Metrohm

Application Bulletin 63/3 e

Determination of calcium, magnesium, iron and aluminum in digested cement samples by photometric titrations

Branch

General analytical chemistry; mineral resources, cement

Keywords

Calcium; magnesium; iron; aluminum; Ca; Mg; Fe; Al; cement; Portland cement; digestion; Optrode; indicator; 6.1115.000; branch 1; branch 15

Summary

Different kinds of cement are known but the contained elements are nearly the same for all types. These elements are mainly calcium, magnesium, iron, aluminum and silicon.

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, respectively. The silicon content has to be determined gravimetrically.

Samples

- Portland Cement

Instruments

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

Electrodes

- Optrode
- pH electrode

Reagents

- Sodium hydroxide, puriss p.a.
- Hydrochloric acid, >= 37%
- Acetic acid, purum, > 99.0%
- Ammonium acetate, > 98%
- Ammonium hydroxide, ~ 25%
- Nitric acid, > 65%
- Sodium chloride, puriss p.a.
- Titriplex® III – solution, c(Na_2EDTA) = 0.1 mol/L
- Zinc sulfate heptahydrate, > 99%
- Methylthymol blue sodium salt
- Murexide
- Sulfosalicylic acid dihydrate, > 98%
- Xylenol orange disodium salt
- Iron(II)sulfate heptahydrate, > 99.5%
- Aluminum powder
- Magnesium, > 99.5%
- Calcium oxide, reagent grade
- Calconcarboxylic acid
- Ethanol, purum

Solutions

c(NaOH) = 2 mol/L	80 g NaOH is dissolved in approx. 600 mL deion. water and transferred to a 1 L volumetric flask. The solution is filled up to the mark with deion. water.
c(NH_3) = 2 mol/L	144 mL w(NH_3) = 25% is given into a 1 L volumetric flask and filled up to the mark with deion. water.
Acetate buffer	60 g ammonium acetate is dissolved in approx. 300 mL deion. 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 deion. water.
Ammonium buffer	54 g ammonium chloride is dissolved in approx. 300 mL deion. 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 deion. water.

c(HCl) = 6 mol/L	590 mL w(HCl) = 37% is given into a 1 L volumetric flask containing already approx. 250 mL deion. water. After cooling down, the solution is filled up to the mark with deion. 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 deion. water. After the solution has cooled down, the solution is filled up to the mark with deion. water.
Murexide indicator	100 mg murexide is added to 10 g sodium chloride and finely ground.
Methylthymol blue indicator	100 mg methylthymol blue sodium salt is added to 10 g sodium chloride and finely ground.
Xylenol orange indicator	100 mg xylenol orange disodium salt is dissolved in 100 mL deion. water.
Sulfosalicylic acid indicator	4 g sulfosalicylic acid dihydrate is dissolved in 100 mL deion. water
Calconcarboxylic acid indicator (HHSNN)	20 mg calconcarboxylic acid is dissolved in 50 mL ethanol
Titrant 1	$c(Na_2EDTA)$ = 0.1 mol/L Should be bought ready-to-use from a supplier, e.g. Merck
Titrant 2	$c(ZnSO_4)$ = 0.1 mol/L 28.7 g $ZnSO_4 \cdot 9\ H_2O$ is dissolved in approx. 500 mL deion. water, transferred into a 1 L volumetric flask and filled up to the mark with deion. 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 deion. water. The solution is filled up to the mark with deion. 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 deion. water. For the titer determination 10 mL of this solution is pipetted into a plastic beaker. 50 mL deion. 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 first equivalence point.

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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 deion. water. For the titer determination 1 mL of this solution is pipetted into a beaker, 50 mL deion. 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 first 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 deion. 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 first equivalence point.

Sample Analysis

All analyses are carried out with the Optrode at a wave length 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 deion. 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 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 deion. water is added. The pH of the solution is adjusted with c(NH_3) = 2 mol/L to pH 10 and a spatula tip of methylthymol blue is added. The solution is titrated with c(Na_2EDTA) = 0.1 mol/L until after the first equivalence point. The equivalence point is visible by a color change from blue to clear.

Determination of iron

10 mL sample solution is pipetted into a plastic beaker and approx. 70 mL deion. 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_3) = 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 deion. water is added. After addition of 10 mL acetate buffer the pH is adjusted with c(HCl) = 6 mol/L to pH 3.5. 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 first 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 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 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 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

$$f(EDTA_{0.1}) = \frac{m(CaCO_3)}{V_{EP1} \times c(EDTA_{0.1}) \times M(CaCO_3)}$$

$f(EDTA_{0.1})$:	Titer of Na_2EDTA solution
$m(CaCO_3)$:	Amount of calcium carbonate used for titer determination in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
$c(EDTA_{0.1})$:	Concentration of the Na_2EDTA solution (0.1 mol/L)
$M(CaCO_3)$:	100.09 g/mol

c(Na_2EDTA) = 0.025 mol/L

$$f(EDTA_{0.025}) = \frac{m(CaCO_3)}{V_{EP1} \times c(EDTA_{0.025}) \times M(CaCO_3)}$$

$f(EDTA_{0.025})$:	Titer of Na_2EDTA solution
$m(CaCO_3)$:	Amount of calcium carbonate used for titer determination in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
$c(EDTA_{0.025})$:	Concentration of the Na_2EDTA solution (0.025 mol/L)
$M(CaCO_3)$:	100.09 g/mol

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

$$f(Bi(NO_3)_3) = \frac{V(EDTA_{0.1}) \times f(EDTA_{0.1}) \times c(EDTA_{0.1})}{V_{EP1} \times c(Bi(NO_3)_3)}$$

$f(Bi(NO_3)_3)$:	Titer of $Bi(NO_3)_3$ solution
$V(EDTA_{0.1})$:	Added volume of Na_2EDTA solution with a concentration of 0.1 mol/L
$f(EDTA_{0.1})$:	Titer of Na_2EDTA solution with a concentration of 0.1 mol/L
$c(EDTA_{0.1})$:	Concentration of Na_2EDTA solution (0.1 mol/L)
V_{EP1}:	Titrant consumption of $Bi(NO_3)_3$ until the first equivalence point
$c(Bi(NO_3)_3)$:	Concentration of $Bi(NO_3)_3$ solution (0.05 mol/L)

Calculation of the different contents

Calcium oxide content

$$w(CaO) = \frac{f(EDTA_{0.1}) \times c(EDTA_{0.1}) \times V_{BP2} \times M(CaO) \times 40}{m(Sample)}$$

w(CaO):	Calcium oxide content in %
$f(EDTA_{0.1})$:	Titer of Na_2EDTA solution
$c(EDTA_{0.1})$:	Concentration of the Na_2EDTA solution (0.1 mol/L)
V_{BP2}:	Titrant consumption until the second break point in mL
M(CaO):	Formula mass of calcium oxide, 56.08 g/mol
m(Sample):	Sample size in g used for digestion
40:	conversion factor (see below)

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

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
$V_{EP1,\ Mg}$:	Titrant consumption until the first equivalence point in mL
$V_{BP2,\ Ca}$:	Titrant consumption until the second break point in mL

$$w(MgO) = \frac{V_{used,\ Mg} \times f(EDTA_{0.1}) \times M(MgO) \times c(EDTA_{0.1}) \times 40}{m(Sample)}$$

$V_{used,\ Mg}$:	Corrected Volume used for magnesium determination
$f(EDTA_{0.1})$:	Titer of Na_2EDTA solution
M(MgO):	Formula mass of magnesium oxide, 40.32 g/mol
$c(EDTA_{0.1})$:	Concentration of the Na_2EDTA solution (0.1 mol/L)
m(Sample):	Sample size in g used for digestion
40:	Conversion factor (see below)

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

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

$$n(Fe_2O_3) = f(EDTA_{0.025}) \times c(EDTA_{0.025}) \times V_{BP1}$$

$n(Fe_2O_3)$:	Amount of substance in mmol
$f(EDTA_{0.025})$:	Titer of Na_2EDTA solution
$c(EDTA_{0.025})$:	Concentration of Na_2EDTA solution (0.025 mol/L)
V_{BP1}:	Consumption of titrant until the first break point in mL

$$w(Fe_2O_3) = \frac{n(Fe_2O_3) \times M(Fe_2O_3) \times 1000 \times 100}{m(Sample) \times 10 \times 1000 \times 2}$$

$w(Fe_2O_3)$:	Content of iron(III)oxide in %
$n(Fe_2O_3)$:	Amount of substance in mmol
$M(Fe_2O_3)$:	Formula mass of iron(III) oxide, 159.7 g/mol
1000:	Digestion solution filled up to 1 L
100:	Conversion factor for %
m(Sample):	Sample size in g used for digestion
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

$$n(EDTA_{0.1}) = V(EDTA_{0.1}) \times f(EDTA_{0.1}) - c(EDTA_{0.1})$$

$n(EDTA_{0.1})$:	Amount of added Na_2EDTA in mmol
$f(EDTA_{0.1})$:	Titer of Na_2EDTA solution
$c(EDTA_{0.1})$:	Concentration of Na_2EDTA solution (0.1 mol/L)

$$n(Al + Fe) = V(Bi(NO_3)_3) \times f(Bi(NO_3)_3) \times c(Bi(NO_3)_3)$$

n(Al + Fe):	Amount of aluminum and iron in mmol
$f(Bi(NO_3)_3)$:	Titer of bismuth nitrate solution
$c(Bi(NO_3)_3)$:	Concentration of bismuth nitrate solution (0.05 mol/L)

$$w(Al_2O_3) = \frac{(n(EDTA_{0.1}) - n(Fe_2O_3) - n(Al + Fe)) \times M(Al_2O_3) \times 10}{m(Sample\ Size)}$$

$w(Al_2O_3)$:	Content of aluminum oxide in %
$w(Al_2O_3)$:	Content of aluminum oxide in %
$n(EDTA_{0.1})$:	Amount of Na_2EDTA in mmol
$n(Fe_2O_3)$:	Amount of iron(III)oxide in mmol
n(Al + Fe):	Amount of aluminum and iron in mmol
$M(Al_2O_3)$:	Formula mass of iron(III) oxide, 101.96 g/mol
M(Sample Size):	Sample size in g used for digestion
10:	Conversion factor (see below)

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

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

Example determination

Titer determination of EDTA

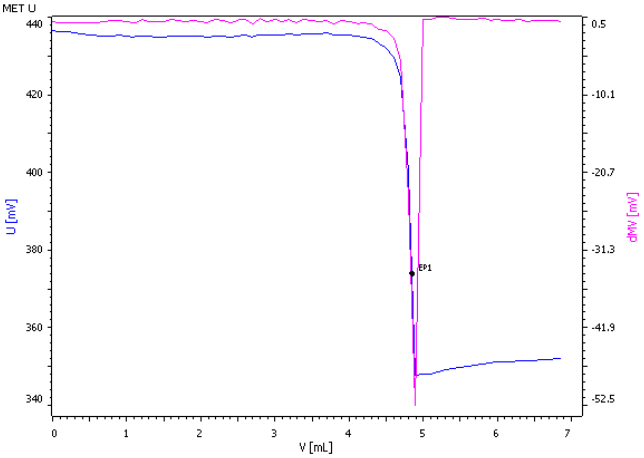

Fig. 1: Potentiometric titer determination of $c(Na_2EDTA)$ = 0.1 mol/L

Titer determination of c(Bi(NO$_3$)$_3$)

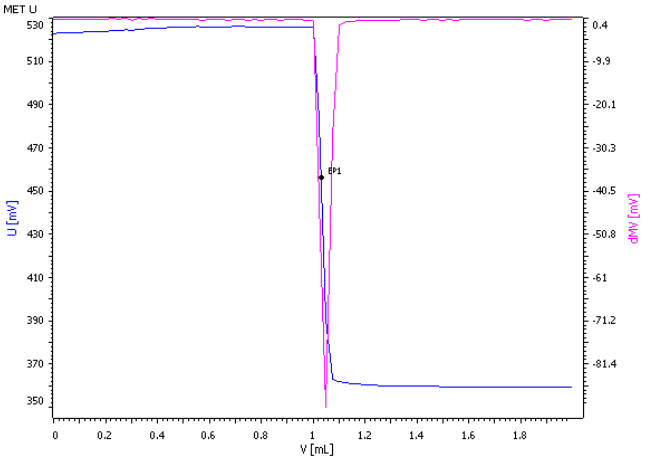

Fig. 2: Potentiometric titer determination of c(Bi(NO$_3$)$_3$) = 0.05 mol/L

Titration of calcium

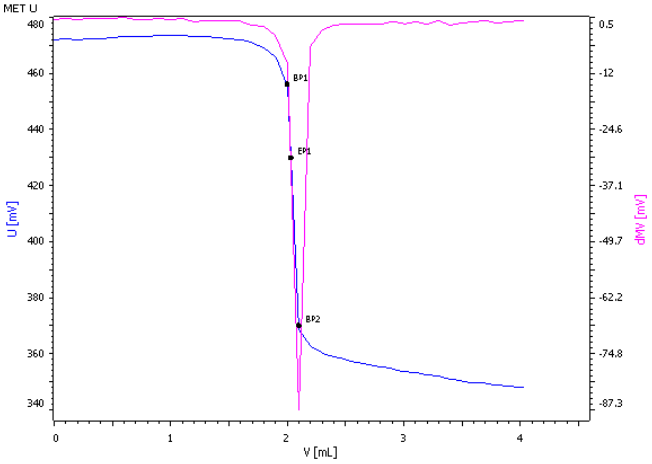

Fig. 3: Potentiometric determination of calcium with c(Na$_2$EDTA) = 0.1 mol/L

Titration of magnesium

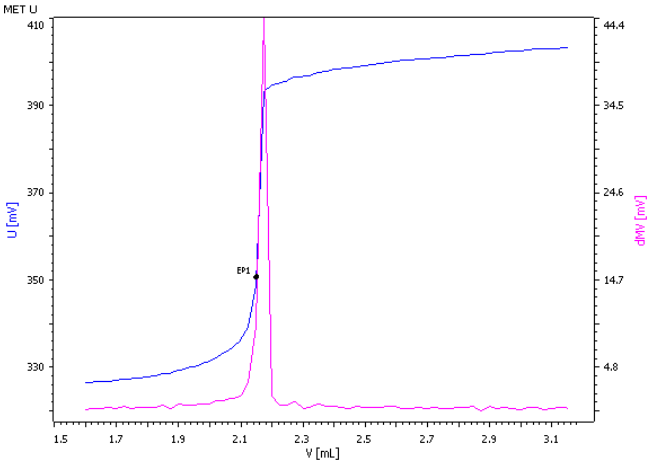

Fig. 4: Potentiometric determination of magnesium with c(Na$_2$EDTA) = 0.1 mol/L

Titration of iron(III)

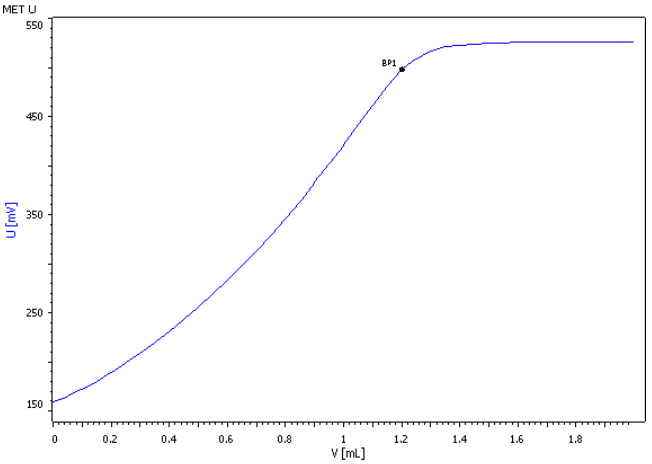

Fig. 5: Potentiometric determination of iron with c(Na$_2$EDTA) = 0.025 mol/L

Titration of aluminum

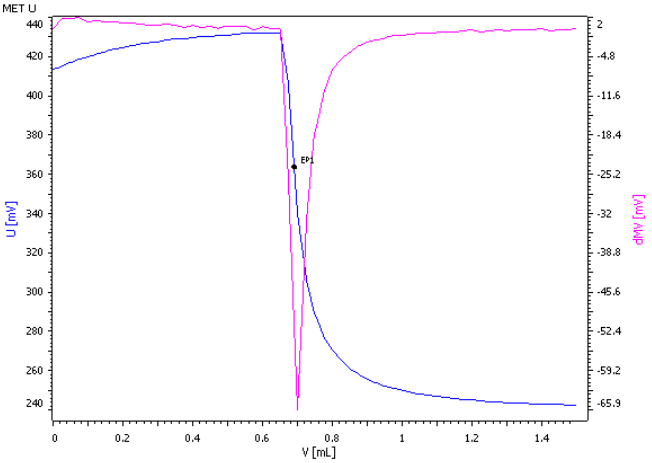

Fig. 6: Potentiometric determination of iron with c(Bi(NO$_3$)$_3$) = 0.025 mol/L

Comments

- According to the norm EN 196-2:2005 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 zinc sulfate bismuth nitrate was used as titrant. It was found that zinc doesn't 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.

Author

Competence Center Titration

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