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

Aciers et fontes — Dosage du phosphore — Méthode par spectrophotométrie au phosphovanadomolybdate

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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.

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.

International Standard ISO 10714 was prepared by Technical Committee ISO/TC 17, *Steel*, Sub-Committee SC 1, *Methods of determination of chemical composition*.

The publication of this International Standard gives rise to the cancellation of ISO 2732:1984.

Annexes A and B of this International Standard are for information only.

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

1 Scope

This International Standard specifies a spectrophotometric method for the determination of phosphorus in steel and iron with the following limitations.

The method is applicable to phosphorus contents between 0,001 0 % (*m*/*m*) and 1,0 % (*m*/*m*).

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 concentration 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 contents of the interfering elements.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377-2:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 2: Samples for the determination of the chemical composition.*

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

Table 1

Maximum content of the interfering elements, % (*m*/*m*)						Test portion	Application range, Δw_P
As	Hf	Nb	Ta	Ti	W	g	% (*m*/*m*)
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

3 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 perchloric and nitric acid solution.

Extraction of phosphovanadomolybdate by 4-methyl-2-pentanone with citric acid present to complex arsenic.

Spectrophotometric measurement at a wavelength of 355 nm.

4 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 (7.2) that the relevant reagents are free from phosphorus or of very low phosphorus content. Whenever necessary, the results shall be corrected accordingly. Grades giving high blank values (above 10 µg) are unsuitable and shall be discarded.

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

4.2 Nitric acid, ρ about 1,40 g/ml.

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

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

4.5 Hydrofluoric acid, 40 % (m/m), ρ about 1,14 g/ml.

4.6 Citric acid, solution.

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

4.7 4-Methyl-2-pentanone (isobutyl methyl ketone).

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

4.8 Hexa-ammonium heptamolybdate, solution.

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

This solution shall be freshly prepared each day.

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

4.9 Ammonium metavanadate, solution.

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

4.10 Sodium nitrite, solution.

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

4.11 Tetrafluoroboric acid, solution.

Dissolve 75 g of orthoboric acid (H_3BO_3) in 600 ml of water in a plastic beaker. Add 50 ml of hydrofluoric acid (4.5), 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.

4.12 Phosphorus, standard solutions.

4.12.1 Stock solution, corresponding to 1 g of P per litre.

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

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

1 ml of this stock solution contains 1 mg of P.

4.12.2 Standard solution, corresponding to 10 mg of P per litre.

Transfer 10,0 ml of the stock solution (4.12.1) to 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 P.

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042 as appropriate.

Ordinary laboratory apparatus, and

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

Using the slitwidth recommended by the manufacturer and 4-methyl-2-pentanone (4.7) as the compensating solution, measure the absorbance of the colour-developed and extracted blank solution (see 7.3.2) 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 1). Use this wavelength for the determination.

NOTE 1 355 nm is not the wavelength of the maximum absorption 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 absorption without giving negative absorption values for low concentration due to the light absorption of the solvent.

5.2 Polytetrafluoroethylene (PTFE) beakers, or **perfluoroalkoxy (PFA) beakers** (see note 2), 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.

NOTE 2 PFA beakers are recommended in this International Standard. They are specially constructed for fuming of acids up to 280 °C.

5.3 Heating source, with controllable surface temperature.

6 Sampling

Carry out sampling in accordance with ISO 377-2 or appropriate national standards for steel and iron.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,1 mg, a test portion of the sample according to table 2.

7.2 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.

7.3 Determination

7.3.1 Preparation of the test solution

7.3.1.1 For phosphorus contents up to 0,1 % (*m*/*m*)

Place the test portion (7.1) in a beaker (5.2). Add 5 ml of nitric acid (4.2) and 5 ml of hydrochloric acid (4.1). For samples containing high amounts of niobium and/or tantalum, also add 7 ml of hydrofluoric acid (4.5). Cover the beaker with a PTFE watch-glass and heat gently on a heating source (5.3) until the reaction ceases.

Table 2

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

Remove the watch-glass and add 10 ml of perchloric acid (4.4). 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 % (*m*/*m*) chromium, remove the chromium as follows.

While partly covering the beaker solution with the watch-glass, with the chromium fully oxidized, add hydrochloric acid (4.1) drop by drop to the fuming solution, until coloured fumes are no longer liberated. Then continue the fuming to oxidize the remaining chromium.

Repeat the treatment until no yellow fumes appear when hydrochloric acid (4.1) is introduced.

After fuming, add 25 ml of nitric acid (4.3) and 6 ml of hydrofluoric acid (4.5) 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 (4.5) and boil again. If the precipitate still does not dissolve, or if any precipitate occurs at a later stage, repeat the determination using a smaller mass of test portion.

Add 10 ml of sodium nitrite solution (4.10) 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. Wash the beaker walls several times with water during the boiling.

Allow the solution to cool slightly and add 40 ml of tetrafluoroboric acid solution (4.11). Cool the solution between 20 °C and 30 °C within 10 min and proceed immediately with the colour development (see 7.3.2), avoiding any delay which might allow the oxides to re-precipitate.

7.3.1.2 For phosphorus contents greater than 0,1 % (*m*/*m*)

Carry out the procedure specified in the first paragraph of 7.3.1.1.

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

Transfer the test solution quantitatively to 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 to a beaker (5.2).

Proceed as specified in 7.3.1.1, from the second paragraph beginning at "add 10 ml of the perchloric acid (4.4)...".

7.3.2 Colour development and extraction

Add 10,0 ml of ammonium metavanadate solution (4.9) and 15,0 ml of hexa-ammonium heptamolybdate solution (4.8) 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 to a 250 ml separating funnel. Add 10 ml of citric acid solution (4.6), mix and immediately add 40,0 ml of 4-methyl-2-pentanone (4.7), 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 measurement (7.3.3).

7.3.3 Spectrophotometric measurement

Carry out the spectrophotometric measurement of the test solution (see 7.3.2) at a constant temperature (± 1 °C) between 18 °C and 25 °C at a wavelength of 355 nm with a cell of 1 cm optical path length, after adjusting the spectrophotometer (5.1) to zero absorbance in relation to 4-methyl-2-pentanone (4.7).

7.4 Establishing the calibration graph

7.4.1 Preparation of calibration solutions

Introduce into a series of five beakers (5.2) the volumes of the phosphorus standard solution (4.12.2) indicated in table 3.

Table 3

Volume of phosphorus standard solution (4.12.2) ml	Corresponding mass of phosphorus in measuring solution µg
0[1]	0
2,5	25
5,0	50
7,5	75
10,0	100

[1] Zero member.

Treat the solutions according to 7.3.1 and 7.3.2.

7.4.2 Spectrophotometric measurement

Carry out spectrophotometric measurements of each solution at a wavelength of 355 nm, after adjusting the spectrophotometer (5.1) to zero absorbance in relation to 4-methyl-2-pentanone (4.7).

7.4.3 Plotting the calibration graph

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

8 Expression of results

8.1 Method of calculation

Convert the absorbance measured in 7.3.3 into the corresponding mass, expressed in micrograms, of phosphorus in the extracted test solution by using the calibration graph (see 7.4.3).

The phosphorus content, w_P, expressed as a percentage by mass, is given by the equation

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

$$= (m_{P,1} - m_{P,0}) \times \frac{D}{10^4 m}$$

where

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

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

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

V is the volume, expressed in millilitres, of a suitable aliquot of the test solution containing not more than 0,1 mg of phosphorus (see 7.3.1.2);

m is the mass, in grams, of the test portion (7.1).

8.2 Precision

A planned trial of this method was carried out by 20 laboratories, at eight levels of phosphorus, each laboratory making three determinations (see notes 3 and 4) of phosphorus content at each level.

The test samples used are listed in table A.1.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a logarithmic relationship between phosphorus content and repeatability (r) and reproducibility (R and R_w) of the test results (see note 5) as summarized in table 4. The graphical representation of the data is shown in figure B.1.

NOTES

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

4 The third determination was carried out on a different time (on a different day) by the same operator as in note 3 using the same apparatus with a new calibration.

5 From the results obtained on day 1, the repeatability (r) and reproducibility (R) were calculated using the procedure specified in ISO 5725. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_w) was calculated.

Table 4

Phosphorus content % (m/m)	**Repeatability** r	**Reproducibility** R	 R_w
0,001	0,000 16	0,000 40	0,000 35
0,002	0,000 30	0,000 73	0,000 62
0,005	0,000 67	0,001 61	0,001 30
0,01	0,001 22	0,002 93	0,002 28
0,02	0,002 23	0,005 32	0,003 99
0,05	0,004 98	0,011 7	0,008 38
0,1	0,009 12	0,021 2	0,014 7
0,2	0,016 7	0,038 6	0,025 8
0,5	0,037 2	0,084 8	0,054 1
1,0	0,068 2	0,154	0,094 8

9 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;

b) the method used by reference to this International Standard;

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

Annex A
(informative)

Additional information on the international co-operative tests

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

The results of the trials were reported in document ISO/TC 17/SC 1 N 835, March 1990. The graphical representation of the precision data is given in annex B.

The test samples used are listed in table A.1.

Table A.1

Sample	Phosphorus content % (m/m)			Precision		
	Certified	Found		Repeatability	Reproducibility	
		$\overline{w}_{P,1}$	$\overline{w}_{P,2}$	r	R	R_w
AMKO iron (Pure iron)	< 0,000 2 [1]	0,000 27	0,000 25	0,000 25	0,000 53	0,000 31
JSS 003-1 (Pure iron)	0,001 1	0,001 10	0,001 12	0,000 34	0,000 48	0,000 51
Sandvik 1 (Alloy 800)	0,009[1]	0,005 34	0,005 19	0,000 44	0,001 38	0,001 35
JK 8F (Austenitic stainless)	0,017 6	0,016 3	0,016 2	0,001 52	0,002 98	0,002 73
Sandvik 2 (Austenitic stainless)	0,022[1]	0,018 6	0,018 8	0,001 56	0,005 78	0,002 33
BCS 485 (Tool steel)	0,046	0,045 7	0,045 4	0,004 80	0,015 0	0,007 70
ECRM 484-1 (Cast iron)	0,121	0,114 0	0,115 2	0,009 95	0,032 9	0,024 8
ECRM 486-1 (Cast iron)	1,00	0,971	0,979	0,090 7	0,117	0,094 1

$\overline{w}_{P,1}$: general mean within a day
$\overline{w}_{P,2}$: general mean within days

1) Non-certified value