



Ferroniobium — Determination of niobium content — Gravimetric method

Ferro-niobium — Dosage du niobium — Méthode gravimétrique

0 Introduction

Studies of the methods specified in this Technical Report have revealed that it is not possible, using wet chemical methods, to obtain results of sufficient accuracy to satisfy the criteria for the publication of an International Standard. For this reason, it has been decided to publish the methods in the form of a Technical report.

1 Scope and field of application

This Technical Report specifies a gravimetric method for the determination of the niobium content of ferroniobium. It also specifies a photometric method for the determination of the titanium content (annex A), a gravimetric method for the determination of tantalum contents greater than 1 % (*m/m*) (annex B) and a photometric method for the determination of tantalum contents less than 1 % (*m/m*) (annex C).

The methods are applicable to ferroniobium having niobium contents between 40 and 75 % (*m/m*), tantalum contents between 0,25 and 8,0 % (*m/m*) and titanium contents between 0,05 and 5,0 % (*m/m*).

Interference may arise if bismuth is present. This will appear in the tantalum fraction, but the element is seldom present in concentrations greater than 0,005 % (*m/m*) in ferroniobium. Trivalent antimony, if present, is eluted with titanium and precipitated with cupferron, but it does not interfere in the photometric method for the determination of titanium.

2 Reference

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

3 Principle

Dissolution of a test portion in a mixture of hydrochloric acid hydrofluoric acid and passing the solution through an anion-exchange column. Elution of titanium, iron and other elements with a mixture of ammonium chloride, hydrochloric acid and hydrofluoric acid.

Treatment of this eluate with boric acid and cupferron, ignition of the precipitate, containing the titanium, fusion with potassium hydrogen sulphate, and leaching with sulphuric acid solution. Oxidation of titanium with hydrogen peroxide to the yellow peritanate and photometric measurement at a wavelength of approximately 410 nm.

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¹⁾ At present at the stage of draft.

Elution of niobium with a mixture of ammonium chloride and hydrofluoric acid and of tantalum with an ammonium chloride/ammonium fluoride solution adjusted to a pH of 5 to 6.

Treatment of the eluates with boric acid to complex the fluorides, precipitation of niobium and tantalum with cupferron ignition, and weighing as the pentoxide.

For tantalum contents of less than 1 % (*m/m*), addition of zirconium as a gatherer in the cupferron separation, conversion of the tantalum to the pyrogallol complex, and photometric measurement at a wavelength of approximately 420 nm.

4 Reagents

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

4.1 Nitric acid ($\rho = 1,42$ g/ml).

4.2 Hydrochloric acid ($\rho = 1,19$ g/ml).

4.3 Hydrofluoric acid ($\rho = 1,14$ g/ml).

4.4 Ammonium chloride, 240 g/l solution.

Dissolve, by warming, 480 g of ammonium chloride (NH_4Cl) in 1 600 ml of water, cool, dilute to 2 000 ml and mix. Filter, if necessary.

Use this stock solution the preparation of the solutions described in 4.5, 4.6 and 4.7.

4.5 Ammonium chloride/ammonium fluoride, neutral solution.

Transfer 600 ml of the ammonium chloride solution (4.4) and 40 ml of the hydrofluoric acid (4.3) to a plastic beaker. Adjust the pH to 5 to 6 with ammonium hydroxide solution [$c(\text{NH}_4\text{OH}) \approx 13$ mol/l; approximately 80 to 85 ml will be required], dilute to 1 000 ml with water, and mix.

NOTE — Prepare this solution with care. If the pH is too low, the volume specified will not completely elute the tantalum; if the pH is too high, tantalum will precipitate in the column, thus leading to errors in this and subsequent determinations.

4.6 Ammonium chloride/hydrochloric acid/hydrofluoric acid mixture.

Transfer 240 ml of the ammonium chloride solution (4.4), 200 ml of the hydrofluoric acid (4.3) and 150 ml of the hydrochloric acid (4.2) to a plastic bottle, dilute to 1 000 ml with water, and mix.

4.7 Ammonium chloride/hydrofluoric acid mixture.

Transfer 600 ml of the ammonium chloride solution (4.4) and 40 ml of the hydrofluoric acid (4.3) to a plastic bottle, dilute to 1 000 ml with water, and mix.

4.8 Ammonium nitrate, 20 g/l wash solution.

Dissolve 20 g of ammonium nitrate (NH_4NO_3) in water, and dilute to 1 000 ml.

4.9 Boric acid (H_3BO_3).

4.10 Cupferron, 60 g/l solution.

Dissolve 60 g of cupferron in 800 ml of cold water, dilute to 1 000 ml and filter.

This solution should be freshly prepared as required and cooled to 5 °C before use.

4.11 Cupferron, wash solution.

Add 25 ml of the cupferron solution (4.10) to 975 ml of cold (1 + 9) hydrochloric acid solution and mix.

Prepare as required.

4.12 Hydrochloric acid/hydrofluoric acid mixture.

Add 250 ml of the hydrochloric acid (4.2) to 300 ml of water, add 200 ml of the hydrofluoric acid (4.3), dilute to 1 000 ml with water, and mix.

4.13 Hydrogen peroxide (H₂O₂), 30 % solution.**4.14 Ion-exchange resin.**

Use a strongly basic anion-exchange resin, of particle size 75 to 38 µm (200 to 400 mesh), with 8 to 10 % divinylbenzene cross linkage.

Since the mesh size of the resin may vary considerably from lot to lot, air-dry the resin and pass it through a sieve of aperture size 53 µm.

NOTE — Material retained on the sieve may be used for other purposes.

Remove most of the fines from the fraction passing the sieve by preparing a suspension of the resin in (1 + 9) hydrochloric acid solution, allowing the coarser fraction to settle for 10 to 15 min and removing the fines by decantation. Repeat the process several times until most of the very fine material has been removed from the suspension.

4.15 Oxalate/citrate/sulphuric acid solution.

Dissolve 35 g of ammonium oxalate [(NH₄)₂C₂O₄ · H₂O] and 35 g of diammonium hydrogen citrate [(NH₄)₂HC₈H₅O₇] in 1 000 ml of (1 + 39) sulphuric acid solution.

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4.16 Pyrogallol [1, 2, 3 - bihydroxybenzene {C₆H₃(OH)₃}]**4.17 Sodium hydroxide, 100 g/l solution.**

Dissolve 20 g of sodium hydroxide (NaOH) in 150 ml of water, cool, dilute to 200 ml, and mix.

Store in a plastic bottle.

4.18 Tantalum, standard solution corresponding to 0,500 mg of Ta per litre.

Transfer 0,122 1 g of tantalum pentoxide (Ta₂O₅) to a platinum crucible. Add 2,5 g of potassium hydrogen sulphate (KHSO₄) and heat to fuse the oxide. Dissolve the cooled melt in warm oxalate/citrate/sulphuric acid solution (4.15). Transfer to a 200 ml one-mark volumetric flask, cool, dilute to the mark with the oxalate/citrate/sulphuric acid solution (4.15) and mix.

1 ml of the standard solution corresponds to 0,500 mg of Ta.

4.19 Titanium, standard solution corresponding to 0,100 mg of Ti per litre.

Transfer 0,083 4 g of titanium dioxide (TiO₂) to a platinum crucible. Add 1 g of potassium hydrogen sulphate, and heat to fuse the oxide. Cool, and dissolve the melt in 50 ml of warm (1 + 9) sulphuric acid solution. Cool, transfer to a 500 ml one-mark volumetric flask, dilute to the mark with (1 + 9) sulphuric acid solution, and mix.

1 ml of this standard solution corresponds to 0,100 mg of Ti.

4.20 Zirconium, 1 g/l solution.

Dissolve 0,5 g of zirconium in 10 ml of the hydrofluoric acid (4.3) in a plastic bottle, and dilute to 500 ml.

NOTE — An equivalent mass of zirconyl chloride may be substituted for the zirconium metal.

5 Apparatus

Usual laboratory equipment, and in particular :

5.1 Ion-exchange columns.

5.1.1 General

The columns shall be constructed of polystyrene tubing and shall be approximately 300 mm long and 25 mm in internal diameter. A suitable column may be prepared as follows :

Insert a waxed, rubber stopper, with a hole of diameter 5 mm, into the bottom of the polystyrene tube. Insert into the hole, and flush with the upper surface of the stopper, a 150 mm length of polystyrene tubing, having an external diameter of 5 mm and a bore of 2 mm. Attach another 150 mm length of this tubing to the smaller tube, using an approximately 50 mm length of polyvinyl tubing, and control the flow rate by means of a stopcock on the polyvinyl tubing.

If a number of determinations are to be made, it is convenient to arrange the columns so that they can be operated with a minimum of attention. Plastic columns equipped with polystyrene fittings have been developed for such an assembly : inlet and outlet tubes are polyethylene; where necessary, flexible connections, are of polyvinyl tubing; the flow rate is controlled by stopcocks on these flexible connections.

The system shall be carefully assembled and checked to avoid possible leakage of solutions containing hydrofluoric acid.

5.1.2 Preparation of ion-exchange column

Place a 6 to 10 mm thick layer of acid-resistant polyvinyl chloride plastic fibre in the bottom of the column. Add the resin suspension (4.14) in small portions to obtain a settled bed of the resin 150 to 180 mm high. Wash the column with approximately 100 ml of (1 + 9) nitric acid solution, and perform three elution cycles with alternate additions of 100 ml of (1 + 9) hydrochloric acid solution and 100 ml of (3 + 1) hydrochloric acid solution to remove the remainder of the fines. Finally, wash the column with 200 ml of (1 + 3) hydrochloric acid solution to a level about 20 mm above the resin.

NOTE — Resin columns prepared in this way have been used for several years; the only maintenance required may be to empty and refill the column with the resin charge if the flow rate becomes excessively slow due to compaction.

5.2 Plastics, laboratory ware, made of polyethylene, polypropylene, or TFE-fluorocarbon.

5.2.1 Bottles, of capacities 250 and 1 000 ml.

5.2.2 Measuring cylinders, of capacities 50 and 250 ml.

5.2.3 Griffin-form beakers, of capacities 250, 600 and 1 000 ml, with covers.

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 $0,5 \pm 0,000$ 1 g.

7.2 Preparation of test solutions

7.2.1 Transfer the test portion to a 250 ml plastic beaker (5.2.3). Add 40 ml of the hydrochloric acid/hydrofluoric acid mixture (4.12). Place a plastic cover on the beaker, and heat gently. After the reaction ceases, add the nitric acid (4.1), drop by drop, until the solution clears.

NOTE — The addition of nitric acid should be kept to a minimum because of its strong replacing power for niobium on the ion-exchange column. Approximately 6 to 8 drops will be required.

Digest on a steam bath for 20 to 30 min to remove nitrous oxide fumes. Rinse the plastic cover and the walls of the beaker with the hydrochloric acid/hydrofluoric acid mixture (4.12), and dilute the solution to 70 ml with the same acid mixture.

7.2.2 Transfer 50 ml of the hydrochloric acid/hydrofluoric acid mixture (4.12) to the column in portions of 5 to 10 ml. Drain the acid to a level 100 mm above the resin bed, collecting the eluate in a 600 ml plastic beaker (5.2.3). Transfer the solution of the test portion in portions of 5 to 10 ml to the column. As the solution passes down the column, continue to add portions until all of the solution has been transferred. Wash the beaker four or five times with 4 ml portions of the hydrochloric acid/hydrofluoric acid mixture (4.12), transferring the washings to the column. Wash the sides of the column with 10 to 15 ml of the hydrochloric acid/hydrofluoric acid mixture, followed by several washings with the ammonium chloride/hydrochloric acid/hydrofluoric acid mixture (4.6).

7.2.3 Pass a total of 300 ml of the ammonium chloride/hydrochloric acid/hydrofluoric acid mixture through the column at a flow rate of approximately 100 to 125 ml/h. Allow the solution to drain to the top of the resin. Remove the beaker containing the first fraction and use this solution for the determination of the titanium content as described in annex A. Replace the beaker with another 600 ml plastic beaker (5.2.3).

7.2.4 Wash the sides of the column with four or five portions (a total of about 25 ml) of the ammonium chloride/hydrofluoric acid mixture (4.7), allowing the solution to drain to the top of the resin each time. Pass a total of 300 ml of this mixture through the column at the flow rate specified in 7.2.3.

NOTE — This point in the preparation of the test solutions provides a convenient and satisfactory place to stop, for example overnight, if the elutions cannot otherwise, be carried out as a continuous operation.

Remove the beaker containing the second fraction and use this solution for the determination of the niobium content as described in 7.3. Replace the beaker with another 600 ml plastic beaker (5.2.3).

7.2.5 For the determination of the tantalum content in accordance with annex B or annex C, wash the sides of the column with five or six 5 ml portions of the solution (4.5). Pass a total of 350 ml of this solution through the column, at the flow rate specified in 7.2.3. Remove the beaker containing the third fraction and use this solution for the determination of the tantalum content described in annex B or annex C, as appropriate.

7.2.6 Prepare the column for the next determination by adding 50 ml of (1 + 3) hydrochloric acid solution, in 10 ml positions, and discarding the eluates.

7.3 Determination

NOTE — Blank tests usually give results of less than 0,5 mg and hence are considered to be compensated for by the few tenths of a milligram of mineral acid lost in the precipitation.

7.3.1 To the second fraction, which contains the niobium (see 7.2.4), add 15 g of the boric acid (4.9), 75 ml of the hydrochloric acid (4.2), and 95 ml of water. Heat at 30 to 35 °C until the boric acid has dissolved. Cool to 5 °C.

7.3.2 Add slowly, while stirring the solution, 65 ml of the cupferron solution (4.10). Add filter paper pulp, stir well, and allow to stand for 10 to 15 min. Filter, using moderate suction, on a Buchner funnel, using double thickness, low-ash, fine filter paper, of diameter 90 mm, precoated with a little filter paper pulp. Transfer the precipitate to the funnel, clean the beaker with a piece of moistened filter paper and place this in the funnel. Wash the paper and precipitate with 400 ml of cold (5 °C) cupferron wash solution (4.11).

7.3.3 Transfer the precipitate and paper to tared platinum crucible, and ignite at a low temperature until the carbon is destroyed. Finally, ignite at 1 200 °C until constant mass is attained and weigh [the niobium is determined as niobium pentoxide (Nb₂O₅)].

8 Expression of results

The niobium content, expressed as a percentage by mass, is given by the formula

$$\frac{0,699 m_1}{m_0} \times 100$$

where

m_0 is the mass, in grams, of the test portion (7.1);

m_1 is the mass, in grams, of niobium pentoxide (Nb_2O_5) determined in 7.3.3;

0,699 is the factor for expressing niobium pentoxide as niobium.

9 Precision

An inter-laboratory trial involving nine laboratories gave the statistical information summarized in table 1.

Table 1

Sample	Determined niobium content % (m/m)	Repeatability	Reproducibility
1 NBS 340	57,51	0,16	0,26
2	65,40	0,29	0,11

10 Test report

The test report shall include the following information :

- 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) details of any operations not specified in this Technical Report or regarded as optional.

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Annex A

Determination of titanium content – Photometric method

A.1 Introduction

The method specified in this annex requires the use of photometric cells of optical path length 2 cm. Cells having other optical path lengths may be used provided that appropriate adjustments are made to the quantities of the test solution and the reagents used.

For this method, the recommended titanium concentration in the test solution (see 7.2.3) is 1,0 to 25,0 mg/l.

The colour of the complex is stable for at least 2 h.

A.2 Additional apparatus

A.2.1 Photometer, single-cell or multiple-cell type, suitable for measurements in the region of 410 nm, together with cells of optical path length 2 cm.

A.2.2 Pipettes, of capacities 1 - 5 - 10 - 15 and 25 ml.

A.2.3 One-mark volumetric flasks, of capacity 100 ml.

A.2.4 Beakers, of capacities 150 and 1 500 ml.

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A.3 Procedure

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A.3.1 Test solution

Use the test solution obtained in 7.2.3 (or prepared as described in clause 7 up to and including 7.2.3).

A.3.2 Preparation of the calibration graph

A.3.2.1 Preparation of calibration solutions

By means of pipettes, transfer into a series of five 100 ml one-mark volumetric flasks (A.2.3) 1 - 5 - 10 - 15 and 25 ml of the standard titanium solution (4.19), dilute to approximately 80 ml with (1 + 9) sulphuric acid solution, and mix.

A.3.2.2 Preparation of reference solutions

By means pipettes, transfer into a series of five 100 ml one-mark volumetric flasks (A.2.3) 1 - 5 - 10 - 15 and 25 ml of the standard titanium (4.19) dilute to the mark with (1 + 9) sulphuric acid solution, and mix.

A.3.2.3 Development of colour

Add to each of the solutions prepared in A.3.2.1 1,0 ml of the hydrogen peroxide solution (4.13), dilute to the mark with (1 + 9) sulphuric acid solution, and mix.

A.3.2.4 Photometric measurements

If using a multiple-cell photometer, determine the cell correction for cells with an optical path length of 2 cm and a light band centered at a wavelength of approximately 410 nm. Using the test cell, perform the photometric measurements on the solutions (A.3.2.3).

If using a single-cell photometer, transfer a suitable portion of the appropriate reference solution (A.3.2.2) to a cell of optical path length 2 cm and adjust the photometer to its initial setting using a light band centered at a wavelength of approximately 410 nm. While maintaining this setting perform the photometric measurements on the solutions (A.3.2.3).

A.3.2.5 Plotting the graph

Plot a graph having, for example, the nett photometric readings of the solutions (A.3.2.3) as ordinates and the corresponding masses, in milligrams, of titanium in the solutions as abscissae.

A.3.3 Determination

A.3.3.1 Transfer the test solution (the first fraction containing the titanium and iron, obtained in 7.2.3) to a 1 500 ml beaker (A.2.4) containing 50 g of the boric acid (4.9) dissolved in 700 ml of warm water. Add 125 ml of the hydrochloric acid (4.2) and cool to 5 °C.

A.3.3.2 Add slowly, while stirring the solution, 50 ml of the cupferron solution (4.10). Add filter paper pulp, stir well, and allow to stand for 10 to 15 min. Filter, using moderate suction, on a Buchner funnel, using double thickness, low-ash, fine filter paper, of diameter 90 mm, precoated with a little filter paper pulp. Transfer the precipitate to the funnel, clean the beaker with a piece of moistened filter paper and place this in the funnel. Wash the paper and precipitate with 400 ml of cold (5°C) cupferron wash solution (4.11).

A.3.3.3 Transfer the paper and precipitate to a porcelain crucible, and ignite at 550 to 600 °C until the carbon is destroyed.

A.3.3.4 If vanadium is present, fuse the ignited oxides with 2 to 3 g of potassium hydrogen sulphate, cool, and dissolve the melt in 30 ml of (1 + 9) hydrochloric acid solution in 150 ml beaker. Add the sodium hydroxide solution (4.17) until alkaline to litmus and then add 5 ml in excess. Boil for 3 min, and then add some filter paper pulp. Filter using a medium filter paper, and wash the precipitate with the ammonium nitrate wash solution (4.8). Transfer the paper and precipitate to a porcelain crucible, and ignite at 550 to 600 °C until the carbon is destroyed.

A.3.3.5 Fuse the ignited oxides obtained in A.3.3.3 or A.3.3.4 with 2 to 3 g of potassium hydrogen sulphate and leach with 30 ml of (1 + 9) sulphuric acid solution.

A.3.3.6 Transfer the solution (see the note) to a volumetric flask of appropriate capacity in accordance with table 2.

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Table 2

Expected titanium content, % (m/m)	Initial dilution, ml	Volume of aliquot portion, ml	Equivalent mass of test portion in the aliquot portion, g
0,05 to 1,25	50	20	0,2
1,24 to 2,50	50	10	0,1
2,49 to 5,00	100	10	0,05

NOTE — If the solution is not clear, filter through a fine filter paper into the volumetric flask and wash with (1 + 9) sulphuric acid solution. Dilute to the mark with the same sulphuric acid solution and mix.

A.3.3.7 Transfer two aliquot portions to 100 ml one-mark volumetric flasks, the volumes of the aliquot portions being in accordance with table 2, and dilute to approximately 80 ml with (1 + 9) sulphuric acid solution. Treat one of the solutions as described in A.3.3.8 and the other as described in A.3.3.9.

A.3.3.8 Dilute the first solution to the mark with (1 + 9) sulphuric acid solution and mix. (This is the reference solution.)

A.3.3.9 Using the second solution, develop the colour as specified in A.3.2.3.

A.3.3.10 Carry out the photometric measurements as specified in A.3.2.4.

A.4 Expression of results

By means of the calibration graph, determine the mass, in milligrams, of titanium corresponding to the nett photometric reading of the solution.

The titanium content, expressed as a percentage by mass, is given by the formula

$$\frac{m_3}{10 m_2}$$

where

m_2 is the mass, in grams, of test portion in 100 ml of the solution used for the photometric measurement;

m_3 is the mass, in milligrams, of titanium corresponding to the nett photometric reading.

A.5 Precision

An inter-laboratory trial involving nine laboratories gave the statistical information summarized in table 3.

Table 3

Sample	Determined titanium content, % (m/m)	Repeatability	Reproducibility
1 NBS 340	0,89	0,10	0,07
2	0,046	0,005	0,010

A.6 Test report

The test report shall include the following information :

- the reference of the method used;
- the results and the method of expression used;
- any unusual features noted during the determination;
- details of any operations not specified in this Technical Report or regarded as optional.

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