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International Standard 4744

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Copper and copper alloys — Determination of chromium content — Flame atomic absorption spectrometric method

Cuivre et alliages de cuivre — Dosage du chrome — Méthode par spectrométrie d'absorption atomique dans la flamme

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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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USA

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Copper and copper alloys — Determination of chromium 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 chromium in chromium-copper, and in alloyed and unalloyed coppers listed in International Standards.

The method is applicable to the determination of chromium contents between 0,003 and 2,0 % (*m/m*).

2 Principle

Dissolution of a test portion in nitric acid and digestion in sulfuric acid. After appropriate dilution, aspiration of the test solution into an air-acetylene flame, and determination of the chromium content by spectrometric measurement of the absorption of the 357,9 nm line emitted by a chromium hollow-cathode lamp.

3 Reagents

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

3.1 Sulfuric acid, ρ 1,84 g/ml.

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

3.3 Nitric acid, ρ 1,2 g/ml, about 34 % (*m/m*) solution.

Dilute 500 ml of nitric acid, ρ 1,4 g/ml, with 500 ml of water, and mix.

3.4 Copper, 20 g/l base solution.

Transfer 20,0 g of chromium-free copper to a 1 000 ml beaker. Add, in small portions, 400 ml of the nitric acid solution (3.3). Cover the beaker. If necessary, warm gently to help dissolution. After cooling, add cautiously 200 ml of the sulfuric acid (3.1); heat to the evolution of copious white fumes and continue for 5 min. Cool and add cautiously about 200 ml of water, and warm to complete the dissolution. Quantitatively transfer the cooled solution to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

50 ml of this solution contains 1,0 g of copper.

45 ml of this solution contains 0,9 g of copper.

3.5 Chromium, standard solution corresponding to 0,5 g of Cr per litre.

Weigh, to the nearest 0,000 1 g, 1,414 2 g of potassium dichromate ($K_2Cr_2O_7$), previously dried at 140 °C and allowed to cool in a desiccator. Place in a 400 ml beaker and dissolve in about 20 ml of water. Add 5 ml of the sulfuric acid (3.1) and, while cooling, cautiously add the hydrogen peroxide solution (3.2), adding an excess of about 2 ml after effervescence has ceased. Allow the solution to stand at ambient temperature until the yellow colour has completely disappeared (several hours), then transfer to a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 0,5 mg of Cr.

3.6 Chromium, standard solution corresponding to 0,025 g of Cr per litre.

Transfer 25,0 ml of the chromium standard solution (3.5) to a 500 ml one-mark volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 0,025 mg of Cr.

4 Apparatus

Ordinary laboratory apparatus, and

4.1 Burette, graduated in 0,05 ml.

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

4.3 Chromium hollow-cathode lamp.

4.4 Compressed air supply.

4.5 Cylinder of acetylene.

5 Sampling[1]

The test sample shall be in the form of fine chips or drillings, obtained by milling or drilling, with a maximum thickness of 0,5 mm.

6 Procedure

6.1 Test portion

Weigh, to the nearest 0,001 g, about 1 g of the test sample (clause 5).

6.2 Preparation of the calibration graph

6.2.1 Preparation of standard matching solutions

Using a burette (4.1), introduce into each of a series of nine 100 ml one-mark volumetric flasks the volumes of standard chromium solutions (3.5 and 3.6) as shown in the table. To each flask, add 50 ml of the copper base solution (3.4). Dilute to the mark and mix.

6.2.2 Adjustment of apparatus

Fit the chromium 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 357,9 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 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 chromium 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.

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.

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

6.3 Determination

6.3.1 Preparation of the test solution

6.3.1.1 Transfer the test portion (6.1) to a 250 ml beaker. Add 20 ml of the nitric acid solution (3.3), cover, and warm gently to complete the dissolution. Allow to cool and cautiously add 20 ml of the sulfuric acid (3.1). Heat to the evolution of copious white fumes. Continue heating for 5 min, swirling the solution if necessary. Allow to cool, add 20 to 30 ml of water and heat to dissolve the salts.

6.3.1.2 In the case of chromium contents between 0,002 and 0,20 % (*m/m*), transfer the test solution (6.3.1) to a 100 ml one-mark volumetric flask. Dilute to the mark and mix.

6.3.1.3 In the case of chromium contents between 0,20 and 2 % (*m/m*), transfer the test solution (6.3.1) to a 100 ml one-mark volumetric flask. Dilute to the mark and mix. Transfer 10,0 ml of the solution obtained into another 100 ml one-mark volumetric flask. Add 45 ml of the copper base solution (3.4). Dilute to the mark and mix.

Table

Standard chromium solution		Corresponding mass of chromium	Corresponding chromium content of test portion	
(3.6)	(3.5)		1 g/100 ml (6.4.1.1)	0,1 g/100 ml (6.4.1.2)
ml	ml	mg	% (*m/m*)	% (*m/m*)
0*	—	0	0	0
1	—	0,025	0,002 5	
2	—	0,05	0,005	
4	—	0,10	0,010	
8	—	0,20	0,020	0,20
20	—	0,50	0,050	0,50
—	2	1,0	0,10	1,0
—	3	1,5	0,15	1,5
—	4	2,0	0,20	2,0

* Blank test on reagents for calibration.

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[1] An International Standard dealing with the sampling of copper and copper alloys is in preparation.

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 chromium 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 chromium 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 chromium solutions (3.5 or 3.6).

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

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

where

c_1 is the concentration, in milligrams 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 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 concentration of 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 Chromium content of the sample

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

$$\frac{c - c_1}{10\,m} \times r$$

where

c is the chromium concentration, expressed in milligrams per 100 ml, of the test solution (6.3.1), obtained according to 7.1;

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

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

r is the ratio between the volume of the test solution (6.3.1) and the standard matching solutions (6.2.1).

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.
