

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION R 681

CHEMICAL ANALYSIS OF CEMENTS

MINOR CONSTITUENTS OF PORTLAND CEMENT

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BRIEF HISTORY

The ISO Recommendation R 681, *Chemical analysis of cements – Minor constituents of Portland cement*, was drawn up by Technical Committee ISO/TC 74, *Hydraulic binders*, the Secretariat of which is held by the Institut Belge de Normalisation (IBN).

Work on this question by the Technical Committee began in 1958 and led, in 1963, to the adoption of a Draft ISO Recommendation.

In February 1965, this Draft ISO Recommendation (No. 774) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Argentina	Ireland	Romania
Australia	Israel	Sweden
Austria	Italy	Turkey
Belgium	Japan	U.A.R.
Czechoslovakia	Korea, Rep. of	United Kingdom
Denmark	Netherlands	U.S.A.
France	New Zealand	U.S.S.R.
Germany	Norway	Yugoslavia
Hungary	Poland	
India	Portugal	

No Member Body opposed the approval of the Draft.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council which decided, in March 1968, to accept it as an ISO RECOMMENDATION.

CHEMICAL ANALYSIS OF CEMENTS

MINOR CONSTITUENTS OF PORTLAND CEMENT

1. GENERAL INSTRUCTIONS

1.1 Reagents

All the reagents should be of the analytical reagent grade.

Special reagents relating to a given determination are described in the section concerning the determination.

1.2 Filter-paper

Filter-papers should be *ash-free*. Filter-papers with a close texture are called *slow*, filter-papers with a medium texture are called *medium* and filter-papers with an open texture are called *fast*.

1.3 Blank determinations

A blank determination is recommended in every case. If possible, it is best carried out with a substance of nearly the same composition as the sample to be analysed, but without the constituent to be determined; otherwise carry out all the described operations without introducing the sample.

1.4 Colorimetry

An approximate determination can be made by visual comparison with a colorimetric scale corresponding with known quantities of the constituent to be determined.

A more precise determination can be made absorptiometrically. Two kinds of spectrophotometric apparatus are in common use: that employing a prism- or grating-monochromator capable of selecting a wave-length band of about one nanometer ($1 \text{ nm} = 10^{-9} \text{ m}$), and that using an optical filter of the ordinary or the interference type allowing the passage of a band of 5 to 20 nm. The narrower the wave band, the more accurately does the additivity law apply to the optical densities measured.

2. COLORIMETRIC DETERMINATION OF TITANIUM

2.1 Principle

Ti^{4+} forms a yellow complex with hydrogen peroxide in an acid medium. For concentrations under 50 mg of Ti^{4+} per litre, the resulting colour is proportional to the titanium present. The most suitable medium is sulphuric acid of 2 N to 3 N concentration.

Interfering ions : Fe^{+++} and V^{5+} .

The interference caused by the coloration due to the Fe^{+++} ions can be neglected in the case of Portland cement. V^{5+} gives a yellow colour similar to Ti^{4+} , and the specified procedure does not take account of this interference, but it is very seldom experienced.

2.2 Special reagents

Hydrogen peroxide solution, 6 % (20 volumes).

Standard titanium solution. Boil for 15 min a mixture of 4.5 g of potassium titanium oxalate, 8 g of ammonium sulphate and 50 ml of concentrated sulphuric acid. Cool and dilute the solution to 1 litre with distilled water. Titanium is determined on 50 ml portions of the solution by precipitation with ammonia solution and final weighing as titanium dioxide.

2.3 Procedure

Treat a 1 g sample of cement following the methods described in ISO Recommendation R 680, *Chemical analysis of cements – Main constituents of Portland cement*, for separating the total silica. If the residue from silica purification is negligible, the filtrate from the silica contains all the titanium. If insoluble residue is appreciable, fuse it with a small amount of (1 + 1) mixture of borax and sodium carbonate and then dissolve in hydrochloric acid. Add the resulting solution to the filtrate from the silica.

Then precipitate the total oxides once, following the method described in ISO Recommendation R 680, after single washing with the ammonium nitrate solution, take up the precipitate in a 100 ml graduated flask, first with water, then with 25 ml hot (1 + 3) sulphuric acid taking care to redissolve all the precipitate. Finally rinse the filter-paper and the funnel with water until the final volume reaches about 90 ml. Cool the graduated flask and its contents. Then add 5 ml of 6 % hydrogen peroxide solution and make up to the mark of 100 ml with water. Then carefully mix the contents of the graduated flask.

2.4 Measuring

Carry out measurement by visual comparison, or instrumentally using a spectrophotometer.

With the monochromator-type apparatus, operate at 410 nm using a 1 cm cell. With the filter-type apparatus choose a filter with a wave-length band as near as possible to 410 nm.

In all cases make a range of standard colorimetric solutions using known quantities of titanium, either for visual comparison or for the construction of a standard curve giving the optical density as a function of known concentration, in the described operational conditions. Refer the optical density obtained for the sample solution on this curve, and read the amount of titanium dioxide in grammes for a sample of 1 g cement. Then

$$\text{TiO}_2 \% = \text{value as read} \times 100$$

3. COLORIMETRIC DETERMINATION OF PHOSPHORUS

3.1 Principle

Phosphorus present in the sample is dissolved as a PO_4^{3-} ion by a mixture of nitric and perchloric acids. Addition of a solution of ammonium vanadomolybdate forms a yellow coloured phosphovanadomolybdate complex. Amyl alcohol allows the extraction of the complex free of interference and thus facilitates the measurement of the phosphate present in the sample.

3.2 Special reagents

3.2.1 Ammonium vanadomolybdate solution. Dissolve 1 g of ammonium vanadate in 300 ml water, if possible with the help of mechanical stirring. After complete solution, add slowly 140 ml nitric acid ($d = 1.42$), then 400 ml of 10 % ammonium molybdate solution. Make the mixture up to 1 litre. Prepare this solution freshly before use.

3.2.2 Standard phosphate solution. Weigh exactly 0.186 g of dry diammonium hydrogen orthophosphate $(\text{NH}_4)_2 \text{HPO}_4$. Dissolve in water and make up to exactly 500 ml.

$$1 \text{ ml} = 0.2 \text{ mg P}_2\text{O}_5$$

3.3 Procedure

Weigh a 0.2 g sample into a 100 ml squat form beaker, add 1 ml of water and 1 ml of concentrated nitric acid ($d = 1.42$). Stir and add 5 ml of 60 % perchloric acid. Cover the beaker with a watch glass and warm on a hotplate, in a fume chamber. Adjust the temperature so that thick white fumes of perchloric acid appear after 3 min. Then move the beaker to a cooler part of the hotplate and continue the reaction for 10 min, allowing to fume gently. Remove the beaker from the hotplate and cool it. Add 20 ml of water, filter through a 9 cm medium filter-paper into a 300 ml conical flask. Wash four times with hot water. Heat the filtrate to just below boiling point and add 25 ml of the ammonium vanadomolybdate solution (3.2.1). Stir, and cool the solution to normal temperature. Run 10 ml amyl alcohol (exactly measured), into a 150 ml conical separating funnel, then add the preceding solution and washings from the conical flask. Shake the contents of the separating funnel vigorously for 2 min and allow to settle for 5 min. Run off the aqueous layer. Run off about 1 ml of the alcoholic layer in order to rinse the stem of the separating funnel and filter the remainder of the extraction through a small dry slow filter paper. Discard the first few drops of the filtrate and collect finally the clear amyl alcohol solution in the measuring cell.

3.4 Measuring

Carry out measurement by visual comparison, or instrumentally using a spectrophotometer.

For measuring the depth of yellow coloration of the phosphovanadomolybdenum complex with the monochromator-type apparatus, operate at 426 nm. With the filter-type apparatus, use a filter of which the wave-length band is as near as possible to 426 nm.

A blank determination is absolutely necessary as amyl alcohol extracts a faint colour from contact with the ammonium vanadomolybdate solution.

The unknown concentration is finally determined from a colorimetric set of standard solutions or a standard curve established from known amounts of standard phosphate solution (3.2.2).

If the value read from the curve corresponds with the phosphoric anhydride concentration in grammes for a 0.2 g sample :

$$P_2O_5 \% = \text{value as read} \times 500$$

4. COLORIMETRIC DETERMINATION OF MANGANESE

4.1 Principle

In an acid medium and in the presence of periodate Mn^{++} is oxidized to MnO_4^- . Addition of phosphoric acid helps the quantitative formation of MnO_4^- , complexes the Fe^{+++} in a colourless ion and stabilizes the colour of the solution.

4.2 Special reagents

4.2.1 Potassium periodate

4.2.2 *Standard potassium permanganate solution.* Dissolve 0.050 g of potassium permanganate in water and make up to exactly 250 ml.

$$1 \text{ ml} = 0.1 \text{ mg } Mn_2O_3$$

Freshly prepare this solution before use.

4.3 Procedure

Weigh exactly 1 g of cement into a 250 ml beaker. While stirring, add 30 or 40 ml of water followed by 6 ml of concentrated nitric acid ($d = 1.42$). Boil the mixture until all the cement has dissolved. Filter off the insoluble residue through a slow filter-paper of 9 cm, then wash with water. The volume of the solution should then be about 60 to 70 ml. Add 5 ml of ortho phosphoric acid ($d = 1.75$) and 0.3 to 0.5 g of potassium periodate (4.2.1) to the filtrate. Boil gently until the permanganate coloration appears. If the permanganate coloration does not develop, reduce the acidity of the solution by cautiously adding ammonia solution.

After the colour has developed, leave the solution on a suitable regulated hotplate, at just below boiling point for 30 min. Cool and make up to exactly 100 ml.

4.4 Measuring

Carry out measurement by visual comparison, or instrumentally, using a spectrophotometer.

With the monochromator-type apparatus, operate at 525 nm. With the filter-type apparatus, use a filter of which the wave-length band is as near as possible to 525 nm.

Determine the unknown concentration from a colorimetric set of standard solutions or a standard curve established from known amounts of standard potassium permanganate solution (4.2.2).

If the value read from the curve corresponds with the manganese oxide concentration for a 1 g sample :

$$\text{Mn}_2\text{O}_3 \% = \text{value as read} \times 100$$

5. DETERMINATION OF FREE LIME

5.1 Glycol method

5.1.1 Principle. Calcium oxide (CaO) and calcium hydroxide (Ca(OH)₂) (free lime) present in cement or clinker are dissolved by hot anhydrous glycol. The resultant alkaline solution is titrated against a strong acid.

5.1.2 Special reagents.

5.1.2.1 Mixed indicator. Dissolve 0.05 g of methyl red in about 40 ml of ethanol and 0.05 g of bromocresol green in about 40 ml of ethanol. Mix both solutions and make up to 100 ml with alcohol.

5.1.2.2 Absolute alcohol. This liquid readily absorbs moisture from the atmosphere. It should be kept in tightly stoppered bottles fitted with an air-tight cap, and opened only for the interval necessary for manipulations.

5.1.2.3 Glycol (1.2 ethane-diol). This reagent should be pure and anhydrous. It absorbs atmospheric moisture and should be treated in the same way as absolute alcohol.

5.1.2.4 Sand. It is best to use ground quartz (grains of about 0.5 mm diameter).

NOTES

1. Water content in absolute alcohol and glycol can be determined by titration by the Karl Fischer method.
2. A blank determination will allow correction for the acidity or alkalinity of the reagents.