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INTERNATIONAL STANDARD ISO 3111

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Copper alloys — Determination of tin as alloying element — Volumetric method

Alliages de cuivre — Dosage de l'étain comme élément d'alliage — Méthode volumétrique

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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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Copper alloys – Determination of tin as alloying element – Volumetric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a volumetric method for the determination of tin in copper alloys.

The method is applicable for the determination of tin as an alloying element in all types of copper alloys listed in ISO Recommendations or International Standards.

2 PRINCIPLE

Separation of tin from the copper by co-precipitation with iron(III) hydroxide and titration with iodine solution in a carbon dioxide atmosphere after reduction with hypophosphorous acid.

3 REAGENTS

All the reagents shall be of analytical grade. Distilled or deionized water shall be used.

3.1 Hydrochloric acid (ρ 1,09 g/ml).

Dilute 100 ml of hydrochloric acid (ρ 1,19 g/ml) with 100 ml of water.

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

3.3 Iron(III) chloride solution.

Dissolve 10 g of iron(III) chloride ($FeCl_3 \cdot 6H_2O$) in water and dilute to 1 000 ml.

3.4 Ammonia solution (ρ 0,945 g/ml).

Dilute 100 ml of ammonia solution (ρ 0,89 g/ml) with 100 ml of water.

3.5 Washing solution.

Dissolve 10 g of ammonium chloride in water, add 50 ml of ammonia solution (3.4) and dilute with water to 1 000 ml.

3.6 Mercury(II) chloride solution.

Dissolve 0,5 g of mercury(II) chloride ($HgCl_2$) in 100 ml of water.

3.7 Hypophosphorous acid solution.

Dilute 600 ml of hypophosphorous acid (H_3PO_2), 50 %, to 1 000 ml with water.

3.8 Ammonium thiocyanate solution.

Dissolve 50 g of ammonium thiocyanate (NH_4CNS) in 100 ml of water.

3.9 Potassium iodide solution.

Dissolve 10 g of potassium iodide (KI) in 100 ml of water.

3.10 Starch solution.

Dissolve 0,5 g of starch in 100 ml of water.

Prepare freshly every 2 days.

3.11 Potassium iodate solution.

Dissolve 0,85 g of sodium hydroxide (NaOH) in 500 ml of water, add 3,0051 g of potassium iodate (KIO_3) and 12 g of potassium iodide (KI) and after dissolving in a 1 000 ml volumetric flask dilute to the mark (1 ml is equivalent to 0,005 g of tin).

3.12 Potassium iodate solution.

Transfer 200,0 ml of potassium iodate solution (3.11) into a 500 ml volumetric flask and dilute to the mark (1 ml is equivalent to 0,002 g of tin).

The tin equivalent of the solution (3.11) and solution (3.12) is determined by the analysis of a known amount of pure tin (corresponding to 1 %, 5 % or 10 % tin respectively) in the presence of a complementary quantity of copper (99 %, 95 % or 90 % respectively). The rules given in clause 6 shall be followed during this calibration.

4 APPARATUS

4.1 Normal laboratory apparatus.

4.2 Attachment for reduction in a carbon dioxide atmosphere (see figure 1)[1], comprising the following parts :

a) **Carbon dioxide bomb,** equipped with a reduction valve.

b) **Two washing bottles,** the first filled with 90 ml of tin(II) chloride solution 10 % and 10 ml of hydrochloric acid (ρ 1,19 g/ml), the second empty.

c) **Rubber stopper** with three holes, the first for a glass tube of 10 mm diameter and 600 mm length as an air cooler, the second for the inlet of carbon dioxide by a glass tube, the third for the burette (figure 2) and for the addition of the solutions of ammonium thiocyanate, potassium iodide and starch. During the reduction and cooling steps, the third hole must be closed by a glass rod.

d) **Conical flask,** 750 to 1 000 ml, with neck diameter of about 55 mm.

e) **Magnetic stirrer** with a PTFE-coated magnet.

f) **Conical flask,** 300 to 500 ml, containing 50 to 100 ml of water.

4.3 Burette, graduated in 0,05 ml with an outlet of 100 mm length (figure 2).

5 SAMPLING

Carry out the sampling in accordance with the requirements of ISO . . .[2]

6 PROCEDURE

The sample should preferably be in the form of fine drillings with a maximum thickness of 0,3 mm.

The mass of the test portion shall be 1 ± 0,000 1 g for tin contents between 3 and 13 % or 2 ± 0,000 1 g for tin contents between 0,5 and 3 %.

Transfer the test portion into a 400 ml beaker, add 20 or 30 ml of the hydrochloric acid (3.1), according to the mass of the test portion, 1 or 2 g respectively, cover with a watch glass and add, drop by drop, 5 to 10 ml of the hydrogen peroxide (3.2). When dissolution is complete, wash the watch glass, add 100 ml of water and heat for 2 min to expel the chlorine.

Add 25 ml of the iron(III) chloride solution (3.3), neutralize with the ammonia (3.4), add ammonia in a slight excess, just enough to dissolve the copper present as the blue-coloured Cu-NH_3-complex (about 5 ml). Cover the beaker and boil for 2 min.

Filter the solution, while still warm, through a paper of about 15 cm diameter. Wash several times with warm washing solution (3.5). Discard the filtrate.

Dissolve the precipitate from the filter and wash the filter with 180 ml of warm hydrochloric acid (3.1) which has been used first for dissolving any traces of precipitate adhering to the walls of the beaker. Finally wash the beaker and the filter with warm water. Collect the solution in the conical flask (4.2 d).

Add 10 ml of the mercury(II) chloride solution (3.6), 10 ml of the hypophosphorous acid (3.7) and the magnetic stirrer (4.2 e), mix well and stopper the flask with the rubber stopper (4.2 c). Introduce a slow stream of carbon dioxide and heat the solution to boiling for 5 min (see figure 1, phase 1), then cool under running water to a temperature below 15 °C (phase 2) without interrupting the gas flow. If a brown precipitate of elementary arsenic, which precedes a black one of metallic mercury, appears at the beginning of boiling, boil only for 1 min, interrupt the gas stream and filter the solution, still warm, through a Gooch crucible, type G3, into another flask (4.2 d), wash the crucible with as little hydrochloric acid as necessary, add 5 ml of the mercury(II) chloride solution and the magnetic stirrer (4.2 e), start again with introducing carbon dioxide, boil for 5 min and cool below 15 °C.

Stir the cooled solution magnetically (4.2 e) and add, after having diminished the gas flow somewhat, by pipettes through the third hole in the rubber stopper 10 ml of the ammonium thiocyanate solution (3.8), 5 ml of the potassium iodide solution (3.9) and 10 ml of the starch solution (3.10), wash the walls of the flask with some freshly de-aerated water, and introduce the outlet of the burette (4.3) through the same hole (see figure 1, phase 3). Fill the burette with potassium iodate solution (3.11) for tin contents between 3 and 13 % (test portion mass 1 g) or with potassium iodate solution (3.12) for contents between 0,5 and 3 % (test portion mass 2 g). Titrate, while stirring, until the blue colour of the iodine/starch complex appears and is stable for at least 20 s.

Carry out a blank determination through all steps of the procedure using the same amounts of reagents as specified above.

7 EXPRESSION OF RESULTS

Calculate the tin content, as a percentage by mass, by the formula

$$\text{Sn}\ \%\ (m/m) = \frac{(V_1 - V_2) \times C}{10\,m}$$

where

V_1 is the volume, in millilitres, of potassium iodate solution used for the determination;

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[1] This equipment may be replaced by a Contat-Göckel trap filled with a saturated sodium hydrogen carbonate solution.

[2] In preparation.

V_2 is the volume, in millilitres, of potassium iodate solution used for the blank test;

C is the tin equivalent, in milligrams of tin per millilitre, of the potassium iodate solution;

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

8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any characteristics noted during the determination;

d) any operation not included in this International Standard or regarded as optional.

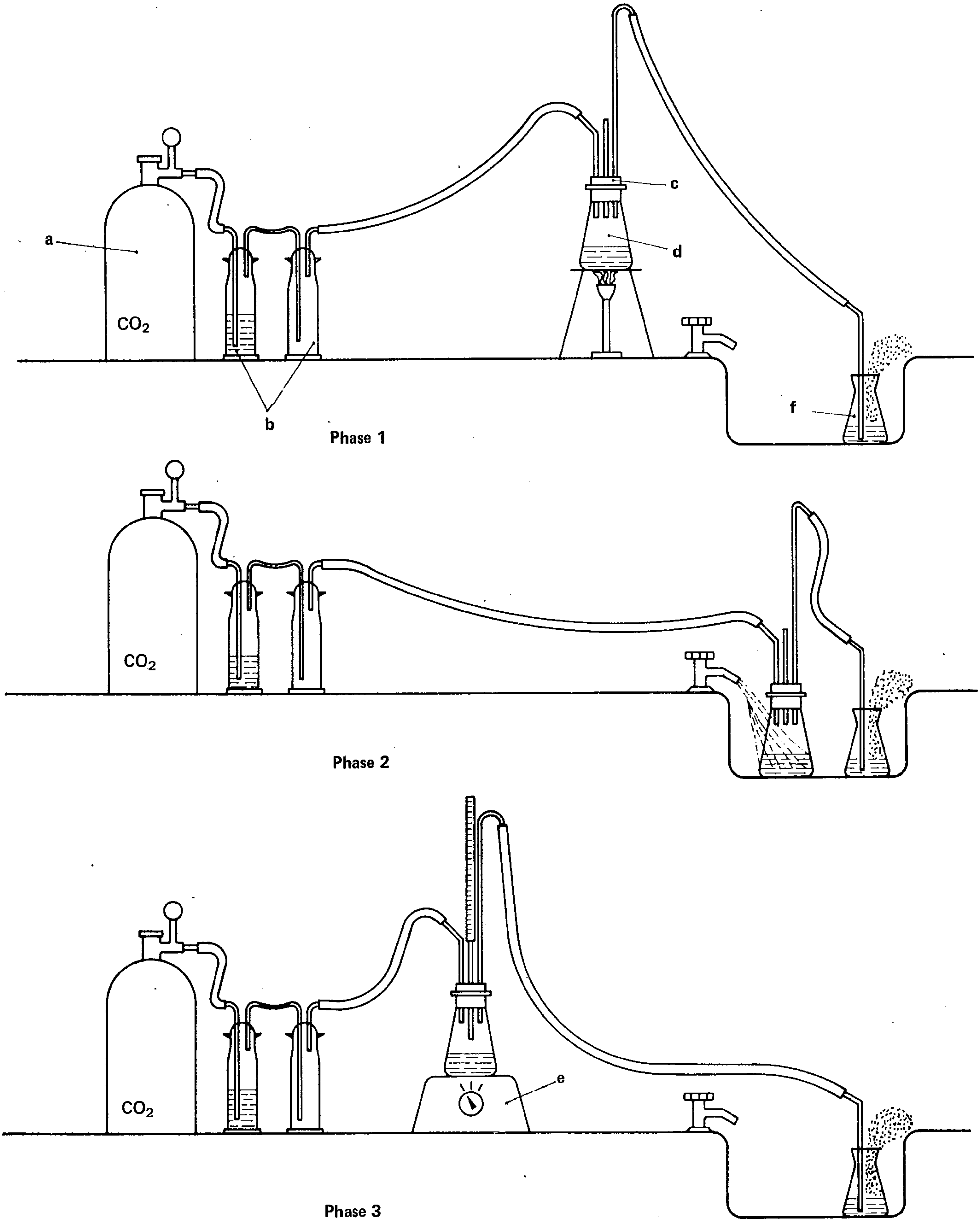

FIGURE 1 — **Attachment for reduction (4.2)**

Dimensions in millimetres

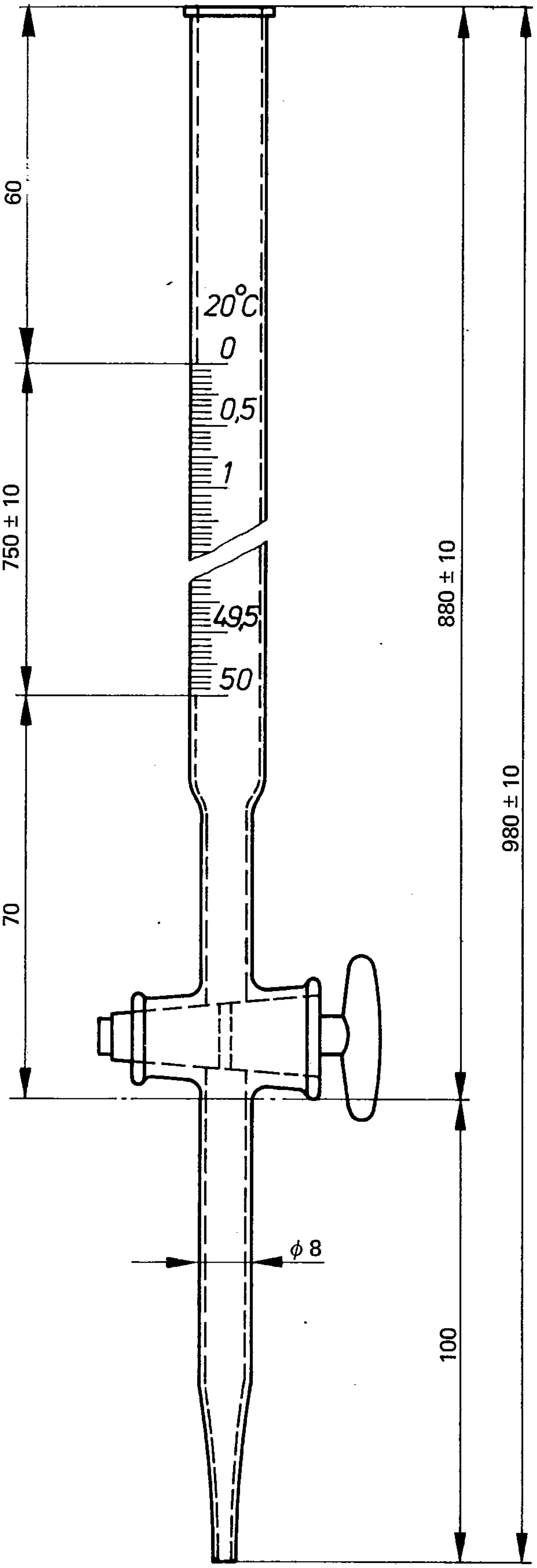

FIGURE 2 — **Burette (4.3)**