INTERNATIONAL STANDARD

ISO 9683-1

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Iron ores — Determination of vanadium —

Part 1:
BPHA spectrophotometric method

Minerais de fer — Dosage du vanadium —

Partie 1: Méthode spectrophotométrique à la BPHA

Reference number
ISO 9683-1:2006(E)

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Contents

Page

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 9683-1 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This first edition of ISO 9683-1 cancels and replaces ISO 9683:1991, which has been technically revised. It has been updated to alter the manner in which precision data are presented.

ISO 9683 consists of the following part, under the general title *Iron ores — Determination of vanadium*:

— *Part 1: BPHA spectrophotometric method*

The following part is under preparation:

— *Part 2: Flame atomic absorption spectrometric method*

INTERNATIONAL STANDARD **ISO 9683-1:2006(E)**

Iron ores — Determination of vanadium —

Part 1:
BPHA spectrophotometric method

WARNING — This part of ISO 9683 may involve hazardous materials, operations and equipment. This part of ISO 9683 does not purport to address all of the safety issues associated with its use. It is the responsibility of the user to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This part of ISO 9683 specifies a spectrophotometric method using *N*-benzoyl-phenylhydroxylamine (BPHA) for the determination of the mass fraction of vanadium in iron ores.

This method is applicable to mass fractions of vanadium between 0,005 and 0,5 % in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

2 Normative references

The following referenced documents are indispensable for the application 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 — One-mark pipettes*

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

ISO 3082, *Iron ores — Sampling and sample preparation procedures*

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

ISO 7764, *Iron ores — Preparation of predried test samples for chemical analysis*

3 Principle

A test portion is decomposed by fusion with sodium peroxide, and leached with water and sulfuric acid.

Orthophosphoric acid is added to an aliquot and the vanadium is oxidized to the pentavalent state by potassium permanganate. The excess permanganate is reduced by sodium nitrite in the presence of urea.

A complex is formed by treatment with BPHA and hydrochloric acid, and the complex is extracted with chloroform.

The absorbance is measured spectrophotometrically at approximately 535 nm.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only water that complies with grade 2 of ISO 3696.

4.1 Iron metal powder, of mass fraction of vanadium $< 0{,}001$ %.

4.2 Sodium peroxide, fine powder.

4.3 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 4 + 1.

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

4.5 Orthophosphoric acid, ρ 1,7 g/ml, diluted 1 + 1.

4.6 Hydrogen peroxide, 300 g/l solution.

4.7 Sodium nitrite, 3 g/l solution.

4.8 Urea, 250 g/l solution.

4.9 Potassium permanganate, 3,2 g/l solution.

Dissolve 3,2 g of potassium permanganate in 100 ml of water. Boil gently for about 1 h, filter through a carefully cleaned fine-texture glass filter funnel into a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix. Store the solution in a brown bottle.

4.10 Sodium tripolyphosphate, 100 g/l solution.

Dissolve 25 g of sodium tripolyphosphate in 170 ml of water, dilute to 250 ml and mix.

4.11 Background solution.

Place 1,300 g of pure iron (4.1) in a zirconium or vitreous carbon crucible (5.1) containing 4,0 g of sodium peroxide (4.2). Add another 4,0 g of sodium peroxide, mix thoroughly with a glass rod or nickel spatula and tamp the mixture. Place the crucible for 1 min or 2 min at the entrance of a muffle furnace (5.2), the temperature of which is regulated at 420 °C ± 10 °C, and then transfer it to the closed furnace for at least 1 h to effect sintering.

Remove the crucible from the furnace and cool to room temperature. Place the crucible containing the sintered mass in a dry 400 ml beaker, cover with a watch-glass and, momentarily lifting the cover, add 5 ml of water around the sinter cake. When the reaction has subsided, add a further 15 ml of water in the same way. After several minutes, when the reaction has subsided again, empty the crucible into the 400 ml beaker, rinsing with approximately 10 ml of water. Cautiously pour 30 ml of sulfuric acid (4.4) into the crucible, heat gently, if necessary, to dissolve any residue, and transfer the solution to the beaker, rinsing with about 10 ml of water.

Cautiously add 100 ml of sulfuric acid (4.4) and mix with a glass rod. Add 1 to 2 drops of hydrogen peroxide (4.6) while stirring, until a clear yellow solution is obtained. Boil for about 2 min, cool, transfer to a 200 ml one-mark volumetric flask, dilute to volume with water and mix.

4.12 Chloroform.

4.13 *N*-Benzoyl-phenylhydroxylamine (BPHA), 2,5 g/l chloroform solution.

4.14 Vanadium, standard solutions.

4.14.1 Vanadium stock solution, 1 000 μg V/ml.

Dry several grams of ammonium metavanadate (NH_4VO_3) in an air oven at 100 °C for 1 h and cool to room temperature in a desiccator. Weigh, to the nearest 0,000 2 g, 2,296 3 g of the dried product into a 600 ml beaker, add 400 ml of hot water and heat gently to dissolve. Cool, carefully add 50 ml of sulfuric acid (4.4), transfer to a 1 000 ml one-mark volumetric flask, quantitatively, dilute to volume with water and mix.

4.14.2 Vanadium standard solution, 50 µg V/ml.

Introduce 5,0 ml of vanadium stock solution (4.14.1) to a 100 ml one-mark volumetric flask containing 70 ml of water and 5 ml of sulfuric acid (4.4). Cool, dilute to volume with water and mix.

4.15 Calibration solutions.

To each of six 125 ml separating funnels, add 25,0 ml of background solution (4.11) and 7 ml of orthophosphoric acid (4.5). Using pipettes, add the quantities of vanadium standard solution (4.14.2) and water as given in Table 1 to the respective separating funnels, and mix by swirling.

Table 1 — Calibration solutions

Vanadium standard solution (4.14.2) ml	**Water** ml	**Vanadium concentration in the measured solution** µg/ml
0	5,0	0
0,5	4,5	0,5
1,0	4,0	1,0
2,0	3,0	2,0
3,5	1,5	3,5
5,0	0	5,0

For colour development and extraction, proceed as directed in 7.4.2, beginning at "Add 0,8 ml of potassium permanganate solution (4.9) ..."

5 Apparatus

Ordinary laboratory apparatus, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042, respectively, and the following.

5.1 Zirconium metal or vitreous carbon crucible, of capacity approximately 50 ml.

5.2 Muffle furnace, capable of being regulated at 420 °C ± 10 °C.

5.3 Spectrophotometer.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 µm particle size which has been taken and prepared in accordance with ISO 3082. In the case of ores having significant contents of combined water or oxidizable compounds, use a particle size of minus 160 µm.

NOTE A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

6.2 Preparation of predried test samples

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a manner that it is representative of the whole contents of the container. Dry the test sample at 105 °C ± 2 °C, as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

7.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with Annex A, independently, on one predried test sample.

NOTE The expression "independently" means that the second and any subsequent result is not affected by the previous result(s). For this particular analytical method, this condition implies that the repetition of the procedure shall be carried out either by the same operator at a different time or by a different operator, including, in both cases, appropriate recalibration.

7.2 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately 0,5 g of the predried test sample obtained in accordance with 6.2.

The test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.

7.3 Blank test and check test

In each run, one blank test and one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analysis of the ore sample(s) under the same conditions. In a blank test, 25 ml of the background solution shall be used in place of the aliquot of the test solution. A predried test sample of the certified reference material shall be prepared as specified in 6.2.

The certified reference material should be of the same type as the sample to be analysed and the properties of the two materials should be sufficiently similar to ensure that, in both cases, no significant changes in the analytical procedure will become necessary.

Where the analysis is carried out on several samples at the same time, the blank value may be represented by one test, provided that the procedure is the same and the reagents used are from the same reagent bottles.

Where the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

7.4 Determination

7.4.1 Decomposition of the test portion

Place 2,00 g of sodium peroxide (4.2) in a zirconium or vitreous carbon crucible (5.1). Immediately add the test portion (7.2) and mix well using a glass rod or a nickel spatula. Fuse over a burner and swirl the crucible until the melt is cherry red and clear. Remove from the heat and swirl cautiously to cause the cooling melt to solidify in a thin layer on the wall of the crucible. Now place the crucible and contents in a dry 300 ml beaker. Cover with a watch-glass and, momentarily lifting the cover, add 5 ml of water to the crucible. When the effervescence has ceased, empty the crucible into the beaker, rinsing with approximately 5 ml of water.

Add 32 ml of sulfuric acid (4.4) to the beaker via the crucible, wash the crucible with 5 ml of water and remove the crucible.

Add 1 to 2 drops of hydrogen peroxide (4.6) until a clear yellow solution appears. Boil for about 2 min, cool, transfer to a 50 ml one-mark volumetric flask, dilute to volume with water and mix. (This is the test solution.)

7.4.2 Colour development and extraction

Using a pipette, introduce appropriate aliquots (see Table 2) of the test solution and background solution into a 125 ml separating funnel, add 7 ml of orthophosphoric acid (4.5) and 5 ml of water, and mix by swirling.

Table 2 — Dilution guide for test solution

Mass fraction of vanadium	**Aliquot of the test solution** (7.4.1)	**Aliquot of the background solution** (4.11)	**Mass of vanadium in the aliquot**
%	ml	ml	µg
0,005 to 0,10	25	0	12,5 to 250
0,10 to 0,20	10	15	100 to 200
0,20 to 0,50	5	20	100 to 250

Add 0,8 ml of potassium permanganate solution (4.9), mix by swirling and stand for 4 min. Add 5 ml of urea solution (4.8), and then add 1 ml of sodium nitrite solution (4.7) drop by drop while swirling, and allow to stand for 1 min. Add 25 ml of hydrochloric acid (4.3) and 10 ml of BPHA solution (4.13), and shake for 45 s. Allow the two layers to separate, draw off the organic layer (main extract) by filtering through absorbent cotton inserted into the stem of the funnel, or through a dry filter paper fitted in an ordinary funnel, into a dry 50 ml one-mark volumetric flask, retaining the aqueous layer.

Add 10 ml of chloroform (4.12) to the separating funnel and shake for 30 s. Allow the two layers to separate, draw off the organic layer by filtering through the absorbent cotton or dry filter paper. Combine it with the main extract, dilute to volume with chloroform (4.12) and mix.

CAUTION — Operations involving the use of chloroform should be conducted in a cool, well ventilated area.

To ensure the same colour-developing conditions in the test solution and the calibration solutions, each solution should be taken separately through the colour development and extraction steps, and batch colour development should be avoided.

For the test solution containing more than 1 mg of titanium in the aliquot, 10 ml of sodium tripolyphosphate solution (4.10) should be added before the addition of potassium permanganate solution (4.9).

7.4.3 Spectrophotometric measurement

Carry out the spectrophotometric measurement of the test solution at a wavelength of about 535 nm, in a cell of 1 cm optical path length, after adjusting the spectrophotometer (5.3) to zero absorbance in relation to chloroform (4.12).

7.4.4 Calibration

7.4.4.1 Spectrophotometric measurement

Carry out the spectrophotometric measurement of absorbance of each calibration solution (4.15), using the calibration solution with 0 ml of vanadium standard solution (4.14.2) as the reference, in accordance with the directions given in 7.4.3.

7.4.4.2 Plotting the calibration graph

Prepare the calibration graph by plotting the absorbance against the vanadium concentrations, expressed in micrograms per millilitre, in the measured solutions.

8 Expression of results

8.1 Calculation of mass fraction of vanadium

Convert the absorbance (7.4.3) of the colour-developed test solution and the blank test solution into the corresponding concentration, expressed in micrograms of vanadium per millilitre, by means of the calibration graph (7.4.4.2).

The mass fraction of vanadium, w_V, expressed as a percentage, is calculated from the equation

$$\begin{aligned} w_\mathrm{V} &= (\rho_{\mathrm{V},1} - \rho_{\mathrm{V},0}) \times \frac{1}{10^6} \times \frac{V_1}{V_2} \times \frac{V_3}{m} \times 100 \\ &= (\rho_{\mathrm{V},1} - \rho_{\mathrm{V},0}) \times \frac{1}{10^6} \times \frac{50}{V_2} \times \frac{50}{m} \times 100 \\ &= (\rho_{\mathrm{V},1} - \rho_{\mathrm{V},0}) \times \frac{1}{4V_2 m} \qquad (1) \end{aligned}$$

where

$\rho_{\mathrm{V},0}$ is the concentration, in micrograms per millilitre, of vanadium in the blank test solution (7.3);

$\rho_{\mathrm{V},1}$ is the concentration, in micrograms per millilitre, of vanadium in the test solution (7.4.1);

V_1 is the volume, in millilitres, of the test solution;

V_2 is the volume, in millilitres, of the aliquot portion (Table 2);

V_3 is the volume, in millilitres, of the colour-developed test solution (7.4.2);

m is the mass, in grams, of the test portion (7.2).

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression equations:[1)]

$$R_\mathrm{d} = 0{,}033\,3\,X + 0{,}001\,0 \qquad (2)$$

$$P = 0{,}050\,8\,X + 0{,}001\,1 \qquad (3)$$

$$\sigma_\mathrm{d} = 0{,}011\,8\,X + 0{,}000\,4 \qquad (4)$$

$$\sigma_\mathrm{L} = 0{,}015\,3\,X + 0{,}000\,3 \qquad (5)$$

[1)] Additional information is given in Annexes B and C.

where

X is the mass fraction of vanadium, expressed as a percentage, of the test sample, calculated as follows:

- within-laboratory Equations (2) and (4): the arithmetic mean of the duplicate values,
- between-laboratory Equations (3) and (5): the arithmetic mean of the final results (8.2.3) of the two laboratories;

R_d is the independent duplicate limit;

P is the permissible tolerance between laboratories;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation.

8.2.2 Determination of analytical result

Having computed the independent duplicate results according to Equation (1), compare them with the independent duplicate limit (R_d), using the procedure given in Annex A, and obtain the final laboratory result μ_c (see 8.2.5).

8.2.3 Between-laboratories precision

Between-laboratories precision is used to determine the agreement between the final results reported by two laboratories. The assumption is that both laboratories followed the same procedure as described in 8.2.2.

Compute the following quantity:

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \tag{6}$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

$\mu_{1,2}$ is the mean of the final results.

Substitute $\mu_{1,2}$ for X in Equation (3) and calculate P.

If $|\mu_1 - \mu_2| \leqslant P$, the final results are in agreement.

8.2.4 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM) (see the second paragraph of 7.3). Calculate the analytical result (μ_c) for the RM/CRM using the procedures in 8.1 and 8.2.1 to 8.2.3, and compare it with the reference or certified value A_c. There are two possibilities:

a) $|\mu_c - A_c| \leqslant C$ in which case, the difference between the reported result and the reference/certified value is statistically insignificant.

b) $|\mu_c - A_c| > C$ in which case, the difference between the reported result and the reference/certified value is statistically significant.

where

μ_c is the analytical result for the CRM/RM;

A_c is the certified/reference value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35:2006, *Reference materials — General and statistical principles for certification.*

For a CRM/RM certified by an interlaboratory test programme

$$C = 2[\sigma_L^2 + \frac{\sigma_d^2}{n} + V(A_c)]^{1/2} \qquad (7)$$

where

$V(A_c)$ is the variance of the certified/reference value A_c (= 0 for a CRM/RM certified by only one laboratory;

n is the number of replicate determinations carried out on the CRM/RM.

CRMs certified by only one laboratory should be avoided unless they are known to have an unbiased certified value.

8.2.5 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample, or as otherwise determined by the operations specified in Annex A, calculated to five decimal places and rounded off to the third decimal place as follows:

a) where the figure in the fourth decimal place is less than 5, it is discarded and the figure in the third decimal place is kept unchanged;

b) where the figure in the fourth decimal place is 5 and there is a figure other than 0 in the fifth decimal place, or when the figure in the fourth decimal place is greater than 5, the figure in the third decimal place is increased by one;

c) where the figure in the fourth decimal place is 5 and the figure 0 is in the fifth decimal place, the 5 is discarded and the figure in the third decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and is increased by one if it is 1, 3, 5, 7 or 9.

8.3 Oxide factor

The oxide factor, expressed as a percent, is given by the following equation:

$$w_{\mathrm{V_2O_5}} = 1{,}785\,2\; w_{\mathrm{V}} \qquad (8)$$

9 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) a reference to this part of ISO 9683;

d) details necessary for the identification of the sample;

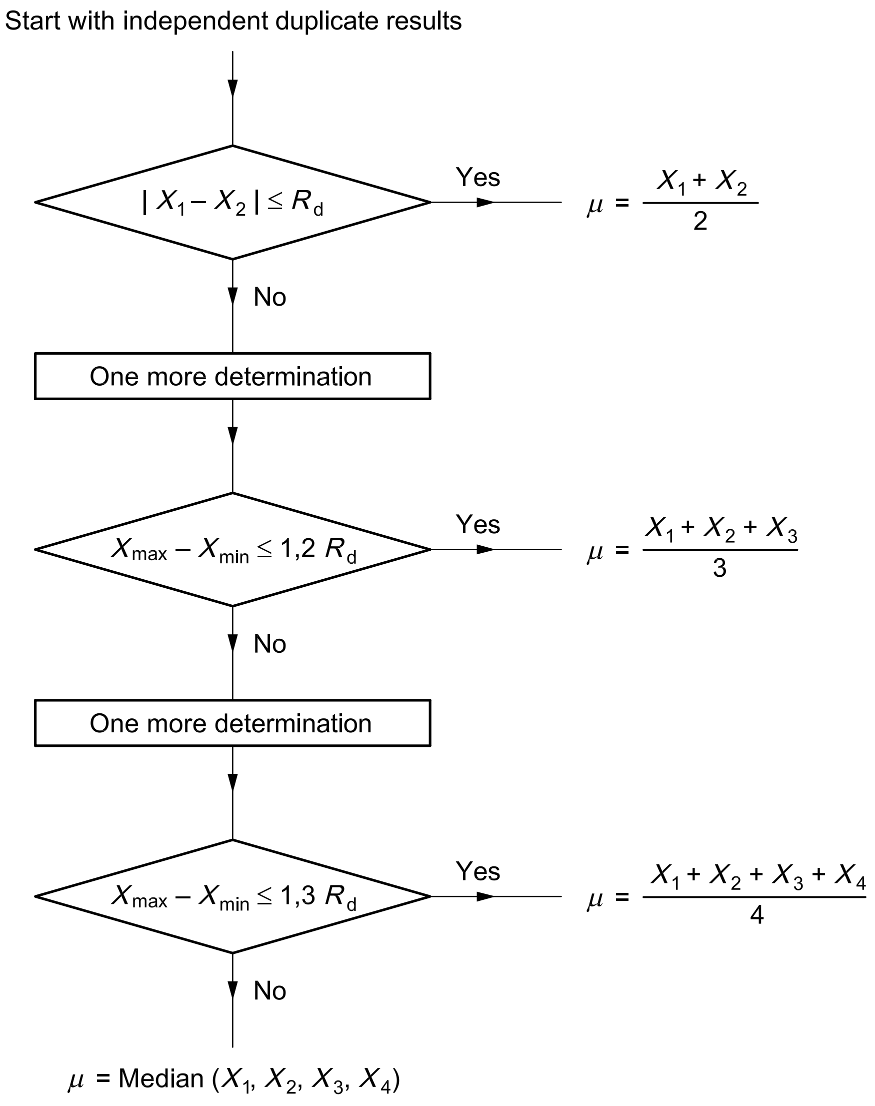
e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the result, either for the test sample or for the certified reference material(s).

Annex A
(normative)

Flowsheet of the procedure for the acceptance of analytical values for test samples



R_d: as defined in 8.2.1.

Annex B
(informative)

Derivation of repeatability and permissible equations

The regression equations in 8.2.1 were obtained by statistical evaluation of the results of international analytical trials carried out in 1985 and 1986 on seven iron ore samples, involving 12 laboratories in seven countries.

The graphical treatment of the precision data is given in Annex C.

The test samples used are listed in Table B.1.

Table B.1 — Mass fractions of vanadium in test samples

Sample	Mass fraction of vanadium %
Savage River pellets	0,523
Phillippine iron sand	0,307
Malmberget MAC 10	0,104
Tuollavaara fines	0,060
IRSID MO2-1	0,034
Whyalla pellets	0,011
Canada SCH-1	0,004

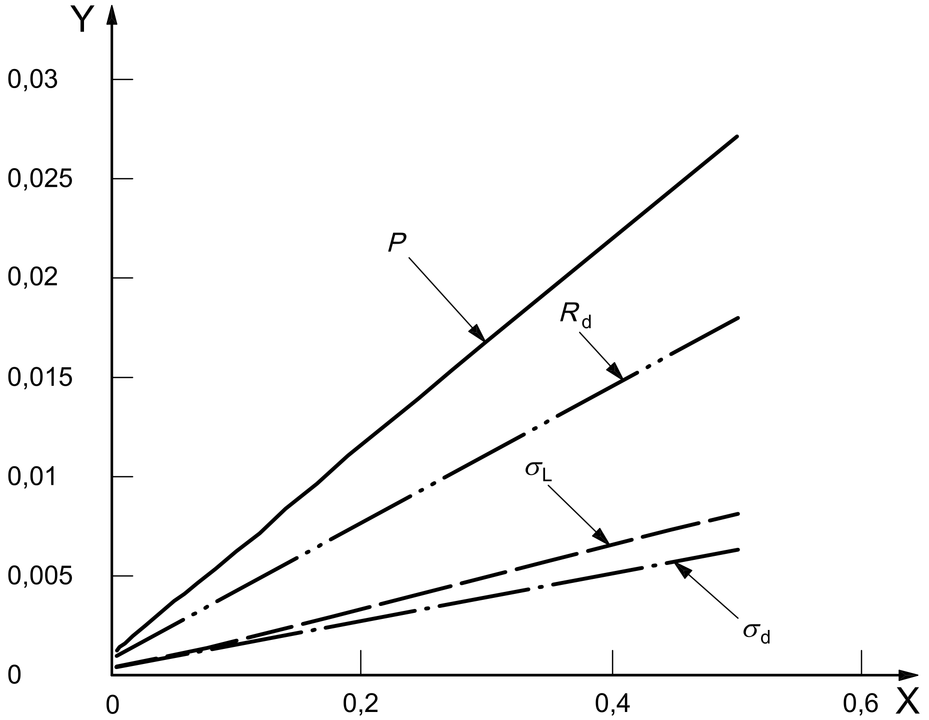
NOTE 1 A report of the international trial and a statistical analysis of the results (Document ISO/TC 102/SC 2 N840, October 1986) is available from the Secretariat of ISO/TC 102/SC 2.

NOTE 2 The statistical analysis was performed in accordance with the principles embodied in ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

Annex C
(informative)

Precision data obtained by international analytical trials

NOTE Figure C.1 is a graphical representation of the equations in 8.2.1.



Key

X mass fraction of vanadium, %

Y precision, %

Figure C.1 — Least-squares fit of precision against X for vanadium

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