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# ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

# ISO RECOMMENDATION

# R 1694

## CRYOLITE (NATURAL AND ARTIFICIAL)

## DETERMINATION OF IRON CONTENT

## 1,10-PHENANTHROLINE PHOTOMETRIC METHOD

**1st EDITION**

August 1970

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## BRIEF HISTORY

The ISO Recommendation R 1694, *Cryolite (natural and artificial) – Determination of iron content – 1,10-phenanthroline photometric method*, was drawn up by Technical Committee ISO/TC 47, *Chemistry*, the Secretariat of which is held by the Ente Nazionale Italiano di Unificazione (UNI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1694, which was circulated to all the ISO Member Bodies for enquiry in March 1969. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Australia
Austria
Belgium
Brazil
Canada
Czechoslovakia
France
Germany
Greece
Hungary
India
Iran
Israel
Italy
Netherlands
New Zealand
Norway
Poland
Portugal
Romania
South Africa, Rep. of
Spain
Switzerland
Turkey
U.A.R.
United Kingdom
U.S.S.R.
Yugoslavia

No Member Body opposed the approval of the Draft.

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

ISO Recommendation R 1694 August 1970

# CRYOLITE (NATURAL AND ARTIFICIAL)

## DETERMINATION OF IRON CONTENT

## 1,10-PHENANTHROLINE PHOTOMETRIC METHOD

### 1. SCOPE

This ISO Recommendation describes a photometric method, using 1,10-phenanthroline, for the determination of the iron content of natural and artificial cryolite.

### 2. FIELD OF APPLICATION

The method is applicable to the determination of iron contents, expressed as $Fe_2O_3$, greater than 0.020 % of natural and artificial cryolite.

NOTE. – The method is also suitable for application to the natural and synthetic materials having a molar ratio $NaF/AlF_3$ between 3 and 1.7.

### 3. PRINCIPLE

Dissolution of a test portion either by 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 at a wavelength of about 510 nm.

### 4. REAGENTS

Distilled water or water of equal purity should be used in the test.

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, $\rho$ 1.4 (g/ml), approximately 68 % (m/m) solution, with water and dilute to 1000 ml.

4.5 *Hydrochloric acid*, approximately 6 N solution.

Dilute 515 ml of hydrochloric acid, ρ 1.14 (g/ml), approximately 38 % (m/m) solution, with water and dilute to 1000 ml.

4.6 *Hydroxylammonium chloride*, 10 g/l solution.

Dissolve 10 g of hydroxylammonium chloride ($NH_2OH.HCl$) in water and dilute to 1000 ml.

4.7 *1,10-phenanthroline hydrochloride*, 2.5 g/l solution.

Dissolve 2.5 g of 1,10-phenanthroline hydrochloride monohydrate ($C_{12}H_8N_2.HCl.H_2O$) in water and dilute to 1000 ml.

NOTE. – 1,10-phenanthroline hydrochloride monohydrate can be replaced by 1,10-phenanthroline monohydrate.

4.8 *Buffer solution*

Dissolve 272 g of sodium acetate trihydrate in approximately 500 ml of water.

Add 240 ml of glacial acetic acid, approximately 17.4 N, and dilute to 1000 ml. Filter, if necessary.

4.9 *Sodium acetate*, 500 g/l solution.

Dissolve 50 g of sodium acetate trihydrate in water and dilute to 100 ml. Filter, if necessary.

4.10 *Acetic acid*, dilute solution.

Dilute 500 ml of glacial acetic acid, approximately 17.4 N, with water and dilute to 1000 ml.

4.11 *Iron*, standard solution containing 0.200 g/l of $Fe_2O_3$.

This solution can be prepared by either of the two following methods :

4.11.1 Weigh, to the nearest 1 mg, 0.982 g of iron (II) ammonium sulphate hexahydrate, place in a beaker of suitable capacity (100 ml, for example) and dissolve in water.

Add 20 ml of sulphuric acid solution, ρ 1.84 (g/ml), 96 % (m/m) solution approximately, transfer quantitatively to a 1000 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 1 mg, 0.200 g of iron trioxide ($Fe_2O_3$) previously ignited at 600 °C and cooled in desiccator. Transfer to a beaker of a suitable capacity (100 ml, for example), add 10 ml of ρ 1.19 (g/ml) hydrochloric acid solution approximately 38 % (m/m) solution, and heat gently to dissolve. Allow to cool, transfer quantitatively to a 1000 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 containing 0.010 g/l of $Fe_2O_3$.

Transfer 50.0 ml of the standard solution (4.11) to a 1000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 10 μg of $Fe_2O_3$.

This solution should be prepared immediately before use.

4.13 *Indicator paper*, covering the pH range 3.5 to 4.2 at intervals of 0.2 units.

## 5. APPARATUS

Ordinary laboratory apparatus and

5.1 *Platinum dish*, flat-bottomed, approximately 80 mm in diameter and approximately 35 mm deep, fitted with a platinum lid.

5.2 *Electric furnace*, controlled at 550 ± 25 °C, for alkaline fusion.

5.3 *Electric furnace*, controlled at 750 ± 25 °C, for alkaline fusion.

5.4 *Electric furnace*, controlled at 700 ± 20 °C, for acid fusion.

5.5 *pH-meter*, fitted with a glass electrode.

5.6 *Spectrophotometer*, or

5.7 *Photoelectric absorptiometer.*

## 6. PROCEDURE

### 6.1 Test portion

Weigh, to the nearest 1 mg, 1 g of the dried test sample*.

### 6.2 Blank test

6.2.1 *Alkaline fusion*. Weigh into the platinum dish (5.1), 12 g of sodium carbonate (4.1) and 4 g of boric acid (4.2) and mix thoroughly 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. Leave the dish in the furnace until the reaction subsides.

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

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) and carefully wash the dish and lid with 18 ml of the nitric acid solution (4.4) and then with hot water, collecting the washings in the beaker; simmer gently for a few minutes until complete dissolution is obtained.

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 sample solution (6.4.1). After cooling, dilute to the mark and mix thoroughly.

Alternatively, the following procedure may be used :

6.2.2 *Acid fusion*. Weigh into the platinum dish (5.1), 10 g of 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, and leave at the temperature of 700 ± 20 °C for a maximum of 10 minutes.

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 and 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 same 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 sample solution (6.4.1). After cooling, dilute to the mark and mix thoroughly.

### 6.3 Preparation of calibration curve

6.3.1 *Preparation of the standard matching solutions*, for photometric measurements with a 1 cm cell. 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.

| Volume of standard iron solution (4.12) | Corresponding mass of $Fe_2O_3$ |
|---|---|
| ml | µg |
| 0 * | 0 |
| 1.0 | 10 |
| 2.5 | 25 |
| 5.0 | 50 |
| 10.0 | 100 |
| 15.0 | 150 |
| 20.0 | 200 |
| 25.0 | 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 thoroughly.

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* See ISO Recommendation R 1619, *Cryolite (natural and artificial) – Preparation and storage of test samples*, clause 2.3.

6.3.2 *Photometric measurement.* After 10 minutes, carry out the photometric measurement with the spectrophotometer (5.6) at a wavelength of about 510 nm or with the photoelectric absorptiometer (5.7) with a suitable filter, adjusting the instrument to zero optical density against the compensation solution.

6.3.3 *Preparation of calibration chart.* Prepare a calibration chart having, for example, the $Fe_2O_3$ content in milligrammes per 100 ml of standard matching solution as abscissae and the corresponding values of optical density as ordinates.

## 6.4 Determination

### 6.4.1 *Preparation of the sample solution*

6.4.1.1 ALKALINE FUSION. Weigh into the platinum dish (5.1) 12 g of sodium carbonate (4.1) and 4 g of boric acid (4.2). Mix thoroughly with a platinum spatula. Add to the mixture 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. Keep at 550 ± 25 °C until the reaction subsides (about 30 minutes).

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 minutes, the operator making sure that the temperature of 750 ± 25 °C is kept for at least 20 minutes.

Remove the dish from the furnace and allow to cool in the 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 trioxide) adhering to the walls of the dish by means of 18 ml of the nitric acid solution (4.4) 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 quantitatively to a one-mark volumetric flask of either 250 or 500 ml capacity, according to the iron content to be determined.

After cooling, dilute to the mark and mix thoroughly.

Alternatively, the following procedure may be used :

6.4.1.2 ACID FUSION. Weigh into the platinum dish (5.1) 10 g of potassium pyrosulphate (4.3). Add the test portion (6.1) and mix carefully 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. Keep for 30 minutes at the temperature of 700 ± 20 °C.

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 is obtained, 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 either 250 or 500 ml capacity according to the iron content to be determined.

After cooling, dilute to the mark and mix thoroughly.

### 6.4.2 *Development of the colour reaction*

6.4.2.1 TAKING OF ALIQUOTS. Take two aliquot portions of the sample solution (6.4.1) each containing between 50 and 250 µg of $Fe_2O_3$ and place one in a beaker of suitable capacity and the other in a 100 ml one-mark volumetric flask.