

COPPER 44

**COPPER
44**

Atomic mass 63.54

<i>Compound</i>	<i>Empirical formula</i>	<i>RMM</i>	<i>% Cu</i>	<i>CAS no</i>
<i>Coppercarbonate</i>	$\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$	221.1	57.47	12069-69-1
<i>Copperoxychloride</i>	$3\text{Cu}(\text{OH})_2 \cdot \text{CuCl}_2$	427.1	59.51	01332-40-7
<i>Copper(II)sulphate</i>	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	249.7	25.45	07758-98-7
<i>Copper(I)oxide</i>	Cu_2O	143.1	88.81	01317-39-1

Formulations Wettable powders and dustable powders

**COPPER IN TECHNICAL COPPER COMPOUNDS
44/TC/M/-**

1 Sampling. Take at least 100 g.

2 Identity test -

3 Copper

***3.1 Electrolytic method** (Referee method)

OUTLINE OF METHOD The free and combined copper is converted to sulphate and determined electrolytically.

REAGENTS

Sulphuric acid density 1.84

Nitric acid density 1.42

Sulphuric-nitric acid mixture. Mix 2 volumes of sulphuric acid with 1 volume of nitric acid

Ethanol 95%

Ammonia solution density 0.880

Diethyl ether

* CIPAC method 1962; revised 1974. Prepared by the French Committee; Chairman: J L H A Prat.

APPARATUS

Flat bottom flask 150 ml with a long neck or

Conical flask 300 ml with narrow neck

Beaker 500 ml, tall form

Split watch glasses to fit

Electrolysis apparatus with magnetic stirrer

Hot plate or *sand bath*

Desiccator

Oven at 80 ± 2 °C

Weighing bottle

PROCEDURE

(a) *Preparation of sample.* Weigh (to the nearest mg) sufficient of the sample (w g) to contain about 250 to 350 mg of copper, and transfer to a 150 ml flat bottom flask (150 ml). Add the sulphuric-nitric acid mixture (10 to 15 ml) and evaporate gently on a hot plate or sand bath until the white fumes of sulphuric acid produced just cease. Add a few drops of sulphuric acid and evaporate again. Dissolve the residue in distilled water, filter, if necessary, into a beaker, wash with water and make up to about 300 ml with water.

(b) *Determination.* Add sulphuric acid (10 drops) and nitric acid (15 ml) and electrolyse using a current density of 1.5 A (*Note*). Do not immerse the cathode (or platinum basket) completely. Stir the solution during the electrolysis with the magnetic stirrer and cover the beaker with two half watch glasses. After 2 h electrolysis, remove a few ml of the solution and add a little ammonia solution. If no blue colour appears, rinse the watch glasses with a jet from a wash bottle, replace them on the beaker without stopping the current, immerse the cathode further in the liquid and continue the electrolysis. Observe whether any red colour appears on the freshly immersed cathode.

If the preceding tests have shown that the copper has not been completely deposited on the cathode, continue the electrolysis for a further 30 min and repeat the tests. Then, without switching off the current, immerse the electrodes in another beaker containing acidified water (25 ml of nitric acid - 300 ml of water) and leave for 10 min. Replace the beaker, in turn, by two other beakers containing distilled water, leaving each in place for 5 min. Switch off the current and immerse the cathode in turn in ethanol and the diethyl ether. Dry the cathode at 80 °C for 1 min, allow to cool and weigh (x g). Remove the copper from the cathode, clean, dry and reweigh (z g).

(c) Calculation

$$\text{Copper content} = \frac{1000(x - z)}{w} \quad \text{g/kg}$$

where:

- w = mass of sample taken (g)
 x = mass of the electrode after the electrolysis (g)
 z = mass of the electrode after removal of the copper (g)

Note Electrolysis in nitric acid, alone, takes longer than in ammonium sulphate and nitrate solution but, in the presence of traces of lead, it is preferable in order to avoid fouling of the cathode.

*3.2 Volumetric thiosulphate method

OUTLINE OF METHOD Cupric ions, formed by digestion with sulphuric acid-nitric acid mixture or hydrochloric acid, afford, with potassium iodide, cuprous iodide and iodine. The latter is titrated with sodium thiosulphate.

REAGENTS

Hydrochloric acid density 1.18. Dilute with water 1 + 1

Sulphuric acid density 1.84

Nitric acid density 1.42

Urea

Ammonium solution density 0.880

Acetic acid glacial

Potassium iodide solution 332 g/l, iodate free

Potassium thiocyanate solution 400 g/l

Starch indicator solution RE 27.1

Sodium thiosulphate standardized solution $c(1/2 \text{Na}_2\text{S}_2\text{O}_3) = 0.1 \text{ mol/l}$; RE 26.3 standardized against pure metallic copper.

Sodium fluoride solution saturated approximately 48 g/l. Store in a polyethylene bottle.

Litmus paper

* CIPAC method 1967, revised 1974. Prepared by a British Committee of PAC; Chairman: H Crossley (The Murphy Chemical Co., Ltd).

APPARATUS

*Weighing bottle**Conical flasks* 250 ml with ground-glass stoppers*Burette* 50 ml*Hot plate**Volumetric flask* 250 ml*Pipette* 50 ml*Beaker* 250 ml*Filterpaper* Whatman No. 2024 or equivalent

PROCEDURE

(i) Samples not containing copper(I)oxide or more than 20% of copper

(a) Preparation of sample. Weigh (to the nearest mg) sufficient sample (w g) to contain about 0.75 g of copper, transfer to a 250 ml conical flask, add hydrochloric acid (25 ml) and a few pumice granules, boil for a few minutes and cool. Transfer, quantitatively to a volumetric flask (250 ml), filtering if necessary, make up to the mark with washings from the conical flask and filter. Pipette 50 ml of the well mixed solution into a 250 ml conical flask.

(b) Determination. Add ammonia solution, keeping the solution constantly swirled, until the precipitate which first forms, re-dissolves to give a deep blue colour. Add acetic acid until just acid to litmus paper, then 2 ml in excess, and cool to 15 to 20 °C. Add sodium fluoride solution (5 ml) and potassium iodide solution (10 ml), close the flask with a stopper previously moistened with water, and swirl to mix. Titrate with the thiosulphate to a pale straw colour, add starch solution (2 ml) and potassium thiocyanate solution (5 ml). Continue the titration until the blue colour is just discharged (t ml). If the blue colour returns within 3 to 5 min insufficient sodium fluoride has been added to mark the excess of iron.

(c) Calculation

$$\text{Copper content} = \frac{317 \times t \times N}{w} \text{ g/kg}$$

where:

N	=	normality of the sodium thiosulphate solution
t	=	volume required for the titration (ml)
w	=	mass of sample taken (g)

(ii) Samples containing copper(I)oxide and not more than 20% copper

(a) Preparation of sample. Weigh (to the nearest 0.1 mg) sufficient sample to contain 0.15 g of copper (w g) into to 500 ml conical flask, add nitric acid (15 ml), sulphuric acid (5 ml), and a few pumice granules. Boil on a hot plate until dense white fumes appear and a blue-green solution with a white sediment remains. If a brown colour persists in the sediment, or brown fumes

are evolved on adding a few drops of nitric acid, add further nitric acid (5 ml) and boil again. Repeat, if necessary. Cool, then add cautiously water (50 ml); heat on a hot plate to boiling, and boil till free from brown fumes. Add urea (0.5 g) and continue boiling for a further 5 min. Cool to room temperature.

(b) *Determination.* As for (i) b.

(c) *Calculation*

$$\text{Copper content} = \frac{63.5 \times t \times N}{w} \text{ g/kg}$$

(iii) *Samples containing more than 20% copper and/or copper(I)oxide*

(a) *Preparation of sample.* Weigh (to the nearest mg) sufficient sample to contain about 0.75 g of copper (w g) into a 250 ml conical flask, add nitric acid (15 ml), sulphuric acid (10 ml) and a few pumice granules. Boil on a hot plate until dense white fumes appear and a blue-green solution with a white sediment remains. If a brown colour persists in the sediment, or brown fumes are evolved on adding a few drops of nitric acid, add further nitric acid (5 ml) and boil again. Repeat if necessary. Cool, then add cautiously water (50 ml); heat on the hot plate to boiling and boil till free from brown fumes. Add urea (0.5 g) and continue boiling for a further 5 min. Cool to room temperature, transfer to the volumetric flask, and make up to the mark with distilled water. Mix well and pipette a 50 ml aliquot into a 250 ml conical flask.

(b) *Determination* As for (i) b.

COPPER WETTABLE POWDERS

44/WP/M/-

1 Sampling. Take at least 500 g.

2 Identity tests -

3 Copper

* **3.1 Electrolytic method** (Referee method). As for copper in technical copper compounds 44/TC/M/3.1.

° **3.2 Volumetric thiosulphate method**

(i) *Samples not containing organic matter or copper(I)oxide.* As for copper in technical copper compounds 44/TC/M/3.2(i).

* CIPAC method 1962, revised 1974.

° CIPAC method 1967, revised 1974.

(ii) *Samples containing less than 20% copper but containing organic matter and/or copper(I)oxide.* As for copper in technical copper compounds 44/TC/3.2 (ii)

(iii) *Samples containing more than 20% copper and organic matter and /or copper(I)oxide.* As for copper in technical copper compounds 44/TC/M/3.2 (iii)

4 Suspensibility

APPARATUS AND REAGENTS As for MT15 and 44/TC/M/3.1

PROCEDURE

(a) *Preparation of the suspension* MT 15.1 (i).

(b) *Determination of sedimentation* MT 15.1 (ii).

(c) *Determination of copper in the bottom 25 ml of suspension.* Transfer the bottom 25 ml to a 50 ml evaporating dish, rinse out any material adhering to the walls of the cylinder with a jet of water, evaporate on a water bath, and then dry to constant weight in an oven at 105 °C.

Transfer the residue quantitatively to a conical flask (250 ml) and determine the mass of copper by 44/TC/M/3.2.

(d) *Calculation*

$$\text{Suspensibility} = \frac{111(c - Q)}{c} \%$$

where:

c = mass of copper in the sample taken for the preparation of the suspension (g)

Q = mass of copper in bottom 25 ml of suspension (g)

COPPER DUSTABLE POWDERS

44/DP/M/-

1 Sampling. Take at least 1 kg.

2 Identity tests -

3 Copper

***3.1 Electrolytic method** (Referee method). As for copper in technical copper compounds 44/TC/M/3.1.

* CIPAC method 1962, revised 1974

° **3.2 Volumetric thiosulphate method.** As for copper in technical copper compounds 44/TC/M/3.2.

4 Sieve test

APPARATUS and REAGENTS As for MT 59.1 and 44/TC/M/3.

PROCEDURE

(a) *Sieve test* As for MT 59.1.

(b) *Copper in the residue on the test sieve.* Invert the test sieve over a piece of tared, glazed, black paper, brush the residue from the sieve on to the paper, and determine the weight of the residue.

If the weight is equal to, or less than, the specification limit for the copper in the residue, then it is unnecessary to determine the copper. If the amount is greater, then determine the copper in the residue on the sieve by 44/TC/M/3 using all the material left on the sieve.

° CIPAC method 1967, revised 1974