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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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Contents

Page

Foreword ..... **iv**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **1**
4 Principle of Methods A and B **2**
5 Sample preparation **2**
6 Interferences **2**
7 Sample disintegration and measurement **2**
8 Calculation and expression of results **9**
9 Test report **10**
Annex A (informative) **Precision** **11**
Bibliography **13**

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*.

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 techniquesI. 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.

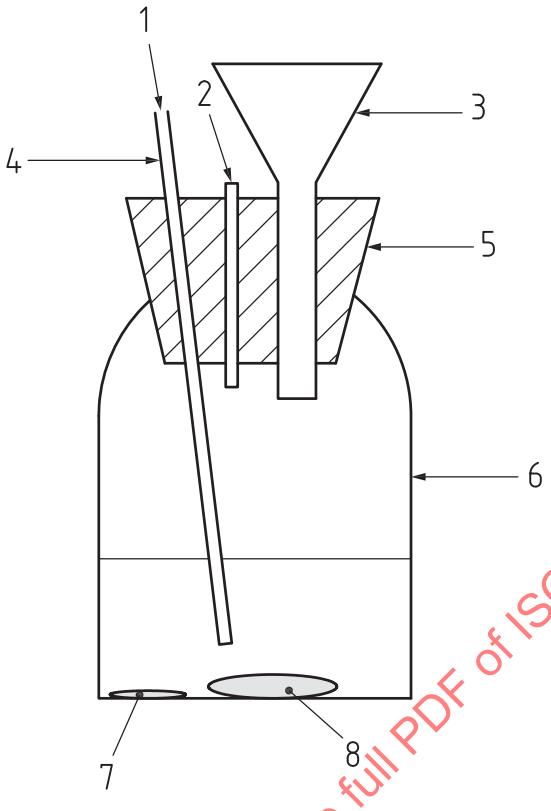
7.1.2.8.5 **Magnetic stirrer bar**, with a plastic covering.

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)

in the vessel. Begin stirring and purge with nitrogen (7.1.1.11) for 5 min. While continuing to purge, transfer 5 ml of sulfuric acid (1 + 1) (7.1.1.3) and 5 ml of hydrofluoric acid (7.1.1.5) through the funnel (7.1.2.8.3). Stir for 30 min. Add 100 ml of hot, boric acid solution (7.1.1.6) (approximately 75 °C) through the funnel and stir for 10 min. Turn off the purge gas.

Transfer the decomposition solution into a 250 ml volumetric flask (7.1.2.2). Allow to cool to room temperature and dilute to volume with deionized water that was stored overnight in order to remove any bubbles.

In the case of oxidized glass, increase the sample amount to 1 g and use the same amount of reagents.

The sample solution cannot be stored for more than one day.

7.1.5 Preparation of the blank solution

Prepare a blank sample solution following the procedure described in 7.1.4 but without any sample.

7.1.6 Determination of Fe^{2+} oxide (FeO)

Transfer a suitable aliquot of the sample solution obtained by applying the instructions of 7.1.4 into the beaker (7.1.2.9). The aliquot of the sample solution depends on the Fe^{2+} concentration in the solution which shall fall within the concentration range adjusted in the calibration graph. Add 5 ml of 1,10-phenanthroline solution (7.1.1.8). Adjust, with a pH meter (7.1.2.10), the pH to 3,5 by adding ammonium acetate (7.1.1.9). Transfer the solution into a 100 ml volumetric flask, dilute to the mark with deionized water and mix well. Allow to stand for 15 min.

Apply the same procedure (by taking the same aliquot) of the blank solution prepared in accordance with 7.1.5.

Correct for the blank by measuring the optical absorbance of the sample measuring solution and blank against water at 510 nm in appropriate cells on the spectrometer (7.1.2.5).

7.1.7 Determination of the total iron content (calculated as Fe_2O_3)

7.1.7.1 Determination of total iron content (calculated as Fe_2O_3) by XRF methods

Follow the instructions of ISO 12677. Ensure that the total iron content is high enough to fit into the calibration curve of the X-ray fluorescence (XRF) spectrometer.

7.1.7.2 Determination of total iron content (calculated as Fe_2O_3) by the spectral photometric method by 1,10-phenanthroline absorption spectrometry

Transfer a suitable aliquot of the sample solution obtained by following the procedure described in 7.1.4 into a beaker (7.1.2.9). The aliquot of the sample solution depends on the Fe^{2+} concentration in the solution which shall fall within the concentration range adjusted in the calibration graph.

Time is critical in this procedure, from the initial purging through the addition of the 1,10-phenanthroline solution (7.1.1.8). The time indicated shall be strictly adhered to.

In the case of oxidized glass, increase the sample amount to 1 g and use the same amount of reagents.

The sample solution cannot be stored for more than 1 day.

Add 5 ml of hydroxyammonium chloride (7.1.1.7) and 5 ml of 1,10-phenanthroline solution (7.1.1.8). Adjust the pH of the solution to 3,5 with a pH meter (7.1.2.10) with ammonium acetate (7.1.1.9). Transfer the solution into a 100 ml volumetric flask (7.1.2.2) and dilute to the mark with deionized water. Mix well. Allow to stand for 15 min.

Apply the same procedure (by taking the same aliquot) to the blank solution prepared previously as in 7.1.4.

Correct for blank value by measuring the optical density of the sample measuring solution against water at 510 nm in appropriate cells on the absorption spectrometer (7.1.2.5).

7.2 Method B

7.2.1 Reagents

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

7.2.1.1 **Water**, according to ISO 3696, of at least grade 3.

7.2.1.2 **Iron parent solution**, ρ(Fe) = 1 000 mg/l: parent solution of the commercially available element with ρ = 1 000 mg/l Fe.

7.2.1.3 **Iron reference solution**, ρ(Fe) = 100 mg/l: 10 ml of the parent solution (7.2.1.2) is transferred to a 100 ml volumetric flask which is filled up to the mark with water (7.2.1.1).

7.2.1.4 **1,10-Phenanthroline**, $C_{12}H_8N_{12}$.

7.2.1.5 **1,10-Phenanthroline solution**, $\rho(C_{12}H_8N_{12})$ = 40 g/l: 2 g of 1,10-phenanthroline (7.2.1.4) are weighed into a beaker and diluted with approximately 30 ml of water (7.2.1.1). The solution shall be transferred into a 50 ml volumetric flask and filled up to the mark with water. The solution may be used for about 4 weeks.

7.2.1.6 **Sodium hydroxide**, NaOH.

7.2.1.7 **Sodium hydroxide solution**, c(NaOH) = 5 mol/l: 200 g of sodium hydroxide (7.2.1.6) are weighed into a beaker and diluted with approximately 800 ml of water (7.2.1.1). The solution shall be transferred into a 1 000 ml plastic volumetric flask and filled up to the mark with water.

7.2.1.8 **Nitrilotriacetic acid**, $N(C_6H_9O_6)_3$.

7.2.1.9 **Nitrilotriacetic acid solution**, $\rho[N(C_6H_9O_6)_3]$ = 40 g/l: 2 g of nitrilotriacetic acid (7.2.1.8) are weighed into a beaker and diluted with 4 ml of sodium hydroxide solution (7.2.1.7) and then 20 ml of water (7.2.1.1) is added. The solution shall be transferred into a 50 ml volumetric flask and filled up to the mark with water. The solution shall be mixed well.

7.2.1.10 **Boric acid**, H_3BO_3.

7.2.1.11 **Boric acid solution**, $\rho(H_3BO_3)$ = 40 g/l: 40 g of boric acid (7.2.1.10) are weighed into a 1 l beaker and diluted with approximately 600 ml of water (7.2.1.1). The solution is warmed slowly on a heating plate until all the crystals are dissolved. Once the solution has cooled back to room temperature, it shall be transferred into a 1 000 ml volumetric flask and filled up to the mark with water. The solution may be used for about 6 months.

7.2.1.12 **Sulfuric acid**, $c(1/2H_2SO_4) \approx 20$ mol/l.

7.2.1.13 **Hydrofluoric acid**, w(HF) = 40 %; ρ = 1,13 g/ml.

7.2.1.14 **Decomposition solution**: 25 ml of sulfuric acid (7.2.1.12) and 25 ml of hydrofluoric acid (7.2.1.13) are poured carefully into a plastic bottle. It is closed thoroughly and shaken.

7.2.1.15 **Ascorbic acid**, $C_6H_8O_6$.

7.2.2 Apparatus

Apparatus as described in 7.1.2, together with the following elements.

7.2.2.1 Polystyrene test tubes.

7.2.2.2 Spectral absorption spectrometer.

7.2.2.3 Polystyrene cuvettes, with 10 mm layer thickness, to be sealed.

7.2.3 Sample disintegration and measurement

7.2.3.1 General

The determination is performed in two steps. In the first step, the mass content of Fe^{2+} is determined. In the second step, Fe^{3+} is reduced to Fe^{2+}. The mass content of the Fe^{2+} formed is determined likewise.

The glass and polystyrene containers, as well as the pipettes, shall be cleaned directly before use with diluted nitric acid. Afterwards they shall be rinsed thoroughly with water.

7.2.3.2 Sample decomposition for the determination of iron species

Polystyrene test tubes should be provided in a test tube rack. For each determination, one test tube shall be taken. Take another six test tubes for the preparation of the standard solutions. Weigh 20 mg to 30 mg of the sample, ground according to Clause 5, into a polystyrene test tube.

Moisten the sample with a drop of water and add a suitable small stirring magnet. Add 0,2 ml of nitrilotriacetic acid solution (7.2.1.9) and 0,2 ml of 1,10-phenanthroline solution (7.2.1.5) with ice cooling.

Stir constantly for 3 min. Afterwards add 0,4 ml of decomposition solution (7.2.1.14), then stir the suspension for a further 30 min. The solution may become slightly hazy.

Add 3 ml of boric acid solution (7.2.1.11) and stir the mixture for another 3 min. After this time. adjust the pH-value to 2,8 by adding 1,5 ml of sodium hydroxide solution (7.2.1.7). Check the pH value with an indicator stick.

If necessary, adjust the pH value by adding decomposition solution (7.2.1.14) or sodium hydroxide solution (7.2.1.7), respectively.

As an alternative, approximately 5,5 ml of sodium acetate buffer solution (pH=4) can be added.

The polystyrene test tubes shall be screwed thoroughly and then shaken.

NOTE 1 While adding the sodium hydroxide solution, a haze might appear. In this case, centrifugation of the test tubes prior to measurement is necessary.

NOTE 2 The polystyrene test tubes (7.2.2.1) typically fit into conventional laboratory centrifuges.

7.2.3.3 Setting up the standard solutions

Prepare six polystyrene test tubes (7.2.2.1) solely with the reagents. Add a drop of water (7.2.1.1) and a small suitable stirring magnet to each of them. Then proceed with these standards by following the steps in accordance with 7.2.3.2.

Then add 0 µl, 20 µl, 50 µl, 100 µl, 150 µl and 200 µl of iron reference solution (7.2.1.3) with a pipette.

Add ascorbic acid to each of the standard solutions until a little sediment remains. The ascorbic acid serves to reduce the Fe^{3+} to Fe^{2+} in the standard solutions. A pink to dark red colour appears in the solution. After

30 min, measure each standard solution and determine the calibration curve. Thereafter determine the Fe^{2+} concentration in the sample according to 7.2.3.4.

7.2.3.4 Determination of Fe^{2+} concentration

Transfer 2 ml of the sample solution prepared according to 7.2.3.2 into a polystyrene cuvette (7.2.2.3) using a microlitre pipette. Measure this solution at a wavelength of 510 nm with the photometer and compare with the standard solutions.

7.2.3.5 Determination of Fe^{3+} concentration

After the measurement of Fe^{2+} ions in the sample solutions, add a spatula-tip-full of ascorbic acid to all the polystyrene cuvettes (7.2.2.3). This serves to reduce the Fe^{3+} ions present to Fe^{2+} ions. Each polystyrene test tube shall be screwed thoroughly and shaken. After a reaction time of 30 min, measure this solution at a wavelength of 510 nm with the photometer and compare with the standard solutions.

8 Calculation and expression of results

The determination of the iron concentration is performed using a calibration curve.

It can be drawn by hand or alternatively it can be provided by an appropriate computer-aided evaluation program.

The mass content of Fe^{2+} (w_1) or calculated as FeO (w_2) shall be determined using Equations (1) and (2):

$$w_1 = \frac{V_1 \cdot F}{10\,000 \cdot m} \tag{1}$$

and

$$w_2 = w_1 \times 1{,}286\,5 \tag{2}$$

where

V_1 is the volume read from the calibration curve, in microlitres;

F is the factor (resulting from the concentration of the iron standard solution (7.1.1.10.2), in milligrams per litre;

m is the net mass, in milligrams.

The mass content of Fe^{3+} (w_3) or calculated as FeO (w_4) shall be determined using Equations (3) and (4):

$$w_3 = \left(\frac{V_2 \cdot F}{10\,000\ m} \right) - w_1 \tag{3}$$

and

$$w_4 = w_3 \times 1{,}429\,8 \tag{4}$$

where

V_2 is the volume read from the calibration curve (see 7.2.3.3), in microlitres;

F is a factor resulting from the concentration of the iron standard solution (7.1.1.10.2), in milligrams per litre;

m is the net mass, in milligrams.

At the most, three significant decimals are to be indicated, but no more than the lower limit of the range of application of this International Standard.

9 Test report

Test reports shall include the following information:

a) a reference to this International Standard;

b) sample identification;

c) test results expressed as a mean of the single values of the multiple determinations;

d) statement of whether method A or B was used in the determination;

NOTE See Tables A.1 and A.2.

e) if required, uncertainty of the mean (see Table A.1 for Method A and Table A.2 for Method B) or standard deviation;

f) if required, information for calibration;

g) any discrepancy of the procedure used for sample testing according to this International Standard;

h) name and address of the laboratory, analysis date and, if required, the signature of the responsible person.