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Nickel, ferronickel and nickel alloys — Determination of phosphorus content — Phosphovanadomolybdate molecular absorption spectrometric method

Nickel, ferronickel et alliages de nickel — Dosage du phosphore — Méthode par spectrométrie d'absorption moléculaire au phosphovanadomolybdate

Reference number
ISO 11400:1992(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 11400 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*, Sub-Committee SC 4, *Analysis of nickel alloys*.

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Nickel, ferronickel and nickel alloys — Determination of phosphorus content — Phosphovanadomolybdate molecular absorption spectrometric method

1 Scope

This International Standard specifies a molecular absorption spectrometric method for the determination of the phosphorus content in nickel, ferronickel and nickel base alloys in the range of 0,000 5 % (*m*/*m*) to 0,05 % (*m*/*m*).

Arsenic, chromium, hafnium, niobium, silicon, tantalum, titanium and tungsten interfere, but the interferences can be avoided by complexation or volatilisation (for Cr). The lowest phosphorus content [0,000 5 % (*m*/*m*)] can only be reached in 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 648:1977, *Laboratory glassware — One-mark pipettes.*

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 a mixture of nitric and hydrochloric acids. Fuming with perchloric acid in a PFA or PTFE beaker and removal of chromium as volatile chromylchloride.

Complexation of silicon and the refractory elements with fluoride ions.

Conversion of phosphorus to phosphovanadomolybdic acid in a perchloric and nitric acid solution.

Extraction of phosphovanadomolybdic acid into 4-methyl-2-pentanone with citric acid present to complex arsenic.

4 Reagents

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

Verify by blank tests (7.6) that the relevant reagents are free from phophorus. Lots giving high blank values are unsuitable and should not be used. The blank value should be below 0,000 5 % (*m*/*m*), calculated for 1 g of sample.

4.1 Nitric acid, $\rho_{20} = 1{,}41$ g/ml, diluted 1 + 4.

4.2 Hydrofluoric acid, [40 % (*m*/*m*)], $\rho_{20} =$ 1,14 g/ml.

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 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.

4.4 4-methyl-2-pentanone (methyl isobutyl ketone).

4.5 **Hexaammonium heptamolybdate**, solution.

Dissolve 15 g of hexaammonium heptamolybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ in water and dilute to 100 ml.

Prepare a fresh solution each day. If high and unstable blank values appear, there might be a problem with the salt used. In such a case, switch to another lot.

4.6 **Ammonium metavanadate**, solution.

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

4.7 **Sodium nitrite**, solution.

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

4.8 **Fluoro-boric acid**, solution.

Suspend 75 g of boric acid (H_3BO_3) in 600 ml of hot water in a plastics beaker. Add 50 ml of hydrofluoric acid (4.2), dilute to 1 000 ml with water and digest until the boric acid dissolves. Keep the solution in a plastics bottle.

The solution should be gently heated if the boric acid tends to crystallize.

4.9 **Phosphorus**, standard reference solution (1,000 g/l).

Weigh, to the nearest 0,000 1 g, 4,394 2 g of potassium dihydrogenorthophosphate (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 and dissolve in water. Make up to the mark with water and mix.

4.10 **Phosphorus**, standard solution (10 mg/l).

Transfer 10,0 ml of the phosphorus standard reference solution (4.9) to a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

5 Apparatus

Glassware shall be cleaned with hot hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml) and rinsed with water.

Ordinary laboratory apparatus and

5.1 **Molecular absorption spectrometer**, capable of measuring absorbance at a wavelength of 355 nm.

5.2 **Heatable plastics beakers**, made of polytetrafluoroethylene (PTFE) or, preferably, of its perfluoroalkoxy copolymer (PFA). The PFA beakers have graphite bases and are specially constructed for fuming of acids up to 280 °C.

The beakers must be thoroughly cleaned before analysis. Fill the beakers with hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml) diluted 1 + 1, and boil for approximately 2 min. Rinse with water.

5.3 **Heating source**, with controllable surface temperature.

6 Sampling and sample preparation

6.1 Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in the case of dispute, according to 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 dried in air.

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

7 Procedure

WARNING — Fuming perchloric acid is a powerful oxidant and can cause explosions when in contact with organic materials. All evaporations must be carried out in fume cupboards suitable for use with perchloric acid.

7.1 Test portion and preparation of test solution

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

7.1.2 Transfer the test portion to the plastics beaker (5.2) and add 5 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml) and then 5 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml). For samples with high contents of Nb, Si, Ta, or Hf, also add 7 ml of hydrofluoric acid (4.2). Fit the beaker with a PTFE cover and heat gently until the reaction ceases. Add 10 ml of perchloric acid ($\rho_{20} = 1{,}66$ g/ml) and, leaving a small opening to release the vapours, evaporate to dense perchloric acid fumes.

Table 1 — Mass of sample to be taken

Expected phosphorus content % (m/m)	Mass of sample g	Maximum concentration of the interfering elements [% (m/m)]					
		As	Hf	Nb	Ta	Ti	W
0,000 5 to 0,010	1,0	0,05	0,1	1	0,1	2	2
0,002 0 to 0,040	0,25	0,2	0,5	5	0,5	10	8
0,005 0 to 0,050	0,10	0,5	1,5	10	1	25	25

NOTE 1 Nickel and some copper-bearing nickel alloys, such as monel, will dissolve more readily in nitric acid (ρ_{20} = 1,41 g/ml) diluted 1 + 1.

7.1.3 For samples containing less than 0,1 % (m/m) chromium, omit the next step (7.2) and proceed directly to 7.3.

7.2 Removal of chromium

Continue fuming until no droplets are observed on the cover and all the chromium is oxidized to the hexavalent state. Start adding hydrochloric acid (ρ_{20} = 1,18 g/ml) drop by drop to the fuming solution in the partly covered beaker, until coloured fumes are no longer liberated. Then resume fuming to reoxidize the remaining chromium. Repeat the treatment until no yellow fumes appear when the hydrochloric acid is added. Cool to room temperature.

7.3 Complexation

7.3.1 Add 25 ml of dilute nitric acid (4.1) and 4 ml of hydrofluoric acid (4.2) to the solution (7.2), and continue heating for 8 min to 10 min until all the precipitate is dissolved.

NOTE 2 It is important that the precipitated refractory oxides dissolve completely. If this does not happen, another 2 ml of hydrofluoric acid (4.2) may be added and the boiling repeated. If the precipitate still remains undissolved, a new test sample of lesser mass must be taken for analysis.

7.3.2 Add 10 ml of the sodium nitrite solution (4.7) and continue to boil the solution for 10 min to reduce any residual dichromate and to expel all nitrous fumes. Wash the beaker walls a few times with water during boiling.

7.3.3 Add 40 ml of the fluoro-boric acid solution (4.8), rapidly cool the mixture to between 20 °C and 30 °C, and proceed immediately with the colour development.

NOTE 3 The oxides might precipitate again if it took more than 10 min to cool the solution.

7.4 Colour development and extraction

7.4.1 Add 10 ml of the ammonium metavanadate solution (4.6) and 15 ml of the hexaammonium heptamolybdate solution (4.5) to the cooled clear solution. Allow to stand at a temperature between 18 °C and 25 °C for a minimum of 7 min, but not longer than 15 min.

7.4.2 Transfer the solution to a 250 ml separating funnel which has been marked at 100 ml volume and, if necessary, make up to the mark with water. Add 10 ml of the citric acid solution (4.3), mix, and immediately follow with 40 ml of 4-methyl-2-pentanone (4.4). 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 organic layer through a dry paper into a small dry beaker. Proceed immediately with the spectrometric measurement.

7.5 Spectrometric measurement

Ensure that the temperature of the solutions is constant to ± 1 °C. Measure the absorbance of the solution with the molecular absorption spectrometer (5.1) at a wavelength of 355 nm. Use 4-methyl-2-pentanone (4.4) as the reference, and cells with 1 cm optical path length.

7.6 Blank test

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

7.7 Calibration

7.7.1 Add 0 ml, 2,5 ml, 5,0 ml and 10,0 ml, respectively, of the phosphorus standard solution (4.10) to four plastics beakers (5.2). The additions correspond to 0 mg, 0,025 mg, 0,05 mg and 0,100 mg of phosphorus. Proceed as directed in 7.1.2 to 7.5.

7.7.2 Subtract the absorbance of the first "zero" solution from that of each solution containing phosphorus and plot the net absorbance against the mass, in milligrams, of phosphorus added.

7.8 Number of determinations

Carry out the determination at least in duplicate.

8 Expression of results

8.1 Calculation

8.1.1 Correct the absorbance reading of the test solution (see 7.5) by subtracting the absorbance reading in the blank test (7.6). Convert the net absorbance of the test solution into milligrams of phosphorus by means of the calibration graph (see 7.7.2).

8.1.2 Calculate the percentage by mass of phosphorus in the test sample using the formula

$$\frac{m_2}{10m_1}$$

where

m_1 is the mass, in grams, of the test portion;

m_2 is the mass, in milligrams, of phosphorus found in the test portion.

8.2 Precision

8.2.1 Laboratory tests

Up to eight laboratories in six countries participated in the testing of this procedure using two nickel metal and four ferronickel samples (7 laboratories in 4 countries), and six nickel base alloys (8 laboratories in 6 countries). The samples were analysed three or four times on different days. The nominal composition of the samples is given in table 2.

8.2.2 Statistical analysis

8.2.2.1 Results from the interlaboratory test programme were evaluated according to ISO 5725. 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 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.

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

<table>
<tr><th colspan="7">Nickel and ferronickel</th></tr>
<tr><th>Sample</th><th>P</th><th>As</th><th>Cr</th><th>Fe</th><th>Si</th><th>Ni</th></tr>
<tr><td>Ni No. 1</td><td>0,000 05</td><td>—</td><td>—</td><td>< 0,01</td><td>—</td><td>Remainder</td></tr>
<tr><td>Ni No. 2</td><td>0,000 8</td><td>—</td><td>—</td><td>0,2</td><td>—</td><td>Remainder</td></tr>
<tr><td>Fe-Ni No. 1</td><td>0,01</td><td>< 0,001</td><td>0,5</td><td>Remainder</td><td>0,5</td><td>25</td></tr>
<tr><td>Fe-Ni No. 2</td><td>0,01</td><td>0,1</td><td>4,5</td><td>Remainder</td><td>5</td><td>25</td></tr>
<tr><td>Fe-Ni No. 3</td><td>0,045</td><td>< 0,001</td><td>0,5</td><td>Remainder</td><td>0,6</td><td>25</td></tr>
<tr><td>Fe-Ni No. 4</td><td>0,045</td><td>0,1</td><td>4,5</td><td>Remainder</td><td>5</td><td>25</td></tr>
</table>

<table>
<tr><th colspan="10">Nickel alloys</th></tr>
<tr><th>Sample</th><th>P</th><th>Co</th><th>Cr</th><th>Cu</th><th>Fe</th><th>Mo</th><th>Ni</th><th>Nb</th><th>W</th></tr>
<tr><td>4D-7</td><td>0,01</td><td>—</td><td>—</td><td>32</td><td>1</td><td>—</td><td>65</td><td>—</td><td>—</td></tr>
<tr><td>4D-8</td><td>0,01</td><td>—</td><td>21</td><td>—</td><td>4</td><td>9</td><td>62</td><td>3</td><td>—</td></tr>
<tr><td>4D-9</td><td>0,02</td><td>—</td><td>18</td><td>—</td><td>19</td><td>3</td><td>53</td><td>5</td><td>—</td></tr>
<tr><td>4D-10</td><td>0,02</td><td>—</td><td>20</td><td>—</td><td>46</td><td>—</td><td>31</td><td>—</td><td>—</td></tr>
<tr><td>4D-11</td><td>0,01</td><td>1</td><td>21</td><td>—</td><td>20</td><td>8</td><td>47</td><td>—</td><td>—</td></tr>
<tr><td>4D-12</td><td>0,005</td><td>42</td><td>21</td><td>—</td><td>2</td><td>4</td><td>20</td><td>4</td><td>4</td></tr>
</table>

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

8.2.2.4 Of the two samples of nickel metal, one laboratory was rejected as a Cochran outlier for sample 2. The phosphorus content of sample 1 was below the scope of the method and no meaningful results were obtained.

In the ferronickel group, one laboratory was rejected as a Cochran outlier for sample 4.

Three laboratories were rejected from the alloys group, one as a Cochran outlier for sample 4D-12 and two as Dixon outliers for samples 4D-9 and 4D-10.

9 Test report

The test report shall include the following information:

a) the 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 3 — Results of statistical analysis

Sample reference	Mean % (*m*/*m*)	Within-laboratory standard deviation	Between-laboratory standard deviation	Repeatability	Reproducibility
Ni No. 2	0,000 91	0,000 07	0,000 12	0,000 2	0,000 4
FeNi No. 1	0,010 0	0,000 4	0,000 2	0,001 2	0,001 4
FeNi No. 2	0,010 0	0,000 4	—	0,001 2	0,001 2
FeNi No. 3	0,043 7	0,001 4	0,002 1	0,003 8	0,006 8
FeNi No. 4	0,042 5	0,001 0	0,001 0	0,002 7	0,003 8
4D-7	0,012 0	0,000 6	0,000 7	0,001 6	0,002 6
4D-8	0,008 9	0,000 9	0,001 5	0,002 4	0,005 0
4D-9	0,014 8	0,000 8	0,000 6	0,002 3	0,002 8
4D-10	0,018 5	0,000 3	0,000 7	0,001 0	0,002 2
4D-11	0,013 5	0,000 6	0,000 8	0,001 6	0,002 7
4D-12 1)	0,005 4	0,000 1	0,000 8	0,000 4	0,002 2

1) Standard reference alloy BAM 328-1, certified 0,005 % (*m*/*m*) P, was used as sample 4D-12.

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Descriptors: nickel, ferronickel, nickel alloys, chemical analysis, determination of content, phosphorus, molecular absorption spectrometry.

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