International Standard ISO 4947

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Steel and cast iron — Determination of vanadium content — Potentiometric titration method

Aciers et fontes — Dosage du vanadium — Méthode par titrage potentiométrique

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Foreword

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INTERNATIONAL STANDARD ISO 4947-1986 (E)

Steel and cast iron — Determination of vanadium content — Potentiometric titration method

1 Scope and field of application

This International Standard specifies a potentiometric titration method for the determination of vanadium in steel and cast iron.

The method is applicable to vanadium contents between 0,04 and 2 % (m/m).

2 Reference

ISO 377, *Wrought steel — Selection and preparation of samples and test pieces*.

3 Principle

Dissolution of a test portion with appropriate acids. Addition of hydrofluoric acid to keep tungsten in solution.

Oxidation of chromium and vanadium by potassium peroxydisulfate. Partial oxidation of chromium.

While checking the potential of the solution,

- reduction of chromium(VI) and vanadium(V) by ammonium iron(II) sulfate;
- oxidation of vanadium by slight excess of potassium permanganate; reduction of the excess permanganate by sodium nitrite, and reduction of the excess sodium nitrite by sulfamic acid.

Potentiometric titration of vanadium by ammonium iron(II) sulfate standard solution.

4 Reagents

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

4.1 Potassium peroxydisulfate ($K_2S_2O_8$).

4.2 Hydrochloric acid, ϱ about 1,19 g/ml.

4.3 Nitric acid, ϱ about 1,40 g/ml.

4.4 Hydrofluoric acid, ϱ about 1,15 g/ml.

4.5 Sulfuric acid, ϱ about 1,84 g/ml, diluted 1 + 4.

4.6 Sulfuric acid, ϱ about 1,84 g/ml, diluted 1 + 50.

4.7 Orthophosphoric acid, ϱ about 1,70 g/ml.

4.8 Ammonium iron(II) sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$], solution in sulfuric acid medium.

Dissolve 40 g of ammonium iron(II) sulfate hexahydrate in approximately 500 ml of water, add 20 ml of sulfuric acid, ϱ about 1,84 g/ml, cool, make up the volume to 1 000 ml and mix.

4.9 Potassium permanganate, 5 g/l solution.

4.10 Sodium nitrite, 3 g/l solution.

4.11 Sulfamic acid (NH_2SO_3H), 100 g/l solution.

This solution is stable for only one week.

4.12 Potassium dichromate, standard reference solution.

Weigh, to the nearest 0,001 g, approximately 1 g of potassium dichromate (the highest purity grade) previously dried at 150 °C until a constant mass is obtained on cooling in the desiccator. Introduce the weighed mass into a 250 ml beaker, dissolve it in 20 ml of water and add 160 ml of sulfuric acid (4.5). Transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, cool, dilute to the the mark with water and mix.

4.13 Ammonium iron(II) sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$], standard solution.

1 ml of this solution corresponds to approximately 1,275 mg of vanadium.

4.13.1 Preparation of the solution

Dissolve 10 g of ammonium iron(II) sulfate hexahydrate in approximately 500 ml of water, add 25 ml of sulfuric acid, ϱ about 1,84 g/ml, make up the volume to 1 000 ml and mix.

4.13.2 Standardization of the solution (to be carried out just before use)

Take 25,0 ml of the potassium dichromate standard reference solution (4.12) and titrate potentiometrically with the ammonium iron(II) sulfate solution (4.13.1). The corresponding concentration (c) of the ammonium iron(II) sulfate standard solution (4.13) is given by the formula:

$$c = \frac{0{,}025 \times m_0}{49{,}03 \times V} \times 50{,}94$$

$$= \frac{m_0}{V} \times 0{,}026$$

where

c is the corresponding concentration of the ammonium iron(II) sulfate standard solution (4.13) expressed in milligrams of vanadium per millilitre;

m_0 is the mass, in milligrams, of the weighed potassium dichromate;

V is the volume, in millilitres, of the ammonium iron(II) sulfate standard solution (4.13) used for titration;

0,025 is the ratio between the volume taken and the total volume of the potassium dichromate standard reference solution;

49,03 is the relative molecular mass of potassium dichromate divided by 6;

50,94 is the relative atomic mass of vanadium.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Potentiometric titration device which permits a difference in potential to be measured with platinum/saturated calomel electrodes.

6 Sampling

Carry out sampling in accordance with ISO 377 or appropriate national standards for cast iron.

7 Procedure

7.1 Test portion

According to the presumed vanadium content, weigh, to the nearest 0,001 g, the following mass of the test portion:

a) for vanadium contents between 0,04 and 0,25 % (m/m): approximately 5 g;

b) for vanadium contents between 0,25 and 1 % (m/m): approximately 2 g;

c) for vanadium contents between 1 and 2 % (m/m): approximately 1 g.

The quantity of vanadium in the test portion may vary between 2 and 20 mg.

7.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure and using the same quantities of all reagents.

7.3 Determination

7.3.1 Preparation of the test solution

7.3.1.1 Samples soluble in sulfuric acid

Introduce the test portion (7.1) into a 400 ml beaker (see notes 1 and 2) and add 40 ml of sulfuric acid (4.5) for a 1 g or 2 g test portion. For a 5 g test portion, add 70 ml of sulfuric acid (4.5). Cover the beaker with a watch-glass and heat gently until effervescence ceases.

For samples with high silicon contents, add 5 to 10 drops of hydrofluoric acid (4.4). Bring to the boil to ensure complete cessation of effervescence.

If the test portion contains tungsten, add a sufficient quantity of hydrofluoric acid (4.4) to keep it in solution. In general 5 ml of hydrofluoric acid (4.4) will suffice for a 1 g test portion, 7 ml for a 2 g test portion, and 13 ml for a 5 g test portion.

Dilute the solution to between 90 and 100 ml with water and proceed as in 7.3.2.

NOTES

1 If hydrofluoric acid (4.4) is used, a fused silica beaker and a fused silica watch-glass shall be employed.

2 The glassware used should not contain more than 0,05 % (m/m) of arsenic.

If the glass contains barium, a barium sulfate precipitate may form; however, this will not adversely affect the determination.

7.3.1.2 Samples not readily soluble in sulfuric acid

For test portions difficult to dissolve in the sulfuric acid medium the initial dissolution may be accomplished with a mixture of nitric acid (4.3) and hydrochloric acid (4.2).

After dissolution, add the quantity of sulfuric acid (4.5) already indicated in 7.3.1.1 and heat until white fumes are given off.

Take up again with water, heating to dissolve the salts, then repeat the evaporation to white fumes to ensure that the nitric acid is completely eliminated.

If the test portion contains tungsten, add a sufficient quantity of hydrofluoric acid (4.4) to keep it in solution. In general 5 ml of hydrofluoric acid (4.4) will suffice for a 1 g test portion, 7 ml for a 2 g test portion, and 13 ml for a 5 g test portion.

Dilute the solution to between 90 and 100 ml with water and proceed as in 7.3.2.

7.3.2 Oxidation of chromium and vanadium

Cool the solution (7.3.1) to approximately 50 °C. Add 3 g of potassium peroxydisulfate (4.1) per gram of test portion, heat slowly to boiling and boil for at least 10 min.

7.3.3 Preparation of the solution for measurement

7.3.3.1 Control of the oxidation of chromium and vanadium

Cool the solution (7.3.2) to room temperature. If it is necessary to remove graphite, filter the solution through a cellulose pulp lined coarse filter paper and wash with sulfuric acid (4.6), adding several drops of hydrofluoric acid (4.4) to facilitate filtering. Make up the final volume of the solution to approximately 150 ml.

Introduce the electrodes of the potentiometric device (5.1) into the beaker and agitate the solution, preferably with an electromagnetic stirrer. The potential should be above 770 mV.

If the potential is lower, or if it falls regularly, remove the electrodes from the solution, and repeat the operations of 7.3.2.

Cool to room temperature and make up the volume to approximately 150 ml.

Verify that the potential is above 770 mV.

7.3.3.2 Reduction of chromium and vanadium

Introduce the electrodes into the beaker and reduce chromium(VI) and vanadium(V) by adding ammonium iron(II) sulfate solution (4.8) (see note) to a slight excess (the potential drops to between 500 and 570 mV), agitating continuously at a constant speed.

NOTE — When the quantity of chromium is large (test portion of 5 g, or high chromium content) it is necessary to use a more concentrated ammonium iron(II) sulfate solution (e.g. 400 g/l) at the start, then finish with the solution 4.8.

7.3.4 Oxidation of vanadium

Cool the solution (7.3.3) to a temperature below 15 °C to avoid partial oxidation of the chromium.

Wait 2 min. Then add, drop by drop, potassium permanganate solution (4.9) until the potential of the indicator electrode stabilizes between 1 100 and 1 160 mV (see note). The potential shall not exceed this range in order to avoid partial oxidation of the chromium.

NOTE — When the solution is not highly coloured, oxidation with the permanganate can be observed (light pink colouring, stable for 2 min).

Wait 2 to 3 min, during which time the potential shall neither increase by more than 30 mV nor drop below 1 100 mV.

Eliminate the excess potassium permanganate by adding sodium nitrite solution (4.10), drop by drop. The potential will drop; when it reaches 850 mV, add a further 15 drops of this solution.

When the potential is stabilized at about 770 mV, wait approximately 30 s and add 5 ml of sulfamic acid solution (4.11). The potential will drop to about 740 mV and then increase again to about 800 mV. Then add 20 ml of orthophosphoric acid (4.7) if the volume is at or below 200 ml. If the volume is above 200 ml, add 30 to 40 ml of orthophosphoric acid (4.7). Wait for the potential to stabilize (approximately 2 to 5 min).

7.4 Titration

When the potential is stable, titrate the vanadium with the ammonium iron(II) sulfate standard solution (4.13) until the equivalence point is reached. The potential at this point is between 570 and 670 mV.

8 Expression of results

8.1 Method of calculation

The vanadium (V) content, as a percentage by mass, is calculated from the following formula:

$$\frac{(V_1 - V_0) \times c}{1\,000} \times \frac{100}{m} = \frac{(V_1 - V_0) \times c}{10 \times m}$$

where

V_0 is the volume, in millilitres, of the ammonium iron(II) sulfate standard solution (4.13) used for titrating the blank solution;

V_1 is the volume, in millilitres, of the ammonium iron(II) sulfate standard solution (4.13) used for titrating the test solution;

c is the corresponding concentration of the ammonium iron(II) sulfate standard solution (4.13), expressed in milligrams of vanadium per millilitre;

m is the mass, in grams, of the test portion.

8.2 Precision

A planned trial of this method was carried out by twelve laboratories, at seven levels of vanadium, each laboratory making three determinations of vanadium at each level.

The test samples used are listed in annex A.

The results obtained were treated statistically in accordance with ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

The data obtained showed a logarithmic relationship between vanadium content and repeatability (r) and reproducibility (R) of the test results, as summarized in table 1. The graphic presentation of the figures is given in annex B.

Table 1

Level of vanadium % (m/m)	Repeatability r	Reproducibility R
0,04	0,003 6	0,005 2
0,10	0,006 1	0,009 0
0,20	0,009 2	0,013 7
0,50	0,015 6	0,023 7
1,00	0,023 4	0,036 0
2,00	0,035 1	0,054 6

9 Test report

The test report shall include the following particulars:

a) the method used, by reference to this International Standard;

b) the results, and the form in which they are expressed;

c) any unusual features noted during the determination;

d) any operation not specified in this International Standard, or any optional operation which may have influenced the results.