International Standard 6437

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Copper alloys — Determination of chromium content — Titrimetric method

Alliages de cuivre — Dosage du chrome — Méthode titrimétrique

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Foreword

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

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Copper alloys — Determination of chromium content — Titrimetric method

WARNING — Throughout this International Standard, normal precautions regarding the use of perchloric acid in laboratory work shall be observed.

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of the total chromium content of copper-chromium alloys listed in International Standards.

The method is applicable to products having chromium contents between 0,10 and 2,0 % (*m*/*m*).

2 Principle

Dissolution of a test portion followed by oxidation of the bulk of chromium by perchloric acid in the presence of orthophosphoric acid to avoid loss of chromium. Oxidation of residual chromium(III) by potassium permanganate. Reduction of chromium(VI) by iron(II) solution, and determination of the equivalence point either using an indicator or by measuring the change in potential as a function of the volume of titrant used.

3 Reagents

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

3.1 Hydrochloric acid, ϱ 1,19 g/ml.

3.2 Nitric acid, ϱ 1,40 g/ml.

3.3 Hydrofluoric acid, ϱ 1,13 g/ml.

3.4 Perchloric acid, ϱ 1,61 g/ml.

3.5 Sulfuric acid, ϱ 1,83 g/ml.

3.6 Hydrochloric acid, solution, 1 + 20.

Dilute 5,0 ml of the hydrochloric acid (3.1) with 100 ml of water.

3.7 Orthophosphoric acid, solution , 1 + 2.

Dilute 100 ml of orthophosphoric acid, ϱ 1,70 g/ml, with 200 ml of water.

3.8 Potassium permanganate, 2,5 g/l solution.

Dissolve 2,5 g of potassium permanganate in water and dilute to 1 000 ml.

3.9 Diphenylamine, 2 g/l in sulfuric acid.

Dissolve 0,2 g of diphenylamine in 100 ml of sulfuric acid (3.5).

3.10 Potassium dichromate, standard solution corresponding to 1,733 g of Cr per litre.

Weigh, to the nearest 0,000 1 g, 4,903 3 g of potassium dichromate ($K_2Cr_2O_7$).

Place in a beaker of suitable capacity and dissolve in reductant-free water. Transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with reductant-free water and mix.

1 ml of this standard solution contains 1,733 mg of Cr.

3.11 Iron(II) ammonium sulfate, 46 g/l solution in 1 mol/l sulfuric acid solution.

3.11.1 Preparation of the solution

Dilute 54 ml of the sulfuric acid (3.5) to 1 litre with water. Dissolve 46 g of iron(II) ammonium sulfate hexahydrate $[Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O)]$ in a small amount of this solution, then dilute to 1 000 ml with the same sulfuric acid solution.

1 ml of this solution is equivalent to approximately 2 mg of Cr.

3.11.2 Standardization of the solution

3.11.2.1 Volumetric standardization with an indicator

Transfer 20 ml of the potassium dichromate solution (3.10) to a 400 ml beaker. Add 25 ml of the orthophosphoric acid solution (3.7) and 150 ml of water. Add 0,1 ml of the diphenylamine solution (3.9) and titrate with the iron(II) ammonium sulfate solution (3.11) rapidly at first until the purple colour appears, then slowly until the colour disappears.

The titre of the iron(II) ammonium sulfate solution, expressed as milligrams of chromium per millilitre of solution, is given by the formula

$$c_{Cr} = \frac{V_1}{V_2} \times 1{,}733$$

where

V_1 is the volume, in millilitres, of the potassium dichromate solution (3.10) used;

V_2 is the volume, in millilitres, of the iron(II) ammonium sulfate solution (3.11.1) used in the titration.

3.11.2.2 Potentiometric standardization

Transfer 30 ml of the potassium dichromate solution (3.10) to a 600 ml beaker containing 15 ml of the sulfuric acid (3.5), 25 ml of the orthophosphoric acid solution (3.7), and about 330 ml of water. Titrate using the procedure specified in 5.4.2.

The titre of the iron(II) ammonium sulfate solution, expressed as milligrams of chromium per millilitre of solution, is given by the formula in 3.11.2.1.

Daily standardization of the iron(II) ammonium sulphate solution is required.

4 Apparatus

Ordinary laboratory apparatus, and

4.1 Beakers, capacity 600 ml, tall form.

4.2 Potentiometric titration apparatus.

5 Procedure

5.1 Test portion

Weigh, to the nearest 0,001 g, about 2 g of the test sample.[1]

5.2 Dissolution of test portion

Transfer the test portion (5.1) to a 600 ml tall-form beaker (4.1). Add 20 ml of the hydrochloric acid (3.1), 10 ml of the nitric acid (3.2), and 1 ml of the hydrofluoric acid (3.3). When effervescence ceases, add 10 ml of the orthophosphoric acid solution (3.7) and 30 ml of the perchloric acid (3.4). Bring to the boil and evaporate until thick white perchloric fumes appear. Maintain until the test portion is totally dissolved. Reduce the heat and boil gently for 5 min. Cool. Add 30 ml of water and boil for 5 min. Cool.

5.3 Oxidation of residual chromium(III)

Add 150 ml of water to the solution (5.2), bring to the boil and add 5 ml of the potassium permanganate solution (3.8). Boil for 3 min., then add 10 ml of the hydrochloric acid solution (3.6) and boil for 15 min. Allow to cool.

5.4 Determination

5.4.1 Volumetric titration with indicator

To the test solution (5.3), add 25 ml of the orthophosphoric acid solution (3.7) and 0,1 ml of the diphenylamine solution (3.9). Titrate rapidly with the iron(II) ammonium sulfate solution (3.11) until a dark ultra-marine blue colour appears, then slowly until the clear blue-green end-point is reached.

5.4.2 Potentiometric titration

Transfer the test solution (5.3) to a 600 ml tall-form beaker (4.1). Add 20 ml of the sulfuric acid (3.5) and 25 ml of the orthophosphoric acid solution (3.7). Dilute to about 400 ml with water. Allow to cool, if necessary. Place the electrodes in the solution, and, while stirring, titrate with the iron(II) ammonium sulfate solution (3.11) until the potentiometric change occurs. Titrate slowly near the end-point. Using a platinum-saturated calomel electrode, the change in potential is of the order of 200 mV, and lies between 900 and 700 mV.

5.5 Check test

Verify the validity of the application of the method using a standard material or a synthetic sample containing a known amount of chromium and of composition similar to the material to be analysed, and carrying out the procedure as specified in 5.1 to 5.4.

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

6 Expression of results

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

$$\frac{V \times c_{\mathrm{Cr}}}{10\,m}$$

where

V is the volume, in millilitres, of the iron(II) ammonium sulfate solution (3.11) used in the determination (5.4);

c_{Cr} is the titre of the iron(II) solution (3.11), expressed as milligrams of chromium per millilitre of solution, calculated in 3.11.2;

m is the mass, in grams, of the test portion.

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.

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