International
Standard

ISO 10714

Second edition
2024-07

Steel and iron — Determination of phosphorus content — Phosphovanadomolybdate spectrophotometric method

Aciers et fontes — Détermination des teneurs en phosphore — Méthode spectrophotométrique au phosphomolybdovanadate

Reference number
ISO 10714:2024(en)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

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.

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 document 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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 459, *ECISS - European Committee for Iron and Steel Standardization,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 10714:1992), which has been technically revised.

The main changes are as follows:

- a complete revaluation of the 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 iron — Determination of phosphorus content — Phosphovanadomolybdate spectrophotometric method

1 Scope

This document specifies a spectrophotometric method for the determination of phosphorus in steel and cast iron.

The method is applicable to phosphorus contents between 0,001 0 % (mass fraction) and 1,0 % (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 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 terminology databases for use in standardization at the following addresses:

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

4 Principle

Dissolution of a test portion in an oxidizing acid mixture.

Fuming with perchloric acid and removal of chromium as volatile chromyl chloride.

Complexing of silicon and the refractory elements with hydrofluoric acid and complexing of the excess of hydrofluoric acid with orthoboric acid.

Conversion of phosphorus to phosphovanadomolybdate in presence of perchloric and nitric acids.

Extraction of phosphovanadomolybdate by 4-methyl-2-pentanone in presence of citric acid to complex arsenic.

Spectrophotometric measurements at a wavelength of 355 nm.

Arsenic, hafnium, niobium, tantalum, titanium and tungsten interfere in determining phosphorus, but the interferences can be partially overcome by formation of complexes and use of small quantities of test portion. Depending on the content of the interfering elements, the application ranges and test portions given in Table 1 apply.

The lower end of the application range can only be reached in test samples with low content of the interfering elements.

Table 1 — Application ranges and test portions

Maximum content of the interfering elements % (mass fraction)						Test portion g	Application range, Δw_p % (mass fraction)
As	Hf	Nb	Ta	Ti	W		
0,05	0,1	1	0,1	2	2	1,0	0,001 to 0,010
0,2	0,5	5	0,5	10	8	0,25	0,005 to 0,040
0,5	1,5	10	1,0	25	25	0,10	0,010 to 0,100
0,2	0,5	5	0,5	10	8	0,25	0,100 to 1,00

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.

Verify by blank tests (8.2) that the reagents are free from phosphorus or of very low phosphorus content. Whenever necessary, the results shall be corrected accordingly. Reagents giving high blank values (above 10 µg) are unsuitable and shall be discarded.

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

5.2 Nitric acid, ρ about 1,40 g/ml.

5.3 Nitric acid solution, ρ about 1,40 g/ml, diluted 1 + 4.

5.4 Perchloric acid, ρ about 1,54 g/ml.

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

5.5 Hydrofluoric acid, ρ about 1,14 g/ml.

5.6 Citric acid, 500 g/l.

Dissolve 500 g of citric acid monohydrate ($H_8C_6O_7 \cdot H_2O$) in water, dilute to 1 000 ml with water and mix.

5.7 4-Methyl-2-pentanone (isobutyl methyl ketone).

The same batch of 4-methyl-2-pentanone shall be used for analysing a series of samples.

5.8 Hexa-ammonium heptamolybdate, 150 g/l.

Dissolve 150 g of hexa-ammonium heptamolybdate tetrahydrate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in water, dilute to 1 000 ml with water and mix.

This solution shall be freshly prepared each day.

High and unstable blank values might be attributed to this reagent in particular. In such a case, change to another batch.

5.9 **Ammonium metavanadate,** 2,5 g/l.

Dissolve 2,5 g of ammonium metavanadate (NH_4VO_3) in water, dilute to 1 000 ml with water and mix.

5.10 **Sodium nitrite,** 50 g/l.

Dissolve 50 g of sodium nitrite ($NaNO_2$) in water, dilute to 1 000 ml with water and mix.

5.11 **Tetrafluoroboric acid.**

Dissolve 75 g of orthoboric acid (H_3BO_3) in 600 ml of water in a plastic beaker. Add 50 ml of hydrofluoric acid (5.5), dilute to 1 000 ml with water and mix. The solution can be gently heated if the boric acid tends to precipitate.

Keep the solution in a plastic bottle.

5.12 **Phosphorus,** standard solutions.

5.12.1 **Phosphorus standard solution,** 1 g/l.

Weigh, to the nearest 0,000 1 g, 4,393 6 g of potassium dihydrogen phosphate (KH_2PO_4) previously dried to constant mass at 110 °C and cooled in a desiccator.

Transfer into a 1 000 ml one-mark volumetric flask, dissolve in water, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of phosphorus.

5.12.2 **Phosphorus standard solution,** 10 mg/l.

Transfer 10,0 ml of the phosphorus standard solution (5.12.1) into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

Prepare this standard solution just before use.

1 ml of this standard solution contains 10 µg of phosphorus.

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 **Spectrophotometer,** equipped to measure absorbance at a wavelength of 355 nm.

Using the slitwidth recommended by the manufacturer and 4-methyl-2-pentanone (5.7) as the compensating solution, measure the absorbance of the blank solution (see 8.2) at a wavelength of about 340 nm. Then, gradually increase the wavelength until maximum absorbance is obtained (this is generally at a wavelength of 355 nm, see NOTE). Use this wavelength for the determination.

NOTE 355 nm is not the wavelength of the maximum absorbance spectrum from the complex. It is not possible to use the maximum point since the 4-methyl-2-pentanone starts to absorb the light at a lower wavelength, where a maximum absorbance value is obtained. 355 nm is selected to give the highest absorbance without giving negative absorbance values for low concentration values due to the light absorption of the solvent.

6.2 **Polytetrafluoroethylene (PTFE) beakers, or perfluoroalkoxy (PFA) beakers**, with graphite bases.

Clean the beakers thoroughly before the analysis by filling with hydrochloric acid, *ρ* about 1,19 g/ml, diluted 1 + 1, and boiling for about 2 min. Then rinse well with water.

PFA beakers are recommended in this document. They are specially constructed for fuming of acids up to 280 °C.

7 Sampling and sample preparation

Carry out the sampling and the sample preparation in accordance with ISO 14284 or appropriate national standards for steels and cast irons.

8 Procedure

8.1 Test portion

Weigh, to the nearest 0,1 mg, a test portion according to Table 2.

Table 2 — Test portion

Expected phosphorus content % (mass fraction)	Maximum content of the interfering elements % (mass fraction)						Test portion g
	As	Hf	Nb	Ta	Ti	W	
0,001 to 0,005	0,05	0,1	1	0,1	2	2	1,0
0,005 to 0,010	0,05	0,1	1	0,1	2	2	1,0
	0,2	0,5	5	0,5	10	8	0,25
0,010 to 0,040	0,2	0,5	5	0,5	10	8	0,25
	0,5	1,5	10	1,0	25	25	0,10
0,040 to 0,100	0,5	1,5	10	1,0	25	25	0,10
0,100 to 1,00	0,2	0,5	5	0,5	10	8	0,25

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 the reagents, except the test portion.

8.3 Determination

8.3.1 Preparation of the test solution

8.3.1.1 Phosphorus contents up to 0,1 % (mass fraction)

8.3.1.1.1 Place the test portion (8.1) in a beaker (6.2). Add 5 ml of nitric acid (5.2) and 5 ml of hydrochloric acid (5.1). For samples containing high contents of niobium and/or tantalum, also add 7 ml of hydrofluoric acid (5.5). Cover the beaker with a PTFE watch-glass and heat gently until the reaction ceases.

8.3.1.1.2 Remove the watch-glass.

8.3.1.1.3 Add 10 ml of perchloric acid (5.4). Replace the watch-glass, leaving a small opening to let the fumes out, and evaporate to dense white fumes. Maintain fuming until no droplets can be seen on the watch-glass. For samples containing more than 0,1 % (mass fraction) chromium, remove the chromium as follows.

8.3.1.1.4 While partly covering the beaker solution with the watch-glass, with the chromium fully oxidized, add hydrochloric acid (5.1) drop by drop to the fuming solution, until coloured fumes are no longer expelled. Then continue the fuming to oxidize the remaining chromium.

8.3.1.1.5 Repeat the treatment until no yellow fumes appear when hydrochloric acid (5.1) is added.

8.3.1.1.6 After fuming, add 25 ml of nitric acid solution (5.3) and 6 ml of hydrofluoric acid (5.5) and boil the solution for 8 min to 10 min to dissolve all the precipitate. If any precipitate remains after boiling, add another 2 ml of hydrofluoric acid (5.5) and boil again. If the precipitate still does not dissolve, or if any precipitate occurs at a later stage, repeat the procedure (8.3.1) using a smaller mass of test portion.

8.3.1.1.7 Add 10 ml of sodium nitrite (5.10) to reduce any dichromate which has not been removed as chromyl chloride and continue to boil the solution for 10 min to expel the nitrous fumes. Rinse the beaker walls several times with water during the boiling.

8.3.1.1.8 Allow the solution to cool slightly and add 40 ml of tetrafluoroboric acid (5.11). Cool the solution between 20 °C and 30 °C within 10 min and proceed immediately with the colour development (see 8.3.2), avoiding any delay which might allow the oxides to re-precipitate.

8.3.1.2 Phosphorus contents greater than 0,1 % (mass fraction)

Follow the procedure specified in 8.3.1.1.1.

Dilute to about 100 ml with water. Cool and filter, if necessary, to remove graphite.

Transfer the test solution quantitatively into a 200 ml plastic volumetric flask, dilute to the mark with water and mix.

Using a pipette, take a suitable volume (V) of the solution containing not more than 0,1 mg of phosphorus and transfer it into a beaker (6.2).

Proceed as specified in 8.3.1.1.3.

8.3.2 Colour development and extraction

Add 10,0 ml of ammonium metavanadate (5.9) and 15,0 ml of hexa-ammonium heptamolybdate (5.8) and then allow to stand at a temperature between 18 °C and 25 °C for a minimum of 7 min, but no longer than 15 min.

Transfer the solution into a 250 ml separating funnel. Add 10 ml of citric acid (5.6), mix and immediately add 40,0 ml of 4-methyl-2-pentanone (5.7), and shake the funnel for 30 s.

Allow the two layers to separate and discard the lower (aqueous) phase.

Dry the inside of the stem of the separating funnel with a small piece of filter paper. Filter the 4-methyl-2-pentanone layer through a dry rapid filter paper into a small dry beaker. Proceed immediately with spectrophotometric measurements (see 8.3.3).

8.3.3 Spectrophotometric measurements

Carry out the spectrophotometric measurement of the test solution (see 8.3.2) at a constant temperature (±1 °C) between 18 °C and 25 °C at a wavelength of 355 nm in a cell of 10 mm optical path length, after adjusting the spectrophotometer (6.1) to zero absorbance in relation to 4-methyl-2-pentanone (5.7).

8.4 Establishment of the calibration curve

8.4.1 Preparation of calibration solutions

Introduce into a series of five beakers (6.2) the volumes of the phosphorus standard solution (5.12.2) indicated in Table 3.

Table 3 — Calibration solutions

Volume of phosphorus standard solution (5.12.2) ml	Corresponding mass of phosphorus µg
0[a]	0
2,5	25
5,0	50
7,5	75
10,0	100
[a] Zero member.	

Treat the solutions according to 8.3.1 and 8.3.2.

8.4.2 Spectrophotometric measurements

Carry out the spectrophotometric measurement of each calibration solution at a wavelength of 355 nm, after adjusting the spectrophotometer (6.1) to zero absorbance in relation to 4-methyl-2-pentanone (5.7).

8.4.3 Plotting the calibration curve

Subtract the absorbance of the zero member from the absorbance of each calibration solution and prepare the calibration curve by plotting the net absorbance values against the mass of phosphorus, expressed in micrograms, in the calibration solutions.

9 Expression of results

9.1 Method of calculation

Convert the absorbance measured in 8.3.3 to the corresponding mass, expressed in micrograms, of phosphorus in the test solution by using the calibration curve (see 8.4.3).

The phosphorus content, w_P, expressed as a percentage by mass, is given by Formula (1).

$$w_\mathrm{P} = \frac{m_{\mathrm{P},1} - m_{\mathrm{P},0}}{m \times 10^6} \times D \times 100 \qquad (1)$$

where

$m_{\mathrm{P},0}$ is the mass, expressed in micrograms, of phosphorus in the blank test;

$m_{\mathrm{P},1}$ is the mass, expressed in micrograms, of phosphorus in the test solution;

D is the dilution factor [for phosphorus contents up to 0,1 % (mass fraction) $D = 1$ and for phosphorus contents greater than 0,1 % (mass fraction) $D = 200/V$];

V is the volume, expressed in millilitres, of the aliquot of the test solution containing not more than 0,1 mg of phosphorus (see 8.3.1.2);

m is the mass, in grams, of the test portion (8.1).

9.2 Precision

A planned trial of this method was carried out by 20 laboratories, at eight levels of phosphorus, each laboratory making three determinations (see NOTE 1 and NOTE 2) of phosphorus content at each level.

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

The results obtained were treated statistically according to ISO 5725-2 and ISO 5725-3.

The data obtained showed a logarithmic relationship between phosphorus content and repeatability limit (r) and reproducibility limits (R_w and R) of the test results (see NOTE 3) as summarized in Table 4. The graphical representation of the data is shown in Figure B.1.

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 of time.

NOTE 2 The third determination was carried out on 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: from the two values obtained on day 1 and the value obtained on day 2, the repeatability limit (r) and reproducibility limits (R_w and R) were calculated using the procedure specified in ISO 5725-3.

Table 4 — Precision data (smoothed values)

Phosphorus content % (mass fraction)	**Repeatability limits** % (mass fraction) r	**Reproducibility limits** % (mass fraction)	
		R_w	R
0,001	0,000 28	0,000 45	0,000 72
0,002	0,000 48	0,000 74	0,001 20
0,005	0,000 95	0,001 44	0,002 37
0,01	0,001 59	0,002 37	0,003 95
0,02	0,002 68	0,003 91	0,006 58
0,05	0,005 32	0,007 57	0,012 9
0,1	0,008 94	0,012 5	0,021 6
0,2	0,015 0	0,020 6	0,036 0
0,5	0,029 9	0,039 8	0,070 7
1,0	0,050 2	0,065 6	0,118

10 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 10714:2024;

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 may have influenced the results.

Annex A

(informative)

Additional information on the international interlaboratory test

Table 4 was derived from the results of an international interlaboratory test carried out in 1989 on two pure iron samples, four steel samples and two cast iron samples in 12 countries involving 20 laboratories.

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

Table A.1 — Test samples and experimental precision data

Sample	**Phosphorus content** % (mass fraction)		**Precision** % (mass fraction)		
	Certified	**Found**	**Repeatability limit**	**Reproducibility limits**	
			r	R_w	R
AMKO iron (Pure Iron)	<0,000 2[a]	0,000 26	0,000 17	0,000 29	0,000 50
JSS 003-1 (Pure Iron)	0,001 1	0,001 14	0,000 43	0,000 46	0,000 61
Sandvik 1 (Alloy 800)	0,009[a]	0,005 22	0,000 70	0,001 38	0,001 51
JK 8F (Austenitic stainless steel)	0,017 6	0,016 2	0,001 5	0,002 3	0,003 9
Sandvik 2 (Austenitic stainless steel)	0,022[a]	0,018 7	0,001 4	0,002 4	0,006 0
BCS 485 (Tool steel)	0,046	0,045 8	0,004 7	0,007 2	0,014 9
ECRM 484-1 (Cast iron)	0,121	0,115	0,010	0,013	0,028
ECRM 486-1 (Cast iron)	1,00	0,976	0,090	0,107	0,139

[a] Non-certified value