International Standard

ISO 4749

Copper alloys — Determination of lead content — Flame atomic absorption spectrometric method

Alliages de cuivre — Dosage du plomb — Méthode par spectrométrie d'absorption atomique dans la flamme

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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 developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized 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.

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.

International Standard ISO 4749 was developed by Technical Committee ISO/TC 26, *Copper and copper alloys*, and was circulated to the member bodies in January 1982.

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

Australia	France	Poland
Austria	Germany, F. R.	Romania
Belgium	Hungary	Spain
Brazil	Italy	Sweden
Bulgaria	Japan	Switzerland
Canada	Korea, Dem. P. Rep. of	Thailand
China	Korea, Rep. of	Turkey
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The member bodies of the following countries expressed disapproval of the document on technical grounds :

Chile
South Africa, Rep. of

Copper alloys — Determination of lead content — Flame atomic absorption spectrometric method

1 Scope and field of application

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the lead content of all types of copper alloys listed in International Standards.

The method is applicable to the determination of lead as alloying element or impurity between 0,01 and 5,0 % (m/m). By appropriate modification of sample mass, the lower limit may be extended to 0,002 % (m/m).

2 Principle

Dissolution of a test portion in fluoroboric-nitric acid mixture. Aspiration of the test solution into an air-acetylene flame, and determination of the lead content by spectrometric measurement of the absorption of the 217,0 nm line emitted by a hollow-cathode lead lamp.

3 Reagents

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

3.1 Fluoroboric-nitric acid, attack reagent.

Mix together 300 ml of boric acid, 40 g/l solution, 30 ml of the hydrofluoric acid, 40 % (V/V) solution, 500 ml of the nitric acid, ϱ 1,40 g/ml, and 150 ml of water.

3.2 Nitric acid, 1 + 1.

Dilute 100 ml of nitric acid, ϱ 1,40 g/ml, with 100 ml of water.

3.3 Copper, 20 g/l base solution.

Transfer 10,0 g of lead-free copper ($<$ 0,000 2 % Pb) to a 600 ml polytetrafluorethylene, polyethylene, or low-pressure polypropylene beaker. Add 400 ml of the attack reagent (3.1), warm until the copper is dissolved, then boil until nitrous fumes have been expelled. In the case of polyethylene or polypropylene beakers, use a water bath for heating. Allow to cool and transfer the solution to a 500 ml one-mark volumetric flask. Dilute to the mark and mix.

50 ml of this solution contains 1 g of copper and 40 ml of the fluoroboric-nitric acid mixture.

3.4 Lead, standard solution corresponding to 1,0 g of Pb per litre.

Weigh, to the nearest 0,001 g, 1,000 g of lead (purity 99,9 % minimum). Transfer to a 250 ml beaker. Add 20 ml of the nitric acid solution (3.2), cover, and warm gently until the lead is dissolved. Boil the solution for a few minutes to expel nitrous fumes. Allow to cool and transfer the solution to a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 0,001 g of Pb.

3.5 Lead, standard solution corresponding to 0,1 g of Pb per litre.

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Pipette 25,0 ml of the lead standard solution (3.4) to a 250 ml one-mark volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 0,1 mg of Pb.

4 Apparatus

Ordinary laboratory apparatus and

4.1 Beakers, polytetrafluorethylene, polyethylene or polypropylene, capacities 250 and 600 ml.

4.2 Atomic absorption spectrometer, equipped with an air-acetylene burner.

4.3 Hollow-cathode lead lamp.

4.4 Compressed air supply.

4.5 Cylinder of acetylene.

5 Sampling[1]

5.1 Test sample

The test sample should preferably be in the form of fine chips or drillings, obtained by milling or drilling, with a maximum thickness of 0,3 mm.

6 Procedure

6.1 Test portion

Weigh, to the nearest 0,001 g, about 1 g of the test sample (5.1).

6.2 Preparation of calibration graph

Prepare a calibration graph each time a series of samples is analysed.

6.2.1 Preparation of standard matching solutions

Into each of a series of eight 100 ml one-mark volumetric flasks, introduce the volumes of lead standard solution (3.5) and copper base solution (3.3) as shown in tables 1, 2 or 3, depending on the expected lead content. Dilute to the mark and mix.

Table 1 — Lead content below 0,2 % (m/m)

Lead standard solution (3.5) ml	Mass of lead contained mg	Copper base solution (3.3) ml	Mass of copper contained g	Corresponding lead content of sample %
0*	0	50	1	0
1	0,1	50	1	0,01
2	0,2	50	1	0,02
5	0,5	50	1	0,05
7	0,7	50	1	0,07
10	1,0	50	1	0,10
15	1,5	50	1	0,15
20	2,0	50	1	0,20

* Blank test on reagents for calibration.

Table 2 — Lead content between 0,1 and 1 % (m/m)

Lead standard solution (3.5) ml	Mass of lead contained mg	Copper base solution (3.3) ml	Mass of copper contained g	Corresponding lead content of sample %
0*	0	10	0,2	0
1	0,1	10	0,2	0,05
2	0,2	10	0,2	0,10
5	0,5	10	0,2	0,25
7	0,7	10	0,2	0,35
10	1,0	10	0,2	0,50
15	1,5	10	0,2	0,75
20	2,0	10	0,2	1,00

* Blank test on reagents for calibration.

Table 3 — Lead content between 0,5 and 5 % (m/m)

Lead standard solution (3.5) ml	Mass of lead contained mg	Copper base solution (3.3) ml	Mass of copper contained g	Corresponding lead content of sample %
0*	0	2	0,04	0
1	0,1	2	0,04	0,25
2	0,2	2	0,04	0,50
5	0,5	2	0,04	1,25
7	0,7	2	0,04	1,75
10	1,0	2	0,04	2,5
15	1,5	2	0,04	3,75
20	2,0	2	0,04	5,00

* Blank test on reagents for calibration.

NOTES

1 The range of standard matching solutions is appropriate for most current models of equipment of average performance. The range and operating conditions should be selected for optimum measurements by the particular equipment available.

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1) An International Standard (ISO 1811) dealing with the sampling of copper alloys is in preparation.

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2 The presence of copper and attack acid in the standard matching solutions compensates for chemical interaction effects of these species.

3 The analytical lead wavelength of 217,0 nm is the most sensitive line and therefore is favoured for the determination of low contents of lead, up to approximately 20 µg of Pb per millilitre. The lead wavelength of 283,3 nm is less sensitive, and is preferred for higher contents of lead, up to approximately 60 µg of Pb per millilitre.

6.2.2 Adjustment of the apparatus

Fit the lead hollow-cathode lamp (4.3) into the apparatus (4.2), switch on the current and allow to stabilize. Adjust the current, the sensitivity and the aperture of the slit according to the characteristics of the apparatus. Adjust the wavelength in the region of 217,0 nm to minimum absorbance. Adjust the pressure of the air and acetylene according to the characteristics of the aspirator burner.

6.2.3 Spectrometric measurements

Aspirate the appropriate series of standard matching solutions (6.2.1) in succession into the flame and measure the absorbance of each. Take care to maintain a constant rate of aspiration throughout the preparation of the calibration graph. Spray water through the burner after each measurement.

6.2.4 Plotting the graph

Plot a graph having, for example, the masses, in milligrams, of lead contained in 100 ml of the standard matching solutions as abscissae, and the corresponding values of the measured absorbances, reduced by the value of the absorbance measured in the blank test on reagents for calibration (6.2.1, term 0), as ordinates.

6.3 Determination

6.3.1 Preparation of the test solution

Transfer the test portion (6.1) to a 250 ml polytetra-fluorethylene, polyethylene, or polypropylene beaker (4.1), and cover. Add 40 ml of the attack reagent (3.1). Cover and warm gently until the sample is dissolved, then heat at a temperature of approximately 90 °C until brown fumes have been expelled. If polyethylene or polypropylene beakers are used, heating shall be carried out in a water bath. Wash down the cover and sides of the beaker, and allow to cool. Transfer the solution to a 100 ml one-mark volumetric flask, dilute to the mark and mix.

Select an aliquot portion from the test solution according to the expected lead content, and prepare a dilution in a volumetric flask as indicated in table 4.

Table 4 — Dilution

Lead content % (m/m)	Aliquot of the test solution (6.3.1) ml	Final volume of diluted solution ml	Dilution ratio r_D
0,01 to 0,2	total sample	—	1
0,1 to 1,0	20,0	100	5
0,5 to 5,0	20,0	500	25

NOTES

1 If the test portion does not contain silica, it may be dissolved in a mixture of hydrochloric and nitric acids. For 1 g of sample, add 5 ml of hydrochloric acid, ϱ 1,19 g/ml, and 10 ml of nitric acid, ϱ 1,40 g/ml, diluted 1 + 1. The copper base solution (3.3) must be prepared in this same mixture of acids, in order to generate the corresponding standard matching solutions.

2 If it is desired to determine lead contents below 0,01 % (m/m) down to 0,002 % (m/m), a 5 g test portion may be used. In all cases, it is necessary to have the same amounts of copper and acid present in the standard matching solutions as in the test solutions.

6.3.2 Spectrometric measurements

6.3.2.1 Preliminary measurement

Carry out a preliminary measurement on the test solution (6.3.1), following the procedure specified in 6.2.3 at the same time as the spectrometric measurements are carried out on the standard matching solutions (6.2.1).

From the calibration graph (6.2.4), calculate the approximate concentration of lead in 100 ml of the test solution (6.3.1).

6.3.2.2 Bracketing measurements

Carry out a second measurement on the test solution (6.3.1), following the procedure specified in 6.2.3, by bracketing between two standard matching solutions of composition similar to that of the standard matching solutions (6.2.1), but having lead contents which differ by smaller increments.

To prepare these standard matching solutions, follow the procedure specified in 6.2.1, using, however, suitable quantities of standard lead solution (3.5).

6.4 Blank test

Carry out a blank test at the same time as the determination and following the same procedure, using the same quantities of reagents as for the determination but omitting the test portion.

7 Expression of results

7.1 Concentration of the test solution

The lead concentration, c, expressed in milligrams of lead per 100 ml of test solution, is given by the formula

$$c = c_1 + (c_2 - c_1)\frac{A_0 - A_1}{A_2 - A_1}$$

where

c_1 is the concentration, in milligrams of lead per 100 ml, of the standard matching solution of lower concentration, used for the bracketing measurement (6.3.2.2);

c_2 is the concentration, in milligrams of lead per 100 ml, of the standard matching solution of higher concentration, used for the bracketing measurement (6.3.2.2);

A_0 is the value of the absorbance corresponding to the test solution (6.3.1);

A_1 is the value of the absorbance corresponding to concentration c_1;

A_2 is the value of the absorbance corresponding to concentration c_2.

7.2 Lead content of the sample

The lead content of the sample, expressed as a percentage by mass, is given by the formula

$$\frac{c - c_1}{10m} \times r_D$$

where

c is the concentration, expressed in milligrams of lead per 100 ml, of the test solution, calculated in accordance with 7.1;

c_1 is the concentration, expressed in milligrams of lead per 100 ml, of the blank test solution (6.4);

m is the mass, in grams, of the test portion (6.1);

r_D is the dilution ratio (see table 4).

8 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.