INTERNATIONAL STANDARD ISO 1694

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Cryolite, natural and artificial — Determination of iron content — 1,10-Phenanthroline photometric method

Cryolithe, naturelle et artificielle — Dosage du fer — Méthode photométrique à la phénanthroline-1,10

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 47, has reviewed ISO Recommendation R 1964 and found it technically suitable for transformation. International Standard ISO 1694 therefore replaces ISO Recommendation R 1694-1970 to which it is technically identical.

ISO Recommendation R 1694 was approved by the Member Bodies of the following countries :

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No Member Body expressed disapproval of the Recommendation.

No Member Body disapproved the transformation of ISO/R 1694 into an International Standard.

Printed in Switzerland

Cryolite, natural and artificial — Determination of iron content — 1,10-Phenanthroline photometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a 1,10-phenanthroline photometric method for the determination of the iron content of natural and artificial cryolite and of natural and synthetic materials having a molar ratio (NaF/AlF_3) between 3 and 1,7 approximately.

The method is applicable to products having an iron content, expressed as iron(III) oxide, equal to or greater than 0,020 % (*m/m*).

2 REFERENCE

ISO 1619, *Cryolite, natural and artificial — Preparation and storage of test samples.*

3 PRINCIPLE

Dissolution of a test portion by either alkaline or acid fusion.

Preliminary reduction of iron(III) by means of hydroxylammonium chloride.

Formation of the complex iron(II)-1,10-phenanthroline in a buffered medium (pH value between 3,5 and 4,2).

Photometric measurement of the coloured complex at a wavelength of about 510 nm.

4 REAGENTS

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Sodium carbonate, anhydrous.

4.2 Boric acid (H_3BO_3).

4.3 Potassium pyrosulphate ($K_2S_2O_7$), finely crushed.

4.4 Nitric acid, approximately 8 N solution.

Dilute 540 ml of nitric acid, ρ approximately 1,40 g/ml, about 68 % (*m/m*) solution, with water and dilute to 1 000 ml.

4.5 Hydrochloric acid, approximately 6 N solution.

Dilute 515 ml of hydrochloric acid, ρ approximately 1,19 g/ml, about 38 % (*m/m*) solution, with water and dilute to 1 000 ml.

4.6 Hydroxylammonium chloride ($NH_2OH.HCl$), 10 g/l solution.

4.7 1,10-Phenanthroline hydrochloride, monohydrate, ($C_{12}H_8N_2.HCl.H_2O$) 2,5 g/l solution.

This reagent may be replaced by a 2,5 g/l solution of 1,10-phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$).

4.8 Buffer solution, of pH 4,9.

Dissolve 272 g of sodium acetate trihydrate ($CH_3COONa.3H_2O$) in approximately 500 ml of water. Add 240 ml of glacial acetic acid, ρ approximately 1,05 g/ml, about 17,4 N. Dilute to 1 000 ml and mix.

4.9 Sodium acetate trihydrate ($CH_3COONa.3H_2O$), 500 g/l solution.

4.10 Acetic acid, dilute solution.

Dilute 500 ml of glacial acetic acid, ρ approximately 1,05 g/ml, about 17,4 N, with water and dilute to 1 000 ml.

4.11 Iron, standard solution corresponding to 0,200 g of iron(III) oxide per litre.

Prepare this solution by either of the following two methods :

4.11.1 Weigh, to the nearest 0,001 g, 0,982 g of ammonium iron(II) sulphate hexahydrate $[(NH_4)_2Fe(SO_4)_2.6H_2O]$. Place in a beaker of suitable capacity (for example 100 ml) and dissolve in water. Add 20 ml of sulphuric acid solution, ρ approximately 1,84 g/ml, allow to cool, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,200 mg of Fe_2O_3.

4.11.2 Weigh, to the nearest 0,001 g, 0,200 g of iron(III) oxide previously ignited at 600 °C and cooled in desiccator. Transfer to a beaker of suitable capacity (for example 100 ml), add 10 ml of hydrochloric acid solution, ρ approximately 1,19 g/ml, and heat gently to dissolve. Allow to cool, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,200 mg of Fe_2O_3.

4.12 Iron, standard solution corresponding to 0,010 g of iron(III) oxide per litre.

Transfer 50,0 ml of the standard solution (4.11) to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,010 mg of Fe_2O_3.

Prepare this solution just before use.

4.13 Indicator paper, covering the pH range 3,5 to 4,2, at intervals of 0,2 unit.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Platinum dish, flat-bottomed, of diameter approximately 80 mm and depth approximately 35 mm, fitted with a platinum lid.

5.2 Electric furnace, capable of being controlled at 550 ± 25 °C, for alkaline fusion.

5.3 Electric furnace, capable of being controlled at 750 ± 25 °C, for alkaline fusion.

5.4 Electric furnace, capable of being controlled at 700 ± 20 °C, for acid fusion.

5.5 pH meter.

5.6 Spectrophotometer, or

5.7 Photoelectric absorptiometer, fitted with filters ensuring a maximum transmission between 500 and 520 nm.

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0,001 g, 1 g of the test sample, dried at 110 °C (see 3.3 of ISO 1619).

6.2 Blank test

6.2.1 *Alkaline fusion*

Weigh into the platinum dish (5.1) 12 g of the sodium carbonate (4.1) and 4 g of the boric acid (4.2) and mix thoroughly, preferably with a platinum spatula.

Cover the dish with its lid and place in the electric furnace (5.2), controlled at 550 ± 25 °C, taking care to isolate the dish from the floor of the furnace by means of a support to avoid the risk of contamination. Maintain at 550 ± 25 °C until the reaction subsides.

Then transfer the dish to the electric furnace (5.3), controlled at 750 ± 25 °C, again taking care to isolate it from the furnace floor, and allow to remain in the furnace for a maximum of 5 min.

Remove the dish from the furnace and allow to cool in air.

Add boiling water to the dish and heat gently until dissolution is complete.

After cooling slightly, transfer the contents of the dish to a beaker of suitable capacity containing 20 ml of the nitric acid solution (4.4). Carefully wash the dish and lid with 18 ml of the nitric acid solution and then with hot water, collecting the washings in the beaker; simmer gently for a few minutes until complete dissolution.

Allow to cool slightly and transfer quantitatively to a one-mark volumetric flask of the same capacity as that used for the preparation of the test solution (6.4.1). After cooling, dilute to the mark and mix.

6.2.2 *Acid fusion*

Weigh into the platinum dish (5.1), 10 g of the potassium pyrosulphate (4.3).

Cover the dish with its lid and place in the electric furnace (5.4), controlled at 700 ± 20 °C, taking care to isolate the dish from the floor of the furnace by means of a support to avoid the risk of contamination. Maintain at 700 ± 20 °C for a maximum of 10 min.

Remove the dish from the furnace and allow to cool in air. Add 10 ml of water and 10 ml of the hydrochloric acid solution (4.5) to the dish. Simmer until dissolution is complete, taking care at the same time to rinse the lid and walls of the dish with hot water, collecting the washings in the dish.

Allow to cool slightly and transfer the solution quantitatively to a one-mark volumetric flask of the same capacity as that used for the preparation of the test solution (6.4.1). After cooling, dilute to the mark and mix.

6.3 Preparation of calibration graph

6.3.1 *Preparation of the standard colorimetric solutions,* for photometric measurements with a cell of 1 cm optical path length

Into each of a series of eight 100 ml one-mark volumetric flasks, transfer respectively the volumes of the standard iron solution (4.12) shown in the following table :

Standard iron solution (4.12)	Corresponding mass of Fe_2O_3
ml	mg
0*	0
1,0	0,010
2,5	0,025
5,0	0,050
10,0	0,100
15,0	0,150
20,0	0,200
25,0	0,250

* Compensation solution.

Add to each flask an amount of water sufficient to dilute to approximately 50 ml, then add 5 ml of the hydroxylammonium chloride solution (4.6), 5 ml of the 1,10-phenanthroline solution (4.7) and 25 ml of the buffer solution (4.8). Dilute to the mark and mix.

6.3.2 *Photometric measurement*

After 10 min, carry out the photometric measurement with the spectrophotometer (5.6) at a wavelength of about 510 nm or with the photoelectric absorptiometer (5.7) fitted with a suitable filter, adjusting the instrument to zero absorbance against the compensation solution.

6.3.3 *Plotting the calibration graph*

Plot a graph having, for example, the iron(III) oxide content in milligrams per 100 ml of standard colorimetric solution as abscissae and the corresponding values of absorbance as ordinates.

6.4 Determination

6.4.1 *Preparation of the test solution*

6.4.1.1 ALKALINE FUSION

Into the platinum dish (5.1), weigh 12 g of the sodium carbonate (4.1) and 4 g of the boric acid (4.2). Mix thoroughly, preferably with a platinum spatula. Add the test portion (6.1) and mix thoroughly.

Cover the dish with its lid and place it in the electric furnace (5.2), controlled at 550 ± 25 °C, taking care to isolate the dish from the floor of the furnace by means of a support to avoid the risk of contamination. Maintain at 550 ± 25 °C until the reaction subsides. (Time necessary : about 30 min.)

Then transfer the dish to the electric furnace (5.3), controlled at 750 ± 25 °C, again taking care to isolate it from the floor of the furnace. Keep the dish in the furnace for 30 min, ensuring that the temperature of 750 ± 25 °C is maintained for at least 20 min.

Remove the dish from the furnace and allow to cool in air. Add boiling water to the dish and heat gently until dissolution is complete.

After cooling slightly, transfer the contents of the dish to a beaker of suitable capacity, containing 20 ml of the nitric acid solution (4.4).

Dissolve the residue (which consists essentially of iron(III) oxide) adhering to the walls of the dish by means of 18 ml of the nitric acid solution and carefully wash the dish and its lid with hot water, collecting the washings in the beaker. Simmer the solution for a few minutes to ensure complete dissolution. Allow to cool slightly and transfer the solution quantitatively to a one-mark volumetric flask of capacity either 250 or 500 ml, according to the iron content to be determined. After cooling, dilute to the mark and mix.

6.4.1.2 ACID FUSION

Into the platinum dish (5.1), weigh 10 g of the potassium pyrosulphate (4.3). Add the test portion (6.1) and mix carefully, preferably with a platinum spatula.

Cover the dish with its lid and place in the electric furnace (5.4), controlled at 700 ± 20 °C, taking care to isolate it from the floor of the furnace by means of a support to avoid the risk of contamination. Maintain at 700 ± 20 °C for 30 min.

Remove the dish from the furnace and allow to cool in air.

Add 10 ml of water and 10 ml of the hydrochloric acid solution (4.5) to the dish. Simmer the solution until complete dissolution, taking care at the same time to rinse the lid and walls of the dish with hot water and collect the washings in the dish.

Allow to cool slightly and transfer the solution quantitatively to a one-mark volumetric flask of capacity either 250 or 500 ml, according to the iron content to be determined. After cooling, dilute to the mark and mix.

6.4.2 *Colour reaction*

6.4.2.1 TAKING OF ALIQUOT PORTIONS

Take two aliquot portions of the test solution (6.4.1) each containing between 0,05 and 0,250 mg of iron (III) oxide and place one in a beaker of suitable capacity and the other in a 100 ml one-mark volumetric flask.

6.4.2.2 PRELIMINARY TEST FOR CONTROL AND ADJUSTMENT OF pH

Dilute the aliquot portion of the test solution in the beaker to approximately 50 ml with water. Then add 5 ml of the hydroxylammonium chloride solution (4.6), 5 ml of the 1,10-phenanthroline solution (4.7) and 25 ml of the buffer solution (4.8).

Check the pH value of the solution using either the indicator paper (4.13) or the pH meter (5.5). This value should be between 3,5 and 4,2; if it is not, adjust the pH value by slowly adding the required volume of the sodium acetate solution (4.9) or the acetic acid solution (4.10), as appropriate; stir after each addition.

Note the volume of reagent used to adjust the pH and discard the solution.

6.4.2.3 COLOUR DEVELOPMENT

To the aliquot portion of the test solution placed in the 100 ml one-mark volumetric flask, add the same quantities of all the reagents as used in the preliminary test (6.4.2.2). Dilute to the mark and mix.

6.4.2.4 PHOTOMETRIC MEASUREMENTS

After 10 min, carry out the photometric measurements of the test solution and blank test solution following the procedure specified in 6.3.2, after having adjusted the instrument to zero absorbance against water (see note to clause 7).

7 EXPRESSION OF RESULTS

By reference to the calibration graph (see 6.3.3), determine the iron content corresponding to the values of the photometric measurements (see 6.4.2.4).

The iron content, expressed as a percentage by mass of iron(III) oxide, is given by the formula

$$(m_1 - m_2) \times \frac{D}{10 \times m_0}$$

where

m_0 is the mass, in grams, of the test portion (6.1);

m_1 is the mass, in milligrams, of iron(III) oxide found in the aliquot portion of the test solution taken for the determination;

m_2 is the mass, in milligrams, of iron(III) oxide found in the aliquot portion corresponding to the blank test solution;

D is the ratio of the volume of the test solution to the volume of the aliquot portion taken for the determination.

NOTE — Generally, the aliquot portion of the blank test solution, after treatment for photometric measurement, shows a slight coloration. In this case, it will be advisable to use it as compensation solution.

In the event, the formula for calculation becomes

$$m_1 \times \frac{D}{10 \times m_0}$$

where the symbols have the same meaning as in the preceding formula.

8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard or in the International Standard to which which reference is made, or regarded as optional.