International Standard 7266

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Copper and copper alloys — Determination of sulfur content — Combustion titrimetric method

Cuivre et alliages de cuivre — Dosage du soufre — Méthode titrimétrique après combustion

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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 7266 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	Italy	Sweden
Belgium	Japan	Switzerland
Canada	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	
Iran	Spain	

No member body expressed disapproval of the document.

Copper and copper alloys — Determination of sulfur content — Combustion titrimetric method

1 Scope and field of application

This International Standard specifies a combustion titrimetric method for the determination of the sulfur content of copper and copper alloys.

The method is applicable to contents of sulfur greater than 0,010 % (m/m) in all types of copper and copper alloys listed in International Standards.

2 Principle

Combustion of a test portion in oxygen at 1 250 °C. Absorption of combustion gases in dilute hydrogen peroxide solution. Titration of the sulfuric acid formed with sodium borate in the presence of a mixed methyl red-methylene blue indicator solution.

3 Reagents

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

3.1 Hydrogen peroxide, approximately 3 g/l solution.

Dilute 10 ml of hydrogen peroxide, 30 % (m/m) to 1 000 ml with water.

3.2 Sulfuric acid, solution, $c(H_2SO_4) \approx 0{,}002\,5$ mol/l

Dilute 14 ml of sulfuric acid (ϱ 1,84 g/l) to 1 000 ml. Dilute 10 ml of this solution to 1 000 ml.

3.3 Sodium borate, standard solution.

Dissolve 1,189 5 g of sodium borate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) in water and dilute to the mark in a 1 000 ml one-mark volumetric flask.

1 ml of this standard solution is equivalent to 100 µg of S.

3.4 Mixed indicator

Dissolve 0,120 g of methyl red and 0,080 g of methylene blue in 100 ml of ethanol.

4 Apparatus

Ordinary laboratory apparatus, and

4.1 Burette, 25 ml, with 0,05 ml graduations.

4.2 Combustion apparatus (see figure 1), consisting of the following :

4.2.1 Oxygen bottle with pressure regulator and flowmeter (D). The oxygen must be sulfur-free.

4.2.2 Purging tubes (A_1 and A_2). A_1 is packed with asbestos treated with sodium hydroxide. The bottom part of A_2 is filled to three-quarters of its height with anhydrous magnesium perchlorate; the top part is filled with phosphorus(V) oxide. The two substances are separated by a plug of glass wool.

4.2.3 Two-way valve (R), with 3 to 4 mm tubing, such that oxygen can flow into the combustion tube T (4.2.6) and the combustion gases can flow into the bubbler tube B (4.3.2).

4.2.4 Mercury check valve (S), with an equilibrium flask and a safety tube. The level of mercury is adjusted, by means of the equilibrium flask, so that a seal is made when, with valve R (4.2.3) open, the gas flows from the combustion tube at a rate of 2,5 l/min. When valve R is opened, an overpressure is created, and the mercury seal operates until normal pressure is established.

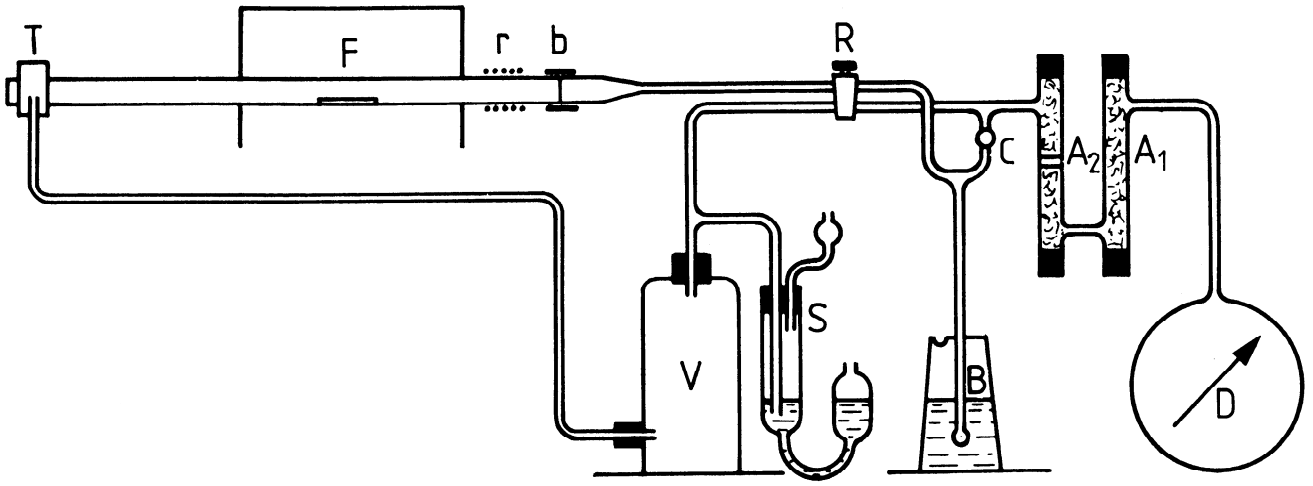
4.2.5 Pressure-release container (V).

4.2.6 Combustion tube (T), made of non-porous refractory material, in which the combustion boat containing the test portion is placed (see 7.2).

4.2.7 Combustion boats, previously calcined at 1 250 °C in a stream of oxygen (see 7.3).

4.2.8 Tube furnace (F), capable of maintaining the heated portion of the combustion tube T (4.2.6) at 1 250 °C, with a metal cooling head for the combustion tube (see figure 3).

4.2.9 Glass outlet tube, of the same diameter as the combustion tube T (4.2.6), connected to the combustion tube by a rubber sleeve (b).



A_1 and A_2	Purging tubes (4.2.2)	F	Combustion furnace (4.2.8)
B	Bubbler tube (4.3.2)	S	Mercury check valve and safety tube (4.2.4)
C	Outlet valve (4.3.3)	R	Two-way valve (4.2.3)
D	Pressure regulator and flowmeter (4.2.1)	V	Pressure-release container (4.2.5)
b	Rubber sleeve (4.2.9)	T	Combustion tube (4.2.6)
r	Cooling coil (4.2.10)		

Figure 1 — Apparatus for the determination of sulfur by combustion

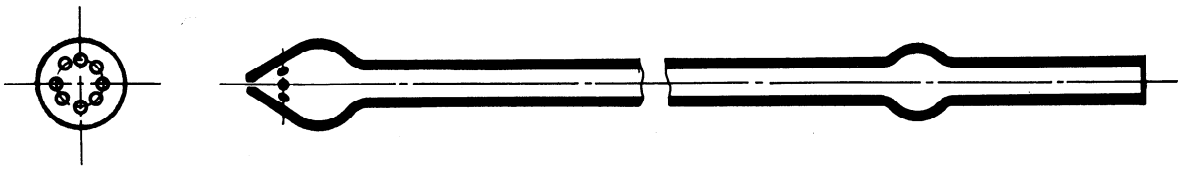


Figure 2 — Bubbler tube B (4.3.2) (Diameter of holes : 0,05 mm)

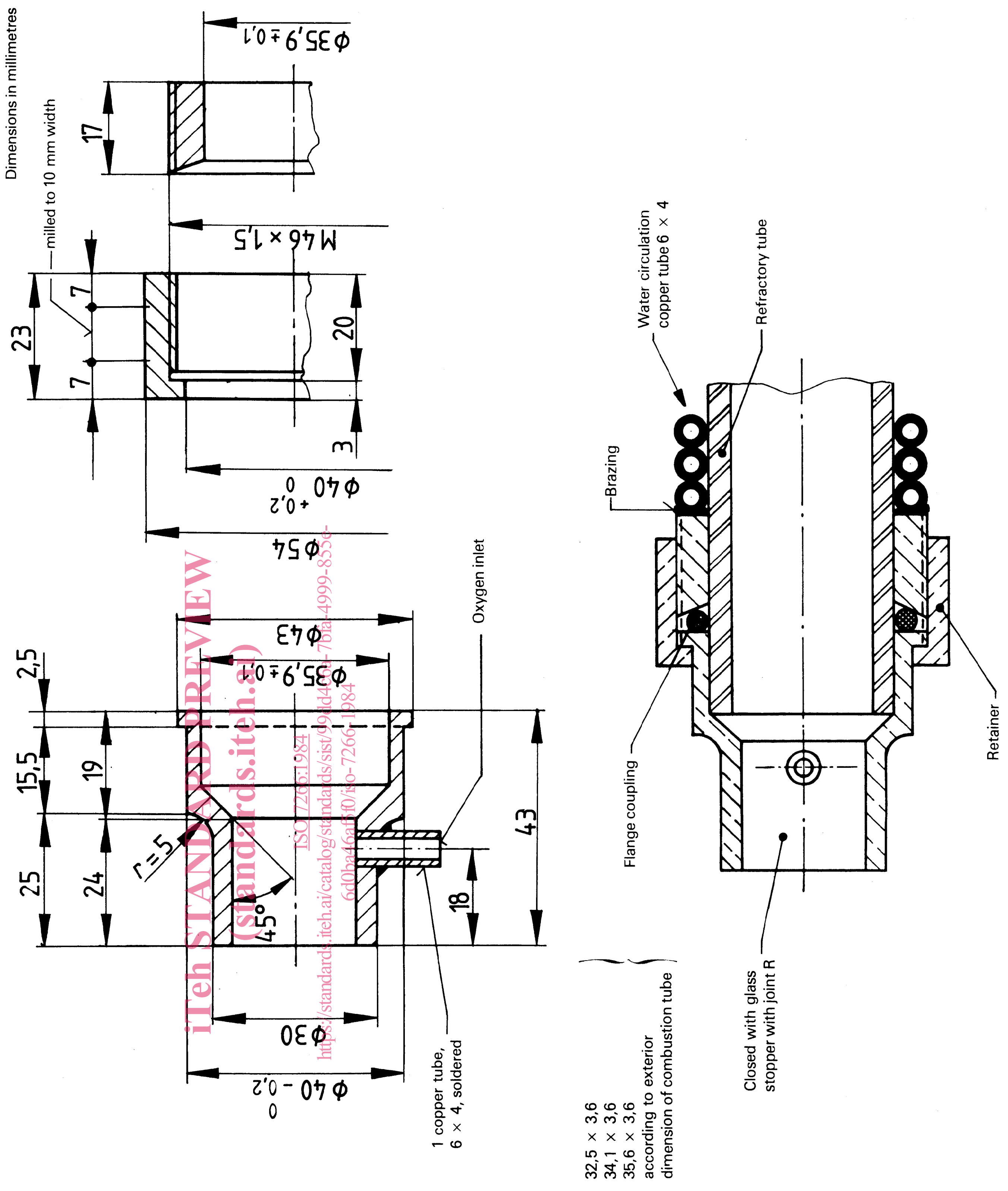


Figure 3 — Metallic cooling head for combustion tube

4.2.10 Water cooling coil (r), to cool combustion gases.

4.2.11 Flexible plastic tubing for all fixed connections.

4.3 Absorption apparatus, consisting of the following (see figures 1 and 2) :

4.3.1 Absorption vessel, 250 ml.

4.3.2 Bubbler tube (B) with holes in one end (see figure 2), immersed in a solution of hydrogen peroxide (3.1).

4.3.3 Outlet valve (C), between purging tubes A_1 and A_2 and bubbler tube B. With this valve, it is possible to maintain a slight oxygen flow into the absorption vessel (4.3.1), thereby preventing the hydrogen peroxide solution (3.1) from flowing up into the bubbler tube B (4.3.2).

5 Procedure

5.1 Test portion

Weigh 1 ± 0,001 g of sample into a combustion boat (4.2.7). For samples with high zinc content, particularly the brasses, add to the sample in the combustion boat five times its mass in pure tin (see 7.1).

5.2 Blank test

Calcination of the combustion tube and combustion boats makes a blank test of this apparatus unnecessary. In the case of high zinc alloys, a blank test shall be carried out using the same mass of tin added to the combustion boat.

5.3 Determination

Pre-heat the furnace F (4.2.8) to 1 250 °C. Ensure that the cooling coil r (4.2.10) is working, and connect the combustion tube T (4.2.6) at both ends.

Open valves R (4.2.3) and C (4.3.3) and pass oxygen through the system at a rate of 2,5 l/min, regulating the flow rate with the pressure regulator and flowmeter D (4.2.1).

Close valve R and adjust the oxygen flow rate to 0,5 l/min by means of valve C. To the absorption vessel (4.3.1) add 40 ml of the hydrogen peroxide solution (3.1), 160 ml of water, and 4 to 6 drops of the mixed indicator solution (3.4). Immerse the bubbler tube B (4.3.2) in the solution. Turn the indicator violet by the addition of sulfuric acid solution (3.2) if necessary.

Open valve R and pass oxygen through the system at a rate of 2,5 l/min for 2 min, in order to expel carbon dioxide. If necessary, readjust the pressure regulator and flowmeter D.

Close valve R and add the sodium borate solution (3.3) to the absorption vessel until the solution is neutralized. The indicator will change from violet through blue to green. Stop adding solution when the indicator changes from blue green to bright green.

Remove the stopper from the furnace head. Insert the combustion boat (4.2.7) containing the test portion into the hottest zone of the furnace using a refractory metal rod.

Replace the stopper on the combustion tube and wait 2 min. Slowly open valve R. Pass oxygen through the combustion tube for 2 min, then close valve R. Remove to stopper and take out the combustion boat (see 7.4).

Titrate the solution in the absorption vessel with the sodium borate solution until the indicator turns bright green.

5.4 Check test

Make a preliminary test of the apparatus using a standard material or a synthetic sample containing a known amount of sulfur and carrying out the procedure as specified in 5.1 to 5.3.

6 Expression of results

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

$$\frac{V \times 0{,}000\,1}{m} \times 100 = \frac{V}{100\,m}$$

where

V is the volume, in millilitres, of the sodium borate solution (3.3) used in the titration;

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

0,000 1 is the mass, in grams, of sulfur equivalent to 1 ml of the sodium borate solution (3.3).

In the case of high zinc alloys, the calculated sulfur content must be reduced by the sulfur content of the tin blank (5.2).

7 Notes on procedure

7.1 Analysis of high-zinc copper alloys

The method can be applied to copper alloys with high zinc content, in particular the copper-zinc alloys (brasses), by adding to the sample in the combustion boat five times its mass in pure tin. If this precaution is omitted, zinc is distilled during heating and the zinc oxide thus formed interferes with the volumetric determination of sulfur.

7.2 Pre-treatment of combustion tubes

When a new tube is used, as much of it as possible must be calcined at or above the temperature at which it is to be used (1 250 °C) by moving the tube lengthwise in the furnace.

7.3 Calcination of combustion boats

Calcination should be carried out on the day the boat is to be used. Boats should be stored in a desiccator. The absence of sulfur must be verified by means of blank tests.

7.4 Multiple determinations

A series of 5 or 6 determinations can be carried out with the same bubbler tube and the same absorption solution. To reduce time loss to a minimum, the next test portion can be inserted as soon as combustion of the previous test portion is completed, and titration can be carried out during the 2 min waiting period.

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, which might affect the results.

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