydrogen; the OH hydrogen splits off as H^+. This converts the boric acid-mannitol ester into a medium-strength acid. The polyalcohol should be present in excess so that a 1:2 compound can be formed. The polyalcohol used in our experiment is D(–)mannitol. The structure of the boric acid complex can be depicted as follows:



Titration of boric acid

Materials and apparatus

Exchange Unit 20 mL

Ecotrode 6.0232.100

Reagents and chemicals

Titrant c(NaOH) = 0.1 mol/L

«Sample» $c(H_3BO_3)$ = approx. 0.1 mol/L. 6.2 g H_3BO_3 is dissolved in dist. H_2O and made up to 1 liter.

D(–)mannitol solution approx. 200 g mannitol is dissolved in 800 mL dist. H_2O. The solution is saturated.

Procedure

5.00 mL $c(H_3BO_3)$ = 0.1 mol/L is diluted with dist. H_2O to approx. 50 mL in a first glass beaker and titrated with c(NaOH) = 0.1 mol/L.

5.00 mL $c(H_3BO_3)$ = 0.1 mol/L is treated with 10 mL mannitol solution and diluted to approx. 50 mL with dist. H_2O in a second glass beaker. It is then titrated with c(NaOH) = 0.1 mol/L.

Calculation

The following formula is entered in the Titrino in order to obtain the concentration of the boric acid:

mol/L H_3BO_3 = EPn x C01 x C30 / C00

EPn = mL NaOH up to endpoint at pH = approx. 10 (EPn = EP1 or EP2)
C00 = sample volume in mL (5)
C01 = 0.1 (concentration of NaOH in mol/L)
C30 = titer of NaOH

Boric acid determination without the addition of mannitol

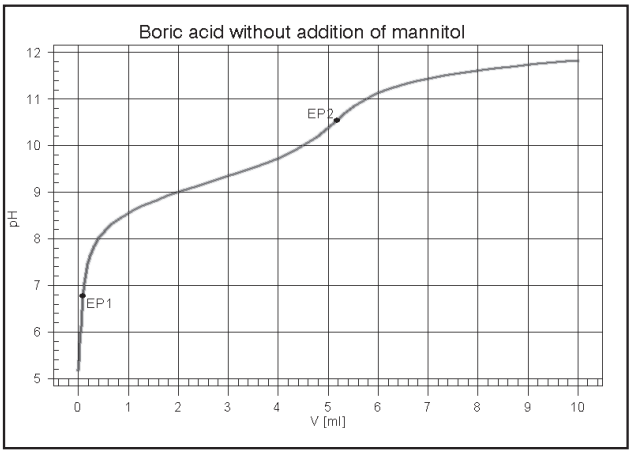
Parameters

```
'pa
794 Titrino            OE2/239    794.0010
date 2002-05-10     time  10:37          3
DET  pH             BOR AC1
parameters
>titration parameters
  meas.pt.density             4
  min.incr.                10.0 µl
  titr.rate                max. ml/min
  signal drift               50 mV/min
  equilibr.time              26 s
  start V:                  OFF
  pause                      0 s
  meas.input:                1
  temperature               25.0 °C
>stop conditions
  stop V:                   abs.
  stop V                     10 ml
  stop pH                   OFF
  stop EP                    9
  filling rate             max. ml/min
>statistics
  status:                   OFF
>evaluation
  EPC                        5
  EP recognition:           all
  fix EP1 at pH            OFF
  pK/HNP:                   OFF
>preselections
  req.ident:                OFF
  req.smpl size:            OFF
  activate pulse:           OFF
          ------------
```

Measured values and statistics

Measured value	Sample size H_3BO_3 (mL)	Consumption of NaOH (mL)	$c(H_3BO_3)$ in mol/L
1	5.00	5.095	0.1019
2	5.00	5.089	0.1018
χ			**0.1019**

Example of a titration curve



Frequently, in the titration of weak acids, the initial curve section has nothing to do with the species to be determined (blank value, EP1). Since the pK_a value is >9, the titration curve rises steeply on the way from the initial pH to the buffer plateau, which is interpreted by the Titrator as a first EP.

Boric acid determination with the addition of mannitol

Parameters

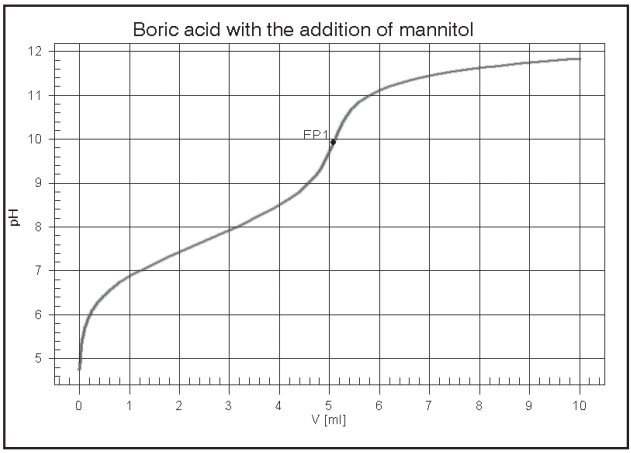
```
'pa
794 Titrino            OE2/239   794.0010
date 2002-05-10     time  10:44         4
DET  pH             BOR AC1
parameters
>titration parameters
  meas.pt.density              4
  min.incr.                 10.0 µl
  titr.rate                 max. ml/min
  signal drift                50 mV/min
  equilibr.time               26 s
  start V:                   OFF
  pause                        0 s
  meas.input:                  1
  temperature               25.0 °C
>stop conditions
  stop V:                    abs.
  stop V                      10 ml
  stop pH                    OFF
  stop EP                      9
  filling rate              max. ml/min
>statistics
  status:                    OFF
>evaluation
  EPC                          5
  EP recognition:            all
  fix EP1 at pH             OFF
  pK/HNP:                    OFF
>preselections
  req.ident:                 OFF
  req.smpl size:             OFF
  activate pulse:            OFF
          ------------
```

Measured values and statistics

Measured value	Sample size H_3BO_3 (mL)	Consumption of NaOH (mL)	c(H_3BO_3) in mol/L
1	5.00	5.078	0.1016
2	5.00	5.082	0.1016
3	5.00	5.114	0.1023
4	5.00	5.083	0.1017
5	5.00	5.105	0.1021
6	5.00	5.079	0.1016
7	5.00	5.087	0.1017
8	5.00	5.120	0.1024
9	5.00	5.089	0.1018
10	5.00	5.083	0.1017
$\bar{\chi}$			**0.1019**
S ±			**0.0003**
Srel ±%			**0.30**

The titration curve with added mannitol is noticeably steeper in the endpoint region.

Example of a titration curve



II.1.10 Titration of the acid and base capacity (p and m values) with fixed EPs and calculation of the carbonate hardness

Learning topics

- Titration of weak bases (salts) with a strong acid.
- Titration curve and position of the endpoints.
- $CO_2/CaHCO_3/CaCO_3$ equilibria in water.
- Water hardness.

Principles

Carbon dioxide gas (CO_2) dissolves in water. Depending upon the pH value three species can be present: carbonate, hydrogen carbonate and free CO_2. If, for example, Ca^{2+} or Mg^{2+} ions are present in the water, their solubility depends upon the counter-ion (anion) and the pH value.

If sufficient free carbonic acid is present then calcium will remain dissolved as the hydrogen carbonate. If additionally excess free carbonic acid is dissolved then it will attack, for example, limestone (corrosion of concrete) – the water is said to be aggressive. If calcareous water is heated then carbon dioxide is driven off and the lime-carbonic acid equilibrium is displaced to the carbonate side: boiler scale is deposited. The sum of the dissolved calcium and magnesium ions in mmol/L that are then precipitated as sparingly soluble salts corresponds to the **carbonate hardness** or **temporary hardness** of the water. Together with the **non-carbonate hardness** or **permanent** or **sulfate hardness** (obtainable as the sum of the concentrations of the two alkaline earth ions minus the hydrogen carbonate concentration) it forms a part of the total harness of the particular water (see below).

The **alkalinity or acid capacity** of a water is equal to the number of mmol hydrochloric acid that is consumed for the titration of 1 mL water to the color change of methyl orange or to pH = 4.3. This titration mainly determines hydroxide, carbonate and hydrogen carbonate anions.

The **acidity or base capacity** of a water is equal to the number of mmol sodium hydroxide consumed for the titration of 1 mL water to the color change of phenolphthalein or to pH = 8.2. This titration mainly determines weak acids, particularly carbonic acid, and hydrogen carbonate. In each of these titrations up to two equivalence points could be found; these correspond to the carbonate/hydrogen carbonate equilibrium and hydrogen carbonate/carbonic acid equilibrium.

The p and m values are given for the analytical characterization of water. If a basic water is titrated with HCl solution to determine the acid capacity then the **p value** corresponds to the consumption of c(HCl) = 1 mol/L in mL for the titration of 1 mL water up to the phenolphthalein endpoint or pH = 8.2. In particular, this determines the amount of CO_3^{2-}. The **m value** (pH = 4.3) corresponds to the consumption of hydrochloric acid c = 1 mol/L in mL up to the color change of methyl orange or pH = 4.3 (0.05 mval/L is subtracted for the m value of neutral water without any buffering constituents); this mainly determines the amount of hydrogen carbonate.

If acidic water samples are titrated with sodium hydroxide to determine the base capacity then the terms used are negative m and p values.

The **carbonate hardness** of a water is that part of the total hardness (see also II.5.4. and II.5.5.) caused by the alkaline earth ion fraction that is equivalent to the carbonate and hydrogen carbonate ions as well as the hydroxyl ions formed by their hydrolysis.

a) The carbonate hardness is calculated from the p and m values; if 2 p is smaller than or equal to m then the carbonate hardness x = m

b) If 2 p is larger than m the carbonate hardness x = 2 (m – p)

c) If p = m the carbonate hardness x = 0

If a higher value is obtained for the carbonate hardness than for the total hardness, then this indicates that in the water there are more carbonate and hydrogen carbonate ion equivalents than alkaline earth ions (determination see II.5.2.). The carbonate hardness is then given as being the total hardness.

Reaction equations

$CO_2 + H_2O \rightarrow H_2CO_3$
(formation of carbonic acid by hydration of CO_2)

$H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+$
(dissociation of first proton)

$HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+$
(dissociation of second proton)

$HCO_3^- + H_3O^+ \rightleftharpoons CO_2 + H_2O$
(displacement of CO_2 from HCO_3^-)

$H_2CO_3 + 2\,H_3O^+ \rightleftharpoons CO_2 + 3\,H_2O$
(displacement of CO_2 from H_2CO_3)

$2\,HCO_3^- \rightleftharpoons CO_2\uparrow + CO_3^{2-} + H_2O$
(formation of boiler scale on heating)

Materials and apparatus

Exchange Unit 10 mL

Aquatrode II 6.0253.100

Reagents and chemicals

Distilled or deionized water

Ready-to-use standard solution *c*(HCl) = 0.1 mol/L, Riedel-de Haën, order no. 35335

Tap water

Procedure

100 mL of a sample of drinking water is pipetted from a volumetric pipet into a 150 mL beaker and a magnetic stirrer bar is added. Always fill off one water sample only and process it immediately as atmospheric CO_2 could dissolve in the sample or CO_2 could be released from the solution.

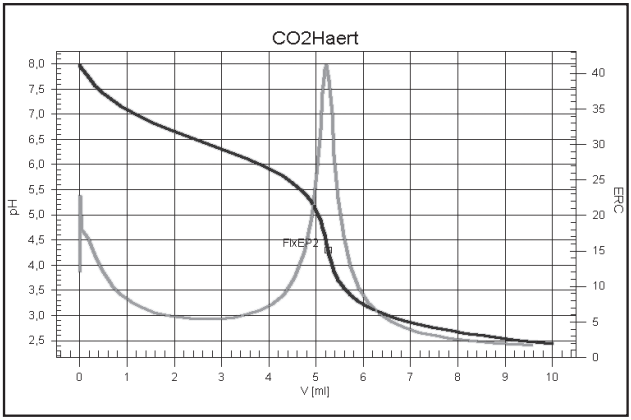
The stirrer speed is set so that no air bubbles are entrained as additional dissolved carbon dioxide would lead to incorrect results. The electrode and the buret tip are immersed in the sample solution so that the flow of freshly added titrant is not directed toward the electrode.

When the water sample has been prepared it is titrated according to the following dynamic pH program:

Dynamic titration program for carbonate hardness in drinking water

```
794 Titrino              01102   794.0010
date  2002-08-23    time  10:24       37
DET  pH             CO2Hard
parameters
>titration parameters
  meas.pt.density           4
  min.incr.                 5 µl
  titr.rate                 5 ml/min
  signal drift             15 mV/min
  equilibr.time            43 s
  start V:                 OFF
  pause                    90 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                    10 ml
  stop pH                  OFF
  stop EP                    9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                        5
  EP recognition:          OFF
  fix EP1 at pH            8.2
  fix EP2 at pH            4.3
  fix EP3 at pH            OFF
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Measured values and statistics

Measured value no.	Sample size water (mL)	Consumption (mL *c*(HCl) = 0.1 mol/L)	Carbonate hardness in mmol/L
1	100	5.253	5.25
2	100	5.257	5.25
3	100	5.252	5.25
4	100	5.251	5.25
5	100	5.253	5.25
6	100	5.250	5.25
7	100	5.253	5.25
8	100	5.251	5.25
9	100	5.251	5.25
10	100	5.249	5.25
$\bar{\chi}$			**5.25**
S ±			**0.003**
S_{rel} ±%			**0.06**

Possible sources of error

Particular care must be taken that the water samples are only filled off directly before the titration as otherwise they would continuously absorb atmospheric carbon dioxide. In order to achieve good results we recommend that you adapt the titration parameters in the «parameter» program.

The titration speed and the measured value drift should be lowered step by step until a correct result is obtained. During this procedure the waiting time for the equilibrium to become established will be automatically increased by the Titrino.

If, apart from carbonic acid and its anions, other substances are present in the water that have a buffering effect at about pH 4.3 or pH 8.2, this titration cannot be used.

II.1.11 Formol number in vegetable juices

Learning topics

- Titration of mixtures of amino acids after reaction with the release of a proton.
- Endpoint titrations and determining the optimal titration endpoint.

Principles

The formol number is purely a characteristic number. It is a cumulative parameter for the amount of all amino acids in certain natural products, chiefly fruit and vegetable juices. The formol number stands for the amount of amino nitrogen that can be titrated by formalin in mg/g dry substance.

The determination has no relationship to the size and amount of amino acid molecules and has been adapted to meet practical requirements. In order to avoid interference by weak acids the titration is carried out at a correspondingly high pH value: All the carboxyl groups present are first neutralized with sodium hydroxide (pH 8.50). The addition of formaldehyde then releases a proton from each amino group. Only primary amines release a proton readily. With secondary amines not all compounds release a proton, while tertiary amines have no proton and therefore cannot react.

A formaldehyde excess must be present in order to ensure complete reaction. The released protons are titrated with NaOH. Monoamino-monocarboxylic acids and monoamino-dicarboxylic acids correspond to 1 H^+, diamino-carboxylic acids to 2 H^+.

Reaction using a monoamino-monocarboxylic acid as an example:

Reaction equation

$$^-OOC - R - NH_3^+ + CH_2=O \rightleftharpoons {}^-OOC - R - NHCH_2OH + H^+$$

Materials and apparatus

Exchange Unit 10 mL

Profitrode 6.0255.100

Reagents and chemicals

Deionized water self-prepared

Formaldehyde solution w(HCHO) = 35% adjusted to pH 8.50 with NaOH

NaOH standard solution
c(NaOH) = 0.1 mol/L Riedel-de Haën 35263

Procedure

25 mL homogenized sample solution is pipetted into a beaker from a volumetric pipet and diluted with water to approx. 40 mL. A magnetic stirrer bar is added and the solution is titrated according to a SET program (FormolN1) in order to adjust the sample to pH 8.50. A Profitrode with double junction is used for detecting the pH value; this must be immersed in the solution until the ground-joint diaphragm is covered.

When the titration has been completed, 15 mL of the formaldehyde solution adjusted to pH 8.50 is added to the beaker from a Dosimat or volumetric pipet and the sample is immediately titrated according to the SET program (FormolN2). The formaldehyde attaches itself to the amino acids in the sample with the release of a proton. When the set waiting time has elapsed the freshly formed protons (oxonium ions) are again titrated to pH = 8.5 with c(NaOH) = 0.1 mol/L.

Parameter settings

```
'pa
794 Titrino            01102   794.0010
date 2002-09-03    time  10:50        5
SET  pH           FormolN1
parameters
>SET1
  EP at pH              8.50
  dynamics               0.5
  max.rate              10.0 ml/min
  min.rate                10 µl/min
  stop crit:           drift
  stop drift              20 µl/min
>SET2
  EP at pH               OFF
>titration parameters
  titr.direction:        auto
  start V:               OFF
  pause                    0 s
  meas.input:              1
  temperature           25.0 °C
>stop conditions
  stop V:                abs.
  stop V                  10 ml
  filling rate          max. ml/min
>statistics
  status:                OFF
>preselections
  conditioning:          OFF
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
         ------------
       'pa
794 Titrino            01102   794.0010
date 2002-09-03    time  10:51        5
SET  pH           FormolN2
parameters
>SET1
  EP at pH              8.50
  Dynamics               0.5
  max.rate              10.0 ml/min
  min.rate                10 µl/min
  stop crit:           drift
  stop drift              20 µl/min
>SET2
  EP at pH               OFF
>titration parameters
  titr.direction:          +
  start V:               OFF
  pause                   60 s
  meas.input:              1
  temperature           25.0 °C
>stop conditions
  stop V:                abs.
  stop V                  10 ml
  filling rate          max. ml/min
>statistics
  status:                OFF
>preselections
  conditioning:          OFF
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
         ------------
```

Calculation

The formol number is given in mL c(NaOH) = 0.1 mol/L per 100 mL sample.

Formol number = EP1 x C01 x C30

EP1 = consumption of c(NaOH) = 0.1 mol/L in mL
C01 = 4
C30 = titer of NaOH

Measured values and statistics

Measured value	Sample size fruit juice (mL)	Consumption of NaOH (mL)	Formol number
1	25.0	6.009	24.04
2	25.0	6.026	24.10
3	25.0	5.973	23.89
4	25.0	5.992	23.97
5	25.0	6.007	24.03
6	25.0	6.026	24.10
7	25.0	5.995	23.98
8	25.0	5.989	23.96
9	25.0	5.998	23.99
10	25.0	6.023	24.09
$\bar{\chi}$			**24.02**
S ±			**0.06**
S_{rel} ±%			**0.23**

Possible sources of error

- Formaldehyde solution not preneutralized.
- Electrode not calibrated or incorrect endpoint selected for the SET titration.

II.2 Acid-base titrations and methods, non-aqueous

II.2.1 General and additional remarks about non-aqueous titrations

Under Sections I.2.1 Acid-base reactions (autoprotolysis) and I.5 Titrants: (I.5.9 and I.5.10), some information on this subject has already been provided. Some additions to it are given here:

Non-aqueous titrations are primarily carried out when:

- the substance is not soluble in water
- the samples are fats or oils, or
- components of mixtures of acids or bases have to be determined separately by titration.

Instead of water (suitable) organic solvents are used. These should:

- dissolve the sample and not react with it,
- permit the determination of components in a mixture, and, if possible, should not be toxic or water-endangering

In most cases only a few solvents are required. These are: acetone, ethanol, isopropanol, methanol, toluene and glacial acetic acid (concentrated acetic acid) or, occasionally, binary mixtures of them.

The titrants are also not prepared with water. Examples are: NaOH in ethanol, KOH in isopropanol, HCl in ethanol or $HClO_4$ in glacial acetic acid.

If acids or bases are dissolved in protic solvents (e.g. H_2O), protolysis occurs. But salts produced during the titration can also be broken down protolytically. In such solvents the differentiation of strong acids with a similar strength is not possible by titration.

The situation is different if the titration is carried out in non-aqueous solvents. Examples are phenol and boric acid in water or ethanol or aromatic amines in water or DMF, which can easily be titrated in a non-aqueous medium.

A further reason why the titrimetric determination of acidic or basic components of a mixture is not possible in protic solvents is leveling. Instead of the strong acid or base itself lyonium or lyate ions of the solvent are produced. In the particular system these represent the strongest acids or bases that can possibly occur in the corresponding solvents. The differences in strength that were present in the original mixture of acids or bases are compensated or, as one says, leveled. A classical example of this is the aqueous solution of strong mineral acids.

With these acids water practically quantitatively forms the oxonium ion H_3O^+. This is why only their total can be determined in aqueous solution

Other frequently used terms:

Amphiprotic solvent

Also known as protic. Noticeable self-dissociation, e.g.:

$$2\ CH_3OH \rightleftarrows CH_3OH_2^+ + CH_3O^-$$

Aprotic solvent
No self-dissociation.

Dielectric constant (DC)

Proportional factor between the electric flux density D and the electric field strength E in vacuum. It is strongly temperature-dependent. Solutions with a higher DC promote the dissociation of electrolytes. In nonpolar solvents with a small DC even strong electrolytes (e.g. KCl, $HClO_4$) are only weakly dissociated. Examples of DCs:

Water	80.4 (20 °C)
Methanol	33.6 (20 °C)
Ethanol	25.1 (20 °C)
Acetone	21.2 (20 °C)
MIBK	18.5 (25 °C)
Pyridine	13.5 (20 °C)
Acetic acid	6.2 (20 °C)
Toluene	2.4 (20 °C)

Dissociation
Formation of ions, e.g. CH_3OOK CH_3COO^- + K^+

Solvents for non-aqueous titrations can be split up into different classes:

a) Amphiprotic – acidic
e.g. glacial acetic acid, trifluoroacetic acid, phenol, cresol. Solvents for bases.

b) Amphiprotic – basic
e.g. ethylenediamine, benzylamine, butylamine. Solvents for weak acids.

c) Amphiprotic – neutral
e.g. ethanol, isopropanol, ethylene glycol. Solvents for strong and weak acids and salts.

d) Aprotic – acidic
e.g. nitromethane, nitroethane. Solvents for strong and weak acids and salts (seldom used, explosion hazard)

e) Aprotic – basic
e.g. pyridine, dimethylformamide (DMF), dimethylsulfoxide (DMSO). Solvents for weak acids.

f) Aprotic – neutral
e.g. acetone, acetonitrile, nitrobenzene, diethyl ether, dioxan, hydrocarbons (hexane, heptane, toluene), chlorinated hydrocarbons (chloroform, methylene chloride). Carbohydrates, ether, dioxan and chlorinated hydrocarbons are only used as solubility promoters (for nonpolar substances such as fats and oils). Potentiometric indication cannot be carried out in these solvents (high electrical resistance). Used as solvents for amines or (if appropriate) for weak acids.

II.2.2. Titer determination of perchloric acid, c($HClO_4$) = 0.1 mol/L in glacial acetic acid

Learning topics

- Use of standard titrimetric substances.
- Coefficient of expansion of organic solvents/titrants.
- Titration curve.
- Use of suitable electrodes.

Principles

As a dilute $HClO_4$ standard solution is frequently not adjusted exactly to a defined concentration, but only has an approximate concentration of e.g. 0.1 mol/L, its accurate concentration must be determined by using a standard titrimetric substance. This also applies when dealing with an acid in a non-aqueous solvent. The titer of $HClO_4$ is determined by using tris(hydroxymethyl)-aminomethane (Tris) as the standard titrimetric substance. The titration of $HClO_4$ is a non-aqueous acid-base titration. As the pH value is only defined for water, the presentation of the pH value for a non-aqueous titration is only a formal transfer of this expression.

Reaction equation

$(CH_2OH)_3C–NH_2 + HClO_4 \rightarrow (CH_2OH)_3C–NH_3^+ + ClO_4^-$

Materials and apparatus

Exchange Unit	20 mL
Solvotrode	6.0229.100
Analytical balance	5-digit Sartorius 1702

Reagents and chemicals

c($HClO_4$) = 0.1 mol/L in glacial acetic acid
(Merck no. 9065)

Tris
(Fluka no. 93350)

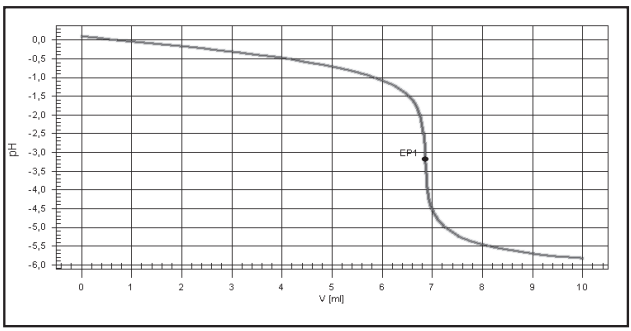
CH_3COOH_{conc}
(Fluka no. 45730)

Procedure

Tris is dried in a weighing bottle in a drying oven for 2 h at 105 °C and then cooled down and stored in a desiccator. 10 samples between 50 and 100 mg are then weighed out accurately to 0.1 mg and each is placed in a 100 mL beaker. 70 mL water-free acetic acid is added and the titration carried out using the following parameters:

```
DET  pH
>titration parameters
  meas.pt.density          4
  min.incr.             10.0 µl
  titr.rate             max. ml/min
  signal drift            50 mV/min
  equilibr.time           26 s
  start V:               abs.
  start V                  0 ml
  dos.rate              max. ml/min
  pause                    0 s
  meas.input:              1
  temperature           25.0 °C
>stop conditions
  stop V:                abs.
  stop V                  10 ml
  stop pH                OFF
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                  ON
  mean                n=     5
  res.tab:            original
>evaluation
  EPC                      5
  EP recognition:         all
  fix EP1 at pH          OFF
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
          ------------
```

Example of a titration curve



Calculation

In order to obtain the titer of perchloric acid the following formula is entered in the instrument:

Titer = C00 x C01 / C02 / EP1;4;

The individual variables are:

EP1 = added volume up to first equivalence point [mL]
C00 = weight of standard titrimetric substance [g]
C01 = correction factor
(*c* = 0.1 mol/L = 10000 mL/mol)
C02 = molar weight of Tris (121.17 g/mol)

The titer has no unit and should be given to 4 decimal places.

Measured values and statistics

Measured value	Sample size Tris (g)	Consumption of $HClO_4$ (mL)	Titer
1	0.1007	8.240	1.0086
2	0.0799	6.535	1.0090
3	0.0613	5.023	1.0072
4	0.0661	5.423	1.0059
5	0.0837	6.863	1.0065
6	0.0608	4.976	1.0084
7	0.1013	8.279	1.0076
8	0.0612	5.020	1.0061
9	0.0859	7.031	1.0083
10	0.0652	5.351	1.0056
$\overline{\chi}$			**1.0073**
S ±			**0.0012**
S_{rel} ±%			**0.12**

Possible sources of error

Possible sources of error in the titration could be incorrectly weighed-out standard titrimetric substance or incorrect handling of the Solvotrode. We recommend that the weighing is carried out with great care. Before each use the Solvotrode should be first rinsed with the solvent, then with distilled water and finally with the solvent again.

II.2.3 Titer determination of alcoholic *c*(KOH) = 0.1 mol/L

Learning topics

- Use of standard titrimetric substances.
- Coefficient of expansion of organic solvents/titrants.
- Influence of CO_2 absorption from the atmosphere on the titrant.
- Titration curve.
- Use of suitable electrodes.

Principles

Strong bases such as NaOH or KOH absorb carbon dioxide to form Na_2CO_3 or K_2CO_3. This changes their titer and a second equivalence point is found, which means that the titrations would be incorrect.

To determine the titer of the KOH solution an alcoholic solution of benzoic acid is used to react volumetrically with the KOH to be determined. The solvent used is ethanol, in which the KOH is also dissolved.

Reaction equation

C_6H_5–COOH + KOH → C_6H_5–COOK + H_2O

Materials and apparatus

Exchange Unit 20 mL

Solvotrode 6.0229.100

Reagents and chemicals

Ethanol analytical grade >99.5%
Fluka

Ready-to-use *c*(KOH) = 0.1 mol/L in isopropanol
Merck 1.05544.1000

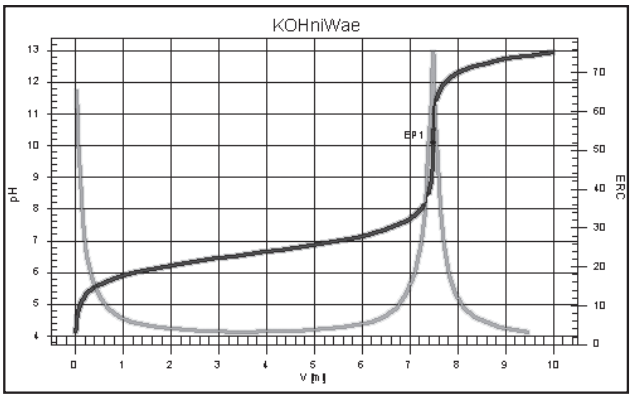
Benzoic acid
Fluka 12349

Procedure

Benzoic acid is dried in a drying oven for 2 hours at 105 °C and then allowed to cool down to room temperature in a desiccator. 10 portions between 60 and 100 mg are weighed out into separate beakers using weighing boats. A magnetic stirrer bar is added and the benzoic acid is dissolved in approx. 50 mL ethanol. When it has completely dissolved the 10 beakers are titrated using the following dynamic pH titration program:

```
794 Titrino              01102   794.0010
date  2002-08-26    time  17:38        37
DET  pH            KOHniWae
Parameters

>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                 OFF
  pause                     0 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                    10 ml
  stop pH                  OFF
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:          all
  fix EP1 at pH           OFF
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

The titer is the quotient of the actual and theoretical values for the concentration of a standard solution.

$$x(X) = \frac{c(X)Ist}{c(X)soll}$$

Titer = C00/C01/EP 1 (input parameters Titrino)

The individual variables are:

EP1 = standard solution KOH in mL consumed up to endpoint
C00 = weight of benzoic acid in mg
C01 = 12.212 (molecular weight of benzoic acid in g/mol x 0.1 = 122.12 x 0.1 in mg/L)

Measured values and statistics

Measured value	Sample size benzoic acid (mg)	Consumption of KOH (mL)	Titer
1	103.77	9.434	0.9007
2	105.44	9.594	0.9000
3	101.24	9.232	0.8980
4	101.28	9.217	0.8998
5	92.81	8.454	0.8990
6	104.81	9.533	0.9003
7	89.60	8.144	0.9009
8	82.26	7.483	0.9002
9	87.57	7.990	0.8975
10	84.75	7.746	0.8959
$\bar{\chi}$			**0.8992**
S ±			**0.0016**
S_{rel} ±%			**0.18**

Possible sources of error

Before the titer is determined, the KOH standard solution should be checked for a fine white precipitate of potassium carbonate. The largest error encountered in the calculation is the relative inaccuracy when weighing out the standard titrimetric substance. During the titration care must be taken that no air bubbles are entrained by the stirrer bar, as any carbon dioxide absorbed from the air could produce a second endpoint caused by freshly formed potassium carbonate (or high-bias results are obtained for the titration of weak acids as a result of leveling).

II.2.4 Titration of nitrating acid (HNO_3 / H_2SO_4 mixture)

Learning topics

- Meaning of relative acid strength (pK_a values).
- Separation of different acids in a single titration.
- Titration sequence according to acid strength:
  EP1 = ½ H_2SO_4 + HNO_3:
  EP2 – EP1 = ½ H_2SO_4
  (reaction equations are given below)

Potentiometric determination of nitrating acid

Principles

In industry nitrating acid is used in the production of nitro compounds such as explosives, pharmaceuticals and plastics. Nitrating acid is a mixture of concentrated sulfuric acid and concentrated nitric acid. In order to obtain the content of nitric acid and sulfuric acid analytically, the nitrating acid is dissolved in methanol and titrated with a standard solution of cyclohexylamine ($C_6H_{11}NH_2$). The first endpoint corresponds to the sum of the first step of the sulfuric acid with the nitric acid. The considerably weaker endpoint of the second step of the sulfuric acid is only reached at a considerably higher «pH value».

Compared with other alkaline titrants, cyclohexylamine has the great advantage that it is not affected by carbon dioxide; the formation of tertiary amines by deamination is also eliminated.

Reaction equations

$$H_2SO_4 + C_6H_{11}NH_2 \rightarrow C_6H_{11}NH_3^+ + HSO_4^-$$

$$HNO_3 + C_6H_{11}NH_2 \rightarrow C_6H_{11}NH_3^+ \; NO_3^-$$

$$HSO_4^- + C_6H_{11}NH_2 \rightarrow C_6H_{11}NH_3^+ + SO_4^{2-}$$

Materials and apparatus

Exchange Unit 5 mL
Solvotrode 6.0229.100

Reagents and chemicals

Methanol, reagent grade >99.8%
Fluka65543

Cyclohexylamine, reagent grade >99.5%
Fluka29300

Nitric acid, reagent grade >65%
Fluka84380

Sulfuric acid, reagent grade 95…97%
Fluka84720

Deionized water
self-prepared

Procedure

2 mL each of nitric acid and sulfuric acid are pipetted into a 200 mL volumetric flask and mixed with 40 mL deionized water. After the cooling fill with methanol to the mark and mix.

If no ready-to-use cyclohexylamine standard solution is available then 49.08 g cyclohexylamine is dissolved in 1 liter of methanol. After thorough mixing the standard solution is ready and can be used for the titration.

A volumetric pipet or a piston pipet is used to pipet 3 mL «nitrating acid» into a 50 mL beaker where it is treated with 25 mL methanol. A magnetic stirrer bar is added and the titration is carried out until 2 endpoints have been detected or the maximum volume has been reached. A DET method is drawn up according to the following parameters and used for titrating the nitrating acid:

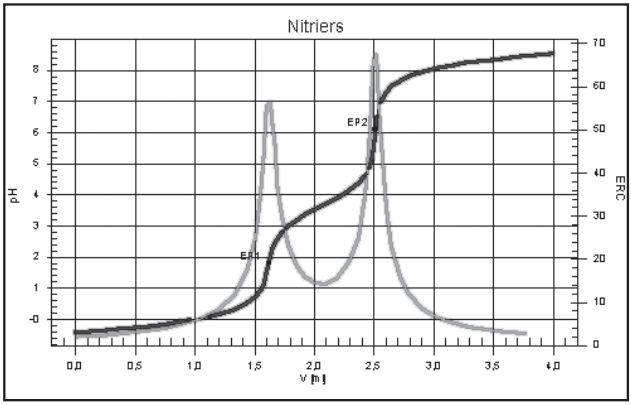
```
794 Titrino              01102   794.0010
date  2002-08-28    time  15:37       55
DET  pH             Nitr.Ac
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             35 mV/min
  equilibr.time            30 s
  start V:                 OFF
  pause                     0 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                    4 ml
  stop pH                  OFF
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:          all
  fix EP1 at pH           OFF
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
         ------------
```

Measured values and statistics

Measured value	Sample size nitric acid (mL)	mL titrant EP1	mL titrant EP2	g/L H_2SO_4	g/L HNO_3
1	2.50	1.6143	2.4964	17.302	9.227
2	2.50	1.6113	2.4927	17.288	9.198
3	2.50	1.6214	2.5114	17.457	9.217
4	2.50	1.6118	2.4949	17.321	9.183
5	2.50	1.6166	2.5046	17.418	9.182
6	2.50	1.6098	2.4917	17.298	9.173
7	2.50	1.6053	2.4809	17.174	9.196
8	2.50	1.6025	2.4780	17.172	9.162
9	2.50	1.6073	2.4878	17.270	9.159
10	2.50	1.6014	2.4725	17.086	9.203
$\bar{\chi}$				**17.279**	**9.190**
S ±				**0.112**	**0.022**
S_{rel} ±%				**0.65**	**0.24**

(A dilute mixture of HNO_3 and H_2SO_4 has been used)

Example of a titration curve



Calculation

g/L H_2SO_4 = (EP2 – EP1) x C01/C00

C00 = sample size in mL
C01 = 49.039
C02 = 31.506

g/L HNO_3 = [EP1 – (EP2 – EP1)] x C02 / C00

II.2.5 Acid number in petrochemical products with alcoholic KOH

Learning topics

- Determination of weak acids, produced by the breakdown of lubricants, by non-aqueous titration with a strong base.

Principles

The so-called acid number TAN (Total Acid Number) is a cumulative parameter for all free acids in petrochemical products that can react with KOH. Lubricants (fats/oils) are subjected to high mechanical and/or thermal stresses when used in motors, gearboxes, etc. The thermal breakdown of lubricants produces acids which could cause corrosion. This is why additives are added to the lubricants to bind the acids produced. These additives could be, for example, amines or metallic soaps.

The determination of the TAN value is used to check the extent to which the additives have already been used up, or how much free acid can already be determined in the oil. The acid number provides information about how long and how intensively the oil has been used. The acids found in the oil have a negative effect on the working life of the motor, which is why the acid number is particularly important.

It is not possible to differentiate between the different acids titrimetrically. Their total content (TAN – Total Acid Number) is determined. In this case the solvent used is a mixture of isopropanol, toluene and water; a Solvotrode is used to detect the endpoint. The titrant is tetra-n-butylammonium hydroxide.

Acids with a pK_a >9 are normally not determined.

Materials and apparatus

Exchange Unit 20 mL
Solvotrode 6.0229.100

Reagents and chemicals

Tetra-n-butylammonium hydroxide standard solution, c = 0.1 mol/L
Merck 1.09162.1000

Toluene analytical grade >99%
Fluka89682

Isopropanol analytical grade >99.5%
Fluka59302

Deionized water
self-prepared

Procedure

If no solvent mixture is already available then it must first be prepared by mixing 500 mL toluene, 495 mL isopropanol and 5 mL water. The sample size depends on the expected acid number. If the acid number is unknown then one or more preliminary titrations must be carried out with the sample size being increased step by step until one or more endpoints can be found. However, the sample size should not exceed 10 g. The oil sample is weighed out into a beaker, a stirrer bar is added and the oil is dissolved in 50 mL of the solvent mixture.

Before the start of the titration care must be taken that the sample has been completely dissolved in the solvent mixture and that no precipitate can be recognized. We recommend that samples that are difficult to dissolve are mixed thoroughly for some time on a magnetic stirrer.

The electrode is immersed in the beaker until the ground-joint diaphragm is completely wetted by the solvent. The titration is then carried out according to the dynamic pH program given below.

At the end of the titration the solvent mixture should be used to rinse thoroughly in order to prevent the carryover of adhering residues to the next titration.

After several measurements the Solvotrode should be immersed in distilled water for some time without moistening the ground-joint diaphragm, as otherwise electrolyte solution would be washed out.

```
794 Titrino              01102   794.0010
date  2002-08-29    time  08:55         0
DET  pH                  TAN
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  min.incr.alternative   100.0 µl
  titr.rate              max. ml/min
  signal drift             10 mV/min
  equilibr.time            38 s
  start V:                OFF
  pause                    50 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                    4 ml
  stop pH                 OFF
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                       5
  EP recognition:        last
  fix EP1 at pH          OFF
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:        value
  activate pulse:         OFF
         ------------
```

Calculation

As the acid number parameter is a cumulative parameter and stands for a number of acidic compounds, it does not refer to a particular acid. The unit of the acid number is:

mg/g (mg KOH per g sample).

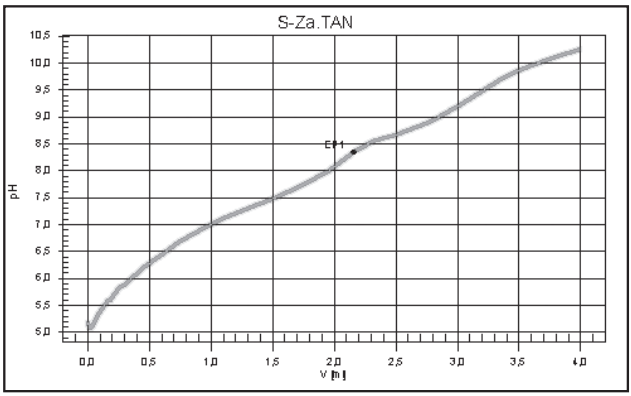
The Titrino calculates the acid number according to the following entered formula:

RS1 = (EP1 – C31) x C01 x C02 x C03 / C00;1;mg/g
EP1 = consumption of titrant in mL up to first endpoint
C00 = sample weight in g
C01 = concentration of standard solution in mol/L (0.1)
C02 = titer of standard solution
C03 = molecular weight KOH in g/mol (56.106)
C31 = blank value for KOH for solvent in mL

Remarks

It is particularly important that the oil sample is completely dissolved in the solvent mixture before the start of the titration. To obtain a better comparison of the results, an internal standard is used, which is dissolved in the solvent before addition. This standard contained an amount of benzoic acid corresponding to a titrant consumption of approx. 3 mL.

Example of a titration curve



II.2.6 Determining the ephedrine hydrochloride content according to Pharm. Europe

Learning topics

- Direct non-aqueous titration of amine hydrochlorides with a strong base. Titration sequence according to acid strength.

Principles

Pharm. Europe describes an elegant, modern method. As the products usually still contain traces of free HCl [pK_a (HCl) < pK_a (hydrochloride)], this means that two endpoints are found in non-aqueous solvents (this cannot be observed in aqueous solutions because of leveling). It is difficult to determine the HCl traces quantitatively. For this reason some HCl is deliberately added to the sample solution. This makes the first endpoint more noticeable. It is important that carbonate-free NaOH is used. If this is not the case then high-bias results will be obtained as the carbonate will be titrated together with the amine hydrochloride.

EP1 = HCl (not used for the calculation)

(EP2 – EP1) = amine hydrochloride

Reaction equation

$R-NH_2 \times HCl + NaOH \rightarrow R-NH_2 + NaCl + H_2O$

Materials and apparatus

Exchange Unit 20 mL
Solvotrode 6.0229.100

Reagents and chemicals

Titrant:
sodium hydroxide c(NaOH) = 0.1 mol/L
ready-to-use standard solution

Auxiliary solution:
hydrochloric acid c(HCl) = 0.01 mol/L
self-prepared

Solvent:
ethanol analytical grade 96%

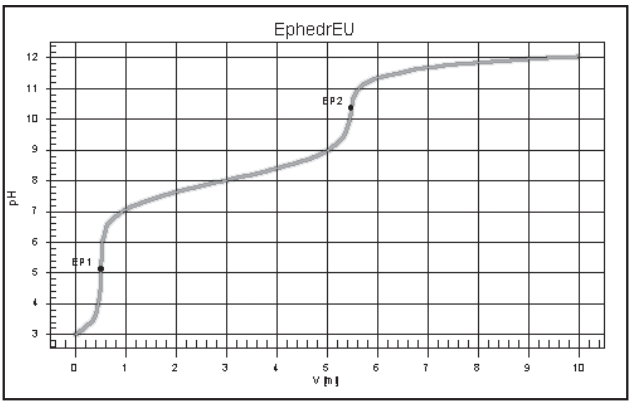
Procedure

The sample containing ephedrine is weighed out into a beaker with an accuracy of 0.1 mg and dissolved in approx. 50 mL ethanol. 5 mL hydrochloric acid is added to the beaker from a volumetric pipet together with a stirrer bar and the sample is thoroughly mixed on a magnetic stirrer.

The endpoint is detected by immersing a Solvotrode in the beaker: The titration is carried out with c(NaOH) = 0.1 mol/L up to the second endpoint using the following program:

```
794 Titrino             01102   794.0010
date  2002-09-12    time  08:26        0
DET  pH            EphedrEU
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                 OFF
  pause                     0 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                    10 ml
  stop pH                  OFF
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:          all
  fix EP1 at pH           OFF
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:         value
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

1 mL *c*(NaOH) = 0.1 mol/L corresponds to 20.17 mg ephedrine

Ephedrine = (EP1–EP2) x C01

EP1 = consumption of mL NaOH up to first endpoint
EP2 = consumption of mL NaOH up to second endpoint
C01 = 20.17 (equivalent weight of ephedrine)

Measured values and statistics

Measured value	Sample size (mL)	mL (EP2 – EP1)	% Ephedrine x HCl
1	10.0	4.965	100.14
2	10.0	4.968	100.20
3	10.0	4.969	100.22
4	10.0	4.973	100.31
5	10.0	4.970	100.24
6	10.0	4.975	100.35
$\overline{\chi}$			**100.24**
S ±			**0.08**
S_{rel} ±%			**0.08**

Possible sources of error

If bases containing carbonate are used then high-bias results will be obtained (carbonate/weak acid leveling).

II.2.7 Determining the ephedrine hydrochloride content according to USP 24/25

Learning topics

- Indirect, non-aqueous titration of amine hydrochlorides with $HClO_4$ in glacial acetic acid.
- Conversion of the hydrochlorides to acetates – conjugated acid-base pairs.

Principles

This method is also used for the analytical determination of amine hydrochlorides in a non-aqueous titration.

This conventional method, which is not environmentally compatible, is still frequently stipulated in the USP instructions. The substance is dissolved in glacial acetic acid, an excess of Hg(II) acetate is added and the amine acetate formed is titrated (as a weak base) with the strong acid $HClO_4$. Acetic acid and mercury(II) acetate convert the amine hydrochlorides ($R–NH_2$ x HCl) to amine acetates ($R–NH_2$ x CH_3COOH) and mercury(II) chloride. Perchloric acid can be used to convert the amine acetate to amine perchlorate ($R–NH_2$ x $HClO_4$) in a displacement reaction.

Reaction equations

$$2\ R-NH_2 \times HCl + Hg(CH_3COO)_2 \rightarrow 2\ R-NH_2 \times CH_3COOH + HgCl_2$$

$$R-NH_2 \times CH_3COOH + HClO_4 \rightarrow R-NH_2 \times HClO_4 + CH_3COOH$$

Materials and apparatus

Exchange Unit 20 mL
Solvotrode 6.0229.100

Reagents and chemicals

Perchloric acid in glacial acetic acid
$c(HClO_4)$ = 0.1 mol/L

$Hg(CH_3COO)_2$ in glacial acetic acid
(3.19 g / 100 mL)

Anhydrous acetic acid (glacial acetic acid)

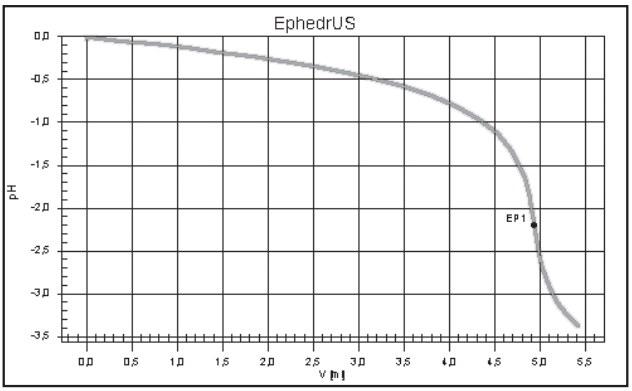
Deionized water

Procedure

Depending on the expected ephedrine content, 0.250 g to 0.500 g sample is weighed out into a titration beaker. The sample is dissolved in glacial acetic acid and treated with 10 mL $Hg(CH_3COO)_2$. A stirrer bar is added and the solution is titrated with $c(HClO_4)$ = 0.1 mol/L up to the first endpoint. The endpoint is detected with the Solvotrode and the following dynamic program is used for the titration:

```
'pa
794 Titrino              01102   794.0010
date  2002-09-12    time  08:15         0
DET  pH            EphedrUS
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                 OFF
  pause                     0 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                   10 ml
  stop pH                  OFF
  stop EP                   1
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:          all
  fix EP1 at pH           OFF
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(HClO_4)$ = 0.1 mol/L corresponds to 20.17 mg ephedrine

Mass fraction of ephedrine = EP1 x C01 x C02 x C31 / C00

EP1 = perchloric acid consumption up to endpoint in mL
C00 = sample weight in mg
C01 = equivalent weight of ephedrine (20.17)
C02 = 100 (for %)
C31 = titer of $HClO_4$

Measured values and statistics

Measured value	Sample size (mg)	mL $c(HClO_4)$ = 0.1 mol/L	% Ephedrine x HCl
1	100.22	4.951	99.64
2	111.25	4.500	99.72
3	106.73	5.285	99.87
4	112.14	5.543	99.70
$\bar{\chi}$			**99.72**
S ±			**0.08**
S_{rel} ±%			**0.08**

Possible sources of error

In this type of titration the glacial acetic acid continuously removes water from the electrode; this could result in an uncontrolled electrode drift. After each titration the glass ring of the ground-joint diaphragm must be checked to ensure that it is seated loosely. A small amount of electrolyte solution should escape. It is necessary to immerse the electrode in a beaker containing deionized water after each sample.

II.2.8 Benzoic acid in H_2O, ethanol, acetone, methyl isobutyl ketone (MIBK) and acetonitrile

Learning topics

- Titration of a weak acid with a strong base in various solvents.
- Influence of the solvent on the shape of the titration curve and the position of the endpoint.
- Autoprotolysis and dielectric constant of the solvent used.
- Choice of a suitable solvent for weak acids.

Principles

Benzoic acid can be titrated directly both in water and in non-aqueous solvents with sodium hydroxide or other strong bases. In this case sodium hydroxide c(NaOH) = 0.1 mol/L dissolved in ethanol is used as the standard solution. A Solvotrode is used to detect the endpoint instead of a colored indicator.

Reaction equation

C_6H_5–COOH + NaOH → C_6H_5–COONa + H_2O

Materials and apparatus

Exchange Unit 20 mL
Solvotrode 6.0229.100

Reagents and chemicals

Benzoic acid
analytical grade >99.5%

Sodium hydroxide
ready-to-use standard solution
c(NaOH) = 0.1 mol/L in ethanol

Acetone
analytical grade

Acetonitrile
analytical grade

Methyl isobutyl ketone (MIBK)
analytical grade

Deionized water

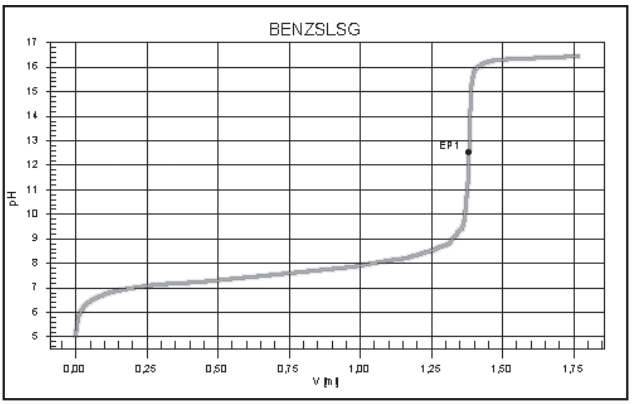
Procedure

Benzoic acid is dried overnight in a drying oven at 105 °C and then allowed to cool down to room temperature in a desiccator for one hour. It is then weighed out into a titration beaker and dissolved in approx. 50 mL of the particular solvent. A stirrer bar is added and the benzoic acid is stirred continuously until it has fully dissolved. The buret and the Solvotrode are positioned in the solution such that the added standard solution is not led directly to the electrode. The titration is carried out according to the following dynamic pH program:

```
'pa
794 Titrino             01102   794.0010
date  2002-09-12    time  08:48        0
DET  pH            BENZOICA
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                    10 ml
  stop pH                 OFF
  stop EP                   1
  filling rate           max. ml/min
>statistics
  status:                   ON
  mean                n=     2
  res.tab:            original
>evaluation
  EPC                       5
  EP recognition:         all
  fix EP1 at pH          OFF
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:        value
  activate pulse:         OFF
          ------------
```

Example of a titration curve

Example of a titration in acetone. Please carry out titrations in the other solvents and compare the titration curves.



Calculation

1 mL *c*(NaOH) = 0.1 mol/L corresponds to 12.212 mg $C_7H_6O_2$

mg benzoic acid / sample weight = EP1 x C01

EP1 = consumption; mL *c*(NaOH) = 0.1 mol/L
C01 = 12.212 (mg/mL)

II.2.9 Aniline in H_2O, ethanol, acetone, dioxan/IPA 1:1 and acetonitrile

Learning topics

- Titration of a weak base with a strong acid in various solvents.
- Influence of the solvent on the shape of the titration curve and the position of the endpoint.
- Autoprotolysis and dielectric constant of the solvent used.
- Choice of a suitable solvent for weak bases.

Principles

Aniline (aminobenzene) is a weakly alkaline compound that reacts with hydrochloric acid to form the so-called aniline salt (aniline hydrochloride). In contrast to aniline itself, this salt is easily soluble in water. Aniline is sparingly soluble in water, but is soluble in alcohols.

Reaction equation

$C_6H_5 - NH_2 + HCl \rightarrow C_6H_5 - NH_2 \times HCl$

Materials and apparatus

Exchange Unit 20 mL
Solvotrode 6.0229.100

Reagents and chemicals

Hydrochloric acid
c(HCl) = 0.1 mol/L in ethanol, ready-to-use standard solution

Deionized water
self-prepared

Ethanol
analytical grade 96%

Acetone
analytical grade

Dioxan
analytical grade

2-Propanol
analytical grade

Acetonitrile
analytical grade

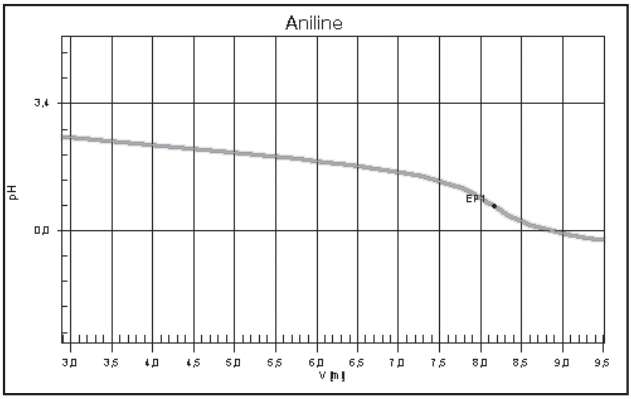
Aniline
analytical grade

Procedure

Approx. 70…80 mg aniline is carefully weighed out into a titration beaker using an analytical balance and dissolved in approx. 50 mL of the particular solvent. A stirrer bar is added and the buret tip and the Solvotrode are immersed in the solution so that the added hydrochloric acid solution is not led directly to the electrode. The sample is then titrated according to the following program up to the first endpoint:

```
`pa
794 Titrino              01102   794.0010
date  2002-09-12    time  09:10         0
DET  pH            ANILINE
parameters
>titration parameters
  meas.pt.density            4
  min.incr.               10.0 µl
  titr.rate               max. ml/min
  signal drift              50 mV/min
  equilibr.time             26 s
  start V:                 OFF
  pause                      0 s
  meas.input:                1
  temperature             25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                    10 ml
  stop pH                  OFF
  stop EP                    1
  filling rate            max. ml/min
>statistics
  status:                    ON
  mean                n=     2
  res.tab:            original
>evaluation
  EPC                        5
  EP recognition:          all
  fix EP1 at pH           OFF
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:         value
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

1 mL *c*(HCl) = 0.1 mol/L corresponds to 9.312 mg C_6H_8N

mg aniline / sample weight = EP1 x C01 x C30

EP1 = consumption; mL c(HCl) = 0.1 mol/L
C01 = 9.312 (M aniline in g/mol x 0.1 = 93.12 x 0.1 in mg/mL)
C30 = titer of HCl solution

II.3 Precipitation titrations and methods

II.3.1 Titer determination of $c(AgNO_3)$ = 0.1 mol/L

Learning topics

- Use of standard titrimetric substances.
- Potentiometric indication.
- Shape of titration curve.
- Choice of suitable electrode.

Principles

As a dilute $AgNO_3$ standard solution is frequently not adjusted exactly to a particular concentration, but only an approximate concentration of, for example, 0.1 mol/L, its accurate concentration must be determined by using a standard titrimetric substance. The titer of the $AgNO_3$ solution is determined by using NaCl as the standard titrimetric substance.

Reaction equation

$Ag^+ + Cl^- \rightarrow AgCl$ (s)
Precipitation of Cl^- by Ag^+

Materials and apparatus

Exchange Unit	20 mL
Ag Titrode	6.0430.100
Analytical balance	5-digit Sartorius 1702

Reagents and chemicals

Titrant:
$c(AgNO_3)$ = 0.1 mol/L
Merck 1.09081.1000

Acid:
$c(HNO_3)$ = 2 mol/L

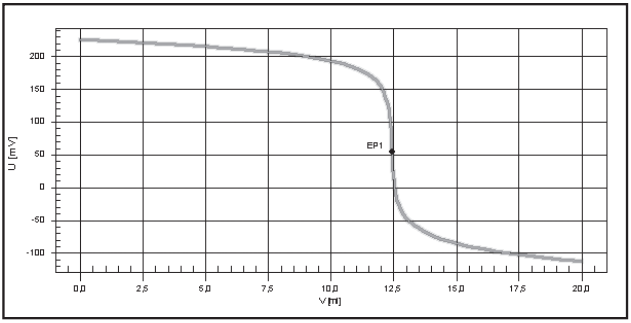
Standard titrimetric substance:
NaCl analytical grade
Fluka 71380

Procedure

The sodium chloride is dried in a drying oven for 2 h at 120 °C and then cooled down and stored in a desiccator. 10 samples of between 80 and 105 mg are weighed out with an accuracy of 0.1 mg into individual 100 mL beakers. Each sample is acidified with 5 mL $c(HNO_3)$ = 2 mol/L and made up to approx. 60 mL with dist. H_2O. The following parameters are used for the titration:

```
DET  U
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                   20 ml
  stop U                  OFF mV
  stop EP                 OFF
  filling rate           max. ml/min
>statistics
  status:                   ON
  mean                n=    10
  res.tab:            original
>evaluation
  EPC                       5
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:        value
  activate pulse:         OFF
          ------------
```

Example of a titration curve



Calculation

In order to obtain the titer of $AgNO_3$, the following formula must be entered in the instrument:

Titer = C00 x C01 / C02 / EP1;4;

The individual variables are:

EP1	added volume up to first endpoint [mL]
C00	weight of standard titrimetric substance [g]
C01	10'000 (correction factor)
C02	molecular weight of NaCl = 58.44 [g/mol]

The titer has no unit and should be given to 4 decimal places.

Measured values and statistics

Measured value	Sample size NaCl (g)	Consumption of $AgNO_3$ (mL)	Titer
1	0.0918	15.766	0.9963
2	0.0881	15.064	1.0007
3	0.1048	17.888	1.0025
4	0.0652	11.172	0.9986
5	0.0762	12.424	0.9999
6	0.0882	15.059	1.0022
7	0.0790	13.510	1.0006
8	0.0821	14.038	1.0007
9	0.0866	14.823	0.9997
10	0.0922	15.766	1.0006
$\bar{\chi}$			**1.0002**
S ±			**0.0018**
S_{rel} ±%			**0.18**

Possible sources of error

Too fast titration leads to inclusions in the precipitate and therefore incorrect results.

II.3.2 Chloride (NaCl) in meat bouillon

Learning topics

- Analysis of foodstuffs.
- Sample preparation.
- Salt content.

Principles

This titration represents applications in the food sector in which the salt content of a product is to be determined. Examples of possible matrices are, for example, crispbread, ready-to-serve meals, spice mixtures.

With the usual salt contents encountered the precipitation titration is a simple and favorably priced method that can be automated.

Reaction equation

$Ag^+ + Cl^- \rightarrow AgCl$ (s)
precipitation of Cl^- by Ag^+

Materials and apparatus

Exchange Unit	20 mL
Ag Titrode	6.0430.100
Analytical balance	5-digit Sartorius 1702

Reagents and chemicals

Titrant:
$c(AgNO_3)$ = 0.1 mol/L
Merck 1.09081.1000

Acid:
$c(HNO_3)$ = 2 mol/L

Bouillon:
0.2 L (one cube dissolved in 200 mL warm H_2O)

Procedure

5 mL bouillon is pipetted into each of 10 beakers (100 mL); care must be taken that the bouillon is always well shaken to prevent its constituents from being deposited. 5 mL $c(HNO_3)$ = 2 mol/L is added to each beaker followed by dist. H_2O to make up to approx. 60 mL. The following parameters are used for the titration:

DET U

```
>titration parameters
  meas.pt.density            4
  min.incr.               10.0 µl
  titr.rate               max. ml/min
  signal drift              50 mV/min
  equilibr.time             26 s
  start V:                 OFF
  pause                     0 s
  meas.input:               1
  temperature             25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                    20 ml
  stop U                   OFF mV
  stop EP                  OFF
  filling rate            max. ml/min
>statistics
  status:                    ON
  mean                n=     10
  res.tab:            original
>evaluation
  EPC                        5
  EP recognition:          all
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve

Calculation

In order to obtain the concentration of NaCl in the bouillon, the following formula is entered in the instrument:

ß(NaCl) = EP1 x CO4 x C05 x C06 / C00;2;g/L

The individual variables are:

EP1 added volume up to first equivalence point [mL]

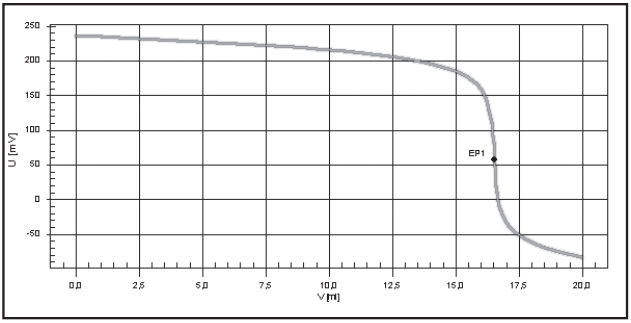
C00 bouillon sample size [mL]

C04 molecular weight of NaCl = 58.44 [g/mol]

C05 concentration of standard solution = 0.1 [mol/L]

C06 titer (1.0000) [–]

This results in ß(NaCl) having the unit [g/L]; the concentration of NaCl should be given to two decimal places.



Measured values and statistics

Measured value	Sample size bouillon (mL)	Consumption of $AgNO_3$ (mL)	g/L NaCl
1	5.00	16.535	19.33
2	5.00	16.524	19.31
3	5.00	16.489	19.27
4	5.00	16.472	19.25
5	5.00	16.573	19.37
6	5.00	16.478	19.26
7	5.00	16.457	19.23
8	5.00	16.529	19.32
9	5.00	16.494	19.28
10	5.00	16.532	19.32
$\bar{\chi}$			**19.29**
S ±			**0.043**
S_{rel} ±%			**0.22**

Possible sources of error

The bouillon should always be thoroughly shaken before pipetting as otherwise its constituents will be deposited. Care must also be taken that any suspended matter in the bouillon, e.g. parsley or vegetable pieces, does not block the pipet.

II.3.3 Chloride in drinking water

Learning topics

- Solubility.
- Solubility product.
- Analysis of drinking water.

Principles

In this case we are concerned with determining very small amounts of chloride, such as are found in drinking water, by a precipitation titration. The determination limit is approx. 3 mg/L chloride.

Reaction equation

$Ag^+ + Cl^- \rightarrow AgCl$ (s)
precipitation of Cl^- by Ag^+

Materials and apparatus

Exchange Unit 20 mL
Ag Titrode with Ag_2S coating 6.0430.100
Analytical balance 5-digit Sartorius 1702

Reagents and chemicals

Titrant:
$c(AgNO_3)$ = 0.01 mol/L Merck

Standard titrimetric substance:
NaCl Fluka 71380

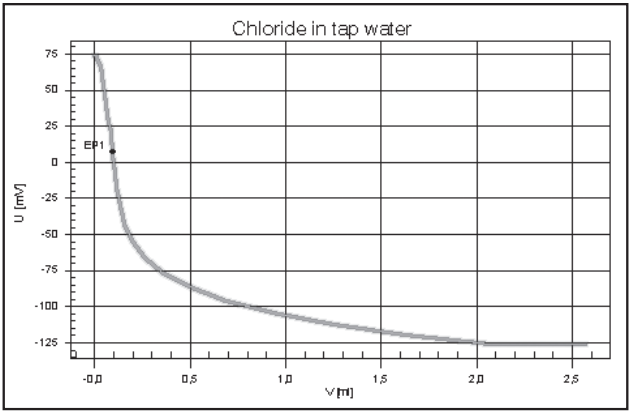
Acid:
$c(HNO_3)$ = 2 mol/L

Tap water from Herisau

Procedure

100 mL tap water is measured out into the titration beaker, treated with 2 mL $c(HNO_3)$ = 2 mol/L and then titrated with $c(AgNO_3)$ = 0.01 mol/L to after the first endpoint:

Example of a titration curve



Calculation

1 mL $c(AgNO_3)$ = 0.01 mol/L corresponds to 0.3545 mg Cl^-

mg/L Cl^- = EP1 x C01 x C02 / C00

C01 = 0.3545
C02 = 1000 (for 1 liter)
C00 = sample size in mL (100)

II.3.4 Sulfide in wastewater

Learning topics

- Environmental analysis.
- Sample preparation.
- Influence of pH and oxygen or air on sulfides.

Principles

Sulfides occur in wastewater and mineral water, among other things (e.g. spas, therapeutic water sources).

Sulfide dissolved in water is precipitated as silver sulfide; the endpoint is determined by potentiometric detection with an Ag Titrode. The water sample must be made alkaline with NaOH in order to prevent the highly volatile H_2S from escaping.

In this case a small amount of sodium sulfide is added to an alkaline water sample (O_2-free) and the free sulfide determined analytically with silver nitrate solution.

Reaction equation

$$H_2S + 2\,AgNO_3 \rightarrow Ag_2S + 2\,HNO_3$$

Materials and apparatus

Exchange Unit	10 mL
Ag Titrode with Ag_2S coating	6.0430.100

Reagents and chemicals

$AgNO_3$ standard solution
$c(AgNO_3)$ = 0.001 mol/L

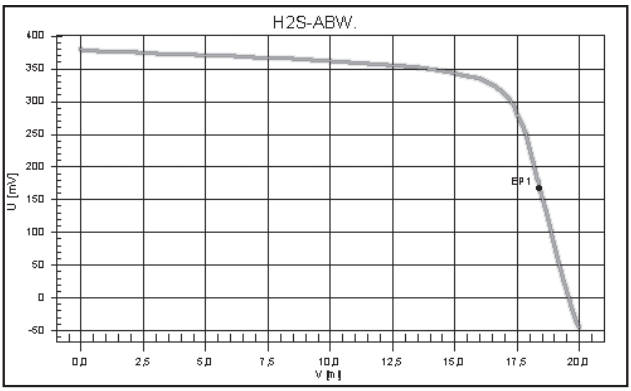
Procedure

100 mL water sample is pipetted into a beaker from a volumetric pipet and made alkaline by the addition of 1 mL w(NaOH) = 30%. A magnetic stirrer bar is added and the water sample is titrated with silver nitrate solution $c(AgNO_3)$ = 0.001 mol/L up to the first endpoint. An Ag Titrode is used for detecting the endpoint. The following parameter settings are used:

'pa

```
794 Titrino              01102   794.0010
date  2002-09-12    time  12:15       12
DET  U              H2S-ABW.
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                 OFF
  pause                     0 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                abs.
  stop V                   20 ml
  stop U                   OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:          all
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(AgNO_3)$ = 0.001 mol/L corresponds to 0.017 mg H_2S

H_2S = EP1 x C01 x C02 / C00;2;mg/L

EP1 = mL silver nitrate solution up to endpoint
C00 = sample size in mL (100)
C01 = 0.017
C02 = 1000 (for 1 liter)

Measured values and statistics:

Measured value	Sample size water (mL)	Consumption of $AgNO_3$ (mL)	mg/L H_2S
1	100	17.820	3.029
2	100	17.721	3.013
3	100	17.514	2.977
4	100	18.403	3.129
5	100	17.952	3.052
$\overline{\chi}$			**3.038**
S ±			**0.057**
S_{rel} ±%			**1.89**

Possible sources of error

Sample not made alkaline – escape of H_2S.

II.3.5 Cyanide in wastewater

Learning topics

- Complex formation constant.
- Solubility product.
- Relative acid strengths.
- Environmental/wastewater analysis.

Principles

Free cyanide ions in aqueous solution can be determined analytically by a potentiometric titration with silver nitrate. The titration endpoint is determined by using an Ag Titrode with a sulfide coating. When working with cyanides particular care should be taken that an alkaline medium is always used, as otherwise volatile hydrocyanic acid would be formed. Apart from the danger to life this would, of course, produce completely incorrect results.

The first endpoint corresponds to the free cyanide, the second to the silver-dicyano complex $[Ag(CN)_2]^-$.

Reaction equations

$Ag^+ + CN^- \rightarrow AgCN$

$AgCN + CN^- \rightarrow [Ag(CN)_2]^-$

Materials and apparatus

Exchange Unit	10 mL
Ag Titrode with Ag_2S coating	6.0430.100

Reagents and chemicals

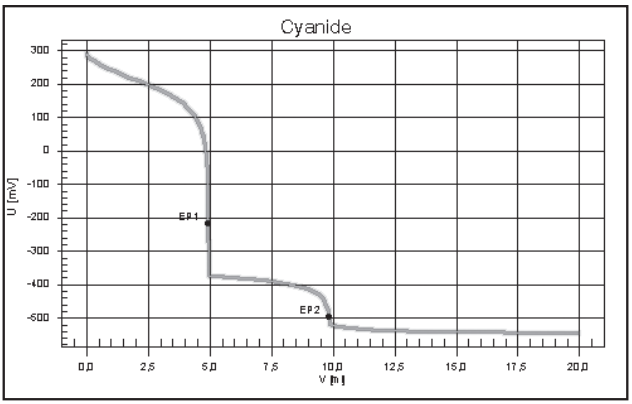
KCN	analytical grade
$AgNO_3$	standard solution $c(AgNO_3)$ = 0.1 mol/L
NaOH solution	w(NaOH) = 30%
Cyanide standard	c(KCN) = 0.1 mol/L in c(NaOH) = 0.1 mol/L

Procedure

Approx. 50 mL deionized water is placed in a beaker and made alkaline with 1 mL w(NaOH) = 30%. A volumetric pipet is used to add 10 mL cyanide standard, a stirrer bar is added and the sample is titrated with silver nitrate standard solution $c(AgNO_3)$ = 0.1 mol/L to the second endpoint according to the following program (in practical work one generally titrates only to the first, more pronounced endpoint).

```
'pa
794 Titrino             01102   794.0010
date  2002-09-12    time  13:36       12
DET  U                Cyanide
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
       >stop conditions
  stop V:                 abs.
  stop V                   10 ml
  stop U                  OFF mV
  stop EP                  9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      5
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(AgNO_3)$ = 0.1 mol/L corresponds to 2.6018 mg CN (at EP2) or 5.2036 mg CN (at EP1)

Cyanide (g/L) = EP1 x C01 / C00

EP1 = consumption of silver nitrate standard solution (mL)
C00 = size of standard in mL (10)
C01 = 5.2036

Measured values and statistics:

Measured value	Sample size standard (mL)	Consumption of $AgNO_3$ (mL at EP1)	Cyanide in g/L
1	10.0	4.998	1.3004
2	10.0	5.002	1.3014
3	10.0	4.999	1.3006
4	10.0	5.003	1.3017
5	10.0	5.001	1.3012
$\bar{\chi}$			**1.3011**
S ±			**0.0005**
S_{rel} ± %			**0.04**

II.3.6 Mixture of chloride, bromide and iodide with and without added acetone

Learning topics

- Solubility and solubility product.
- Precipitation.
- Differentiation.
- Shape of titration curve.
- Titration according to solubility product.
- Reducing the solubility.

Principles

Because of their different solubility products, chloride, bromide and iodide present in a mixture can be determined individually by titration. In the example given below, a solution is prepared that contains comparable amounts of all the ions. The standard solution contains 0.1 mol/L each of NaCl, KBr and KI. The mixture is acidified with nitric acid and titrated up to the third endpoint with silver nitrate. The difficulty with this particular titration is caused by the low difference in solubility between silver chloride and silver bromide. An investigation is made into whether acetone improves the separation.

Reaction equations

$KI + AgNO_3 \rightarrow AgI + KNO_3$
$KBr + AgNO_3 \rightarrow AgBr + KNO_3$
$KCl + AgNO_3 \rightarrow AgCl + KNO_3$

Materials and apparatus

Exchange Unit	20 mL
Ag Titrode with Ag_2S coating	6.0430.100

Reagents and chemicals

Sodium chloride	analytical grade
Potassium bromide	analytical grade
Potassium iodide	analytical grade
Silver nitrate ready-to-use standard solution	$c(AgNO_3)$ = 0.1 mol/L
Nitric acid	$c(HNO_3)$ = 2 mol/L

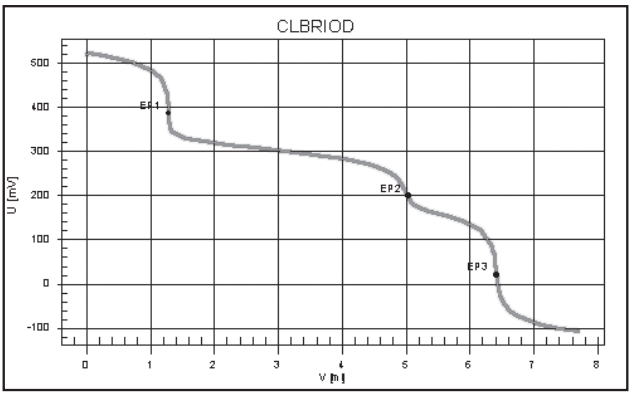
Procedure

6 mL of the thoroughly mixed halides mixture is pipetted into a beaker from a volumetric pipet and acidified with 1 mL $c(HNO_3)$ = 2 mol/L. After the addition of approx. 50 mL deionized water and a magnetic stirrer bar the titration is carried out according to the following DET program:

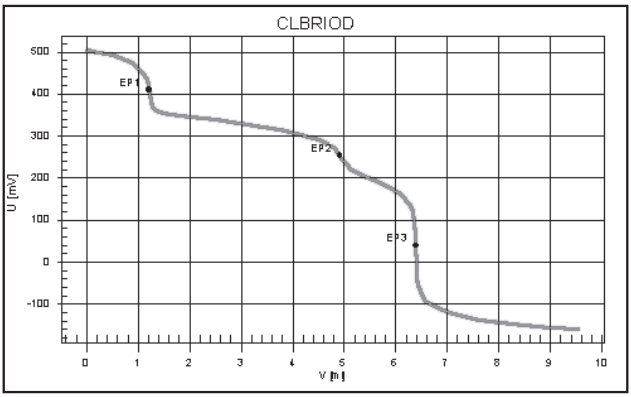
```
'pa
794 Titrino              01102   794.0010
date  2002-09-12    time  14:26       16
DET  U              Cl,Br,I
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                   6 ml
  stop U                  OFF mV
  stop EP                  9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      5
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
          ------------
```

Examples of titration curves

Titration without acetone



Titration with acetone



Calculation

1 mL $c(AgNO_3)$ = 0.1 mol/L corresponds to 3.5453 mg Cl^- or 7.9909 mg Br^- or 12.69 mg I^-

mg/L chloride = (EP3–EP2) x C01 / C00

mg/L bromide = (EP2–EP1) x C02 / C00

mg/L iodide = EP1 x C03 / C00

C00 = sample size in mL
C01 = 3.5453
C02 = 7.9909
C03 = 12.69

II.3.7 Cationic surfactant in mouth rinses

Learning topics

- Substantivity*.
- Disinfectants.
- Analysis of drugs.

* In this case substantivity is understood to be the characteristic property of surfactants (particularly cationic surfactants) of adhering to surfaces. With respect to washing agents this is also known as the so-called Lenor effect (fabric conditioners).

Principles

In order to determine cetylpyridinium chloride (CPCl), a cationic surfactant, the mouth rinse sample is titrated with sodium dodecylsulfate (SDS), an anionic surfactant. Cetylpyridinium chloride is used in these formulations as a mouth and throat disinfectant.

For many years surfactants were determined by the classical two-phase titration with colored indicators and visual indication. As this involved the use of chloroform, the potentiometrically indicated surfactant titration today offers an environmentally more favorable alternative. An ion-sensitive surfactant electrode is used, namely a PVC liquid-membrane electrode whose membrane composition has been optimized for the determination of surfactants. The measurement is made against a reference electrode.

Reaction equation

CPCl + SDS → CPCl – SDS (ion associate)

Materials and apparatus

Exchange Unit	20 mL
Ionic Surfactant Electrode	6.0507.120
Ag/AgCl reference electrode	6.0726.100

Reagents and chemicals

Buffer solution	pH = 3.0 citrate/HCL Merck Titrisol no. 109883
Titrant:	*c*(SDS) = 0.004 mol/L.

Procedure

10 mL portions of mouth rinse are pipetted into 10 beakers (100 mL), 5 mL buffer is added and the solution is made up to approx. 50 mL with dist. H_2O.

The following parameters are used for the titration:

```
MET  U
parameters
>titration parameters
  V step                  0.10 ml
  titr.rate               max. ml/min
  signal drift             OFF mV/min
  equilibr.time             10 s
  start V:                 OFF
  pause                     30 s
  meas.input:                1
  temperature             25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                     5 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                        1 mV
  EP recognition:    greatest
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve

Calculation

In order to determine the CPCl content in a mouth rinse, the following formula must be entered in the instrument:

CPCl = EP1 x C01 x C02 x C03 / C00;1;ppm

The individual variables are:

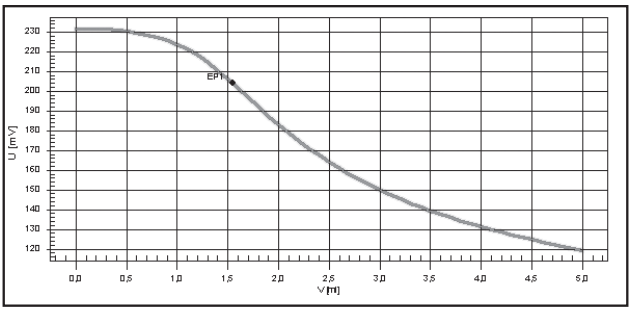
EP1 = mL titrant up to first equivalence point

C00 = sample size in mL

C01 = conversion factor: 1 mL SDS 0.004 mol/L corresponds to 1.432 mg CPCl

C02 = correction factor for mg/L (1000)

C03 = titer (1)



Measured values and statistics

Measured value	Sample size (mL)	Consumption of SDS (mL)	ppm CPCl
1	100	1.550	222.0
2	100	1.532	219.4
3	100	1.500	214.8
4	100	1.500	214.8
5	100	1.550	224.4
6	100	1.567	222.0
7	100	1.550	224.4
8	100	1.481	212.1
9	100	1.477	211.5
10	100	1.500	214.8
$\overline{\chi}$			**218.0**
S ±			**5.0**
S_{rel} ±%			**2.29**

Possible sources of error

In surfactant titrations it must be noted that the otherwise usual degree of accuracy cannot be achieved. This is primarily because of the reaction mechanism, but inhomogeneities are also involved.

Methanol can be added if foam is produced. If the electrode is allowed to remain too long in the titrated solution, it will either not respond at all in the following titration or respond incorrectly. In such cases the electrode must be rinsed with methanol and placed in sodium dodecylsulfate solution, *c*(DSS) = 0.004 mol/L, for several minutes.

Three to four conditioning titrations should be carried out before the titration proper. Before each titration the electrode should be immersed in the sample solution for approx. 20…30 s in order to ensure that it is adapted to the sample matrix. The working life of the electrode can be lengthened by storing it dry.

II.3.8 Anionic surfactants and soaps in washing powder, potentiometric two-phase titration

Learning topics

- Surfactant analysis.
- Characteristics of anionic surfactants and soaps.
- pH dependency of surfactant group structure.
- Titration curve.
- Two-phase titration.
- Choice of a suitable electrode.

Principles

The separation of anionic surfactants and soaps is based on the fact that soaps lose their wash-active properties under acidic conditions. In an acidic medium soaps are present as undissociated fatty acids; these cannot be determined analytically with Hyamine. In contrast, anionic surfactants can be titrated with Hyamine – a cationic surfactant – in both acidic and alkaline solution as in each case they are present as an ionic compounds.

This means that the analytical determination of both types of surfactant in a single sample is only possible by carrying out two separate titrations.

- In the first titration at pH 2.0 only the anionic surfactants are determined.
- In a second titration at pH 11.5 both anionic surfactants and soaps are determined.

The surfactants are determined in a two-phase titration in which a solvent mixture consisting of a 1 : 1 mixture of methyl isobutyl ketone and ethanol is used.

The ion-sensitive electrode Surfactrode Refill is used for detection (together with an Ag/AgCl reference electrode).

Before the start of the titration the pH must be adjusted with NaOH or HCl. This is done using a combined pH glass electrode that can be used in addition to the Surfactrode Refill.

Materials and apparatus

Exchange Unit	20 mL
Viscotrode	6.0239.100
Surfactrode Refill	6.0507.140
Ag/AgCl reference electrode	6.0726.107
Propeller stirrer	727

Reagents and chemicals

Hyamine standard solution
c(Hyamine) = 0.005 mol/L

Solvent mixture
methyl isobutyl ketone / ethanol 1 : 1 (V/V)

Solubility promoter
Metrohm TEGOadd

Deionized water
self-prepared

Procedure

Step 1: Anionic surfactants

Approx. 0.2 g of the homogenized sample is weighed out into a 150 mL beaker and fully dissolved in approx. 70 mL deionized water. After the addition of 0.2 mL TEGOadd, the combined glass electrode is immersed in the solution and the pH is adjusted to 2.0 by the addition of hydrochloric acid.

The Surfactrode Refill is then immersed in the beaker in place of the combined glass electrode and 20 mL of the solvent mixture is added. The propeller stirrer is immersed deeply in the sample so that the sample and solvent can be thoroughly mixed. A homogeneous suspension of the solvent mixture and dissolved sample should be formed. The titration is then carried out up to the endpoint using the Hyamine standard solution and a DET program.

Step 2: Sum of the anionic surfactants and soaps

Approx. 0.2 g of the homogenized sample is weighed out into a 150 mL beaker and fully dissolved in approx. 70 mL deionized water. After the addition of 0.2 mL TEGOadd, the combined glass electrode is immersed in the solution and the pH value is adjusted to 11.50 by the addition of sodium hydroxide.

The Surfactrode Refill is then immersed in the beaker in place of the combined glass electrode and 20 mL of the solvent mixture is added. The propeller stirrer is immersed deeply in the sample so that the sample and solvent can be thoroughly mixed. Care must be taken that no air bubbles are entrained and that no deep vortex is formed. Nevertheless, a homogeneous suspension of the solvent mixture and dissolved sample should still be formed.

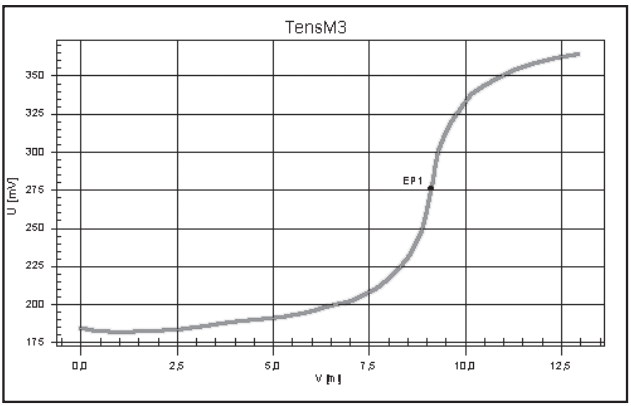
A magnetic stirrer bar cannot mix the solvent mixture and the dissolved sample satisfactorily and cannot be used for such a determination.

The following parameters are used for the titration:

```
pa
794 Titrino              01102   794.0010
date 2002-09-06     time  16:07        47
DET  U               TensM3
parameters
>titration parameters
  meas.pt.density            2
  min.incr.               50.0 µl
  titr.rate               max. ml/min
  signal drift             OFF mV/min
  equilibr.time             15 s
  start V:                 OFF
  pause                     30 s
  meas.input:                1
  temperature             25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                    20 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate           max. ml/min
>statistics
  status:                   ON
  mean                n=     3
  res.tab:            original
>evaluation
  EPC                        2
  EP recognition:    greatest
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
         ------------
```

Example of a titration curve

(Titration curve at pH = 11.5)



Calculation

mmol/100 g surfactants = EP1 x C01 x C02 / C00

EP1 = consumption of Hyamine standard solution
C01 = concentration of Hyamine = 0.005 mol/L
C02 = 100 (for 100 g)
C00 = sample size in g

Measured values and statistics

Measured value	Sample size (g)	Hyamine consumption (mL)	Total A.T. mmol/ 100 g
1	0.2022	17.414	43.061
2	0.2315	19.477	44.065
3	0.2210	19.461	44.029
4	0.2255	18.944	42.004
5	0.2004	17.275	43.101
$\overline{\chi}$			**43.252**
S ±			**0.849**
S_{rel} ± %			**1.96**

3.9 Calibration factor for nonionic surfactants

Learning topics

- Use of a calibration factor instead of determining the titer.
- Non-stoichiometric behavior.
- Pseudo-complexes*.
- Choice of suitable electrodes.

* See Application Bulletin no. 230 for additional information.

Principles

In many formulations, nonionic surfactants are used as co-surfactants to increase effectiveness (washing power, emulsifiability, etc. – see also literature reference 17).

The calibration factor states how much standard surfactant (e.g. polyethylene glycol) reacts with one milliliter of the standard solution.

Reaction equations

$NIO + x\,Ba^{2+} \rightarrow [NIOBa_x]^{2x+}$

$[NIOBa_x]^{2x+} + 2xTPB^- \; [NIOBa_x]TPB_{2x}$

TPB^- = tetraphenylborate ion

Materials and apparatus

Exchange Unit	10 mL
NIO surfactant electrode	6.0507.010
Ag/AgCl reference electrode (outer electrolyte NaCl, *c* = 1 mol/L)	6.0726.100

Reagents and chemicals

Buffer solution pH 10
1.24 g H_3BO_3 is treated with 10 mL *c*(NaOH) = 1 mol/L and made up to 100 mL with H_2O.

$BaCl_2$ solution 21 g
$BaCl_2 \times 2\,H_2O$ + 1 mL conc. HCl is made up to 100 mL with H_2O.

STPB standard solution
3.4223 g sodium tetraphenylborate is dissolved in 300 mL H_2O. In a second beaker 10 g polyvinyl alcohol is dissolved in 300 mL water under heating. Add 10 mL buffer solution pH = 10. Combine and make up to 1000 mL with H_2O.

Polyethylene glycol
Make up 1 g/L with deionized water.

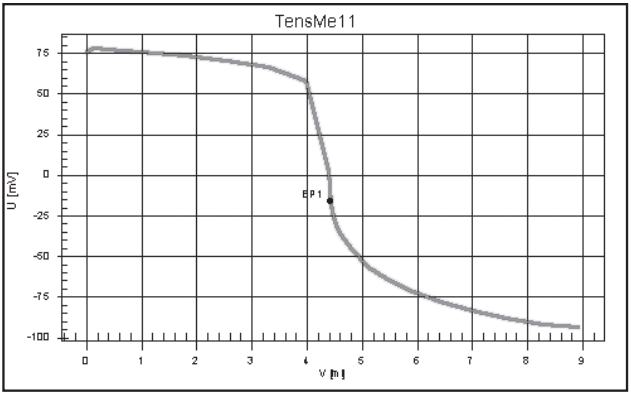
Procedure

10 mL standard surfactant solution is pipetted from a volumetric pipet into a beaker and diluted to approx. 60 mL with water. 10 mL barium chloride solution is added followed by a magnetic stirrer bar and the solution is thoroughly mixed. The solution is then titrated with the STPB standard solution up to the first endpoint using the DET program given below.

The electrode must be rinsed with methanol after every 3 to 4 titrations or wiped with a methanol-moistened tissue.

```
'pa
794 Titrino              01102   794.0010
date  2002-09-12    time  10:57         0
DET  U             TensMe11
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              50.0 µl
  titr.rate              max. ml/min
  signal drift            OFF mV/min
  equilibr.time            20 s
  start V:                OFF
  pause                    30 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                   20 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:    greatest
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

mg NIO surfactant / mL STPB standard solution = C00 x EP1

EP1 = consumption of STPB standard solution
C00 = volume of standard surfactant solution used

Measured values and statistics

Measured value	Sample size standard (mg)	Consumption of STPB (mL)	Calibration factor (mg/mL)
1	10.0	4.354	2.2967
2	10.0	4.427	2.2589
3	10.0	4.414	2.2655
4	10.0	4.412	2.2665
5	10.0	4.265	2.3477
6	10.0	4.207	2.3770
$\overline{\chi}$			**2.2966**
S ±			**0.0488**
S_{rel} ± %			**2.12**

II.3.10 Nonionic surfactants in household cleaners

Learning topics

- Special surfactant analysis.
- Influence of ionic surfactants.
- Shape of titration curve.

Principles

Household cleaners can contain up to 5% nonionic surfactants in addition to cationic surfactants. In the titration with STPB standard solution the pH only plays a minor role, but it should not be below pH = 3 or above pH = 9.

If the cleaning agent contains sulfates, incorrect results may be obtained because of the precipitation of barium sulfate. In such cases more $BaCl_2$ must be added.

As barium also forms a precipitate with carbonates, the titration should be carried out under slightly acidic conditions to prevent any precipitation.

Materials and apparatus

Exchange Unit 20 mL

NIO surfactant electrode 6.0507.010

Ag/AgCl reference electrode 6.0726.100
(outer electrolyte c(NaCl) = 1 mol/L)

Reagents and chemicals

Buffer solution pH 10
1.24 g H_3BO_3 is treated with 10 mL c(NaOH) = 1 mol/L and made up to 100 mL with H_2O.

$BaCl_2$ solution 21 g $BaCl_2 \times 2H_2O$ + 1 mL conc. HCl is made up to 100 mL with H_2O.

STPB standard solution
3.4223 g sodium tetraphenylborate is dissolved in 300 mL H_2O. In a second beaker 10 g polyvinyl alcohol is dissolved in 300 mL water under heating. Add 10 mL buffer solution pH = 10. Combine and make up to 1000 mL with H_2O.

Acetic acid c = 2 mol/L

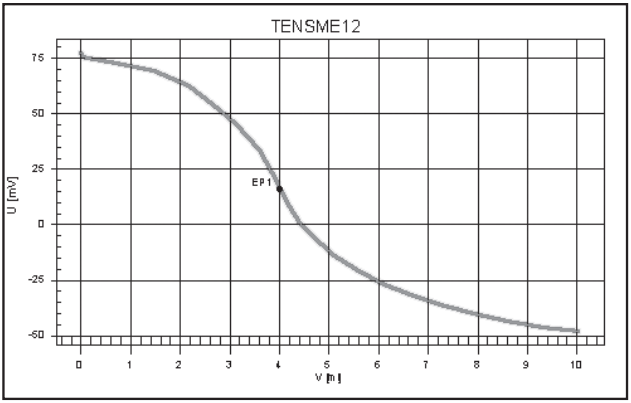
Deionized water

Procedure

Approx. 1 g household cleaner is weighed out exactly on an analytical balance and dissolved in approx. 80 mL deionized water. The pH is adjusted to approx. 4 with dilute acetic acid and a magnetic stirrer bar is added followed by 10 mL barium chloride solution. The solution is stirred vigorously and titrated with STPB standard solution using the following parameter settings:

```
'pa
794 Titrino              01102   794.0010
date  2002-09-12    time  11:31         0
DET  U              TENSME12
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              50.0 µl
  titr.rate              max. ml/min
  signal drift            OFF mV/min
  equilibr.time            20 s
  start V:                OFF
  pause                    30 s
  meas.input:               1
  temperature            25.0 °C
       >stop conditions
  stop V:                 abs.
  stop V                   20 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:    greatest
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

% NIO surfactants = EP1 x C01 x C02 / C00

EP1 = consumption of STPB standard solution in mL
C00 = sample weight in g
C01 = 0.1 (for %)
C02 = 2.2966 (calibration factor)

Measured values and statistics

Measured value	Sample size (g)	Consumption of STPB (mL)	% NIOs
1	0.2975	0.440	0.3397
2	0.4648	0.746	0.3658
3	2.0518	3.072	0.3439
4	2.5060	3.624	0.3321
5	2.5836	3.743	0.3327
6	2.8033	4.020	0.3293
$\bar{\chi}$			**0.3400**
S ±			**0.0135**
S_{rel} ±%			**3.98**

II.4 Redox titrations and methods

II.4.1 Iodometry (iodine/thiosulfate)

Learning topics

- Redox reactions.
- Redox potential; titration curve.
- Choice of suitable electrode.

Principles and reaction equations

Iodometry is probably the most versatile method used in redox titrations. The wide range of applications is based on the oxidizing effect of iodine and the reducing effect of the iodide ions. The basic process is completely reversible:

$$I_2 + 2\,e^- \rightleftharpoons 2\,I^-$$

This means that there are two possible ways of using iodometry:

A) Reducing agents can be titrated directly with iodine, for example:

$$Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2\,I^-$$

B) Oxidizing agents are treated with an excess of KI solution (usually in an acidic solution) and the released iodine is titrated, for example with thiosulfate solution:

$$2\,Fe^{3+} + 2\,I^- \rightarrow 2\,Fe^{2+} + I_2$$

$$2\,S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\,I^-$$

As iodine solutions are unstable and their iodine content changes rapidly (iodine sublimates off), this means that titer determinations have to be carried out frequently. As an alternative to KI_3 solutions, a mixture of KI / KIO_3 in a 5:1 molar ratio can be used; this solution releases iodine when acidified:

$$IO_3^- + 5\,I^- + 6\,H_3O^+ \rightarrow 3\,I_2 + 9\,H_2O$$

In this case the reaction rate depends strongly on the pH (Landolt reaction) – this is why work is usually carried out under strongly acidic solutions (H_2SO_4).

In order to analytically determine the concentration of an unknown iodine solution, it is titrated against a thiosulfate solution. The thiosulfate ($S_2O_3^{2-}$) reduces the iodine to be determined to iodide (I^-) and oxidizes the thiosulfate to tetrathionate ($S_4O_6^{2-}$).

*Mechanism**

The mechanism of this redox reaction is similar to that observed in organic nucleophilic substitution reactions. In the first step iodine undergoes nucleophilic attack by the thiosulfate with the formation of iodide and an intermediate product ($^-OSO_2SI$). In the second step the iodine undergoes nucleophilic displacement from the intermediate product ($^-OSO_2SI$) as iodide with the formation of tetrathionate.

* According to A.D. Awtrey and R.E. Connick, J. Am. Chem. Soc. 73 (1951) 1341

Materials and apparatus

Exchange Unit	20 mL
Pt Titrode	6.0431.100

Reagents and chemicals

Na thiosulfate solution
$c(Na_2S_2O_3) = 0.1$ mol/L

Triiodide solution
$c(KI_3) = 0.05$ mol/L Fluka 57665

Acid
$c(H_2SO_4) = 0.5$ mol/L

Procedure

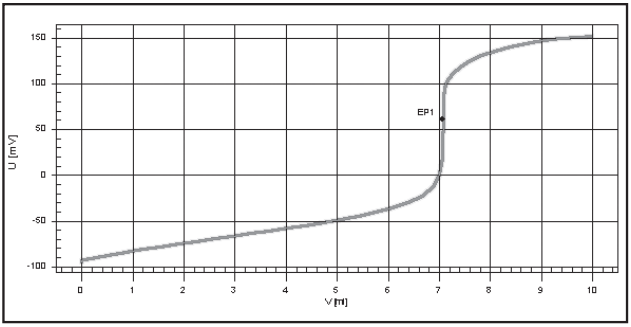
7 mL of the triiodide solution is pipetted into a beaker (100 mL), 10 mL $c(H_2SO_4)$ = 0.5 mol/L is then added and made up to approx. 60 mL with dist. H_2O.

As iodine sublimates very easily, only that particular beaker which is to be titrated immediately is prepared. A total of 10 samples is titrated.

The titration is carried out using the following parameters:

```
DET  U
>titration parameters
  meas.pt.density            4
  min.incr.               10.0 µl
  titr.rate               max. ml/min
  signal drift              20 mV/min
  equilibr.time             38 s
  start V:                 OFF
  pause                      0 s
  meas.input:                1
  temperature             25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                    10 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate           max. ml/min
       >statistics
  status:                   ON
  mean                n=    10
  res.tab:            original
>evaluation
  EPC                        5
  EP recognition:          all
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

To obtain the concentration of the iodine solution, the following formula must be entered in the instrument:

c(iodine) = EP1 x C01 / C02 / C00

Variables used

EP1	=	added volume up to equivalence point [mL]
C00	=	volume of triiodide solution [mL]
C01	=	concentration of thiosulfate solution (0,1) [mol/L]
C02	=	stchiometric factor (2) [–]

This results in c(iodine) having the unit [mol/L]. The concentration should be given to four decimal places.

Measured values and statistics

Measured value	Sample size of triiodide solution (mL)	Consumption of thiosulfate (mL)	$c(I_2)$ in mol/L
1	7.000	7.095	0.0507
2	7.000	7.061	0.0504
3	7.000	7.074	0.0505
4	7.000	7.072	0.0505
5	7.000	7.090	0.0506
6	7.000	7.070	0.0505
7	7.000	7.080	0.0506
8	7.000	7.062	0.0504
9	7.000	7.079	0.0506
10	7.000	7.078	0.0506
χ			**0.0505**
S ±			**0.0001**
S_{rel} ±%			**0.19**

Possible sources of error:

Possible sources of error in the titration could be, for example, pipetting errors or the premature sublimation of iodine from the triiodide solution. We recommend that pipetting should be carried out as carefully as possible and that each individual sample is prepared immediately before it is titrated so that as little iodine as possible sublimates off.

II.4.2 Chromatometry

Learning topics

- Redox potential.
- pH dependency of redox potential.
- Altering the oxidation state.

Principles

Chromium(VI) is a relatively strong oxidizing agent and is able to oxidize a large number of reducing agents under acidic conditions. In this process (which also involves hydrogen ions) dichromate, which is stable in acidic solution, accepts 6 electrons supplied by the particular reducing agent and is reduced to chromium(III):

$Cr_2O_7^{2-} + 14\ H_3O^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 21\ H_2O$

Dichromates have the advantage that they are very stable and can also be prepared from a standard titrimetric substance – $K_2Cr_2O_7$.

In our example the Fe(II) content of a solution is titrated. The Fe(II) in an inorganic acid solution is oxidized to Fe(III) even at room temperature.

Reaction equation

$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14\ H_3O^+ \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 21\ H_2O$

Materials and apparatus

Exchange Unit	10 mL
Pt Titrode	6.0431.100

Reagents and chemicals

Potassium dichromate standard solution
$c(1/6\ K_2Cr_2O_7) = 0.1$ mol/L

$(NH_4)_2Fe(SO_4)_2$
analytical grade

Sulfuric acid
$w(H_2SO_4) = 96\%$

Procedure

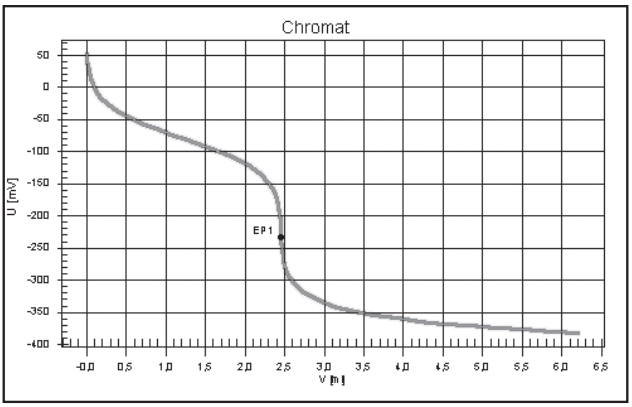
$K_2Cr_2O_7$ is dried overnight at 130 °C in a drying oven and left to cool down in a desiccator for at least 2 h. 4.9032 g $K_2Cr_2O_7$ is dissolved in dist. H_2O in a 1000 mL volumetric flask, made up to the mark and mixed.

$c(1/6\ K_2Cr_2O_7) = 0.1$ mol/L (or $c(K_2Cr_2O_7) = 1/60$ mol/L)

Approx. 2 g ammonium iron(II) sulfate is dissolved in 100 mL water and 10 mL portions are pipetted into beakers. Approx. 50 mL water is added and the solution is carefully acidified with 1 mL concentrated sulfuric acid. A magnetic stirrer bar is added and the solution is titrated with $K_2Cr_2O_7$ standard solution $c = 0.1$ mol/L up to the first endpoint. A Pt Titrode is used for recognizing the endpoint; the titration is carried out according to the following program:

```
'pa
794 Titrino              01102   794.0010
date  2002-09-12    time  17:50       12
DET  U              Chromate
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                   10 ml
  stop U                  OFF mV
  stop EP                  9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      5
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(1/6\ K_2Cr_2O_7)$ = 0.1 mol/L corresponds to 28.404 mg $(NH_4)_2Fe(SO_4)_2$

g/L $(NH_4)_2Fe(SO_4)_2$ = EP1 x C01 / C00

EP1 = mL dichromate solution up to endpoint
C00 = sample size in mL
C01 = 28.404

II.4.3 Cerimetry

Learning topics

- «Strength» of the oxidizing agent, «oxidation performance».
- pH dependency.

Principles

Ce(IV) is a very strong oxidizing agent. Solutions in sulfuric acid are also stable when warm. Ce(IV) can only be used under acidic conditions. The reaction takes place in one step, no interfering intermediate products are formed:

$$Ce^{4+} + e^- \rightarrow Ce^{3+}$$

Ce(IV) can be used for the determination of reducing agents in the presence of large amounts of chloride.

Our example shows the titration with hexacyanoferrate(II).

Reaction equation

$$[Fe(CN)_6]^{4-} + Ce^{4+} \rightarrow [Fe(CN)_6]^{3-} + Ce^{3+}$$

Materials and apparatus

Exchange Unit	10 or 20 mL
Pt Titrode	6.0431.100

Reagents and chemicals

Deionized water

Cerium(IV) sulfate solution
ready-to-use standard solution
Merck 1.09092.100

Potassium hexacyanoferrate(II) trihydrate
ultrapure analytical grade
Fluka 60280

Concentrated sulfuric acid
95...97% Fluka 84720

Procedure

Approx. 250 mg potassium hexacyanoferrate(II) is dissolved in 100 mL water. 10 mL portions of the solution are pipetted into 100 mL beakers from a volumetric pipet. The portions are diluted to approx. 50 mL with deionized water and a magnetic stirrer bar is added.

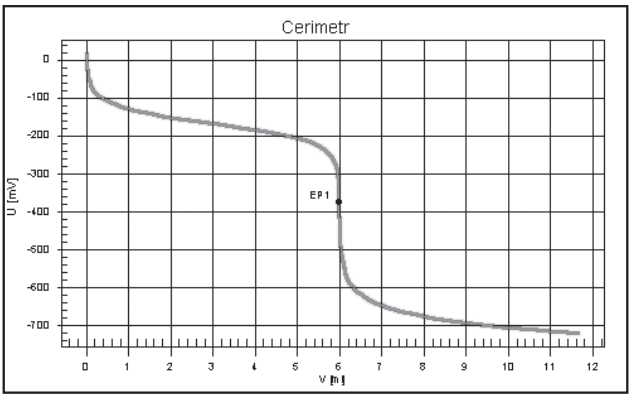
A graduated pipet is used to carefully add 5 mL concentrated sulfuric acid under vigorous stirring; care must be taken that the solution does not become too hot. If necessary it should be cooled in an ice bath so that delayed boiling cannot occur.

Although the solution can also be titrated when warm, it is advisable to allow it to cool down to room temperature.

The sample is then titrated according to the following DET U program (Pt Titrode):

```
‘pa
794 Titrino              01102   794.0010
date  2002-09-12    time  17:10       12
DET  U             Cerimetr
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
       >stop conditions
  stop V:                abs.
  stop V                   20 ml
  stop U                  OFF mV
  stop EP                  9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      5
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
```

Example of a titration curve



Calculation

1 mL Ce(IV), c = 0.1 mol/L corresponds to 36.8346 mg $K_4[Fe(CN)_6]$

% = EP1 x C01 x C02 / C00

EP1 = mL Ce(IV) solution up to endpoint
C00 = sample weight in mg (250)
C01 = 36.8346
C02 = 100 (for %)

Measured values and statistics

Measured value	Sample size (mg)	Consumption of Ce(IV) (mL)	% $K_4[Fe(CN)_6]$
1	246.2	5.890	88.12
2	253.8	6.068	88.07
3	250.3	5.980	88.00
4	261.7	6.256	88.05
$\bar{\chi}$			**88.06**
S ±			**0.05**
S_{rel} ±%			**0.06**

II.4.4 Permanganatometry

Learning topics

- Alteration of the oxidation state.
- Redox processes.
- pH dependency of redox potential.

Principles and reaction equations

$KMnO_4$ is always used for standard solutions. This utilizes the high oxidation performance of this compound. The majority of titrations are carried out under strongly acidic solutions (but not in HCl, which is oxidized to chlorine and chlorine dioxide and would therefore interfere).

In strongly acidic solutions, Mn(VII) is reduced to Mn(II):

$$MnO_4^- + 8\ H_3O^+ + 5\ e^- \rightarrow Mn^{2+} + 12\ H_2O$$

In weakly acidic or neutral solutions, Mn(VII) is reduced to Mn(IV) and manganese dioxide is formed:

$$MnO_4^- + 4\ H_3O^+ + 3\ e^- \rightarrow \{MnO_2\}\downarrow + 6\ H_2O$$

and in alkaline solutions manganate:

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}$$

Our example is the determination of oxalic acid:

$$2\ MnO_4^- + 5\ C_2O_4^{2-} + 16\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$$

Materials and apparatus

Exchange Unit	20 mL
Pt Titrode	6.0431.100

Reagents and chemicals

Oxalic acid dihydrate
standard titrimetric substance

Sulfuric acid
$c(H_2SO_4) = 2$ mol/L

Potassium permanganate
standard solution $c(KMnO_4) = 0.02$ mol/L

Manganese sulfate
analytical grade >99.5% Fluka 84720

Procedure

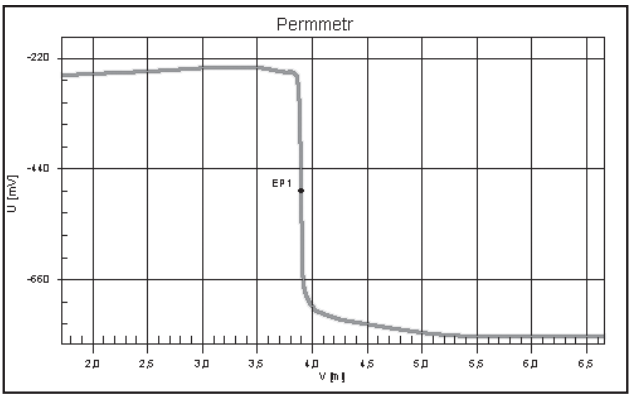
Approx. 20 mg oxalic acid dihydrate is weighed out into a beaker on an analytical balance and diluted with 50 mL deionized water. 5 mL sulfuric acid and 0.5 g manganese sulfate* are then added, followed by a magnetic stirrer bar, and the fine deposit of manganese sulfate is completely dissolved by vigorous stirring. A Pt Titrode is used for endpoint recognition.

* Used as a catalyst so that the titration can be carried out at room temperature.

The titration is carried out with the following parameter settings:

```
'pa
794 Titrino              01102   794.0010
date  2002-09-13    time  09:18         0
DET  U             Perm.
parameters
>titration parameters
  meas.pt.density            4
  min.incr.               10.0 µl
  titr.rate               max. ml/min
  signal drift              50 mV/min
  equilibr.time             26 s
  start V:                 OFF
  pause                      0 s
  meas.input:                1
  temperature             25.0 °C
       >stop conditions
  stop V:                 abs.
  stop V                    20 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                        5
  EP recognition:          all
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(KMnO_4)$ = 0.02 mol/L corresponds to 6.303 mg $H_2C_2O_4$ x 2 H_2O

% = EP1 x C01 x C02 / C00

EP1 = mL permanganate solution up to endpoint
C00 = sample weight in mg
C01 = 6.303
C02 = 100 (for %)

II.4.5 Thiosulfate with iodine; potentiometric, biamperometric and bivoltametric titration

Learning topics

- Indication methods.
- Dilute solutions.
- Shape of titration curve.
- Choice of suitable electrode.

Determination of thiosulfate with iodine solution

Principles

The irreversible reaction between iodine and thiosulfate leads to the formation of iodide and tetrathionate.

The endpoint of the titration can be indicated biamperometrically, potentiometrically as well as bivoltametrically.

For potentiometric titration a platinum ring electrode is used, whereas for bivoltametric and biamperometric titration a separate double Pt-sheet electrode is used.

Reaction equation

$$2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^-$$

Materials and apparatus

Exchange Unit	20 mL
Combined Pt-ring electrode	6.0451.100
Separate double Pt-sheet electrode	6.0309.100

Reagents and chemicals

Iodine solution
$c(I_2) = 0.05$ mol/L

Sulfuric acid
$c(H_2SO_4) = 2$ mol/L

Potassium iodide
analytical grade

Sodium thiosulfate
standard solution $c(Na_2S_2O_3) = 0.1$ mol/L

Procedure

10 mL sodium thiosulfate standard solution c = 0.1 mol/L is pipetted into a beaker from a volumetric pipet and treated with 2 mL $c(H_2SO_4) = 2$ mol/L. The solution is made up to approx. 50 mL with deionized water and thoroughly stirred. The sodium thiosulfate is titrated with the standard iodine solution using the following MET program:

MET program for potentiometric titration

```
794 Titrino              01102   794.0010
date  2002-09-13    time  08:46         0
MET  U              Thiosul1
parameters
>titration parameters
  V step                  0.10 ml
  titr.rate               max. ml/min
  signal drift              50 mV/min
  equilibr.time             26 s
  start V:                  OFF
  pause                      0 s
  meas.input:                1
  temperature             25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                    10 ml
  stop U                  OFF mV
  stop EP                    9
  filling rate           max. ml/min
>statistics
  status:                   OFF
>evaluation
  EPC                        30 mV
  EP recognition:           all
  fix EP1 at U            OFF mV
  pK/HNP:                   OFF
>preselections
  req.ident:                OFF
  req.smpl size:            OFF
  activate pulse:           OFF
          ------------
```

MET program for biamperometric titration

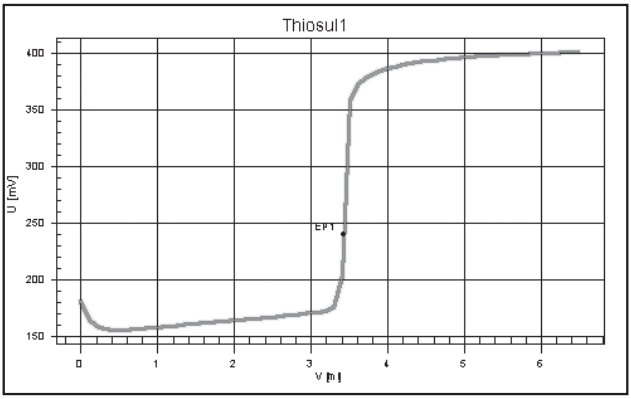
```
'pa
794 Titrino              01102   794.0010
date  2002-09-13    time  09:07        0
MET  Upol          Thiosul2
parameters
>titration parameters
  V step                0.10 ml
  titr.rate             max. ml/min
  signal drift            50 µA/min
  equilibr.time           26 s
  start V:               OFF
  pause                    0 s
  U(pol)                 200 mV
  electrode test:        OFF
  temperature           25.0 °C
       >stop conditions
  stop V:               abs.
  stop V                  20 ml
  stop I                 OFF µA
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                OFF
>evaluation
  EPC                      2 µA
  EP recognition:        all
  fix EP1 at I           OFF µA
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
          ------------
```

MET program for bivoltametric titration

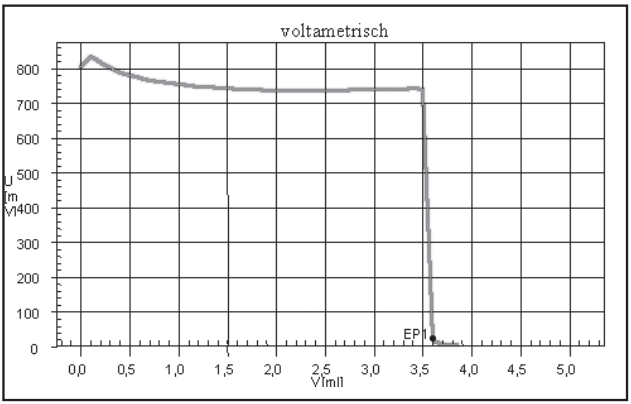
```
'pa
794 Titrino              01102   794.0010
date  2002-09-13    time  09:09        0
MET  Ipol          Thiosul3
parameters
>titration parameters
  V step                0.10 ml
  titr.rate             max. ml/min
  signal drift            50 mV/min
  equilibr.time           26 s
  start V:               OFF
  pause                    0 s
  I(pol)                   1 µA
  electrode test:        OFF
  temperature           25.0 °C
       >stop conditions
  stop V:               abs.
  stop V                  20 ml
  stop U                 OFF mV
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                OFF
>evaluation
  EPC                      30 mV
  EP recognition:        all
  fix EP1 at U           OFF mV
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
          ------------
```

Examples of titration curves

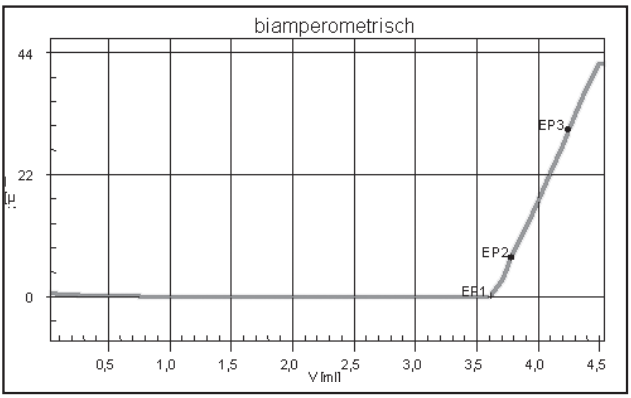
Potentiometric titration



Bivoltametric titration



Biamperometric titration



With the biamperometric titration the true enpoint coincides with the first breaking point (EP1). However, if the titrator evaluates a potentiometric titration curve independently, additional, wrong endpoints can appear (EP2 and EP3 in the example shown).

Calculation

1 mL $c(I_2)$ = 0.05 mol/L corresponds to 15.810 mg $Na_2S_2O_3$

g/L $Na_2S_2O_3$ = EP1 x C01 x C30 / C00

EP1 = mL iodine solution up to endpoint
C00 = sample size in mL
C01 = 15.81
C30 = titer of iodine solution

II.4.6 Bromine index in petrochemical products

Learning topics

- Non-aqueous redox titration.
- Polarized electrodes.
- Analysis of petrochemical products.
- Electrophilic addition of bromine at double bonds:

  $R - CH = CH - R + Br_2 \rightarrow R - CHBr - CHBr - R$

Principles

Bromium is added electrophilically at C=C double bonds and becomes decolorized. This reaction is regarded as being a specific identification for olefines and is also know as the Bayer Test.

The bromine index or bromine number is the amount of bromine consumed by 100 g sample. Under cold conditions bromine reacts with numerous unsaturated compounds in the petrochemical product. Instead of the exact identification and quantification of the individual olefines, the bromine consumption is given as a cumulative parameter. This is purely a characteristic number, with the bromine index being used for substances with a low bromine consumption and given in mg Br_2/100g sample. In contrast, the bromine number is determined for substances whose bromine consumption lies in the range from one to several g Br_2 / 100 g sample.

Reaction equation

$R - CH = CH - R + Br_2 \rightarrow R - CHBr - CHBr - R$

Materials and apparatus

Exchange Unit	10 mL
Separate double Pt-sheet electrode	6.0309.100
Temperature sensor Pt 1000	6.1110.100
Ice bath or thermostat	

Reagents and chemicals

Titrant:
bromide – bromate solution
c = 0.00333 mol/L (0.02 N)

Solvent mixture consisting of:
714 mL glacial acetic acid
134 mL tetrachloromethane
or 1,1,1-trichloroethene
or 1-methyl-2-pyrrolidone
134 mL methanol
18 mL H_2SO_4 w(H_2SO_4) = 20%

Procedure

When connecting the electrode please make sure that the connector for the platinum electrode is plugged into the «POL» socket.

The sample size depends on the expected bromine index. For a bromine index of approx. 100 the sample size is one gram. When making up the solvent mixture the toxic and not readily degradable chlorinated hydrocarbons should, if possible, be replaced by non-chlorinated products.

The sample is dissolved in 100 mL of the solvent mixture and cooled to 0…5 °C in an ice bath or with a thermostat. The mixture should be thoroughly stirred with a magnetic stirrer bar.

The following program is used for the titration:

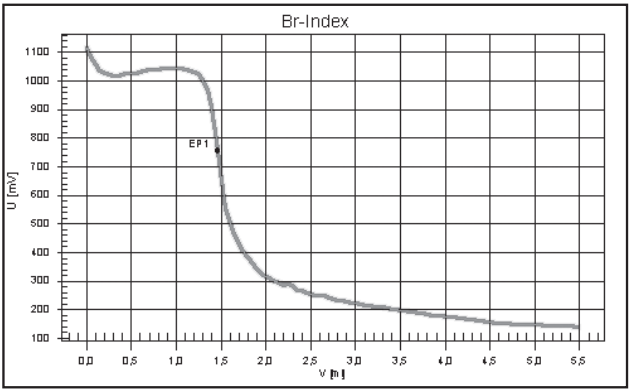
```
'pa
794 Titrino             01102   794.0010
date  2002-09-09    time  13:59       15
MET  Ipol          Br index
parameters
>titration parameters
  V step                 0.05 ml
  titr.rate             max. ml/min
  signal drift           OFF mV/min
  equilibr.time           30 s
  start V:               OFF
  pause                   60 s
  I(pol)                   1 µA
  electrode test:        OFF
  temperature           14.1 °C
       >stop conditions
  stop V:               abs.
  stop V                  50 ml
  stop U                 OFF mV
  stop EP                   9
  filling rate          max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                     200 mV
  EP recognition:         all
  fix EP1 at U           OFF mV
>preselections
  req.ident:              Id1
  req.smpl size:          all
  activate pulse:         OFF
          ------------
```

Example of a titration curve

Calculation

Bromine index (mg Br_2 / 100 g) = EP1 x C01 x C02 / C00

EP1 = consumption of bromide/bromate solution
c = 0.00333 mol/L («0.02 N»)
C00 = sample weight of petrol
C01 = 0.02 («normality» of bromide/bromate solution)
C02 = 7990



Measured values and statistics

Measured value	Sample size (g)	Consumption of titrant (mL)	BI engine oil (mg Br_2 / 100 g)
1	22.253	1.502	10.79
2	20.047	1.249	9.96
3	25.532	1.779	11.13
$\bar{\chi}$			**10.63**
S ±			**0.60**
S_{rel} ± %			**5.66**

II.4.7 Free sulfurous acid (SO_2) in wine

Learning topics
- Analysis of foodstuffs.
- Dilute solutions.
- Polarized electrodes.

Principles

Sulfite (sulfurous acid) is added to wine for two reasons:

- to stop enzymatic sugar degradation (alcoholic fermentation)
- as an antioxidant (protection against atmospheric oxygen)

Different countries permit different maximum levels in wine. The majority of the SO_2 is present in the wine in bound form. In order to determine the total SO_2 the wine must first be saponified with NaOH. Sulfite is oxidized to sulfate by iodine. The titration of sulfites with iodine solution is indicated by bivoltametric endpoint recognition with a double Pt-sheet electrode. The potential is measured between two polarized platinum sheets. As long as there is an excess of free sulfite in the solution, the potential remains at approx. 300 mV. As soon as the sulfite has been consumed and only iodine and sulfate or sulfuric acid are present in the solution, the potential drops to approx. 0 mV.

Reaction equations

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$
$$H_2SO_3 + 2\,H_2O \rightleftharpoons SO_3^{2-} + 2\,H_3O^+$$
$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2\,HI$$

Materials and apparatus

Exchange Unit	20 mL
Separate double Pt-sheet electrode	6.0309.100

Reagents and chemicals

Iodide/iodate standard solution
$c(I_2)$ = 1/128 mol/L
Sulfuric acid w = 25%
Potassium iodide analytical grade >99%

Procedure

50 mL wine is pipetted into a beaker from a volumetric pipet and approx. 1 g potassium iodide is added followed by 5 mL sulfuric acid w = 25% and a magnetic stirrer bar. A separate double Pt-sheet electrode is used for endpoint recognition; this continuously measures the potential in the solution.

The sample is titrated with the standard solution $c(I_2)$ = 1/128 mol/L using the following program:

```
'pa
794 Titrino              01102   794.0010
date  2002-09-09    time  15:22       19
SET  Ipol          SO2 wine
parameters
>SET1
  EP at U                  20 mV
  dynamics                300 mV
  max.rate                  5 ml/min
  min.rate                 10 µl/min
  stop crit:              time
  t(delay)                 10 s
>SET2
  EP at U                 OFF mV
>titration parameters
  titr.direction:         auto
  start V:                 OFF
  pause                    20 s
  I(pol)                    1 µA
  electrode test:          OFF
  temperature             25.0 °C
       >stop conditions
  stop V:                 abs.
  stop V                   10 ml
  filling rate           max. ml/min
>statistics
  status:                  OFF
>preselections
  conditioning:            OFF
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
      ------------
```

Calculation

1 mL $c(I_2)$ = 1/128 mol/L corresponds to 0.50 mg SO_2

mg/L SO_2 = EP1 x C01 x C02 / C00

EP1 = mL iodine solution up to endpoint
C00 = sample size in mL (50)
C01 = 0.5
C02 = 1000 (for 1 liter)

Measured values and statistics

Measured value	Sample size wine (mL)	Consumption of titrant (mL)	Free SO_2 in mg/L
1	50	2.115	21.15
2	50	2.134	21.34
3	50	2.199	21.99
4	50	2.177	21.77
5	50	2.130	21.30
6	50	2.252	22.52
$\bar{\chi}$			**21.68**
S ±			**0.52**
S_{rel} ± %			**2.40**

II.4.8 Oxygen content in water – Winkler method

Learning topics

- Redox processes.
- Iodometry.
- Water analysis.

Principles

The Winkler method is an elegant method for determining the oxygen content in water.

Manganese(II) chloride and NaOH solution are added to the water sample. The oxygen leads to the formation of Mn(III) hydroxide. After being dissolved in acid, the Mn(III) is reduced to Mn(II) in the presence of iodide ions. At the same time an amount of iodine that is equivalent to the oxygen is released and can be titrated with thiosulfate.

Reaction equations

$MnCl_2 + 2\,NaOH \rightarrow Mn(OH)_2 + 2\,NaCl$

$2\,Mn(OH)_2 + O_2 + H_2O \rightarrow 2\,Mn(OH)_3 + 2\,H_3O^+$

$2\,Mn(OH)_3 + 6\,HCl \rightarrow 2\,MnCl_3 + 6\,H_2O$

$2\,MnCl_3 + 2\,KI \rightarrow 2\,MnCl_2 + 2\,KCl + I_2$

Materials and apparatus

Exchange Unit	10 mL
Separate double Pt-sheet electrode	6.0309.100
Combined Pt-ring electrode	6.0451.100

Reagents and chemicals

Titrant
$c(Na_2S_2O_3)$ = 0.05 mol/L

Winkler I
400 g $MnCl_2$ x 4 H_2O is dissolved in dist. H_2O and made up to 1 liter

Winkler II
500 g NaOH, 1 g NaN_3 et 150 potassium iodide are dissolved in dist. H_2O and made up to 1 liter

Acid mixture 350
mL each of $w(H_3PO_4)$ = 85% and w(HCl) = 36% are mixed and made up to 1 liter with dist. H_2O

Procedure

The water sample is filled bubble-free into the sample bottle, e.g. with a tube that «fills the bottle from below», with inclined stopper until it overflows and then sealed. After removing the stopper, 2 mL each of Winkler solution I (40% $MnCl_2$ x 4 H_2O) and Winkler solution II (50% NaOH and 15% KI) are added just below the surface of the water, the bottle is immediately sealed again and the contents mixed. After deposition of the precipitate (several hours) approx. 1/3 of the supernatant water is carefully aspirated off, 10 mL acid mixture is added (conc. HCl / conc. H_3PO_4 1:1), the bottle is then sealed and the contents mixed. A magnetic stirrer bar is added and the released iodine is titrated with $c(Na_2S_2O_3)$ = 0.05 mol/L to SET Ipol (1 μA, separate double Pt-sheet electrode).

The iodine formed is titrated with $c(Na_2S_2O_3)$ = 0.05 mol/L according to the following SET or MET programs:

MET titration

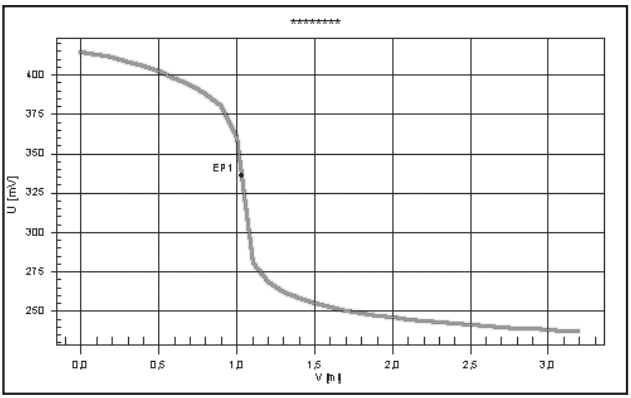
```
'pa
794 Titrino              01102   794.0010

date  2002-09-12    time  16:26       12
MET  Ipol           O2WiMET
parameters
>titration parameters
  V step                 0.10 ml
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                 OFF
  pause                     0 s
  I(pol)                    1 µA
  electrode test:          OFF
  temperature             25.0 °C
       >stop conditions
  stop V:                abs.
  stop V                   20 ml
  stop U                   OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

SET titration:

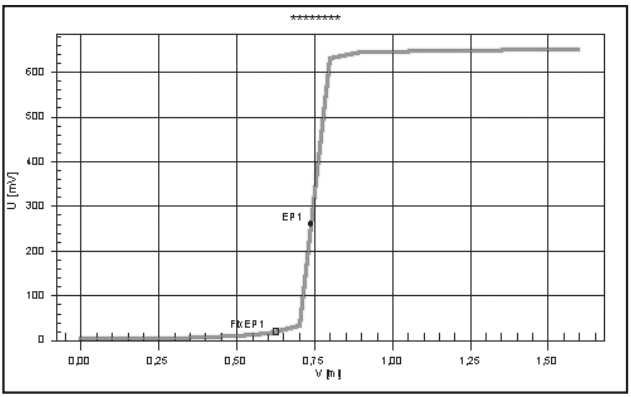
```
794 Titrino              01102   794.0010
date  2002-09-12    time  16:27       12
SET  Ipol           O2Winkl
parameters
>SET1
  EP at U                  240 mV
  dynamics                 220 mV
  max.rate                   5 ml/min
  min.rate                  10 µl/min
  stop crit:              time
  t(delay)                  10 s
>SET2
  EP at U                  OFF mV
>titration parameters
  titr.direction:         auto
  start V:                 OFF
  pause                     0 s
  I(pol)                    1 µA
  electrode test:          OFF
  temperature             25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                    20 ml
  filling rate            max. ml/min
>statistics
  status:                  OFF
>preselections
  conditioning:            OFF
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
  EPC                       30 mV
  EP recognition:          all
  fix EP1 at U             20 mV
  fix EP2 at U            OFF mV
          ------------
```

Examples of titration curves

Oxygen by Winkler method with combined Pt-ring electrode – MET method



Oxygen by Winkler method with separate double Pt-sheet electrode – SET method



Calculation

1 mL $c(Na_2S_2O_3)$ = 0.05 mol/L corresponds to 0.40 mg O_2

mg/L O_2 = EP1 x C01 x C02 x C30 / (C00 – 4)

EP1 = mL thiosulfate solution up to endpoint
C00 = sample size/bottle contents in mL
C01 = 0.4
C02 = 1000 (for 1 liter)
C30 = titer of thiosulfate solution
«4» = mL Winkler solution I and II

Additional remarks

The oxygen absorption ability of water depends on three different factors:

- Temperature: As the temperature increases, the oxygen absorption decreases.
- Pressure: As the pressure increases, the oxygen absorption increases.
- Salt content: As the salt content increases, the oxygen absorption decreases – by approx. 0.554% per g/L salt (rule of thumb).

The following tables give an overview:

Air pressure as a function of the height above sea level

101.325 kPa = 1 atm = 760 mm Hg

SL/m = height above sea level in meters, kPa = mean air pressure in kilopascal

SL/m	kPa	SL/m	kPa
0	101.3	900	90.5
100	100.1	1000	89.4
200	98.8	1100	88.3
300	97.6	1200	87.2
400	96.4	1300	86.1
500	95.2	1400	85.0
600	94.0	1500	84.0
700	92.8	1600	82.9
800	91.7	1700	81.9

Oxygen solubility (oxygen saturation in mg/L O_2) as a function of the temperature and air pressure

Temp. in °C	111.5 kPa (1.1 atm)	101.3 kPa (1.0 atm)	91.2 kPa (0.9 atm)	81.1 kPa (0.8 atm)	70.9 kPa (0.7 atm)
0.0	16.09	14.62	13.14	11.69	10.21
5.0	14.06	12.77	11.48	10.20	8.91
10.0	12.43	11.29	10.15	9.00	7.86
15.0	11.10	10.08	9.05	8.03	7.01
20.0	10.02	9.09	8.14	7.23	6.30
25.0	9.12	8.62	7.40	6.56	5.70
30.0	8.35	7.56	6.76	5.99	5.19
35.0	7.69	6.95	6.22	5.47	4.75

To be able to calculate the oxygen saturation of a sample, the air pressure, the temperature (at the time the sample was taken) and the salt content of the sample have to be taken into account.

II.4.9 Hydrogen peroxide (H_2O_2) in disinfectants with $KMnO_4$

Learning topics

- Redox potential.
- Redox pairs.
- Relativity of oxidation / reducing agents («redox amphotery»).

Principles

Hydrogen peroxide is redox-amphoteric. It oxidizes reducing agents such as the thiol groups of hair proteins when applied for a permanent wave and is itself reduced to water. However, strong oxidizing agents such as permanganate oxidize it to oxygen.

In this case an aqueous solution of hydrogen peroxide is titrated up to the first endpoint with potassium permanganate standard solution in the presence of sulfuric acid. A combined Pt-ring electrode is used to detect the endpoint.

Reaction equation

$$2\ MnO_4^- + 5\ H_2O_2 + 6\ H_3O^+ \rightarrow 2\ Mn^{2+} + 5\ O_2 + 14\ H_2O$$

Materials and apparatus

Exchange Unit	10 mL
Combined Pt-ring electrode	6.0451.100

Reagents and chemicals

Hydrogen peroxide solution

Sulfuric acid
concentrated, approx. 96%

Potassium permanganate
Ready-to-use titrant c = 0.02 mol/L (0.1 N)

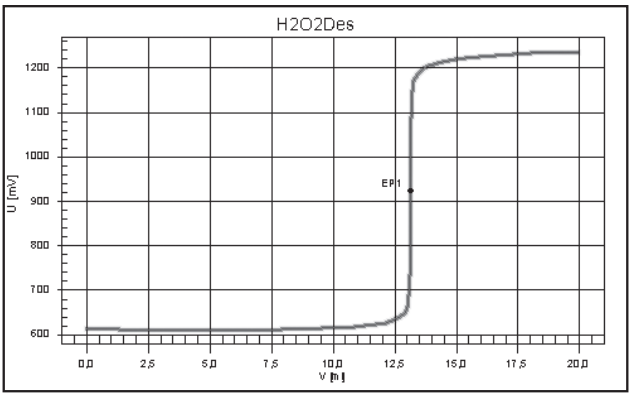
Deionized water

Procedure

75 mL of the sample solution is pipetted into a beaker from a volumetric pipet. A magnetic stirrer bar is added and 5 mL concentrated sulfuric acid is carefully added under vigorous stirring. Care must be taken that the solution does not become too hot. It is then titrated with potassium permanganate solution up to the first endpoint according to the following program:

```
'pa
794 Titrino              01102   794.0010
date  2002-09-12    time  14:26       12
DET  U              H2O2Des
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
       >stop conditions
  stop V:                 abs.
  stop V                   20 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                       5
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(KMnO_4)$ = 0.02 mol/L corresponds to 1.701 mg H_2O_2

% H_2O_2 = EP1 x C01 x C02 / C00

EP1 = mL permanganate up to endpoint
C00 = sample size in mL (75)
C01 = 1.701
C02 = 0.1 (for %)

Measured values and statistics

Measured value	Sample size H_2O_2 (mL)	Consumption of $KMnO_4$ (mL)	% H_2O_2
1	75.0	13.150	0.0298
2	75.0	13.159	0.0298
3	75.0	13.162	0.0299
4	75.0	13.055	0.0296
5	75.0	13.088	0.0297
$\overline{\chi}$			**0.0298**
S ±			**0.0001**
S_{rel} ± %			**0.67**

II.4.10 Diazotization titration with $NaNO_2$

Learning topic

- Diazotization of primary amines, analysis of drugs, nitrite titrations.

Principles

Primary amino groups can be diazotized by nitrous acid in a solution of hydrochloric acid whereby the diazonium salt is formed.

As nitrous acid is not stable, sodium nitrite is used as the titrant. The acid used is normally HCl – in order to accelerate the diazotization reaction, bromide ions can also be added (usually HBr as a catalyst). As $NaNO_2$ and hydrochloric acid immediately form (volatile) HNO_2, this means that vigorous stirring must be applied during the titration and the solution cooled down to approx. 15 °C.

Instructions according to this method can be found, for example, in the USP for the determination of sulfonamides and other drugs.

Reaction equation

$R\text{–}NH_2 + HNO_2 + HCl \rightarrow [R\text{–}N^+{\equiv}N]Cl^- + 2\,H_2O$

Materials and apparatus

Exchange Unit	20 mL
Combined Pt-ring electrode	6.0451.100

Reagents and chemicals

Titrant
$c(NaNO_2)$ = 0.1 mol/L

Hydrochloric acid
w(HCl) = 10%

Procedure

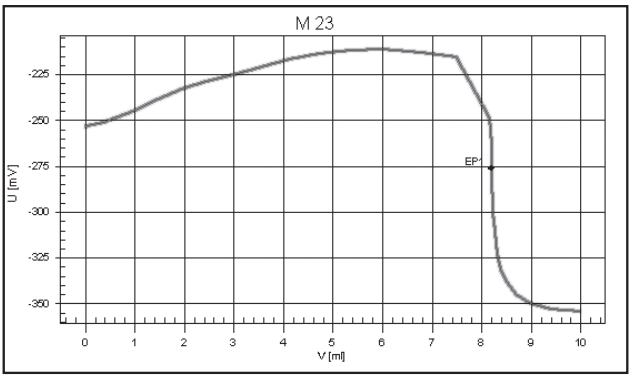
Using sulfanilamide as an example

Approx. 0.140 g sample is weighed out into the titration vessel and dissolved in 50 mL w(HCl) = 10%. The mixture is cooled down to approx. 10 °C and then titrated with $c(NaNO_2)$ = 0.1 mol/L to after the first endpoint (combined Pt-ring electrode).

Parameters

```
'pa
794 Titrino              01102
794.0010
date   2003-01-30     time  08:18
0
DET  U                 M 23
parameters
>titration parameters
  meas.pt.density           3
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            17.3 °C
>stop conditions
  stop V:                 abs.
  stop V                   20 ml
  stop U                  OFF mV
  stop EP                  9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      5
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          all
  activate pulse:         OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(NaNO_2)$ = 0.1 mol/L corresponds to 17.22 mg $C_6H_8N_2O_2S$

w = EP1 x C01 x C02 x C36 / C00;2;%

C00 = sample weight in mg
C01 = equivalent weight of titrated substance (17.22)
C02 = conversion factor to % (100)
C36 = titer of the $NaNO_2$

Measured values

Measured value	Sample size (mg)	Consumption of $NaNO_2$ (mL)	% Sulfanilamide
1	142.5	8.215	99.30
2	155.8	8.984	99.30

II.4.11 Bromatometry

Learning topics

- Bromate/bromium as oxidizing agent.
- Direct and indirect determination methods.
- Determination of drugs and metal ions.

Principles and reaction equations

Bromates are strong oxidizing agents and can be used under acidic conditions for the direct determination of e.g. As(III), Sb(III), Sn(II), Cu(I) and hydrazine. In an acidic solution the bromate is reduced to bromide:

$$BrO_3^- + 6\,H_3O^+ + 6\,e^- \rightarrow Br^- + 9\,H_2O$$

The titration makes use of the fact that bromate comproportionates with bromide to form elemental bromine.

$$BrO_3^- + 5\,Br^- + 6\,H_3O^+ \rightarrow 9\,H_2O + 3\,Br_2$$

Under acidic conditions an excess of bromate is added to the dissolved substance, which is oxidized. The excess bromate is allowed to react with potassium iodide and the iodine formed is titrated with thiosulfate.

A large number of indirect determinations is possible. Examples from the pharmaceutical sector and determinations of metal ions are mentioned below.

Preparation of the titrant $c(1/6\ KBrO_3)$ = 0.1 mol/L

$KBrO_3$ is available in very pure form as a standard titrimetric substance. It is dried in a drying oven for two to three hours at 180 °C and allowed to cool down in a desiccator for at least 2 h.

2.7833 g $KBrO_3$ is weighed out into a 1000 mL volumetric flask, dissolved in dist. H_2O, made up to the mark and mixed. The solution is very stable and also has a stable titer, but must not contain any bromide ions!

Analytical use in the pharmaceutical sector

A suitable amount of substance is weighed out into an Erlenmeyer flask and dissolved in dist. H_2O. It is treated with an excess of $c(1/6\ KBrO_3)$ = 0.1 mol/L, KBr and acid are added and the flask is then sealed and the contents mixed. After a reaction time of 15 min the potassium iodide is added and the released iodine is titrated with $c(Na_2S_2O_3)$ = 0.1 mol/L (Pt Titrode).

Titrant $c(Na_2S_2O_3)$ = 0.1 mol/L

According to the Pharm. Europe and the USP the content of the following substances can be determined by this method: chlorocresol, cysteine, hexylresorcinol, hydroxyethylsalicylate, parachlorophenol, phenol, phenylephrine hydrochloride and resorcinol.

Determination of metal ions

The method is based on the fact that numerous metal ions under suitable pH conditions can be precipitated as oxinate complexes by 8-hydroxyquinoline (bivalent metal ions bind two, trivalent metal ions bind three oxine ligands).

The precipitate formed is filtered through a glass filter crucible and rinsed with warm water. A dilute solution of hydrochloric acid is then added. This releases oxine, which is converted to 5,7-dibromo-8-hydroxyquinoline with Br_2.

This is done by adding an excess of $c(KBrO_3)$ = 0.1 mol/L and some KBr solution and allowing the reaction to take place for 5 min in a sealed Erlenmeyer flask. After the addition of potassium iodide solution the released iodine is titrated with $c(Na_2S_2O_3)$ = 0.1 mol/L (Pt Titrode).

Literature reference

Jander/Jahr

Massanalyse (titrimetric analisis)

Walter de Gruiter, Berlin 1989

ISBN 3-11-011975-7

Calculation

1 mol oxine corresponds to 2 mol Br_2 (or 4 mol Br). $KBrO_3$ and KBr together produce 3 mol Br_2 from 1 mol $KBrO_3$. 1 equivalent of a bivalent metal ion corresponds to 8 equivalents of bromine; a trivalent metal ion to 12 equivalents of bromine. Or:

1 mL c(1/6 $KBrO_3$) = 0.1 mol/L corresponds to, e.g.:

0.22485 mg Al
1.4050 mg Cd
0.73667 mg Co
0.7943 mg Cu
0.46539 mg Fe
0.30381 mg Mg
0.68673 mg Mn
0.733 mg Ni
1.9836 mg U and
081713 mg Zn

Example: determination of resorcinol

Materials and apparatus

Exchange Unit	20 mL
Pt Titrode	6.0431.100

Reagents and chemicals

Reaction solution
c($KBrO_3$) = 1/60 mol/L

Hydrochloric acid solution
w(HCl) = 35%

Potassium iodide solution
w(KI) = 10%

Titrant
c($Na_2S_2O_3$) = 0.1 mol/L

Procedure

Approx. 0.7 g sample is weighed out into a 500 mL volumetric flask, dissolved in dist. H_2O, made up to the mark and mixed.

25.0 mL (1/20 of the sample weight) is pipetted into an Erlenmeyer flask, 25.00 mL c($KBrO_3$) = 1/60 mol/L and 5 mL w(HCl) = 35% are added and the flask is immediately sealed. It is swirled around for 1 min and then allowed to stand for 2 min. 10 mL w(KI) = 10% is added, the flask is sealed again and thoroughly mixed. The flask walls and stopper are rinsed with dist. H_2O and the contents are titrated with c($Na_2S_2O_3$) = 0.1 mol/L to after the first endpoint. A blank containing 25.00 mL c($KBrO_3$) = 1/60 mol/L is treated in the same manner as the sample.

Parameters

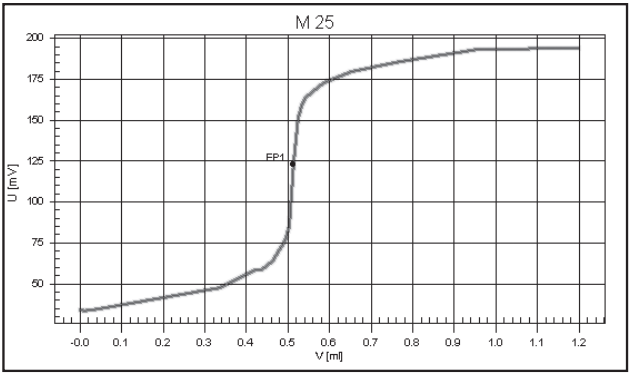
```
'pa
794 Titrino              01102   794.0010
date 2003-01-30     time  09:06         0
DET  U                  M 25
parameters
>titration parameters
  meas.pt.density           2
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             30 mV/min
  equilibr.time            32 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            40.8 °C
>stop conditions
  stop V:                 abs.
  stop V                   20 ml
  stop U                  OFF mV
  stop EP                  9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      5
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          all
  activate pulse:         OFF
          ------------
```

Calculation

w = (C33 – EP1) x C01 x C02 / C00;2;%

C00 = sample weight in mg
C01 = equivalent weight of the titrated substance (1.835)
C02 = conversion factor to % (100)
C33 = blank value

Example of a titration curve



Measured values

Measured value	Sample size resorcinol (mg)	Consumption (C33 – EP1) mL)	% Resorcinol
1	36.2	19.234	97.50
2	36.2	19.307	97.87

II.5 Complexometry / Chelometry methods

II.5.1 Titer determination of $c(Na_2EDTA) = 0.1$ mol/L with $CaCO_3$

Learning topics

- Use of standard titrimetric substances.
- Complex formation.
- Complex formation constant.
- Indication methods.

Principle

$CaCO_3$ is suitable for use as the standard titrimetric substance for determining the titer of Na EDTA solutions.

Reaction equation

$Ca^{2+} + Na_2EDTA \rightarrow CaEDTA + 2\ Na^+$

Materials and apparatus

Exchange Unit	20 mL
Cu ISE	6.0502.140
Ag/AgCl reference electrode	6.0726.107

Reagents and chemicals

Titrant
$c(Na_2EDTA) = 0.1$ mol/L

Auxiliary solution
$c(Cu(NH_4)_2EDTA) = 0.1$ mol/L

Buffer solution
NH_3/NH_4Cl, pH = 10

Hydrochloric acid solution
$c(HCl) = 5$ mol/L

Standard titrimetric substance
$CaCO_3$

Procedure

$CaCO_3$ is dried overnight in a drying oven at 140 °C and allowed to cool down in a desiccator for at least 2 h.

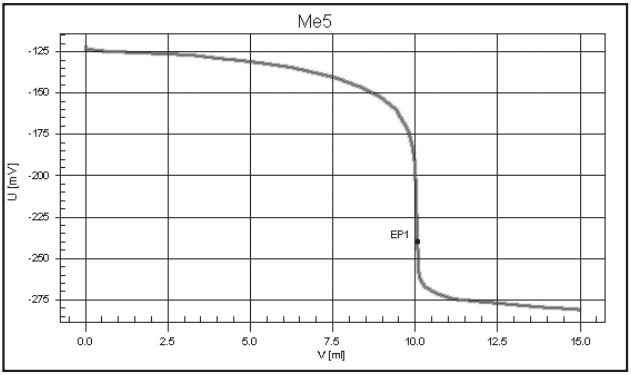
Approx. 100 mg $CaCO_3$ is weighed out accurately to 0.1 mg into a titration beaker and suspended in approx. 20 mL dist. H_2O. Under stirring $c(HCl) = 5$ mol/L is added drop by drop until everything has dissolved. After the addition of approx. 30 mL dist. H_2O, 5 mL buffer solution pH = 10 and 1 mL auxiliary solution, the mixture is titrated with $c(Na_2EDTA) = 0.1$ mol/L to after the first endpoint.

Care must be taken that the temperature remains constant during the titration. The titer determination is normally carried out three times and the mean value is used.

Parameters

```
'pa
794 Titrino              01102   794.0010
date  2003-01-29    time  08:47       12
DET  U                   Me5
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                 OFF
  pause                    30 s
  meas.input:               1
  temperature            25.0 °C
       >stop conditions
  stop V:                 abs.
  stop V                    20 ml
  stop U                   OFF mV
  stop EP                  OFF
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:    greatest
  up lim.1 U             2000 mV
  low lim.2 U              OFF mV
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           all
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

Titer = C00 / C01 / EP1;4

EP1 = mL Na_2EDTA up to endpoint
C00 = weight of $CaCO_3$ in mg
C01 = equivalent weight of the titrated substance (10.009)

Measured values and statistics

Measured value	Sample size $CaCO_3$ (mg)	Consumption of Na_2EDTA (mL)	Titer
1	100.7	9.877	1.0186
2	104.8	10.302	1.0164
3	102.5	10.067	1.0173
4	103.7	10.195	1.0163
5	99.8	9.815	1.0159
6	105.6	10.352	1.0191
7	104.2	10.225	1.0182
8	103.8	10.206	1.0163
9	100.9	9.913	1.0169
10	100.7	9.898	1.0184
$\bar{\chi}$			**1.0173**
S ±			**0.0011**
S_{rel} ±%			**0.11**

II.5.2 Ca and sulfate content in tap water with the Ca ISE

Learning topics

- Complex formation constant.
- Solubility product.
- Selectivity.
- Titration curve.

Principles

The following instructions describe an elegant method that allows the sulfate and calcium content of water to be determined in one run. In the acidified sample (so that carbonate does not interfere) the sulfate is treated with an excess of barium chloride and precipitated as barium sulfate. After alkaline buffering the (unprecipitated) excess barium is back-titrated with EGTA. Two endpoints are found. EP1 corresponds to the Ca and the difference EP2 – EP1 to the Ba (Mg does not interfere as EGTA only forms weak complexes with it).

Reaction equations

$Ba^{2+} + SO_4^{2+} \rightarrow \{BaSO_4\}$

Excess $BaCl_2$:

$Ba^{2+} + Na_2H_2EGTA + 2\ H_2O \rightarrow Na_2BaEGTA + 2\ H_3O^+$

Materials and apparatus

Exchange Unit	20 mL
Ca ISE	6.0508.110
Ag/AgCl reference electrode	6.0726.107

Reagents and chemicals

Titrant
c(EGTA) = 0.05 mol/L

Barium chloride solution
$c(BaCl_2)$ = 0.05 mol/L in c(HCl) = 0.001 mol/L

Buffer solution
NH_3/NH_4Cl, pH = 10

Hydrochloric acid solution
c(HCl) = 2 mol/L

Procedure

If necessary, the sample solution is adjusted to pH <4 with HCl and treated with 5 mL $c(BaCl_2)$ = 0.05 mol/L. The reaction is allowed to take place for 3 min under stirring. Then 5 mL buffer solution pH = 10 is added, allowed to react for a further 30 s and then titrated with EGTA, c(EGTA) = 0.05 mol/L.

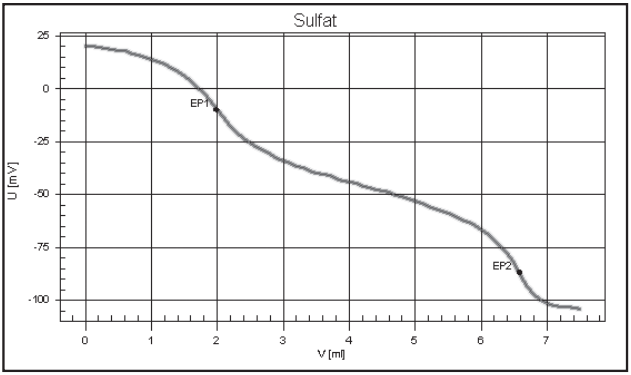
Two equivalence points are obtained, the first one corresponding to the Ca^{2+} content and the difference between the second and the first equivalence point to the excess Ba^{2+}.

By using a blank sample (without sulfate), which is prepared and titrated in the same way, the titrant consumption for the added amount of $c(BaCl_2)$ = 0.05 mol/L is first determined. This blank value is stored in the titrator as common variable C30.

Parameters

```
'pa
794 Titrino              01102   794.0010
date  2003-01-29    time  10:40         0
MET  U              Sulfate
parameters
>titration parameters
  V step                  0.10 ml
  titr.rate               max. ml/min
  signal drift              50 mV/min
  equilibr.time             26 s
  start V:                 OFF
  pause                      0 s
  meas.input:                1
  temperature             25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                    25 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                        5 mV
  EP recognition:       window
  low lim.1 U              -50 mV
  up lim.1 U                 0 mV
  low lim.2 U             -100 mV
  up lim.2 U               -75 mV
  low lim.3 U              OFF mV
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

1 mL *c*(EGTA) = 0.05 mol/L corresponds to 2.004 mg Ca or 4.803 mg SO_4

Ca = EP1 x C01 x C02 / C00;2;mg/L

RS2 = EP2–EP1;2;mL

SO_4 = (C30 – RS2) x C03 xC02 / C00;2;mg/L

C00 = sample size in mL
C01 = 2.004 for Ca
C02 = 1000 (conversion factor mL/L)
C03 = 4.803 for sulfate
C30 = blank consumption in mL

Measured values

Measured value	Sample size water (mL)	EP1 (mL)	EP2 (mL)	β(Ca) (mg/L)	β(SO_4) (mg/L)
1	50.0	1.999	6.684	80.12	30.26
2	50.0	1.990	6.675	79.76	30.26

II.5.3 Ca and Mg content (total hardness) in water with the Ca ISE

Learning topics

- Ca ISE. Response behavior and selectivity.
- Recomplexing/auxiliary complexing agents.
- Titration curve.
- Water analysis.

Principles

The chief hardness formers in water are Ca and Mg salts. The more calcium and/or magnesium dissolved in the water, the harder it is. Objects that remain in contact with hard water for a long time frequently acquire a scale deposit made up of the precipitated salts of these metals. Higher fatty acids form precipitates that are insoluble in water with these metals; these can also be found on the walls of baths.

The sum of the two alkaline earth ions in mmol/L corresponds to the total hardness (see also II.5.4. and II.5.5.). In this experiment calcium and magnesium are determined separately in a complexometric titration. In order to obtain a better differentiation between the Ca and Mg «jumps» in the titration curve, an auxiliary complexing agent is added, this also masks interfering Fe^{3+} and Al^{3+}.

Reaction equation

$$Mg^{2+} + Ca^{2+} + 2\ Na_2H_2EDTA + 4\ H_2O \rightarrow Na_2MgEDTA + Na_2CaEDTA + 4\ H_3O^+$$

Materials and apparatus

Exchange Unit	20 mL
Ca ISE	6.0508.110
Ag/AgCl reference electrode	6.0726.107

Reagents and chemicals

Titrant
c(Na_2EDTA) = 0.05 mol/L in
c(KOH) = 0.1 mol/L

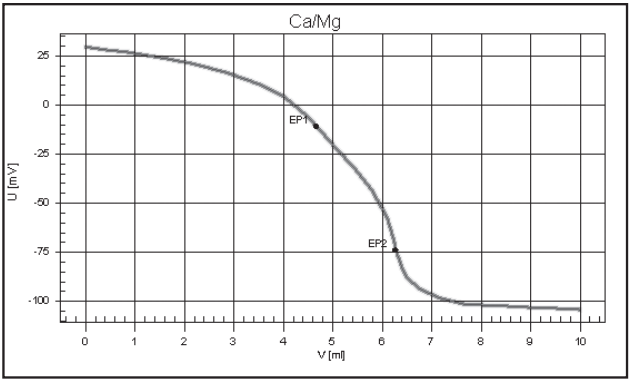
Auxiliary complexing agent
c(acetylacetone) = 0.1 mol/L in
c(Tris) = 0.2 mol/L

Procedure

100 mL sample is placed in the titration beaker. 15 mL auxiliary complexing agent solution is then added and, after a short waiting period, the solution is titrated with Na_2EDTA using the Ca ISE. The first equivalence point corresponds to the Ca^{2+} content, the difference between the second and first equivalence point to the Mg^{2+} content.

```
'pa
794 Titrino              01102   794.0010
date  2003-01-28    time  10:50         0
DET  U                 Ca/Mg
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
       >stop conditions
  stop V:                 abs.
  stop V                   10 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      30
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(Na_2EDTA)$ = 0.05 mol/L corresponds to 2.004 mg Ca or 1.216 mg Mg

Ca = EP1 x C01 x C02 / C00;2;mg/L

Mg = (EP2 – EP1) x C03 x C02 / C00;2;mg/L

C00 = sample size in mL (100)
C01 = 2.004 for Ca
C02 = 1000 (conversion factor in mL/L)
C03 = 1.216 for Mg

Measured values and statistics

Measured value	EP1 (mL)	EP2 (mL)	*c*(Ca) mmol/L	β(Ca) mg/L	*c*(Mg) mmol/L	β(Mg) mg/L
1	2.151	2.903	2.151	86.21	0.752	18.28
2	2.150	2.882	2.150	86.17	0.732	17.80
3	2.148	2.871	2.148	86.09	0.723	17.58
4	2.155	2.901	2.155	86.37	0.746	18.14
5	2.150	2.890	2.150	86.17	0.740	17.99
6	2.199	2.925	2.199	88.14	0.726	17.65
7	2.153	2.883	2.153	86.29	0.730	17.75
8	2.153	2.923	2.153	86.29	0.770	18.72
9	2.149	2.874	2.149	86.13	0.725	17.63
10	2.152	2.884	2.152	86.25	0.732	17.80
$\bar{\chi}$			**2.156**	**86.41**	**0.738**	**17.93**
S ±			**0.015**	**0.61**	**0.015**	**0.36**
S_{rel} ±%			**0.70**	**0.71**	**2.00**	**2.07**

II.5.4 Total hardness in drinking water with the Ca ISE

Learning topics

- Recomplexing.
- ISE.
- Selectivity.
- Calculation of water hardness.

Principles *(see also II.1.10 and II.5.3)*

The total hardness of a water is given in mmol alkaline earth ions/L and replaces the different and confusing «units» such as German, French, USA hardness degrees, etc. The knowledge of the water hardness plays a great role in the daily use of water; for example in adding the right amount of washing powder to washing machines, water softening (hot water production), etc. Coarse divisions into different types of water are made: soft, medium-hard, hard and very hard water:

Alkaline earth ion content in mmol/L	Water type
Below 1.3	soft
1,3…2,5	medium-hard
2,5…3,8	hard
Above 3.8	very hard

Soft waters can be expected in sources in granite areas, medium-hard water in lakes and hard waters in areas with a predominantly limestone-containing subsurface.

The titration curve shows two equivalence points; the first equivalence point corresponds to the Ca^{2+} content, the difference between the second and first equivalence point to the Mg^{2+} content.

Reaction equations

Frequently, the anion ETDA is shortened with Y; the equations then present themselves as follows:

1. $Ca^{2+} + H_2Y^{2-} + 2\ H_2O \rightarrow CaY^{2-} + 2\ H_3O^+$

2. $Mg^{2+} + H_2Y^{2-} + 2\ H_2O \rightarrow MgY^{2-} + 2\ H_3O^+$

Materials and apparatus

Exchange Unit	20 mL
Ca ISE	6.0508.110
Ag/AgCl reference electrode	6.0726.107

Reagents and chemicals

Titrant
$c(Na_2EDTA) = 0.1$ mol/L

Auxiliary complexing agent
c(acetylacetone) = 0.1 mol/L in
c(Tris) = 0.2 mol/L

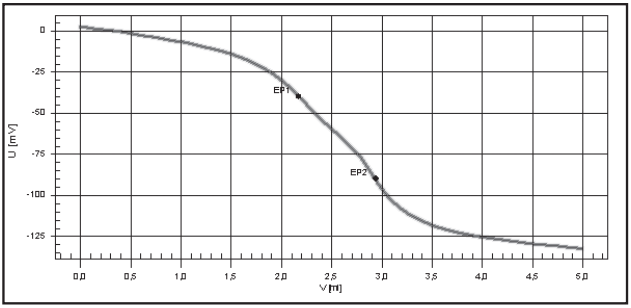
Procedure

100 mL water is pipetted into each of 10 beakers (150 mL). 15 mL auxiliary complexing solution is added and, after a waiting period of approx. 5 min, the solution is titrated with $c(Na_2EDTA) = 0.1$ mol/L.

The titration is carried out using the following parameters:

```
DET  U
parameters
>titration parameters
  meas.pt.density            1
  min.incr.               10.0 µl
  titr.rate               max. ml/min
  signal drift              20 mV/min
  equilibr.time             38 s
  start V:                 OFF
  pause                     0 s
  meas.input:               1
  temperature             25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                     5 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate            max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                        5
  EP recognition:          all
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculations of hardness

To obtain the total hardness and the concentrations of the calcium and magnesium ions, the following formulas must be entered in the instrument:

Calcium =
EP1 x C01 x C02 / C00;2;mmol/L

Magnesium =
(EP2 – EP1) x C01 x C02 / C00;2;mmol/L

TH =
EP2 xC01 x C02 / C00;2;mmol/L

The individual variables are:

EP1 = added volume up to first endpoint [mL]
EP2 = added volume up to second endpoint [[mL]
C00 = sample size (100) [mL]
C01 = correction factor (1000) [–]
C02 = concentration of EDTA solution (0.1) [mol/L]

The total hardness is given in mmol/L, with 0.1 mmol Ca/Mg corresponding to 4.008 mg Ca or 2.431 mg Mg. The total hardness should be given to two decimal places.

Measured values and statistics

Measured value	EP1 (mL)	EP2 (mL)	*c*(Ca) mmol/L	*c*(Mg) mmol/L	*c*(TH) mmol/L
1	2.1806	2.9472	2.181	0.766	2.947
2	2.1748	2.9414	2.175	0.766	2.941
3	2.1715	2.9386	2.172	0.767	2.939
4	2.1757	2.9386	2.176	0.763	2.939
5	2.1758	2.9358	2.176	0.760	2.936
6	2.1761	2.9439	2.176	0.768	2.944
7	2.1642	2.9383	2.164	0.774	2.938
8	2.1693	2.9431	2.169	0.774	2.943
9	2.1760	2.9343	2.176	0.758	2.934
10	2.1759	2.9394	2.176	0.763	2.939
$\bar{\chi}$			**2.174**	**0.766**	**2.940**
S ±			**0.005**	**0.005**	**0.004**
S_{rel} ± %			**0.22**	**0.65**	**0.13**

Possible sources of error

In order to obtain reliable results we recommend that you always prepare only the beaker that is to be titrated immediately. Care should also be taken that no air bubbles are entrained. Ca electrodes that have been stored dry are conditioned for 10 min in $c(CaCl_2)$ = 0.01 mol/L before the titration.

II.5.5 Total hardness in drinking water with the Spectrosense 610 nm

Learning topics

- Colored indicators; photometric titration.
- Complex formation, recomplexing.
- Color change.
- pH dependency.
- Titration curve.

Determining the total hardness of drinking water

Principles

As the complex formation constants of EDTA are very small in acidic or neutral solution, the solution must be buffered to pH = 10 during the whole titration. The indicator used for the titration is eriochrome black T, the color change of the indicator is determined photometrically using the Metrohm Spectrosense 610 nm.

Reaction equations

1. $Ca^{2+} + H_2Y^{2-}$ (EDTA) + 2 $H_2O \rightarrow CaY^{2-} + 2\ H_3O^+$

2. $Mg^{2+} + H_2Y^{2-}$ (EDTA) + 2 $H_2O \rightarrow MgY^{2-} + 2\ H_3O^+$

Materials and apparatus

Exchange Unit	20 mL
Spectrosense 610 nm	6.1109.110

Reagents and chemicals

Titrant
$c(Na_2EDTA)$ = 0.1 mol/L

Buffer solution
NH_3/NH_4Cl, pH = 10

Indicator solution
w(eriochrome black T) = 0.1%

Auxiliary reagent
magnesium complexonate (MgEDTA)

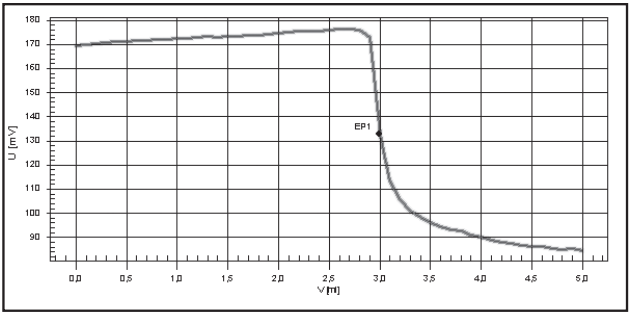
Procedure

100 mL water is pipetted into each of 10 glass beakers (150 mL). Approx. 0.1 g MgEDTA and 10 mL buffer solution are added. The solution is then treated with 0.5 mL eriochrome black indicator and titrated with $c(Na_2EDTA)$ = 0.1 mol/L. Correct results will only be obtained if the Spectrosense 610 nm is allowed to warm up for approx. 15 min before the titration.

The titration is carried out using the following parameters:

```
MET  U
parameters
>titration parameters
  V step                  0.10 ml
  titr.rate               max. ml/min
  signal drift              50 mV/min
  equilibr.time             26 s
  start V:                 OFF
  pause                      0 s
  meas.input:                1
  temperature             25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                     5 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       30 mV
  EP recognition:          all
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

In order to obtain the total hardness, the following formula must be entered in the instrument:

TH = EP1 x C01 x C02 / C00;2;mmol/L

The individual variables are:

EP1 = added volume up to equivalence point [mL]
C00 = water sample size (100) [mL]
C01 = correction factor (1000) [–]
C02 = concentration of EDTA solution (0.1) [mol/L]

The total hardness is given in mmol/L, with 0.1 mmol Ca/Mg corresponding to 4.008 mg Ca or 2.4305 mg Mg. The total hardness should be given to two decimal places.

Measured values and statistics

Measured value	Sample size water (mL)	Consumption of Na_2EDTA (mL)	c(TH) mmol/L
1	100.0	3.000	3.000
2	100.0	2.998	2.998
3	100.0	2.998	2.998
4	100.0	2.997	2.997
5	100.0	2.999	2.999
6	100.0	2.999	2.999
7	100.0	2.999	2.999
8	100.0	2.997	2.997
9	100.0	2.999	2.999
10	100.0	2.997	2.997
$\overline{\chi}$			**2.998**
S ±			**0.001**
S_{rel} ±%			**0.04**

Possible sources of error

In order to obtain good results we recommend that you always prepare only that beaker which is to be titrated immediately. Care should also be taken that no air bubbles are entrained and that no air bubbles adhere to the mirror of the Spectrosense, as these could affect the measurement.

II.5.6 Nickel in a nickel electroplating bath with the Cu ISE

Learning topics

- Recomplexing.
- Selectivity.
- Analysis of metals.

Principles

In certain cases, ion-selective electrodes are suitable for the indication of the titration process. In this example, a Cu-selective electrode is used (see also under II.5.2).

The main constituent of nickel-plating baths is, of course, nickel. This metal has to be monitored; its content is normally in the region of 70 g/L Ni. The starting substances used are normally sulfates or sulfamates (salts of amidosulfonic acid). Depending on whether the baths are matt or bright nickel baths, various additives are used to ensure optimal nickel deposition. In matt nickel baths these could include boric acid, ammonium and Mg(II), in bright nickel baths cobalt, formate, formaldehyde, sulfonic acid, saccharin, etc.

Reaction equation

$$CuEDTA + Ni(II) \rightarrow NiEDTA + Cu(II)$$

Materials and apparatus

Exchange Unit	20 mL
Cu ISE	6.0502.140
Ag/AgCl reference electrode	6.0726.107

Reagents and chemicals

Titrant
$c(Na_2EDTA) = 0.1$ mol/L

Auxiliary solution
$c(Cu(NH_4)_2EDTA) = 0.1$ mol/L

Buffer solution
NH_3/NH_4Cl, pH = 10

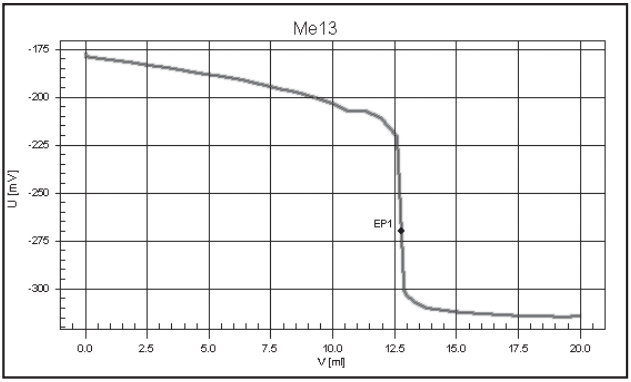
Procedure

Approx. 50 mL dist. H_2O and 1.00 mL bath sample are placed in a glass beaker. After the addition of 1 mL auxiliary solution and 10 mL buffer solution the titration is carried out with $c(Na_2EDTA) = 0.1$ mol/L to after the first endpoint.

Parameters

```
'pa
794 Titrino              01102   794.0010
date  2003-01-28    time  11:25         0
DET  U                  Me13
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                 OFF
  pause                     0 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                    20 ml
  stop U                   OFF mV
  stop EP                  OFF
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5 mV
  EP recognition:    greatest
  up lim.1 U             2000 mV
  low lim.2 U             OFF mV
  fix EP1 at U           OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           all
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(Na_2EDTA)$ = 0.1 mol/L corresponds to 5.869 mg Ni

Ni = EP1 x C01 x C34 / C00;2;g/L

C00 = sample size in mL (100)
C01 = equivalent weight of Ni (5.869)
C34 = titer of the Na_2EDTA solution

Measured values

Measured value	Sample size Ni bath (mL)	Consumption of Na_2EDTA (mL)	g/L Ni
1	1.00	13.038	76.52
2	1.00	12.995	76.27

II.5.7 Calcium in milk with the Cu ISE

Learning topics

- Ca bonding forms.
- Food analysis.

Principles

In addition to water, dairy products are one of the main sources of calcium in human nutrition. Their calcium is easily taken up by the human body. Calcium supply plays a key role in preventing symptoms of malnutrition (keyword: osteoporosis – particularly in women, but recently also more frequent in men). Calcium in milk is only partly in an ionogenic state. The majority is present in bound form, but can be complexed by EGTA in alkaline solution. With EGTA, calcium(II) can be selectively determined in the presence of Mg(II) (Mg only forms weak complexes with EGTA).

Reaction equation

$$CuEGTA + Ca^{2+} \rightarrow CaEGTA + Cu^{2+}$$

Materials and apparatus

Exchange Unit	20 mL
Cu ISE	6.0502.140
Ag/AgCl reference electrode	6.0726.107

Reagents and chemicals

Titrant
c(EGTA) = 0.1 mol/L

Auxiliary solution
$c(Cu(NH_4)_2EGTA)$ = 0.1 mol/L

Buffer solution
NH_3/NH_4Cl, pH = 10

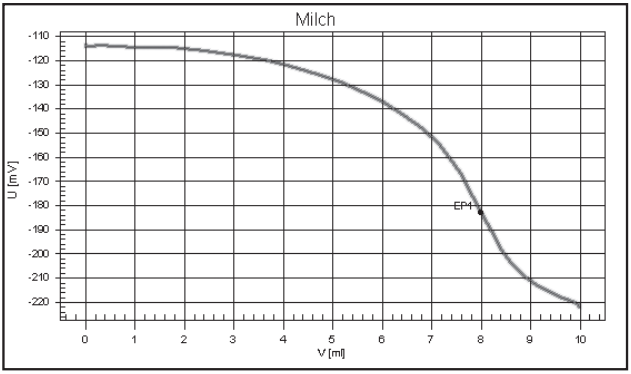
Procedure

Approx. 10 g sample is weighed out exactly into a glass beaker and diluted with approx. 90 mL dist. water. The prepared sample is treated with 1 mL CuEGTA solution and 10 mL buffer solution pH = 10. It is allowed to react under stirring for 10 to 30 s and then titrated with c(EGTA) = 0.1 mol/L to after the first endpoint.

Parameters

```
'pa
794 Titrino              01102   794.0010
date  2003-01-29    time  09:58        0
DET  U                  Milk
parameters
>titration parameters
  meas.pt.density           1
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift            OFF mV/min
  equilibr.time             5 s
  start V:                OFF
  pause                    20 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                    5 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:          all
  fix EP1 at U            OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           all
  activate pulse:          OFF
          ------------
```

Example of a titration curve



Calculation

1 mL *c*(EGTA) = 0.1 mol/L corresponds to 4.008 mg Ca

Calcium = EP1 x C01 x C02 / C00;3;%

EP1 = mL EGTA up to endpoint
C00 = sample size in g
C01 = 4.008 for Ca
C02 = 0.1 (conversion factor to %)

Measured values

Measured value	Sample size milk (g)	Consumption of EGTA (mL)	% Ca
1	11.565	9.218	0.319
2	10.020	7.997	0.320

II.5.8 Aluminum in stomach tablets (antacids) with the Spectrosense 610 nm

Learning topics

- Complex formation.
- Complex formation constant.
- pH dependency of complex formation.

Principles

Hyperacidity (HCl) can cause gastric disorders (heartburn) that may also affect the esophagus. So-called antacids are taken to alleviate these disorders. They neutralize the acid, but are not a cure and only provide short-term relief. Previously $NaHCO_3$ was mainly used. It only helps very briefly, as it stimulates acid production. Modern antacids contain, among other things, $MgCO_3$, $CaCO_3$, $Al(OH)_3$ and/or silicates of these cations. Here we are titrating Al(III) with EDTA.

At room temperature aluminum only forms the complex very slowly. This is why an excess of EDTA is added, the solution heated and, after the reaction, the excess EDTA back-titrated with $ZnSO_4$.

Reaction equation

$Al^{3+} + Na_2H_2EDTA \rightarrow NaAlEDTA + 2\ H_3O^+$

Materials and apparatus

Exchange Unit	20 mL
Spectrosense 610 nm	6.1109.110

Reagents and chemicals

Titrant I
$c(Na_2EDTA) = 0.1$ mol/L

Titrant II
$c(ZnSO_4) = 0.1$ mol/L

Buffer solution
acetate buffer, pH = 4.7

Hydrochloric acid
$w(HCl) = 25\%$

Indicator solution
dithizone, 25.6 mg / 100 mL ethanol

Alcohol
ethanol, analytical grade

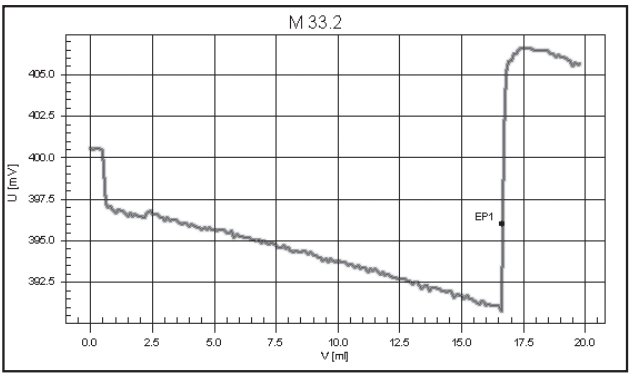
Procedure

20 tablets are weighed out and pulverized. A portion of sample containing approx. 2 g $Al(OH)_3$ is weighed out into a beaker. 20 mL dist. H_2O and, under stirring, 15 mL $w(HCl) = 25\%$ are added. The mixture is carefully heated until all the $Al(OH)_3$ has dissolved. After cooling down the solution is filtered into a 200 mL volumetric flask, the filter is rinsed with dist. H_2O and the solution is then made up to the mark and mixed. A 10.00 mL aliquot is pipetted into the titration beaker, 20.00 mL $c(Na_2EDTA) = 0.1$ mol/L and 20 mL acetate buffer are added, heated and boiled for 5 min. After cooling down, 50 mL ethanol and 2 mL dithizone indicator are added and titrated with $c(ZnSO_4) = 0.1$ mol/L to after the first endpoint. A blank containing 20.00 mL $c(Na_2EDTA) = 0.1$ mol/L is also titrated.

Parameters

```
‘pa
794 Titrino              01102   794.0010
Date 2003-01-30     time  11:51         0
MET  U                M 33.2
parameters
>titration parameters
  V step                 0.1 ml
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:                OFF
  pause                    0 s
  meas.input:              1
  temperature            25.0 °C
>stop conditions
  stop V:                abs.
  stop V                   20 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      10 mV
  EP recognition:         all
  fix EP1 at U           OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          all
  activate pulse:         OFF
          ------------
```

Example of a titration curve



Calculation

1 mL $c(Na_2EDTA)$ = 0.1 mol/L corresponds to 7.80 mg $Al(OH)_3$

$Al(OH)_3$ = (C33 – EP1) x C01 / (C00 x C02);2;%

EP1 = mL $ZnSO_4$ up to endpoint
C00 = sample size
C01 = 7.8 for Al
C02 = 10 (conversion factor)
C33 = «blank value» (mL $ZnSO_4$ used in the back-titration)

Measured values

Measured value	Sample size tablets (mg)	Consumption of Na_2EDTA (mL)	% $Al(OH)_3$
1	906.6	16.667	14.34
2	906.6	16.668	14.34

II.5.9 Iron in cement with the Spectrosense 610 nm

Learning topics

- Complex formation.
- Complex formation constant.
- pH dependency of complex formation.
- Colored indicators.
- Specificity.

Principles

Cements are finely ground hydraulic binders which, on absorbing water, harden like stone and are water-resistant when they have hardened. They consist mainly of Ca silicates, Ca aluminates and Ca ferrites. They are made of mixtures of raw materials (limestone, clay, marl) by heating them (at approx. 1500 °C), usually in revolving cylindrical furnaces, to form the so-called clinkers. Depending on the application, other constituents may be added (aggregates), these then determine the most important properties of the cement (time taken for setting and hardening, strength, chemical resistance, etc.). Example of composition:

Tricalcium silicate	40…80%
Dicalcium silicate	0…30%
Tricalcium aluminate	7…15%
Calcium-aluminate ferrite	4…15%

Reaction equation

$Fe^{3+} + Na_2H_2EDTA + 2\,H_2O \rightarrow NaFeEDTA + 2\,H_3O^+ + Na^+$

Materials and apparatus

Exchange Unit 20 mL

Spectrosense 610 nm 6.1109.110

Reagents and chemicals

Titrant
$c(Na_2EDTA) = 0.1$ mol/L

Hydrochloric acid
$w(HCl) = 36\%$

Nitric acid
$w(HNO_3) = 32.5\%$

Ammonia solution
$w(NH_3) = 25\%$

Indicator solution
w(sulfosalicylic acid) = 4% in dist. H_2O

Procedure

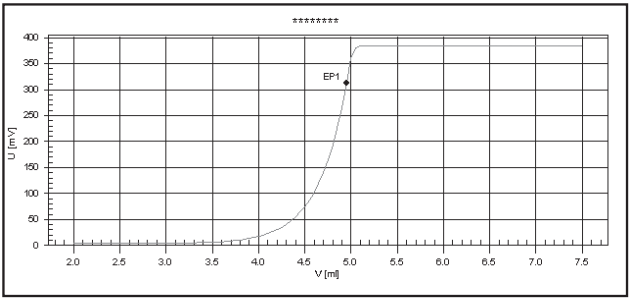
Approx. 1 g cement is mixed with 1.5 g NH_4Cl and treated with 8 mL HCl and 0.5 mL HNO_3. The mixture is boiled and stirred occasionally with a glass rod. After the addition of 50 mL hot water the mixture is filtered through a black ribbon filter into a 500 mL volumetric flask and the filter thoroughly rinsed with hot water. The combined filtrate is allowed to cool down and then made up to the mark with dist. water.

25 mL sample solution is diluted to 50 mL with 25 mL dist. water. 1 g ammonium chloride and 20 drops of the indicator solution are added and the mixture is heated to boiling. Ammonia is used to adjust the pH to 1.5...2.0 and the solution is then diluted to 150 mL with dist. water. This solution is then titrated with $c(Na_2EDTA) = 0.1$ mol/L until the color changes from red-violet to colorless/slightly yellow.

Parameters

```
`pa
794 Titrino              01102   794.0010
Date 2003-01-29     time  11:44        0
SET  U               Cement
parameters
>SET1
  EP at U                 400 mV
  dynamics                150 mV
  max.rate               10.0 ml/min
  min.rate               25.0 µl/min
  stop crit:            drift
  stop drift               20 µl/min
>SET2
  EP at U                 OFF mV
>titration parameters
  titr.direction         auto
  start V:                OFF
  pause                     0 s
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                   10 ml
  filling rate           max. ml/min >sta-
tistics
  status:                 OFF
>preselections
  conditioning:           OFF
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
       ------------
```

Example of a titration curve



Calculation

1 mL $c(Na_2EDTA)$ = 0.1 mol/L corresponds to 7.985 mg Fe_2O_3

Fe_2O_3 = EP1 x C01 x C02 / (C03 x C00 x C04);2;%

EP1 = mL Na_2EDTA up to endpoint
C00 = weight of cement in g (1.1026)
C01 = 7.8985 for Fe_2O_3
C02 = volume of whole sample solution (500)
C03 = sample volume (25)
C04 = 10 (conversion factor to %)

Measured values

Measured value	Sample size cement (mg)	Consumption of Na_2EDTA (mL)	% Fe_2O_3
1	55.0	0.304	4.41
2	55.0	0.302	4.38

III. Appendix

Further and/or cited literature

Metrohm Application Bulletins, Application Notes and Monographs can be obtained free of charge from your local Metrohm agency). Much information can also be found on the Metrohm Internet page

www.metrohm.com

1.	Bruttel, P.	**Non-aqueous titration of acids and bases with potentiometric endpoint indication**	Metrohm monograph 50243 – 04.1999
2.	Derek Cooper, Chris Doran,	**Analytical Chemistry by Open Learning. Classical Methods Vol. 1.**	John Wiley & Sons. Chichester 1987
3.	Metrohm	**FOOD PAC** The know-how package for the titrimetric/potentiometric determination of foodstuffs	Metrohm no. 6.6055.003
4.	Fritz, J.S., Schenk G.H.	**Quantitative Analytische Chemie.** Translation from the American by Ingo Lüderwald and Leo Gros	Vieweg Verlag, Wiesbaden, 1989 ISBN 3-528-08484-7
5.	Galster, H.	**pH Measurement. Fundamentals, Methods, Applications, Instrumentation**	VCH Weinheim, 1991 ISBN 3-527-28237-8
6.	Thomas Gassner	**Systematische Untersuchungen zur Genauigkeit von Titrationen**	Metrohm monograph in German 50021 - 1979
7.	Harris, D.C.	**Lehrbuch der Quantitativen Analyse**	Vieweg-Verlag, Wiesbaden 1997, ISBN 3-528-06756-X
8.	Huber, W.	**Titrationen in nichtwässrigen Lösungen**	Akademische Verlagsgesellschaft, Frankfurt a.M. (1964)
9.	Kunze, U.R. / Schwedt, G.	**Grundlagen der qualitativen und quantitativen Analyse**	Wiley-VCH, Weinheim 2002 ISBN 3-527-30858-X
10.	MERCK	**Die Untersuchung von Wasser**	
11.	Metrohm	**Application Bulletins**	Please ask the table of contents
12.	Metrohm	**Ti Application Notes**	Please ask the table of contents
13.	Metrohm	**OIL PAC** The know-how package for the determination of petrochemical products	Metrohm no. 6.6040.003

14.	Metrohm	**PHARM PAC** The know-how package for the titrimetric/potentiometric determination of pharmaceutical ingredients	Metrohm no. 6.6042.003
15.	Metrohm	**PLATE PAC** The know-how package for the titrimetric/ potentiometric analysis of electroplating baths	Metrohm no. 6.6044.003
16.	Richter, W., Tinner, U.	**La technique des titrages**	Metrohm monograph in French 8.016 – 5002
17.	Schulz, R.	**Titrimetric determination of surfactants and pharmaceuticals. Modern methods for analytical practice**	Metrohm monograph 1999 – 52243
18.	Georg Schwedt	**Analytische Chemie. Grundlagen, Methoden und Praxis**	Thieme Verlag Stuttgart 1995
19.	Metrohm	**SURF PAC** The know-how package for the titrimetric/ potentiometric determination of surfactants	Metrohm no. 6.6041.003
20.	Tinner, U.	**Electrodes in Potentiometry**	Metrohm monograph 8.015.5003
21.	Julian Tyson	**Analysis** What Analytical Chemists Do.	Royal Society of Chemistry Paperbacks. London 1988
22.	Valcárcel, M.	**Principles of Analytical Chemistry**	Springer, Berlin, Heidelberg 2000 ISBN 3-540-64007-X
23.	Metrohm	**WINE PAC** The know-how package for the titrimetric/ potentiometric analysis of wine and must	Metrohm no. 6.6043.003

Standardized methods

Metrohm always attempts to meet the requirements of company-specific, national and international standards with its instruments and large range of accessories. To a considerable extent we have been successful in this and our customers can be sure that they have purchased the correct instrument/correct accessories for working in accordance with such standards. From the great number of such standards a few are mentioned below that concern titrimetric methods and which indicate how universal the use of such methods is. Abbreviations:

AOAC Official Methods of Analysis of the Official Analytical Chemists (USA)
ASTM American Society for Testing and Materials
DIN Deutscher Normenausschuss
EN European Norm
EPA US Environmental Protection Agency
ISO International Organization for Standardization

- AOAC 950.07 Acidity (total) of beer. Potentiometric titration method
- AOAC 960.14 Quarternary ammonium compounds. Potentiometric titration method
- AOAC 970.37 Monosodium gluconate in food. Potentiometric titration method
- AOAC 971.27 Sodium chloride in canned vegetables. Method III. Potentiometric method
- AOAC 979.02 Fentin in pesticide formulations. Potentiometric titration method
- ASTM D 664-04
  Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration
- ASTM D 6174-97
  Standard Test Method for Hydroxyl Groups Using Reaction with p-Toluene Sulfonyl Isocyanate (TSI) and Potentiometric Titration with Tetrabutylammonium Hydroxide
- ASTM D 3341-91
  Standard Test Method for Lead in Gasoline – Iodine Monochloride Method
- ASTM D 6174-97
  Standard Test Method for Inorganic Sulfate in Surfactants by Potentiometric Lead Titration
- DIN EN 25663 Water quality; determination of Kjeldahl nitrogen
- DIN EN 25813 Water quality; determination of dissolved oxygen; iodometric method
- DIN 38406-3
  Determination of calcium and magnesium, complexometric tritation (E 3)
- DIN 38409-7
  Determination of acid and base capacity (waters)
- DIN EN ISO 8467
  Water quality – Determination of permanganate index
- EPA method 325.3 Chloride (drinking water)
- EPA method 330.1 Chlorine (waters)
- EPA method 360.2 Dissolved oxygen (waters)
- European Pharmacopoeia 4th Edition & Supplements
- ISO 13756
  Determination of silver in silver jewellery alloys – Volumetric (potentiometric) method using sodium chloride or potassium chloride
- ISO 3839
  Petroleum products – Determination of bromine number of distillates and aliphatic olefins – Electrometric method
- ISO 4220
  Ambient air – Determination of a gaseous acid air pollution index – Titrimetric method with indicator or potentiometric endpoint detection
- ISO 6326-3
  Natural gas – Determination of sulfur compounds – Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry
- ISO 8298
  Nuclear fuel technology – Determination of milligram amounts of plutonium in nitric acid solutions – Potentiometric titration with potassium dichromate after oxidation by Ce(IV) and reduction by Fe(II)
- U.S. Pharmacopeia USP 26 NF-23, 2003

275 years – the history of titrimetric analysis

Year	Who ?	What ?
1729	G.J. Geoffroy	Acidity of vinegar with potash
1747	L.G. Le Monnier	Carbonate content of mineral water with H_2SO_4
1750	G.F. Venel	Mineral water analysis with violet excerpt as indicator
1756	F. Home	First titrations with volumetric measurements (K_2CO_3 with HNO_3; water hardness with Na_2CO_3)
1767	W. Lewis	Titration of K_2CO_3 with HCl and litmus as colored indicator
1779	V.A. Gioanette	Titrates carbonate in drinking water with acetic acid
1782	L.B. Guyton de Morveau	Content of HCl and HNO_3 in mother liquors with K_2CO_3 and Curcuma indicator
1784	L.B. Guyton de Morveau	Prototype of a buret (gaso-mètre), glass tube with scale
1809	F.A.H. Descroizilles	Describes for the first time a measuring flask
1824	J.L. Gay-Lussac	Use of the names pipette (mesure petite) and burette
1828	J.L. Gay-Lussac	Term «titre» for content and/or quality designation
1840	A. Du Pascier	Uses iodine in ethanol as measuring solution
1843	M.J. Fordos, A. Gélis	Titrate sulfite and thiosulfate with iodine solution
1851	J. von Liebig	Oldest complex formation titration (cyanide with $AgNO_3$)
1855	F. Mohr	Publishes textbook on titration methods
1877	E. Luck	Uses phenolphthalein as the first synthetic color indicator
1893	R. Behrend	First potentiometric titration (argentometry)
1894	H. Tromssdorff	Describes 14 synthetic acid-base indicators
1897	W. Böttger	Acid-base titrations using the hydrogen electrode (potentiometric)
1900	F. Crotogino	Pt electrode for the indication of redox titrations
1909	F. Haber, Z. Klemensiewicz	pH electrode for the indication of potentiometric acid-base titrations
1915	J. Knop	Diphenylamine as the first redox indicator
1923	E. Müller	First monograph about potentiometric titrations
1926	C.W. Foulk, A.T. Bawden	Dead-stop titrations (U_{pol} – biamperometry) with two polarized Pt electrodes
1935	K. Fischer	Determinations with Karl Fischer reagent (KFR)
1936	Schellbach, C.R. Fresenius	Strip as a reading-off assistance of rod burettes
1945	G. Schwarzenbach	Complexometric titrations with EDTA
1947	M.D. Cannon	First combined pH glass electrode
1956	Metrohm	First piston burette
1958	Metrohm	First automatic titrator (E 336 Potentiograph)
1964	Metrohm	First Exchange Unit
1968	Metrohm	First digital titrator (Titroprint)
1973	Metrohm	Automatic analyzer (E 553 Sample Changer)
1979	Metrohm	First Titroprocessor (636)
1989	Metrohm	First Titrino (701 KF)
2002	Metrohm	First Titrando