INTERNATIONAL STANDARD

ISO 29581-2

First edition
2010-03-01

Cement — Test methods —

Part 2: Chemical analysis by X-ray fluorescence

Ciments — Méthodes d'essais —

Partie 2: Analyse chimique par spectrométrie de fluorescence X

Reference number
ISO 29581-2:2010(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 29581-2 was prepared by Technical Committee ISO/TC 74, *Cement and lime*.

ISO 29581 consists of the following parts, under the general title *Cement — Test methods*:

— *Part 1: Analysis by wet chemistry*

— *Part 2: Chemical analysis by X-ray fluorescence*

Introduction

This part of ISO 29581 incorporates the following technical principles based on comments received by the Secretariat.

a) It provides an analytical method based on X-ray fluorescence (XRF) for use as the alternative method for the analysis of cement. When correctly calibrated according to the specified procedures and reference materials, it provides a method of suitable precision for conformity and information purposes.

b) It introduces a reference method for TiO_2, P_2O_5, SrO and Br analysis.

c) Traceability of the method relies upon reference materials and “pure” chemicals so that the ultimate traceability to basic international chemical standards relies upon classical analytical methods that are outside of the scope of this part of ISO 29581.

XRF and other instrumental methods, such as differential thermal analysis for determination of carbon dioxide, atomic absorption spectroscopy, etc., can be used as alternative methods, provided they are calibrated against the reference methods, or against internationally accepted reference materials.

Cement — Test methods —

Part 2: Chemical analysis by X-ray fluorescence

1 Scope

This part of ISO 29581 describes a performance-based method for the chemical analysis of cement for SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, K_2O, Na_2O, TiO_2, P_2O_5, Mn_2O_3, SrO, Cl and Br using X-ray fluorescence (XRF). It can be applied to other relevant elements when adequate calibrations have been established.

This part of ISO 29581 describes an alternative method for analyses of cement for conformity and information purposes, based on beads of fused sample and analytical validation using certified reference materials, together with performance criteria.

A method based on pressed pellets of unfused sample can be considered as equivalent, providing that the analytical performance satisfies the same criteria.

NOTE 1 The use of fused beads generally improves the accuracy of analysis for non-volatile elements, since it eliminates variability arising from differences in mineralogical forms or oxidation states. Pressed pellets generally improve the accuracy of analysis for volatile elements and can give adequate accuracy for the routine analysis of non-volatile elements.

NOTE 2 The presence of sulfide in a sample also leads to restrictions on the scope of the analysis that can be undertaken using the XRF technique based upon fused beads. In particular, sulfate (SO_3) cannot be determined directly from such a fused bead because of the contribution to the analysis from the unknown amount of sulfide. In addition, sulfide cannot be determined directly (or accurately, indirectly) because of the contribution of the unknown amount of sulfate to the analysis and because of the possibility that some sulfide can be lost by volatilization during fusion. Consequently, the method of ISO 29581-1, included as Annex D to this part of ISO 29581, is the reference method for determining the sulfate content of samples containing sulfide species.

Other methods can be used, provided they are calibrated, either against the reference method or against internationally accepted reference materials, in order to demonstrate their equivalence.

In the case of dispute, unless otherwise agreed by all parties, only the reference method in ISO 29581-1 can be used.

This part of ISO 29581 describes methods that apply principally to cements, but which can also be applied to their constituent materials and to other materials, the standards for which call up these methods.

International Standard specifications state which methods can be used.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO Guide 30, *Terms and definitions used in connection with reference materials*

ISO Guide 31, *Reference materials — Contents of certificates and labels*

ISO 29581-1, *Cement — Test methods — Part 1: Analysis by wet chemistry*

EN 196-7, *Methods of testing cement — Part 7: Methods of taking and preparing samples of cement*

EN 197-1, *Cement — Part 1: Composition, specifications and conformity criteria for common cements*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
beads
glassy discs of fused sample for analysis by X-rays in the spectrometer

3.2
pellets
compressed discs of finely ground sample for analysis by X-rays in the spectrometer

3.3
calibration beads or pellets
beads or pellets used for establishing the calibration equation

3.4
analysis beads or pellets
beads or pellets containing the sample being analysed

3.5
accuracy
closeness of agreement between a test result and the certified value for a reference material

3.6
repeatability
closeness of agreement among independent test results obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time

3.7
reproducibility
closeness of agreement between independent test results obtained with the same method on identical test items in different laboratories with different operators using different equipment

3.8
expert laboratory
laboratory capable of consistently meeting the expert performance criteria set out in Clause 14

3.9
normal laboratory
laboratory capable of consistently meeting the normal performance criteria set out in Clause 14

4 General requirements for testing

4.1 Number of tests

Analysis of a cement can require the determination of a number of its chemical elements. For each determination, one or more tests shall be carried out in which the number of measurements taken shall be as specified in the relevant clause of this part of ISO 29581.

Where the analysis is one of a series subject to statistical control, the determination of each chemical element by a single test shall be the minimum required.

Where the analysis method (including preparation and measurement) is checked at least once a week, as in accordance with 12.5.1, a determination of each chemical element by a single test shall be the minimum required. In the other cases, the number of tests for the determination of each chemical element shall be two; see also Clause 13.

4.2 Accuracy and precision limits

4.2.1 Accuracy limit

The accuracy performance criterion in this part of ISO 29581 is measured as a limit on the closeness of agreement between a test result and an accepted reference value for a certified reference material. The limits for accuracy, expressed in percent absolute, are set out in Table 2; one set is appropriate to the performance it is expected that an "expert" laboratory can achieve, whereas the other is appropriate for a "normal" laboratory.

4.2.2 Repeatability limit

The repeatability performance criterion in this part of ISO 29581 is measured as a limit on the repeatability where independent test results are obtained with the same method on identical test items (material) in the same laboratory by the same operator using the same equipment within a short interval of time. The limits for repeatability, expressed in percent absolute, are set out in Table 1; one set is appropriate to the performance it is expected that an "expert" laboratory can achieve, whereas the other is appropriate to a "normal" laboratory.

4.2.3 Reproducibility limit

The reproducibility performance criterion in this part of ISO 29581 is measured as a limit on the reproducibility where test results are obtained with the same method on identical test items (material) in different laboratories with different operators using different equipment. The limits for reproducibility, expressed in percent absolute, are set out in Table 3; one set is appropriate to the performance it is expected that an "expert" laboratory can achieve, whereas the other is appropriate to a "normal" laboratory.

4.2.4 Laboratory competence

The laboratory shall demonstrate that it can achieve the required performance in accordance with 12.3.3 and 12.3.4.

4.3 Expression of mass

Express mass in grams to the nearest 0,000 5.

4.4 Other methods

Other methods may be used, provided they are calibrated, either against the reference method or against internationally accepted reference materials, in order to demonstrate their equivalence.

5 Reagents and reference materials

5.1 Pure reagents

Reagents shall be of analytical quality and, wherever possible, pure oxides or carbonates, except for the calibration of such elements as sulfur, chlorine, bromine or phosphorus, which do not form stable oxides or carbonates, where some guarantee of stoichiometry is required.

Reagents shall be free of (or corrected for) the presence of water (and, in the case of oxides, carbon dioxide) when weighed out for fusion. Also, the reagents shall be in a known oxidation state. The specified procedure ensures that the correct oxidation state is obtained.

The reagents used to prepare the standard beads for cations shall be pure oxides or carbonates of at least 99,95 % purity (excluding moisture or CO_2).

Reagents shall be used in a known stoichiometry in terms of content. In order to achieve this, they can be treated before use as follows.

a) Determine the loss on ignition for silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and magnesium oxide (MgO) as follows.

   1) Ignite the reagent at, for example, (1 175 ± 25) °C and maintain at this temperature for 30 min.

   2) Cool in a desiccator to room temperature and reweigh.

   3) After allowing for this loss, weigh the appropriate amount of the unignited material to prepare the bead.

b) Dry manganese oxide (Mn_2O_3) and titanium(IV) oxide (TiO_2) as follows.

   1) Ignite the reagent at, for example, (1 000 ± 25) °C and maintain at this temperature for 30 min.

   2) Cool in a desiccator to room temperature before use.

c) Dry iron (III) oxide (Fe_2O_3) as follows.

   1) Ignite the reagent at, for example, (700 ± 25) °C and maintain at this temperature for 30 min.

   2) Cool in a desiccator to room temperature before use.

d) Dry calcium carbonate ($CaCO_3$), strontium carbonate ($SrCO_3$), potassium carbonate (K_2CO_3) and sodium carbonate (Na_2CO_3).

   1) Heat the reagent at, for example, (250 ± 10) °C and maintain at this temperature for 2 h.

   2) Cool in a desiccator to room temperature before use.

5.2 Reference materials

5.2.1 Certified reference materials

Certified reference materials (CRMs) are materials, e.g. cement, supplied by an organization conforming to the requirements for the competence of reference material producers in accordance with ISO Guide 30.

CRMs shall be supplied with a certificate of analysis giving information on the average value and standard deviation in accordance with ISO Guide 31.

5.2.2 Industrial reference materials

Industrial reference materials (IRMs) are materials, e.g. cement, prepared and homogenized by a laboratory. The reference analysis of an IRM shall be the average result from inter-laboratory co-operative testing involving at least four laboratories able to meet the performance criteria given in 12.3.

5.3 Calibration standards

Calibration standards are prepared in the laboratory from pure, analytical-grade reagents, IRMs, CRMs or a combination of these. They shall be formulated to provide a series of calibration standards covering the range of maximum to minimum values for each element being analysed and shall be evenly distributed between those limits. The variation in concentrations of the elements shall be independent of each other. There shall be a minimum of seven calibration standards in a series.

5.4 Binding agent

A binding agent, e.g. wax, whose influence on the elements being analysed has been determined, is used in the grinding of samples during the preparation of pressed pellets. Carry out a pellet-preparation monitoring check (see 12.5) whenever the batch of binding agent is changed.

6 Apparatus

6.1 Balance, capable of weighing to an accuracy of ± 0,000 5 g.

6.2 Fusion vessels and **casting moulds**, of a non-wetted platinum alloy, such as Pt/5 % Au or Pt/Rh.

Vessels that serve both as a fusion vessel and as a casting mould (i.e. a combined fusion mould) may be used. If moulds become distorted in use, then they shall be reshaped by pressing in a suitable former. If the bottom (flat) surface of the bead is used for analysis, it is necessary that the internal base of the mould also be kept flat and free from blemishes.

NOTE Cleanliness of fusion vessels is important in achieving accurate analyses. This can be achieved, for example, by boiling in dilute hydrochloric acid, 1:10 by volume or citric acid, 100 g/l.

6.3 Lids, optional, of a platinum alloy (not necessarily non-wetted).

6.4 Furnace, e.g. an electric resistance, muffle or high-frequency induction furnace, capable of operating at (250 ± 10) °C, (700 ± 25) °C, (950 ± 25) °C, (1 000 ± 25) °C and (1 175 ± 25) °C.

6.5 Automatic fusion apparatus, for use in automatic bead preparation (see 11.4).

An automatic fusion apparatus may be used, provided that the performance criteria in 12.3 can be met.

6.6 Cooling apparatus, consisting of any device, such as a narrow jet of air that can be directed to the centre of the base of the casting mould (for example, by the base of a bunsen burner without a barrel) or a water-cooled metal plate.

NOTE Normally, cooling in air is sufficient but some difficult samples can require a cooling apparatus in order to cool the melt rapidly. This is necessary to obtain a homogeneous bead and to free the melt from the casting mould.

6.7 Heat reservoir, for the casting mould, required in special circumstances when using moulds of small sizes, so that the mould does not cool too rapidly when removed from the furnace.

6.8 Spectrometer, X-ray fluorescence, capable of meeting the performance criteria given in 12.3.

NOTE It is required to set appropriate measuring conditions to satisfy the performance criteria based on the type of samples, the type of apparatus, elements being analysed and their content, etc.

6.9 Flow gas, maintained at as constant a room temperature as possible.

The temperature of the flow gas cylinder and of the connecting pipework is critical in order to prevent drift in sensitivity of the flow proportional counters. Pipework shall be as short as practical and run, whenever possible, within the temperature-controlled room housing the spectrometer. Where this is not possible, the cylinder shall be kept in a temperature-controlled cabinet (room temperature ± 2 °C) or otherwise maintained at a constant room temperature. For the same reason, new cylinders shall be allowed to equilibrate for at least 2 h to room temperature before use.

NOTE 1 The flow gas is used in the gas flow proportional counter of the XRF spectrometer.

NOTE 2 The composition of gas can change as the cylinder becomes exhausted. Cylinders should be replaced before they become completely empty.

6.10 Grinding equipment, capable of grinding the sample, with binding agent if necessary, to a suitable fineness.

6.11 Pellet press, capable of applying a pressure suitable for production of pellets with a consistent, consolidated surface to meet the performance requirements given in 12.3.

6.12 Mould, usually of steel, of suitable strength to withstand the press without distortion and of suitable size to produce a pellet to fit the spectrometer.

7 Preparation of a test sample of cement

Before chemical analysis, treat the laboratory sample, taken in accordance with EN 196-7, as follows to obtain a homogeneous test sample.

a) Take approximately 100 g of the laboratory sample by means of a sample divider or by quartering.

b) Sieve this portion on a 150 µm or 125 µm sieve until the residue remains constant.

c) Remove metallic iron from the material retained on the sieve by means of a magnet (see Note 1).

d) Grind the iron-free fraction of the retained material so that it completely passes the 150 µm or 125 µm sieve.

e) Transfer the sample to a clean, dry container with an airtight closure and shake vigorously to mix it thoroughly.

f) Carry out all operations as quickly as possible to ensure that the test sample is exposed to ambient air for only the minimum time.

NOTE 1 Where the analysis is one of a series subject to statistical control and the level of the metallic iron content has been shown to be insignificant in relation to the chemical properties being determined, it is not necessary to remove metallic iron. Where the level of metallic iron is significant, it is required to record and report the amount in the results.

NOTE 2 Where the sample contains quartz, it can be necessary to grind the sample to pass a 90 µm sieve in order to obtain a satisfactory fusion (see Clause 11). The time and temperature required to obtain a satisfactory fusion is affected by the fineness of the sample.

NOTE 3 Where pressed pellets are used, accuracy can be improved by grinding the sample more finely.