Metrohm

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Automated potentiometric titration of aluminum and magnesium in the same solution

Branch

General analytical laboratories; pharmaceutical industry; metals, electroplating

Keywords

Titration; automation; aluminum; magnesium; Cu ISE; complexometric titration; back-titration; DCTA; branch 1; branch 4; branch 10; 6.0502.140

Summary

Mixtures of aluminum and magnesium ions can be analyzed automatically by potentiometric titration. After addition of 1,2-diaminocyclohexanetetraacetic acid (DCTA) and complex formation the DCTA excess is back-titrated with copper(II) sulfate. The ion-selective copper electrode is used as indicator electrode. First the aluminum is determined in acidic solution, then the magnesium in alkaline solution.

Instruments

- Titrator with MET mode
- 10 mL buret, 2x
- Sample changer

Electrodes

Cu ISE	6.0502.140
LL ISE Reference	6.0750.100

Reagents

- Copper sulfate pentahydrate, $CuSO_4 \cdot 5\ H_2O$
- 1,2-Diaminocyclohexanetetraacetic acid monohydrate, DCTA
- Sodium acetate
- Glacial acetic acid
- Sulfuric acid, concentrated, H_2SO_4
- Ammonia, w(NH_3) = 10%
- Calcium standard, 6. 2303.070
- $Cu(NH_4)_2EDTA$, Cu-EDTA
- NaOH

Solutions

Titrant	c($CuSO_4$) = 0.1 mol/L If possible this solution should be bought from a supplier. Dissolve 24.968 g $CuSO_4 \cdot 5\ H_2O$ in approx. 500 mL deion. H_2O, add 0.5 mL conc. H_2SO_4 and make up to 1 L with deion. H_2O.
DCTA solution	c(DCTA) = 0.1 mol/L Dissolve 36.463 g DCTA in 400 mL c(NaOH) = 0.5 mol/L and make up to 1 L with deion. H_2O.
Buffer solution	Dissolve 123 g sodium acetate and 86 mL conc. acetic acid in deion. H_2O and make up to 1 L.
Cu-EDTA	c($Cu(NH_4)_2EDTA$) = 0.1 mol/L If possible this solution should be bought from a supplier.
NaOH solution	c(NaOH) = 1 mol/L

Standard solution

Calcium standard	c(Ca^{2+}) = 0.1 mol/L 6.2303.070

Sample preparation

No sample preparation is required.

Analysis

Titer DCTA

3 to 5 mL calcium standard is dosed into a titration vessel. 50 mL deion. H_2O and 10 mL w(NH_3) = 10% and 1 mL Cu-EDTA are added. The solution is then titrated with c(DCTA) = 0.1 mol/L until after the first equivalence point.

Titer $CuSO_4$

3 to 5 mL c(DCTA) = 0.1 mol/L is dosed into a titration vessel. 50 mL deion. H_2O and 10 mL $w(NH_3)$ = 10% are added. The solution is then titrated with $c(CuSO_4)$ = 0.1 mol/L until after the first equivalence point.

Sample

Strongly acidic sample solutions (e.g. from acid digestions) are pre-neutralized to pH = 2 … 3 with c(NaOH) = 1 mol/L.

Pipet a sample volume containing not more than 12 mg Al^{3+} and 20 mg Mg^{2+} into a titration vessel and dilute with 50 mL deion. H_2O. First the aluminum is determined. Add 6.00 mL c(DCTA) = 0.1 mol/L and 5 mL buffer solution and allow to react for 1 min under stirring. Afterwards the DCTA excess is back-titrated with $c(CuSO_4)$ = 0.1 mol/L until after the first equivalence point.

Now the magnesium can be determined. Add another 6.00 mL c(DCTA) = 0.1 mol/L and 20 mL $w(NH_3)$ = 10% to the titrated sample solution and back-titrate the DCTA excess with $c(CuSO_4)$ = 0.1 mol/L until after the first equivalence point.

Parameters

Titer DCTA and $CuSO_4$

Mode	MET U
Stirring rate	8
Signal drift	50 mV/min
Min. waiting time	5 s
Max. waiting time	26 s
Volume increment	0.1 mL
EP criterion	30 mV
EP recognition	greatest

Al determination

Mode	MET U
Stirring rate	8
Signal drift	50 mV/min
Min. waiting time	5 s
Max. waiting time	26 s
Volume increment	0.1 mL
Stop EP	1
Volume after EP	1 mL
EP criterion	30 mV
EP recognition	greatest

Mg determination

Mode	MET U
Stirring rate	8
Signal drift	50 mV/min
Min. waiting time	5 s
Max. waiting time	26 s
Volume increment	0.1 mL
EP criterion	15 mV
EP recognition	greatest

Calculation

Titer DCTA

$$f_1 = \frac{V_{Std} \times c_{Std}}{V_{EP1} \times c_{DCTA}}$$

f_1: Titer of DCTA
V_{Std}: Added volume of standard solution in mL
c_{Std}: Concentration of the standard solution in mol/L
V_{EP1}: Titrant consumption until the first equivalence point in mL
c_{DCTA}: Concentration of DCTA in mol/L

Titer $CuSO_4$

$$f_2 = \frac{V_{DCTA} \times f_1 \times c_{DCTA}}{V_{EP1} \times c_{CuSO_4}}$$

f_2: Titer of $CuSO_4$
V_{DCTA}: Added volume of DCTA in mL
f_1: Titer of DCTA
c_{DCTA}: Concentration of DCTA in mol/L
V_{EP1}: Titrant consumption until the first equivalence point in mL
c_{CuSO_4}: Concentration of $CuSO_4$ in mol/L

Sample

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

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

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

β_{Al}: Aluminum content in g/L
β_{Mg}: Magnesium content in g/L

V_{DCTA}:	Added volume of DCTA in mL
$V_{EP1.1}$:	Titrant consumption until the first equivalence point of the aluminum titration in mL
$V_{EP1.2}$:	Titrant consumption until the first equivalence point of the magnesium titration in mL
V_{Ex}:	Excess of titrant added in the aluminum titration in mL
V_{End}:	End volume of the aluminum titration in mL
f_1:	Titer of DCTA
f_2:	Titer of $CuSO_4$
c_{DCTA}:	Concentration of DCTA in mol/L
c_{CuSO_4}:	Concentration of $CuSO_4$ in mol/L
M_{Al}:	Molecular mass of aluminum; 26.982 g/mol
M_{Mg}:	Molecular mass of magnesium; 24.305 g/mol
V_S:	Sample size in mL

Example determination

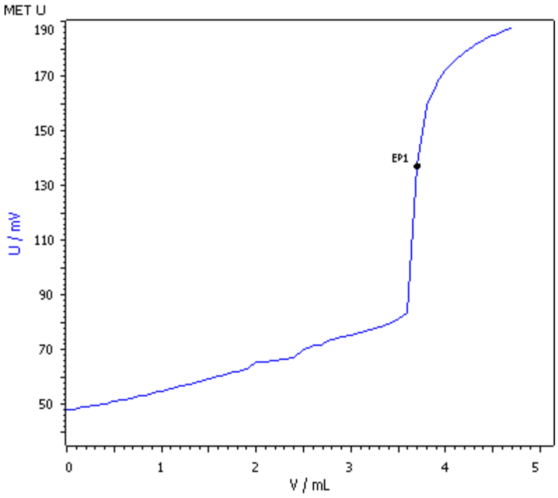

Fig. 1: Titration curve of the aluminum determination

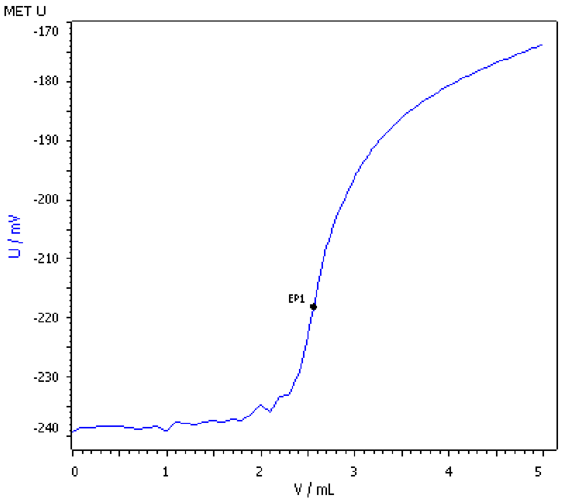

Fig. 2: Titration curve of the magnesium determination

Comments

- The surface of the Cu ISE has to be polished from time to time with aluminum oxide powder (6.2802.000 polishing set).
- A waiting time of at least 1 min before the titration of the aluminum is recommended, due to the slow reaction of aluminum with DCTA.

Author

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