Metrohm

Application Bulletin 101/4 e

Complexometric titrations with the copper ion-selective electrode

Branch

General analytical chemistry; metals, electroplating; pharmaceutical industry; water, wastewater; mineral resources, cement

Keywords

Titration; complexometric titration; potentiometric titration; 6.0502.140; Ion-selective electrode, Cu ISE; copper; branch 1; branch 2; branch 4; branch 10; branch 15

Summary

This bulletin describes the complexometric, potentiometric titration of metal ions. An ion-selective copper electrode is used to indicate the equivalence point of the titration. Since the electrode does not respond directly to complexing agents, the corresponding Cu-complex is added to the solution. With the described electrode, it is possible to determine water hardness and to analyze metal concentrations in electroplating baths, metal salts, minerals and ores. The following metal ions can be determined:

Al^{3+}, Ba^{2+}, Bi^{3+}, Ca^{2+}, Co^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+} and Zn^{2+}

Instruments

- Titrator with MET mode
- 10 mL buret
- Stirrer
- Sample processor (optional)
- Pumps for rinsing and waste removal (optional)

Electrodes

Ion-selective electrode, Cu	6.0502.140
LL ISE Reference	6.0750.100

Reagents

- Disodium ethylendiaminetetraacetic acid, Na_2EDTA
- Calcium carbonate, $CaCO_3$
- Copper sulfate, $CuSO_4$
- Ethylendiaminetetraacetic acid diammonium copper salt, $Cu(NH_4)_2EDTA$
- CO_2-free dest. H_2O

Not all of the following reagents are needed, depending on the chosen buffer solution:

- Sodium acetate
- Glacial acetic acid
- Ammonium chloride, NH_4Cl
- Ammonia, $w(NH_3) = 25\%$
- Sodium hydroxide
- Boric acid, H_3BO_3

Solutions

Titrant for back titration	$c(CuSO_4) = 0.1$ mol/L in H_2O If possible this solution should be bought from a supplier
EDTA solution or Titrant	$c(Na_2EDTA) = 0.1$ mol/L in H_2O If possible this solution should be bought from a supplier
Auxiliary solution	$c(Cu(NH_4)_2EDTA) = 0.1$ mol/L in H_2O If possible this solution should be bought from a supplier
Acetate buffer	123 g Sodium acetate is weighed into a 1 L volumetric flask and dissolved in distilled water. 86 mL glacial acetic acid is added and the mixture made up to 1 L with distilled water.
Ammonia buffer	54 g NH_4Cl is weighed into a 1 L volumetric flask and dissolved in distilled water. 350 mL $w(NH_3) = 25\%$ is added and the mixture made up to 1 L with distilled water.
Alkaline borate buffer	40 g NaOH is weighed into a 1 L volumetric flask, dissolved in approximately 500 mL distilled water: 65 g H_3BO_3 is then dissolved in this solution. After

	cooling to room temperature the mixture is made up to 1 L with distilled water.

Standard solutions

Calcium carbonate	$CaCO_3$ is dried over night in a drying oven at 140 °C and allowed to cool down in a desiccator for at least 2 h.

Sample preparation

No sample preparation required.

Analysis

Titer

100 … 200 mg dried $CaCO_3$ is weighed out into a titration beaker with an accuracy of 0.1 mg and suspended in 20 mL dist. H_2O. Under stirring, c(HCl) = 5.0 mol/L is added dropwise until the $CaCO_3$ has dissolved completely. After the addition of 30 mL dist. H_2O, 5 mL ammonia buffer and 1 mL auxiliary solution, the solution is titrated with c(Na_2EDTA) = 0.1 mol/L until after the first equivalence point.

For back titrations additionally the titer of c($CuSO_4$) = 0.1 mol/L is determined. Therefore 10 mL of the standardized c(Na_2EDTA) = 0.1 mol/L is diluted with 50 mL dist. H_2O. 10 mL buffer solution is added and the solution then titrated with c($CuSO_4$) = 0.1 mol/L until after the first equivalence point.

Direct titration

If necessary the sample is pre-neutralized to pH = 5 ... 7. Then 5 mL buffer solution (pH = 10) and 1 mL auxiliary solution are added to the sample solution. While stirring, wait 30 s, then titrate the solution with c(Na_2EDTA) = 0.1 mol/L until after the first equivalence point. The following metals can be determined in this manner:

- Total hardness in water (Ca + Mg) with alkaline borate buffer
- Ca, Mg, Ba, Sr, Co, Ni, Pb, Zn with ammonia buffer pH = 10

Back titration

5 mL acetate buffer and an excess of c(Na_2EDTA) = 0.1 mol/L are added to the sample solution. After waiting a minimum of 3 min, while stirring, the excess of EDTA is titrated back with c($CuSO_4$) = 0.1 mol/L until after the first equivalence point (MET U mode with 30 s fixed waiting time). This method is used for metal ions with low complex formation speed.

- In acetate buffer pH = 4.7, it is possible to determine: Al, Bi and Fe.

Parameters

Titer

Mode	MET U
Pause	30 s
Stirrer speed	8
Volume. increment	100 µL
Signal drift	50 mV/min
Max. waiting time	26 s
EP criterion	30 mV
EP recognition	greatest

Direct titration

Mode	MET U
Pause	30 s
Stirrer speed	8
Volume. increment	100 µL
Signal drift	50 mV/min
Max. waiting time	26 s
EP criterion	30 mV
EP recognition	greatest

Back titration

Mode	MET U
Pause	3 min
Stirrer speed	8
Volume. increment	100 µL
Signal drift	50 mV/min
Min. waiting time	30 s
Max. waiting time	30 s
EP criterion	5 mV
EP recognition	all

For some applications improved parameters allowing faster titrations can be used. See AN-T-107 for iron, AN-T-103 for aluminum and AN-T-105 for bismuth.

Calculation

Titer

$$\text{Titer EDTA} = \frac{m_s}{V_{EP1} \times c_{Na_2EDTA} \times M_{CaCO_3}}$$

m_s: Sample size of dried $CaCO_3$ in mg

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

c_{Na_2EDTA}: Concentration of titrant in mol/L; here $c(Na_2EDTA) = 0.1$ mol/L

M_{CaCO_3}: Molar mass of $CaCO_3$, 100.089 g/mol

$$\text{Titer } CuSO_4 = \frac{V_{EDTA} \times f_{EDTA}}{V_{EP1}}$$

V_{EDTA}: Volume of added excess $c(Na_2EDTA) = 0.1$ mol/L in mL

f_{EDTA}: Titer of the EDTA solution

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

Direct titration

$$\beta_{Me} = \frac{V_{EP1} \times M_{Me} \times c_{Na_2EDTA}}{V_s}$$

β_{Me}: Content of the analyte in sample in g/L

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

M_{Me}: Molar mass of analyte in g/mol

c_{Na_2EDTA}: Concentration of titrant in mol/L; here $c(Na_2EDTA) = 0.1$ mol/L

V_s: Sample volume in mL

Back titration

$$\beta_{Me} = \frac{(V_{EDTA} - V_{EP1}) \times c_{CuSO_4} \times M_{Me}}{V_s}$$

β_{Me}: Content of the analyte in sample in g/L

V_{EDTA}: Volume of added excess $c(Na_2EDTA) = 0.1$ mol/L in mL

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

c_{CuSO_4}: Concentration of titrant in mol/L; here $c(CuSO_4) = 0.1$ mol/L

M_{Me}: Molar mass of analyte in g/mol

V_s: Sample volume in mL

Example determination

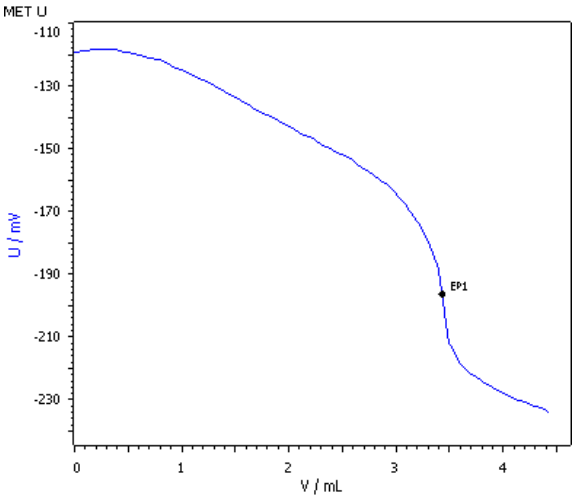

Fig. 1: Titration curve of calcium in milk (direct titration)

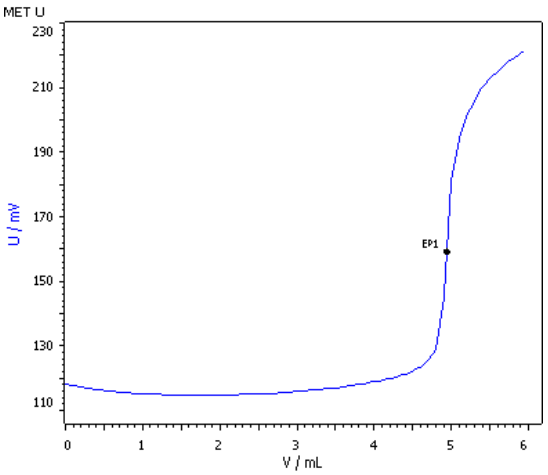

Fig. 2: Titration curve of iron in aqueous solution (back titration)

Comments

General remarks

- The larger the complex formation constant (usually log K_f is specified), the more stable the complex. The effective complex formation constants are generally lowered by protons (acids) since these compete with the metal ions in reaction with the complexing agent. The following rule of thumb holds:
  - Metals with complex formation constants ≤ 10 are titrated in alkaline solution.
  - Metals with complex formation constants ≥ 15 should be titrated in weakly acidic solutions (Fe^{3+} and Bi^{3+} can even be titrated at pH = 2).
- A table of complex formation constants can be found in the appendix.

- The surface of the Cu ISE must occasionally be polished with the Metrohm polishing kit (6.2802.000).
- Highly acidic or highly alkaline sample solutions must first be neutralized or more buffer solution added (pH check).
- For ions with high complex formation constants better titration curves are obtained with monotonic titrations (MET mode) and fixed waiting times.
- By complexometric titrations it is not possible to determine a mixture of metal ions in the same solution simultaneously.
- Usually two equivalence points are obtained by the titration of total hardness in water. The calculations must be done with the second equivalence point only because the first does not give accurate results. When a sample changer is used and the pH value has to be determined too, it is recommended to work with borate buffer. The released ammonia from the ammonia buffer would falsify the pH value of the sample.
- The total amount of aluminum in the titration beaker should not exceed 15 mg (overload of ion selective electrode). After about 20 titrations or the observation of flatter potential jumps at the endpoint the surface of the copper ion selective electrode should be polished with a polishing set.
- As an aid in the case of Mg ions, which cannot increase the amount of free Cu ions, ammonia is added to the solution. It forms relatively stable Cu-tetramine complexes. The stability constant of CuEDTA is lowered and the availability of free Cu ions increased.
- At the titration equivalence point, a quantity of complexing agent, equivalent to the metal ion to be determined, is present and the concentration of free Cu ions is thus lowered to the value of the complex formation constant. Through further additions of complexing agent, the equilibrium is shifted further to the left by a decrease in the Cu^{2+} concentration in the equation. These changes of the concentration of Cu ions form the basis of the potentiometric titration curve.

References

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Author

Competence Center Titration

Metrohm International Headquarters

Appendix

A few important complex formation constants (log K_f) for various metals and complexing agents are listed below.

Metal ions	EDTA	NTA	DCTA	DIGITA	DTPA
Ca^{2+}	10.7	6.4	13.2	11.0	10.9
Mg^{2+}	8.7	5.4	11.0	5.2	/
Sr^{2+}	8.6	5.0	10.5	8.5	/
Ba^{2+}	7.8	4.8	8.6	8.4	/
Mn^{2+}	13.8	7.4	17.4	12.3	15.6
Fe^{2+}	14.3	8.8	/	11.8	16.0
Fe^{3+}	25.1	15.9	29.3	/	27.9
Co^{2+}	16.3	10.4	19.6	12.3	19.3
Cu^{2+}	18.8	13.0	22.0	17.8	21.5
Ni^{2+}	18.6	11.5	/	11.8	20.2
Zn^{2+}	16.5	10.7	19.3	12.9	18.6
Cd^{2+}	16.5	9.8	19.0	16.1	19.3
Pb^{2+}	18.0	11.4	20.3	11.8	18.9
Hg^{2+}	21.8	/	25.0	23.2	26.7
Al^{3+}	16.1	/	18.3	/	/
Bi^{3+}	27.9	/	/	/	/

Abbreviations:

EDTA Ethylenediamine tetraacetic acid

NTA Nitrilo triacetic acid

DCTA trans-diaminocyclohexane tetraacetic acid

DIGITA bis-(aminoethyl)-glycolether tetraacetic acid

DTPA Diethylenetriamine pentaacetic acid