Application Bulletin 101/5 e

Complexometric titrations with the copper-selective electrode

Industry sector

Chemical; environmental testing; pharmaceuticals; food & beverage; metal products, plating & finishing; personal care & cosmetics; raw materials, mining & metals

Keywords

Titration; back titration; direct titration; potentiometric titration; complexometric titration; ion-selective electrode, Cu; copper-selective electrode; Cu-ISE; EDTA, metal ions; rare earth elements; REE; 6.0502.140; S01; S010; S02; S020; S021; S022; S023; S027; S04; S040; S07; S070; S10; S100; S101; S102; S104; S12; S120; S15; S150; S151; S152

Summary

This Application Bulletin describes the complexometric, potentiometric determinations of metal ions using the copper-selective electrode, also known as Cu-ISE. The electrode consists of a robust and shatter-proof plastic shaft made of EP (epoxy resin/polymer) and a crystal membrane.

In the first section of this document, the working principle, the theory behind complexometric titration, and some general tips are given for electrode handling and for the determination of metal ions. In the second part, practical examples are used to demonstrate how determinations can be performed using either direct titration or back-titration. The described Cu-ISE can be used to determine water hardness, metal concentrations in rare earth elements (REEs), electroplating baths, metal salts, minerals, and ores. The following metal ions can be determined:

Al^{3+}, Ba^{2+}, Bi^{3+}, Ca^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, In^{3+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, Tl^{3+}, Zn^{2+}, Zr^{4+}, and the REEs which include Sc^{3+}, Y^{3+}, as well as the lanthanides.

Instruments and accessories

- Titrator with the modes MET U and/or DET U
- Stirrer
- Buret(s)

Electrodes

Ion-selective electrode, Cu	6.0502.140
LL ISE reference electrode	6.0750.100

Reagents

- Disodium ethylenediaminetetraacetic acid solution, $c(Na_2EDTA) = 0.1$ mol/L
- Copper sulfate solution, $c(CuSO_4) = 0.1$ mol/L
- Calcium carbonate, $CaCO_3$, ≥ 99.8%
- Copper di-ammonium EDTA solution, $c(Cu(NH_4)_2\text{-EDTA}) = 0.1$ mol/L
- Hydrochloric acid solution, $c(HCl) = 1.0$ mol/L

Depending on the chosen buffer solution, not all of the following reagents are needed:

- Sodium acetate, CH_3COONa, ≥ 99.0%
- Glacial acetic acid, CH_3COOH, 100%
- Ammonium chloride, NH_4Cl, ≥ 99.5%
- Ammonium hydroxide solution, ~25% NH_3 basis
- Sodium hydroxide, NaOH, pellets, ≥ 98.0%
- Boric acid, H_3BO_3, ≥ 99.5%

Solutions

Titrant for back-titration	$c(CuSO_4) = 0.1$ mol/L If possible, this solution should be bought from a supplier.
EDTA solution or titrant	$c(Na_2EDTA) = 0.1$ mol/L If possible, this solution should be bought from a supplier.
Auxiliary solution	$c(Cu(NH_4)_2\text{-EDTA}) = 0.1$ mol/L If possible, this solution should be bought from a supplier.
Acetate buffer pH = 4.76	123 g sodium acetate is weighed into a 1000 mL volumetric flask.

	Approximately 600 mL deionized water is added and the sodium acetate is dissolved completely. 86 mL glacial acetic acid is added, and then the flask is filled up to the mark with deionized water.
Ammonia buffer pH = 10	54 g NH_4Cl is weighed into a 1000 mL volumetric flask. Approximately 500 mL deionized water is added, and the ammonium chloride is dissolved completely. 350 mL ammonium hydroxide solution is added, and then the flask is filled up to the mark with deionized water.
Alkaline borate buffer pH = 10.5	40 g NaOH pellets are weighed into a 1000 mL volumetric flask. Approximately 500 mL deionized water is added, and the sodium hydroxide is dissolved completely. 65 g H_3BO_3 is then dissolved in this solution. After cooling to room temperature, the flask is filled up to the mark with deionized water.

Standard

Calcium carbonate	$CaCO_3$ was dried for 2 h in a drying oven at 105 °C and allowed to cool overnight in a desiccator.

Working principle

Crystal membrane

The electrode's ion-selective crystal membrane consists of a solid mixed crystal made of copper and silver sulfide (CuS/Ag_2S). The crystal's selectivity arises from the equilibrium between the Cu^{2+} ions in the sample solution and the sulfide in the crystal matrix.

The measuring range of the Cu-ISE lies between 10^{-8} and 0.1 mol/L Cu^{2+} (corresponding to approximately 0.64 µg/L to 6.4 g/L Cu^{2+}).

The Cu-ISE can be used within a pH range of 2 to 12 and a temperature range of 0–80 °C without adversely affecting the results or the electrode material.

The Cu-ISE can be used in organic solvents for short periods of time. Additionally, both the crystal and the plastic shaft are resistant to dilute hydrofluoric acid (HF).

Complexometric titration

A complex is a chemical structure composed of individual ions or molecules, written as $[ML_n]^{\pm Z}$, where M is the metal, L is the ligand, and Z is the total charge. Aminopolycarboxylic acids (APCAs) can form stable 1:1 complexes with nearly all polyvalent metal ions. One of the best-known and widely used complexing agents is ethylenediaminetetraacetic acid (EDTA).

The stability of complexes is determined by thermodynamic and kinetic factors. One measure of thermodynamic stability is the complex formation constant, K_f. In tables, this is usually given as log K_f. The larger log K_f is, the more stable the complex. The stability of metal complexes can be described by the following simplified equation, where EDTA as the ligand reacts with a divalent metal ion (Me^{2+}):

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

The effective complex formation constants are generally lowered by protons (acids), as they compete with the metal ions when they react with the complexing agent. The following rules of thumb apply:

- Metals with complex formation constants ≤ 10 are titrated in alkaline solution (e.g., Ca^{2+} or Mg^{2+}).
- Metals with complex formation constants ≥ 15 should be titrated in weakly acidic solutions (e.g., Al^{3+} or Pb^{2+}).

Titrations must be performed in buffered solutions since protons are always released during complex formation reactions. The following examples with Ca^{2+} and Al^{3+} illustrate this in a simplified manner:

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

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

Table 2 lists the logarithmic K_f values for the formation of the metal ions analyzed in this Application Bulletin using common titrants. Please note that K_f values always depend on pH, temperature, and ionic strength. Consequently, different values may be reported for the same metal ion, depending on the source.

The values in **Table 2** only apply to a moderate ionic strength of approximately 0.1 mol/L, at a temperature of 25 °C, for fully deprotonated ligands, and under conditions of 1:1 complex formation. Please note, the log K_f values can vary significantly depending on the pH value.

Table 1. The complexing agents with abbreviations and full names.

Abbreviation	Description
EDTA	Ethylenediaminetetraacetic acid
EGTA	Ethylene glycol-bis(β-aminoethyl ether)-N,N,N′,N′-tetraacetic acid
CDTA	Trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid
DTPA	Diethylenetriaminepentaacetic acid
NTA	Nitrilotriacetic acid

Table 2. Typical logarithmic K_f values for the formation of different complexes with specific metal ions.

Metal ion	EDTA	EGTA	CDTA	DTPA	NTA
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)	27.4	23.8	31.2	29.7	17.5
Ca(II)	10.7	11.0	12.5	10.7	6.4
Cd(II)	16.5	16.7	19.2	19.3	9.5
Ce(III)	15.9	16.3	18.8	20.2	15.8
Co(II)	16.5	12.5	18.9	18.4	10.4
Cu(II)	18.8	17.8	21.3	21.5	13.0
Dy(III)	18.3	16.8	19.3	22.3	16.8
Eu(III)	17.3	17.0	19.0	22.4	16.9
Er(III)	18.8	17.5	19.9	22.8	17.4
Fe(III)	25.1	20.5	28.1	28.6	15.9
Gd(III)	17.4	17.1	19.4	22.6	17.0
Ho(III)	18.6	17.2	19.6	22.7	17.2
In(III)	24.9	21.8	28.8	29.0	16.9
La(III)	15.5	15.9	17.8	19.8	15.8
Lu(III)	19.8	17.8	20.4	22.9	17.8
Mg(II)	8.8	5.2	10.3	9.3	5.5
Mn(II)	13.9	12.3	16.8	15.6	7.4
Nd(III)	16.6	16.3	18.5	21.0	16.2
Ni(II)	18.4	13.6	19.4	20.3	11.5
Pb(II)	18.0	14.7	19.7	18.8	11.4
Pm(III)	16.2	16.5	18.7	21.4	16.4
Pr(III)	16.4	16.1	18.3	20.5	16.0
Sc(III)	23.1	21.3	23.8	24.3	18.8
Sm(III)	17.1	16.6	18.9	21.8	16.5
Sr(II)	8.7	8.5	10.5	9.7	5.0
Tb(III)	17.9	17.1	19.5	22.4	17.0
Tl(III)	19.0	16.5	18.0	19.5	13.5
Tm(III)	21.9	17.6	20.1	22.8	17.5
Y(III)	18.1	17.4	19.9	22.5	17.3
Yb(III)	19.5	17.8	20.3	23.0	17.7
Zn(II)	16.5	14.5	18.7	18.8	10.7
Zr(IV)	29.3	26.5	20.7	36.9	20.9

General tips

For optimal titration results, the following points are essential to follow:

- The Cu-ISE should be stored dry and with its protective cap on. After a long period of storage, or if the curves become unstable, the Cu-ISE should be polished with the 6.2802.000 polishing set.
- You can find a video showing the best way to polish the Cu-ISE here: «How to polish a crystal ion-selective electrode».
  Only one ISE type must be polished with each polishing set. If several ion-selective electrodes are to be polished, a dedicated polishing set should be reserved for each type.
- The crystal membrane is sensitive to light due to its composition. Therefore, protect the Cu-ISE from direct sunlight.
- Avoid scratching the membrane. It should neither be touched with bare hands nor cleaned with abrasive materials (except for polishing with the recommended material). It is also sensitive to mechanical shocks.
- Check that the measuring surface of the electrode is clean.
- Clean the electrode using the spray rinse and/or dip rinse after each measurement with either deionized water or the recommended solvent.
- **Never** put electrodes in ultrasonic baths as they are damaged by such treatment.
- Do not rub the electrode dry after rinsing.
- The crystal membrane reacts particularly strongly with Ag^{+}, Hg^{2+}, and S^{2-} ions due to its composition. Very high concentrations of these ions negatively affect the titration result. For example, the total amount of aluminum in the titration beaker should not exceed 15 mg, as this would overload the Cu-ISE. More detailed information about interfering ions and other interferences can be found in the leaflet: «Manual for ion-selective electrodes» 8.109.8042.
- The membrane surface must be free of air bubbles before and during the titration.

Practical examples

Analysis

Titer EDTA

Approximately 100 mg dried $CaCO_3$ is weighed into the titration beaker with an accuracy of 0.1 mg. Then, 20 mL of deionized water and as little c(HCl) = 1.0 mol/L as possible is added dropwise until the $CaCO_3$ dissolves completely. While stirring, 30 mL of deionized water, 5 mL ammonia buffer, as well as 1 mL auxiliary solution are added, and the solution is titrated with c(Na_2EDTA) = 0.1 mol/L until after the equivalence point.

After each titration, the buret tips as well as the electrodes are rinsed thoroughly with deionized water.

Titer $CuSO_4$

Additionally, the titer of c($CuSO_4$) = 0.1 mol/L is determined for back-titrations.

10.0 mL of the standardized EDTA solution is dosed into the titration beaker. While stirring, 50 mL of deionized water as well as 10 mL of acetate buffer pH = 4.76 are added and the solution is titrated with c($CuSO_4$) = 0.1 mol/L until after the first equivalence point.

After each titration, the buret tips as well as the electrodes are rinsed thoroughly with deionized water.

Direct titration

The sample volume is chosen so that the amount of titrant consumed is approximately half the volume of the buret.

If necessary, highly acidic samples are pre-neutralized to a pH of approximately 7. Then, 5 mL of alkaline buffer solution (corresponding to the metal ions to be determined—see information below) and 1 mL of auxiliary solution is added to the sample solution. While stirring, wait for 30 seconds and then titrate the solution with standardized c(Na_2EDTA) = 0.1 mol/L until after the equivalence point.

After each titration, the buret tips as well as the electrodes are rinsed thoroughly with deionized water.

Direct titration is used for metal ions with a complex formation constant $K_f \leq 10$. It can be used to determine the following metals:

- Total hardness in water (Ca^{2+} + Mg^{2+}) with alkaline borate buffer (pH = 10.5)
- Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, or Zn^{2+}, with ammonia buffer (pH = 10)

No auxiliary solution needs to be added when determining Cu^{2+}.

Back-titration

The sample volume and the amount of excess EDTA are chosen so that approximately half of the buret volume is consumed by the titrant.

If necessary, highly alkaline samples are pre-neutralized to a pH of approximately 5. Then, 5 mL acetate buffer (pH = 4.76) and an excess of standardized $c(Na_2EDTA)$ = 0.1 mol/L are added to the sample solution. After a minimum waiting time of three minutes, while stirring, the excess of EDTA is back-titrated with standardized $c(CuSO_4)$ = 0.1 mol/L until after the equivalence point.

After each titration, the buret tips as well as the electrodes are rinsed thoroughly with deionized water.

Back-titration is used for metal ions with a complex formation constant $K_f \geq 15$. It can be used to determine the following metals:

- Al^{3+}, Bi^{3+}, Fe^{3+}, In^{3+}, Mn^{2+}, Tl^{3+}, Zr^{4+}, and the REEs which include Sc^{3+}, Y^{3+}, as well as the lanthanides, with acetate buffer (pH = 4.76)

In addition to direct titration, Mn^{2+} can also be determined by back-titration. However, for back-titration, the ammonia buffer (pH = 10) is used instead of the acetate buffer (pH = 4.76).

In^{3+} can be back-titrated using either the ammonia buffer (pH = 10) or the acetate buffer (pH = 4.76).

Parameters

Titer EDTA, titer $CuSO_4$, and direct titration

Mode	MET U
Stirring rate	8
Pause	30 s
Volume increment	0.10 mL
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
EP criterion	30 mV
EP recognition	Greatest

Back-titration

Mode	MET U
Stirring rate	8
Pause	180 s
Volume increment	0.10 mL
Signal drift	50 mV/min
Min. waiting time	30 s
Max. waiting time	30 s
EP criterion	5 mV
EP recognition	All

For certain applications, improved parameters that allow for faster titrations can be used. See the example AN-T-103 for Al^{3+}, AN-T-105 for Bi^{3+} or AN-T-107 for Fe^{3+}.

Calculations

Titer EDTA

$$f_{EDTA} = \frac{m_{CaCO_3}}{V_{EP1} \times c_{EDTA} \times M_{CaCO_3}}$$

f_{EDTA} Titer of titrant, c(Na_2EDTA) = 0.1 mol/L
m_{CaCO3}: Sample size of $CaCO_3$ in mg
V_{EP1}: Titrant consumption until the first equivalence point in mL
c_{EDTA}: Concentration of titrant, c(Na_2EDTA) = 0.1 mol/L
M_{CaCO3}: Molecular weight of calcium carbonate, M($CaCO_3$) = 100.089 g/mol

Titer $CuSO_4$

$$f_{CuSO4} = \frac{V_{EDTA} \times f_{EDTA}}{V_{EP1}}$$

f_{CuSO4} Titer of titrant, c($CuSO_4$) = 0.1 mol/L
V_{EDTA}: Volume of added excess EDTA in mL
f_{EDTA} Titer of added excess EDTA
V_{EP1}: Titrant consumption until the first equivalence point in mL

Direct titration

$$\beta_{Me} = \frac{V_{EP1} \times c_{EDTA} \times f_{EDTA} \times M_{Me}}{V_S}$$

β_{Me}: Mass concentration of the analyte in the sample in g/L
V_{EP1}: Titrant consumption until the first equivalence point in mL
c_{EDTA}: Concentration of titrant, c(Na_2EDTA) = 0.1 mol/L
f_{EDTA}: Titer of titrant, c(Na_2EDTA) = 0.1 mol/L
M_{Me}: Molecular weight of the analyte in g/mol
V_S: Sample size in mL

Back-titration

$$\beta_{Me} = \frac{(V_{EDTA} \times c_{EDTA} \times f_{EDTA} - V_{EP1} \times c_{CuSO4} \times f_{CuSO4}) \times M_{Me}}{V_S}$$

β_{Me}: Mass concentration of the analyte in the sample in g/L
V_{EDTA}: Volume of added excess EDTA in mL
c_{EDTA}: Concentration of added excess EDTA, c(Na_2EDTA) = 0.1 mol/L
f_{EDTA}: Titer of c(Na_2EDTA) = 0.1 mol/L
V_{EP1}: Titrant consumption until the first equivalence point in mL
c_{CuSO4}: Concentration of titrant, c($CuSO_4$) = 0.1 mol/L
f_{CuSO4} Titer of titrant, c($CuSO_4$) = 0.1 mol/L
M_{Me}: Molecular weight of the analyte in g/mol
V_S: Sample size in mL

Example

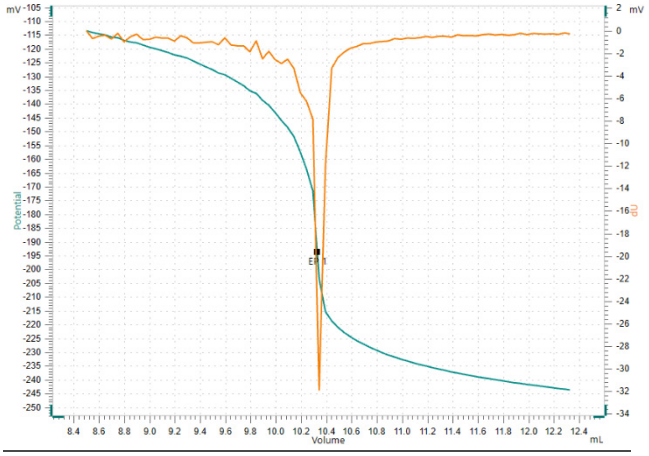

Figure 1. Titer determination of c(Na_2EDTA) = 0.1 mol/L with $CaCO_3$.

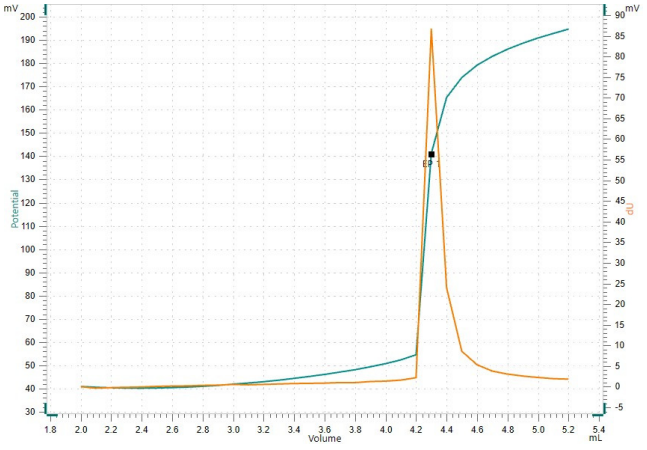

Figure 2. Back-titration of yttrium at pH = 4.76 with the Cu-ISE.

Comments

The analyses are performed in MET U mode because better titration curves are obtained for ions with high complex formation constants. However, an equivalent DET U mode also provides very accurate results.

With complexometric titrations it is normally not possible to determine a mixture of metal ions in the same solution simultaneously.

When determining water hardness, two equivalence points are typically obtained. However, the second equivalence point is used for calculations, as the first does not produce accurate results.

In the case of Mg^{2+} ions, which cannot increase the amount of free Cu^{2+} ions, ammonia is added to the solution as an auxiliary agent, leading to the formation of stable Cu-tetramine complexes. This lowers the stability constant of CuEDTA and increases the availability of free Cu^{2+} ions.

References

Monograph: Complexometric (chelatometric) Titrations, 8.108.5042

Leaflet: Manual for ion-selective electrodes, 8.109.8042

Seel, F. (1966), Die komplexometrische Titration. Die chemische Analyse. Band 45. Von G. Schwarzenbach und H. Flaschka. Ferdinand Enke Verlag, Stuttgart 1965. 5. neubearbeitete Aufl., XVI, 339 S., 42 Abb., 12 Tab., 48,– DM. Angewandte Chemie, 78: 455-455. https://doi.org/10.1002/ange.19660780817

Ross, J.W., & Frant, M.S. (1969). Chelometric indicator titrations with the solid-state cupric ion-selective electrode. Analytical Chemistry, 41, 1900-1902. https://doi.org/10.1021/ac60282a026

Baumann, E.W. / Wallace, R.M.
Cupric-selective electrode with copper(II)-EDTA for end point detection in chelometric titrations of metal ions Analytical Chemistry, 41, (1969) 2072 – 2074 https://pubs.acs.org/doi/10.1021/ac50159a050

Alumaa, P., Pentchuk, J. Ionic strength dependence of heavy metal tartrate complex stabilities. *Chromatographia* 47, 77–80 (1998). https://doi.org/10.1007/BF02466789

Misumi, S, & Taketatsu, T (1959). Complexometric titration of rare earth elements. Dissolution of the rare earth oxalate with ethylenediaminetetraacetic acid and back titration with magnesium sulfate. *Bull. Chem. Soc. Japan*, *Vol: 32*. https://doi.org/10.1246/bcsj.32.873

Flaschka, H. A., & Barnard, A. J. (Eds.). (1967). *Chelates in analytical chemistry* (Vol. 3). Marcel Dekker.

S.J. Lyle, Md.M. Rahman, Complexometric titration of yttrium and the lanthanons—I: A comparison of direct methods, Talanta, Volume 10, Issue 11, 1963, Pages 1177-1182, ISSN 0039-9140 https://doi.org/10.1016/0039-9140(63)80170-8

Author

Competence Center Titration

Metrohm International Headquarters