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

*Acier et fonte — Détermination des teneurs en vanadium — Méthode
par titrage potentiométrique*

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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

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This second edition cancels and replaces the first edition (ISO 4947:1986), which has been technically revised. The main changes compared to the previous edition are as follows:

- introduction of an optional electrode;
- re-assessment of precision data.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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

1 Scope

This document 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 % (mass fraction) and 2 % (mass fraction).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

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3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <http://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

4 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 a slight excess of potassium permanganate; reduction of the excess of permanganate by sodium nitrite, and reduction of the excess of sodium nitrite by sulfamic acid.

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

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696, free from reducing or oxidizing activity.

5.1 Potassium peroxydisulfate ($K_2S_2O_8$).

5.2 Hydrochloric acid, ρ approximately 1,19 g/ml.

5.3 Nitric acid, ρ approximately 1,40 g/ml.

5.4 Hydrofluoric acid, ρ approximately 1,15 g/ml.

5.5 Sulfuric acid, ρ approximately 1,84 g/ml, diluted 1 + 4.

5.6 Sulfuric acid, ρ approximately 1,84 g/ml, diluted 1 + 50.

5.7 Orthophosphoric acid, ρ approximately 1,70 g/ml.

5.8 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 approximately 1,84 g/ml, allow to cool, make up the volume to 1 000 ml with water and mix.

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5.9 Potassium permanganate, 5 g/l.

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5.10 Sodium nitrite, 3 g/l. <https://standards.iteh.ai/catalog/standards/sist/885cfa8f-f0e7-41ec-a646-1ab10c748609/iso-4947-2020>

5.11 Sulfamic acid (NH_2SO_3H), 100 g/l.

This solution is stable for only one week.

5.12 Potassium dichromate, standard solution.

Weigh, to the nearest 0,001 g, approximately 1 g of potassium dichromate (high purity grade) previously dried at 150 °C until a constant mass (the mass difference shall not exceed 0,3 mg) is obtained after cooling in a desiccator. Transfer the weighed mass into a 250 ml beaker, dissolve it in 20 ml of water and add 160 ml of sulfuric acid (5.5). Transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, allow to cool, dilute to the mark with water and mix.

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

1 ml of this solution corresponds to approximately 1,299 mg of vanadium.

5.13.1 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 1,84 g/ml approximately, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, allow to cool, dilute to the mark with water and mix.

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

Transfer 25,0 ml of the potassium dichromate standard solution (5.12) into a beaker of appropriate size and titrate potentiometrically with the ammonium iron(II) sulfate solution (5.13.1). The corresponding concentration (ρ) of the ammonium iron(II) sulfate standard solution (5.13) is given by Formula (1):

$$\rho = \frac{0,025 \times m_0}{49,03 \times V} \times 50,94 \quad (1)$$

where

ρ is the corresponding concentration of the ammonium iron(II) sulfate standard solution (5.13) expressed in milligrams of vanadium per millilitre;

m_0 is the mass of the weighted potassium dichromate expressed in milligrams;

V is the volume of the ammonium iron(II) sulfate standard solution (5.13) used for the titration expressed in millilitres;

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

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

50,94 is the molar mass of vanadium.

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6 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385, ISO 648 or ISO 1042 as appropriate.

Ordinary laboratory apparatus and the following shall be used.

6.1 Potentiometric titration device which permits a difference in potential to be measured with platinum-saturated calomel electrodes or platinum-Ag/AgCl electrodes.

7 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel and cast iron.

8 Procedure

8.1 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 % (mass fraction) and 0,25 % (mass fraction): approximately 5 g;
- b) for vanadium contents between 0,25 % (mass fraction) and 1 % (mass fraction): approximately 2 g;
- c) for vanadium contents between 1 % (mass fraction) and 2 % (mass fraction): approximately 1 g.

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

8.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all reagents as used for the determination, except the test portion.

8.3 Determination

8.3.1 Preparation of the test solution

8.3.1.1 Samples soluble in sulfuric acid

Transfer the test portion (8.1) into a 400 ml beaker.

If hydrofluoric acid (5.4) is used, a fused silica beaker and a fused silica watch-glass should be employed. The glassware used should not contain more than 0,05 % (mass fraction) of arsenic.

NOTE If the glassware contains barium, a barium sulfate precipitate can form; however, this will not adversely affect the determination.

Add 40 ml of sulfuric acid (5.5) for a 1 g or 2 g test portion. For a 5 g test portion, add 70 ml of sulfuric acid (5.5). 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 (5.4). Bring to the boil to ensure complete cessation of effervescence.

If the sample contains tungsten, add a sufficient quantity of hydrofluoric acid (5.4) to keep it in solution. In general, 5 ml of hydrofluoric acid (5.4) 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 a volume between 90 ml and 100 ml with water and proceed as described in 8.3.2.

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8.3.1.2 Samples not readily soluble in sulfuric acid

For test portions difficult to dissolve in the sulfuric acid medium, the initial dissolution may be carried out with a mixture of nitric acid (5.3) and hydrochloric acid (5.2).

After dissolution, add the quantity of sulfuric acid (5.5) specified in 8.3.1.1 and heat until white fumes are given off.

Add water and heat to dissolve the salts. 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 (5.4) to keep it in solution. In general, 5 ml of hydrofluoric acid (5.4) 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 a volume between 90 ml and 100 ml with water and proceed as described in 8.3.2.

8.3.2 Oxidation of chromium and vanadium

Cool the solution (8.3.1) to approximately 50 °C. Add 3 g of potassium peroxydisulfate (5.1) per gram of test portion, heat slowly to boiling and boil for at least 10 min.

8.3.3 Preparation of the solution for titration

8.3.3.1 Control of the oxidation of chromium and vanadium

Cool the solution (8.3.2) to room temperature. If graphite is present in the solution, filter the solution through a cellulose pulp lined coarse filter paper and rinse with sulfuric acid (5.6), adding several

drops of hydrofluoric acid (5.4) to facilitate filtering. Make up the final volume of the solution to approximately 150 ml.

Introduce the electrodes of the potentiometric device (6.1) into the beaker and stir 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 described in 8.3.2.

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

Verify that the potential is above 770 mV.

8.3.3.2 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 (5.8) to a slight excess (the potential drops to between 500 mV and 570 mV) and agitating continuously at a constant speed.

When the quantity of chromium is high (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 beginning, then finish with the solution (5.8).

8.3.4 Oxidation of vanadium

Cool the solution (8.3.3) to a temperature below 15 °C to avoid partial oxidation of chromium.

Wait 2 min. Then add, drop by drop, potassium permanganate solution (5.9) until the potential stabilizes between 1 100 mV 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 colour, stable for 2 min).

Wait 2 min 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 (5.10), drop by drop. The potential will drop; when it reaches 850 mV, add 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 (5.11). The potential will drop to about 740 mV and then increase again to about 800 mV. Then add 20 ml of orthophosphoric acid (5.7) if the volume is at or below 200 ml. If the volume is above 200 ml, add 30 ml to 40 ml of orthophosphoric acid (5.7). Wait until the potential stabilizes (approximately 2 min to 5 min).

8.4 Titration

When the potential is stable, titrate the vanadium with the ammonium iron(II) sulfate standard solution (5.13) until the equivalence point is reached. The potential at this point is between 570 mV and 670 mV.