Metrohm

Application Bulletin 63/3 e

Calcium, magnesium, iron and aluminum in hydraulic cement samples

Accurate determination by photometric titration

Branch

Raw materials, mining & metals; Cement & other non-metals

Keywords

Calcium; magnesium; iron; aluminum; Ca; Mg; Fe; Al; cement; titration; photometric titration; Portland cement; hydraulic cement; digestion; Optrode; indicator; 6.1115.000; S15; S151

Summary

Two types of cement materials can be distinguished: non-hydraulic cement and hydraulic cement. While non-hydraulic cement, such as hydrated lime, hardens in contact with air, hydraulic cement, such as Portland cement, requires the presence of water to harden. Still the contained elements in the various cement types are nearly the same for all. These elements are mainly calcium, magnesium, iron, aluminum and silica.

This Application Bulletin describes the determination of calcium, magnesium, iron, and aluminum by photometric titration. After digestion of the cement sample calcium, magnesium, iron and aluminum can be determined by photometric titration with the Optrode at 610 nm and different indicators.

Instruments

- Titrator with MET mode
- 2 mL buret (2×)
- 5 mL buret

Electrodes

- Optrode
- pH electrode

Reagents

- Sodium hydroxide, NaOH, puriss p.a.
- Hydrochloric acid, conc. HCl, w(HCl) >= 37%
- Glacial acetic acid, CH_3COOH, purum, > 99.0%
- Ammonium acetate, NH_4CH_3COO, > 98%
- Ammonium hydroxide, w(NH_4OH) ~ 25%
- Nitric acid, conc. HNO_3, w(HNO_3) > 65%
- Sodium chloride, NaCl, puriss p.a.
- Calcium carbonate, $CaCO_3$, puriss, p.a.
- Disodium ethylendiaminetetraacetate dihydrate, c(Na_2EDTA) = 0.1 mol/L
- Bismuth nitrate heptahydrate, $Bi(NO_3)_3 \cdot 5\ H_2O$, > 99%
- Methylthymol blue sodium salt
- Murexide
- Sulfosalicylic acid dihydrate, > 98%
- Xylenol orange disodium salt
- Calconcarboxylic acid, HHSNN
- Ethanol, purum

Solutions

Titrant 1 Ca^{2+} and Mg^{2+}	c(Na_2EDTA) = 0.1 mol/L Should be bought ready-to-use from a supplier.
Titrant 2 Fe^{3+}	c(Na_2EDTA) = 0.025 mol/L 250 mL c(Na_2EDTA) = 0.1 mol/L is pipetted into a 1 L volumetric flask and the flask is filled up to the mark with deionized water.
Titrant 3 Al^{3+}	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 c(HNO_3) = 2 mol/L and transfer into a 1 L volumetric flask. Next, make up to 1 L with deionized water.
c(NaOH) = 2 mol/L	80 g NaOH is dissolved in approx. 600 mL deionized water and transferred to a 1 L volumetric flask. The solution is filled up to the mark with deionized water.
c(NH_4OH) = 2 mol/L	144 mL w(NH_3) = 25% is given into a 1 L volumetric flask and

	filled up to the mark with deionized water.
Acetate buffer	60 g ammonium acetate is dissolved in approx. 300 mL deionized water and transferred into a 1 L volumetric flask. Afterwards 400 mL acetic acid is added and the solution is filled up to the mark with deionized water.
Ammonium buffer	54 g ammonium chloride is dissolved in approx. 300 mL deionized water and transferred into a 1 L volumetric flask. 350 mL w(NH3) = 25% is added and the solution is filled up to the mark with deionized water.
c(HCl) = 6 mol/L	590 mL w(HCl) = 37% is given into a 1 L volumetric flask containing already approx. 250 mL deionized water. After cooling down, the solution is filled up to the mark with deionized water.
c(HNO_3) = 2 mol/L	192 mL w(HNO_3) = 65% is given into a 1 L volumetric flask containing already approx. 500 mL deionized water. After cooling down, the solution is filled up to the mark with deionized water.
Murexide indicator (Ca indicator)	100 mg murexide is added to 10 g sodium chloride and finely ground.
Methylthymol blue indicator (Mg indicator)	100 mg methylthymol blue sodium salt is added to 10 g sodium chloride and finely ground.
Xylenol orange indicator (Al indicator)	100 mg xylenol orange disodium salt is dissolved in 100 mL deionized water.
Sulfosalicylic acid indicator (Fe indicator)	4 g sulfosalicylic acid dihydrate is dissolved in 100 mL deionized water
HHSNN indicator (titer Na_2EDTA)	20 mg calconcarboxylic acid is dissolved in 50 mL ethanol

Standards

$CaCO_3$ standard solution	$CaCO_3$ is dried over night in a drying oven at 140 °C and allowed to cool down in a desiccator for at least 2 h. 250 mg dried $CaCO_3$ is weighed into a 100 mL beaker and dissolved with as much c(HCl) = 6 mol/L as needed. The solution is transferred into a 100 mL volumetric flask and filled up to the mark with deionized water.

Sample preparation

Cement samples

4 g Portland cement is given into a 250 mL beaker and 6 g ammonium chloride is added. For the digestion 48 mL w(HCl) = 37% is added slowly along the beaker walls. Caution! A fierce reaction occurs. After the fierceness of the reaction has decreased, 3 mL w(HNO_3) = 65% is added. The reaction become fiercer again. After the reaction has weakened, the beaker is placed on a heating plate at 200 °C for 1 h.

The suspension, containing the undigested silicon oxide and the digested metal compounds is filtered through a folded filter into a 500 mL volumetric flask and rinsed with hot deionized water. The solution is filled up to the mark with deionized water.

Analysis

Titer determination

c(Na_2EDTA) = 0.1 mol/L

250 mg $CaCO_3$ is given into a 100 mL beaker and dissolved with as much c(HCl) = 6 mol/L as needed. The solution is transferred into a 100 mL volumetric flask and filled up to the mark with deionized water. For the titer determination 10 mL of this solution is pipetted into a plastic beaker. 50 mL deionized water is added and the solution is pre-neutralized with c(NaOH) = 2 mol/L to pH 5–7. After addition of 2 mL c(NaOH) = 2 mol/L and 1.5 mL HHSNN indicator solution the solution is titrated with c(Na_2EDTA) = 0.025 mol/L until after the equivalence point.

c(Na_2EDTA) = 0.025 mol/L

250 mg $CaCO_3$ is given into a 100 mL beaker and dissolved with as much c(HCl) = 6 mol/L as needed. After dissolution, the solution is transferred into a 100 mL volumetric flask and filled up to the mark with deionized water. For the titer determination 1 mL of this solution is pipetted into a beaker,

50 mL deionized water is added and the solution is pre-neutralized with c(NaOH) = 2 mol/L to pH 5–7. After addition of 2 mL c(NaOH) = 2 mol/L and 1.5 mL HHSNN indicator solution the solution is titrated with c(Na_2EDTA) = 0.025 mol/L until after the equivalence point.

c($Bi(NO_3)_3$) = 0.05 mol/L

Before determining the titer of the bismuth nitrate solution it is necessary to determine the titer of c(Na_2EDTA) = 0.1 mol/L because the titer is used for the titer determination of the bismuth nitrate solution.

0.5 mL of the c(Na_2EDTA) = 0.1 mol/L solution is dosed into a plastic beaker and 70 mL deionized water is added. After addition of 1 mL xylenol orange indicator solution and 1 mL c(HNO_3) = 2 mol/L, the solution is titrated with c($Bi(NO_3)_3$) = 0.05 mol/L until after the equivalence point.

Sample determination

All analyses are carried out with the Optrode at a wavelength of 610 nm. Before using the Optrode it is recommended that the LED is switched on for a minimum of 5 minutes prior to titration.

Determination of calcium

2.5 mL sample solution is pipetted into a plastic beaker and approx. 70 mL deionized water is added. The pH of the solution is adjusted with c(NaOH) = 2 mol/L to pH 12 and a spatula tip of murexide indicator is added. The solution is titrated with c(Na_2EDTA) = 0.1 mol/L until after the second break point. The equivalence point is visible by a color change from pink to purple. The mean value of the consumption is saved as common variable because this value is used for the calculation of the magnesium content.

Determination of magnesium

2.5 mL sample solution is pipetted into a plastic beaker and approx. 70 mL deionized water is added. The pH of the solution is adjusted with c(NH_4OH) = 2 mol/L to pH 10 and a spatula tip of methylthymol blue indicator is added. The solution is titrated with c(Na_2EDTA) = 0.1 mol/L until after the equivalence point. The equivalence point is visible by a color change from blue to clear. For a fast titration, a start volume corresponding to the volume obtained for the calcium determination is added.

Determination of iron

10 mL sample solution is pipetted into a plastic beaker and approx. 70 mL deionized water is added. The pH of the solution is adjusted depending on the actual pH with c(HCl) = 6 mol/L or with c(NH_4OH) = 2 mol/L to a pH between 1.5 and 2. After addition of 1 mL sulfosalicylic acid indicator solution the sample solution is titrated with c(Na_2EDTA) = 0.025 mol/L until after the first break point. The endpoint is visible by a color change of claret-red to clear. For the calculation of the aluminum content the mean value of the consumption is saved a common variable.

Determination of aluminum

10 mL sample solution is pipetted into a plastic beaker and 70 mL deionized water is added. After addition of 10 mL acetate buffer the pH is adjusted with c(HCl) = 6 mol/L to pH 3.5. Then, 1.25 mL c(Na_2EDTA) = 0.1 mol/L is added and the solution is stirred for a reaction time of at least 3 min. For the titration 1 mL xylenol orange indicator solution is added and the titration is carried out with c($Bi(NO_3)_3$) = 0.05 mol/L until after the equivalence point. The equivalence point is visible by a color change of orange/pink to purple/blue.

Parameters

Titer determination

c(Na_2EDTA) = 0.1 mol/L and c(Na_2EDTA) = 0.025 mol/L

Mode	MET U
Titration rate	slow
Stirring rate	off
Signal drift	20 mV/min
Min. waiting time	0 s
Max. waiting time	38 s
Volume increment	0.05 mL
Stop volume	2 mL (5 mL)*
Stop EP	1
Volume after EP	0.5
EP criterion	15
EP recognition	all

* For c(Na_2EDTA) = 0.1 mol/L

c($Bi(NO_3)_3$) = 0.05 mol/L

Mode	MET U
Titration rate	user
Stirring rate	off
Signal drift	20 mV/min
Min. waiting time	0 s
Max. waiting time	38 s
Volume increment	0.025 mL
Stop volume	2 mL
Stop EP	1
Volume after EP	0.5
EP criterion	15
EP recognition	all

Sample determination

Determination of calcium

Mode	MET U
Titration rate	optimal
Stirring rate	off
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Volume increment	0.1 mL
Stop volume	5 mL
Stop EP	1
Volume after EP	1
EP recognition	off
Additional Eval.	break point evaluation
EP criterion	0.3
Slope	0.9
Smoothing factor	5
Window	off

Determination of magnesium

Mode	MET U
Titration rate	user
Stirring rate	off
Start volume	$V_{BP2, Ca}$ – 0.5 mL
Signal drift	30 mV/min
Min. waiting time	0 s
Max. waiting time	32 s
Volume increment	0.025 mL
Stop volume	5 mL
Stop EP	1
Volume after EP	1
EP criterion	15
EP recognition	all

$V_{BP2, Ca}$ = Used volume for the calcium determination until the second break point in mL

Determination of iron

Mode	MET U
Titration rate	slow
Stirring rate	off
Signal drift	20 mV/min
Min. waiting time	0 s
Max. waiting time	38 s
Volume increment	0.05 mL
Stop volume	2 mL
Stop EP	1
Volume after EP	0.5
EP recognition	off
Additional Eval.	break point evaluation
EP criterion	0.7
Slope	0.9
Smoothing factor	5
Window	off

Determination of aluminum

Mode	MET U
Titration rate	user
Stirring rate	off
Signal drift	20 mV/min
Min. waiting time	0 s
Max. waiting time	38 s
Volume increment	0.025 mL
Stop volume	2 mL
Stop EP	1
Volume after EP	1
EP criterion	15
EP recognition	greatest

Calculation

Titer determination

c(Na_2EDTA) = 0.1 mol/L and 0.025 mol/L

$$f_{EDTA} = \frac{m_{S,\,A}}{V_{EP1} \times c_{EDTA} \times M_A}$$

with:

$$m_{S,\,A} = \frac{m_{S,\,S} \times V_A}{V_S}$$

f_{EDTA}: Titer of Na_2EDTA solution

$m_{S,\,A}$: Amount of calcium carbonate in the aliquot used for titer determination in mg

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

c_{EDTA}: Concentration of the Na_2EDTA solution; c(Na_2EDTA) = 0.1 mol/L or 0.025 mol/L

M_A: Molar mass of calcium carbonate; 100.09 g/mol

$m_{S,\,S}$: Amount of calcium carbonate in the stock solution used for titer determination in mg

V_A: Aliquot volume used for the titer determination in mL; 10 or 1 mL

V_S: Total volume of the stock solution in mL

c($Bi(NO_3)_3$) = 0.05 mol/L

$$f_{Bi(NO3)3} = \frac{V_{EDTA,\,0.1} \times f_{EDTA,\,0.1} \times c_{EDTA,\,0.1}}{V_{EP1} \times c_{Bi(NO3)3}}$$

$f_{Bi(NO3)3}$: Titer of $Bi(NO_3)_3$ solution

$V_{EDTA,\,0.1}$: Added volume of c(Na_2EDTA) = 0.1 mol/L in mL

$f_{EDTA,\,0.1}$: Titer of c(Na_2EDTA) = 0.1 mol/L

$c_{EDTA,\,0.1}$: Concentration of Na_2EDTA solution; c(Na_2EDTA) = 0.1 mol/L

V_{EP1}: Titrant consumption of $Bi(NO_3)_3$ until the first equivalence point

$c_{Bi(NO3)3}$: Concentration of $Bi(NO_3)_3$ solution; c($Bi(NO_3)_3$) = 0.05 mol/L

Sample determination

Calcium oxide content

$$w_{CaO} = \frac{f_{EDTA,\,0.1} \times c_{EDTA,\,0.1} \times V_{BP2} \times M_{CaO} \times 40}{m_S}$$

w_{CaO}: Calcium oxide content in %

$f_{EDTA,\,0.1}$: Titer of c(Na_2EDTA) = 0.1 mol/L

$c_{EDTA,\,0.1}$: Concentration of Na_2EDTA solution; c(Na_2EDTA) = 0.1 mol/L

V_{BP2}: Titrant consumption until the second break point in mL

M_{CaO}: Molar mass of calcium oxide; 56.08 g/mol

40: Conversion factor (see below)

m_S: Sample size used for digestion in g

$$40 = \frac{1000 \times 100}{2.5 \times 1000}$$

1000: Digestion solution filled up to 1 L

100: Conversion factor for %

1000: Conversion factor mg to g

2.5: Used amount of digested solution in mL

Magnesium oxide content

$$V_{used,\,Mg} = V_{EP1,\,Mg} - V_{BP2,\,Ca}$$

$V_{used,\,Mg}$: Corrected volume used for magnesium determination in mL

$V_{EP1,\,Mg}$; Titrant consumption until the first equivalence point in mL

$V_{BP2,\,Ca}$: Titrant consumption until the second break point in mL

$$w_{MgO} = \frac{V_{used,\,Mg} \times f_{EDTA,\,0.1} \times M_{MgO} \times c_{EDTA,\,0.1} \times 40}{m_S}$$

w_{CaO}: Calcium oxide content in %

$V_{used,\,Mg}$: Corrected volume used for magnesium determination in mL

$f_{EDTA,\,0.1}$: Titer of c(Na_2EDTA) = 0.1 mol/L

M_{MgO}: Molar mass of magnesium oxide; 40.32 g/mol

$c_{EDTA,\,0.1}$: Concentration of Na_2EDTA solution; c(Na_2EDTA) = 0.1 mol/L

40: Conversion factor (see below)

m_S: Sample size used for digestion in g

$$40 = \frac{1000 \times 100}{2.5 \times 1000}$$

1000: Digestion solution filled up to 1 L

100: Conversion factor for %

1000: Conversion factor mg to g

2.5: Used amount of digested solution in mL

Iron(III)oxide content

$$n_{Fe2O3} = f_{EDTA,\,0.025} \times c_{EDTA,\,0.025} \times V_{BP1}$$

n_{Fe2O3}: Amount of iron oxide in mmol

$f_{EDTA,\,0.025}$: Titer of c(Na_2EDTA) = 0.025 mol/L

$c_{EDTA,\,0.025}$: Concentration of Na_2EDTA solution; c(Na_2EDTA) = 0.025 mol/L

V_{BP1}: Titrant consumption until the first break point in mL

$$w_{Fe2O3} = \frac{n_{Fe2O3} \times M_{Fe2O3} \times 5}{m_S}$$

w_{Fe2O3}: Iron oxide content in %
n_{Fe2O3}: Amount of iron oxide in mmol
M_{Fe2O3}: Molar mass of iron(III) oxide; 159.7 g/mol
5: Conversion factor (see below)
m_S: Sample size used for digestion in g

$$5 = \frac{1000 \times 100}{10 \times 1000 \times 2}$$

1000: Digestion solution filled up to 1 L
100: Conversion factor for %
1000: Conversion factor mg to g
10: Used amount of digested solution in mL
2: Stoichiometric factor (Fe to Fe_2O_3)

Aluminum oxide content

$$n_{EDTA,\,0.1} = V_{EDTA,\,0.1} \times f_{EDTA,\,0.1} \times c_{EDTA,\,0.1}$$

$n_{EDTA,\,0.1}$: Amount of added Na_2EDTA in mmol
$V_{EDTA,\,0.1}$: Volume of c(Na_2EDTA) = 0.1 mol/L added for back-titration in mL
$f_{EDTA,\,0.1}$: Titer of c(Na_2EDTA) = 0.1 mol/L
$c_{EDTA,\,0.1}$: Concentration of Na_2EDTA solution; c(Na_2EDTA) = 0.1 mol/L

$$n_{Al + Fe} = V_{EP1} \times f_{Bi(NO3)3} \times c_{Bi(NO3)3}$$

$n_{Al + Fe}$: Amount of aluminum and iron in mmol
V_{EP1}: Titrant consumption until the first equivalence point in mL
$f_{Bi(NO3)3}$: Titer of c($Bi(NO_3)_3$) = 0.1 mol/L
$c_{Bi(NO3)3}$: Concentration of $Bi(NO_3)_3$ solution; c($Bi(NO_3)_3$) = 0.05 mol/L

$$w_{Al2O3} = \frac{(n_{EDTA,\,0.1} - n_{Fe2O3} - n_{Al + Fe}) \times M_{Al2O3} \times 5}{m_S}$$

w_{Al2O3}: Aluminum oxide content in %
$n_{EDTA,\,0.1}$: Amount of added Na_2EDTA in mmol
n_{Fe2O3}: Amount of iron oxide in mmol
$n_{Al + Fe}$: Amount of aluminum and iron in mmol
M_{Al2O3}: Molar mass of aluminum oxide; 101.96 g/mol
5: Conversion factor (see below)
m_S: Sample size used for digestion in g

$$5 = \frac{1000 \times 100}{10 \times 1000 \times 2}$$

1000: Digestion solution filled up to 1 L
100: Conversion factor for %
1000: Conversion factor mg to g
10: Used amount of digested solution in mL
2: Stoichiometric factor (Al to Al_2O_3)

Example determination

Titer determination

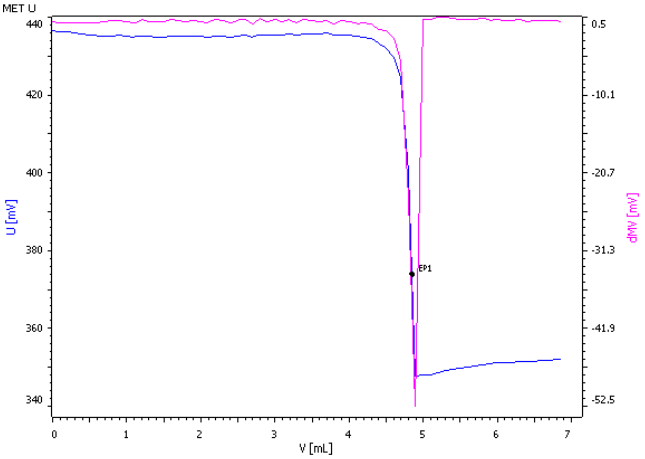

Fig. 1: Potentiometric titer determination of c(Na_2EDTA) = 0.1 mol/L

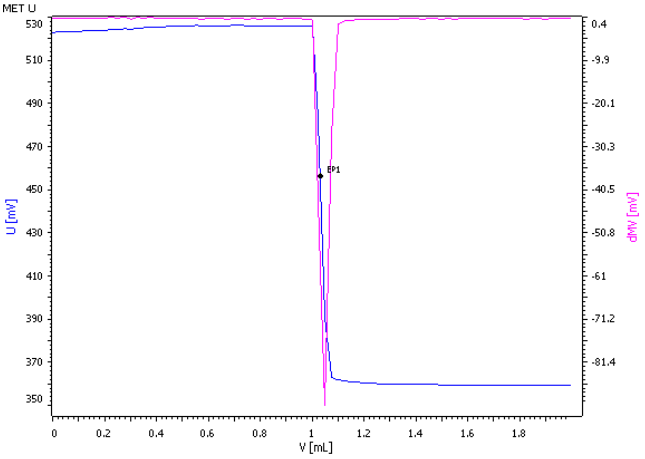

Fig. 2: Potentiometric titer determination of c($Bi(NO_3)_3$) = 0.05 mol/L

Sample determination

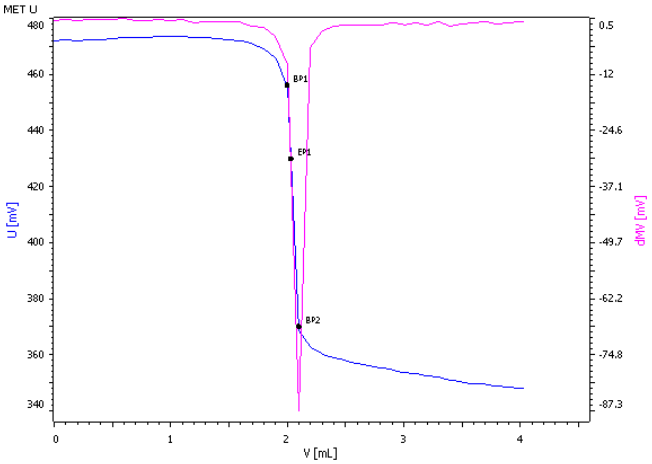

Fig. 3: Potentiometric determination of calcium with c(Na_2EDTA) = 0.1 mol/L

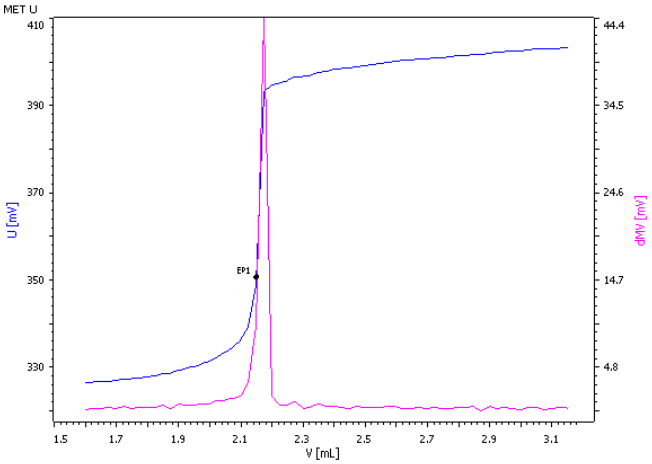

Fig. 4: Potentiometric determination of magnesium with c(Na_2EDTA) = 0.1 mol/L

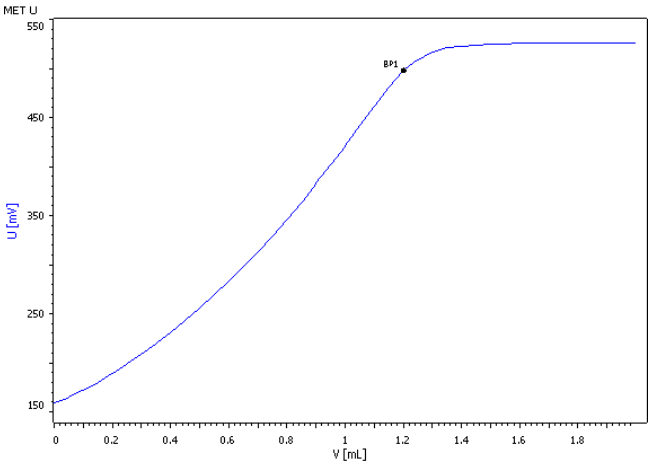

Fig. 5: Potentiometric determination of iron with c(Na_2EDTA) = 0.025 mol/L

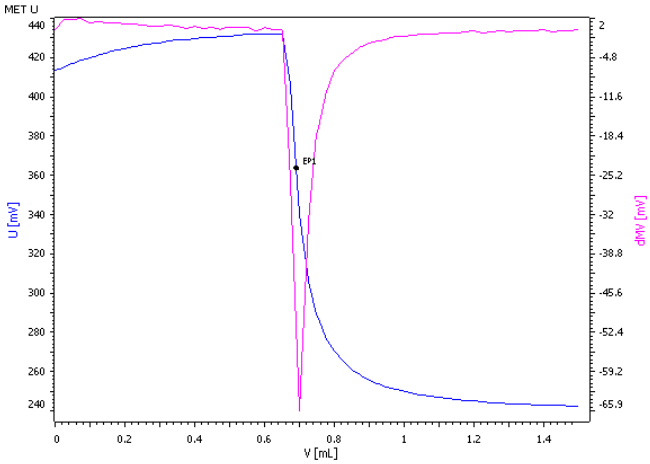

Fig. 6: Potentiometric determination of iron with c($Bi(NO_3)_3$) = 0.025 mol/L

Comments

- The herein proposed methods for the calcium and magnesium content determination have the advantage that inexpensive EDTA can be used in comparison to the EGTA and DCTA.
- According to the norm EN 196-2 the aluminum content is determined by direct titration with EDTA solution. As aluminum reacts very slowly with EDTA the titration is carried out in a boiling solution. By using a back-titration the boiling is avoided.
- For the back-titration of aluminum a minimum waiting time of 200 s have to be kept between the addition of EDTA and the titration, or the solution has to be boiled for at least 60 s after addition of the EDTA solution.
- Instead of the commonly used zinc sulfate for EDTA back-titration, bismuth nitrate was used as titrant. It was found that zinc does not form stable complexes at pH 3.5. Higher pH values are not recommended as the aluminum starts to form hydroxide complexes, which will not be detected by complexometric titration.
- With the given analysis description for the iron content determination, it is not necessary to titrate at elevated temperatures.

References

- ISO 29581-1
  Cement — Test methods — Part 1: Analysis by wet chemistry
- EN 196-2
  Methods of testing cement; Part 2: Chemical analysis of cement

Date

March 2020

Author

Competence Center Titration

Metrohm International Headquarters