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Chemical analysis of refractory material glass and glazes — Determination of Fe^{2+} and Fe^{3+} by the spectral photometric method with 1,10-phenanthroline

Analyse chimique de matériaux réfractaires, du verre et d'émaux — Dosage de Fe^{2+} et Fe^{3+} par la méthode spectrophotométrique en utilisant la 1,10-phénanthroline

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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 14719 was prepared by Technical Committee ISO/TC 33, *Refractories*.

INTERNATIONAL STANDARD **ISO 14719:2011(E)**

Chemical analysis of refractory material glass and glazes — Determination of Fe^{2+} and Fe^{3+} by the spectral photometric method with 1,10-phenanthroline

1 Scope

This International Standard specifies a spectral photometric method with 1,10-phenanthroline for the quantitative determination of Fe^{2+} and Fe^{3+} in oxidic raw and basic materials for ceramics, glass and glazes, e.g. feldspar, kaolinites, clay, limestone, quartz refractory materials. This International Standard could be extended to other aluminosilicate materials, providing that uncertainty data is produced to support it. However, there might be problems in the decomposition of high-purity alumina and chrome ore samples.

The method is not suitable for reduced materials, such as silicon carbide, graphite-magnesia, etc.

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 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5022, *Shaped refractory products — Sampling and acceptance testing*

ISO 6286, *Molecular absorption spectrometry — Vocabulary — General — Apparatus*

ISO 8656-1, *Refractory products — Sampling of raw materials and unshaped products — Part 1: Sampling scheme*

ISO 10725, *Acceptance sampling plans and procedures for the inspection of bulk materials*

ISO 11648-2, *Statistical aspects of sampling from bulk materials — Part 2: Sampling of particulate materials*

ISO 12677, *Chemical analysis of refractory products by X-ray fluorescence (XRF) — Fused cast-bead method*

ISO 26845, *Chemical analysis of refractories — General requirements for wet chemical analysis, atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) methods*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 26845 apply.

4 Principle of Methods A and B

Samples are digested in a mixture of hydrofluoric acid and sulfuric acid. In the presence of a complexing agent, 1,10-phenanthroline, Fe^{2+} ions form a pink complex. The pink complex is measured photometrically at 510 nm in an aqueous solution. Quantitative results are obtained by calibration with reference solutions. The sum of the determination of both iron species corresponds to the total iron content.

This International Standard provides two sample dissolution techniquesl. In Method A, ten times more sample (500 mg) is necessary than for Method B (20 mg to 30 mg). As a consequence, the amount of reagents needed are reduced for Method B. In both methods, a HF-H_2SO_4 dissolution of the sample is carried out.

Methods A and B implement different strategies to avoid oxidation of Fe^{2+} to Fe^{3+} during the sample dissolution and measurement: while in Method A the samples react in an air- and light-tight reaction vessel with nitrogen, in Method B the solution is stabilized with nitrilotriacetic acid in simple polystyrene cuvettes cooled by ice.

Both methods are applicable for the full range of materials covered by the scope of this International Standard. For samples which appear more heterogeneous, a higher sample mass for the preparation may lead to more reproducible results. In this case, Method A shall be applied.

5 Sample preparation

The sampling shall be performed in accordance with ISO 5022 or ISO 8656-1 with reference, where appropriate, to ISO 10725 and ISO 11648-2.

The sample shall be ground to a particle size less than 63 µm and stored afterwards in a stoppered sample bottle in a desiccator.

The samples shall be dried to constant mass at 110 °C before the determination of Fe^{2+}/Fe^{3+}.

Weigh precisely the correct sample amount for the dissolution.

NOTE The drying of samples will not change the Fe^{2+} content in almost all refractory materials; the moisture content might vary with time.

6 Interferences

Interferences in the determination of Fe^{2+}/Fe^{3+} can be caused by other polyvalent ions, e.g. As^{5+}/As^{3+}, Sb^{5+}/Sb^{3+}, etc. The formation of an insoluble precipitate, e.g. lead and barium sulfate, may also interfere in the determination.

7 Sample disintegration and measurement

7.1 Method A

7.1.1 Reagents

Reagents of a recognized analytical grade shall be used for this analysis.

7.1.1.1 **Water**, according to ISO 3696, at least of Grade 2.

7.1.1.2 **Sulfuric acid**, H_2SO_4, $\rho = 1{,}84$ g/cm^3.

7.1.1.3 **Sulfuric acid** (1 + 1).

7.1.1.4 **Hydrofluoric acid**, HF, $\rho = 1{,}13$ g/cm^3.

7.1.1.5 **Hydrofluoric acid**, without reducing agents.

Transfer 50 ml of hydrofluoric acid (7.1.1.4) into a platinum dish. Add one drop of 0,02 mol/l $KMnO_4$ (7.1.1.15) solution. Heat on a steam bath until the permanganate is reduced. Cool for use and store in a polyethylene bottle.

7.1.1.6 **Boric acid solution**.

Add 90 g of boric acid (H_3BO_3) to 1 800 ml of water.

7.1.1.7 **Hydroxylammonium chloride**, $NH_2OH{\cdot}HCl$ (100 g/l).

7.1.1.8 **1,10-Phenanthroline solution** (5 g/l).

7.1.1.9 **Ammonium acetate**, CH_3COONH_4 (approximately 50 % by mass).

Dissolve 50 g of ammonium acetate in 50 ml of water.

7.1.1.10 **Ammonium iron(II) sulfate hexahydrate**, $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$.

7.1.1.10.1 **Iron stock solution** (1 ml = 1 mg Fe).

Weigh 3,510 8 g of ammonium iron(II) sulfate hexahydrate [$Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$] (7.1.1.10) and transfer to a 500 ml volumetric flask. Dissolve in water, add 8 ml to 10 ml of hydrochloric acid ($\rho = 1{,}19$ g/cm^3), dilute to volume and mix.

7.1.1.10.2 **Iron standard solution** (1 ml = 0,01 mg Fe).

Dilute 10 ml of the iron stock solution to 1 000 ml in a volumetric flask with deionized water.

7.1.1.11 **Nitrogen gas**, white spot (high quality).

The gas cylinder should be provided with a two-stage reducing valve and a gas-flow regulator for a flow rate of 28 l/h to 280 l/h.

7.1.1.12 **Hydrochloric acid**, HCl, $\rho = 1{,}19$ g/cm^3.

7.1.1.13 **Hydrochloric acid** (1 + 4).

7.1.1.14 **Hydrochloric acid** (1 + 12).

7.1.1.15 **Potassium permanganate solution**, $KMnO_4$, 0,02 mol/l (3,160 64 g/l).

7.1.2 Apparatus

For solutions that do not contain hydrofluoric acid, ordinary laboratory apparatus and the usual laboratory glassware made from borosilicate glass and complying with the requirements of relevant International Standards shall be used.

For solutions containing hydrofluoric acid or any acidic fluoride, plastic apparatus shall be used. Graduated plastic graduated flasks shall be used for sample stock solutions and calibration standards, etc.

Beakers, storing bottles, volumetric flasks and pipettes shall be prepared by filling them to 90 % of the overflow capacity with hydrochloric acid (7.1.1.14) overnight. After the soaking, they shall be washed thoroughly with water.

7.1.2.1 **Analytical balance**, capable of reading to the nearest 0,1 mg.

7.1.2.2 **Volumetric flasks**, complying with the requirements of class A in ISO 1042.

7.1.2.3 **Pipettes**, of suitable capacities complying with the requirements of class A in ISO 648.

7.1.2.4 **Magnetic stirrer**.

7.1.2.5 **Molecular absorption spectrometer**, conforming to the requirements of ISO 6286.

7.1.2.6 **Optical cells**, as recommended by the spectrometer manufacturer.

7.1.2.7 **Hotplate**.

7.1.2.8 **Reaction vessel**. Plastic or polytetrafluoroethylene (PTFE) bottle or beaker of 250 ml capacity.

The vessel will be used to exclude air (oxygen) when reacting the sample with the reagents. The vessel can be fitted with a rubber stopper, as shown in Figure 1, or the vessel can be a beaker with the lip removed and the bottom of another container placed on top, with the appropriate openings for introduction of purge gas, reagents, and vent tubing. In order to exclude light, the vessel shall be covered with black paint on the surface.

The vessel comprises the components described in 7.1.2.8.1 to 7.1.2.8.5.

7.1.2.8.1 **Plastic** or **TFE-fluorocarbon bottle or beaker**, of 250 ml capacity.

7.1.2.8.2 **Plastic tube**, used to introduce the purge gas into the vessel. It is advisable to use a connection between the plastic tubing and the gas cylinder that will allow it to be easily connected and disconnected.

7.1.2.8.3 **Plastic powder funnel**, that allows for the addition of the reagents to the sample without interfering with the purged atmosphere in the vessel.

7.1.2.8.4 **Vent tube**, to allow the escape of gas when reagents are being added through the powder funnel.

If it is not present, reagents could be forced back through the powder funnel when they are added because the vessel is under positive pressure.

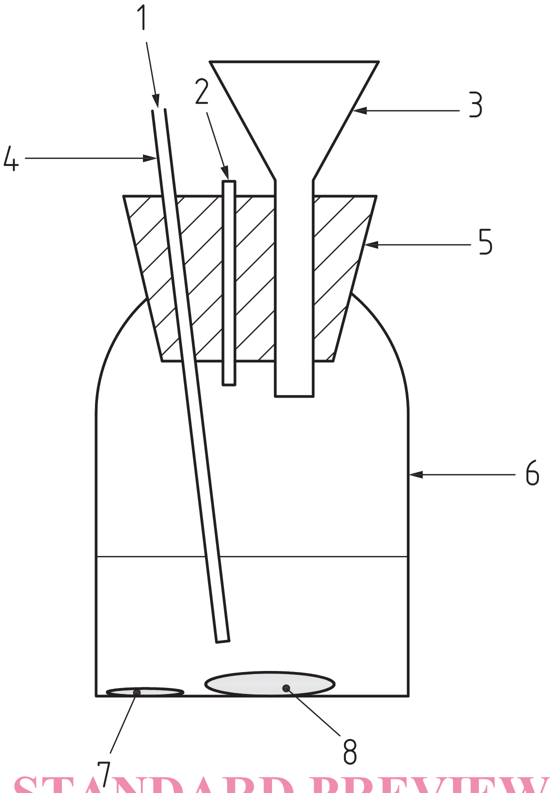
7.1.2.8.5 **Magnetic stirrer bar**, with a plastic covering.

7.1.2.9 **Beakers**, of 100 ml capacity.

7.1.2.10 **pH meter**.

7.1.2.11 **Platinum dish**, of suitable capacity.

7.1.2.12 **Commercially available black paint**, in an aerosol canister.



Key

1	gas inlet
2	vent tube
3	plastic powder funnel
4	plastic tube
5	rubber stopper
6	PTFE or plastic bottle or beaker
7	sample
8	magnetic stirrer bar

Figure 1 — Ferrous-iron reaction vessel

7.1.3 Iron calibration curve

Into a series of 100 ml beakers (7.1.2.9), add appropriate aliquots of diluted iron standard solution (7.1.1.10.2) to cover the range of 0 to 400 µg of Fe^{2+}. Dilute the solution in each beaker to 50 ml with water. Add to each beaker 5 ml of hydroxylammonium chloride solution (7.1.1.7) and 5 ml of 1,10-phenanthroline solution (7.1.1.8). Adjust the pH of the solutions to 3,5 with a pH meter (7.1.2.10) by using hydrochloric acid (7.1.1.14) or ammonium acetate (7.1.1.9). Transfer the solutions to 100 ml volumetric flasks (7.1.2.2). Dilute to volume with water and mix thoroughly. Allow to stand for 15 min.

Measure the optical absorbance of the solutions against water in appropriate cells at 510 nm on the spectrophotometer (7.1.2.5).

Plot the concentration (micrograms of iron per millilitre of measuring solution) versus optical absorbance on linear graph paper.

7.1.4 Preparation of the sample solution

Transfer 500 mg of the powdered glass with a little water into a 250 ml plastic or PTFE reaction vessel (7.1.2.8) containing a small magnetic stirrer bar (7.1.2.8.5). Place the purging apparatus (see Figure 1)