International Standard ISO 6685

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# Chemical products for industrial use — General method for determination of iron content — 1,10-Phenanthroline spectrophotometric method

*Produits chimiques à usage industriel — Méthode générale de dosage du fer — Méthode spectrophotométrique à la phénanthroline-1,10*

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# Foreword

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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.

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# Chemical products for industrial use — General method for determination of iron content — 1,10-Phenanthroline spectrophotometric method

## 1 Scope

This International Standard specifies a general 1,10-phenanthroline spectrophotometric method for the determination of the iron content of chemical products for industrial use.

It describes a technique for the determination of the content of iron in a solution. Reference should be made, for the preparation of the test solution, to the International Standard relating to the product to be analysed, which should indicate the modifications necessary to make the method applicable to that product.

## 2 Field of application

The method is applicable to test solutions from which an aliquot portion can be taken containing between 10 and 500 µg of Fe in a volume of not more than 60 ml.

Large amounts of alkali metals, calcium, strontium, barium, magnesium, manganese(II), arsenic(III), arsenic(V), uranium(VI), lead, chloride, bromide, iodide, thiocyanate, acetate, chlorate, nitrate, sulphate, sulphide, metaborate, selenate, citrate, tartrate, phosphate and up to 100 mg of germanium(IV), in the test solution, do not interfere. In the presence of tartrate, citrate, arsenate or more than 100 mg of phosphate, colour development is, however, liable to be slower.

Details of certain interferences and means by which they can be overcome are given in the annex.

## 3 Principle

Reduction of all the iron(III) present in the test solution to iron(II) with ascorbic acid. Formation of the orange-red complex between iron(II) and 1,10-phenanthroline at a pH between 2 and 9, and spectrophotometric measurement of the absorbance of the complex at the wavelength of maximum absorption (510 nm).

Under the specified conditions, the complex is measured at a pH between 4 and 6.

## 4 Reagents

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

**4.1 Hydrochloric acid,** 180 g/l solution.

Dilute, taking all necessary precautions, 409 ml of 38 % $(m/m)$ hydrochloric acid solution, $\varrho = 1{,}19$ g/ml, to 1 000 ml with water and mix well.

**4.2 Ammonia,** 85 g/l solution.

Dilute 374 ml of 25 % $(m/m)$ ammonia solution, $\varrho = 0{,}910$ g/ml, to 1 000 ml with water and mix well.

**4.3 Sodium acetate/acetic acid buffer solution,** pH 4,5 at 20 °C.

Dissolve 164 g of anhydrous sodium acetate in about 500 ml of water, add 240 ml of glacial acetic acid, and dilute to 1 000 ml with water.

**4.4 Ascorbic acid,** 100 g/l solution.

Discard this solution after 1 week.

**4.5 1,10-Phenanthroline hydrochloride monohydrate** ($C_{12}H_8N_2.HCl.H_2O$), or **1,10-phenanthroline monohydrate** ($C_{12}H_8N_2.H_2O$), 1 g/l solution.

Dissolve 1 g of either 1,10-phenanthroline hydrochloride monohydrate or 1,10-phenanthroline monohydrate in water and dilute to 1 000 ml.

Store the solution away from light. Use only colourless solutions.

**4.6 Iron,** standard solution corresponding to 0,200 g of Fe per litre.

Prepare by one of the following methods.

**4.6.1** Weigh, to the nearest 0,001 g, 1,727 g of ammonium iron(III) sulphate dodecahydrate [$NH_4Fe(SO_4)_2.12H_2O$] and dissolve it in about 200 ml of water. Transfer quantitatively to a 1 000 ml one-mark volumetric flask, add 20 ml of a (1 + 1) solution of concentrated sulphuric acid, dilute to the mark and mix.

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

**4.6.2** Weigh, to the nearest 0,001 g, 0,200 g of pure (99,9 %) iron wire, place in a 100 ml beaker and add 10 ml of concentrated hydrochloric acid, $\rho$ = 1,19 g/ml. Warm gently until completely dissolved, cool, transfer 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.

**4.7 Iron,** standard solution corresponding to 0,020 g of Fe per litre.

Transfer 50,0 ml of the standard iron solution (4.6) to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 20 µg of Fe.

Prepare this solution at the time of use.

## 5 Apparatus

Ordinary laboratory apparatus and

**5.1 Spectrophotometer,** fitted with cells of optical path length 1, 2 and 4 or 5 cm.

## 6 Procedure

### 6.1 Test portion and preparation of the test solution

The mass of the test portion and details for preparation of the test solution will be given in the International Standard relating to the product concerned.

### 6.2 Blank test

Prepare a blank test solution simultaneously with the test solution using exactly the same quantity of all the reagents used for the determination, diluting to the same volume and taking an aliquot portion having the same volume as that used in the determination.

### 6.3 Preparation of the calibration graphs

**6.3.1 Preparation of standard colorimetric solutions** for spectrophotometric measurements with cells of optical path length 1, 2 and 4 or 5 cm

According to the expected iron content of the test solution, place the volumes of the standard iron solution (4.7), shown in table 1, in a series of 100 ml one-mark volumetric flasks.

**6.3.2 Colour development**

Treat the contents of each flask as follows.

Dilute, if necessary, to approximately 60 ml with water and, if necessary, adjust the pH to approximately 2 with the hydrochloric acid solution (4.1), using narrow-range indicator paper to check the pH. Add 1 ml of the ascorbic acid solution (4.4), followed by 20 ml of the buffer solution (4.3), and 10 ml of the 1,10-phenanthroline solution (4.5), dilute to the mark with water and mix. Allow to stand for not less than 15 min.

**6.3.3 Spectrophotometric measurements**

Carry out the spectrophotometric measurements using the spectrophotometer (5.1) at the wavelength of maximum absorption (about 510 nm) and in cells of appropriate optical path length (see table 1) after having adjusted the instrument to zero absorbance against water.

**6.3.4 Plotting the graphs**

Deduct the absorbance of the blank test on the reagents for calibration from that of each standard colorimetric solution and plot a graph having, for example, the mass, in micrograms, of iron (Fe) contained in 100 ml of standard colorimetric solution as abscissae and the corresponding values of absorbance as ordinates.

**Table 1**

| Expected iron content of the aliquot portion of the test solution taken for the determination, µg | | | | | |
|---|---|---|---|---|---|
| 50 to 500 | | 25 to 250 | | 10 to 100 | |
| **Standard iron solution (4.7)** | **Corresponding mass of Fe** | **Standard iron solution (4.7)** | **Corresponding mass of Fe** | **Standard iron solution (4.7)** | **Corresponding mass of Fe** |
| ml | µg | ml | µg | ml | µg |
| 0* | 0 | 0* | 0 | 0* | 0 |
| 2,50 | 50 | 3,00 | 60 | 0,50 | 10 |
| 5,00 | 100 | 5,00 | 100 | 1,00 | 20 |
| 10,00 | 200 | 7,00 | 140 | 2,00 | 40 |
| 15,00 | 300 | 9,00 | 180 | 3,00 | 60 |
| 20,00 | 400 | 11,00 | 220 | 4,00 | 80 |
| 25,00 | 500 | 13,00 | 260 | 5,00 | 100 |
| **Optical path length of spectrophotometer cell,** cm | | | | | |
| 1 | | 2 | | 4 or 5 | |

* Blank test on the reagents for calibration.

### 6.4 Determination

#### 6.4.1 Colour development

Take an aliquot portion of the test solution (6.1) containing not more than 500 µg of iron (Fe) in a volume of 60 ml and a similar aliquot portion of the blank test solution. Dilute, if necessary, to about 60 ml and adjust the pH, if necessary, to approximately 2 with either the ammonia solution (4.2) or the hydrochloric acid solution (4.1), using a narrow-range indicator paper to check the pH. Transfer quantitatively the solutions to 100 ml one-mark volumetric flasks and develop the colour as specified in 6.3.2, starting from "Add 1 ml of the ascorbic acid solution (4.4)...".

#### 6.4.2 Spectrophotometric measurements

Carry out the spectrophotometric measurements on the two solutions (6.4.1), after colour development, by the procedure specified in 6.3.3.

## 7 Expression of results

### 7.1 Calculation

By means of the calibration graphs (6.3.4), determine the masses of Fe corresponding to the absorbances of the aliquot portions of the test and blank test solutions taken for colour development.

The International Standards relating to the product in question will give the formulae to be applied for the final calculation.

### 7.2 Repeatability and reproducibility

Experimental trials carried out in seven laboratories on aluminium sulphate, ammonium sulphate and disodium tetraborate, each containing three levels of iron, gave the statistical results given in table 2.

## 8 Test-report

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the general method used and of the International Standard relating to the product being analysed;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or in the International Standard relating to the product being analysed, or regarded as optional.

Table 2

| | Aluminium sulphate | | | Ammonium sulphate | | | Disodium tetraborate | | |
|---|---|---|---|---|---|---|---|---|---|
| **Mean, µg of Fe/ml** | 2,209 | 3,874 | 6,833 | 1,552 | 3,973 | 5,375 | 1,189 | 2,825 | 5,727 |
| **Relative standard deviation of repeatability*** | 1,00 | 1,16 | 1,17 | 0,77 | 1,11 | 1,15 | 1,35 | 1,77 | 0,77 |
| **Relative standard deviation of reproducibility*** | 5,9 | 3,6 | 2,5 | 5,6 | 4,4 | 2,2 | 7,0 | 3,6 | 2,3 |

* $\frac{\text{Standard deviation}}{\text{Mean}} \times 100$

# Annex

## Interferences

**A.1** Certain **cations**, notably **tin(IV)**, **antimony(III)**, **antimony(V)**, **titanium**, **zirconium**, **cerium(III)** and **bismuth**, are hydrolysed in acetate solution at about pH 4; they will, however, remain in solution if sufficient citrate or tartrate is present. Up to 100 mg of these cations will not be precipitated if sodium citrate (or tartrate) buffer solution is used instead of the acetate buffer solution (4.3). Colour development will be accelerated if the temperature of the solution is raised to boiling point. If citrate or tartrate buffer solutions are used, it is essential that the order of addition of reagents, specified in 6.4.1, be adhered to.

The addition of citrate also prevents the formation of insoluble phosphates.

**A.2** In the presence of **aluminium**, hydrolysis will occur if the general procedure is followed. Whilst this interference can be overcome by the substitution of citrate or tartrate buffer for acetate buffer (as in the case of presence of titanium or zirconium), if colour development is carried out between pH 3,5 and 4,2, aluminium will not interfere (see ISO 805*).

**A.3** **Cadmium**, **zinc**, **nickel**, **cobalt** and **copper** form soluble complexes with 1,10-phenanthroline. If these metals are present, colour development is retarded and the absorbance is reduced. The minimum amount of the reagent (4.5) required for each 0,1 mg of iron present is 1,7 ml but, in the presence of these interfering metals, additional reagent is required. Additional reagents should be used in the proportion of 1 ml for each 0,1 mg of **nickel**, **cobalt** or **copper**, each 0,5 mg of **zinc** and each 3 mg of **cadmium**.

**A.4** Solutions containing **coloured ions** cannot be measured against water. A solution of the same composition as that of the test solution, but without the 1,10-phenanthroline solution, should be used in the reference cell.

**A.5** In the presence of **tungsten(V)** or **molybdenum(VI)**, particularly in large amounts, the reaction should be carried out at about pH 7, by introducing the following modifications :

To the test solution containing **tungsten** or **molybdenum**, add 1 ml of a 300 g/l tartaric acid solution and adjust with the hydrochloric acid solution (4.1) or the ammonia solution (4.2) until only slightly alkaline to litmus. Add 1 to 2 ml of the ammonia solution (4.2) in excess, dilute to about 75 ml, add 1 ml of the ascorbic acid solution (4.4) and 10 ml of the reagent (4.5), heat for 5 to 10 min, at between 90 and 100 °C, cool to room temperature, and dilute to 100 ml. Using this method, up to 250 mg of **tungsten** or **molybdenum** in the test solution does not interfere.

**A.6** **Silver** forms an unstable complex with the reagent and hydrochloric acid, but this can be prevented by the addition of thiosulphate by the following procedure :

Precipitate all the **silver** by adding sufficient sodium chloride solution. Adjust the pH to between 3 and 5, and add the ascorbic acid and buffer solution as specified in 6.3.2. Then add a 25 g/l solution of sodium thiosulphate pentahydrate until the precipitate just dissolves, add 10 ml of the reagent (4.5) and continue as specified in 6.3.2. Using this method, up to 100 mg of **silver** in the test solution does not interfere.

**A.7** If **mercury(I)** or **mercury(II)** is present in the test solution, then chloride cannot be tolerated. Adjustment of pH should, in these circumstances, be carried out with a 252 g/l nitric acid solution and, for each 5 mg of **mercury** present in the test solution, 10 ml of the reagent solution (4.5) in addition to that specified should be used.

**A.8** More than 10 mg of **rhenium** in the test solution forms a precipitate of 1,10-phenanthrolinium perrhenate.

**A.9** The presence of **pyrophosphate** ions slows down colour development and affects the reduction of iron(III) to iron(II). Up to 2 mg in the test solution does not cause serious interference if absorbances are read after 30 min. Colour development can be accelerated by raising the pH; at pH 8,8, up to 30 mg of **pyrophosphate** in the test solution can be tolerated.

**A.10** Up to 500 mg of **oxalates** in the test solution can be tolerated, above which colour development tends to be incomplete.

**A.11** Up to 250 mg of **fluorides** in the test solution can be tolerated, above which colour development tends to be incomplete. The reduction of iron(III) to iron(II) is affected.

**A.12** Up to 200 mg of **vanadium(V)** in the test solution does not interfere.

**A.13** Any **selenite** present in the test solution should be oxidized to selenate. Up to 1 000 mg of **selenate** does not interfere.

**A.14** Up to 1 mg of **cyanide** does not interfere.

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* ISO 805, *Aluminium oxide primarily used for the production of aluminium — Determination of iron content — 1,10-Phenanthroline photometric method.*

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