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Copper and copper alloys — Determination of phosphorus content — Molybdovanadate spectrometric method

Cuivre et alliages de cuivre — Dosage du phosphore — Méthode spectrométrique au molybdovanadate

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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It has been approved by the member bodies of the following countries:

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Australia
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Copper and copper alloys — Determination of phosphorus content — Molybdovanadate spectrometric method

1 Scope and field of application

This International Standard specifies a molybdovanadate spectrometric method for the determination of the phosphorus content of copper and copper alloys.

The method is applicable to the determination of phosphorus contents between 0,000 5 and 0,5 % *(m/m)* in all types of copper and copper alloys listed in International Standards.

2 Principle

Dissolution of a test portion with nitric acid. Elimination of interfering elements by fuming with perchloric, hydrofluoric and hydrobromic acids. Decomposition of insoluble phosphates by fusion with sodium carbonate.

For concentrations below 0,01 % *(m/m)*, extraction of phosphorus as phosphomolybdic acid and spectrometric determination as molybdenum blue; for concentrations between 0,005 and 0,5 % *(m/m)*, extraction and spectrometric determination as phosphovanadomolybdic acid.

3 Reagents

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

3.1 Nitric acid, ϱ 1,2 g/ml.

3.2 Hydrofluoric acid, 40 % *(V/V)*, ϱ 1,14 g/ml.

3.3 Perchloric acid, ϱ 1,67 g/ml.

3.4 Hydrobromic acid, ϱ 1,50 g/ml.

3.5 Isobutanol.

3.6 Methanol.

3.7 Methyl isobutyl ketone.

3.8 Ammonium molybdate solution I.

Dissolve 50 g of ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ in 250 ml of water. Add a solution of 115 ml of the perchloric acid (3.3) and 500 ml of water at room temperature. Dilute to 1 000 ml with water.

After prolonged storage, a white precipitate may form. While this residue will not affect the analysis, care should be taken to prevent its contamination of the aliquot used in the analysis.

Immediately before use, the aliquot used in the analysis should be purified by shaking with 10 ml of the isobutanol (3.5).

3.9 Ammonium molybdate solution II.

Dissolve 150 g of ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$, in 1 000 ml of water.

3.10 Tin(II) chloride, stock solution.

Dissolve 10 g of tin(II) chloride dihydrate $(SnCl_2.2H_2O)$ in 25 ml of hydrochloric acid, ϱ 1,19 g/ml.

Prepare this solution fresh before use.

3.11 Tin(II) chloride, working solution.

Dilute 1 ml of the tin(II) chloride stock solution (3.10) with 10 ml of sulfuric acid, ϱ 1,54 g/ml, and water to 200 ml.

Prepare this solution fresh before use.

3.12 Ammonium vanadate solution.

Dissolve 2,5 g of ammonium vanadate (NH_4VO_3) in 1 000 ml of water.

3.13 Citric acid solution.

Dissolve 500 g of citric acid in 1 000 ml of water.

3.14 Phosphorus, standard solution, corresponding to 10 mg of P per litre.

Dissolve 0,878 6 g of potassium dihydrogen orthophosphate (KH_2PO_4), freshly dried at 105 °C, with water and dilute to 1 000 ml. Dilute a 50 ml aliquot portion of this solution to 1 000 ml.

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

4 Apparatus

All vessels shall be free of contamination by phosphorus. Cleaning with hot hydrochloric acid, ϱ 1,19 g/ml, is recommended.

Ordinary laboratory apparatus, and

4.1 PTFE *beakers*, capacity 100 ml.

4.2 Spectrometer, fitted with cells of optical path lengths 1 and 4 cm.

5 Procedure

5.1 For copper and copper alloys free of zirconium, titanium, niobium and/or tantalum, with phosphorus contents between 0,000 5 and 0,01 % *(m/m)*

5.1.1 Weigh, to the nearest 0,001 g, 1,000 g of the test sample.

5.1.2 Dissolve the test portion in a PTFE beaker (4.1) with 10,0 ml of the nitric acid (3.1). Heat gently, if necessary. To eliminate silicon, add 0,50 ml of the hydrofluoric acid (3.2) and 10,0 ml of the perchloric acid (3.3) and heat until fuming begins.

5.1.3 Dilute the solution with 10 ml of water and add 10,0 ml of the hydrobromic acid (3.4). To eliminate interference from arsenic, antimony and tin, heat gently until fuming begins again. If tin contents of > 1 % *(m/m)* are present, repeat the fuming step with 10,0 ml of the hydrobromic acid (3.4).

5.1.4 Dissolve the copper bromide formed during the fuming steps by adding several millilitres of the nitric acid (3.1) and bring to fuming. Dilute this solution with 30 ml of water. Heat to boiling for 10 min, then cool to room temperature.

5.1.5 If the phosphorus content is expected to be < 0,005 % *(m/m)*, transfer the entire solution from 5.1.4 to a 125 ml separating funnel and dilute to 50 ml with water. If the phosphorus content is expected to be > 0,005 % *(m/m)*, dilute the solution from 5.1.4 to the mark with water in a 100 ml one-mark volumetric flask, and transfer a 50 ml aliquot portion to a 125 ml separating funnel.

5.1.6 Add 10 ml of the ammonium molybdate solution I (3.8) and extract the phosphomolybdic acid with 15,0 ml of the isobutanol (3.5) by shaking for about 30 s. After separation of the two phases, transfer the aqueous phase to another separating funnel and repeat the extraction with 6,0 ml of the isobutanol (3.5). Repeat the extraction a third time with 5,0 ml of the isobutanol, then discard the aqueous phase.

5.1.7 Combine the three butanolic extracts in the first separating funnel and wash by shaking twice with 5 ml of water, discarding the wash water each time. To the organic phase, add 15 ml of the tin(II) chloride solution (3.11) and shake for about 30 s. Discard the aqueous layer after separation of the phases. Transfer the blue-coloured organic phase to a 50 ml one-mark volumetric flask and dilute with the methanol (3.6) to the mark.

5.1.8 Measure the absorbance immediately using the spectrometer (4.2), fitted with a 1 cm photometric cell, at 623 nm, using a 1 + 1 mixture of the isobutanol (3.5) and the methanol (3.6) in the reference cell.

Carry a blank test through all steps and correct each result accordingly.

5.1.9 Prepare a calibration graph. Take aliquot portions of 0 to 8 ml of the standard phosphorus solution (3.14) and carry them through all steps of the procedure using exactly the same amounts of reagents. The calibration graph is linear and shows an absorbance of 1 for about 90 µg of phosphorus.

5.2 For copper and copper alloys free of zirconium, titanium, niobium and/or tantalum, with phosphorus contents between 0,005 and 0,5 % *(m/m)*

5.2.1 Weigh, to the nearest 0,001 g, 1,000 g of the test sample.

5.2.2 Dissolve the test portion in a PTFE beaker (4.1) with 10,0 ml of the nitric acid (3.1). Heat gently, if necessary. To eliminate silicon, add 0,50 ml of the hydrofluoric acid (3.2) and 10,0 ml of the perchloric acid (3.3) and heat until fuming begins.

5.2.3 Dilute the solution with 10 ml of water and add 10,0 ml of the hydrobromic acid (3.4). To eliminate interference from arsenic, antimony and tin, heat gently until fuming begins again.

5.2.4 Dilute the solution with 50 ml of water and 10 ml of the nitric acid (3.1). Heat to boiling for 10 min, then cool to room temperature.

5.2.5 If the phosphorus content is expected to be < 0,10 % *(m/m)*, add to the solution from 5.2.4 10 ml of the ammonium vanadate solution (3.12) and 15 ml of the ammonium molybdate solution II (3.9), while swirling. If the phosphorus content is expected to be > 0,10 % *(m/m)*, dilute the solution from 5.2.4 to the mark with water in a 100 ml one-mark volumetric flask. Transfer a 20 ml aliquot portion to a beaker, add 8 ml of the nitric acid (3.1) and 8 ml of the perchloric acid (3.3), and dilute with water to about 60 ml, then add 10 ml of the ammonium vanadate solution (3.12) and 15 ml of the ammonium molybdate solution II (3.9), while swirling.

5.2.6 After 10 min, transfer the solution to a separating funnel. Wash the beaker with water and add the washings to the funnel. Dilute with water to a total volume of about 100 ml.

5.2.7 Add 10 ml of the citric acid solution (3.13) and extract the phosphovanadomolybdic acid by shaking with 20 ml of the methyl isobutyl ketone (3.7) for 30 s. After separation of the phases, draw off the aqueous phase into the original PTFE beaker. Filter the organic phase through a cotton wool plug into a dry 50 ml one-mark volumetric flask.

5.2.8 Transfer the aqueous phase to the separating funnel and repeat the extraction with 20 ml of the methyl isobutyl ketone. Discard the aqueous phase and filter the organic phase into the 50 ml one-mark volumetric flask as in 5.2.7. Wash the separating funnel with 5 ml of the methyl isobutyl ketone, filter into the volumetric flask, and dilute to the mark with the methyl isobutyl ketone.

5.2.9 Measure the absorbance immediately using the spectrometer (4.2), fitted with a 4 cm photometric cell for phosphorus contents between 0,005 and 0,03 % (m/m) or with a 1 cm cell for phosphorus contents between 0,03 and 0,5 % (m/m), at 436 nm. Use methyl isobutyl ketone in the reference cell.

Carry a blank test through all steps and correct each result accordingly.

5.2.10 Prepare a calibration graph. Take aliquot portions of 0 to 30 ml of the standard phosphorus solution (3.14) and carry them through all steps of the procedure using exactly the same amounts of reagents. The calibration graph is linear and shows an absorbance of about 0,15 for 50 µg of phosphorus.

5.3 For copper and copper alloys containing zirconium, titanium, niobium and/or tantalum

If the sample contains zirconium, titanium, niobium and/or tantalum, phosphorus can be found totally or partially as insoluble phosphates. The procedure for dissolving these residues is described below.

5.3.1 Dissolve the test portion according to 5.1 or 5.2. After fuming off the F^-, Br^-, and NO_3^-, filter the solution through a millipore filter. Wash the filter with hot water until free of acid, then dry and ignite the filter in a small porcelain crucible. Transfer the residue to a small platinum crucible, mix with about 0,3 g of sodium carbonate and fuse. After cooling, dissolve the melt with a small amount of water. Filter off any insoluble residue and wash with hot water, adding the washings to the filtrate.

5.3.2 Neutralize the combined filtrate and washings with the perchloric acid (3.3). Add the neutralized solution to the original copper-containing filtrate. The total volume should not exceed 60 ml; if necessary, the volume should be reduced by evaporating.

5.3.3 Continue as described in 5.1 or 5.2.

5.4 Check test

Make a preliminary check of the apparatus by preparing a solution of standard material or a synthetic sample containing a known amount of phosphorus and of composition similar to the material to be analysed, and carrying out the procedure as specified in 5.1, 5.2 or 5.3.

6 Expression of results

By means of the calibration graph (5.1.9, 5.2.10), determine the mass of phosphorus, expressed in micrograms, of the test portion, corresponding to the absorbance obtained. The phosphorus content, expressed as a percentage by mass, is given by the formula

$$\frac{m_1}{m_0 \times 10^6} \times 100$$

$$= \frac{m_1}{m_0 \times 10^4}$$

where

m_0 is the mass, in grams, of the test portion (5.1.1, 5.2.1) or of the aliquot portion taken (5.1.5, 5.2.5);

m_1 is the mass, in micrograms, of phosphorus found in the test solution (5.1.7, 5.2.8).

7 Test report

The test report shall include the following particulars:

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or regarded as optional which might affect the results.