

JIS

JAPANESE
INDUSTRIAL
STANDARD

Translated and Published by
Japanese Standards Association

JIS G 1221 : 1998

Iron and steel — Methods for deter-
mination of vanadium content

ICS 77.080.01

Descriptors : iron, transition metals, steels, ferrous metals, ferrous alloys, vanadium,
determination of content, chemical analysis and testing

Reference number : JIS G 1221 : 1998 (E)

G 1221:1998

Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of International Trade and Industry through deliberations at Japanese Industrial Standards Committee in accordance with the Industrial Standardization Law. Consequently **JIS G 1221:1992** is replaced with **JIS G 1221:1998**.

In this revision, Annex 2 and Annex 4 are prepared based on the corresponding ISO Standards.

Date of Establishment: 1954-03-29

Date of Revision: 1998-02-20

Date of Public Notice in Official Gazette: 1998-02-20

Investigated by: Japanese Industrial Standards Committee

Divisional Council on Iron and Steel

JIS G 1221:1998, First English edition published in 1999-02

Translated and published by: Japanese Standards Association
4-1-24, Akasaka, Minato-ku, Tokyo, 107-8440 JAPAN

In the event of any doubts arising as to the contents,
the original JIS is to be the final authority.

© JSA 1999

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

Printed in Japan

Iron and steel—Methods for determination of vanadium content

Introduction In this Japanese Industrial Standards, Annex 2 is prepared based on **ISO 4947**, *Steel and cast iron—Determination of vanadium content—Potentiometric titration method* issued in 1986 and Annex 4 is prepared based on **ISO 4942**, *Steel and iron—Determination of vanadium content—N-BPHA spectrophotometric method* issued in 1988, without changing original technical contents. Items not specified in the corresponding International Standards are added as Japanese Industrial Standard.

The "informative reference" underlined with dotted line in this Standard is the item which does not exist in the original International Standard.

1 Scope This Japanese Industrial Standard specifies the methods for determination of vanadium in iron and steel.

Remarks : The International Standards corresponding to this Standard are shown below.

ISO 4947 *Steel and cast iron—Determination of vanadium content—Potentiometric titration method*

ISO 4942 *Steel and iron—Determination of vanadium content—N-BPHA spectrophotometric method*

2 Normative references The following standards contain provisions which, through reference in this Standard, constitute provisions of this Standard. The most recent editions of the standards indicated below shall be applied.

JIS G 1201 *General rules for chemical analysis of iron and steel*

JIS K 0557 *Water used for industrial water and wastewater analysis*

JIS K 8001 *General rule for test methods of reagents*

JIS Z 8402 *General rules for permissible tolerance of chemical analyses and physical tests*

3 General matters General matters common to determination method shall be as given in JIS G 1201. However, JIS G 1201 is not applied to Annexes 2 and 4.

4 Classification of determination methods The method for determination of vanadium shall be any one of following methods:

- a) **Potassium permanganate oxidation ammonium iron (II) sulfate titration method**
This method applied to the sample of 0.10 % (m/m) or over up to and incl. 6.0 % (m/m) and shall be as specified in Annex 1 (normative).

- b) **Potassium permanganate oxidation ammonium iron (II) sulfate potentiometric titration method (ISO 4947)** This method applies to the sample of 0.04 % (*m/m*) or over up to and incl. 2 % (*m/m*) vanadium content, and shall be as specified in Annex 2 (normative).
- c) **N-benzoylphenylhydroxylamine extraction absorptiometry (1)** This method applies to the sample of 0.005 % (*m/m*) or over up to and incl. 0.50 % (*m/m*) vanadium content, and shall be as specified in Annex 3 (normative).
- d) **N-benzoylphenylhydroxylamine extraction absorptiometry (2) (ISO 4942) [N-BPHA spectrophotometric method]** This method applies to the sample of 0.005 % (*m/m*) or over up to and incl. 0.50 % (*m/m*), and shall be as specified in Annex 4 (normative).

Annex 1 (normative)
Potassium permanganate oxidation ammonium iron (II)
sulfate titration method

1 Summary Decompose a sample with appropriate acid after reducing chromium, manganese, etc., with ammonium iron (II) sulfate, oxidize vanadium with potassium permanganate. After decomposing excess permanganic acid with urea and sodium nitrite, titrate with ammonium iron (II) sulfate standard solution by using diphenylamine as an indicator.

2 Reagents The reagents shall be as follows.

- a) **Hydrochloric acid (1+1)**
- b) **Nitric acid**
- c) **Perchloric acid**
- d) **Phosphoric acid**
- e) **Aqua regia** (3 volumes of hydrochloric acid and one volume of nitric acid)
- f) **Mixed acid** (3 volumes of sulfuric acid, 13 volumes phosphoric acid, and 14 volumes of water)
- g) **Sodium chloride**
- h) **Ammonium hydrogendifluoride**
- i) **Sodium fluoride**
- j) **Sodium nitrite solution (30 g/l)**
- k) **Ammonium iron (II) sulfate solution** Dissolve 40 g of ammonium iron (II) sulfate hexahydrate by adding about 100 ml of water and 100 ml of sulfuric acid (1+1), and dilute the solution with water to 1 000 ml.
- l) **Diarsenic trioxide solution** Dissolve 0.85 g of diarsenic trioxide in 5 ml of sodium hydroxide solution (50 g/l), and add 50 ml of water, neutralize it with sulfuric acid (1+5), dissolve by adding 3 g of sodium hydrogencarbonate, and dilute the solution to 1 000 ml with water.
- m) **Potassium permanganate solution (3 g/l)**
- n) **Urea**
- o) **1/30 mol/l Ammonium iron (II) sulfate standard solution** Dissolve 13.1 g of ammonium iron (II) sulfate hexahydrate by adding about 100 ml of water and 100 ml of sulfuric acid (1+1). After cooling to ordinary temperature, transfer the solution to a 1 000 ml one-mark volumetric flask with water, and dilute to the mark with water. Determine a factor of the standard solution for each service as follows; Accurately sample 100 ml of water, 10 ml of sulfuric acid (1+1), and 25 ml of 1/30 mol/l ammonium iron (II) sulfate standard solution into a conical beaker (300 ml).

After cooling to room temperature, titrate with 0.008 mol/l potassium permanganate standard solution ⁽¹⁾, obtain the amount of potassium permanganate solution used for the titration by taking a point when the color of solution turns red purple as the end point, and calculate the factor according to the following formula:

$$F_1 = \frac{F_2 \times V \times 1.2}{25}$$

where, F_1 : factor of 1/30 mol/l ammonium iron (II) sulfate standard solution

F_2 : factor of 0.008 mol/l potassium permanganate standard solution

V : amount of 0.008 mol/l potassium permanganate standard solution used (ml)

Note ⁽¹⁾ Dilute accurately 0.02 mol/l potassium permanganate standard solution, which is prepared and standardized according to (7) of 4.5 of JIS K 8001, 2.5 times with the water of grade A2 or upward stated in Table 1 of 3 of JIS K 0557. The factor of 0.02 mol/l potassium permanganate standard solution is used.

p) **Diphenylamine phosphoric acid solution** Dissolve 1.0 g of diphenylamine $[(C_6H_5)_2NH]$ in 100 ml of phosphoric acid.

3 **Test portion** The test portion shall be as given in Annex 1 Table 1.

Annex 1 Table 1 Test portion

Vanadium content % (<i>m / m</i>)	Test portion g
0.10 or over to and excl. 3.0	1.0
3.0 or over up to and incl. 6.0	0.50

4 Procedure

Informative reference : WARNING The vapour of perchloric acid has a risk of explosion under existence of ammonia, nitrous acid vapour, or organic matter. The treatment for vaporizing perchloric acid shall be carried out at a place equipped with an exhaust facility which ensures safety even though perchloric acid is used.

4.1 **Preparation of sample solution** Prepare a sample solution in accordance with any one of the following procedures:

a) **Sample easily decomposed with mixed acid**

1) Weigh the sample, transfer into a beaker (300 ml), cover with a watch-glass, add

30 ml of mixed acid and 20 ml of water, decompose by heating gently, further add 3 ml of nitric acid, and heat. Wash the bottom face of the watch glass, remove the watch glass, and generate white fume of sulfuric acid by heating successively.

- 2) After standing to cool, add 30 ml of water, dissolve salts by sufficiently shaking, cover with a watch glass, and heat to boiling. Wash the bottom face of the watch glass with a small amount of warm water, remove the watch glass, filter the solution with filter paper (class 5 A) ⁽²⁾, and wash the filter paper and insoluble residue several times with warm water. Mix the filtrate and washings together, transfer into a conical beaker (500 ml), and cool to room temperature. Thereafter, dilute the solution to about 200 ml with water. Discard the residue.

Note ⁽²⁾ In the case where insoluble residue is not observed, omit the filtrating operation.

b) Sample not easily decomposed with mixed acid

- 1) Weigh the sample, transfer into a beaker (300 ml), cover with a watch glass, add 20 ml of aqua regia, decompose by heating gently, further add 30 ml of mixed acid, and heat. Wash the bottom face of the watch glass with water, remove the watch glass, and generate white fume of sulfuric acid by heating successively.
- 2) Carry out the operation of a)2).

c) Sample containing cast iron and a great amount of silicon

- 1) Weigh the sample, transfer into a beaker (300 ml), cover with a watch glass, add 0.5 g to 1 g of ammonium hydrogen fluoride and 50 ml of aqua regia, decompose by heating gently, further add 30 ml of mixed acid, and heat. Wash the bottom face of the watch glass with water, remove the watch glass, and generate white fume of sulfuric acid by heating successively.
- 2) Carry out the operation of a)2).

d) Sample containing tungsten, niobium or tantalum

- 1) Carry out the operation of a)1).
- 2) After standing to cool, add 30 ml of water, 3 g of ammonium hydrogen fluoride or 2 g of sodium fluoride, dissolve salts by shaking sufficiently, cover with a watch glass, and heat until boiling. Wash the bottom face of the watch glass with a small amount of warm water, remove the watch glass, filter the solution with filter paper (class 5A) ⁽²⁾, and wash the insoluble residue several times with warm water. Mix the filtrate and washings together, transfer into a conical beaker (500 ml) and cool to room temperature. Thereafter, dilute the solution to about 200 ml with water, and discard the residue.

e) Sample into which vanadium carbide or the like may be undecomposable because of high carbon content

- 1) Carry out the operation of a)1).
- 2) After standing to cool for a short time, add 5 ml of nitric acid, and generate white fume of sulfuric acid by heating.

- 3) Repeat the operation of 2) two or three times, and decompose the carbide of vanadium or the like.
- 4) Carry out the operation of a)2).

f) Sample containing 10 % (m/m) chromium

- 1) Weigh the sample, transfer into a beaker (300 ml), cover with a watch glass, add 30 ml of hydrochloric acid (1+1), and decompose most of the sample by heating gently. Add 5 ml of nitric acid and 30 ml of perchloric acid, generate white fume of perchloric acid by heating, and oxidize chromium to dichromic acid. Thereafter, shift the watch glass, add little by little 1 g to 2 g of sodium chloride heating, and repeat the addition of sodium chloride until brown fume is not generated. After standing to cool for a short time, wash the bottom face of the watch glass with water, remove the watch glass, and reduce the residual amount of perchloric acid to about 5 ml by heating successively.
- 2) After standing to cool, add 50 ml of water, dissolve solts by shaking sufficiently, filter the solution with filter paper (class 5A) ⁽²⁾, and wash the filter paper and insoluble residue several times with warm water. Mix the filtrate and washings together, transfer into a conical beaker (500 ml), add 20 ml of phosphoric acid, and cool to room temperature. Thereafter dilute the solution to about 200 ml with water. Discard the residue.

4.2 Oxidization of vanadium Reduce dichromic acid by dripping ammonium iron (II) sulfate solution [2 k]) to the solution obtained in a) 2), b) 2), c) 2), d) 2), e) 4) or f) 2) of 4.1, and further add 2 ml per 1 % (m/m) of manganese content. After the solution turns slightly red purple by dripping potassium permanganate solution while mixing by shaking, add further 0.5 ml to 1.0 ml, and allow to stand for several min. Add about 5 g of urea, after dissolving by shaking, add drop by drop sodium nitrite solution while mixing the solution by shaking, and make red purple of permanganic acid disappear. Add 5 ml of diarsenic trioxide [2 l]), mix by shaking sufficiently, and allow to stand for 3 min.

4.3 Titration Add accurately 0.05 ml of diphenylamine phosphoric acid solution [2 p]) as an indicator to the solution obtained in 4.2, mix by shaking. After the color of the solution turns purple, titrate with 1/30 mol/l ammonium iron (II) sulfate standard solution [2 o]) while mixing by shaking the solution ⁽³⁾. Take the point when the purple disappears by the last one drop as the end point ⁽⁴⁾, and obtain the used amount of ammonium iron (II) sulfate standard solution.

Notes ⁽³⁾ In the case where the vanadium content in the sample is 0.3% (m/m) or under, a microburet is used.

⁽⁴⁾ Titrate while mixing by shaking sufficiently, especially near the end point.

5 Blank test Carry out the same operation as that for a sample in parallel without using the sample.

6 Calculation Calculate the vanadium content in the sample according to the following formula;

$$V = \frac{F_1 \times (V_1 - V_2) \times 0.001698}{m} \times 100$$

where V : vanadium content in sample [% (m/m)]

F_1 : factor of 1/30 mol/l ammonium iron (II) sulfate standard solution [2 o)]

V_1 : used amount of 1/30 mol/l ammonium iron (II) sulfate standard solution [2 o)] in titration of sample solution (ml)

V_2 : used amount of 1/30 mol/l ammonium iron (II) sulfate standard solution [2 o)] in titration of blank test solution (ml)

m : test portion (g)

7. Precision The precision ⁽⁵⁾ shall be as specified in Annex 1 Table 2.

Annex 1 Table 2 Precision

Unit : % (m/m)

Vanadium content	Within-laboratory reproducibility	Reproducibility
0.10 or over to and excl. 3.2	$D [0.0030 \times (V) + 0.0028]$	$D [0.0059 \times (V) + 0.0041]$

Note ⁽⁵⁾ The D in the precision calculation formula means $D(n, 0.95)$, and its value shall be as given in Table 4 of **JIS Z 8402**. In the case of within-laboratory reproducibility, the value of n is the number of analyses in the same laboratory. In the case of reproducibility, the value of n is the number of laboratories related to the analyses (when $n=2$, $D=2.8$).

The (V) is vanadium content in the sample for which the precision is obtained [% (m/m)].

Informative reference : This precision is obtained from the co-operative test results by using the sample of 0.16 % (m/m) or over up to and incl. 3.21 % (m/m) vanadium content.

Annex 2 (normative)**Potassium permanganate oxidation ammonium iron (II)
sulfate potentiometric titration method (ISO 4947)**

1 Scope and field of application This Annex 2 specifies a potentiometric titration method for 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 : 1985 *Wrought steel – Selection and preparation of samples and test pieces.*

Informative reference : ISO 377 has been replaced with the following standard.

ISO 14284 : 1996 *Steel and iron – Sampling and preparation of samples for the determination of chemical composition.*

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 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 (V) 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