INTERNATIONAL
STANDARD

ISO
9388

First edition
1992-08-15

Nickel alloys — Determination of phosphorus content — Molybdenum blue molecular absorption spectrometric method

Alliages de nickel — Dosage du phosphore — Méthode par spectrométrie d'absorption moléculaire au bleu de molybdène

Reference number
ISO 9388:1992(E)

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 9388 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*, Sub-Committee SC 4, *Analysis of nickel alloys*.

Annex A of this International Standard is for information only.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

Nickel alloys — Determination of phosphorus content — Molybdenum blue molecular absorption spectrometric method

1 Scope

This International Standard specifies a molecular absorption spectrometric method for the determination of the phosphorus content of nickel alloys in the range 0,001 % (*m*/*m*) to 0,025 % (*m*/*m*). Typical compositions of some nickel alloys are given in annex A.

Chromium(III) and silica cause interference which is eliminated in the procedure. See clause 9.

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

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

3 Principle

Dissolution of a test portion in nitric and hydrochloric acids. Removal of hydrochloric acid by fuming with sulfuric acid, and oxidation of chromium(III) to chromium(VI) with ammonium peroxydisulfate.

Precipitation of iron(III) phosphate and redissolution of the precipitate in a hydrofluoric-nitric acid mixture.

Addition of boric, tartaric, and sulfamic acids to complex free fluoride, eliminate arsenic interference, and remove oxides of nitrogen.

Formation and extraction of molybdophosphoric acid into isobutyl alcohol, reduction of the heteropoly acid to molybdenum blue and back-extraction into an aqueous phase.

Measurement of the absorbance of the aqueous solution at 700 nm.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Nitric/hydrochloric acid, mixture.

WARNING — This acid mixture is highly corrosive and unstable. Noxious gases (chlorine) are liberated on standing. It shall be prepared and used in a fume cupboard and shall not be kept in a closed container.

Carefully mix 25 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml) and 125 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml). This mixture should be prepared just before use.

4.2 Hydrofluoric acid, $\rho_{20} = 1{,}15$ g/ml, 48 % (*m*/*m*) HF.

WARNING — Hydrofluoric acid is extremely irritating and corrosive to skin and mucous membranes, producing severe skin burns which are slow to heal. In the case of contact with skin, wash well with water and seek medical advice.

4.3 Sulfuric acid, $\rho_{20} = 1{,}84$ g/ml, diluted 1 + 1.

Slowly, and with constant stirring, add 100 ml of sulfuric acid to 100 ml of water.

4.4 Boric acid, solution.

Dissolve 40 g of boric acid (H_3BO_3) in 1 litre of water and mix.

4.5 Oxalic acid, solution.

Dissolve 1 g of oxalic acid dihydrate [$(COOH)_2 \cdot 2H_2O$] in 100 ml of water and mix.

4.6 Sulfamic acid, solution.

Dissolve 5 g of sulfamic acid (NH_2SO_3H) in 100 ml of water and mix.

4.7 Tartaric acid, solution.

Dissolve 10 g of tartaric acid [$(CHOH \cdot COOH)_2$] in 100 ml of water and mix.

4.8 Chloroform ($CHCl_3$).

4.9 Isobutyl alcohol, (2-methyl-1-propanol) [$(CH_3)_2CH \cdot CH_2OH$].

4.10 Ammonia, solution, $\rho_{20} = 0{,}89$ g/ml.

4.11 Ammonium nitrate, solution.

Dissolve 5 g of ammonium nitrate (NH_4NO_3) in 500 ml of water.

4.12 Ammonium peroxydisulfate, solution.

Dissolve 20 g of ammonium peroxydisulfate [$(NH_4)_2S_2O_8$] in water and dilute to 200 ml. Prepare a fresh solution every three days.

4.13 Iron(III) nitrate, solution.

Dissolve 7,2 g of iron(III) nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in about 75 ml of water containing 3 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml), dilute to 100 ml with water and mix.

4.14 Silver nitrate, solution.

Dissolve 3 g of silver nitrate ($AgNO_3$) in 200 ml of water. Store in a dark glass bottle.

4.15 Sodium molybdate, solution.

Dissolve 10 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) and 8 g of sodium hydroxide (NaOH) in 200 ml of water.

4.16 Sodium chloride, wash solution.

Dissolve 23 g of sodium chloride (NaCl) in water, add 50 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml) and dilute to about 900 ml. Add 60 ml of isobutyl alcohol (4.9) and shake to dissolve. Dilute to a final volume of 1 litre and mix.

4.17 Reducing solution.

4.17.1 Dissolve 10 g of stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) in 25 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml) and heat until dissolved. Cool to ambient temperature and dilute to 50 ml with water. The solution is stable for at least one week when kept in a stoppered flask.

4.17.2 Transfer 5 ml of this solution to a 250 ml one-mark volumetric flask, add 10 ml of the sulfuric acid (4.3), make up to the mark with water and mix. Prepare a fresh solution each day.

4.18 Phosphorus, standard reference solution (100 mg/l).

Transfer exactly 0,439 4 g of potassium dihydrogen phosphate (KH_2PO_4) to a 1 000 ml one-mark volumetric flask, add 100 ml of water and 5 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml) diluted 1 + 1. Dissolve the salt, make up to the mark with water and mix.

5 Apparatus

Ordinary laboratory glassware, and

5.1 Plastics beakers, of capacity 250 ml and usable up to 150 °C. Polymethylpentene or fluorocarbon polymers have been found satisfactory.

5.2 Plastics filtration funnels.

5.3 Separating funnels, of capacity 125 ml. Two funnels are required for the analysis of each test sample. Polytetrafluoroethylene stopcocks and plastics stoppers are preferred.

5.4 One-mark volumetric flasks, complying with the requirements of ISO 1042, class A.

5.5 Mechanical micropipettes, of capacities 100 µl, 250 µl and 500 µl.

5.6 Molecular absorption spectrometer, suitable for measuring absorbance at 700 nm and equipped with optically matched 1 cm or 2 cm glass cells.

6 Sampling and sample preparation

6.1 Sampling and preparation of the laboratory sample shall be carried out according to normal agreed procedures or, in case of dispute, the relevant International Standard.

6.2 The laboratory sample is normally in the form of millings or drillings and no further preparation of the sample is necessary.

6.3 If it is suspected that the laboratory sample is contaminated with oil or grease from the milling or drilling process, it shall be cleaned by washing with high purity acetone and drying in air.

6.4 If the laboratory sample contains particles or pieces of widely varying sizes, the test portion should be obtained by riffling.

7 Procedure

7.1 Test portion and preparation of test solution

7.1.1 Weigh a test portion containing between 3 µg and 50 µg of phosphorus according to table 1, and transfer it to a 150 ml glass beaker.

Table 1 — Mass of sample to be taken

Expected phosphorus content % (*m*/*m*)	Mass of sample g	Weighing accuracy g
0,001 to 0,01	0,29 to 0,31	0,005
0,01 to 0,025	0,19 to 0,21	0,002

7.1.2 Add 7 ml of the acid mixture (4.1), cover the beaker and warm. Remove the beaker from the heat and allow the reaction to proceed and subside. Heat again to complete the dissolution.

7.1.3 Add 5 ml of the sulfuric acid (4.3) and evaporate to dense fumes. Do not evaporate to dryness. Cool to room temperature and dissolve the salts in 5 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml) and 30 ml of water. Transfer the solution, which may contain hydrolysed products of refractory metals, quantitatively to a 400 ml beaker. Use a rubber policeman if necessary.

NOTE 1 Usually, the dissolution is rapid and no extensive heating is required. Some alloys, particularly those high in copper, are best dissolved in 7 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml), diluted 1 + 1. In such instances, omit 7.1.3 and proceed as directed in 7.2.

7.2 Separation of chromium

7.2.1 Dilute the solution to 150 ml, add 3 ml of the iron(III) nitrate solution (4.13), and heat almost to boiling. Add 10 ml of the silver nitrate solution (4.14) and 30 ml of the ammonium peroxydisulfate solution (4.12). Boil the mixture for 10 min to 15 min to decompose the excess oxidant. Dilute to 250 ml with water and add, while stirring, the ammonia solution (4.10) until a permanent precipitate of iron(III) hydroxide forms. Add 15 ml of ammonia solution in excess and digest the hot mixture for about 15 min. Filter the precipitate through a fast filter paper containing some wet filter pulp. Wash the precipitate and filter thorougly with the ammonium nitrate solution (4.11) until all of the yellow colour due to the chromate ions has been removed.

7.2.2 Transfer the filter with the precipitate to a plastics beaker (5.1) containing 2 ml of hydrofluoric acid (4.2). Wash the precipitation beaker with 10 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml) diluted 1 + 1 and add the washings to the plastics beaker. Heat carefully to dissolve the precipitate, and break up the filter with a plastics stirring rod. Filter through an 11 cm medium speed filter and plastics funnel into a 100 ml plastics beaker. Wash twice with 5 ml portions of water and then once with 30 ml of the boric acid solution (4.4). Finish washing the filter with water so that the total volume of the filtrate does not exceed 60 ml to 70 ml.

NOTE 2 It is important to ensure that all the chromium is oxidized to chromium(VI) before the precipitation, and to wash the precipitate and filter until it is completely free of chromium(VI). The filtration and washing of the precipitate of hydrous oxides is very fast in the presence of filter pulp.

7.3 Extraction of molybdophosphoric acid

7.3.1 Transfer the filtrate to a separating funnel (5.3). Add 2 ml of the tartaric acid solution (4.7), 1 ml of the sulfamic acid solution (4.6), and 10 ml of the sodium molybdate solution (4.15). Mix by swirling, add 20 ml of the isobutyl alcohol (4.9) and extract by shaking the funnel vigorously for 2 min. Allow the phases to separate and transfer the lower aqueous layer into a second separating funnel. Add, to this aqueous phase, 5 ml of sodium molybdate solution and 10 ml of isobutyl alcohol. Shake vigorously for 2 min, allow the phases to separate and discard the lower aqueous phase. Combine the remaining organic phase with that in the first separating funnel. Swirl, allow to settle and discard any residual aqueous phase which may separate on standing.

7.3.2 Wash the combined extracts by adding 20 ml of the sodium chloride wash solution (4.16) and shaking for 30 s. Drain off and discard the lower aqueous phase. Repeat the washing of the organic phase twice more, each time using 20 ml of the sodium chloride wash solution. Discard the aqueous washings.

7.4 Molybdenum blue development

To the washed extract add, in order, 40 ml of the chloroform (4.8), 30 ml of water, 10 ml of the diluted reducing solution (4.17.2), and 2 ml of the oxalic acid solution (4.5). Without delay, shake for 1 min. Allow the phases to separate and discard the heavier chloroform layer. Transfer the blue aqueous solution into a 100 ml one-mark volumetric flask containing 5 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml) diluted 1 + 1. Rinse the funnel with water and dilute the solution in the flask to the mark. Mix and allow to stand for at least 20 min before measurement.

NOTE 3 The mixtures should not be left standing after the reducing and oxalic acid solutions have been added. Proceed immediately with the equilibration. A minimum of 20 min is required for the colour to develop fully. The solution then remains stable for at least 20 h.

7.5 Spectrometric measurement

Measure the absorbance of the test solution in a 1 cm cell at a wavelength of 700 nm against water as the reference. Use 2 cm cells when determining phosphorus contents of 0,001 % (m/m).

7.6 Blank test

Carry out a blank test in parallel with the determination, following the same procedure, using the same quantities of all the reagents as in the determination, but omitting the test portion.

7.7 Calibration

7.7.1 To four 400 ml glass beakers add, using a micropipette (5.5), 0 µl, 100 µl, 250 µl and 500 µl, respectively, of the phosphorus standard solution (4.18). The additions correspond to 0 µg, 10 µg, 25 µg and 50 µg of phosphorus. To each beaker add 5 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml) and proceed as described in 7.2 to 7.4.

7.7.2 Measure the absorbance of the phosphorus-containing calibration solutions in 1 cm (or 2 cm) cells at 700 nm against the "zero" solution as reference.

7.7.3 Plot the measured absorbance readings against the mass, in micrograms, of phosphorus added.

NOTES

4 By carrying the calibration through the precipitation and extraction steps, and using the "zero" solution as the reference, the blank from reagents used in the calibration is eliminated. The absorbance readings therefore correspond to the net phosphorus additions made.

5 Absorbance readings show a linear relationship and their absolute values have been found to be reproducible on different days during a period of more than three months.

7.8 Number of determinations

Carry out the determination at least in duplicate.

8 Expression of results

8.1 Calculation

8.1.1 Convert the absorbance readings of the test solution (see 7.5) and of the reagent blank (see 7.6) into micrograms of phosphorus using the calibration graph (see 7.7.3).

8.1.2 The phosphorus content, expressed as a percentage by mass, of the test portion, is given by the formula

$$\frac{m_1 - m_2}{m_0} \times 10^{-4}$$

where

m_0 is the mass, in grams, of the test portion (see 7.1.1);

m_1 is the mass, in micrograms, of phosphorus found in the test portion;

m_2 is the mass, in micrograms, of phosphorus in the blank test.

8.2 Precision

8.2.1 Laboratory tests

Originally 14 laboratories participated in the testing of this method. After technical revisions were made, seven laboratories in five countries participated in the second precision testing of this method, in which six alloy samples of the nominal composition given in table 2 were used. Each sample was analysed in duplicate on different days.

8.2.2 Statistical analysis

8.2.2.1 Results from the interlaboratory test programme were evaluated according to ISO 5725, using the means of the duplicate results. The data were tested for statistical outliers by the Cochran and Dixon tests given in ISO 5725.

8.2.2.2 The principle of the Cochran test is that a set of results is an outlier if the within-laboratory variance is too large in relation to others. Dixon's test is used to determine if the mean from a laboratory is too far from the other laboratory means. Both tests were applied at the 95 % confidence level.

8.2.2.3 Repeatability and reproducibility were calculated according to ISO 5725 at the 95 % confidence level. The results of the statistical analysis are given in table 3.

8.2.2.4 One laboratory was rejected because of incomplete data. One laboratory was rejected as a Cochran outlier for sample 2.

9 Interferences

9.1 Chromium(III) interferes in the phosphorus determination causing low recoveries. To eliminate this interference, chromium(III) is oxidized to chromium(VI) and phosphorus is precipitated as iron(III) phosphate leaving the chromium in solution as chromate ion.

9.2 Silica interference is eliminated by forming the stable fluorosilicate ion. The formation of fluorocomplexes of titanium, zirconium, niobium and tantalum prevents their hydrolysis and the loss of phosphorus by adsorption on hydrous oxides and/or by the formation of stable phosphates. Boric acid is used to complex free fluoride ions which would otherwise mask the molybdate reagent. Tartaric acid eliminates interference by traces of arsenic and sulfamic acid removes oxides of nitrogen.

10 Test report

The test report shall include the following information:

a) a reference to the method used;

b) the results of the analysis;

c) the number of independent replications;

d) any unusual features noted during the analysis;

e) any operation not included in this International Standard or regarded as optional.

Table 2 — Nominal composition of test samples [% (m/m)]

Sample reference	Ni	Fe	Cr	Cu	Mo	Nb	Ti
1	64	2	—	33	—	—	—
2	75	10	15	—	—	—	—
3	60	5	22	—	9	4	—
4	55	17	20	—	3	5	—
5	31	45	20	—	0,5	—	0,5
6	42	36	12	—	6	—	3

Table 3 — Results of statistical analysis

Sample reference	Mean % (m/m)	Within-laboratory standard deviation	Between-laboratory standard deviation	Repeatability	Reproducibility
1	0,014 1	0,000 39	0,000 65	0,001 1	0,002 1
2	0,005 0	0,000 44	0,000 65	0,001 2	0,002 2
3	0,008 2	0,000 51	0,000 87	0,001 4	0,002 8
4	0,014 8	0,000 36	0,000 61	0,001 0	0,002 0
5	0,016 0	0,000 42	0,001 12	0,001 2	0,003 4
6	0,006 0	0,000 61	0,000 60	0,001 7	0,002 4

Annex A

(informative)

Examples of composition of some nickel alloys

The examples of composition given in table A.1 are not to be interpreted as specifications for chemical compositions.

Table A.1 — Examples of composition of some nickel alloys [% (*m*/*m*)]

Alloy[1]	Al	B	C	Co[2]	Cr	Cu	Fe	Mn	Mo	Ni	P	S	Si	Ti	Others
A	—	—	0,30	—	—	28,0 34,0	2,5	2,0	—	63,0[3]	—	0,025	0,5	—	—
B	—	—	0,15	—	14,0 17,0	0,5	6,0 10,0	1,0	—	72,0[3]	—	0,015	0,5	—	—
C	0,4 1,0	—	0,08	—	14,0 17,0	0,5	5,0 9,0	1,0	—	70,0[3]	—	0,015	0,5	2,2 2,8	Nb plus Ta: 0,7 to 1,2
D	0,2 0,8	0,006	0,08	—	17,0 21,0	0,3	Remainder	0,4	2,8 3,3	50,0 55,0	0,015	0,015	0,4	0,6 1,2	Nb plus Ta: 4,7 to 5,5
E	0,15 0,60	—	0,10	—	19,0 23,0	0,7	Remainder	1,5	—	30,0 35,0	—	0,015	1,0	0,15 0,60	—
F	—	—	0,08 0,15	5,0	18,0 21,0	0,5	5,0	1,0	—	Remainder[3]	—	0,020	1,0	0,2 0,6	Pb: 0,005
G	1,0 2,0	0,020	0,13	15,0 21,0	18,0 21,0	0,2	1,5	1,0	—	Remainder	—	0,015	1,0	2,0 3,0	Zr: 0,15
H	4,5 4,9	0,003 0,010	0,12 0,17	18,0 22,0	14,0 15,7	0,2	1,0	1,0	4,5 5,5	Remainder	—	0,015	1,0	0,9 1,5	Zr: 0,15
I	0,3 0,6	0,005	0,04 0,08	19,0 21,0	19,0 21,0	0,2	0,7	0,6	5,6 6,1	Remainder	—	0,007	0,4	1,9 2,4	Ti plus Al: 2,4 to 2,8
J	—	—	0,02	1,0	1,0	—	2,0	1,0	26,0 30,0	Remainder[3]	0,040	0,035	0,1	—	—
K	1,2 1,6	0,003 0,010	0,02 0,10	12,0 15,0	18,0 21,0	0,1	2,0	1,0	3,5 5,0	Remainder	0,015	0,015	0,1	2,8 3,3	Zr: 0,02 to 0,08
L	—	—	0,02	2,5	14,5 16,5	—	4,0 7,0	1,0	15,0 17,0	Remainder	0,040	0,035	0,08	—	V: 0,35 W: 3,0 to 4,5

NOTE — Single values are maximum limits, except for nickel, where single values are minimum values.

[1] Alloy letters are used instead of commercial names, until a neutral ISO designation is developed.

[2] Where no limits are given, the maximum cobalt content is 1,5 % (*m*/*m*).

[3] Cobalt counts as nickel in some alloys.

This page intentionally left blank