

Application Bulletin



Of interest for:
Cement industry
General analytical laboratories

No. 63/2 e

Determination of silicon, calcium, magnesium, iron and aluminium in cements by photometric titration of the solubilized product

Summary

The insoluble silicon dioxide remaining after dissolution of cement is determined gravimetrically. The calcium, magnesium, iron and aluminium in the filtrate are determined by photometric EDTA (0.1 mol/L) titration using a 662 Photometer.

The following directions conform to the analytical methods of 11.11.81 recommended by the Association of Austrian Cement Manufacturers.

1. Determination of silicon

Method

1 g cement is mixed with 1.5 g NH_4Cl and treated with 8 mL conc. HCl and 0.5 mL HNO_3 (1:1). The mixture is boiled over a flame for 40 min with occasional agitation.

After uptake of the residue in 50 mL hot water, the solution is filtered through a black band filter S&S 589¹ into a 500 mL volumetric flask and the filter well rinsed with hot water. After cooling, the combined filtrate and washings are made up to the mark with distilled water (sample solution). The filter is then dried at 140°C for 30 min, incinerated over a flame and finally ignited in a muffle furnace at 1100°C for 15 min (residue).

Berechnung

$$\% \text{SiO}_2 = \frac{\text{weight of residue in g}}{\text{weight of sample in g}} \cdot 100 \%$$

2. Instruments for subsequent determinations

- ▶ 2.536.0110 Potentiograph or
- 2.686.0100 Titroprocessor or
- 2.682.0010 Titroprocessor

- ▶ 2.665.0030 Multi Dosimat Titrating Stand
- ▶ 2.662.XXXX Photometer with Light Guide
- ▶ 2.632.0010 pH Meter
- ▶ 2.586.0012 Labograph

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3. Determination of calcium

Reagents	<ul style="list-style-type: none"> ▶ Titrant c(EDTA) = 0.1 mol/L containing c(KOH) = 0.1 mol/L or c(EDTA) = 0.05 mol/L containing c(KOH) = 0.1 mol/L ▶ Hydroxide c(NaOH) = saturated ▶ Indicator w(murexide) = 0.01 (1% finely ground within NaCl) ▶ Hydroxylamine hydrochloride solution 100 g NH₂OH·HCl p.a./L 												
Method	<p>10 or 20 mL of sample solution are diluted to 200 mL with distilled water and the pH adjusted to 12.0 with NaOH solution. After addition of enough murexide to cover the tip of a spatula, the transmission is compensated to 20% on the photometer and titrated with EDTA at $\lambda = 450 \text{ nm}$.</p> <p>The colour changes from pink to violet.</p>												
Instrument settings	<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;">536 Potentiograph</td> <td style="width: 50%; vertical-align: top;">682 Titroprocessor (Set U)</td> </tr> <tr> <td>range 750 mV</td> <td>electr. input 1</td> </tr> <tr> <td>compensation + 400 mV</td> <td>EP1 U 225 mV</td> </tr> <tr> <td>speed 15 min/100 % vol.</td> <td>dyn.ΔU 1 35 mV</td> </tr> <tr> <td>auto control off</td> <td>drift1 10.0 mV/s</td> </tr> <tr> <td>chart speed 200 mm/100 % vol.</td> <td>t(delay) 1 10 s</td> </tr> </table>	536 Potentiograph	682 Titroprocessor (Set U)	range 750 mV	electr. input 1	compensation + 400 mV	EP1 U 225 mV	speed 15 min/100 % vol.	dyn.ΔU 1 35 mV	auto control off	drift1 10.0 mV/s	chart speed 200 mm/100 % vol.	t(delay) 1 10 s
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Calculation	<p>1 mL 0.1 mol/L EDTA solution corresponds to 5.608 mg CaO. 1 mL 0.05 mol/L EDTA solution corresponds to 2.804 mg CaO.</p> $\% \text{CaO} = \frac{B \text{ mL} \cdot f(\text{EDTA}) \cdot N \cdot \text{dilution factor} \cdot 5.608}{\text{weight of sample in g}} \cdot \%$ <p style="text-align: center;">$B = \text{mL consumed in Ca determination}$</p>												
Note	<ul style="list-style-type: none"> ▶ If any bromine is observed after filtration of the sesquioxide, it can be destroyed by addition of a few mL of hydroxylamine hydrochloride solution. ▶ In many cases, HHSNN is preferred as an indicator to murexide since the colour change observed with the former is much more distinct (λ_{max} with HHSNN = 620 nm). 												

4. Determination of magnesium

Reagents	<ul style="list-style-type: none"> ▶ Titrant c(EDTA) = 0.1 mol/L containing c(KOH) = 0.1 mol/L or c(EDTA) = 0.05 mol/L containing c(KOH) = 0.1 mol/L ▶ Ammonia w(NH₃) = 0.25 (conc.) ▶ Indicator w(methylthymol blue Na-salt) = 0.01 (1% finely ground with NaCl) ▶ Hydroxylamine hydrochloride solution 100 g NH₂OH·HCl p.a./L
Method	<p>10 or 20 mL of sample solution are diluted to approx. 100 mL with distilled water. The pH is adjusted to 10 with ammonia. The transmission is compensated to 100% at $\lambda = 600 \text{ nm}$, and methylthymol blue added until the transmission value reaches approx. 30...40%. Titration is now carried out with EDTA until the colour changes from blue to brownish pink.</p>

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Instrument settings	536 Potentiograph range 750 mV compensation + 400 mV speed 15 min/100 % vol. auto control off chart speed 200 mm/100 % vol.	682 Titroprocessor (Set U) electr. input 1 EP1 U 590 mV dyn.ΔU 1 200 mV drift1 10.0 mV/s t(delay) 1 10 s
Calculation	1 mL 0.1 mol/L EDTA solution corresponds to 4.030 mg MgO. 1 mL 0.05 mol/L EDTA solution corresponds to 2.015 mg MgO. $\% \text{MgO} = \frac{(A - B) \cdot f(\text{EDTA}) \cdot N \cdot \text{dilution factor} \cdot 4.030}{\text{weight of sample in g}} \cdot \%$ <p style="text-align: center;">A = mL consumed in Mg determination B = mL consumed in Ca determination</p>	
Note	<ul style="list-style-type: none"> ▶ If any bromine is observed after filtration of the sesquioxide, it can be destroyed by addition of a few mL of hydroxylamine hydrochloride solution. ▶ In the determination of calcium and magnesium, solutions of the same normality should be used. Sample quantities should also be the same. 	
5. Determination of iron		
Reagents	<ul style="list-style-type: none"> ▶ Titrant c(EDTA) = 0.1 mol/L or 0.05 mol/L ▶ Ammonium chloride NH₄Cl p.a. ▶ Ammonia w(NH₃) = 0.25 (conc.) ▶ Indicator w(sulfosalicylic acid) = 0.04 (4 g in 100 mL water) 	
Method	25 mL of sample solution are diluted to 50 mL with distilled water. 1 g ammonium chloride and 20 drops indicator solution are added and the solution heated to boiling. The pH is adjusted to 1.5...2.0 with ammonia and the whole diluted to 150 mL with distilled water. After compensation of the transmission to 30%, an EDTA titration is performed until the colour changes from reddish violet to colourless or faintly yellow (λ = 620 nm).	
Instrument settings	536 Potentiograph range 750 mV compensation + 400 mV speed 15 min/100 % vol. auto control off chart speed 400 mm/100 % vol.	682 Titroprocessor (Set U) electr. input 1 EP1 U 430 mV dyn.ΔU 1 150 mV drift1 10.0 mV/s t(delay) 1 10 s

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Calculation	<p>1 mL 0.1 mol/L EDTA solution corresponds to 7.985 mg Fe₂O₃. 1 mL 0.05 mol/L EDTA solution corresponds to 3.992 mg Fe₂O₃.</p> $\% Fe_2O_3 = \frac{mL\ consumed \cdot N \cdot f(EDTA) \cdot dilution\ factor \cdot 7.985}{weight\ of\ sample\ in\ g} \cdot \%$
Note	When the pH is adjusted to 1.5...2.0, ensure that no precipitation occurs, otherwise the ensuring light scattering causes large fluctuations in the transmission.

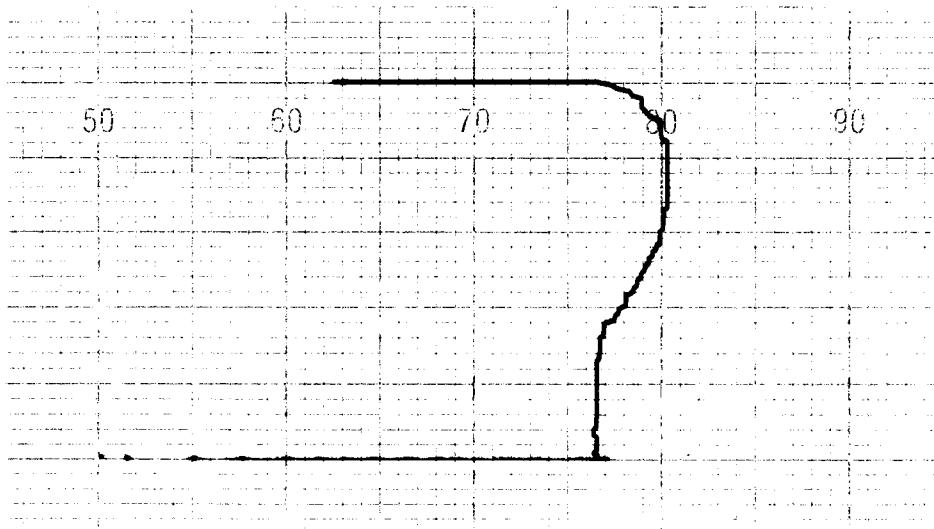
6. Determination of aluminium

Reagents	<ul style="list-style-type: none"> ▶ Titrant c(ZnSO₄) = 0.05 mol/L ▶ Additive c(EDTA) = 0.05 mol/L ▶ Acetate buffer 60 g ammonium acetate and 400 mL acetic acid/L ▶ Buffer pH = 10 54 g ammonium chloride and 350 mL ammonia w = 0.25 made up to 1 litre. ▶ Indicator w(xylene orange Na salt) = 0.01 (1% in dist. water) 		
Method	5.00 mL EDTA and 10 mL acetate buffer are added to 20 mL sample solution. The pH is adjusted to 5.5 with pH 10 buffer. The solution is boiled for a short time, diluted to approx. 100 mL with distilled water and allowed to cool to room temperature. After compensation of the transmission to 100%, indicator solution is added until the transmission is 80%. Back titration with ZnSO ₄ solution is then performed at λ = 570 nm until the colour changes from yellow to reddish violet.		
Instrument settings	<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;"> 536 Potentiograph range 1000 mV compensation +400 mV speed 15 min/100 % vol. auto control off chart speed 200 mm/100 % vol. </td> <td style="width: 50%; vertical-align: top;"> 682 Titroprocessor (Set U) electr. input 1 EP1 U 655 mV dyn.ΔU 1 150 mV drift1 10.0 mV/s t(delay) 1 10 s </td> </tr> </table>	536 Potentiograph range 1000 mV compensation +400 mV speed 15 min/100 % vol. auto control off chart speed 200 mm/100 % vol.	682 Titroprocessor (Set U) electr. input 1 EP1 U 655 mV dyn.ΔU 1 150 mV drift1 10.0 mV/s t(delay) 1 10 s
536 Potentiograph range 1000 mV compensation +400 mV speed 15 min/100 % vol. auto control off chart speed 200 mm/100 % vol.	682 Titroprocessor (Set U) electr. input 1 EP1 U 655 mV dyn.ΔU 1 150 mV drift1 10.0 mV/s t(delay) 1 10 s		
Calculation	<p>1 mL 0.1 mol/L EDTA solution corresponds to 5.098 mg Al₂O₃. 1 mL 0.05 mol/L EDTA solution corresponds to 2.549 mg Al₂O₃.</p> $\% Al_2O_3 = \frac{\left[\left\{ 5.00 \cdot f(EDTA) \cdot N \right\} - \left\{ mL\ consum. \cdot f \cdot N \right\} - mmol Fe_2O_3 \right] \cdot dil. \cdot 5.098}{weight\ of\ sample\ in\ g} \cdot \%$		
Note	Since aluminium is determined in the presence of iron, the content of the latter must be allowed for.		

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7. Examples of curves

Determination of calcium with 682 Titroprocessor



```

SET U *****
electr. input 1
EP1 U          225 mV
dyn.ΔU 1       35 mV
drift1         10.0 mV/s
t(delay) 1     10 s
temp.          25.0 °C
stop V         12.00 ml
=====
    
```

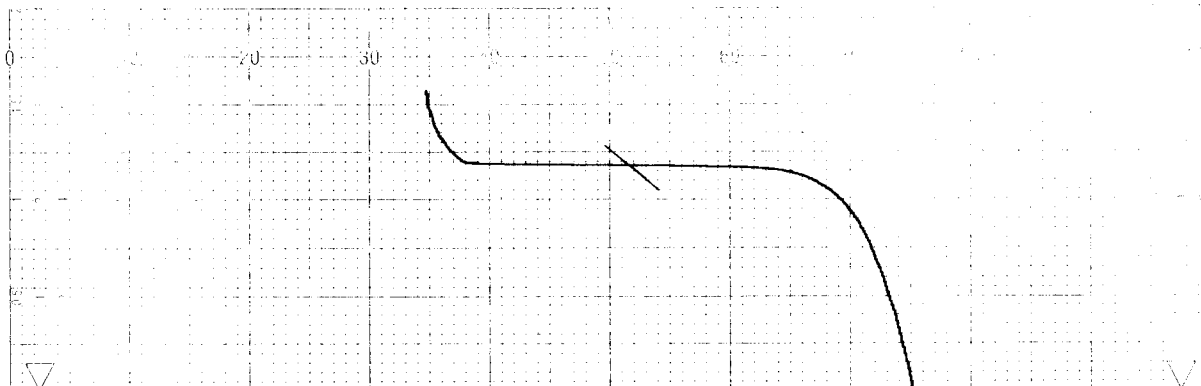
```

date 84-07-25 time 13:05
SET U ***** # 8
Id.#1          1
Id.#2          25.0
U(init)        198 mV
               V/ml      U/mV
EP1            8.762     225
RS1            62.36 %
=====
    
```

```

SET U *****
F1=EP1*C01*C02*C03*C04/C
05;2;%
C01=           1.0136
C02=           1.25
C03=           .05608
C04=           100
C05=           .9984
=====
    
```

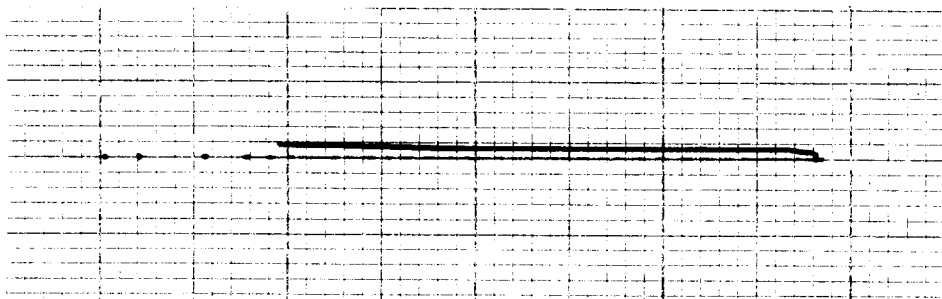
Determination of magnesium with 536 Potentiograph



Sample / Probe 10 ml Stammlösung	Reagent c(EDTA) = 0,05 mol/l Electr 662 Photometer, λ=600 nm	Range / Bereich 750 mV Compensation +400 mV	Speed / Geschw. 15 min/100% Vis. off Auto-Control off Dat 29.6.84
20 ml $\times \frac{400}{200}$ mm/100 % Vol	POTENTIOPHANT	Metrohm Herisau Switzerland	6.2232.000

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Determination of iron with 682 Titroprocessor



SET U 25.7.84
 electr. input 1
 EP1 U 430 mV
 dyn.ΔU 1 150 mV
 drift1 10.0 mV/s
 t(delay) 1 10 s
 temp. 25.0 °C
 stop V 12.00 ml
 =====

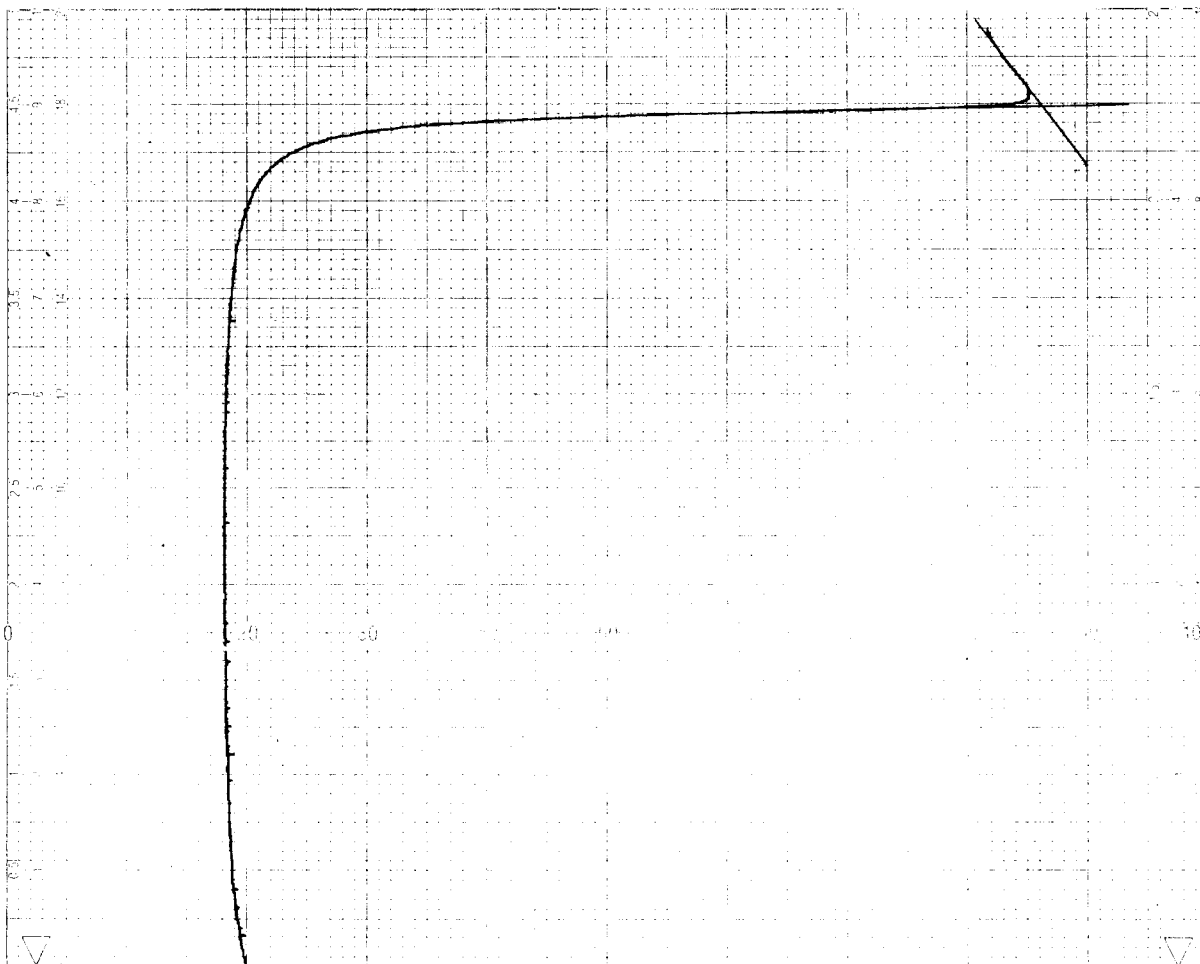
date 84-07-26 time 09:59
 SET U 25.7.84 # 4
 Id.#1 1
 Id.#2 25.0
 U(init) 299 mV

	V/ml	U/mV
EP1	.358	430
RS1	2.90	%

 =====

SET U 25.7.84
 F1=EP1*C01*C02*C03*C04/C
 05;2;%
 C01= .05
 C02= 1.0126
 C03= .05
 C04= 7.98455
 C05= .9984
 =====

Determination of aluminium with 536 Potentiograph



Sample / Probe: 20 ml Stammlösung +10 ml K III 0.05 M Reagent: c(ZnSO₄) = 0,05 M Range / Bereich: 1V Speed / Geschw: 15 min/100% Vis. Compensation: + 400 mV Auto-Control: off Det: 4.7.84

10 X

mm/100 % Vol

POTENTIOPHANT

Metrohm Herisau Switzerland

6.2232.000