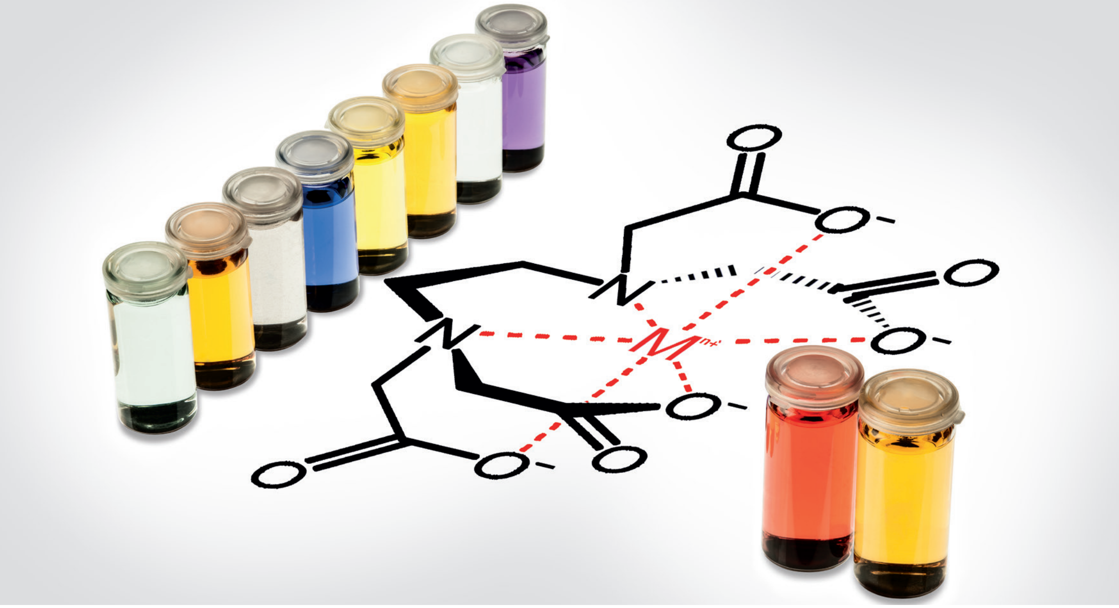
Monograph



Complexometric (Chelometric) Titrations

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Metrohm

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Preface

In 1945, Gerold Schwarzenbach discovered that aminocarboxylic acids (e.g., NTA, EDTA) form stable complexes with metal ions. On the basis of this discovery, he developed the complexometric titration technique, which became increasing popular from 1950 onwards, particularly for determining water hardness. Soon, in addition to calcium and magnesium, other metal ions could also be titrated. The use of new metal indicators and masking agents also enabled determinations of metal ion mixtures. Nowadays, together with acid/base, redox, and precipitation titrations, complexometric titrations are the most frequently used volumetric methods, and are recommended in many international standards and directives.

Theoretical fundamentals

The term *complex* refers to species composed of individual ions or molecules with the formula $[ML_n]^{\pm z}$.

The *coordination number* specifies how many monodentate ligands (or complexing agents) are bound. Cations are usually present in aqueous solutions as *aqua complexes* with the formula $[M(OH_2)_4]^{2+}$ or $[M(OH_2)_6]^{2+}$.

The term *denticity* refers to the number of coordination sites of the respective ligand. Complexes with multidentate ligands are known as *chelates*.

The stability of a complex is determined by thermodynamic and kinetic factors. A measure of the thermodynamic stability is the *complex formation constant* K_f or the *dissociation constant* $K = 1/K_f$.

The stability of metal complexes can be described, for example, by the following simplified equation, which uses EDTA as ligand:

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

The complex formation constant is usually given as log K_f in data tables. The stability of the complex increases with increasing magnitude of log K_f.

The effective complex formation constants are generally lowered in the presence of protons (acids) because these compete with the metal ions in the reaction with the complexing agent, for example, by protonating the carboxyl group(s).

As a general rule:

- Complex formation constant < 10; alkaline titration (e.g., Ca^{2+}, Mg^{2+})
- Complex formation constant > 15; slightly acidic titration (e.g., Al^{3+}, Pb^{2+}) (Fe^{3+} and Bi^{3+} can even be titrated at pH = 2).

Titrations must be carried out in buffered solutions because the complexation reaction always liberates protons. This is illustrated briefly by the following examples:

$$Ca^{2+} + Na_2H_2EDTA + 2\ H_2O \rightarrow [CaEDTA]^{2-} + 2\ Na^+ + 2\ H_3O^+$$

$$Al^{3+} + Na_2H_2EDTA + 2\ H_2O \rightarrow [AlEDTA]^- + 2\ H_3O^+ + 2\ Na^+$$

Apart from a few exceptions, the chelating agents used for titration form 1:1 complexes with metal ions, regardless of whether the metal ions have a charge $z = 2+$ or $z = 3+$.

The following table contains a few selected complex formation constants (log K_f) for common titrants and metal ions:

Metal ion	**EDTA**[1]	**EGTA**[2]	**DCTA**[2]	**DTPA**[2]	**NTA**[2]
Al(III)	16.4	13.9	18.6	18.4	9.5
Ba(II)	7.9	8.4	8.6	8.6	4.8
Bi(III)	27.8[a]	23.8	31.2	29.7	–
Ca(II)	10.7	11.0	12.5	10.7	6.4
Cd(II)	16.5	16.7	19.2	19.3	9.5
Co(II)	16.5	12.5	18.9	18.4	10.4
Co(III)	41.4	–	–	–	–
Cr(II)	13.6[a]	–	–	–	–
Cr(III)	23.4[a]	2.5	–	–	> 10.0
Cu(II)	18.8	17.8	21.3	21.5	13.0
Fe(II)	14.3	11.9	16.3	16.6	8.8
Fe(III)	25.1	20.5	28.1	28.6	15.9
Ga(III)	21.7	–	22.9	23.0	13.6
Hf(IV)	29.5	–	–	35.4	20.3
Hg(II)	21.5	23.1	24.3	27.0	14.6
In(III)	24.9	–	28.8	29.0	16.9
Mg(II)	8.8	5.2	10.3	9.3	5.5
Mn(II)	13.9	12.3	16.8	15.6	7.4
Ni(II)	18.4	13.6	19.4	20.3	11.5
Pb(II)	18.0	14.7	19.7	18.8	11.4
Pd(II)	25.6[a]	–	–	–	–
Sn(II)	18.3[b]	23.9	–	–	–
Sr(II)	8.7	8.5	10.5	9.7	5.0
Th(IV)	23.2	–	29.3	28.8	12.4
Tl(I)	6.4	–	5.3	6.0	4.8
Tl(III)	35.3	–	38.3	48.0	18.0
Zn(II)	16.5	14.5	18.7	18.8	10.7
Zr(IV)	29.3	–	20.7	36.9	20.85

DCTA	trans-Diaminocyclohexanetetraacetic acid
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EGTA	Ethylene glycol bis-(2-aminoethyl)tetraacetic acid
NTA	Nitrilotriacetic acid

The following conclusions can be drawn from the above table:

- Metal ions with a triple positive charge form stronger complexes than metal ions with a double positive charge (cf. Fe^{2+} – Fe^{3+}).
- Ligands with a higher denticity form stronger complexes (cf. NTA – DTPA).
- The weakest complex is formed between Ba and NTA, and the strongest between Tl^{3+} and DTPA.

[1] If not otherwise indicated, the values are based on measurements at 25 °C and an ionic strength of 0.1 mol/L.
[a] Values measured at 20 °C and an ionic strength of 0.1 mol/L.
[b] Values measured at 20 °C and an ionic strength of 1 mol/L.
Harris, Daniel (2007): Quantitative Chemical Analysis. 7th ed., New York.
[2] Values were taken from Dojindo Molecular Technologies (publisher) **http://www.dojindo.com** (Issued 28.9.2015).

Indication of the equivalence point of the titration

Visual or photometric

Visual indication with color indicators is the oldest method of determining the equivalence point of a titration, and it is still frequently used. It is inexpensive and requires little equipment. The particular drawback of this method is that it cannot be automated and is difficult to validate. The color sensitivity of individuals differs, and also depends on the lighting conditions. Furthermore, the endpoint is even more difficult to observe in colored and/or turbid solutions.

The endpoint detection can be improved by the use of photometric indication. In this case, the subjective human eye is replaced by an objective sensor. This kind of indication can be automated and validated – provided that the correct color indicator is chosen and the solutions are not too turbid before or during the titration.

Color indicators do not have a precise *color change point* – rather, they have a *color change range*. This has a considerable influence on the accuracy of the results of titrations where visual indication of the equivalence point is employed. As a general rule: the human eye can perceive a color change when the concentration ratio changes from roughly 1/10 to 10/1. It is thus expedient to select color indicators that have a sharp color change with very different colors.

The color indicators react with the analyte metal ions to form a color complex whose color suddenly changes when all the metal ions have been (re)complexed or titrated by the titrant.

Photometric titration is carried out with fiber-optic sensors. These comprise a light source, two glass fiber (optical) conductors, and an amplifier. Monochromatic light exits the fiber-optic conductor and enters the solution where its color is partially absorbed. Depending on the design of the photometric sensor, the optical signal is sent to a photodiode directly or via a concave mirror and a second fiber-optic conductor. This generates a voltage signal in the amplifier that is sent to the titrator via its electrode input.

During photometric titrations, attention should be paid to the fact that air bubbles in the sample solution may have an unfavorable effect on the shape of the titration curve, and may also influence the results, leading to spikes or equivalence point artifacts.

The following procedure generally applies:

- Stirring is adjusted so that the solution is thoroughly mixed, but no air bubbles are entrained.
- The solution is degassed under vacuum or in an ultrasonic bath before the analysis. If necessary, the sample solution is diluted with dist. H_2O and preneutralized.

Potentiometric

The measuring setup for potentiometric measurements always consists of two electrodes – an indicator electrode (measuring electrode) and a reference electrode. These do not measure potentials (also known as Galvanic potentials), but potential differences (voltages).

The indicator electrode (ion-selective electrode, ISE) provides an electrode potential that depends on the composition of the measuring solution (specifically, the concentration of the measuring ion).

The reference electrode (usually Ag/AgCl) provides an electrode signal (reference potential) that is as independent as possible from the measuring solution.

The potential is measured under almost zero-current conditions using a voltmeter (e.g., the titrator) with a high-resistance measuring input. This is important because it avoids voltage drops.

If a suitable measuring setup is used, the potential U measured between the two electrodes depends only on the measuring solution, or to be more precise, on the activity a_i of the measuring ion, since only dissociated ions are measured. In case of ISE measurements, this relationship is described by the Nernst equation:

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

U:	Measured potential between measuring and reference electrodes
U_0:	Standard potential of the measuring chain (depends on its configuration)
2.303:	Conversion factor from the natural to the decadic logarithm
R:	Gas constant (8.31441 J/K/mol)
T:	Absolute temperature in Kelvin (273.15 + x °C)
z:	Charge of the measuring ion, including algebraic sign (e.g., +2 for Ca^{2+})
F:	Faraday constant (96484.56 C/mol)
a_i:	Activity of the measuring ion
U_N:	Nernst slope (e.g., 29.58 mV at 25 °C and z = +2)

The Nernst slope U_N is the theoretical electrode slope. It corresponds to a potential change induced by a change in a_i by one order of magnitude. It depends on the temperature of the measuring solution and on the charge z of the measuring ion. The following table illustrates these dependencies:

Temperature / °C	U / mV, z = +1	U / mV, z = +2
0	54.20	27.10
10	56.18	28.09
20	58.17	29.09
25	59.16	29.58
30	60.15	30.08
40	62.14	31.07
50	64.12	32.06

Ion-selective electrodes

As their name indicates, ion-selective electrodes respond more or less selectively to the ion for whose measurement they are designed. This suggests that a corresponding ISE is required for each measuring ion to be determined, which would make indication of the equivalence point using ion-selective electrodes extremely unattractive. Furthermore, such a concept would be much too expensive and also difficult to implement with certain measuring ions. How to manage with only one ion-selective electrode is explained in the chapter Cu-ISE.

a) Ca-ISE

The Ca-ISE is a polymer membrane electrode and, as its name indicates, it is particularly responsive to Ca ions. It is therefore mainly used in the titration of calcium. However, there is a trick that allows simultaneous titration of Ca and Mg (e.g., to determine the water hardness). This involves treating the measuring solution with an auxiliary complexing agent (acetylacetone in TRIS buffer). If the mixture is then titrated with EDTA, Ca is complexed first. When there is no Ca left, the auxiliary complexing agent comes into play. Mg reacts with CaEDTA to form MgEDTA. The corresponding quantity of Ca is liberated and can then be titrated with EDTA.

The determination of sulfate exploits the cross-sensitivity of Ca ISE with respect to Ba ions. The sulfate is precipitated with $BaCl_2$, and the excess Ba is then back-titrated with EDTA. In the presence of Ca, the titration has two equivalence points. The first equivalence point corresponds to that of Ca and the second to that of Ba.

More details of these two strategies are given in the practical examples (determination of water hardness and of sulfate).

b) Cu-ISE

The Cu-ISE is a crystal membrane electrode. In theory, it responds only to Cu ions. However, once again a trick allows it to be used not only for titrating Cu ions. To do this, a small amount of CuEDTA is added to the sample solution. CuEDTA is a very stable complex, and liberates only a very small fraction of the Cu(II) ions. However, in alkaline solutions and in the presence of Ni(II) ions, for example, all Cu(II) ions are liberated from the complex, and the NiEDTA complex forms instead. If the mixture is then titrated with EDTA, the concentration of the Cu(II) ions decreases continuously until it reaches its very small initial value at the equivalence point. The following equations illustrate the three steps:

CuEDTA → Cu(II) + EDTA
CuEDTA + Ni(II) → NiEDTA + Cu(II)
Cu(II) + EDTA → CuEDTA

Commonly used complexing agents/titrants

The first complexing agent used for titrations was NTA or its trisodium salt. NTA is cheap, but it has the disadvantage that its complex formation constants are relatively small. It was therefore soon replaced by EDTA, which is still the most common agent used today, and is the specified titrant in many national and international standards.

Additional complexing agents were developed for special purposes (e.g., better selectivity, higher complex formation constants, better separation of mixtures); however, most of them are relatively expensive.

Commercially available complexing agents include:

NTA
- Nitrilotriacetic acid $C_6H_9NO_6$; $M_R = 191.14$ g/mol
- Nitrilotriacetic acid trisodium salt monohydrate $C_6H_6NNa_3O_6 \cdot H_2O$; $M_R = 275.12$ g/mol

EDTA
- Ethylenediaminetetraacetic acid $C_{10}H_{16}N_2O_8$; $M_R = 292.25$ g/mol
- Ethylenediaminetetraacetic acid disodium salt dihydrate $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$; $M_R = 372.24$ g/mol

EGTA
- Ethylene glycol-bis-(2-aminoethyl)tetraacetic acid $C_{14}H_{24}N_2O_{10}$; $M_R = 380.35$ g/mol

DCTA
- trans-1,2-Diaminocyclohexanetetraacetic acid monohydrate $C_{14}H_{22}N_2O_6 \cdot H_2O$; $M_R = 364.36$ g/mol

DTPA
- Diethylenetriaminepentaacetic acid $C_{14}H_{23}N_3O_{10}$; $M_R = 393.35$ g/mol

Buffer solutions

As already mentioned in the section on theoretical fundamentals, two protons are liberated per metal ion during complexation. The sample solution must be buffered to prevent the formation of metal complexes being hindered at lower pH. This is particularly important for metal ions that must be titrated in alkaline solutions.

Ca^{2+} + Na_2H_2EDTA + 2 H_2O →
$CaNa_2EDTA$ + 2 H_3O^+

a) Alkaline buffer solutions

The most commonly buffer is probably a mixture of ammonia and ammonium chloride – its pH value is approx. 10.

The solution normally contains
5–8 mol/L NH_3 and 1 mol/L NH_4Cl.

In special cases, the following alternatives can be used:

- 1 mol/L each of NaOH and H_3BO_3
- 0.2 mol/L tris(hydroxymethyl)aminomethane (TRIS)
- 1 mol/L triethanolamine, adjusted to pH 8 with HCl

b) Acidic buffer solutions

The most commonly used solution in this case is the acetic acid/ammonium acetate buffer: a mixture of 1.4 mol/L CH_3COOH and 1.5 mol/L NH_4CH_3COO has a pH value of approx. 4.7. Buffer solutions can be prepared in the pH range between 4 and 5, mainly by varying the amount of acetic acid.

Highly acidic buffer solutions (pH 2–3) are prepared by adding HCl to 0.5 mol/L glycine.

For all buffer solutions, it is important that their constituents do not form a stronger complex with the analyte metal ion than does the titrant.

Masking

Masking agents can be added to the sample solution to prevent interfering metal ions from reacting with the titrant. These form stronger complexes or bonds with the interfering ions than does the titrant. In this case, it is important that the metal ion being determined is not masked itself.

a) Masking by precipitation

Masking by precipitation means that the interfering metal ions are precipitated from the solution; however, in contrast to a physical separation, the precipitates are left in the solution and are not removed by filtration.

This method was used at an early stage in the photometric determination of water hardness. The sum of calcium and magnesium (total hardness) is determined in a first titration at pH = 10. The second titration is then carried out at pH = 12. Magnesium is precipitated as $Mg(OH)_2$ and can thus no longer interfere in the titration – only the calcium is determined. However, the results for calcium are generally too low because some of it adsorbs onto the precipitate. This is a general problem in precipitation masking. A further disadvantage of this method is that the color indicator is often adsorbed, or its color change is more difficult to detect.

b) Masking by complexation

The masking agent used for masking by complexation must be a selective complexing agent that binds the analyte metal ion as weakly as possible and the interfering ion as strongly as possible.

A small selection of commonly used masking agents

Masking agent	Element
Ammonium fluoride	Al, Ti, Be, Ca, Mg, Sr, Ba
Potassium cyanide	Zn, Cd, Hg, Cu, Ag, Ni, Co
Acetylacetone	Fe, Al, Pd, UO_2
Tiron (dihydroxybenzenedisulfonic acid)	Al, Fe, Ti
Triethanolamine	Fe, Al
2,3-Dimercaptopropanol (BAL)	Zn, Cd, Hg, As, Sb, Sn, Pb, Bi

Color indicators

A large number of color indicators have already been described, and all have advantages and disadvantages. Some of them have become well established and can be used for most complexometric titrations. A small overview of such metallochromic indicators is given below:

Indicator	Element	Color with metal ion	Color with-out metal ion
Pyrocatechol violet	Bi^{3+}, Cd^{2+}, Co^{2+}, In^{3+}, Mn^{2+}, Zn^{2+}	blue	yellow
Dithizone	Zn^{2+}	red	green-violet
Eriochrome Black T	Ca^{2+}, Cd^{2+}, Hg^{2+}, Mg^{2+}, Pb^{2+}, Zn^{2+}	red	blue
Calconcarboxylic acid	Ca^{2+} in the presence of significant Mg^{2+}	red	blue
Hydroxynaphthol blue	Ca^{2+}, Mg^{2+}	red	blue
Murexide	Co^{2+}, Cu^{2+}, Ni^{2+}	yellow	violet
PAN	Cd^{2+}, Cu^{2+}, Zn^{2+}	red	yellow
Phthalein purple	Ba^{2+}, Ca^{2+}, Sr^{2+}	purple	colorless
Tiron	Fe^{3+}, SO_4^{2-}	blue	yellow
Xylenol orange	Al^{3+}, Bi^{3+}, La^{3+}, Sc^{3+}, Th^{4+}, Zr^{4+}	red	yellow

Most metallochromic indicators are unstable in solution. They are thus often added in a solid form (as tablets or triturations with NaCl) to the solution being titrated. This circumstance, however, makes it poorly suited or even unsuitable for automation purposes. This can be overcome by preparing alcoholic or stabilized aqueous solutions. The shelf life of the resulting indicator solution must be determined on a case-by-case basis.

The visible spectra of some common indicators are shown below.

a) Pyrocatechol violet

Pyrocatecholsulfonephthalein; $C_{19}H_{14}O_7S$
0.1% in water

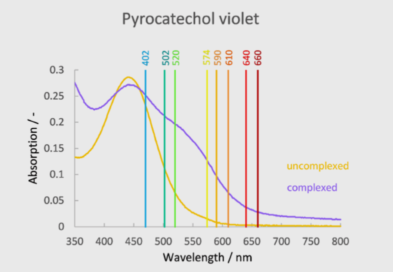

Figure 1 Overlaid Vis spectra of complexed and uncomplexed pyrocatechol violet

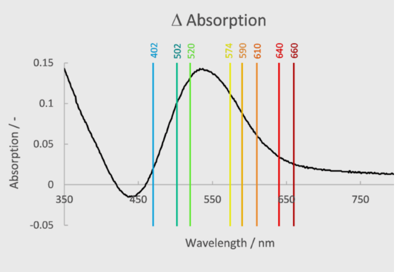

Figure 2 Vis absorption difference spectrum of complexed and uncomplexed pyrocatechol violet

b) Dithizone

1,5-Diphenylthiocarbazone; $C_{13}H_{12}N_4S$
Approx. 30 mg in 100 mL ethanol (shelf life of 1 month in a refrigerator)

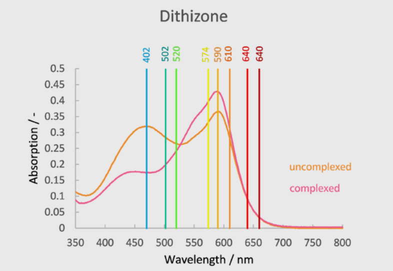

Figure 3 Overlaid Vis spectra of complexed and uncomplexed dithizone

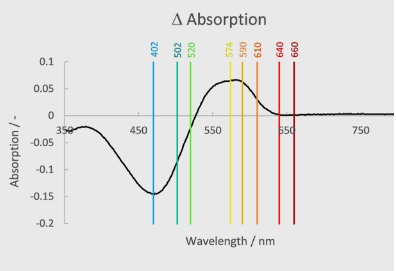

Figure 4 Vis absorption difference spectrum of complexed and uncomplexed dithizone

c) Eriochrome Black T

1-(1-Hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid sodium salt; $C_{20}H_{12}N_3NaO_7S$

1% triturated in NaCl or 100 mg in 100 mL ethanol or 100 mg in 100 mL water and stabilized with 100 mg ascorbic acid

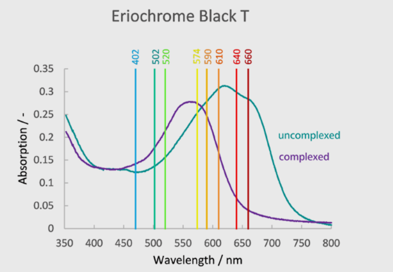

Figure 5 Overlaid Vis spectra of complexed and uncomplexed Eriochrome Black T

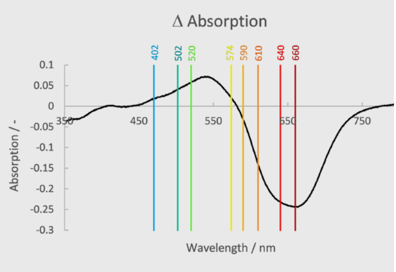

Figure 6 Vis absorption difference spectrum of complexed and uncomplexed Eriochrome Black T

d) Calconcarboxylic acid (HHSNN)

2-Hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid; $C_{21}H_{14}N_2O_7S$

1% triturated in NaCl or 50 mg in 100 mL c(NaOH) = 0.1 mol/L (shelf life of one day)

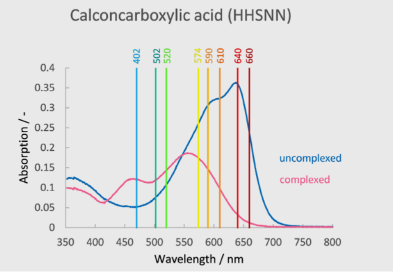

Figure 7 Overlaid Vis spectra of complexed and uncomplexed calconcarboxylic acid

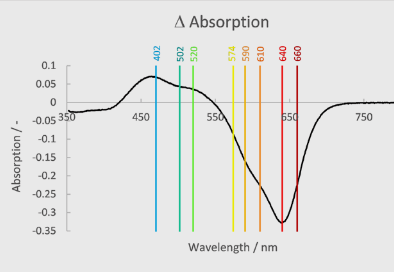

Figure 8 Vis absorption difference spectrum of complexed and uncomplexed calconcarboxylic acid

e) Hydroxynaphthol blue

2,2'-Dihydroxy-1,1'-azonaphthalene-3',4,6'-trisulfonic acid trisodium salt;
$C_{20}H_{11}N_2Na_3O_{11}S_3$
10% triturated in NaCl

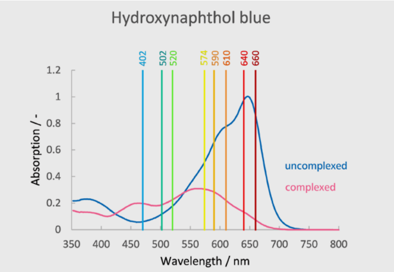

Figure 9 Overlaid Vis spectra of complexed and uncomplexed hydroxynaphthol blue

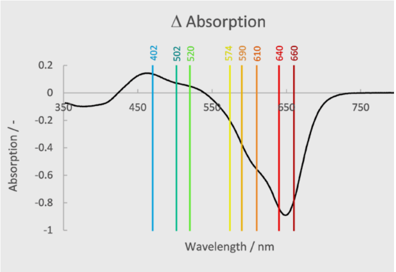

Figure 10 Vis absorption difference spectrum of complexed and uncomplexed hydroxynaphthol blue

f) Methylthymol blue

3,3’-Bis[N,N-di(carboxymethyl)aminomethyl]thymolsulfonephthalein tetrasodium salt; $C_{37}H_{40}N_2Na_4O_{13}S$
100 mg in 100 mL ethanol

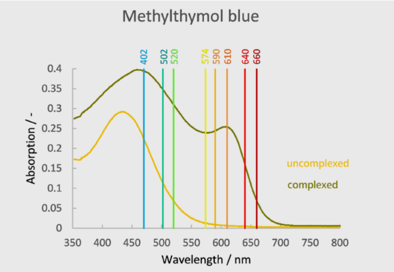

Figure 11 Overlaid Vis spectra of complexed and uncomplexed methylthymol blue

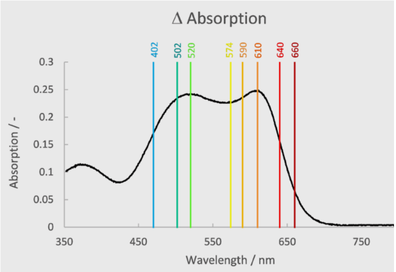

Figure 12 Vis absorption difference spectrum of complexed and uncomplexed methylthymol blue

g) Murexide

Ammonium purpurate; $C_8H_8N_6O_6$
1% triturated in NaCl or 50 mg in 100 mL dist. H_2O

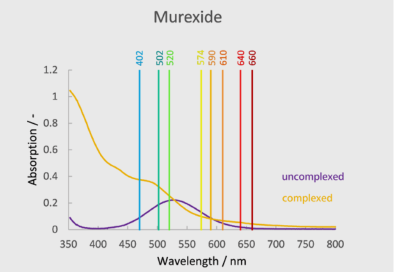

Figure 13 Overlaid Vis spectra of complexed and uncomplexed murexide

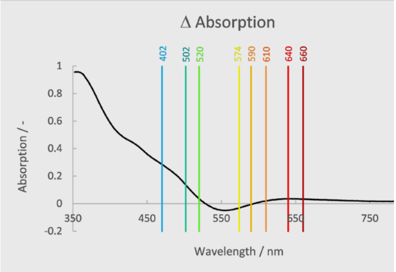

Figure 14 Vis absorption difference spectrum of complexed and uncomplexed murexide

h) PAN

1-(2-Pyridylazo)-2-naphthol; $C_{15}H_{11}NO_3$
100 mg in 100 mL ethanol

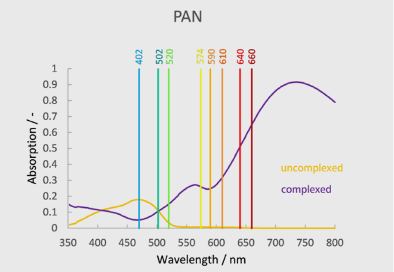

Figure 15 Overlaid Vis spectra of complexed and uncomplexed PAN

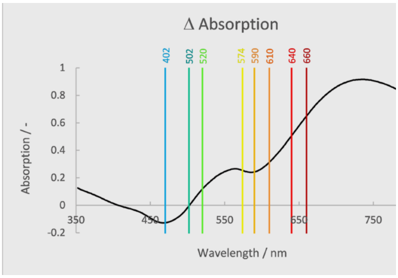

Figure 16 Vis absorption difference spectrum of complexed and uncomplexed PAN

i) Phthalein purple

3,3′-Bis[bis-(carboxymethyl)-aminomethyl]-cresolphthalein; $C_{32}H_{32}N_2O_{12} \cdot H_2O$
100 g in 100 mL dist. H_2O containing 1 mL w/w(NH_3) = 25% (not stable)

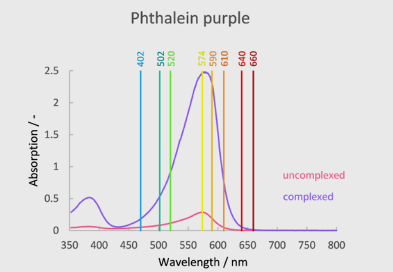

Figure 17 Overlaid Vis spectra of complexed and uncomplexed phthalein purple

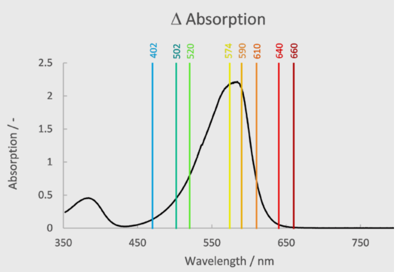

Figure 18 Vis absorption difference spectrum of complexed and uncomplexed phthalein purple

j) Tiron

Pyrocatechol-3,5-disulfonic acid disodium salt; $C_6H_4Na_2O_2S_2$
Added as a solid or 2% in dist. H_2O

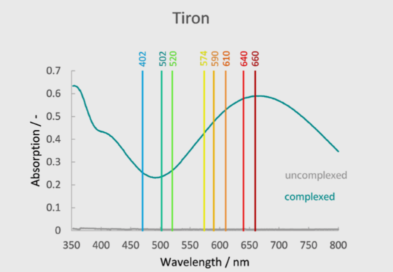

Figure 19 Overlaid Vis spectra of complexed and uncomplexed Tiron

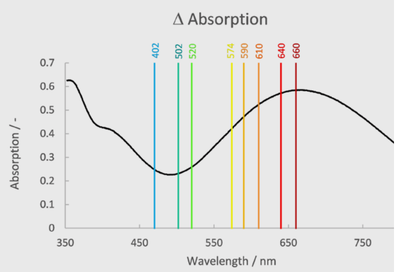

Figure 20 Vis absorption difference spectrum of complexed and uncomplexed Tiron

k) Xylenol orange

3,3′-Bis[N,N-bis(carboxymethyl)aminomethyl]-cresolsulfonephthalein tetrasodium salt; $C_{31}H_{28}N_2Na_4O_{13}S$
100 mg are dissolved in 100 mL deion. H_2O

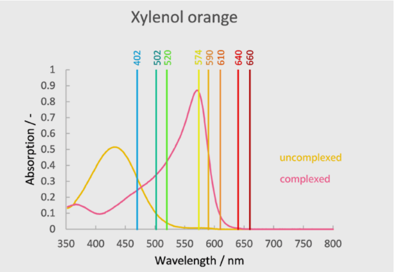

Figure 21 Overlaid Vis spectra of complexed and uncomplexed xylenol orange

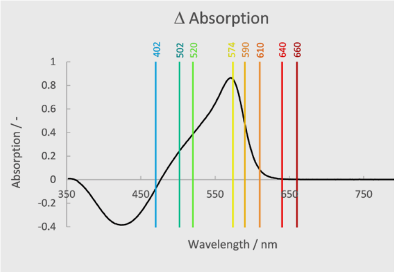

Figure 22 Vis absorption difference spectrum of complexed and uncomplexed xylenol orange

l) Eriochrome Cyanine R

3,3'-(1,1-Dioxido-3H-2,1-benzoxathiol-3-ylidene)bis[6-hydroxy-5-methylbenzoic acid] trisodium salt; $C_{23}H_{15}Na_3O_9S$
Dissolve 40 mg in 100 mL dist. H_2O

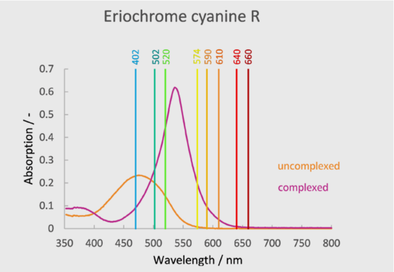

Figure 23 Overlaid Vis spectra of complexed and uncomplexed Eriochrome Cyanine R

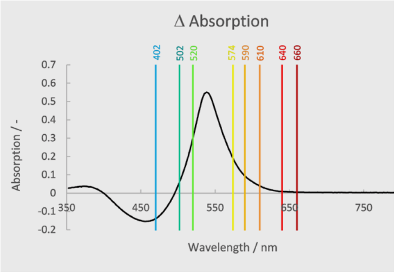

Figure 24 Vis absorption difference spectrum of complexed and uncomplexed Eriochrome Cyanine R

Preparation of standard solutions

Many standard solutions are commercially available as ready-to-use products – and these should be given precedence. The manufacturer has adjusted their titer to 1.0000 at 20 °C.

a) Direct titration

Most complexing agents are available in a pure form as an acid. These have very poor solubility in water and must be converted into their soluble di- or trisodium salts during preparation. The substance concentration c is usually 0.1 mol/L. The solutions have a stable titer.

The preparation of $c(Na_2EDTA) = 0.1$ mol/L is described as an example:

Weigh 29.5 g EDTA ($C_{10}H_{16}N_2O_8$) into a glass beaker and, while stirring, slurry in approx. 300 mL dist. H_2O. Add c(NaOH) = 5 mol/L until everything has dissolved. Allow to cool, mix, and make up to 1 L with dist. H_2O.

b) Back titration

Cu^{2+} or Zn^{2+} solutions are usually used for back titrations. These solutions also have a stable titer and are generally prepared with a concentration of c(Me) = 0.1 mol/L.

$c(CuSO_4) = 0.1$ mol/L
Dissolve 25.2 g $CuSO_4 \cdot 5\ H_2O$ (99%) in approx. 500 mL dist. H_2O. Add 0.5 mL $w/w(H_2SO_4) = 96\%$ and then make up to 1 L with dist. H_2O and mix.

$c(ZnSO_4) = 0.1$ mol/L
Dissolve 28.9 g $ZnSO_4 \cdot 7\ H_2O$ (99.5%) in approx. 500 mL dist. H_2O. Add 0.5 mL $w/w(H_2SO_4) = 96\%$ and then make up to 1 L with dist. H_2O and mix.

Titer determinations

Calcium carbonate is the primary standard for complexing agents (CA in the following). $CaCO_3$ is dried overnight in a drying oven at 140 °C and then left to cool in a desiccator for at least 2 h.

The titer is usually determined in triplicate, and the mean value is used as titer.

Titer determination for direct titration:

Weigh approx. 100 mg $CaCO_3$ with an accuracy of 0.1 mg into a titration beaker and add 20 mL dist. H_2O. Add c(HCl) = 3 mol/L while stirring until the $CaCO_3$ has completely dissolved. Add approx. 80 mL dist. H_2O and 10 mL ammoniacal buffer solution, and titrate with c(CA) = 0.1 mol/L.

Calculation

$$\text{Titer} = \frac{m_S}{V_{EP1} \times c_{KB} \times M_{CaCO_3}}$$

m_S:	Weight of $CaCO_3$ in mg
V_{EP1}:	Volume of CA consumed up to the first equivalence point in mL
c_{CA}:	Concentration of the complexing agent in mol/L
M_{CaCO_3}:	Molecular mass of calcium carbonate; 100.09 g/mol

Titer determination for back titration:

To a titration beaker, add approx. 50 mL dist. H_2O, 10 mL c(CA) = 0.1 mol/L, and 10 mL buffer solution (alkaline or acidic). Then titrate with $c(Cu^{2+}) = 0.1$ mol/L or $c(Zn^{2+}) = 0.1$ mol/L.

Calculation

$$\text{Titer} = \frac{V_S \times f_{KB}}{V_{EP1}}$$

V_S:	Added volume of c(CA) = 0.1 mol/L in mL
f_{CA}:	Titer of the CA solution
V_{EP1}:	Volume of Cu^{2+} or Zn^{2+} solution consumed up to the first equivalence point in mL

Examples: Titer determination of EDTA and EGTA with $CaCO_3$

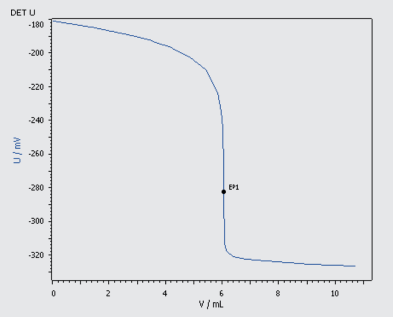

Figure 25 Titration curve of the potentiometric titer determination of EDTA with the Ca-ISE

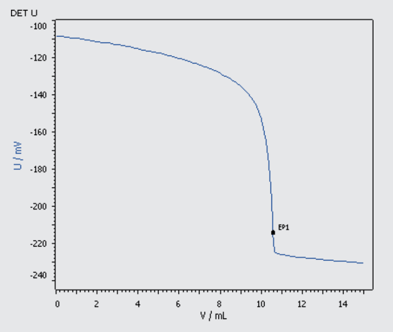

Figure 26 Titration curve of the potentiometric titer determination of EGTA with the Ca-ISE

Practical examples

Water hardness, calcium, and magnesium

General

Hardness constituents in water are usually calcium and magnesium ions. They are mainly present as hydrogen carbonates and sulfates or, in rare cases, as chlorides. Barium and strontium, which are also determined in the total hardness determination, are present only in very small quantities, if at all, and thus do not interfere (0.1 mg/L Ba^{2+} would consume only 0.7 µL $c(Na_2EDTA) = 0.1$ mol/L for a sample size of 100 mL).

Water hardness is given in mmol/L. Terms such as "soft", "hard", "°dH", "°fH" etc. are also used for information purposes, for example, on detergent packaging. The relationships are shown in the following table:

mmol/L	mg/L $CaCO_3$	°fH	°dH	°USH	Hardness
0–0.7	0–70	0–7	0–3.92	0–3.77	very soft
0.7–1.5	70–150	7–15	3.92–8.4	3.77–8.07	soft
1.5–2.5	150–250	15–25	8.4–14.0	8.07–9.50	moderately hard
2.5–3.2	250–320	25–32	14.0–17.92	9.50–17.22	fairly hard
3.2–4.2	320–420	32–42	17.92–23.5	17.22–22.6	hard
> 4.2	> 420	> 42	> 23.5	> 22.6	very hard

Conversion factors

mmol/L × 100 →	mg/L $CaCO_3$
mmol/L × 10 →	°fH (French degree of hardness)
mmol/L × 5.6 →	°dH (German degree of hardness)
mmol/L × 5.38 →	°USH (US degree of hardness)

If the water being investigated has an unfavorable Ca^{2+}/Mg^{2+} ratio (small amount of Mg^{2+} and a large amount of Ca^{2+}), this leads to errors in all titrimetric methods. In such cases, the recommendation is to use a buffer solution with an accurately added amount of Mg^{2+} standard (e.g., 2.4305 mg Mg^{2+}, which corresponds to 1 mL $c(Na_2EDTA) = 0.1$ mol/L) and then to subtract this value during the calculation.

In the case of soft water, the best method is to titrate with $c(Na_2EDTA) = 0.05$ mol/L.

Potentiometric titration with the Ca ISE

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L in $c(KOH) = 0.1$ mol/L
- Auxiliary complex solution: weigh 24.3 g tris(hydroxymethyl)aminomethane (TRIS) into a 1 L volumetric flask and dissolve in approx. 500 mL dist. H_2O. Add 10 mL acetylacetone, mix, and make up to the mark with dist. H_2O. Allow the solution to stand for 24 h before use (max. shelf life is 1 week).

Analyses

Measure a 100 mL water sample into a titration beaker and add 15 mL auxiliary complex solution. Using the "DET U" mode, titrate with $c(Na_2EDTA) = 0.1$ mol/L past the second equivalence point (EP_2). EP_1 corresponds to Ca^{2+} and the difference $EP_2 - EP_1$ corresponds to Mg^{2+}.

Calculation

$$\text{Calcium hardness} = \frac{V_{EP1} \times c_{EDTA} \times f \times 1000}{V_S}$$

$$\text{Magnesium hardness} = \frac{(V_{EP2} - V_{EP1}) \times c_{EDTA} \times f \times 1000}{V_S}$$

$$\text{Total hardness} = \frac{V_{EP2} \times c_{EDTA} \times f \times 1000}{V_S}$$

$$\text{Calcium content} = \frac{V_{EP1} \times c_{EDTA} \times f \times 1000 \times M_{Ca}}{V_S}$$

$$\text{Magnesium cont.} = \frac{(V_{EP2} - V_{EP1}) \times c_{EDTA} \times f \times 1000 \times M_{Mg}}{V_S}$$

Calcium hardness: Calcium content in mmol/L

Magnesium hardn.: Magnesium content in mmol/L

Total hardness: Total hardness in mmol/L

Calcium content: Calcium content in mg/L

Magnesium cont.: Magnesium content in mg/L

V_{EP1}: Volume of EDTA consumed up to the first equivalence point in mL

V_{EP2}: Volume of EDTA consumed up to the second equival. point in mL

c_{EDTA}: Concentration of EDTA in mol/L

f: Titer of the EDTA solution

1000: Conversion factor

V_S: Sample size in mL

M_{Ca}: Molar mass of calcium; 40.078 g/mol

M_{Mg}: Molar mass of magnesium; 24.305 g/mol

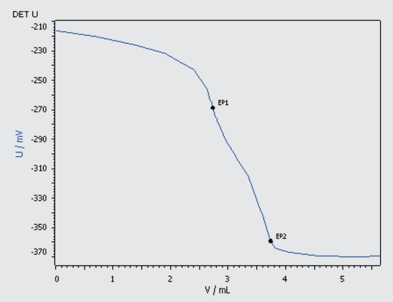

Figure 27 Titration curve of tap water from Herisau (Switzerland), measured with the Ca-ISE

Further literature on this topic can be accessed using the Application Finder under
www.metrohm.com/applications

- *Application Bulletin AB-125 – Simultaneous determination of calcium, magnesium, and alkalinity by complexometric titration with potentiometric or photometric indication in water and beverage samples*

Potentiometric with the Cu ISE

Reagents

- Titrant 1: $c(Na_2EDTA) = 0.1$ mol/L
- Titrant 2: $c(Na_2EGTA) = 0.1$ mol/L
- Buffer solution: dissolve 54 g NH_4Cl and 350 mL $w/w(NH_3) = 25\%$ in dist. H_2O, mix, and make up to 1 L with dist. H_2O.
- Cu complex solution: $c[Cu(NH_4)_2EDTA] = 0.1$ mol/L (e.g., Merck No. 105217)
- CuEGTA: dissolve 2.497 g $CuSO_4 \cdot 5\ H_2O$ in dist. H_2O, make up to 100 mL and mix well. Add 25.0 mL of this solution to 25.0 mL $c(Na_2EGTA) = 0.1$ mol/L.

Analysis

Total hardness (sum of Ca^{2+} & Mg^{2+})

Measure a 100 mL water sample into a titration beaker and add 5 mL buffer solution. Add 0.5 mL Cu complex solution, wait for 20 s while stirring, and titrate in the "MET U" mode with $c(Na_2EDTA) = 0.1$ mol/L. There may be two equivalence points, whereby EP_2 corresponds to the sum $Ca^{2+} + Mg^{2+}$ (EP_1 cannot be used for the calculations because it would give inaccurate results). Since only the largest equivalence point is required, select "largest" as the EP criterion so that only one EP is shown.

Calcium (hardness)

Measure a 100 mL water sample into a titration beaker and add 5 mL buffer solution. Add 0.5 mL CuEGTA, wait for 20 s while stirring, and titrate in the "MET U" mode with $c(Na_2EGTA) = 0.1$ mol/L past the first equivalence point.

Magnesium (hardness)

This is calculated by subtracting the calcium hardness from the total hardness.

Calculation

$$\text{Total hardness} = \frac{V_{EP1.1} \times c_{EDTA} \times f_{EDTA} \times 1000}{V_S}$$

$$\text{Calcium hardn.} = \frac{V_{EP1.2} \times c_{EGTA} \times f_{EGTA} \times 1000}{V_S}$$

Magnesium hardn. = total hardness - calcium hardness

Total hardness:	Total hardness in mmol/L
Calcium hardness:	Calcium content in mmol/L
Magnesium hardn.:	Magnesium content in mmol/L

$V_{EP1.1}$:	Volume of EDTA consumed up to the largest equivalence point of the total hardness titration in mL
c_{EDTA}:	Concentration of EDTA in mol/L
f_{EDTA}:	Titer of the EDTA solution

1000: Conversion factor

V_S: Sample size in mL

$V_{EP1.2}$: Volume of EGTA consumed up to the first equivalence point of the calcium hardness titration in mL

c_{EGTA}: Concentration of EGTA in mol/L

f_{EGTA}: Titer of the EGTA solution

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-131 – Automatic determination of calcium, magnesium, and total hardness in water with the Cu-ISE*

Examples: Titration curves of Herisau tap water with the Cu ISE

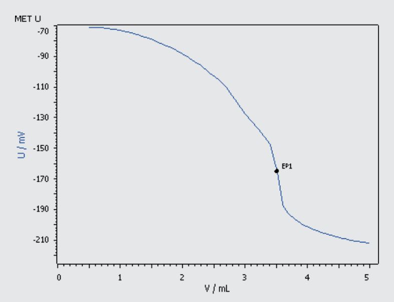

Figure 28 Titration curve of the total hardness determination

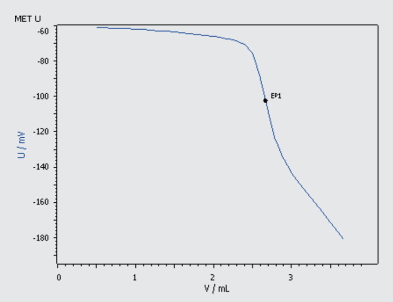

Figure 29 Titration curve of the calcium hardness determination

Photometric with the Optrode at 610 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Buffer solution: Dissolve 54 g NH_4Cl in dist. water and add 350 mL w/w(NH3) = 25%. Mix the solution and make up to 1 L with dist. water.
- Sodium hydroxide: $c(NaOH) =$ 2 mol/L
- $Na_2MgEDTA \cdot H_2O$
- Indicator Solution 1: Eriochrome Black T; dissolve 100 mg Eriochrome Black T in 100 mL ethanol.
- Indicator Solution 2: HHSNN; dissolve 50 mg HHSNN in 100 mL $c(NaOH) =$ 0.1 mol/L.

General remarks

There are a few special requirements that must be taken into account when carrying out photometric titration with optical sensors:

- No interfering gas bubbles should be present in the light path. For this reason, we recommend degassing the water samples before adding the buffer and adjusting the stirrer speed so that no gas bubbles are entrained.
- During determination of the calcium hardness, precipitation of magnesium hydroxide leads to ever increasing turbidity. The mixture must therefore be titrated immediately after adding NaOH and preferably with a start volume. Although the resulting titration curves are not very smooth and look unattractive, this does not affect the accuracy of the results.

Analysis

Total hardness (sum of Ca^{2+} & Mg^{2+})

Measure a 100 mL water sample into a titration beaker, add 0.1 g $Na_2MgEDTA \cdot H_2O$, 10 mL buffer solution, and 0.25 mL Indicator Solution 1, and titrate with $c(Na_2EDTA) = 0.1$ mol/L in the "MET U" mode past the color change.

Calcium (hardness)

Measure a 100 mL water sample into the titration beaker, add 2 mL $c(NaOH) = 2$ mol/L (pH > 12) and 1.5 mL Indicator Solution 2, and titrate immediately with $c(Na_2EDTA) = 0.1$ mol/L in the "MET U" mode up to the color change.

Magnesium (hardness)

This is calculated by subtracting the calcium hardness from the total hardness.

Calculation

$$\text{Total hardness} = \frac{V_{EP1.1} \times c_{EDTA} \times f \times 1000}{V_S}$$

$$\text{Calcium hardn.} = \frac{V_{EP1.2} \times c_{EDTA} \times f \times 1000}{V_S}$$

Magnesium hardn. = total hardness – calcium hardness

Total hardness: Total hardness in mmol/L
Calcium hardness: Calcium content in mmol/L
Magnesium hardn.: Magnesium content in mmol/L

$V_{EP1.1}$: Volume of EDTA consumed up to the first equivalence point of the total hardness titration in mL
c_{EDTA}: Concentration of EDTA in mol/L
f: Titer of the EDTA solution
1000: Conversion factor
V_S: Sample size in mL
$V_{EP1.2}$: Volume of EDTA consumed up to the first equivalence point of the calcium hardness titration in mL

Examples: Photometric titration curves of Herisau tap water

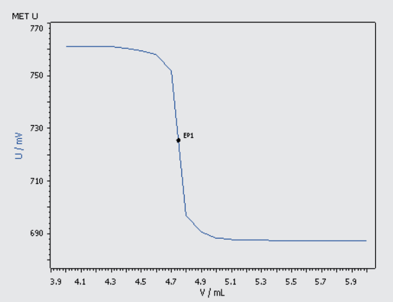

Figure 30 Titration curve of the total hardness determination with the Optrode at 610 nm

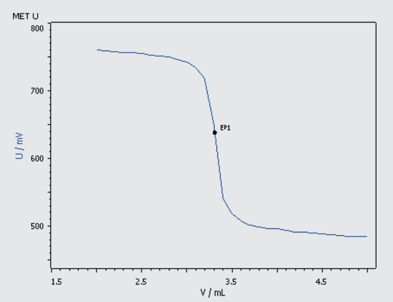

Figure 31 Titration curve of the calcium hardness determination with the Optrode at 610 nm

Further literature on this topic is given in

- *Application Bulletin AB-125 – Simultaneous determination of calcium, magnesium, and alkalinity by complexometric titration with potentiometric or photometric indication in water and beverage samples*
- *Titration Application Note AN-T-084 – Fully automatic determination of the total, calcium and magnesium hardness of water samples using photometric titration*

Aluminum and magnesium, alloys and antacids

Potentiometric with the Cu ISE

Reagents

- Titrant 1: c(DCTA) = 0.1 mol/L; dissolve 36.463 g *trans*-1,2-diaminocyclohexanetetraacetic acid monohydrate in 400 mL c(NaOH) = 0.5 mol/L. Allow to cool, then mix and make up to 1 L with dist. H_2O.
- Titrant 2: c($CuSO_4$) = 0.1 mol/L; dissolve 24.968 g $CuSO_4 \cdot 5H_2O$ in approx. 500 mL dist. H_2O. Add 0.5 mL w/w(H_2SO_4) = 96%, mix, and make up to 1 L with dist. H_2O.
- Buffer solution pH = 4.7: Dissolve 123 g sodium acetate in approx. 200 mL dist. H_2O and add 86 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Ammonia solution: w/w(NH_3) = 10%
- Sodium hydroxide: c(NaOH) = 2 mol/L

Sample preparation

Preneutralize the acidic sample solution, which should not contain more than 12 mg Al^{3+} and/or 20 mg Mg^{2+}, with c(NaOH) = 2 mol/L to pH 2–3, and then dilute with dist. H_2O to approx. 50 mL.

Analysis

To the prepared sample solution, add 5 mL buffer solution pH 4.7 and 6 mL c(DCTA) = 0.1 mol/L. Allow the mixture to react for 1 min while stirring. Next, titrate with $c(CuSO_4)$ = 0.1 mol/L past the first equivalence point → aluminum content. Store the value of the excess titrant of Titrant 2 as a "common variable".

To the completely titrated sample solution, add 20 mL ammonia solution and a further 6 mL c(DCTA) = 0.1 mol/L. Next, titrate with $c(CuSO_4)$ = 0.1 mol/L past the first equivalence point → magnesium content.

Calculation

$$\beta_{Al} = \frac{(V_{DCTA} \times f_1 \times c_{DCTA} - V_{EP1.1} \times f_2 \times c_{CuSO_4}) \times M_{Al}}{V_S}$$

$$V_{Ex} = V_{End} - V_{EP1.1}$$

$$\beta_{Mg} = \frac{(V_{DCTA} \times f_1 \times c_{DCTA} - (V_{EP1.2} + V_{Ex}) \times f_2 \times c_{CuSO_4}) \times M_{Mg}}{V_S}$$

β_{Al}: Aluminum content of the sample in g/L

β_{Mg}: Magnesium content of the sample in g/L

V_{DCTA}: Added quantity of DCTA standard solution in mL

$V_{EP1.1}$: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point of the aluminum titration in mL

$V_{EP1.2}$: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point of the magnesium titration in mL

V_{Ex}: Excess quantity of titrant after the aluminum titration in mL

V_{End}: End volume of the aluminum titration in mL

f_1: Titer of the DCTA standard solution

f_2: Titer of the $CuSO_4$ standard solution

c_{DCTA}: Concentration of the DCTA standard solution in mol/L

c_{CuSO_4}: Concentration of the $CuSO_4$ standard solution in mol/L

M_{Al}: Molar mass of aluminum; 26.982 g/mol

M_{Mg}: Molar mass of magnesium; 24.305 g/mol

V_S: Sample size in mL

Remarks

The surface of the Cu ISE must be polished occasionally with aluminum oxide power (e.g., polishing set 6.2802.000).

Example: Al^{3+} and Mg^{2+} in aqueous solution

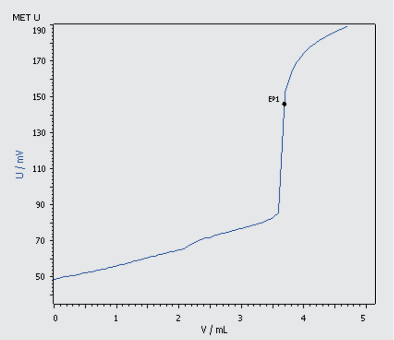

Figure 32 Titration curve of the potentiometric aluminum determination with the Cu-ISE

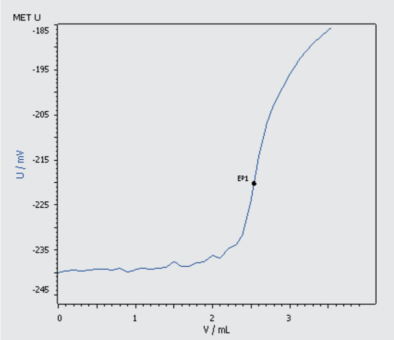

Figure 33 Titration curve of the potentiometric magnesium determination with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-181 – Automated potentiometric titration of aluminum and magnesium in the same solution*
- *Titration Application Note No. AN-T-117 – Automatic determination of aluminum and magnesium mixtures with ion-selective copper electrode (Cu-ISE)*

Magnesium and zinc

Potentiometric with the Cu ISE

Reagents

- Titrant 1: c(Na_2EDTA) = 0.1 mol/L
- Titrant 2: c($CuSO_4$) = 0.1 mol/L; dissolve 24.968 g $CuSO_4 \cdot 5\ H_2O$ in approx. 500 mL dist. H_2O. Add 0.5 mL w/w(H_2SO_4) = 96%, mix, and make up to 1 L with dist. H_2O.
- Acetate buffer, pH = 4.7: Dissolve 123 g sodium acetate in approx. 500 mL dist. H_2O and add 86 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Ammonia buffer, pH = 10: Dissolve 54 g NH_4Cl in approx. 500 mL dist. H_2O and add 350 mL w/w(NH_3) = 25%. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: c(NaOH) = 1 mol/L

Sample preparation

If necessary, dilute the sample solution, which should not contain more than 50 mg Zn^{2+} and/or 20 mg Mg^{2+}, with dist. H_2O to approx. 50 mL and adjust to pH 4–4.5 with c(NaOH) = 1 mol/L.

Analysis

To the prepared sample solution, add 5 mL acetate buffer and 10 mL c(DCTA) = 0.1 mol/L, and allow the mixture to react for 1 min while stirring. Next, titrate with $c(CuSO_4)$ = 0.1 mol/L past the first equivalence point → zinc content. Store the value of the excess titrant of Titrant 2 as a "common variable".

To the completely titrated sample solution, add 10 mL ammonia buffer and a further 10 mL c(DCTA) = 0.1 mol/L. Next, titrate with $c(CuSO_4)$ = 0.1 mol/L past the first equivalence point → magnesium content.

Calculation

$$\beta_{Zn} = \frac{(V_{DCTA} \times f_1 \times c_{DCTA} - V_{EP1.1} \times f_2 \times c_{CuSO_4}) \times M_{Zn}}{V_S}$$

$$V_{Ex} = V_{End} - V_{EP1.1}$$

$$\beta_{Mg} = \frac{(V_{DCTA} \times f_1 \times c_{DCTA} - (V_{EP1.2} + V_{Ex}) \times f_2 \times c_{CuSO_4}) \times M_{Mg}}{V_S}$$

β_{Zn}: Zinc content of the sample in g/L

β_{Mg}: Magnesium content of the sample in g/L

V_{DCTA}: Added quantity of DCTA standard solution in mL

$V_{EP1.1}$: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point of the zinc titration in mL

$V_{EP1.2}$: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point of the magnesium titration in mL

V_{Ex}: Excess quantity of titrant after the zinc titration in mL

V_{End}: End volume of the zinc titration in mL

f_1: Titer of the DCTA standard solution

f_2: Titer of the $CuSO_4$ standard solution

c_{DCTA}: Concentration of the DCTA standard solution in mol/L

c_{CuSO_4}: Concentration of the $CuSO_4$ standard solution in mol/L

M_{Zn}: Molar mass of zinc; 65.409 g/mol

M_{Mg}: Molar mass of magnesium; 24.305 g/mol

V_S: Sample size in mL

Remarks

The surface of the Cu-ISE must be polished occasionally with aluminum oxide power (e.g., polishing set 6.2802.000).

Example: Zn^{2+} and Mg^{2+} in aqueous solution

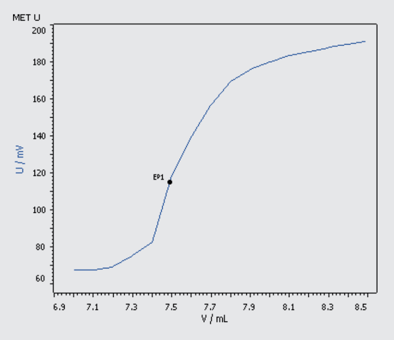

Figure 34 Titration curve of the potentiometric zinc determination with the Cu-ISE

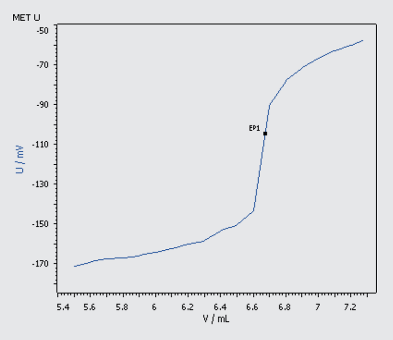

Figure 35 Titration curve of the potentiometric magnesium determination with the Cu-ISE

Further literature on this topic is given in

- *Titration Application Note AN-T-118 – Automatic determination of zinc and magnesium mixtures with ion-selective copper electrode (Cu-ISE)*

Aluminum, calcium, iron, and magnesium in cement and clinker

Photometric with the Optrode at 610 nm

Reagents

- Hydrochloric acid: w/w(HCl) = 36%
- Nitric acid: w/w(HNO_3) = approx. 65%
- Sodium hydroxide: w/w(NaOH) > 99%
- Ammonia: w/w(NH_3) = 25%
- Ammonium chloride: NH_4Cl p.a.
- Titrant 1 for Ca^{2+} and Mg^{2+}: c(Na_2EDTA) = 0.1 mol/L
- Titrant 2 for Fe^{3+}: c(Na_2EDTA) = 0.025 mol/L
- Titrant 3 for Al^{3+}: c($Bi(NO_3)_3$) = 0.05 mol/L; dissolve 24.25 g $Bi(NO_3)_3 \cdot 5H_2O$ in approx. 500 mL HNO_3 (2 mol/L) and transfer into a 1 L volumetric flask. Next, make up to 1 L with dist. H_2O.

- Ammonia: $c(NH_3) = 2$ mol/L; add 144 mL $w/w(NH_3) = 25\%$ to a 1 L volumetric flask and make up to the mark with dist. H_2O.
- Sodium hydroxide: $c(NaOH) = 2$ mol/L; dissolve 80 g NaOH in approx. 600 mL dist. H_2O, transfer into a 1 L volumetric flask, and make up to the mark with dist. H_2O.
- Hydrochloric acid: $c(HCl) = 6$ mol/L; add 590 mL $w/w(HCl) = 37\%$ to a 1 L volumetric flask that already contains approx. 200 mL dist. H_2O. After the solution has cooled, make up to the mark with dist. H_2O.
- Nitric acid: $c(HNO_3) = 2$ mol/L; add 192 mL $w/w(HNO_3) = 65\%$ to a 1 L volumetric flask that already contains approx. 500 mL dist. H_2O. After the solution has cooled, make up to the mark with dist. H_2O.
- Acetate buffer: Dissolve 60 g ammonium acetate in approx. 200 mL dist. H_2O and add 400 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Ammonia buffer: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Mix and make up to 1 L with dist. H_2O.
- Indicator for Ca^{2+}, murexide: triturate 100 mg murexide with 10 g NaCl.
- Indicator for Mg^{2+}, methylthymol blue: triturate 100 mg methylthymol blue with 10 g NaCl.
- Indicator solution for Fe^{3+}, sulfosalicylic acid: dissolve 4 g sulfosalicylic acid in 100 mL dist. H_2O.
- Indicator solution for Al^{3+}, xylenol orange: dissolve 100 mg xylenol orange disodium salt in 100 mL dist. H_2O.

Sample preparation

Mix approx. 4 g cement with 4 g NH_4Cl, add 48 mL $c(HCl) = 6$ mol/L and 3 mL $c(HNO_3) = 2$ mol/L. Heat the mixture and boil for a while. Stir the mixture with a magnetic stirrer for approx. 60 min. Take up the mixture in 50 mL hot dist. H_2O and filter it through a black band filter into a 500 mL volumetric flask. Rinse the filter thoroughly with hot dist. H_2O. Allow to cool, then mix the combined filtrates and make up to the mark with dist. H_2O.

Analyses

Carry out all analyses with the Optrode at a wavelength of 610 nm.

Calcium

To a 2.5 mL sample solution, add approx. 70 mL dist. H_2O and adjust to pH 12 with $c(NaOH) = 2$ mol/L. Add a spatula tip of murexide indicator, then titrate the solution with $c(Na_2EDTA) = 0.1$ mol/L past the second breakpoint. Store the titrant consumption up to BP_2 as a "common variable" because it will be used in the determination of the Mg^{2+} content.

Calculation

$$\text{CaO \%} = \frac{V_{BP2} \times c_{EDTA} \times f_{EDTA} \times 40 \times M_{CaO}}{m_S}$$

CaO%: Calcium content as calcium oxide in %
V_{BP2}: Volume of EDTA consumed up to the second breakpoint in mL
c_{EDTA}: Concentration of EDTA in mol/L; c(EDTA) = 0.1 mol/L
f_{EDTA}: Titer of the EDTA solution
40: Conversion factor
M_{CaO}: Molar mass of calcium oxide; 56.08 g/mol
m_S: Sample size in g

Magnesium

This titration is used to determine the sum of Ca^{2+} and Mg^{2+}, and to calculate the magnesium content by subtracting the titrant consumption for the Ca^{2+} determination from the total consumption.

Pipette 2.5 mL of the digested solution into a titration beaker and dilute to approx. 80 mL with dist. H_2O. Adjust the solution to pH 10 with c(NaOH) = 2 mol/L, and add a spatula tip of methylthymol blue. Next, titrate the solution with c(Na_2EDTA) = 0.1 mol/L past the first equivalence point.

Calculation

$$\text{MgO \%} = \frac{(V_{EP1} - V_{Ca,\ BP2}) \times c_{EDTA} \times f_{EDTA} \times 40 \times M_{MgO}}{m_S}$$

MgO%: Magnesium content as magnesium oxide in %
V_{EP1}: Volume of EDTA consumed up to the first equivalence point in mL
$V_{Ca,\ BP2}$: Volume of EDTA consumed in the calcium determination in mL
c_{EDTA}: Concentration of EDTA in mol/L; c(EDTA) = 0.1 mol/L
f_{EDTA}: Titer of the EDTA solution
40: Conversion factor
M_{MgO}: Molar mass of magnesium oxide; 40.32 g/mol
m_S: Sample size in g

Iron

Pipette 10 mL of the digested solution into a titration beaker, dilute with dist. H_2O, and add 1 mL sulfosalicylic acid indicator. Adjust the mixture to pH 1.5–2 with c(NH_3) = 2 mol/L or with c(HCl) = 6 mol/L, as appropriate. Next, titrate with c(Na_2EDTA) = 0.025 mol/L past the first breakpoint. (Use small volume increments – e.g., 25 µL).

Store the titrant consumption up to BP_1 as a "common variable" because it will be used in the determination of Al^{3+}.

Calculation

$$Fe_2O_3\,\% = \frac{V_{EP1} \times c_{EDTA} \times f_{EDTA} \times 10 \times M_{Fe_2O_3}}{m_S \times 2}$$

$Fe_2O_3\%$: Iron content as iron oxide in %

V_{EP1}: Volume of EDTA consumed up to the first equivalence point in mL

c_{EDTA}: Concentration of EDTA in mol/L; c(EDTA) = 0.025 mol/L

f_{EDTA}: Titer of the EDTA solution

10: Conversion factor

$M_{Fe_2O_3}$: Molar mass of iron oxide; 159.69 g/mol

m_S: Sample size in g

2: Stoichiometric factor

Aluminum

As in the Mg^{2+} determination, this is also a cumulative determination method. Al^{3+} and Fe^{3+} are detected together. The aluminum content is then calculated by subtracting the titrant consumption for the Fe^{3+} determination from the total consumption.

Pipette 10 mL sample into a glass beaker and add 70 mL dist. H_2O. Add 10 mL acetate buffer, adjust to pH 3.5 with c(HCl) = 6 mol/L, and add 1.25 mL $c(Na_2EDTA)$ = 0.1 mol/L and 1 mL xylenol orange indicator solution. Titrate the solution with $c(Bi(NO_3)_3)$ = 0.05 mol/L past the first equivalence point.

Calculation

$$Al_2O_3\,\% = \frac{((V_{EDTA1} \times c_{EDTA1} \times f_{EDTA1}) - (V_{EDTA2} \times c_{EDTA2} \times f_{EDTA2}) - (V_{EP1} \times c_{Bi} \times f_{Bi})) \times M_{Al_2O_3} \times 10}{m_S \times 2}$$

$Al_2O_3\%$: Aluminum content as aluminum oxide in %

V_{EDTA1}: Initial volume of $c(Na_2EDTA)$ = 0.1 mol/L in mL

c_{EDTA1}: Concentration of the Na_2EDTA solution in mol/L; c(EDTA) = 0.1 mol/L

f_{EDTA1}: Titer of the Na_2EDTA solution $c(Na_2EDTA)$ = 0.1 mol/L

V_{EDTA2}: Volume of $c(Na_2EDTA)$ = 0.025 mol/L consumed for the iron determination in mL

c_{EDTA2}: Concentration of the Na_2EDTA solution in mol/L; c(EDTA) = 0.025 mol/L

f_{EDTA2}: Titer of the Na_2EDTA solution $c(Na_2EDTA)$ = 0.025 mol/L

V_{EP1}: Volume of $c(Bi(NO_3)_3)$ = 0.05 mol/L consumed up to the first equivalence point in mL

c_{Bi}: Concentration of the $Bi(NO_3)_3$ solution in mol/L; $c(BiNO_3)_3)$ = 0.05 mol/L

f_{Bi}: Titer of the $Bi(NO_3)_3$ solution; $c(Bi(NO_3)_3)$ = 0.05 mol/L

10: Conversion factor

$M_{Al_2O_3}$: Molar mass of aluminum oxide; 101.96 g/mol

m_S: Sample size in g

2: Stoichiometric factor

Examples: Titration curves of a cement sample

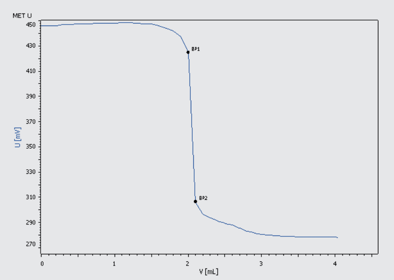

Figure 36 Titration curve of the photometric determination of calcium in cement with the Optrode at 610 nm

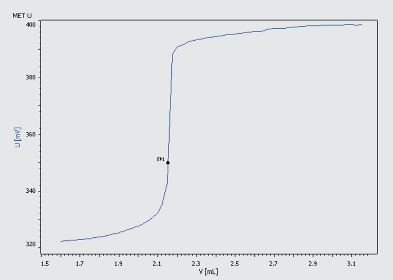

Figure 37 Titration curve of the photometric determination of magnesium in cement with the Optrode at 610 nm

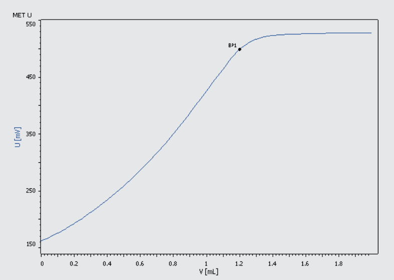

Figure 38 Titration curve of the photometric determination of iron in cement with the Optrode at 610 nm

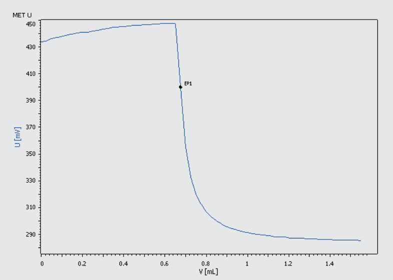

Figure 39 Titration curve of the photometric determination of aluminum in cement with the Optrode at 610 nm

Further literature on this topic is given in

- *Application Bulletin AB-063 – Determination of silicon, calcium, magnesium, iron, and aluminum in digested cement samples by photometric titrations*
- *Titration Application Note AN-T-078 – Determination of aluminum in cement using photometric titration*
- *Titration Application Note AN-T-079 – Determination of calcium in cement by photometric titration of the solubilized product according to EN 196-2*
- *Titration Application Note AN-T-080 – Determination of iron in cement using photometric titration*
- *Titration Application Note AN-T-081 – Determination of magnesium in cement using photometric titration*

Sulfate

Potentiometric with the Ca ISE

Reagents

- Titrant: $c(Na_2EGTA) = 0.05$ mol/L; slurry 19.4 g ethylene glycol-bis(2-aminoethylether)tetraacetic acid ($w = 98\%$) in approx. 200 mL dist. H_2O. Add $c(NaOH) = 10$ mol/L while stirring until everything has dissolved. Allow to cool, mix, and make up to 1 L with dist. H_2O.
- Barium chloride solution: $c(BaCl_2) = 0.05$ mol/L; dissolve 12.34 g $BaCl_2 \cdot 2H_2O$ ($w = 99\%$) in $c(HCl) = 0.01$ mol/L, mix, and make up to 1 L with dist. H_2O.
- Buffer solution pH = 10: dissolve 9 g NH_4Cl and 60 mL $w/w(NH_3) = 25\%$ in dist. H_2O, mix, and make up to 1 L with dist. H_2O.
- Ca^{2+} standard: $c(Ca^{2+}) = 0.1$ mol/L; e.g., Metrohm No. 6.2301.070
- Nitric acid: $c(HNO_3) = 1$ mol/L

Blank value determination

To a glass beaker, add approx. 50 mL dist. H_2O, 1 mL $c(HNO_3) = 1$ mol/L, 0.5 mL Ca^{2+} standard ($c(Ca^{2+}) = 0.1$ mol/L), and 7.5 mL $c(BaCl_2) = 0.05$ mol/L. Allow to react for 3 min while stirring. Add 5 mL buffer solution pH 10, allow to react for a further 30 s, and titrate with $c(Na_2EGTA) = 0.05$ mol/L past the second equivalence point. EP_1 corresponds to the calcium content and the difference $EP_2–EP_1$ to the barium content. Store $EP_2–EP_1$ (mL) as blank value (common variable).

Analysis

If necessary, dilute the sample solution, which should not contain more than 20 mg sulfate, with dist. H_2O to approx. 50 mL and adjust to pH < 4 with $c(HNO_3) = 1$ mol/L. Add 0.5 mL Ca^{2+} standard ($c(Ca^{2+}) = 0.1$ mol/L) and 7.5 mL $c(BaCl_2) = 0.05$ mol/L, and allow to react for 3 min while stirring. Add 5 mL buffer solution pH 10, allow to react for a further 30 s, and titrate with $c(Na_2EGTA) = 0.05$ mol/L past the second equivalence point.

Calculation

$$\beta_{SO_4^{2-}} = \frac{\left(\text{Blank} - (V_{EP2} - V_{EP1})\right) \times c_{EGTA} \times f \times M_{SO_4^{2-}}}{V_S}$$

$\beta_{SO_4^{2-}}$: Sulfate content of the sample in g/L

Blank: Blank value in mL

V_{EP2}: Volume of EGTA standard solution consumed up to the second equivalence point in mL

V_{EP1}: Volume of EGTA standard solution consumed up to the first equivalence point in mL

c_{EGTA}: Concentration of the EGTA standard solution in mol/L

f: Titer of the EGTA standard solution

$M_{SO_4^{2-}}$: Molar mass of sulfate; 96.063 g/mol

V_S: Sample size in mL

Example: Sulfate in aqueous solution

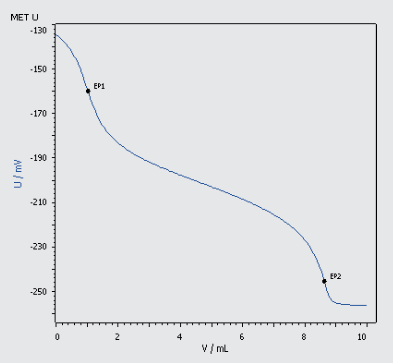

Figure 40 Titration curve of the blank value determination with the Ca ISE

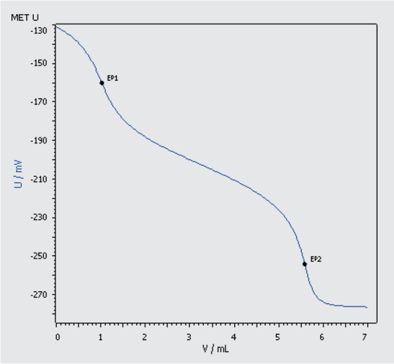

Figure 41 Titration curve of the sulfate determination with the Ca ISE

Further literature on this topic is given in

- *Application Bulletin AB-140 – Titrimetric sulfate determination*
- *Titration Application Note AN-T-116 – Automatic sulfate determination in aqueous solution using a combined ion-selective calcium electrode (Ca-ISE)*

Single determinations

Al – Aluminum

General

The complexometric titration of aluminum is associated with a particularities that should be taken into consideration when determining this metal.

Reaction rate

Complexation is slow at room temperature. For this reason, many titration procedures were formerly carried out in a hot solution. However, if the titrant excess is sufficiently large (> 50%), the reaction is fast and the titration can be performed at room temperature. Hence, Al^{3+} can be determined by back titration.

Formation of hydroxo complexes

Al forms hydroxo complexes that react very sluggishly (if at all) with the complexing agent. Al must thus be titrated in acidic solutions. If the preneutralization is carried out by adding hydroxide ions, for example, this must be taken into account and the solution should only be neutralized to pH ≈ 4. Otherwise, these hydroxo complexes may form (also locally during the addition), thus falsifying the result. Al is best titrated at pH values between 4 and 5.

Since the titration is carried out in slightly acidic solution, Ca^{2+} and Mg^{2+} do not interfere, if present. Fe^{3+} is also detected quantitatively and must be determined separately.

Table of equivalent masses

1 mL $c(Na_2EDTA) = 0.1$ mol/L = x mg equivalent:

Formula	Molar mass in g/mol	Equivalent in mg
Al	26.982	2.698
$Al(OH)_3$	78.004	7.800
Al_2O_3	101.961	5.098
$AlCl_3$	133.341	13.334
$Al(NO_3)_3$	212.996	21.300
$Al(NO_3)_3 \cdot 9\ H_2O$	375.134	37.513
$Al_2(SO_4)_3$	342.151	17.108
$Al_2(SO_4)_3 \cdot 18\ H_2O$	666.426	33.321

Potentiometric with the Cu-ISE

Reagents

- Titrant 1: $c(Na_2EDTA) = 0.1$ mol/L
- Titrant 2: $c(CuSO_4) = 0.1$ mol/L; dissolve 24.97 g $CuSO_4 \cdot 5\ H_2O$ in approx. 500 mL dist. H_2O, add 0.5 mL $w/w(H_2SO_4) = 96\%$, mix, and make up to 1 L with dist. H_2O.
- Acetate buffer, pH = 4.7: Dissolve 116 g ammonium acetate in approx. 200 mL dist. H_2O and add 86 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.

Analysis

If necessary, dilute the sample solution, which should not contain more than 15 mg Al^{3+}, with dist. H_2O to approx. 50 mL. Add 5 mL acetate buffer and 10 mL $c(Na_2EDTA) = 0.1$ mol/L, allow to react for 1–3 min while stirring, and titrate with $c(CuSO_4) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Al} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{CuSO_4}) \times M_{Al}}{V_S}$$

β_{Al}: Aluminum content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $CuSO_4$ standard solution

C_{CuSO_4}: Concentration of the $CuSO_4$ standard solution in mol/L

M_{Al}: Molar mass of aluminum; 26.982 g/mol

V_S: Sample size in mL

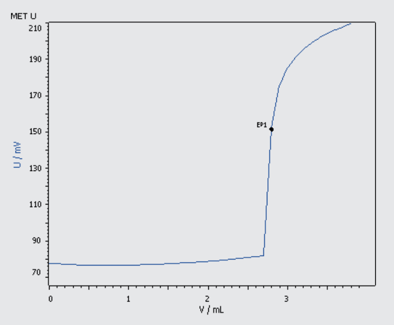

Figure 42 Example curve of a potentiometric aluminum determination

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-103 – Fully automated determination of aluminum in aqueous solution*

Photometric with the Optrode at 610 nm

Reagents

- Titrant: $c(Bi(NO_3)_3) = 0.05$ mol/L; dissolve 24.25 g $Bi(NO_3)_3 \cdot 5\ H_2O$ in approx. 500 mL HNO_3 (2 mol/L) and transfer into a 1 L volumetric flask. Next, make up to 1 L with dist. H_2O.
- Auxiliary solution: $c(Na_2EDTA) =$ 0.1 mol/L
- Hydrochloric acid: $c(HCl) = 6$ mol/L; add 590 mL $w/w(HCl) = 37\%$ to a 1 L volumetric flask that already contains approx. 200 mL dist. H_2O. After the solution has cooled, make up to the mark with dist. H_2O.
- Acetate buffer: Dissolve 60 g ammonium acetate in approx. 200 mL dist. H_2O and add 400 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Indicator solution: Xylenol orange; dissolve 100 mg xylenol orange disodium salt in 100 mL dist. H_2O.

Analysis

Pipette 10 mL sample solution into a glass beaker and add 70 mL dist. H_2O. Add 10 mL acetate buffer, adjust to pH 3.5 with c(HCl) = 6 mol/L, and then add 1.25 mL $c(Na_2EDTA) = 0.1$ mol/L and 1 mL indicator solution. Titrate the solution with $c(Bi(NO_3)_3) = 0.05$ mol/L past the first equivalence point.

Calculation

$$Al_2O_3\ \% = \frac{((V_{EDTA} \times c_{EDTA} \times f_{EDTA}) - (V_{EP1} \times c_{Bi} \times f_{Bi})) \times M_{Al_2O_3} \times 10}{m_S \times 2}$$

$Al_2O_3\%$:	Aluminum content as aluminum oxide in %
V_{EDTA}:	Added volume of EDTA standard solution in mL
c_{EDTA}:	Concentration of the EDTA standard solution in mol/L
f_{EDTA}:	Titer of the EDTA standard solution
V_{EP1}:	Volume of $c(Bi(NO_3)_3) =$ 0.05 mol/L consumed up to the first equivalence point in mL
c_{Bi}:	Concentration of the $Bi(NO_3)_3$ solution in mol/L
f_{Bi}:	Titer of the $Bi(NO_3)_3$ solution; $c(Bi(NO_3)_3) = 0.05$ mol/L
10:	Conversion factor
$M_{Al_2O_3}$:	Molar mass of aluminum oxide; 101.96 g/mol
m_S:	Sample size in g
2:	Stoichiometric factor

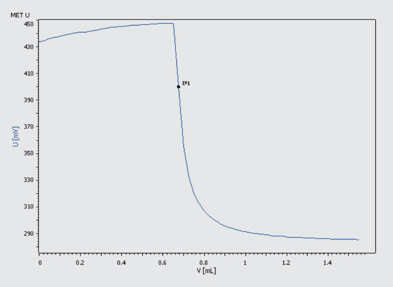

Figure 43 Example of a photometric titration curve of aluminum at 610 nm

Further literature on this topic is given in

- *Application Bulletin AB-063 – Determination of silicon, calcium, magnesium, iron, and aluminum in digested cement samples by photometric titrations*

Ba – Barium and Sr – Strontium

General

Barium and strontium can be titrated either directly or indirectly in alkaline solution. Ca^{2+} and Mg^{2+} are also determined. Ba^{2+} can be separated by precipitation as $BaSO_4$ (Caution: $BaSO_4$ dissolves in excess Na_2EDTA). Heavy metal ions are masked by adding KCN. Since the titration can only be performed in alkaline solution, in which both barium and strontium form sparingly soluble carbonates, the results of the determination may be too low. This is why the determinations are often carried out using back titration.

The following table contains some solubility products as pK_{sp} values as a guide

$K_{sp} = a[A] \cdot a[B]$

pK_{sp} is the negative logarithm of K_{sp}. As pK_{sp} increases, the solubility of the respective compound decreases.

Compound	pK_{sp}
$BaCO_3$	8.2
$BaSO_4$	10.0
$CaCO_3$	7.9
$CaSO_4$	4.3
$MgCO_3$	3.8
$SrCO_3$	8.8
$SrSO_4$	6.6

Table of equivalent masses

1 mL $c(Na_2EDTA) = 0.1$ mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Ba	137.327	13.733
$BaCO_3$	197.336	19.734
$BaCl_2$	208.233	20.823
$Ba(NO_3)_2$	261.337	26.134
BaO	153.326	15.333
$Ba(OH)_2$	171.342	17.134
$BaSO_4$	233.390	23.339
Sr	87.620	8.762
$SrCO_3$	147.629	14.763
$SrCl_2$	158.526	15.853
$Sr(NO_3)_2$	211.630	21.163
SrO	103.619	10.362
$Sr(OH)_2$	121.635	12.164
$SrSO_4$	183.683	18.368

Potentiometric with the Cu-ISE

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Cu complex solution: $c[Cu(NH_4)_2EDTA] = 0.1$ mol/L (e.g., Merck No. 105217)
- Ammonia buffer, pH = 10: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: $c(NaOH) = 1$ mol/L

Analysis

Preneutralize very acidic sample solutions to approx. pH 4 with $c(NaOH) = 1$ mol/L. If necessary, dilute the sample solution with dist. H_2O to approx. 50 mL. Add 1 mL Cu complex solution and 5 mL ammonia buffer, wait for 10–20 s while stirring, and then titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Ba/Sr} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Ba/Sr}}{V_S}$$

$\beta_{Ba/Sr}$: Barium or strontium content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

$M_{Ba/Sr}$: Molar mass of barium and strontium; 137.327 g/mol and 87.620 g/mol, respectively

V_S: Sample size in mL

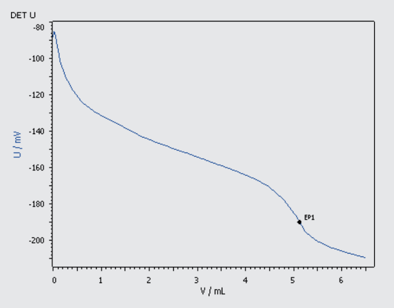

Figure 44 Example of a potentiometric titration curve of barium with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the copper ion-selective electrode*
- *Titration Application Note AN-T-104 – Fully automated determination of barium in aqueous solution*

Photometric with the Optrode at 574 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Indicator solution: Phthalein purple; dissolve 0.1 g phthalein purple in approx. 75 mL dist. H_2O and 1 mL $w/w(NH_3) = 25\%$. Mix and make up to 100 mL with dist. H_2O.
- Ammonia: $w/w(NH_3) = 25\%$
- Sodium hydroxide: $c(NaOH) = 1$ mol/L

Analysis

Preneutralize very acidic samples to pH 4–5 with $c(NaOH) = 1$ mol/L. To 50 mL sample solution, which should not contain more than 100 mg Ba^{2+} or 80 mg Sr^{2+}, add 100 mL dist. H_2O. Add 5 mL $w/w(NH_3) = 25\%$ and 0.5 mL indicator solution, and titrate *immediately* with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point (colorless).

Calculation

$$\beta_{Ba/Sr} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Ba/Sr}}{V_S}$$

$\beta_{Ba/Sr}$: Barium or strontium content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

$M_{Ba/Sr}$: Molar mass of barium and strontium; 137.327 g/mol and 87.620 g/mol, respectively

V_S: Sample size in mL

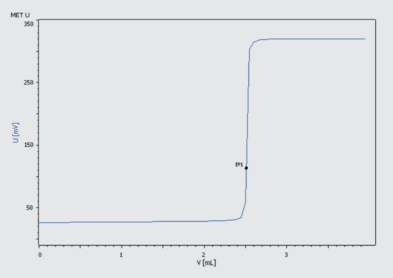

Figure 45 Photometric titration curve of barium with the Optrode at 574 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-142 – Determination of barium using automatic photometric titration*

Bi – Bismuth

General

Similar to Al^{3+}, Bi^{3+} also forms hydroxo complexes in aqueous solutions. Bi^{3+} reacts sluggishly with the complexing agent but, on the other hand, Bi complexes have a very high complex formation constant. This enables Bi^{3+} to be titrated without problems even in very acidic solutions (pH 1–2). Complexometric determination of Bi is thus very selective. Interference can only be expected from metal ions whose complex formation constant is > 20 (Fe^{3+}, Hg^{2+}, Sn^{2+}, Sn^{4+}). Determination of Bi in some pharmaceuticals (e.g., Bi subgallate, Bi subsalicylate) is carried out after digestion of the sample.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Bi	208.980	20.898
$Bi(OH)_3$	261.013	26.101
Bi_2O_3	465.959	23.298
$(BiO)_2CO_3$	509.969	25.498
$BiONO_3 \cdot H_2O$	305.000	30.500
$Bi(NO_3)_3$	394.995	39.500

Potentiometric with the Cu ISE

Reagents

- Titrant 1: c(Na_2EDTA) = 0.1 mol/L
- Titrant 2: c($CuSO_4$) = 0.1 mol/L; dissolve 24.97 g $CuSO_4 \cdot 5\ H_2O$ in approx. 500 mL dist. H_2O. Add 0.5 mL w/w(H_2SO_4) = 96%, mix, and make up to 1 L with dist. H_2O.
- Acetate buffer, pH = 4.7: Dissolve 116 g ammonium acetate in approx. 200 mL dist. H_2O and add 86 mL glacial acetic acid. Mix, and make up to 1 L with dist. H_2O.
- Ammonia: w/w(NH_3) = 25%

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 160 mg Bi^{3+}, with dist. H_2O to approx. 50 mL. Add 5 mL acetate buffer and 10 mL c(Na_2EDTA) = 0.1 mol/L, and, if necessary, adjust to pH 4.7 with w/w(NH_3) = 25%. Allow to react for approx. 1 min while stirring, and titrate with c($CuSO_4$) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Bi} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{CuSO_4}) \times M_{Bi}}{V_S}$$

β_{Bi}: Bismuth content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $CuSO_4$ standard solution

C_{CuSO_4}: Concentration of the $CuSO_4$ standard solution in mol/L

M_{Bi}: Molar mass of bismuth; 208.980 g/mol

V_S: Sample size in mL

Photometric with the Optrode at 520 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Nitric acid: $w/w(HNO_3) = 65\%$
- Indicator solution: Xylenol orange; dissolve 100 mg xylenol orange disodium salt in 100 mL dist. H_2O.

Analysis

Dissolve the sample in a small amount of $w/w(HNO_3) = 65\%$, and dilute to approx. 100 mL with dist. H_2O. Add 0.5 mL indicator solution, and titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

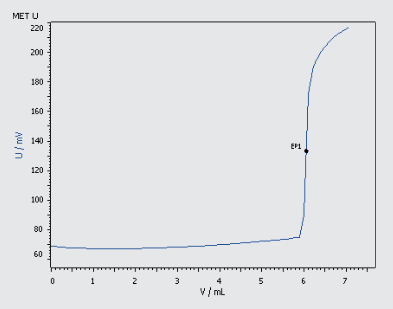

Figure 46 Potentiometric titration curve of bismuth with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-105 – Fully automated determination of bismuth(III) in aqueous solution*

Calculation

$$\beta_{Bi} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Bi}}{V_S}$$

β_{Bi}: Bismuth content of the sample in g/L

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

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Bi}: Molar mass of bismuth; 208.980 g/mol

V_S: Sample size in mL

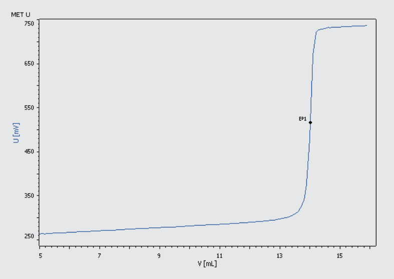

Figure 47 Example of a photometric titration curve of bismuth at 520 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-088 – Photometric EDTA titration of bismuth nitrate according to Ph. Eur. and USP*

Ca – Calcium

General

Ca^{2+} is one of the first metals that was determined using complexometric titration. Since then, hundreds, if not thousands, of publications on this topic have appeared. In this chapter, we will only discuss the determination of Ca^{2+}. If the sample contains both Ca^{2+} with Mg^{2+}, please refer to the section on "Water hardness".

Since Ca^{2+} is always titrated in alkaline solution, there is always a risk that it may absorb CO_2 from the air and precipitate as $CaCO_3$. If the titration is carried out too quickly, this could lead to incorrect results that are too low. ($CaCO_3$ reacts slowly with the titrant, which is acting as a complexing agent, and the resulting turbidity interferes, particularly in the case of photometric titration).

If Ca^{2+} is to be determined in the presence of Mg^{2+}, the EDTA can be replaced by EGTA, which is a more selective titrant (or by the Cu-EGTA complex if a Cu ISE is used).

Table of equivalent masses

1 mL c(CA) = 0.1 mol/L = x mg equivalent (CA = complexing agent)

Formula	Molar mass in g/mol	Equivalent in mg
Ca	40.078	4.008
CaC_2O_4	128.097	12.810
$CaCO_3$	100.087	10.009
$CaCl_2$	110.984	11.098
$Ca(NO_3)_2$	164.088	16.409
CaO	56.077	5.608
$Ca(OH)_2$	74.093	7.409
$CaSO_3$	120.141	12.014
$CaSO_4$	136.141	13.614

Potentiometric with the Ca-ISE

Reagents

- Titrant: c(Na_2EDTA) = 0.1 mol/L
- Buffer solution: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL w/w(NH_3) = 25%. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: c(NaOH) = 1 mol/L

Analysis

Preneutralize acidic sample solutions with c(NaOH) = 1 mol/L to pH 5–7 and dilute, if necessary, with dist. H_2O to approx. 50 mL. Add 5 mL buffer solution and titrate with c(Na_2EDTA) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Ca} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Ca}}{V_S}$$

β_{Ca}:	Calcium content of the sample in g/L
V_{EP1}:	Volume of EDTA standard solution consumed up to the first equivalence point in mL
f:	Titer of the EDTA standard solution
c_{EDTA}:	Concentration of the EDTA standard solution in mol/L
M_{Ca}:	Molar mass of calcium; 40.078 g/mol
V_S:	Sample size in mL

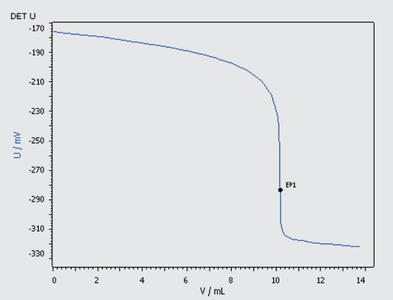

Figure 48 Example curve of a potentiometric calcium determination with the Ca-ISE

Further literature on this topic is given in

- *Application Bulletin AB-125 – Simultaneous determination of calcium, magnesium, and alkalinity by complexometric titration with potentiometric or photometric indication in water and beverage samples*

Potentiometric with the Cu ISE

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Buffer solution: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Mix and make up to 1 L with dist. H_2O.
- Cu complex solution: $c[Cu(NH_4)_2EDTA] = 0.1$ mol/L (e.g., Merck No. 105217)
- Sodium hydroxide: $c(NaOH) = 1$ mol/L

Analysis

Preneutralize acidic sample solutions with $c(NaOH) = 1$ mol/L to pH 5–7 and dilute, if necessary, with dist. H_2O to approx. 50 mL. Add 5 mL buffer solution and 0.5 mL Cu complex solution, wait 20 s while stirring, and titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Ca} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Ca}}{V_S}$$

β_{Ca}: Calcium content of the sample in g/L

V_{EP1}: Volume in mL of EDTA standard solution consumed up to the first equivalence point

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Ca}: Molar mass of calcium; 40.078 g/mol

V_S: Sample size in mL

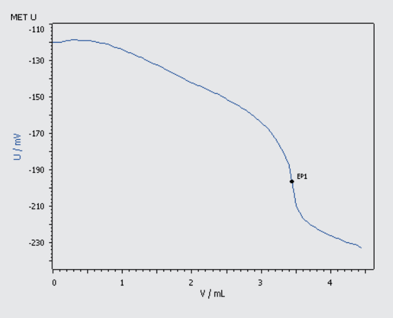

Figure 49 Potentiometric titration curve of the determination of calcium in milk with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-106 – Fully automated determination of calcium in milk*

Photometric with the Optrode at 610 nm

Reagents

- Titrant: c(Na_2EDTA) = 0.1 mol/L
- Sodium hydroxide: c(NaOH) = 1 mol/L
- Indicator solution: HHSNN; dissolve 20 mg HHSNN in 50 mL ethanol.

Analysis

Preneutralize acidic sample solutions with c(NaOH) = 1 mol/L to pH 5–7 and dilute, if necessary, with dist. H_2O to approx. 50 mL. Add 4 mL c(NaOH) = 1 mol/L and 1.5 mL indicator solution, and titrate *immediately* with c(Na_2EDTA) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Ca} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Ca}}{V_S}$$

β_{Ca}: Calcium content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Ca}: Molar mass of calcium; 40.078 g/mol

V_S: Sample size in mL

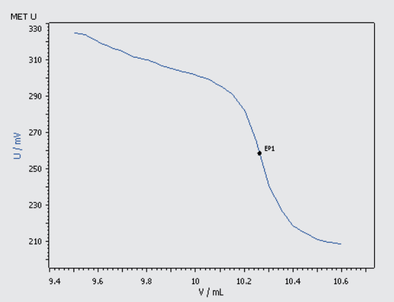

Figure 50 Example of a photometric titration curve of the calcium determination with the Optrode at 610 nm

Further literature on this topic is given in

- *Application Bulletin AB-125 – Simultaneous determination of calcium, magnesium, and alkalinity by complexometric titration with potentiometric or photometric indication in water and beverage samples*

Cd – Cadmium

General

The complexation behavior of Cd^{2+} is very similar to that of zinc. It can be titrated in alkaline solution without problems. However, Ca^{2+} and Mg^{2+} interfere if present because they are also determined.

Table of equivalent masses

1 mL $c(Na_2EDTA) = 0.1$ mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Cd	112.411	11.241
$CdCO_3$	172.420	17.242
$CdCl_2$	183.317	18.332
$Cd(NO_3)_2$	236.421	23.642
$Cd(NO_3)_2 \cdot 2H_2O$	272.451	27.245
CdO	128.410	12.841
$Cd(OH)_2$	146.426	14.643
$CdSO_4$	208.474	20.847

Potentiometric with the Cu-ISE

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Ammonia buffer: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Mix and make up to 1 L with dist. H_2O.
- Cu complex solution: $c[Cu(NH_4)_2EDTA] = 0.1$ mol/L (e.g., Merck No. 105217)
- Sodium hydroxide: $c(NaOH) =$ 1 mol/L

Analysis

Preneutralize acidic sample solutions with $c(NaOH) = 1$ mol/L to pH 4–5 and dilute, if necessary, with dist. H_2O to approx. 50 mL. Add 5 mL ammonia buffer and 0.5 mL Cu complex solution, wait 20 s while stirring, and titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Cd} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Cd}}{V_S}$$

β_{Cd}:	Cadmium content of the sample in g/L
V_{EP1}:	Volume of EDTA standard solution consumed up to the first equivalence point in mL
f:	Titer of the EDTA standard solution
c_{EDTA}:	Concentration of the EDTA standard solution in mol/L
M_{Cd}:	Molar mass of cadmium; 112.411 g/mol
V_S:	Sample size in mL

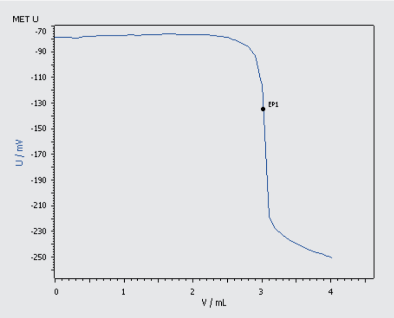

Figure 51 Potentiometric titration curve of cadmium with the Cu-ISE

Photometric with the Optrode at 610 nm

Reagents

- Titrant 1: $c(Na_2EDTA) = 0.1$ mol/L
- Titrant 2: $c(ZnSO_4) = 0.1$ mol/L; dissolve 28.8 g $ZnSO_4 \cdot 7\ H_2O$ in approx. 500 mL dist. H_2O, add 0.5 mL $w/w(H_2SO_4) = 96\%$, mix, and make up to 1 L with dist. H_2O.
- Ammonia buffer, pH = 10: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: $c(NaOH) = 1$ mol/L
- Indicator solution: Eriochrome Black T; dissolve 100 mg Eriochrome Black T in 100 mL ethanol.

Analysis

Preneutralize acidic sample solutions with $c(NaOH) = 1$ mol/L to approx. pH 5 and dilute, if necessary, with dist. H_2O to approx. 50 mL. Add 5 mL ammonia buffer, 10 mL $c(Na_2EDTA) = 0.1$ mol/L, and 0.25 mL indicator solution. Then titrate with $c(ZnSO_4) = 0.1$ mol/L past the first equivalence point.

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-125 – Automatic determination of cadmium in aqueous solution with the Cu-ISE*

Calculation

$$\beta_{Cd} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{ZnSO_4}) \times M_{Cd}}{V_S}$$

β_{Cd}: Cadmium content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $ZnSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $ZnSO_4$ standard solution

c_{ZnSO_4}: Concentration of the $ZnSO_4$ standard solution in mol/L

M_{Cd}: Molar mass of cadmium; 112.411 g/mol

V_S: Sample size in mL

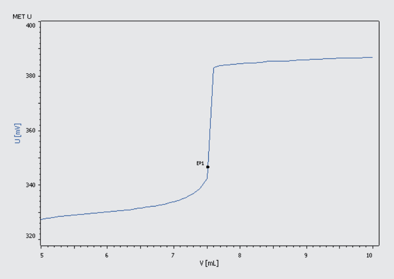

Figure 52 Photometric titration curve of the cadmium determination with the Optrode at 610 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-153 – Determination of cadmium using automatic photometric titration*

Co – Cobalt

General

The complexation behavior of cobalt is similar to that of nickel, and it has almost the same complex formation constants. In alkaline solution and in the presence of excess EDTA as well as added H_2O_2, Co^{2+} forms extremely robust and strongly colored Co^{3+}-EDTA complexes that are also stable in acidic media. This situation was used by various authors for the complexometric determination of cobalt with enhanced selectivity. These methods, however, did not gain acceptance because the quantity of added H_2O_2 is critical and, in the case of photometric titration, the intrinsic color of the Co^{3+} complex interferes with the color change of the indicator.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Co	58.933	5.893
$Co(CH_3COO)_2 \cdot 4\ H_2O$	249.083	24.908
$CoCO_3$	118.942	11.894
$CoCl_2$	129.839	12.984
$CoCl_2 \cdot 6H_2O$	237.930	23.793
$Co(NO_3)_2$	182.943	18.294
$Co(NO_3)_2 \cdot 6\ H_2O$	291.034	29.103
CoO	74.933	7.493
Co_2O_3	165.865	8.293
$CoSO_4$	154.996	15.500
$CoSO_4 \cdot 7H_2O$	281.103	28.110

Potentiometric with the Cu-ISE

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Cu complex solution: $c[Cu(NH_4)_2EDTA] = 0.1$ mol/L (e.g., Merck No. 105217)
- Ammonia buffer: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: $c(NaOH) = 1$ mol/L

Analysis

If necessary, dilute the sample solution with dist. H_2O to approx. 50 mL and pre-neutralize, if necessary, to pH 4–5 with $c(NaOH) = 1$ mol/L. Add 5 mL ammonia buffer and 0.5 mL Cu complex solution, wait for 10–20 s while stirring, and titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Co} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Co}}{V_S}$$

β_{Co}: Cobalt content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Co}: Molar mass of cobalt; 58.933 g/mol

V_S: Sample size in mL

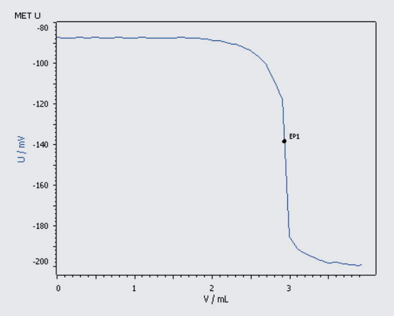

Figure 53 Example of a potentiometric titration curve of cobalt with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-126 – Automatic determination of cobalt in aqueous solution with the Cu-ISE*

Photometric with the Optrode at 574 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Indicator solution: murexide; dissolve 0.2 g murexide (triturated 1:100 with NaCl) in 50 mL dist. H_2O.
- Ammonia buffer: Dissolve 54 g NH_4Cl in approx. 500 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Adjust to pH 9 with $c(HCl) = 6$ mol/L, mix, and make up to 1 L with dist. H_2O.

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 40 mg Co^{2+}, with dist. H_2O to 100 mL and degas. Add 10 mL ammonia buffer solution and 5 mL indicator solution, and then titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Co} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Co}}{V_S}$$

β_{Co}: Cobalt content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Co}: Molar mass of cobalt; 58.933 g/mol

V_S: Sample size in mL

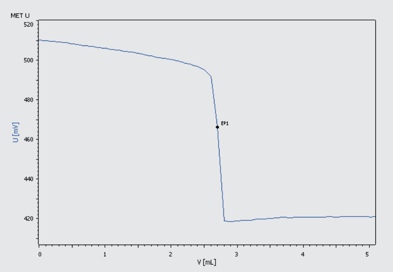

Figure 54 Photometric titration curve of cobalt with the Optrode at 574 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-143 – Determination of cobalt using automatic photometric titration*

Cu – Copper

General

Owing to its relatively high complex formation constant, copper can be titrated in both alkaline and slightly acidic solutions. Only the Cu^{2+} ion can be determined. In case of photometric titration in an ammoniacal solution, the ammonia excess should not be too large and the titrations should always be carried out in dilute solutions. This is because the Cu^{2+}-amine complex is relatively stable and strongly colored and thus competes with the color indicator (e.g., murexide).

Keep adding NH_3 to the sample solution until $Cu(OH)_2$ precipitates. Then add further NH_3 until everything has re-dissolved. Dilute with dist. H_2O to at least 1:1. Add murexide, and titrate with $c(Na_2EDTA) = 0.1$ mol/L.

Better results are obtained by photometric titration at pH = 5.0 with PAN as indicator. To avoid having to titrate at high temperatures, dilute the sample solution with ethanol in an approx. 1:1 ratio.

Table of equivalent masses

1 mL $c(Na_2EDTA) = 0.1$ mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Cu	63.546	6.355
$Cu(CH_3COO)_2 \cdot H_2O$	199.650	19.965
$CuCN$	89.564	8.956
$Cu(CN)_2$	115.581	11.558
$CuCl_2$	134.452	13.445
$CuCl_2 \cdot 2\ H_2O$	170.842	17.084
$Cu(NO_3)_2$	187.556	18.756
$Cu(NO_3)_2 \cdot 3\ H_2O$	241.601	24.160
CuO	79.544	7.954
$Cu(OH)_2$	97.561	9.756
$CuSO_4$	159.600	15.960
$CuSO_4 \cdot 5\ H_2O$	249.680	24.968

Potentiometric with the Cu-ISE

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Ammonia buffer, pH = 10: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: $c(NaOH) = 1$ mol/L

Analysis

If necessary, dilute acidic sample solutions with dist. H_2O to approx. 50 mL and preneutralize to pH 4–5 with $c(NaOH) = 1$ mol/L. Add 5 mL ammonia buffer, and titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Cu} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Cu}}{V_S}$$

β_{Cu}:	Copper content of the sample in g/L
V_{EP1}:	Volume of EDTA standard solution consumed up to the first equivalence point in mL
f:	Titer of the EDTA standard solution
c_{EDTA}:	Concentration of the EDTA standard solution in mol/L
M_{Cu}:	Molar mass of copper; 63.546 g/mol
V_S:	Sample size in mL

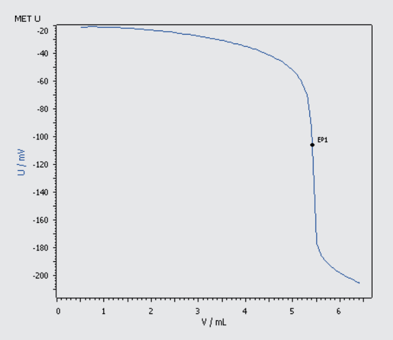

Figure 55 Potentiometric titration curve of copper with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-127 – Automatic determination of copper in aqueous solution with the Cu-ISE*

Photometric with the Optrode at 520 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Acetate buffer, pH = 5.0: dissolve 116 g ammonium acetate in approx. 500 mL dist. H_2O. Adjust to pH 5.0 with glacial acetic acid, mix, and make up to 1 L with dist. H_2O.
- Sodium hydroxide: $c(NaOH) =$ 1 mol/L
- Ethanol: w/w(ethanol) = 96–98%
- Indicator solution: PAN; dissolve 100 mg PAN in 100 mL ethanol.

Analysis

If necessary, dilute acidic sample solutions with dist. H_2O to approx. 50 mL and then preneutralize to approx. pH 4–5 with $c(NaOH) = 1$ mol/L. Add 50 mL ethanol and degas. Add 5 mL acetate buffer and 0.5 mL indicator solution, and titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Cu} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Cu}}{V_S}$$

β_{Cu}: Copper content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Cu}: Molar mass of copper; 63.546 g/mol

V_S: Sample size in mL

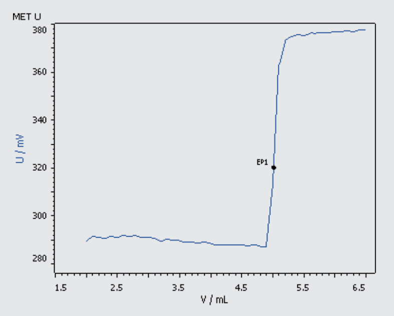

Figure 56 Photometric titration curve of copper with the Optrode at 520 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-124 – Photometric copper determination in aqueous solution*

Fe – Iron

General

Iron forms complexes in both its divalent and trivalent states. The complex formation constants, however, are very different (approx. 12 orders of magnitude). Fe^{3+} forms very strong complexes that are also stable in acidic solution. This means that Fe can be titrated in the presence of other metal ions almost without interference. In the presence of, for example, EDTA, Fe^{2+} becomes a very strong reducing agent (standard potential -0.1 V), which can even reduce Ag^+ to its metal.

As a general rule, titration of Fe^{2+} ions is not advisable. Owing to the relatively low complex formation constant, it must be titrated in alkaline solution under inert gas to prevent oxidation to Fe^{3+}. Conversely, interfering Fe^{3+} can be masked by reducing it, for example, with ascorbic acid. Thus, only the Fe^{3+} ion is titrated in practice. Fe^{2+} can be oxidized using H_2O_2 or peroxydisulfate.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Fe	55.845	5.585
$FeCO_3$	115.856	11.586
$FeCl_2$	126.753	12.675
$FeCl_2 \cdot 4H_2O$	198.813	19.881
$FeCl_3$	162.206	16.221
$FeCl_3 \cdot 6H_2O$	270.297	27.030
$Fe(NO_3)_3$	241.862	24.186
$Fe(NO_3)_3 \cdot 6H_2O$	349.953	34.995
FeO	71.846	7.185
Fe_2O_3	159.692	7.985
$FeSO_4$	151.910	15.191
$FeSO_4 \cdot 7H_2O$	278.010	27.801
$Fe_2(SO_4)_3$	399.870	19.994
$Fe_2(SO_4)_3 \cdot 9H_2O$	562.010	28.101
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	392.130	39.213
$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	482.180	48.218

Potentiometric with the Cu-ISE

Reagents

- Titrant 1: $c(Na_2EDTA) = 0.1$ mol/L
- Titrant 2: $c(CuSO_4) = 0.1$ mol/L; dissolve 24.97 g $CuSO_4 \cdot 5\ H_2O$ in approx. 500 mL dist. H_2O, add 0.5 mL $w/w(H_2SO_4) = 96\%$, mix, and make up to 1 L with dist. H_2O.
- Acetate buffer, pH = 4.7: Dissolve 116 g ammonium acetate in approx. 200 mL dist. H_2O and add 86 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: $c(NaOH) = 1$ mol/L

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 50 mg Fe^{3+}, with dist. H_2O to approx. 50 mL, add 5 mL acetate buffer, and adjust to pH 4.7 with $c(NaOH) = 1$ mol/L. Add 10 mL $c(Na_2EDTA) = 0.1$ mol/L, allow to react for 1–2 min while stirring, and titrate with $c(CuSO_4) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Fe} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{CuSO_4}) \times M_{Fe}}{V_S}$$

β_{Fe}: Iron content of the sample in g/L
V_{EDTA}: Added volume of EDTA standard solution in mL
f_1: Titer of the EDTA standard solution
c_{EDTA}: Concentration of the EDTA standard solution in mol/L
V_{EP1}: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point in mL
f_2: Titer of the $CuSO_4$ standard solution
c_{CuSO_4}: Concentration of the $CuSO_4$ standard solution in mol/L
M_{Fe}: Molar mass of iron; 55.845 g/mol
V_S: Sample size in mL

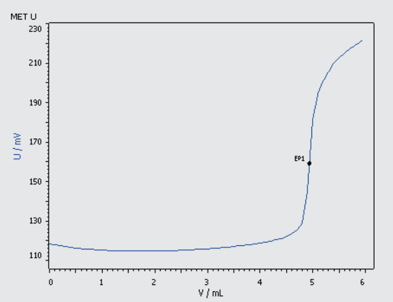

Figure 57 Example of a potentiometric titration curve of iron with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-107 – Fully automated determination of total iron in cement*

Photometric with the Optrode at 610 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Ammonia: $w/w(NH_3) = 25\%$
- Indicator solution: sulfosalicylic acid; dissolve 4 g sulfosalicylic acid in 100 mL dist. H_2O.
- Glycine

Analysis

If necessary, dilute the acidic sample solution with dist. H_2O to approx. 100 mL. Add 0.5 g glycine and 1 mL indicator solution, and adjust to pH 1.5–2 with $w/w(NH_3) = 25\%$. Heat the mixture to 50 °C to dissolve the glycine. Allow to cool, then titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Fe} = \frac{V_{BP1} \times f \times c_{EDTA} \times M_{Fe}}{V_S}$$

β_{Fe}: Iron content of the sample in g/L

V_{BP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_A: Molar mass of iron; 55.847 g/mol

V_S: Sample size in mL

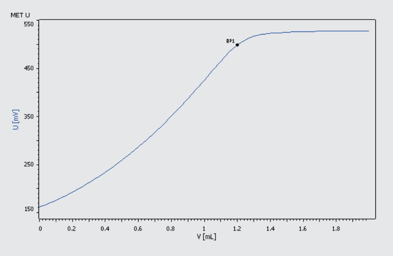

Figure 58 Photometric titration curve of iron with the Optrode at 610 nm

Further literature on this topic is given in

- *Application Bulletin AB-063 – Determination of silicon, calcium, magnesium, iron, and aluminum in digested cement samples by photometric titrations.*
- *Titration Application Note AN-T-080 – Determination of iron in cement by photometric titration*

Ga – Gallium and In – Indium

General

Gallium and indium form complexes with quite high formation constants (e.g., InEDTA; log K_f = 24.9). However, they also tend to form hydroxo complexes that cannot be completely titrated, if at all. Therefore acetate ions are added as auxiliary complexing agents, and the metals are determined by back titration in slightly acidic solution. This avoids possible interference by Ca^{2+}- and/or Mg^{2+} ions.

Photometric back titration with a Mn standard solution with Eriochrome Black T indicator would also be possible in alkaline solution. However, the usual ammonia buffer pH 10 cannot be used for pH adjustment in this case, because this would lead to precipitation of Ga and In as $Ga(OH)_3$ and $In(OH)_3$., respectively. To avoid this, tartrate is added as auxiliary complexing agent before adjusting the pH to 8.5–9 using ammonia. If present, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+} can be masked with KCN.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Ga	69.723	6.972
$Ga(NO_3)_3 \cdot 8H_2O$	399.860	39.986
Ga_2O_3	187.444	9.372
$Ga_2(SO_4)_3$	427.634	21.382
$Ga_2(SO_4)_3 \cdot 18H_2O$	751.909	37.595
In	114.818	11.482
$InCl_3$	221.177	22.118
In_2O_3	277.634	13.882
$In_2(SO_4)_3$	517.824	25.891
$In_2(SO_4)_3 \cdot 9H_2O$	679.961	33.998

Potentiometric with the Cu-ISE

Reagents

- Titrant 1: c(Na_2EDTA) = 0.1 mol/L
- Titrant 2: c($CuSO_4$) = 0.1 mol/L; dissolve 24.97 g $CuSO_4 \cdot 5H_2O$ in approx. 500 mL dist. H_2O, add 0.5 mL w/w(H_2SO_4) = 96%, mix, and make up to 1 L with dist. H_2O.
- Acetate buffer, pH = 4.7: Dissolve 116 g ammonium acetate in approx. 200 mL dist. H_2O and add 86 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Ammonia: w/w(NH_3) = 25%

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 60 mg Ga^{3+} and/or 100 mg In^{3+}, with dist. H_2O to approx. 50 mL. Add 5 mL acetate buffer and 10 mL $c(Na_2EDTA) = 0.1$ mol/L, and, if necessary, adjust to pH 4.7 with $w/w(NH_3) = 25\%$. Allow to react for approx. 30 s while stirring, and then titrate with $c(CuSO_4) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Ga/In} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{CuSO_4}) \times M_{Ga/In}}{V_S}$$

$\beta_{Ga/In}$: Gallium or indium content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $CuSO_4$ standard solution

c_{CuSO_4}: Concentration of the $CuSO_4$ standard solution in mol/L

$M_{Ga/In}$: Molar mass of gallium and indium; 69.723 g/mol and 114.818 g/mol, respectively

V_S: Sample size in mL

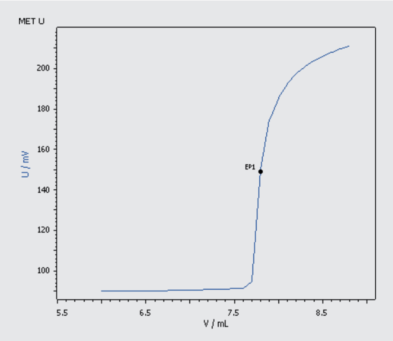

Figure 59 Potentiometric titration curve of indium with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-121 – Automatic indium determination in aqueous solution using the ion-selective copper electrode (Cu-ISE)*

Photometric with the Optrode at 610 nm

Reagents

- Titrant 1: $c(Na_2EDTA) = 0.1$ mol/L
- Titrant 2: $c(ZnSO_4) = 0.1$ mol/L; dissolve 28.8 g $ZnSO_4 \cdot 7H_2O$ in approx. 500 mL dist. H_2O, add 0.5 mL $w/w(H_2SO_4) = 96\%$, mix, and make up to 1 L with dist. H_2O.
- Acetate buffer, pH = 4.7: Dissolve 116 g ammonium acetate in approx. 200 mL dist. H_2O and add 86 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Indicator solution: xylenol orange; dissolve 25 mg xylenol orange disodium salt in 100 mL dist. H_2O.

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 60 mg Ga^{3+} and/or 100 mg In^{3+}, with dist. H_2O to approx. 100 mL and degas. Add 5 mL acetate buffer, 10 mL $c(Na_2EDTA) = 0.1$ mol/L, and 2 mL indicator solution and titrate with $c(ZnSO_4) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Ga/In} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{ZnSO_4}) \times M_{Ga/In}}{V_S}$$

$\beta_{Ga/In}$: Gallium or indium content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $ZnSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $ZnSO_4$ standard solution

c_{ZnSO_4}: Concentration of the $ZnSO_4$ standard solution in mol/L

$M_{Ga/In}$: Molar mass of gallium and indium; 69.723 g/mol and 114.818 g/mol, respectively

V_S: Sample size in mL

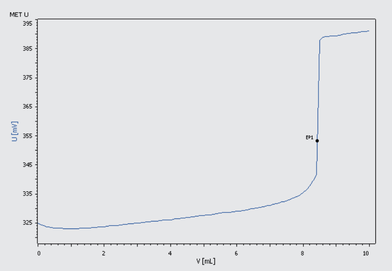

Figure 60 Example of a photometric titration curve of gallium with the Optrode at 610 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-158 – Determination of gallium using automatic photometric titration*

Hg – Mercury

General

Mercury forms relatively strong complexes and is thus suitable for titration. However, it must be present as Hg^{2+} because Hg^{+} disproportionates into Hg^{2+} and metallic Hg in the presence of, e.g., EDTA. Hg^{2+} can be masked relatively easily. It can be precipitated as HgI_2 by adding potassium iodide solution, which liberates the corresponding amount of complexing agent (e.g., EDTA). This allows consecutive titrations, for example, in the presence of Cu^{2+}.

In some pharmaceutical formulations, Hg^{2+} can be titrated directly without having to separate it from the organic matrix beforehand.

The Cu-ISE cannot be used for potentiometric indication because Hg^{2+} poisons the crystal membrane, making the electrode inoperable.

Hg complexes are serious environmental pollutants! The solutions used during the titration should thus be collected and detoxified. We recommend the following procedure for this:

The collected solutions are made alkaline, for example, by adding NaOH. Excess sodium sulfide solution is then added to the stirred mixture. The precipitated (very sparingly soluble) Hg_2S can be collected and disposed of separately.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Hg	200.590	20.059
$HgCl_2$	271.496	27.150
$Hg(NO_3)_2$	324.600	32.460
$Hg(NO_3)_2 \cdot H_2O$	342.615	34.262
HgO	216.589	21.659
$HgSO_4$	296.653	29.665

Photometric with the Optrode at 502 nm

Reagents

- Titrant 1: c(Na_2EDTA) = 0.1 mol/L
- Titrant 2: c($ZnSO_4$) = 0.1 mol/L; dissolve 28.8 g $ZnSO_4 \cdot 7H_2O$ in dist. H_2O, mix, and make up to 1 L with dist. H_2O.
- Ammonia buffer, pH = 10: dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL w/w(NH_3) = 25%. Mix, and make up to 1 L with dist. H_2O.
- Sodium hydroxide: c(NaOH) = 1 mol/L
- Indicator solution: Eriochrome Black T; dissolve 100 mg Eriochrome Black T in 100 mL ethanol.

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 75 mg Hg^{2+}, with dist. H_2O to approx. 50 mL. Add 5.00 mL c(Na_2EDTA) = 0.1 mol/L and neutralize the solution with c(NaOH) = 1 mol/L to approx. pH 5–7. Add 5 mL ammonia buffer and 1 mL indicator solution, and titrate with c($ZnSO_4$) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Hg} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{ZnSO_4}) \times M_{Hg}}{V_S}$$

β_{Hg}: Mercury content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $ZnSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $ZnSO_4$ standard solution

c_{ZnSO_4}: Concentration of the $ZnSO_4$ standard solution in mol/L

M_{Hg}: Molar mass of mercury; 200.590 g/mol

V_S: Sample size in mL

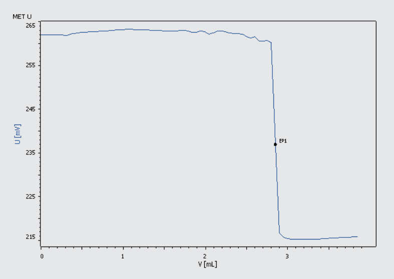

Figure 61 Photometric titration curve of mercury with the Optrode at 502 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-144 – Mercury analysis using automatic photometric titration*

Mg – Magnesium

General

Along with calcium, magnesium was one of the first metals to be titrated complexometrically. The titration is generally carried out in a buffered ammoniacal solution at pH = 10 and can be performed directly. Since Mg^{2+} is very often accompanied by Ca^{2+}, please refer to the separate determination of the two metals in the section on "Water hardness".

Interfering metals, such as Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, and Mn^{2+} can be eliminated by precipitating them with Na_2S solution. The sample should then be filtered and the excess sulfides destroyed by oxidizing them to sulfate (e.g., with H_2O_2).

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Mg	24.305	2.431
$Mg(CH_3COO)_2 \cdot 4H_2O$	214.450	21.445
$MgCO_3$	84.318	8.432
$MgCl_2$	95.211	9.521
$MgCl_2 \cdot 6H_2O$	203.302	20.330
$Mg(NO_3)_2$	148.315	14.832
$Mg(NO_3)_2 \cdot 6H_2O$	256.406	25.641
MgO	40.304	4.030
$Mg(OH)_2$	58.320	5.832
$MgSO_4$	120.360	12.036
$MgSO_4 \cdot H_2O$	138.380	13.838
$MgSO_4 \cdot 7H_2O$	246.470	24.647

Potentiometric with the Cu-ISE

Reagents

- Titrant: c(Na_2EDTA) = 0.1 mol/L
- Cu complex solution: c[$Cu(NH_4)_2$EDTA] = 0.1 mol/L (e.g., Merck No. 105217)
- Ammonia buffer, pH = 10: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL w/w(NH_3) = 25%. Mix and make up to 1 L with dist. H_2O.
- Ammonia: w/w(NH_3) = 25%

Analysis

If necessary, dilute acidic sample solutions with dist. H_2O to approx. 50 mL and pre-neutralize to approx. pH 4–5 with w/w(NH_3) = 25%. Add 0.5 mL Cu complex solution and 5 mL ammonia buffer, wait for 10–20 s while stirring, and titrate with c(Na_2EDTA) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Mg} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Mg}}{V_S}$$

β_{Mg}: Magnesium content of the sample in g/L
V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL
f: Titer of the EDTA standard solution
c_{EDTA}: Concentration of the EDTA standard solution in mol/L
M_{Mg}: Molar mass of magnesium; 24.305 g/mol
V_S: Sample size in mL

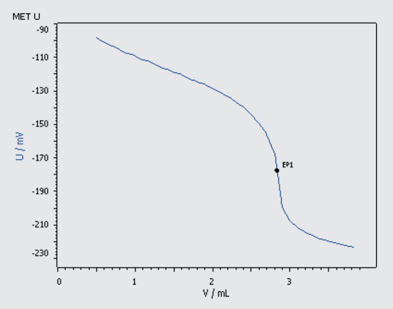

Figure 62 Example of a potentiometric titration curve of magnesium with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-128 – Automatic determination of magnesium in aqueous solution with the Cu-ISE*

Photometric with the Optrode at 610 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Ammonia buffer, pH = 10: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Mix and make up to 1 L with dist. H_2O.
- Ammonia: $w/w(NH_3) = 25\%$
- Indicator solution: Eriochrome Black T; dissolve 100 mg Eriochrome Black T in 100 mL ethanol.

Analysis

If necessary, dilute acidic sample solutions with dist. H_2O to approx. 100 mL and preneutralize to approx. pH 4–5 with $w/w(NH_3) = 25\%$. Add 5 mL ammonia buffer and 0.5 mL indicator solution, and titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Mg} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Mg}}{V_S}$$

β_{Mg}: Magnesium content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Mg}: Molar mass of magnesium; 24.305 g/mol

V_S: Sample size in mL

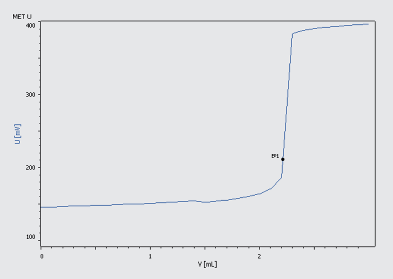

Figure 63 Photometric titration curve of magnesium with the Optrode at 610 nm

Further literature on this topic is given in

- *Application Bulletin AB-125 – Simultaneous determination of calcium, magnesium, and alkalinity by complexometric titration with potentiometric or photometric indication in water and beverage samples*

Mn – Manganese

General

Manganese behaves very similarly to Mg^{2+} in complexometric titrations. However, account must be taken of the fact that only Mn^{2+} can be titrated. In alkaline solution, $Mn(OH)_2$ forms first and then, by reaction with atmospheric oxygen, $Mn(OH)_3$. Therefore, some precautions must be taken when performing a photometric titration. Ascorbic acid is added to the sample solution to reduce any Mn^{3+}, as well as triethanolamine hydrochloride to prevent precipitation of $Mn(OH)_2$. This also masks Fe^{3+} and Al^{3+} ions. Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and the Pt-group metals can be masked with KCN in case of photometric titration. Ca^{2+} and Mg^{2+} are also determined. If they are present, manganese must be separated beforehand, for example, as MnO_2. (MnO_2 can be reduced by oxalic acid).

Table of equivalent masses

1 mL $c(Na_2EDTA) = 0.1$ mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Mn	54.938	5.494
$MnCO_3$	114.974	11.497
$MnCl_2$	125.844	12.584
$MnCl_2 \cdot 4H_2O$	197.905	19.791
$Mn(NO_3)_2 \cdot 4H_2O$	251.009	25.101
MnO	70.937	7.094
MnO_2	86.937	8.694
$Mn(OH)_2$	88.953	8.895
$MnSO_4$	151.000	15.100
$MnSO_4 \cdot H_2O$	169.015	16.902
$MnSO_4 \cdot 4H_2O$	223.060	22.306

Potentiometric with the Cu ISE

Reagents

- Titrant 1: $c(Na_2EDTA) = 0.1$ mol/L
- Titrant 2: $c(CuSO_4) = 0.1$ mol/L; dissolve 24.97 g $CuSO_4 \cdot 5H_2O$ in dist. H_2O, mix, and make up to 1 L with dist. H_2O.
- Ammonia buffer: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL $w/w(NH_3) = 25\%$. Mix and make up to 1 L with dist. H_2O.
- Ammonia: $w/w(NH_3) = 25\%$

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 45 mg Mn^{2+}, with dist. H_2O to approx. 50 mL and then, if necessary, preneutralize to pH 3–4 with $w/w(NH_3) = 25\%$. Add 10 mL $c(Na_2EDTA) = 0.1$ mol/L and 5 mL ammonia buffer, and titrate with $c(CuSO_4) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Mn} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{CuSO_4}) \times M_{Mn}}{V_S}$$

β_{Mn}: Manganese content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $CuSO_4$ standard solution

c_{CuSO_4}: Concentration of the $CuSO_4$ standard solution in mol/L

M_{Mn}: Molar mass of manganese; 54.938 g/mol

V_S: Sample size in mL

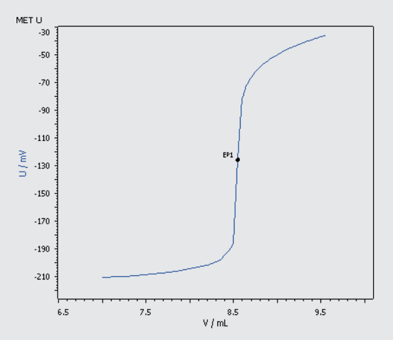

Figure 64 Potentiometric titration curve of manganese with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-120 – Automatic manganese determination in aqueous solution using the ion-selective copper electrode (Cu-ISE)*

Photometric with the Optrode at 610 nm

Reagents

- Titrant: c(Na_2EDTA) = 0.1 mol/L
- Triethanolamine hydrochloride: w/w($C_6H_{15}NO_3 \cdot HCl$) = 20%; dissolve 100 g $C_6H_{15}NO_3 \cdot HCl$ in dist. H_2O, mix, and make up to 500 mL with dist. H_2O.
- Ascorbic acid: (vitamin C), p.a.
- Ammonia buffer: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL w/w(NH_3) = 25%. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: c(NaOH) = 1 mol/L
- Indicator solution: Eriochrome Black T; dissolve 100 mg Eriochrome Black T in 100 mL ethanol.

Analysis

To the acidic sample solution, add 10 mL w/w($C_6H_{15}NO_3 \cdot HCl$) = 20% and a spatula tip of ascorbic acid. If necessary, dilute to approx. 75 mL with dist. H_2O. Preneutralize with c(NaOH) = 1 mol/L to approx. pH 7. Add 5 mL ammonia buffer and 0.25 mL indicator solution, and titrate with c(Na_2EDTA) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Mn} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Mn}}{V_S}$$

β_{Mn}: Manganese content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Mn}: Molar mass of manganese; 54.938 g/mol

V_S: Sample size in mL

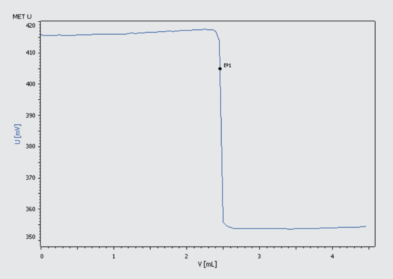

Figure 65 Example of a photometric titration curve of manganese with the Optrode at 610 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-141 – Automatic photometric determination of manganese using the Optrode*

Ni – Nickel

General

Nickel can be titrated very successfully in ammoniacal solutions. However, alkaline earth ions are also determined if they are present in large quantities. High concentrations of Al^{3+}, Fe^{3+}, and Mn^{2+} can be masked by adding triethanolamine.

Ni^{2+} can be separated from interfering metal ions (exception Pd^{2+}) by precipitating it with dimethylglyoxime. The precipitate is dissolved in conc. HCl, treated with excess Na_2EDTA, and the pH is adjusted to 10 with NH_3 before being titrated with, for example, a Zn^{2+} standard solution and Eriochrome Black T indicator.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Ni	58.693	5.869
$NiCO_3$	118.702	11.870
$NiCl_2$	129.599	12.960
$NiCl_2 \cdot 6H_2O$	237.691	23.769
$Ni(NO_3)_2$	182.703	18.270
$Ni(NO_3)_2 \cdot 6H_2O$	290.795	29.080
NiO	74.693	7.469
$NiSO_4$	154.756	15.476
$NiSO_4 \cdot 7H_2O$	280.863	28.086

Potentiometric with the Cu-ISE

Reagents

- Titrant: c(Na_2EDTA) = 0.1 mol/L
- Cu complex solution: c[$Cu(NH_4)_2$EDTA] = 0.1 mol/L (e.g., Merck No. 105217)
- Ammonia buffer: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL w/w(NH_3) = 25%. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: c(NaOH) = 1 mol/L

Analysis

If necessary, dilute the sample solution with dist. H_2O to approx. 50 mL and pre-neutralize, if necessary, to pH 4–5 with c(NaOH) = 1 mol/L. Add 5 mL ammonia buffer and 0.5 mL Cu complex solution, wait for 10–20 s while stirring, and titrate with c(Na_2EDTA) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Ni} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Ni}}{V_S}$$

β_{Ni}: Nickel content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Ni}: Molar mass of nickel; 58.693 g/mol

V_S: Sample size in mL

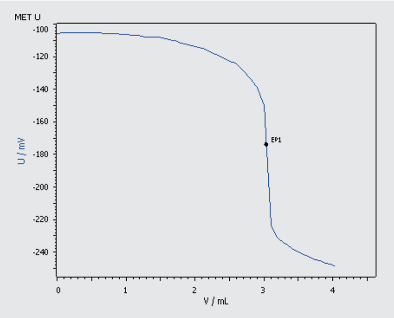

Figure 66 Potentiometric titration curve of nickel with the Cu-ISE

Photometric with the Optrode at 574 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Ammonia buffer: dissolve 54 g NH_4Cl and 350 mL $w/w(NH_3) = 25\%$ in dist. H_2O, mix, and make up to 1 L with dist. H_2O.
- Sodium hydroxide: $c(NaOH) =$ 1 mol/L
- Indicator solution: murexide; dissolve 0.2 g murexide (mixed 1:100 with NaCl) in 50 mL dist. H_2O.

Analysis

If necessary, dilute the sample solution with dist. H_2O to approx. 50 mL and then preneutralize, if necessary, to pH 4–5 with $c(NaOH) = 1$ mol/L. Add 5 mL ammonia buffer and 5 mL indicator solution, and then titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point. Titrate slowly when close to the color change.

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-129 – Automatic determination of nickel in aqueous solution with the Cu-ISE*

Calculation

$$\beta_{Ni} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Ni}}{V_S}$$

β_{Ni}: Nickel content of the sample in g/L
V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL
f: Titer of the EDTA standard solution
c_{EDTA}: Concentration of the EDTA standard solution in mol/L
M_{Ni}: Molar mass of nickel; 58.693 g/mol
V_S: Sample size in mL

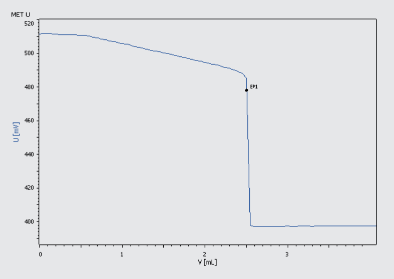

Figure 67 Example of a photometric titration curve of nickel with the Optrode at 574 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-150 – Determination of nickel using automatic photometric titration*

Pb – Lead

General

Complexometric titration of Pb^{2+} can be carried out directly, via displacement reactions (e.g., with MgEDTA), or by back titration in alkaline solution. Sulfates should not be present, if possible, because Pb^{2+} precipitates as $PbSO_4$ in their presence. The alkaline solution should be adjusted to pH 10 with NaOH, and tartrate should be used as an auxiliary complexing agent. This prevents precipitation of Pb^{2+} as $Pb(OH)_2$. However, the tartrate excess must not be too large otherwise the effective stability constant of the indicator (Eriochrome Black T) or of the PbEDTA complex would be lowered too much.

Furthermore, photometric titration in slightly acidic medium enables determination of Pb in the presence of phosphate and alkaline earth ions and is also suitable for determinations in low concentration ranges.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Pb	207.200	20.720
$Pb(CH_3COO)_2$	325.288	32.529
$Pb(CH_3COO)_2 \cdot 3H_2O$	379.334	37.933
$Pb(CH_3CH_2)_4$	323.444	32.344
$PbCO_3$	267.209	26.721
$PbCl_2$	278.106	27.811
PbO	223.199	22.320
$Pb(OH)_2$	241.215	24.122
$Pb_3(PO_4)_2$	811.543	27.051
$PbSO_4$	303.263	30.326
$Pb(NO_3)_2$	331.210	33.121

Potentiometric with the Cu-ISE

Reagents

- Titrant: c(Na_2EDTA) = 0.1 mol/L
- Cu complex solution: c[Cu(NH_4)$_2$EDTA] = 0.1 mol/L (e.g., Merck No. 105217)
- Ammonia buffer: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL w/w(NH_3) = 25%. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: c(NaOH) = 2 mol/L
- Ammonium tartrate solution: $\beta((NH_4)_2C_4H_4O_6)$ = 250 g/L

Analysis

If necessary, preneutralize acidic sample solutions to pH 4–5 with c(NaOH) = 2 mol/L. Add 50 mL ammonium tartrate, 1 mL ammonia buffer, 0.5 mL Cu complex solution, and 5 mL c(NaOH) = 2 mol/L, wait for 30 s while stirring, and then titrate with c(Na_2EDTA) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Pb} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Pb}}{V_S}$$

β_{Pb}: Lead content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Pb}: Molar mass of lead; 207.200 g/mol

V_S: Sample size in mL

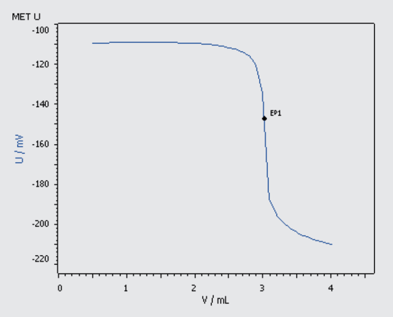

Figure 68 Potentiometric titration curve of lead with the Cu-ISE

Photometric with the Optrode at 574 nm

Reagents

- Titrant 1: c(Na_2EDTA) = 0.1 mol/L
- Titrant 2: c($ZnSO_4$) = 0.1 mol/L; dissolve 28.8 g $ZnSO_4 \cdot 7H_2O$ in dist. H_2O, mix, and make up to 1 L with dist. H_2O.
- Acetate buffer: Dissolve 123 g sodium acetate in approx. 200 mL dist. H_2O and add 50 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Sodium hydroxide: c(NaOH) = 1 mol/L
- Indicator solution: Xylenol orange; dissolve 50 mg xylenol orange disodium salt in 50 mL dist. H_2O.

Analysis

If necessary, dilute the sample solution with dist. H_2O to approx. 50 mL and adjust, if necessary, to pH 5–6 with c(NaOH) = 1 mol/L. Add 10 mL acetate buffer, 5 mL c(Na_2EDTA) = 0.1 mol/L, and 0.5 mL indicator solution. Allow to react for 1 min, and titrate with c($ZnSO_4$) = 0.1 mol/L past the first equivalence point.

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-130 – Automatic determination of lead in aqueous solution with the Cu-ISE*

Calculation

$$\beta_{Pb} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{ZnSO_4}) \times M_{Pb}}{V_S}$$

β_{Pb}: Lead content of the sample in g/L
V_{EDTA}: Added volume of EDTA standard solution in mL
f_1: Titer of the EDTA standard solution
c_{EDTA}: Concentration of the EDTA standard solution in mol/L
V_{EP1}: Volume of $ZnSO_4$ standard solution consumed up to the first equivalence point in mL
f_2: Titer of the $ZnSO_4$ standard solution
c_{ZnSO_4}: Concentration of the $ZnSO_4$ standard solution in mol/L
M_{Pb}: Molar mass of lead; 207.200 g/mol
V_S: Sample size in mL

Further literature on this topic is given in

- *Titration Application Note AN-T-140 – Automated photometric determination of lead using the Optrode*

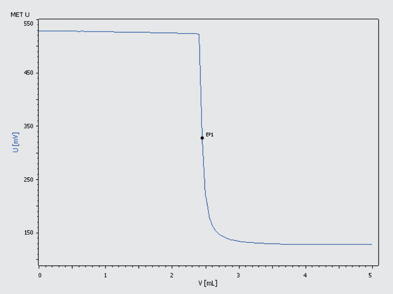

Figure 69 Example of a photometric titration curve of lead with the Optrode at 574 nm

Pd – Palladium

General

There is relatively little data in the literature on complexometric titration of the platinum group metals. Pd^{2+} is usually determined by back titration of excess EDTA. This excess is titrated with a suitable standard solution, for example, with Zn^{2+} in alkaline solution and Eriochrome Black T indicator. (In this case, the solution must be made alkaline with NaOH because Pd^{2+} reacts with ammonia to form very stable, non-titratable Pd-amine complexes). The excess EDTA is then back-titrated with xylenol orange indicator and Th^{4+} at pH = 3.0 or Tl^{3+} at pH 4 to 5. In our example, we titrate at pH 4–5 with xylenol orange indicator using the less toxic Zn^{2+} as the titrant.

Since Pt forms very stable complexes with chloride ions, Pd^{2+} can be determined alongside Pt without interference in the presence of chloride ions.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Pd	106.420	10.642
$PdCl_2$	177.326	17.733
$PdCl_2 \cdot 2H_2O$	213.357	21.336
$PdCl_4$	248.232	24.823
$PdCl_6$	319.138	31.914
$Pd(NO_3)_2$	230.430	23.043
PdO	122.419	12.242
$PdSO_4$	202.483	20.248
$PdSO_4 \cdot 2H_2O$	238.513	23.851

Photometric with the Optrode at 610 nm

Reagents

- Titrant 1: $c(Na_2EDTA) = 0.1$ mol/L
- Titrant 2: $c(ZnSO_4) = 0.1$ mol/L; dissolve 28.8 g $ZnSO_4 \cdot 7H_2O$ in approx. 500 mL dist. H_2O. Add 0.5 mL $w/w(H_2SO_4) = 96\%$, mix, and make up to 1 L with dist. H_2O. Mix 100 mL of this solution, and make up to 1 L with dist. H_2O.
- Acetate buffer, pH = 4.7: Dissolve 123 g sodium acetate in approx. 200 mL dist. H_2O and add 50 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Indicator solution: Xylenol orange; dissolve 100 mg xylenol orange disodium salt in 100 mL dist. H_2O.

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 20 mg Pd^{2+}, with dist. H_2O to approx. 100 mL and degas. Add 10 mL acetate buffer, 5 mL $c(Na_2EDTA) = 0.1$ mol/L, and 10 mL indicator solution, and titrate with $c(ZnSO_4) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Pd} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{ZnSO_4}) \times M_{Pd}}{V_S}$$

β_{Pd}: Palladium content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $ZnSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $ZnSO_4$ standard solution

c_{ZnSO_4}: Concentration of the $ZnSO_4$ standard solution in mol/L

M_{Pd}: Molar mass of palladium; 106.420 g/mol

V_S: Sample size in mL

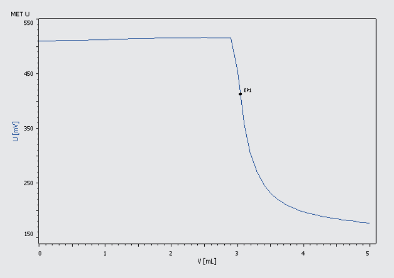

Figure 70 Photometric titration curve of palladium with the Optrode at 610 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-145 – Determination of palladium using automatic photometric titration*

Sn – Tin

General

Both valence states of tin (II and IV) form stable complexes, for example with EDTA, which can be titrated in acidic solutions owing to their high complex formation constants (log K_f = approx. 22).

Furthermore, acidic solutions should also be used because tin ions form stable hydroxo complexes that are difficult or impossible to titrate. Preneutralization must be carried out carefully with vigorous stirring.

Interfering Pb^{2+} ions are usually precipitated as $PbSO_4$ and then removed from the solution by filtration.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Sn	118.710	11.871
$SnCl_2$	189.616	18.962
$SnCl_2 \cdot 2H_2O$	225.647	22.565
$SnCl_4$	260.522	26.052
$SnCl_4 \cdot 5H_2O$	350.598	35.060
SnF_2	156.707	15.671
SnF_4	194.704	19.470
SnO	134.709	13.471
SnO_2	150.709	15.071
$Sn(OH)_2$	152.725	15.273
$Sn(OH)_4$	186.739	18.674
$SnSO_4$	214.773	21.477

Photometric with the Optrode at 574 nm

Reagents

- Titrant: c(Na_2EDTA) = 0.1 mol/L
- Buffer: pH = 2.1; dissolve 5.88 g citric acid and 3.58 g NaCl in 700 mL c(HCl) = 0.1 mol/L, and then adjust to pH 2.1 with c(NaOH) = 2 mol/L. Transfer the solution into a 1 L volumetric flask and make up to the mark with dist. H_2O.
- Indicator solution: Xylenol orange; dissolve 25 mg xylenol orange disodium salt in 100 mL dist. H_2O.

Analysis

To the very acidic sample solution, which should not contain more than 100 mg Sn^{2+} or Sn^{4+}, add 10 mL of buffer pH 2.1 and 80 mL deion. H_2O. Next, add 0.5 mL indicator solution, and titrate with $c(Na_2EDTA)$ = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Sn} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Sn}}{V_S}$$

β_{Sn}: Tin content of the sample in g/L
V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL
f: Titer of the EDTA standard solution
c_{EDTA}: Concentration of the EDTA standard solution in mol/L
M_{Sn}: Molar mass of tin; 118.710 g/mol
V_S: Sample size in mL

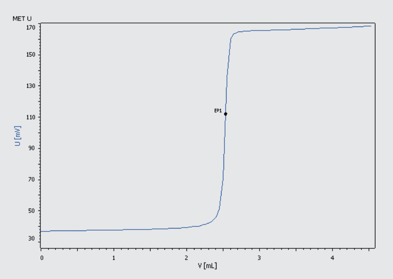

Figure 71 Example of a photometric titration curve of tin with the Optrode at 574 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-146 – Automatic determination of tin using photometric titration*

Th – Thorium

General

Thorium reacts with complexing agents to form very strong complexes with high complex formation constants. Thus it can even be titrated at pH < 1, for example, with Na_2EDTA and xylenol orange indicator. Divalent cations (except Hg^{2+}) do not interfere at such low pH values. Some authors (Pribil, R., Burger, K., Milner, G. W. C., Edwards, J. W.) have pointed out that thorium can form even stronger complexes with sulfates so that EDTA can be liberated again at pH > 1. They exploited this situation to determine Th^{4+} in the presence of Zr^{4+}. The sum of Th^{4+} and Zr^{4+}

is determined in the first step by back-titrating excess EDTA at pH 2.5–2.7 with a Bi^{3+} standard solution and xylenol orange indicator. Next, the fully titrated solution is acidified with HNO_3 to pH 1.2–1.3, and then approx. 2 g ammonium sulfate is added. The thus liberated EDTA molecules are subsequently titrated with Bi^{3+} standard solution and the same indicator.

Table of equivalent masses

1 mL $c(Na_2EDTA) = 0.1$ mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Th	232.038	23.204
$Th(NO_3)_4 \cdot 5H_2O$	570.134	57.013
ThO_2	264.037	26.404
$Th(OH)_4$	300.067	30.007
$Th(SO_4)_2$	424.150	42.415
$Th(SO_4)_2 \cdot 9H_2O$	586.290	58.629

Photometric with the Optrode at 574 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Acetate buffer: add 123 g sodium acetate and 50 mL $w/w(NH_3) = 25\%$ to a 1 L volumetric flask, mix, and make up to the mark with dist. H_2O.
- Indicator solution: Xylenol orange; dissolve 50 mg xylenol orange disodium salt in 50 mL dist. H_2O.

Analysis

If necessary, dilute the sample solution with dist. H_2O to approx. 100 mL. Degas the mixture, and add 0.5 mL indicator solution and 10 mL acetate buffer. Titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Th} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Th}}{V_S}$$

β_{Th}: Thorium content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Th}: Molar mass of thorium; 232.038 g/mol

V_S: Sample size in mL

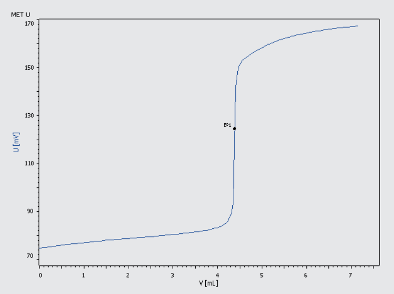

Figure 72 Photometric titration curve of thorium with the Optrode at 574 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-149 – Determination of thorium using automatic photometric titration*

Tl – Thallium

General

Tl^+ forms very weak complexes, whereas Tl^{3+} forms strong complexes with a high complex formation constant. This metal is thus titrated in its trivalent state. The determinations are carried out in slightly acidic solution so that there is no interference, for example, from any alkaline earth ions that may be present.

Thallium is often present in its monovalent state (Tl^+). The best method of oxidizing it to Tl^{3+} is to use aqua regia (mixture of HNO_3 and HCl) because nitric acid alone is insufficient. The sample is treated with aqua regia and then evaporated until it is almost dry.

Tl^+ can be separated well from interfering metal ions by adding some potassium iodide solution to the sample solution. The thus precipitated TlI is removed by filtration and then oxidized to Tl^{3+} with aqua regia as described above.

Table of equivalent masses

1 mL $c(Na_2EDTA) = 0.1$ mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Tl	204.383	20.438
Tl_2CO_3	468.775	23.439
$TlCl$	239.836	23.439
$TlCl_3$	310.742	31.074
TlI	331.287	33.129
$TlNO_3$	266.387	26.639
$Tl(NO_3)_3$	444.765	44.477
Tl_2O	424.762	21.238
Tl_2O_3	456.764	22.838
Tl_2SO_4	504.829	25.241
$Tl_2(SO_4)_3 \cdot 7H_2O$	823.061	41.153

Potentiometric with the Cu-ISE

Reagents

- Titrant 1: $c(Na_2EDTA) = 0.1$ mol/L
- Titrant 2: $c(CuSO_4) = 0.1$ mol/L dissolve 24.97 g $CuSO_4 \cdot 5\ H_2O$ in approx. 500 mL dist. H_2O, add 0.5 mL $w/w(H_2SO_4) = 96\%$, mix, and make up to 1 L with dist. H_2O.
- Acetate buffer, pH = 4.7: Dissolve 116 g ammonium acetate in approx. 200 mL dist. H_2O and add 86 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Ammonia: $w/w(NH_3) = 25\%$

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 150 mg Tl^{3+}, with dist. H_2O to approx. 50 mL. Add 5 mL acetate buffer and 10 mL $c(Na_2EDTA) = 0.1$ mol/L, and then, if necessary, adjust to pH 4.5–4.7 with $w/w(NH_3) = 25\%$. Next, titrate with $c(CuSO_4) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Tl} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{CuSO_4}) \times M_{Tl}}{V_S}$$

β_{Tl}: Thallium content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $CuSO_4$ standard solution

c_{CuSO_4}: Concentration of the $CuSO_4$ standard solution in mol/L

M_{Tl}: Molar mass of thallium; 204.383 g/mol

V_S: Sample size in mL

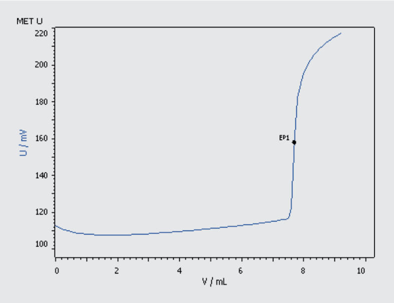

Figure 73 Potentiometric titration curve of thallium with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-122 – Automatic thallium determination in aqueous solution using the ion-selective copper electrode (Cu-ISE)*

Photometric with the Optrode at 574 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Acetate buffer, pH = 4.9: Dissolve 123 g sodium acetate in approx. 200 mL dist. H_2O and add 50 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Indicator solution: Xylenol orange; dissolve 50 mg xylenol orange disodium salt in 50 mL H_2O.

Analysis

To the acidic sample solution, add 5 mL acetate buffer and, if necessary, dilute with dist. H_2O to approx. 100 mL. Degas the mixture, add 0.5 mL indicator solution, and titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Tl} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Tl}}{V_S}$$

β_{Tl}: Thallium content of the sample in g/L
V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL
f: Titer of the EDTA standard solution
c_{EDTA}: Concentration of the EDTA standard solution in mol/L
M_{Tl}: Molar mass of thallium; 204.383 g/mol
V_S: Sample size in mL

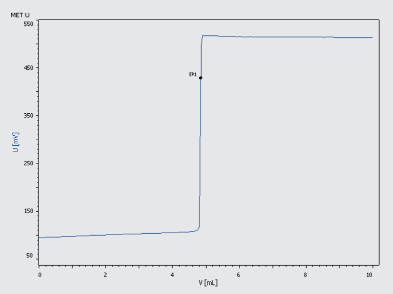

Figure 74 Example of a photometric titration curve of thallium with the Optrode at 610 nm

Metrohm Literature on this topic

- *Titration Application Note AN-T-147 – Determination of thallium using automatic photometric titration*

Zn – Zinc

General

The complexation behavior of Zn^{2+} is very similar to that of cadmium. It can be titrated in alkaline solution without problems. However, Ca^{2+} and Mg^{2+} interfere if present because they are also determined. In alkaline solution, a possible strategy is to use a first titration to determine the total sum of Zn^{2+} plus Ca^{2+} and Mg^{2+} with Eriochrome Black T indicator. Next, the Zn^{2+} is masked with KCN and the liberated Na_2EDTA is determined by means of a consecutive titration, for example, back titration with $MgSO_4$ standard solution.

However, it is much simpler to carry out the (photometric) titration at approx. pH 5 because Ca^{2+} and Mg^{2+} no longer interfere.

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Zn	65.409	6.541
$Zn(CH_3COO)_2$	183.497	18.350
$Zn(CH_3COO)_2 \cdot 2\ H_2O$	219.528	21.953
$Zn(CN)_2$	117.444	11.744
$ZnCO_3$	125.418	12.542
$ZnCl_2$	136.315	13.632
$Zn(NO_3)_2$	189.419	18.942
$Zn(NO_3)_2 \cdot 6\ H_2O$	297.510	29.751
ZnO	81.408	8.142
$Zn(OH)_2$	99.424	9.942
$ZnSO_4$	161.472	16.147
$ZnSO_4 \cdot 7\ H_2O$	287.579	28.758

Potentiometric with the Cu-ISE

Reagents

- Titrant: c(Na_2EDTA) = 0.1 mol/L
- Ammonia buffer: Dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL w/w(NH_3) = 25%. Mix and make up to 1 L with dist. H_2O.
- Cu complex solution: c[$Cu(NH_4)_2EDTA$] = 0.1 mol/L (e.g., Merck No. 105217)
- Sodium hydroxide: c(NaOH) = 1 mol/L

Analysis

If necessary, preneutralize acidic sample solutions with c(NaOH) = 1 mol/L to approx. pH 5–7 and, if necessary, make up to approx. 50 mL with dist. H_2O. Add 5 mL buffer solution and 1 mL Cu complex solution, wait for 20 s while stirring, and titrate with c(Na_2EDTA) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Zn} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Zn}}{V_S}$$

β_{Zn}:	Zinc content of the sample in g/L
V_{EP1}:	Volume of EDTA standard solution consumed up to the first equivalence point in mL
f:	Titer of the EDTA standard solution
c_{EDTA}:	Concentration of the EDTA standard solution in mol/L
M_{Zn}:	Molar mass of zinc; 65.409 g/mol
V_S:	Sample size in mL

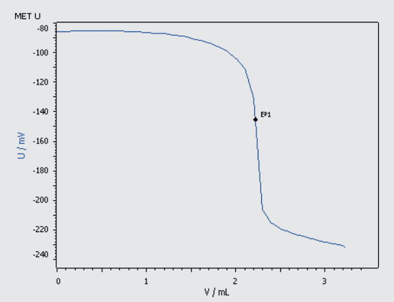

Figure 75 Potentiometric titration curve of zinc with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-108 – Fully automated determination of zinc(II) in aqueous solution*

Photometric with the Optrode at 610 nm

Reagents

- Titrant: c(Na_2EDTA) = 0.1 mol/L
- Ammonia buffer, pH = 10: dissolve 54 g NH_4Cl in approx. 200 mL dist. H_2O and add 350 mL w/w(NH_3) = 25%. Mix and make up to 1 L with dist. H_2O.
- Indicator solution: Eriochrome Black T; dissolve 100 mg each of Eriochrome Black T and ascorbic acid in 100 mL dist. H_2O.
- Sodium hydroxide: c(NaOH) = 1 mol/L

Analysis

If necessary, preneutralize acidic sample solutions with c(NaOH) = 1 mol/L to approx. pH 5 and dilute, if necessary, with dist. H_2O to approx. 50 mL. Add 5 mL ammonia buffer and 0.25 mL indicator solution, and titrate with c(Na_2EDTA) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Zn} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Zn}}{V_S}$$

β_{Zn}: Zinc content of the sample in g/L

V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL

f: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

M_{Zn}: Molar mass of zinc; 65.409 g/mol

V_S: Sample size in mL

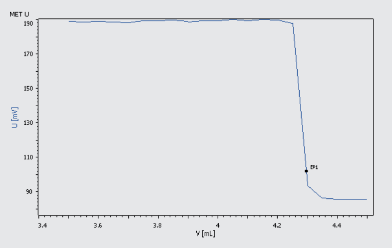

Figure 76 Example of a photometric titration curve of zinc with the Optrode at 610 nm

Metrohm Literature on this topic

- *Titration Application Note AN-T-090 – Photometric EDTA titration of zinc sulfate according to Ph. Eur. and USP*

Zr – Zirconium and Hf – Hafnium

General

Similar to Al^{3+}, zirconium has a tendency to form hydroxo complexes and must therefore be titrated in acidic solution. Fe^{3+} ions interfere, but they can be reduced to non-interfering Fe^{2+} ions by adding ascorbic acid (vitamin C) (only applies to photometric titration).

Hafnium behaves exactly like Zr^{4+} and is titrated using the same procedures. Titrimetric separation of the two metals is not possible.

The EDTA complexes of both metals are relatively stable (log K_f Zr = 19.4 / log K_f Hf = 19.1).

Table of equivalent masses

1 mL c(Na_2EDTA) = 0.1 mol/L = x mg equivalent

Formula	Molar mass in g/mol	Equivalent in mg
Hf	178.490	17.849
$HfCl_4$	320.302	32.030
$Hf(NO_3)_4$	426.510	42.651
HfO_2	210.489	21.049
$HfSO_4$	274.553	27.455
Zr	91.224	9.122
$ZrCl_4$	233.036	23.304
$ZrOCl_2 \cdot 8H_2O$	322.252	32.225
$Zr(NO_3)_4$	339.244	33.924
$Zr(NO_3)_4 \cdot 5H_2O$	429.320	42.932
ZrO_2	123.223	12.322
$Zr(OH)_4$	159.253	15.925
$Zr(SO_4)_2$	283.349	28.335
$Zr(SO_4)_2 \cdot 4H_2O$	355.410	35.541

Potentiometric with the Cu-ISE

Reagents

- Titrant 1: c(Na_2EDTA) = 0.1 mol/L
- Titrant 2: c($CuSO_4$) = 0.1 mol/L; dissolve 24.97 g $CuSO_4 \cdot 5H_2O$ in approx. 500 mL dist. H_2O. Add 0.5 mL w/w(H_2SO_4) = 96%, mix, and make up to 1 L with dist. H_2O.
- Acetate buffer, pH = 4.7: Dissolve 116 g ammonium acetate in approx. 200 mL dist. H_2O and add 86 mL glacial acetic acid. Mix and make up to 1 L with dist. H_2O.
- Ammonia: w/w(NH_3) = 25%

Analysis

If necessary, dilute the acidic sample solution, which should not contain more than 70 mg Zr^{4+} and/or 130 mg Hf^{4+}, with dist. H_2O to approx. 50 mL. Add 5 mL acetate buffer and 10 mL c(Na_2EDTA) = 0.1 mol/L, and, if necessary, adjust to pH 4.7 with w/w(NH_3) = 25%. Allow to react for approx. 1 min while stirring, and titrate with c($CuSO_4$) = 0.1 mol/L past the first equivalence point.

Calculation

$$\beta_{Zr/Hf} = \frac{(V_{EDTA} \times f_1 \times c_{EDTA} - V_{EP1} \times f_2 \times c_{CuSO_4}) \times M_{Zr/Hf}}{V_S}$$

$\beta_{Zr/Hf}$: Zirconium or hafnium content of the sample in g/L

V_{EDTA}: Added volume of EDTA standard solution in mL

f_1: Titer of the EDTA standard solution

c_{EDTA}: Concentration of the EDTA standard solution in mol/L

V_{EP1}: Volume of $CuSO_4$ standard solution consumed up to the first equivalence point in mL

f_2: Titer of the $CuSO_4$ standard solution

c_{CuSO_4}: Concentration of the $CuSO_4$ standard solution in mol/L

$M_{Zr/Hf}$: Molar mass of zirconium and hafnium; 91.224 g/mol and 178.490 g/mol, respectively

V_S: Sample size in mL

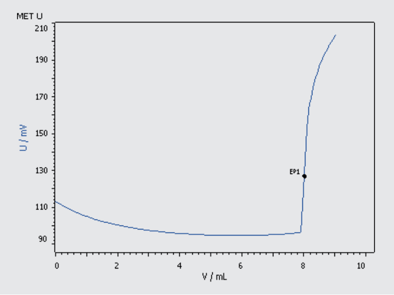

Figure 77 Example of a potentiometric titration curve of zirconium with the Cu-ISE

Further literature on this topic is given in

- *Application Bulletin AB-101 – Complexometric titrations with the Cu-ISE*
- *Titration Application Note AN-T-123 – Automatic zirconium determination in aqueous solution with ion-selective copper electrode (Cu-ISE)*

Photometric with the Optrode at 520 nm

Reagents

- Titrant: $c(Na_2EDTA) = 0.1$ mol/L
- Buffer pH = 1 (glycine / hydrochloric acid): e.g., Merck 109881
- Indicator solution: Eriochrome Cyanine; dissolve 40 mg Eriochrome Cyanine in 100 mL dist. H_2O.

Analysis

To the acidic sample solution, which should not contain more than 70 mg Zr^{4+} and/or 130 mg Hf^{4+}, add 10 mL of buffer pH 1 and 1 mL indicator solution. To the solution, add 80 mL dist. H_2O and titrate with $c(Na_2EDTA) = 0.1$ mol/L past the first equivalence point.

Calculation

$$\beta_{Zr/Hf} = \frac{V_{EP1} \times f \times c_{EDTA} \times M_{Zr/Hf}}{V_S}$$

$\beta_{Zr/Hf}$: Zirconium or hafnium content of the sample in g/L
f: Titer of the EDTA standard solution
c_{EDTA}: Concentration of the EDTA standard solution in mol/L
V_{EP1}: Volume of EDTA standard solution consumed up to the first equivalence point in mL
$M_{Zr/Hf}$: Molar mass of zirconium and hafnium; 91.224 g/mol and 178.490 g/mol, respectively
V_S: Sample size in mL

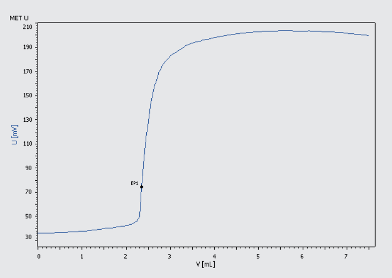

Figure 78 Photometric titration curve of zirconium with the Optrode at 520 nm

Further literature on this topic is given in

- *Titration Application Note AN-T-148 – Determination of zirconium using automatic photometric titration*

Appendix

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Photometric indication of the titration equivalence point

Species	Indicator	Wavelength
Al	Xylenol orange	610 nm
Al in cement	Xylenol orange	610 nm
Ba	Phthalein purple	574 nm
Bi	Xylenol orange	520 nm
Ca	HHSNN	610 nm
Ca in cement	Murexide	610 nm
Cd	Eriochrome Black T	610 nm
Co	Murexide	574 nm
Cu	PAN	520 nm
Fe	Sulfosalicylic acid	610 nm
Fe in cement	Sulfosalicylic acid	610 nm
Ga	Xylenol orange	610 nm
Hf	Eriochrome Cyanine	520 nm
Hg	Eriochrome Black T	502 nm
In	Xylenol orange	610 nm
Mg	Eriochrome Black T	610 nm
Mg in cement	Methylthymol blue	610 nm
Mn	Eriochrome Black T	610 nm
Ni	Murexide	574 nm
Pb	Xylenol orange	574 nm
Pd	Xylenol orange	610 nm
Sn	Xylenol orange	574 nm
Sr	Phthalein purple	574 nm
Th	Xylenol orange	574 nm
Tl	Xylenol orange	574 nm
Water, calcium hardness	HHSNN	610 nm
Water, total hardness	Eriochrome Black T	610 nm
Zn	Eriochrome Black T	610 nm
Zr	Eriochrome Cyanine	520 nm

Table of figures

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