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Copper and copper alloys — Determination of bismuth content — Diethyldithiocarbamate spectrometric method

Cuivre et alliages de cuivre — Dosage du bismuth — Méthode spectrométrique au diéthyldithiocarbamate

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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.

International Standard ISO 5959 was developed by Technical Committee ISO/TC 26, *Copper and copper alloys*, and was circulated to the member bodies in February 1983.

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

Australia	Iran	Spain
Belgium	Italy	Sweden
Canada	Japan	Switzerland
China	Korea, Dem. P. Rep. of	Thailand
Czechoslovakia	Mexico	Turkey
Finland	Netherlands	USA
France	Poland	USSR
Germany, F.R.	Romania	Venezuela
Hungary	South Africa, Rep. of	

No member body expressed disapproval of the document.

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INTERNATIONAL STANDARD ISO 5959-1984 (E)

Copper and copper alloys — Determination of bismuth content — Diethyldithiocarbamate spectrometric method

1 Scope and field of application

This International Standard specifies a diethyldithiocarbamate spectrometric method for the determination of the bismuth content in copper and copper alloys.

The method is applicable to bismuth contents between 0,000 05 and 0,02 % (*m/m*) in all types of copper and copper alloys listed in International Standards.

2 Principle

Separation of bismuth by precipitation as bismuth hydroxide on a manganese dioxide carrier. Dissolution of the precipitate and extraction of bismuth into chloroform as the diethyldithiocarbamate complex. Spectrometric measurement of the absorbance of the complex at a wavelength of 405 nm.

3 Reagents

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

3.1 Ammonia, solution, ϱ 0,91 g/ml.

3.2 Chloroform.

3.3 Hydrogen peroxide, 30 % (*m/m*) solution.

3.4 Nitric acid, diluted 1 + 1.

Dilute 500 ml of nitric acid (ϱ 1,40 g/ml) with 500 ml of water.

3.5 Hydrochloric acid, diluted 1 + 1.

Dilute 500 ml of hydrochloric acid (ϱ 1,19 g/ml) with 500 ml of water.

3.6 Bromine-hydrochloric acid, solution.

Dissolve 100 ml of bromine in 1 000 ml of hydrochloric acid (ϱ 1,19 g/ml).

3.7 Manganese nitrate, 50 g/l solution.

Dissolve 50 g of manganese nitrate tetrahydrate [$Mn(NO_3)_2 \cdot 4H_2O$] in water and dilute to 1 000 ml.

3.8 Potassium permanganate, 6 g/l solution.

Dissolve 6 g of potassium permanganate [$KMnO_4$] in 1 000 ml of water.

3.9 Tartaric acid, 400 g/l solution.

Dissolve 400 g of tartaric acid ($C_4H_6O_6$) in water and dilute to 1 000 ml.

3.10 *Di*sodiumethylenediaminetetraacetate, dihydrate (Na_2EDTA), 100 g/l solution.

Dissolve 100 g of Na_2EDTA in water and dilute to 1 000 ml.

3.11 Hydroxylammonium chloride, 200 g/l solution.

Dissolve 20 g of hydroxylammonium chloride ($NH_2OH \cdot HCl$) in water and dilute to 100 ml.

3.12 Potassium cyanide, 100 g/l solution.

Dissolve 100 g of potassium cyanide (KCN) in water and dilute to 1 000 ml.

3.13 Sodium diethyldithiocarbamate, 2 g/l solution.

Dissolve 0,2 g of sodium diethyldithiocarbamate ($NaC_5H_{10}NS_2 \cdot 3H_2O$) in water and dilute to 100 ml.

3.14 Sodium hydroxide, 20 g/l solution.

Dissolve 20 g of sodium hydroxide (NaOH) in water and dilute to 1 000 ml.

3.15 Bismuth, standard solution corresponding to 0,400 g of Bi per litre.

Dissolve 0,100 g of pure bismuth metal in 50 ml of nitric acid (ϱ 1,40 g/ml). Boil to expel nitrous oxides. Cool and dilute to the mark with water in a 250 ml one-mark volumetric flask.

1 ml of this standard solution contains 0,400 mg of Bi.

3.16 Bismuth, standard solution corresponding to 0,040 g of Bi per litre.

Dilute 25,00 ml of the bismuth standard solution (3.15) and 50 ml of nitric acid (ϱ 1,40 g/ml) to the mark with water in a 250 ml one-mark volumetric flask.

1 ml of this standard solution contains 40 µg of Bi.

4 Apparatus

Ordinary laboratory apparatus, and

4.1 Spectrometer, with 50 mm cells, to detect absorbance at 405 nm.

4.2 Mechanical shaker.

5 Procedure

5.1 Test portion

Weigh a test portion of finely divided material such that it contains between 5 and 200 µg of bismuth, but with a maximum mass of 10 g.

5.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test in the absence of bismuth, using the same quantities of reagents as used for the determination.

5.3 Preparation of the calibration curve

5.3.1 Preparation of the standard matching solutions

Into a series of six 150 ml beakers, pipette the volumes of standard bismuth solution (3.16) shown in the following table.

Standard bismuth solution (3.16)	Corresponding mass of Bi
ml	µg
0 *	0
1	40
2	80
3	120
4	160
5	200

* Blank test on the reagents for calibration.

To each beaker, add 10 ml of the tartaric acid solution (3.9), 5 ml of the Na_2EDTA solution (3.10), sufficient ammonia solution (3.1) to neutralize the solution and provide a 5 ml excess, and 5 ml of the potassium cyanide solution (3.12).

Extract the bismuth as specified in 5.4.4.

5.3.2 Photometric measurements

Carry out the photometric measurements within 30 min after extraction using the spectrometer set at 405 nm, after having, in each case, first adjusted the apparatus to zero absorbance against the chloroform (3.2), and using cells of 50 mm thickness.

Subtract the absorbance of the blank test solution of the reagents for calibration from those of the standard matching solutions.

5.3.3 Plotting of the calibration curve

Plot a graph having, for example, the masses, in micrograms, of bismuth contained in 25 ml of the standard matching solutions (5.3.1) as abscissae and the corresponding values of the absorbance as ordinates.

5.4 Determination

5.4.1 Dissolution and pH adjustment

Dissolve the test portion (5.1) in as little nitric acid solution (3.4) as necessary in a 750 ml conical flask. Expel nitrous oxide fumes by boiling. Dilute with water to 300 to 400 ml and add the ammonia solution (3.1) until only a small amount of copper hydroxide remains undissolved. Dissolve this residue with a minimum of the nitric acid solution (3.4). The pH of the solution should now be between 3,0 and 3,5.

NOTE — If the test portion contains significant amounts of antimony or tin, these hydroxides will begin to precipitate before the appearance of copper hydroxide. In this case, adjust the test solution to the desired pH using an indicator paper.

5.4.2 Precipitation of bismuth hydroxide

To the test solution (5.4.1), add 5 ml of the manganese nitrate solution (3.7) and 10 ml of the potassium permanganate solution (3.8). Heat to boiling while swirling the solution. Boil until the permanganate colour disappears. Filter while hot and wash the precipitate with hot water. Discard the filtrate.

5.4.3 Dissolution of precipitate

Dissolve the precipitate from the filter into a 250 ml beaker using the hydrochloric acid solution (3.5) in the presence of a small amount of the hydrogen peroxide solution (3.3). To the beaker, add 20 ml of the bromine-hydrochloric acid solution (3.6) and evaporate gently. From time to time, add several drops of the hydrogen peroxide solution (3.3) until the bromine is completely expelled. Continue the evaporation to a volume of about 5 ml, then add 10 ml of the tartaric acid solution (3.9) and 5 ml of the Na_2EDTA solution (3.10). Add ammonia solution (3.1) until the solution is neutral; then add 5 ml in excess. Add 2 ml of the hydroxylammonium chloride solution (3.11) and 5 ml of the potassium cyanide solution (3.12). At this point the volume of the test solution should range between 80 and 150 ml with a pH of approximately 12.

5.4.4 Complex formation and extraction

Carry out the complex formation and extraction using low-actinic or amber glassware, and avoid direct sunlight or artificial light.

Transfer the test solution (5.4.3) to a 250 ml separating funnel. Add 3 ml of the diethyldithiocarbamate solution (3.13) and 10 ml of the chloroform (3.2). Shake vigorously for 10 min, preferably using the mechanical shaker (4.2).

Allow the phases to separate and drain the chloroform layer into another 250 ml separating funnel containing 20 ml of the sodium hydroxide solution (3.14).

Extract the aqueous phase twice more with 10 ml of the chloroform, shaking vigorously for 2 min each time. Combine the two resulting chloroform phases with the original in the second 250 ml separating funnel.

Shake the three combined organic phases with the sodium hydroxide solution for 5 min. Add 5 ml of the Na_2EDTA solution (3.10) and 5 ml of the potassium cyanide solution (3.12) and shake for 10 s more. Dilute with 40 to 50 ml of water, add 3 ml of the diethyldithiocarbamate solution, and shake vigorously for 10 min.

Drain the chloroform phase into a 25 ml one-mark volumetric flask. Wash the aqueous phase with 1 to 2 ml of the chloroform by shaking vigorously for 10 s. Add the chloroform washings to the volumetric flask and dilute to the mark with the chloroform.

NOTE — Due to the solubility of chloroform in water, the total volume of the chloroform phase after extraction will be less than 25 ml.

5.4.5 Spectrometric measurements

The spectrometric measurements should be carried out immediately if possible, and not more than 15 min after extraction.

Determine the absorbance of the bismuth-diethyldithiocarbamate complex obtained from the test solution (5.4.4) and from the blank test solution (5.2), using cells of 50 mm thickness, with the spectrometer set at 405 nm, after first adjusting the apparatus to zero absorbance against the chloroform (3.2).

5.5 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 bismuth and of composition similar to the material to be analysed, and carrying out the procedure as specified in 5.1 to 5.4.

6 Expression of results

6.1 Calculation

By means of the calibration curve (5.3.3), determine the masses of bismuth corresponding to the absorbances of the chloroform extracts obtained from the test solution (5.4.4) and from the blank test solution (5.2).

The bismuth content, expressed as a percentage by mass, is given by the formula

$$\frac{m_1 - m_2}{m_0 \times 10^6} \times 100$$

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

where

m_0 is the mass, in grams, of the test portion (5.1);

m_1 is the mass, in micrograms, of bismuth found in the 25 ml chloroform extract of the test solution (5.4.4);

m_2 is the mass, in micrograms, of bismuth found in the 25 ml chloroform extract of the blank test solution (5.2).

Express the result to five decimal places.

6.2 Repeatability and reproducibility

Comparative tests carried out on three samples by six laboratories gave the following statistical data :

Characteristic		Sample 1	Sample 2	Sample 3
Average, % (*m*/*m*)		$0{,}000\,2^2$	$0{,}000\,1^0$	$0{,}009\,9^9$
Standard deviation of repeatability,	ϱ_r :	$0{,}000\,0^1$	$0{,}000\,0^1$	$0{,}000\,1^1$
Standard deviation of reproducibility,	ϱ_R :	$0{,}000\,0^2$	$0{,}000\,0^1$	$0{,}000\,4^8$

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.