G-25-21

International Standard ISO 7692

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Ferrotitanium — Determination of titanium content — Titrimetric method

Ferro-titane — Dosage du titane — Méthode titrimétrique

First edition — 1983-12-15

UDC 669.15'295-198 : 543.24 : 546.82 **Ref. No. ISO 7692-1983 (E)**

Descriptors : ferroalloys, ferrotitanium, chemical analysis, determination of content, titanium, volumetric analysis.

Price based on 5 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (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 authorized 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.

International Standard ISO 7692 was developed by Technical Committee ISO/TC 132, *Ferroalloys,* and was circulated to the member bodies in May 1982.

It has been approved by the member bodies of the following countries :

Austria
Brazil
Canada
China
Czechoslovakia
Egypt, Arab Rep. of
France
India
Iran
Italy
Japan
Korea, Rep. of
Mexico
Norway
Poland
Romania
South Africa, Rep. of
Spain
Sweden
United Kingdom
USSR

The member body of the following country expressed disapproval of the document on technical grounds :

Australia

Printed in Switzerland

Ferrotitanium — Determination of titanium content — Titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of the titanium content of ferrotitanium.

The method is applicable to ferrotitanium having titanium contents between 20 and 80 % (*m*/*m*).

2 Reference

ISO 3713, *Ferroalloys — Sampling and preparation of samples — General rules.*[1]

3 Principle

Dissolution of a test portion using sulphuric, hydrofluoric, nitric and hydrochloric acids.

Separation of the interfering elements (chromium, vanadium, molybdenum and tin), if present, by precipitation of titanium hydroxide in the presence of hydrogen peroxide.

Reduction of the titanium to Ti^{3+} by aluminium metal in an atmosphere of carbon dioxide or nitrogen.

Titration of the Ti^{3+} with standard volumetric iron(III) ammonium sulphate solution in the presence of thiocyanate as indicator.

4 Reagents

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

4.1 Aluminium, of minimum purity 99,5 %, in the form of foil 0,05 mm thick, and free from titanium.

4.2 Sodium hydrogen carbonate ($NaHCO_3$).

4.3 Nitric acid, ρ 1,42 g/ml.

4.4 Sulphuric acid, ρ 1,84 g/ml.

4.5 Hydrochloric acid, ρ 1,19 g/ml.

4.6 Hydrofluoric acid, ρ 1,14 g/ml.

4.7 Sulphuric acid, diluted (1 + 1).

Add carefully 1 volume of the sulphuric acid (4.4) to 1 volume of water. Cool while mixing.

4.8 Sulphuric acid, diluted (1 + 4).

Add carefully 1 volume of the sulphuric acid (4.4) to 4 volumes of water. Cool while mixing.

4.9 Sodium hydroxide, 100 g/l solution.

4.10 Sodium hydroxide, 20 g/l solution.

4.11 Ammonium thiocyanate, 100 g/l solution.

4.12 Nitrogen, practically oxygen free (less than 10 ppm by volume), 99,998 % pure, or **carbon dioxide** of similar purity.

4.13 Hydrogen peroxide, 30 % or 100 volume solution.

---

[1] At present at the stage of draft.

4.14 Iron(III) ammonium sulphate $[Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O]$, standard volumetric solution.

Place 10,2 g of the iron(III) ammonium sulphate in a 400 ml beaker and add 100 ml of cold water and 50 ml of the sulphuric acid (4.7) Transfer quantitatively to a 1 000 ml one-mark volumetric flask and dilute to the mark.

1 ml of this solution corresponds to about 1 mg of titanium.

4.15 Iron(III) sulphate solution.

Dissolve 2 g of pure iron (for example BCS 149/3) in 50 ml of the hydrochloric acid (4.5), oxidize with 10 ml of the nitric acid (4.3), add 40 ml of the sulphuric acid solution (4.7) and heat until white fumes are evolved. Cool, dilute to 200 ml and boil for 15 min. Cool, transfer quantitatively to a 500 ml one-mark volumetric flask and dilute to the mark.

4.16 Titanium sponge or other **metallic titanium** of purity greater than 99,9 %.

4.17 Titanium, standard solution corresponding to 0,500 0 g of Ti per litre, prepared by one of the following methods.

4.17.1 Preparation from titanium dioxide

Weigh 0,834 0 ± 0,000 2 g of titanium dioxide which has been previously calcined for 2 h at 800 °C. Fuse it gently with 10 g of potassium pyrosulphate either in a platinum crucible with a cover of the same material, or in a quartz crucible, of capacity 170 ml, with a cover in the form of a plate, or in a quartz conical flask.

After cooling, dissolve the fusion product directly in the quartz crucible or in the quartz conical flask with 100 ml of warm water, then decant the solution into a 400 ml beaker.

Rinse the quartz crucible or the quartz conical flask several times. If a platinum crucible is used, place it, after cooling, in a 400 ml beaker with 100 ml of warm water to dissolve the fusion product. When the product is dissolved, withdraw the crucible, rinsing it several times in the water.

Add 50 ml of the sulphuric acid solution (4.8) to the solution of the fusion product. Heat gently on a hot-plate until the solution becomes completely clear. Cool, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.17.2 Preparation from potassium hexafluorotitanate

Weigh 2,506 0 ± 0,000 2 g of potassium hexafluorotitanate (K_2TiF_6) which has been previously dried for 2 h at 105 °C into a platinum crucible. Place the crucible in a 100 ml beaker, add 50 ml of the sulphuric acid solution (4.8) and heat until the potassium hexafluorotitanate is dissolved (about 15 min). Cool, withdraw the crucible, rinsing it several times with the water. Transfer quantitatively to a 1 000 ml one-mark volumetric flask and, after cooling, dilute to the mark with water and mix.

5 Apparatus

Usual laboratory equipment and in particular

5.1 PTFE beakers, of capacity 250 ml.

5.2 Glass beakers, of capacity 600 ml.

5.3 Flask, conical or round with a flat-base, of capacity 500 ml.

5.4 Bunsen valve or Goeckel condenser/bulb.

The Bunsen valve (see figure 1) comprises a rubber bung (1) through which two glass tubes (2 and 6) pass. Rubber tubes (3) are fitted onto these glass tubes, the upper ends being closed by glass plugs (5). The rubber tube (3), which is fitted on the glass tube (2), is slitted (4) for a length of 10 to 15 mm in the middle of its length by a razor blade. The tube (6) which ends 5 cm above the level of the solution to be titrated makes it possible to introduce nitrogen or carbon dioxide by substituting the tube through which the gas is delivered for the rubber tube (3).

5.5 Magnetic stirrer, with a PTFE covered stirring bar.

5.6 Apparatus for titration in an atmosphere of nitrogen (see figure 2).

6 Sample

Use powder which will pass through a sieve of aperture size 160 µm, prepared in accordance with ISO 3713.

7 Procedure

7.1 Test portion

Take a test portion of 1 ± 0,000 2 g.

7.2 Blank test

Carry out a blank test in parallel with the determination, following the same procedure and using the same quantities of all the reagents [except the iron(III) ammonium sulphate solution (4.14)], but omitting the test portion.

7.3 Control test

Check the validity of the operating procedures used by carrying out, in parallel with the determination and following the same procedure, the determination(s) of the titanium content(s) of one or several samples of the same type, having known titanium content(s).

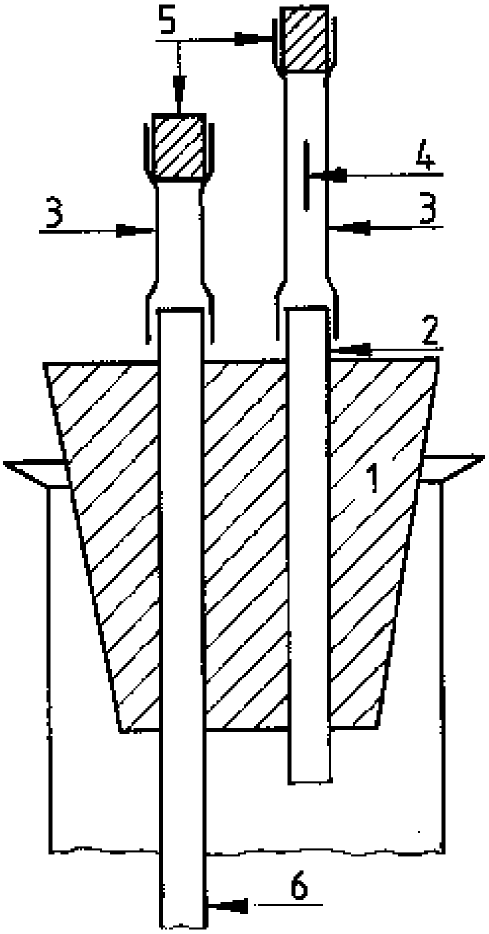

Figure 1 — Bunsen valve

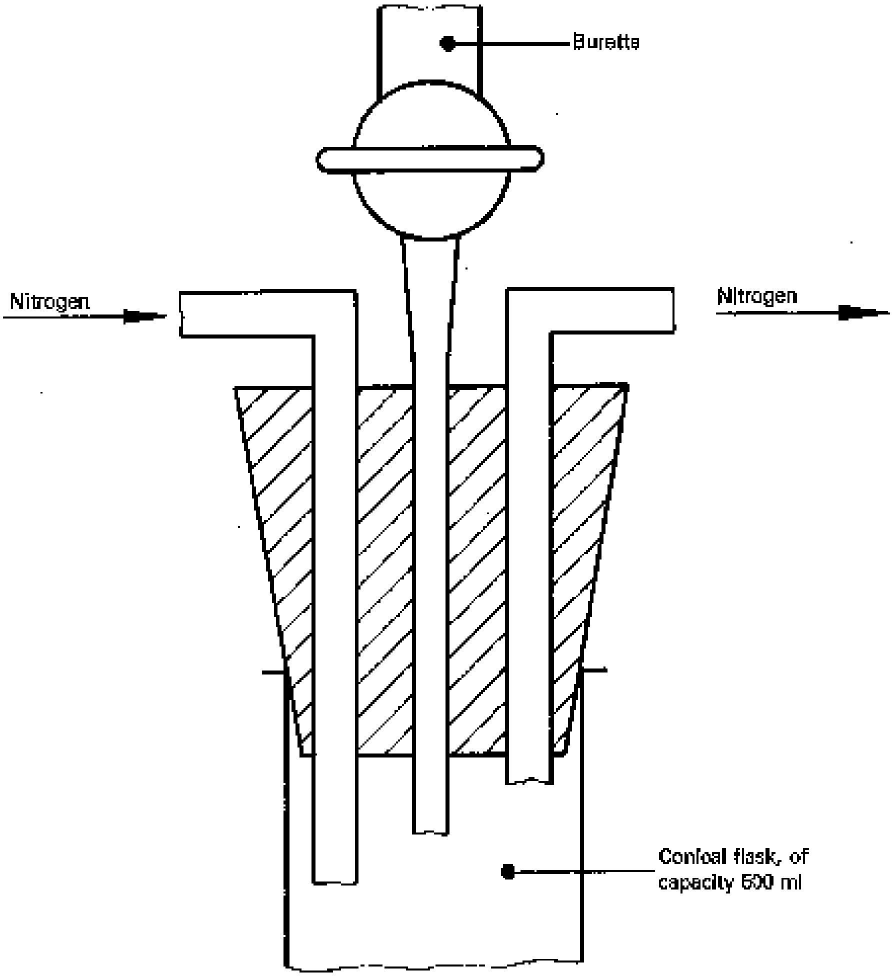

Figure 2 — Apparatus for titration in an atmosphere of nitrogen

7.4 Standardization of the iron(III) ammonium sulphate solution

7.4.1 Method using titanium sponge

Carry out the determination on a test portion of the titanium sponge (4.16) weighing 0,75 to 0,85 g.

7.4.2 Method using standard titanium solution

By means of a pipette, transfer to a 500 ml conical flask, 50 ml of the standard titanium solution (4.17), 5 ml of the sulphuric acid solution (4.7) and 80 ml of the hydrochloric acid (4.5).

Proceed as specified in 7.5.3.2.

Carry out a blank test under the same conditions in order to verify the absence of titanium in the reagents used for preparation of the standard solution.

7.5 Determination

7.5.1 Dissolution of the test portion

Place the test portion in a 250 ml PTFE beaker, and add about 20 ml of water and 35 ml of the sulphuric acid solution (4.7). When the reaction has slowed, add 20 ml of the hydrochloric acid (4.5) and 1 ml of the hydrofluoric acid (4.6). Cover the beaker with a PTFE cover. Oxidize while cold by adding, drop by drop, 5 ml of the nitric acid (4.3).

When the reaction is complete, remove the cover and heat gently until white fumes are evolved. Continue heating for about 5 min. Cool, add 30 ml of the hydrochloric acid (4.5), stir gently, cover and heat on a hot-plate until the solution becomes clear. Rinse the cover with 5 ml of the hydrochloric acid (4.5).

Cool and transfer the solution to a 500 ml one-mark volumetric flask, rinse the beaker and dilute to the mark with water (solution A).

If the expected titanium content of the sample lies in the range 20 to 45 % (*m*/*m*), take exactly 50 ml of solution A; if the expected titanium content lies in the range 45 to 75 % (*m*/*m*), take exactly 25 ml of solution A.

Transfer this aliquot portion to a 250 ml squat beaker containing 10 ml of the iron(III) sulphate solution (4.15) if interfering elements are to be separated, proceeding as specified in 7.5.2, or into a 500 ml conical flask if this separation is not to be carried out, proceeding as specified in 7.5.3.1.

7.5.2 Separation of interfering elements

Add to the aliquot portion of solution A in the 250 ml beaker 60 ml of the sodium hydroxide solution (4.9) and 2 ml of the hydrogen peroxide solution (4.13), heat to boiling and keep boiling for 5 min.

Allow the precipitate to settle and filter either through a fast double filter or through a filter lined with paper pulp. After having transferred all the hydroxide precipitate onto the filter, wash the filter assembly and the precipitate with the sodium hydroxide solution (4.10) and rinse the beaker and the precipitate six times with about 10 ml of the sodium hydroxide solution (4.10).

Rinse the stem of the funnel with water and place the funnel on a 500 ml conical flask.

Place in the 250 ml beaker 45 ml of the hydrochloric acid (4.5) and 15 ml of the sulphuric acid solution (4.8) and heat to 60 to 70 °C. Using this acid mixture, dissolve the hydroxide precipitate on the filter, adding the mixture in fractions of 10 ml and allowing each fraction to run away completely before repeating the addition. When the beaker is empty, add 35 ml of the hydrochloric acid (4.5), heat as before, and wash the filter with fractions of about 10 ml of the hydrochloric acid. Finally rinse the beaker, the filter and the stem of the funnel with hot water (70 to 80 °C), using a total volume not exceeding 40 ml.

Proceed as specified in 7.5.3.2.

7.5.3 Titration

7.5.3.1 Absence of interfering elements

Add to the aliquot portion of solution A in the 500 ml conical flask 85 ml of the hydrochloric acid (4.5) and 25 ml of water.

Proceed as specified in 7.5.3.2.

7.5.3.2 Reduction of titanium

Add to the test solution (prepared in 7.5.2 or 7.5.3.1) 2 ± 0,2 g of the sodium hydrogen carbonate (4.2) and 4 ± 0,2 g of the aluminium (4.1), cut into several pieces. Immediately stopper the flask with the Bunsen valve or Goeckel condenser/bulb (see 5.4) filled with saturated sodium hydrogen carbonate solution[1]. Agitate very frequently during the reduction.

7.5.3.3 Titration in an atmosphere of nitrogen

Before the aluminium is totally dissolved, connect the descending tube (6) of the Bunsen valve to the nitrogen source after having withdrawn the rubber tube (3). Adjust the nitrogen flow to 0,7 ± 0,1 l/min. When the aluminium is dissolved (cessation of effervescence), immerse the flask totally in cold water and allow the nitrogen to escape through the slit (4) in the rubber tube (3) and leave until the solution is at ambient temperature (about 7 min is required).

Without interrupting the flow of nitrogen, lift the Bunsen valve and add 10 ml of the ammonium thiocyanate solution (4.11) and the bar of the magnetic stirrer (see 5.5); rinse the descending tube (6) with cold boiled water and replace the Bunsen valve with the titration assembly (see figure 2), after having connected it to the source of nitrogen.

---

[1] At the end of the reduction, suction may be produced in the Goeckel valve and it will then be necessary to add the saturated sodium hydrogen carbonate solution rapidly.

Place on the magnetic stirrer (5.6) and titrate with the iron(III) ammonium sulphate solution (4.14) until a persistent pink colour is obtained.

7.5.3.4 Titration in an atmosphere of carbon dioxide

When the aluminium is dissolved, cool the solution and withdraw the Bunsen valve or the Goeckel condenser bulb. Add 10 ml of the ammonium thiocyanate solution (4.11) and titrate with the iron(III) ammonium sulphate solution (4.14) until a persistent pink colour is obtained.

8 Expression of results

8.1 If the iron(III) ammonium sulphate solution was standardized by the method using titanium sponge (see 7.4.1), the titanium content, expressed as a percentage by mass, is given by the formula

$$\frac{m_1}{V_2 \quad V_1} \times \frac{V_3 - V_1}{m_2} \times 100$$

where

V_1 is the volume, in millilitres, of iron(III) ammonium sulphate solution (4.14) used in the blank test;

V_2 is the volume, in millilitres, of iron(III) ammonium sulphate solution (4.14) used for the standardization using titanium sponge;

V_3 is the volume, in millilitres, of iron(III) ammonium sulphate solution (4.14) used in the determination;

m_1 is the mass, in grams, of titanium sponge (4.16) contained in the aliquot portion taken in 7.5.1;

m_2 is the mass, in grams, of ferrotitanium contained in the aliquot portion taken in 7.5.1.

8.2 If the iron(III) ammonium sulphate solution was standardized by the method using standard titanium solution (see 7.4.2), the titanium content, expressed as a percentage by mass, is given by the formula

$$\frac{m_1}{V_2 - V_1} \times \frac{V_3 - V_4}{m_2} \times 100$$

where

V_1 is the volume, in millilitres, of iron(III) ammonium sulphate solution (4.14) used in the reagent blank for standardization;

V_2 is the volume, in millilitres, of iron(III) ammonium sulphate solution (4.14) used to titrate 50 ml of the standard titanium solution (4.17);

V_3 is the volume, in millilitres, of iron(III) ammonium sulphate solution (4.14) used in the determination;

V_4 is the volume, in millilitres, of iron(III) ammonium sulphate solution (4.14) used in the blank test;

m_1 is the mass, in grams, of titanium contained in 50 ml of the standard titanium solution (4.17);

m_2 is the mass, in grams, of ferrotitanium contained in the aliquot portion taken in 7.5.1.

9 Test report

The test report shall include the following information :

a) a reference to this International Standard;

b) identification of the sample;

c) the result and the method of expression used;

d) any unusual features noted during the determination;

e) details of any operations not specified in this International Standard or regarded as optional.