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Steel — Determination of vanadium content — Flame atomic absorption spectrometric method (FAAS)

Aciers — Détermination des teneurs en vanadium — Méthode par spectrométrie d'absorption atomique dans la flamme (SAAF)

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Foreword

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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).

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For an explanation on 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 the following URL: 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*.

This second edition cancels and replaces the first edition (ISO 9647:1989), which has been technically revised. The main changes compared to the previous edition are as follows:

- a complete revaluation of the precision data;
- amendment of the field of application.

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 — Determination of vanadium content — Flame atomic absorption spectrometric method (FAAS)

1 Scope

This document specifies a flame atomic absorption spectrometric method (FAAS) for the determination of the vanadium content in steel.

The method is applicable to vanadium contents between 0,01 % (mass fraction) and 0,80 % (mass fraction), provided that the tungsten content in a 1,0 g test portion is not higher than 1,0 % and/or the titanium content is not higher than 0,5 %.

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 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*

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 https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Dissolution of a test portion in hydrochloric, nitric and perchloric acids.

Addition of an aluminium chloride solution as spectrochemical buffer.

Nebulisation of the test solution into an acetylene/nitrous oxide flame of an atomic absorption spectrometer.

Spectrometric measurement of the atomic absorption of the 318,4 nm spectral line emitted by a vanadium hollow-cathode lamp.

NOTE Other suitable radiation sources can also be used.

5 Reagents

During the analysis, unless otherwise specified, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696.

5.1 Pure iron, containing <0,000 5 % of vanadium or of low and known vanadium content.

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

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

5.4 Perchloric acid, ρ approximately 1,67 g/ml.

WARNING — Perchloric acid vapour can cause explosions in the presence of ammonia, nitrous fumes or organic material in general.

5.5 Hydrochloric acid solution, 1 + 50.

Add 10 ml of hydrochloric acid (5.2) to 500 ml of water and mix.

5.6 Aluminium solution, 20 g/l.

Dissolve 90 g of aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) in about 300 ml of water, add 5 ml of hydrochloric acid (5.2), dilute to 500 ml with water and mix.

5.7 Vanadium standard solution, 2,0 g/l.

5.7.1 Preparation using vanadium metal

Weigh (1,000 ± 0,001) g of vanadium (V ≥ 99,9 %) and transfer it into a 400 ml beaker. Add 30 ml of a mixture of three volumes of hydrochloric acid (5.2) and one volume of nitric acid (5.3).

Cover with a watch glass and if necessary, heat gently to assist dissolution. When dissolution is complete evaporate the solution to just before dryness and add 20 ml of hydrochloric acid (5.2).

Allow to cool to room temperature and transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 2,0 mg of vanadium.

5.7.2 Preparation using ammonium metavanadate

Dry several grams of ammonium metavanadate (NH_4VO_3) (purity >99,9 %) in an oven at 100 °C to 105 °C for at least one hour and allow to cool to room temperature in a desiccator.

NOTE A drying temperature over 110 °C will cause decomposition of ammonium metavanadate. Keep strictly to the drying temperature specified.

Weight 2,296 g of the dried product into a 600 ml beaker, add about 400 ml of hot water and gently simmer to dissolve.

Allow to cool, transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 2,0 mg of vanadium.

5.8 **Vanadium standard solution**, 0,08 g/l.

Transfer 10,0 ml of vanadium standard solution (5.7) into a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Prepare this solution immediately prior to use.

1 ml of this solution contains 0,08 mg of vanadium.

6 Apparatus

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

Ordinary laboratory apparatus and the following shall be used.

6.1 Atomic absorption spectrometer

The spectrometer shall be equipped with a vanadium hollow-cathode lamp and supplied with dinitrogen monoxide and acetylene sufficiently pure to give a steady clear fuel-lean flame, free from water and oil, and free from vanadium.

The atomic absorption spectrometer used will be satisfactory if, after optimization according to 8.3.3, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and it meets the performance criteria given in 6.1.1 to 6.1.3.

The instrument should also conform to the additional performance requirement given in 6.1.4.

6.1.1 Minimum precision (see Annex C)

The standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution shall not exceed 1,0 % of the mean absorbance of this solution.

The standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero member) shall not exceed 0,5 % of the mean absorbance of the most concentrated calibration solution.

6.1.2 Limit of detection (see Annex C)

The limit of detection is a number, expressed in units of concentration (or amount) that describes the lowest concentration level (or amount) of an element that can be determined to be statistically different from an analytical blank.

The limit of detection of vanadium in a matrix similar to the final test solution shall be less than 0,3 µg/ml.

6.1.3 Calibration linearity (see Annex C)

The slope of the calibration line covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 times the value of the slope for the bottom 20 % of the concentration range determined in the same way.

For instruments with automatic calibration using two or more standard solutions, it shall be established prior to the analysis, by obtaining absorbance readings, that the above requirements for calibration linearity are fulfilled.

6.1.4 Characteristic concentration (see Annex C)

The characteristic concentration for vanadium in a matrix similar to the final test solution shall be greater than 1 µg/ml.

6.2 Ancillary equipment

Scale expansion can be used until the noise observed is greater than the readout error and is always recommended for absorbances below 0,1. If scale expansion has to be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring a suitable solution with and without scale expansion and then dividing the signals obtained.

7 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steels.

8 Procedure

8.1 Test portion

Weigh to the nearest 0,001 g a test portion according to the presumed vanadium content as follows:

a) for vanadium contents from 0,01 % to less than 0,20 %: a test portion of approximately 1,00 g;

b) for vanadium contents from 0,2 % to 1,0 %: a test portion of approximately 0,20 g.

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, including pure iron (5.1) instead of the test portion.

8.3 Determination

8.3.1 Preparation of the test solution

Place the test portion (8.1) into a 250 ml beaker. Add 10 ml of hydrochloric acid (5.2) and 4 ml of nitric acid (5.3), and cover the beaker with a watch-glass. After effervescence ceases, add 10 ml of perchloric acid (5.4) and evaporate the solution until fumes of perchloric acid are visible, then remove the watch-glass and evaporate until no more fumes come out of the beaker.

Allow to cool, add 10 ml of hydrochloric acid (5.2) and 20 ml of water, and heat gently to dissolve the salts. Filter through a medium texture filter paper into a 100 ml one-mark volumetric flask. Wash with warm hydrochloric acid (5.5) and add the washing fractions to the flask.

Allow to cool, add 10,0 ml of aluminium solution (5.6), dilute to the mark with water and mix.

8.3.2 Preparation of the calibration solutions

8.3.2.1 Vanadium contents <0,2 %

Transfer into a series of 250 ml beakers (1,00 ± 0,01) g of the pure iron (5.1), add 10 ml of hydrochloric acid (5.2) and 4 ml of nitric acid (5.3) to each beaker and cover them with watch-glasses. After effervescence ceases, allow to cool and then respectively add the volumes of vanadium standard solution (5.8) given in Table 1.

Table 1 — Calibration solutions for vanadium contents <0,2 %

Vanadium standard solution volume (5.8) ml	Corresponding vanadium mass mg
0[a]	0
1,0	0,08
2,0	0,16
2,5	0,20
5,0	0,40
10,0	0,80
15,0	1,20
20,0	1,60
25,0	2,00

[a] Zero member.

Proceed as specified in 8.3.1 from "...add 10 ml of perchloric acid (5.4)..." (2nd sentence of 1st paragraph) to the end.

8.3.2.2 Vanadium contents between 0,2 % and 1,0 %

Transfer into a series of 250 ml beakers (0,20 ± 0,01) g of the pure iron (5.1), add 10 ml of hydrochloric acid (5.2) and 4 ml of nitric acid (5.3) to each beaker and cover them with watch-glasses. After effervescence ceases, allow to cool and then respectively add the volumes of vanadium standard solution (5.8) given in Table 2.

Table 2 — Calibration solutions for vanadium contents between 0,2 % and 1,0 %

Vanadium standard solution volume (5.8) ml	Corresponding vanadium mass mg
0[a]	0
5,0	0,40
10,0	0,80
15,0	1,20
20,0	1,60
25,0	2,00

[a] Zero member.

Proceed as specified in 8.3.1 from "...add 10 ml of perchloric acid (5.4)..." (2nd sentence of 1st paragraph) to the end.

8.3.3 Adjustment of the atomic absorption spectrometer

Fit the vanadium hollow-cathode lamp (see 6.1) to the atomic absorption spectrometer (6.1), switch on the current and allow it to stabilize. Adjust the wavelength in the region of 318,4 nm to minimum absorbance, if possible. Following manufacturer's instructions, fit the correct burner, light the flame, adjust it to a red feather and the observation height in the flame to about 20 mm and then allow the burner temperature to stabilize. Taking careful note of the manufacturer's instructions regarding the minimum flow rate of acetylene, nebulize alternately the calibration solution of highest concentration and the zero member, adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solutions is at a maximum.

NOTE Other suitable radiation sources can also be used.

WARNING — The manufacturer's recommendations should be closely followed, and particular attention is drawn to the following safety points:

a) **the explosive nature of acetylene, and regulations concerning its use;**

b) **the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;**

c) **the need to keep the burner head clear of deposits because a badly clogged burner may cause a flashback;**

d) **the need to ensure that the liquid trap is filled with water;**

e) **the need always to spray water between the test solutions, blank solution and/or calibration solutions.**

Evaluate the criteria of 6.1.1 to 6.1.3 and the additional performance requirement of 6.1.4 to ensure that the instrument is suitable for the determination.

8.3.4 Spectrometric measurements

8.3.4.1 Spectrometric measurement of the calibration solutions

Nebulize the relevant series of calibration solutions (8.3.2.1 or 8.3.2.2) depending on the expected vanadium content in succession into the flame and measure the absorbance for each solution. Take care to keep the aspiration rate constant throughout the preparation of the calibration curve. Nebulize water through the burner after each measurement, see note.

NOTE For certain types of apparatus it is preferable to use a solution containing the attack reagents in the same concentrations as in the test portion solutions, instead of water.

8.3.4.1.1 Calibration curves

Subtract the mean absorbance value obtained for the zero-member calibration solution from the mean absorbance values obtained for the other calibration solutions.

Establish the appropriate calibration curve by plotting the net absorbance values of the calibration solutions against the concentration of vanadium, expressed in micrograms per millilitre. Use appropriate spectrometer software or an off-line computer for regression calculations or prepare a graphical representation.

If pure metals and reagents have been used, the zero member should have a negligibly small absorbance.

If, however, the zero member has a significant absorbance a more complicated procedure is required. In this case, the concentration of vanadium c_z, expressed in micrograms per millilitre (µg/ml), in the zero member can be calculated using Formula (1)

$$c_z = c_{c1} \times \frac{A_z}{A_{c1} - A_z} \qquad (1)$$

where

c_{c1} is the concentration of vanadium, expressed in micrograms per millilitre (µg/ml) added to the first calibration solution;

A_z is the absorbance of the zero member;

A_{c1} is the absorbance of the first calibration solution.

The c_z value is then added to each of the nominal calibration concentrations in order to obtain a mean calibration graph passing through the origin.

8.3.4.2 Spectrometric measurement of the test solutions

8.3.4.2.1 Preliminary spectrometric measurement

Carry out a preliminary measurement on the test solution (8.3.1) at the same time as the spectrometric measurements are carried out on the calibration solutions (see 8.3.2). Estimate the preliminary analyte amount by using the calibration curve (8.3.4.1.1).

8.3.4.2.2 Spectrometric measurement

8.3.4.2.2.1 Use of the calibration curve

Measure the absorbance of the blank test solution (8.2) and repeat the measurements of the test solution (see 8.3.4.2.1).

Convert the absorbance values of the blank test solution and the test solutions to micrograms of vanadium per millilitre by means on the calibration curve.

8.3.4.2.2.2 Use of bracketing method

Carry out a second measurement on the test solution (see 8.3.1) by bracketing between the two calibration solutions having vanadium contents slightly higher and slightly lower than the estimated vanadium concentration of the test solution.

9 Expression of results

9.1 Use of the calibration curve

Calculate the vanadium content (w_V), as a percentage by mass, using Formula (2)

$$w_V = \frac{c_1 - c_0}{100 \times m} + C \tag{2}$$

where

c_1 is the vanadium concentration in the test solution, derived from the calibration curve, in micrograms per millilitre (µg/ml);

c_0 is the vanadium concentration in the blank test, from the calibration curve, in micrograms per millilitre (µg/ml);

m is the mass of the test portion, in grams (g);

C is the vanadium content in the iron used in the blank test, expressed as a percentage by mass.

9.2 Use of bracketing method

Calculate the vanadium content (w_V), as a percentage by mass, using Formula (3)

$$w_V = \frac{c_2 - c_0}{100 \times m} + C \tag{3}$$

where c_2 is the vanadium concentration, in micrograms per millilitre (μg/ml), calculated using Formula (4):

$$c_2 = c_3 + (c_4 - c_3) \times \frac{A_0 - A_1}{A_2 - A_1} \tag{4}$$

where

c_3 is the vanadium concentration of the lower calibration solution used, expressed in micrograms per millilitre (μg/ml);

c_4 is the vanadium concentration of the higher calibration solution used, expressed in micrograms per millilitre (μg/ml);

A_0 is the absorbance value of the test solution;

A_1 is the absorbance value of the calibration solution corresponding to concentration c_3;

A_2 is the absorbance value of the calibration solution corresponding to concentration c_4.

10 Precision

A planned test of this method was carried out by 23 laboratories, at seven levels of vanadium, each laboratory making three determinations (see Notes 1 and 2) of the vanadium content at each level.

The test samples used are listed in Table A.1, and the experimental precision data obtained are shown in Table A.2.

The results obtained were treated statistically in accordance with ISO 5725-2:1994 and ISO 5725-3:1994.

A graphical representation of the experimental precision data is given in Annex B.

The smoothed precision data, expressed as a percentage (mass fraction), shown in Table 3 were calculated from the relationships between the vanadium content mean values and repeatability and reproducibility experimental data (see Annex A and Annex B).

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725-1, i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period.

NOTE 2 The third determination was carried out at a different time (on a different day) by the same operator as in note 1 using the same apparatus with a new calibration.

NOTE 3 When revising the present document, the precision data were re-evaluated: this new statistical treatment has led to the removal of a sample (lowest vanadium content level), since the reproducibility parameters (R_w and R) found were not in line with those corresponding to the other samples (see Table A.2).

Table 3 — Precision data (smoothed values)

Vanadium content % (mass fraction)	Repeatability limit % r	Reproducibility limits % R_w	 R
0,01	0,000 8	0,001 7	0,001 8
0,02	0,001 4	0,002 6	0,002 9
0,05	0,002 7	0,004 5	0,005 4
0,10	0,004 5	0,006 8	0,008 8
0,20	0,007 4	0,010 4	0,014 1
0,50	0,014	0,018	0,027
0,80	0,020	0,024	0,037

11 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis or of the test report;

b) method used by reference to this document, i.e. ISO 9647:2020;

c) results and unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which might have influenced the results.

Annex A
(informative)

Additional information on the international interlaboratory test

Table 3 was derived from the results of an international interlaboratory test carried out in 1985 on six steel samples and one pig iron sample in 10 countries and involving 23 laboratories.

The results of the test were reported in document ISO/TC 17/SC 1 N 646, March 1986.

Table A.1 — Test samples used for the precision test

Sample	Chemical composition %									
	V	C	Si	Mn	Ni	Cr	Mo	W	Ti	Co
JSS 113-2 (Pig iron)	0,007	4,29	1,19	0,12	0,011	0,013	—	—	0,066	—
JSS 516-4 (Low alloy steel)	0,010	0,22	0,28	0,97	3,02	1,69	0,41	—	—	—
JSS 652-7 (Stainless steel)	0,038[a]	0,050	0,74	1,68	11,34	17,26	2,33	—	—	0,22
JSS 152-8 (Low alloy steel)	0,10	0,32	0,37	0,42	2,06	0,50	0,97	—	—	—
JSS 153-7 (Low alloy steel)	0,21	0,23	0,27	0,77	1,02	1,02	1,21	—	—	—
JSS 604-7 (Tool steel)	0,51	0,37	1,05	0,35	0,17	4,92	1,07	0,016	—	—
CMIEC CE 056 (Low alloy steel)[b]	0,75	0,30	0,22	0,55	—	2,65	0,56	0,65	—	—

[a] Non-certified value.

[b] CMIEC: Standard sample prepared by CHINA Metallurgical Import and Export Corporation.

Table A.2 — Experimental data obtained from the interlaboratory test

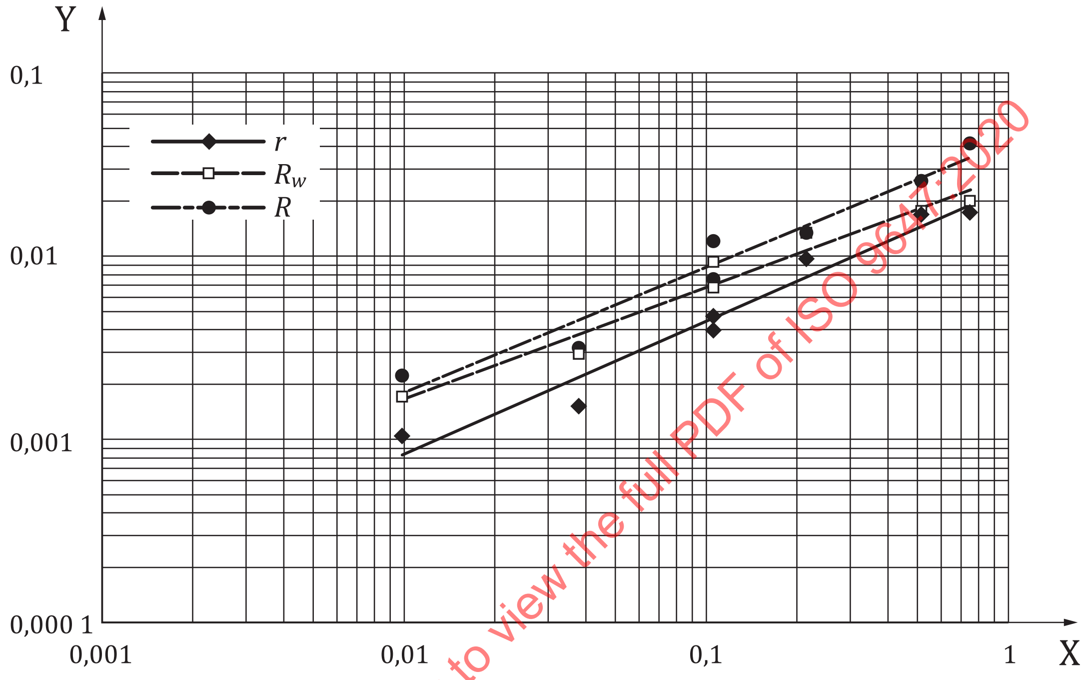
Sample	Vanadium content %		Experimental precision data %		
	Certified	Found	Repeatability limit	Reproducibility limits	
			r	R_W	R
JSS 113-2 (Pig iron)	0,007	0,007 1	0,000 8	0,002 5	0,002 8
JSS 516-4 (Low alloy steel)	0,010	0,009 8	0,001 0	0,001 7	0,002 2
JSS 652-7 (Stainless steel)	0,038[a]	0,037 8	0,001 5	0,002 9	0,003 2
JSS 152-8 (Low alloy steel) (1 gram test portion)	0,10	0,106 0	0,004 8	0,006 7	0,007 5
JSS 152-8 (Low alloy steel) (0,2 gram test portion)	0,10	0,105 8	0,004 0	0,009 3	0,012 1
JSS 153-7 (Low alloy steel)	0,21	0,214	0,010	0,013	0,013
JSS 604-7 (Tool steel)	0,51	0,516	0,017	0,018	0,026
CMIEC CE 056 (Low alloy steel)[b]	0,75	0,748	0,017	0,020	0,042

[a] Non-certified value.

[b] CMIEC: Standard sample prepared by CHINA Metallurgical Import and Export Corporation.

Annex B
(informative)

Graphical representation of precision data



Key

X vanadium content, % (mass fraction)

Y precision data, % (mass fraction)

r repeatability

R_w interlaboratory reproducibility

R reproducibility

$\lg r = 0{,}727 \lg w_V - 1{,}624$	Coefficient of correlation = 0,980
$\lg R_w = 0{,}608 \lg w_V - 1{,}557$	Coefficient of correlation = 0,979
$\lg R = 0{,}690 \lg w_V - 1{,}367$	Coefficient of correlation = 0,974

where w_V is the vanadium mean value, expressed in %, obtained from three determinations in each laboratory.

Figure B.1 — Relationships between vanadium content and repeatability limit, *r*, and reproducibility limits, R_w and *R*