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Cement — Test methods — Chemical analysis

Ciments — Méthodes d'essai — Analyse chimique



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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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Cement — Test methods — Chemical analysis

1 Scope

This International Standard describes the procedures for the chemical analysis of cement.

It gives the reference procedures and, in certain cases, an alternative method which can be considered as giving equivalent results.

If other methods are used, it is necessary to show that they give results equivalent to those given by the reference methods. In case of dispute, only the reference procedures may be used.

This International Standard applies to cements, and also to their constituent materials such as clinker and blastfurnace slag.

Standard specifications state which methods are to be used.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3534:1977, *Statistics — Vocabulary and symbols*.

EN 196-7:1987, *Methods for testing cement; methods of taking and preparing samples of cement*.

3 General requirements for testing

3.1 Number of tests

The number of tests for the various determinations (clause 7 to clause 13) is fixed at two (see also 3.3).

3.2 Repeatability and reproducibility

The standard deviation of repeatability gives the closeness of agreement between successive results obtained with the same method on identical material tested under the same conditions (same operator, same apparatus, same laboratory and short time interval).

The standard deviation of reproducibility gives the closeness of agreement between individual results obtained with the same method on identical material but tested under different conditions (different operators, different apparatus, different laboratories and/or different times).

These deviations are exactly defined in ISO 3534.

The standard deviations of repeatability and reproducibility are expressed in absolute percentages.¹⁾

1) The values of the standard deviation for repeatability and standard deviation for reproducibility given are to be considered as provisional. These values will subsequently be stipulated according to experience acquired in laboratories.

3.3 Expression of masses, volumes, factors and results

Express masses in grams to the nearest 0,000 1 g and volumes from the burette in millilitres to the nearest 0,05 ml.

Express the factors of solutions, given by the mean of three determinations, to three decimal places.

Express the results of the tests, given by the mean of two determinations, as a percentage, generally to two decimal places.

If the difference between two determinations is more than twice the repeatability standard deviation, repeat the test and take the mean of the two closest values.

3.4 Ignitions

Carry out the ignitions as follows.

Place the filter paper and its contents into a crucible which has been previously ignited and tared. Dry it, then incinerate it slowly in an oxidizing atmosphere, without flaming while ensuring complete combustion. Then ignite at the stated temperature. Allow the crucible and its contents to cool to the laboratory temperature in a desiccator. Weigh the crucible and its contents.

3.5 Determination of constant mass

Determine constant mass by making successive 15 min ignitions followed each time by cooling and then weighing. Constant mass is reached when the difference between two successive weighings is less than 0,000 5 g.

3.6 Check for the absence of Cl^- ions (silver nitrate test)

After generally five to six washes of a precipitate, rinse the base of the filter stem with a few drops of water. Wash the filter and its contents with several millilitres of water and collect this in a test tube. Add several drops of silver nitrate solution (4.33). Check the absence of turbidity or precipitate in the solution. If present, continue washing while carrying out periodic checks until the silver nitrate test is negative.

4 Reagents

General requirements for reagents are as follows.

Use only reagents of analytical quality and distilled water, or water of equal purity, during the analysis.

Unless otherwise stated % means % by mass: % (m/m).

The concentrated liquid reagents used in this International Standard have the following densities (ρ) (in g/cm³ at 20 °C):

- hydrochloric acid 1,18 to 1,19
- hydrofluoric acid 1,13
- nitric acid 1,40 to 1,42
- sulfuric acid 1,84
- phosphoric acid 1,71 to 1,75
- acetic acid 1,05 to 1,06
- ammonium hydroxide 0,88 to 0,91
- triethanolamine 1,12

The degree of dilution is always given as a volumetric sum, for example: hydrochloric acid 1 + 2 means that 1 volume of concentrated hydrochloric acid is to be mixed with 2 volumes of water.

4.1 Hydrochloric acid (HCl), concentrated.

4.2 Hydrochloric acid, diluted 1 + 1.

4.3 Hydrochloric acid, diluted 1 + 2.

4.4 Hydrochloric acid, diluted 1 + 3.

4.5 Hydrochloric acid, diluted 1 + 9.

4.6 Hydrochloric acid, diluted 1 + 11.

4.7 Hydrochloric acid, diluted 1 + 19.

4.8 Hydrochloric acid, diluted 1 + 99.

4.9 Hydrochloric acid of pH 1,6, diluted.

Add five or six drops of concentrated hydrochloric acid to 2 l water. Check the pH value by means of a pH-meter. Store the solution in a polyethylene flask.

4.10 Hydrofluoric acid (HF), concentrated.

4.11 Hydrofluoric acid, diluted 1 + 3.

4.12 Nitric acid (HNO_3).

4.13 Sulfuric acid (H_2SO_4), concentrated.

4.14 Sulfuric acid, diluted 1 + 1.

4.15 Phosphoric acid (H_3PO_4).

4.16 Boric acid (H_3BO_3).

4.17 Acetic acid (CH_3COOH).

4.18 Amino-acetic acid ($\text{NH}_2\text{CH}_2\text{COOH}$).

4.19 Metallic chromium powder form (Cr).

4.20 Ammonium hydroxide (NH_4OH), concentrated.

4.21 Ammonium hydroxide, diluted 1 + 1.

4.22 Ammonium hydroxide, diluted 1 + 10.

4.23 Ammonium hydroxide, diluted 1 + 16.

4.24 Sodium hydroxide (NaOH).

4.25 Sodium hydroxide, 4 mol/l solution.

Dissolve 160 g of sodium hydroxide in water and make up to 1 000 ml. Store in a polyethylene flask.

4.26 Sodium hydroxide, 2 mol/l solution.

Dissolve 80 g of sodium hydroxide in water and make up to 1 000 ml. Store in a polyethylene flask.

4.27 Ammonium chloride (NH_4Cl).

4.28 Tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$).

4.29 Potassium periodate (KIO_4).

4.30 Sodium peroxide (Na_2O_2) in powder form.

4.31 Mixture of sodium carbonate and sodium chloride.

Mix 7 g of sodium carbonate (anhydrous Na_2CO_3) with 1 g sodium chloride (NaCl).

4.32 Barium chloride, solution

Dissolve 120 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water and make up to 1 000 ml.

4.33 Silver nitrate, solution.

Dissolve 5 g of silver nitrate (AgNO_3) in water, add 10 ml of concentrated nitric acid (HNO_3) and make up to 1 000 ml with water.

4.34 Sodium carbonate, solution.

Dissolve 50 g of sodium carbonate (anhydrous Na_2CO_3) in water and make up to 1 000 ml.

4.35 Potassium hydroxide, solution.

Dissolve 250 g of potassium hydroxide (KOH) in water and make up to 1 000 ml. Store in a polyethylene flask.

4.36 Ammoniacal zinc sulfate, solution.

Dissolve 50 g of zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) in 150 ml water and add 350 ml of concentrated ammonium hydroxide (NH_4OH). Leave to stand for at least 24 h and filter.

4.37 Lead acetate, solution.

Dissolve approximately 0,2 g of lead(II) acetate trihydrate [$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$] in water and make up to 100 ml.

4.38 Starch, solution.

To 1 g of starch (water soluble), add 1 g of potassium iodide (KI), dissolve in water and make up to 100 ml.

4.39 Polyethylene oxide, solution.

Dissolve 0,25 g of polyethylene oxide ($-\text{CH}_2-\text{CH}_2-\text{O}-$)_n of average molecular mass 200 000 to 600 000, in 100 ml water while stirring vigorously.

This solution is stable for approximately two weeks.

4.40 Boric acid, saturated solution.

Dissolve approximately 50 g of boric acid (H_3BO_3) in water and make up to 1 000 ml.

4.41 Citric acid, solution.

Dissolve 10 g of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) in water and make up to 100 ml.

4.42 Ammonium molybdate, solution.

Dissolve 10 g of ammonium molybdate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$] in water and make up to 100 ml. Store the solution in a polyethylene flask. This keeps for approximately one week.

4.43 Copper sulfate, solution.

In a 50 ml volumetric flask dissolve 0,45 g of copper (II)sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in water and make up to the mark.

4.44 Ammonium acetate, solution.

Dissolve 250 g of ammonium acetate ($\text{CH}_3\text{COONH}_4$) in water and make up to 1000 ml.

4.45 Triethanolamine $[\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3]$, solution 1 + 4.**4.46 Reducing solution.**

Dissolve successively in water 0,15 g of 1-amino-2-hydroxy naphthalene-4-sulfonic acid ($\text{C}_{10}\text{H}_9\text{NO}_4\text{S}$), 0,7 g of sodium sulfite (anhydrous Na_2SO_3) and 9 g of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and make up to 100 ml.

This solution will keep for a maximum of one week.

4.47 Buffer solution, of pH 1,4.

Dissolve 7,505 g of amino-acetic acid ($\text{NH}_2\text{CH}_2\text{COOH}$) and 5,85 g of sodium chloride (NaCl) in water and make up to 1000 ml. Dilute 300 ml of this solution to 1000 ml with dilute hydrochloric acid 1 + 99.

4.48 Potassium iodate, standard solution containing approximately 0,0166 mol/l²⁾.

Dissolve successively in freshly boiled and cooled water in a 1000 ml volumetric flask, 3,6 g $\pm$ 0,1 g of potassium iodate (KIO_3 , dried at 120° C), sufficient sodium hydroxide (NaOH) in the solid form (approximately 3 g) to render the solution alkaline and 25 g of potassium iodide (KI). Make up to the mark with freshly boiled and cooled water.

The factor F of this solution is calculated from the following formula:

$$F = \frac{m_1}{3,5668} \quad (1)$$

where m_1 is the mass of the portion of potassium iodate.

4.49 Sodium thiosulfate solution, approximately 0,1 mol/l²⁾.**4.49.1 Preparation**

Dissolve 24,82 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in water and make up to 1000 ml. Before each test series, determine the factor f of this solution as described in 4.49.2.

4.49.2 Standardization

4.49.2.1 This standardization is carried out preferably in relation to the standard potassium iodate solution (4.48). For this standardization, pipette 20 ml of the standard potassium iodate solution into a 500 ml conical flask and dilute with approximately 150 ml of water. Acidify with 25 ml of hydrochloric acid 1 + 1 and titrate with the approximately 0,1 mol/l sodium thiosulfate solution to a pale yellow colour.

Then add 2 ml of the starch solution (4.38) and continue the titration until the colour changes from blue to colourless.

The factor f of this solution is calculated from the formula:

$$f = \frac{20 \times 0,01667 \times 214,01 \times F}{3,5668 \times V_1} = 20 \cdot \frac{F}{V_1} \quad \dots (2)$$

where

F	is the factor of the standard potassium iodate solution (4.48), expressed in mol/l;
V_1	is the volume of the approximately 0,1 mol/l sodium thiosulfate solution used for the titration;
3,566 8	is the mass of potassium iodate corresponding to a solution with exactly 0,016 67 mol/l of KIO_3 ;
214,01	is the molecular mass of potassium iodate.

4.49.2.2 The standardization may also be carried out in relation to a known quality of potassium iodate.

For this standardization, place in a 500 ml conical flask 0,07 g $\pm$ 0,005 g of potassium iodate and dissolve in approximately 150 ml of water.

Add about 1 g of potassium iodide, acidify with 25 ml of hydrochloric acid 1 + 1 and titrate with the approximately 0,1 mol/l sodium thiosulfate solution until a pale yellow colour is obtained. Then add 2 ml of the starch solution (4.38) and titrate until the colour changes from blue to colourless.

2) If the sulfide content is low (< 0,1 %), solutions ten times less concentrated should be used. They are prepared by pipetting 100 ml of the solutions 4.48 and 4.49 into 1000 ml volumetric flasks and making up to the mark with water.

The factor f of this solution is calculated from the formula:

$$f = \frac{1000 \times m_2}{3,5668 \times V_2} = 280,3634 \frac{m_2}{V_2} \quad \dots (3)$$

where

m_2 is the mass of the portion of potassium iodate;

V_2 is the volume of the approximately 0,1 mol/l sodium thiosulfate solution used for the titration;

3,5668 is the mass of potassium iodate corresponding to a solution with exactly 0,01667 mol/l of KIO_3 .

4.50 Manganese(II) ion, standard solution.

4.50.1 Anhydrous manganese sulfate.

Dry some hydrated manganese sulfate ($\text{MnSO}_4 \cdot x\text{H}_2\text{O}$) to constant mass at a temperature of $250^\circ\text{C} \pm 10^\circ\text{C}$. The composition of the product obtained corresponds to the formula MnSO_4 .

4.50.2 Preparation

Into a 1 000 ml volumetric flask, weigh approximately 2,75 g of anhydrous manganese sulfate; dissolve in water and make up to the mark. The content G of manganese(II) ions of this solution, expressed in milligrams of Mn^{2+} per millilitre, is calculated from the formula:

$$G = \frac{m_3}{2,7485} \quad \dots (4)$$

where m_3 is the mass of the portion of anhydrous manganese sulfate.

4.50.3 Construction of calibration graph

Into each of two volumetric flasks, respectively 500 ml (No. 1) and 1 000 ml (No. 2), pipette 20 ml of the standard manganese ion solution. Make up to the mark with water. Into each of three volumetric flasks, respectively 200 ml (No. 3), 500 ml (No. 4) and 1 000 ml (No. 5), pipette 100 ml of the solution from flask No. 2 and make up to the mark with water.

Take 100 ml of each solution from flasks 1 to 5 and pipette each portion into a 400 ml beaker. Add 20 ml of concentrated nitric acid, 1,5 g of potassium periodate (4.29) and 10 ml of phosphoric acid (4.15), heat to boiling and boil gently for 30 min. Cool to 20°C and transfer the contents of each beaker to a

200 ml volumetric flask. Cool the flasks and their contents to 20°C and make up to the mark with water. Measure the optical density of the solutions using a photometer (5.9) at a wavelength of around 525 nm, against water [use one or more cells (5.10) of appropriate sizes]. Record the optical density values to three decimal places.

For each cell optical length, plot a separate graph of the optical densities of these standard solutions E 1 to E 5 as a function of the corresponding manganese concentrations in milligrams of Mn per 200 ml. The corresponding manganese concentrations are given in table 1. They can be used as given if the content G obtained in accordance with 4.50.2 has the value 1. Otherwise, multiply the manganese concentrations in table 1 by G .

Table 1 — Concentrations of manganese standard solutions

Standard solution	E 1	E 2	E 3	E 4	E 5
Concentration of manganese in mg of Mn per 200 ml	4	2	1	0,4	0,2

4.51 Silica, standard solution.

4.51.1 Silica (SiO_2), of purity $> 99,9\%$ after ignition.

4.51.2 Sodium carbonate, anhydrous (Na_2CO_3).

4.51.3 Basic solution.

Weigh 0,2 g of silica, freshly ignited at $1175^\circ\text{C} \pm 25^\circ\text{C}$, in a platinum crucible already containing 2 g of sodium carbonate.

Heat the mixture and fuse it at a bright-red heat for at least 15 min. After cooling to room temperature, place the fused solid in a polyethylene beaker and dissolve it in water, then transfer the solution quantitatively to a 200 ml volumetric flask and make up to the mark with water.

Store the solution in a polyethylene bottle.

1 ml of solution contains 1 mg of SiO_2 .

4.51.4 Standard solution.

Pipette 5 ml of the basic solution into a 250 ml volumetric flask and make up to the mark with water. Store the solution in a polyethylene bottle. 1 ml of the solution contains 0,02 mg of silica. This solution will keep for a maximum of one week.

4.51.5 Compensating solutions.

Prepare the compensating solutions according to the procedure adopted for the silica content (13.3 to 13.5), by dissolving the amounts of the reagents given in table 2 in water and making up to 500 ml.

4.51.6 Construction of calibration curve

Add from a burette the volumes of the silica calibration solution given in table 3 into 100 ml polyethylene beakers each containing a magnetic stirrer bar. Add 20 ml of the compensating solution by pipette and make up to 40 ml with water from a burette. The volumes required for this are also given in table 3. While stirring with a magnetic stirrer, add 15 drops of hydrofluoric acid 1 + 3. Stir for at least 1 min. Then pipette 15 ml of the boric acid solution (4.40) into the solution.

Adjust the pH of the solution to $1,15 \pm 0,05$ by adding, drop by drop, either the sodium hydroxide solution (4.25), or hydrochloric acid 1 + 2. Carry out this operation with the aid of a pH-meter calibrated using a buffer (4.47) with a neighbouring pH value (e.g. 1,4). Pipette 5 ml of the ammonium molybdate solution (4.42) into the solution (time 0). Adjust the pH of this solution to 1,6 by adding, drop by drop, either the sodium hydroxide solution (4.25) or hydrochloric acid 1 + 2. Transfer the solution to a

100 ml volumetric flask rinsing with dilute hydrochloric acid of pH 1,6 (4.9).

After 20 min, pipette 5 ml of the citric acid solution (4.41) into the volumetric flask, stir and leave to stand for 5 min.

Then pipette 2 ml of the reducing solution (4.46) into the volumetric flask. Make up to the mark with dilute hydrochloric acid of pH 1,6 (4.9) and mix thoroughly. Exactly 30 min after introducing the ammonium molybdate (time 0 + 30), measure the optical density with a photometer (5.9) using a cell of 1 cm optical length against the blank solution prepared in the same way, using the wavelength of maximum extinction near 815 nm. Construct a graph giving the measured optical densities as a function of the corresponding silica contents given in table 3.

The blank solution used in constructing the calibration curve may be used as the blank solution here. The calibration curve enables the silica content in mg SiO_2 /100 ml to be determined.

4.52 Calcium ions, standard solution approximately 0,01 mol/l.

4.52.1 Calcium carbonate (CaCO_3), dried at 200 °C of purity > 99,9 %.

Table 2 — Composition of compensating solutions for volume of 500 ml

Reagent	Precipitation by polyethylene oxide (13.3)	Precipitation by double evaporation (13.4)	Decomposition by HCl and NH_4Cl (13.5)
HCl concentrated, ml	70	75	15
H_2SO_4 1 + 1, ml	1	1	—
HNO_3 concentrated, ml	—	—	1
Polyethylene oxide solution, ml	5	—	—
NH_4Cl , g	—	—	1
Na_2CO_3 , g	1,75	1,75	1,75
NaCl, g	0,25	0,25	0,25
Na_2O_2 , g	3	3	—

Table 3 — Composition of silica calibration solutions and their silica content

Serial No.	Blank	1	2	3	4	5	6	7	8
Standard (SiO_2), solution, ml	0	2	4	5	6	8	10	15	20
Water, ml	20	18	16	15	14	12	10	5	0
Silica content, mg SiO_2 /100 ml	0	0,04	0,08	0,1	0,12	0,16	0,2	0,3	0,4