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Methods of analysis of

Wood preservatives and treated timber —

Part 4: Quantitative analysis of preservatives and treated timber containing copper naphthenate

NOTE It is essential that this Part is read in conjunction with Part 1 *"General considerations and sampling and preparation of materials for analysis"*.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 4, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Amendments issued since publication

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Contents

		Page
1	Scope and field of application	1
2	References	1
3	Method 1. Atomic absorption spectrophotometric method	1
4	Method 2. Colorimetric method	2
5	Test report	4
Publications referred to		Inside back cover

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1 Scope and field of application

This Part of this British Standard details procedures for the determination of copper naphthenate, expressed as the amount of copper present, in preservatives and in treated timber containing this preservative. The methods have been found suitable for the determination of copper in the presence of tributyltin oxide, pentachlorophenol, *o*-phenylphenol, monochloronaphthalene, polychloronaphthalene, γ-HCH, dieldrin, zinc naphthenate, potassium salts and sodium salts. The wood sample may be in the form of sawdust, wood flour, or thin sections.

The procedure for the analysis of preservatives has been primarily designed for solutions complying with the requirements of BS 5056; for samples of other compositions it may be necessary to make adjustments. It is difficult to make recommendations as to the quantity of sample to be taken in the case of treated wood because the predominant factor is the quantity of preservative within the wood rather than the mass of the wood itself. It may thus be necessary to make some adjustment to the values quoted in the standard, either to the mass of the treated wood sample taken for analysis or to the level of dilution of the copper solution resulting from extraction.

Two methods are described, the first involving atomic absorption spectrophotometry and the second colorimetry.

2 References

The titles of the publications referred to in this Part of this standard are listed on the inside back cover.

3 Method 1. Atomic absorption spectrophotometric method

3.1 Principle. The copper is extracted quantitatively from wood samples or preservatives with a hydrochloric acid solution. The resulting copper solution is analysed using an atomic absorption spectrophotometer.

3.2 Reagents. All reagents shall be of recognized analytical reagent quality, and water complying with the requirements of BS 3978 shall be used throughout.

3.2.1 *Hydrochloric acid solution, approximately* 5M. Dilute 500 ml of hydrochloric acid solution (ρ_{20} = 1.18 g/ml) to 1 litre with water.

3.2.2 *Hydrochloric acid solution, approximately* 1M. Dilute 100 ml of hydrochloric acid solution (ρ_{20} = 1.18 g/ml) to 1 litre with water.

3.2.3 *White spirit,* complying with the requirements of BS 245.

3.2.4 *Standard copper solution.* (1 ml = 200 µg of copper). Weigh 0.1000 g of oxide-free copper foil or turnings into a 100 ml conical flask, add 3 ml of water and 3 ml of nitric acid solution (ρ_{20} = 1.42 g/ml) and heat on a hot-plate until digestion is complete. When the fuming subsides, evaporate the solution to dryness. Add a few drops of hydrochloric acid solution (ρ_{20} = 1.18 g/ml) and again evaporate to dryness. Repeat the addition and evaporation of a few drops of the hydrochloric acid solution. Remove from the hot-plate and when cool, dissolve the resulting residue in hydrochloric acid solution (**3.2.2**). Transfer to a 500 ml one-mark volumetric flask, make up to the mark with hydrochloric acid solution (**3.2.2**), and mix.

3.3 Apparatus

3.3.1 *Volumetric glassware*, complying with the requirements for class A quality in accordance with BS 700 (type II), BS 846, BS 1583 or BS 1792, as appropriate.

3.3.2 *Atomic absorption spectrophotometer,* together with a suitable source of resonance radiation for copper, e.g. a hollow cathode lamp.

3.4 Procedure

3.4.1 *Instrument settings and operation.* The instrument settings and operating conditions for the determination of copper shall be as recommended in the Instrument Users' Manual. Copper is determined in a fuel-lean air/acetylene flame at 324.8 nm.

3.4.2 *Preparation of calibration solutions.* Transfer aliquot portions of 0.50 ml, 1.00 ml, 2.50 ml, 5.00 ml, 10.0 ml, 20.0 ml and 30.0 ml of the standard copper solution (**3.2.4**) to a series of 100 ml one-mark volumetric flasks, dilute to the mark with hydrochloric acid solution (**3.2.2**) and mix each solution. This will provide solutions containing 1 µg/ml, 2 µg/ml, 5 µg/ml, 10 µg/ml, 20 µg/ml, 40 µg/ml and 60 µg/ml, respectively, of copper

NOTE Calibration solutions of different concentrations may be necessary to suit the sensitivity of the spectrophotometer used.

3.4.3 *Analysis of preservative.* Weigh out accurately a suitable quantity[1] of the copper naphthenate preservative and dilute it in approximately 50 ml of white spirit (**3.2.3**). Transfer the solution quantitatively to a 100 ml one-mark volumetric flask, make up to the mark with white spirit (**3.2.3**) and mix thoroughly. Filter the solution through a filter paper[2], discard the first runnings and collect approximately 50 ml of the filtrate. Transfer 5 ml of this solution to a 50 ml separating funnel and make up to approximately 10 ml with white spirit (**3.2.3**). Add 20 ml of hydrochloric acid solution (**3.2.2**) and extract the copper from the organic layer by shaking vigorously for at least 90 s. Allow the two phases to separate and run off the aqueous layer into a 100 ml one-mark volumetric flask. Repeat the extraction procedure three more times, each time using a fresh 20 ml aliquot portion of hydrochloric acid solution (**3.2.2**). When all extracts have been combined in the 100 ml one-mark volumetric flask, make up to the mark with hydrochloric acid solution (**3.2.2**) and mix to give the test solution.

Using the operating conditions suitable for the instrument being used, aspirate successively, the hydrochloric acid solution (**3.2.2**) to obtain the blank absorbance, a suitable range of the calibration solutions and, then, the test solution(s). Check the calibration solutions after the last test solution has been run.

NOTE If a number of samples are to be analysed it may be advisable to check the instrument stability by bracketing each test solution with appropriate standard solutions.

Plot a calibration curve of µg/ml of copper against absorbance. Determine the copper content in the test solution by comparing the absorbance reading with the calibration curve and express the result as µg/ml of copper in the test solution.

3.4.4 *Analysis of treated wood.* Accurately weigh approximately 0.1 g[3] of the wood sample into a 50 ml conical flask. Add 10 ml of hydrochloric acid solution (**3.2.1**) and stand the flask in a water bath at a temperature of 55 °C to 60 °C for 30 min with occasional swirling. Remove the flask from the water bath, cool to room temperature, and filter the flask contents through a filter paper[4] into a 50 ml one-mark volumetric flask. Wash the residue and the filter paper thoroughly with water and add the washings to the filtrate in the one-mark volumetric flask. Make up to the mark with water and mix to give the test solution.

Using the operating conditions suitable for the instrument being used, aspirate successively, the hydrochloric acid solution (**3.2.2**) to obtain the blank absorbance, a suitable range of the calibration solutions and, then, the test solution(s). Check the calibration solutions after the last test solution has been run (see note in **3.4.3**).

Plot a calibration curve of µg/ml of copper against absorbance. Determine the copper content in the test solution by comparing the absorbance reading with the calibration curve and express the result as µg/ml of copper in the test solution.

3.4.5 ***Calculations***

3.4.5.1 *The percentage of copper in a preservative.* The percentage, by mass, of copper in the preservative is given by the formula:

$$\frac{C}{5m_1}$$

where

C is the concentration in µg/ml of copper in the test solution;

m_1 is the mass in grams of the copper naphthenate preservative solution taken.

3.4.5.2 *The percentage of copper in treated wood.* The percentage, by mass, of copper in the dry wood is given by the formula:

$$\frac{C}{200m_2}$$

where

C is the concentration in µg/ml of copper in the test solution;

m_2 is the oven-dry equivalent mass in grams of the wood sample taken.

To calculate the oven-dry equivalent mass, determine the moisture content (see Part 1) of a similar sample of wood to that used for the analysis.

4 Method 2. Colorimetric method

4.1 Principle. The copper is extracted quantitatively from wood samples or preservatives with a hydrochloric acid solution. The resulting copper solution is allowed to react with a zinc dibenzyldithiocarbamate solution and the concentration of the resulting coloured complex is measured spectrophotometrically.

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[1] For solutions complying with the requirements of BS 5056, 0.800 g is suitable.

[2] A Whatman no. 42 filter paper has been found to be suitable.

[3] See clause **1**.

[4] Whatman no. 44 filter paper has been round to be suitable.

4.2 Reagents. All reagents shall be of recognized analytical reagent quality, and water complying with the requirements of BS 3978 shall be used throughout.

4.2.1 *Hydrochloric acid, approximately* 5M. Dilute 500 ml of hydrochloric acid solution (ρ_{20} = 1.18 g/ml) to 1 litre with water.

4.2.2 *Hydrochloric acid, approximately* 1M. Dilute 100 ml of hydrochloric acid solution (ρ_{20} = 1.18 g/ml) to 1 litre with water.

4.2.3 *White spirit,* complying with the requirements of BS 245.

4.2.4 *Standard copper solution.* (1 ml ≡ 2 µg of copper). Weigh 0.1000 g of oxide-free copper foil or turnings into a 100 ml conical flask, add 3 ml of water and 3 ml of nitric acid (ρ_{20} = 1.42 g/ml) and heat on a hot-plate until digestion is complete. When the fuming subsides, evaporate the solution to dryness. Add a few drops of hydrochloric acid solution (ρ_{20} = 1.18 g/ml) and again evaporate to dryness. Repeat the addition and evaporation of a few drops of the hydrochloric acid solution. Remove from the hot-plate and when cool dissolve the resulting residue in hydrochloric acid solution (**4.2.2**). Transfer to a 100 ml one-mark volumetric flask, make up to the mark with hydrochloric acid solution (**4.2.2**), and mix. Transfer 10 ml of this solution to a 100 ml one-mark volumetric flask, make up to the mark with hydrochloric acid solution (**4.2.2**), and mix. Transfer 2 ml of this second solution to a 100 ml one-mark volumetric flask, make up to the mark with hydrochloric acid solution (**4.2.2**), and mix to give the standard copper solution.

4.2.5 *Zinc dibenzyldithiocarbamate solution.* Dissolve 0.5 g of zinc dibenzyldithiocarbamate in 500 ml of carbon tetrachloride.

WARNING NOTE. Carbon tetrachloride is toxic and the necessary precautions should be taken to avoid contact with it or inhalation of the vapour.

4.3 Apparatus

4.3.1 *Volumetric glassware,* complying with the requirements for class A quality in accordance with BS 700 (type II), BS 846, BS 1583 or BS 1792, as appropriate.

4.3.2 *Spectrophotometer or photoelectric absorptiometer,* suitable for the measurement of absorbance at 435 nm, with appropriate cells.

4.4 Procedure

4.4.1 *Preparation of the calibration curve.* Transfer aliquot portions of 2 ml, 5 ml, 10 ml, 15 ml and 20 ml of the standard copper solution (**4.2.4**) to a series of 150 ml separating funnels. The aliquot portions contain the equivalent of 4 µg, 10 µg, 20 µg, 30 µg and 40 µg, respectively, of copper. Treat each aliquot portion as follows. Dilute to 100 ml with the hydrochloric acid solution (**4.2.2**) and swirl to mix. Add 10 ml of the zinc dibenzyldithiocarbamate solution (**4.2.5**) and vigorously shake the separating funnel for 90 s. Allow the two phases to separate. Run off the carbon tetrachloride layer through a dry 70 mm filter paper[5], discarding the first runnings, into one of the spectrophotometer cells. Measure the absorbance of the yellow complex against a reagent blank, prepared in a similar way, at a wavelength of 435 nm. Prepare the calibration curve by plotting the absorbance values against micrograms of copper.

4.4.2 *Analysis of preservatives.* Weigh out accurately a suitable quantity[6] of the copper naphthenate preservative, and add approximately 50 ml of white spirit (**4.2.3**). Transfer the mixture quantitatively to a 100 ml one-mark volumetric flask, make up to the mark with white spirit (**4.2.3**) and mix thoroughly. Filter the solution through a filter paper[7], discard the first runnings and collect about 50 ml of the filtrate. Transfer 5 ml of this solution to a 50 ml separating funnel and make up to approximately 10 ml with white spirit (**4.2.3**). Add 20 ml of hydrochloric acid solution (**4.2.2**) and extract the copper from the organic layer by shaking vigorously for at least 90 s. Allow the two phases to separate and run off the aqueous layer into a 100 ml one-mark volumetric flask. Repeat the extraction procedure three more times, each time using a fresh 20 ml aliquot portion of hydrochloric acid solution (**4.2.2**). Add further hydrochloric acid solution (**4.2.2**) to the combined extracts to make up to the mark, and mix. Transfer 2 ml of this solution to a 250 ml separating funnel and make up to approximately 100 ml with hydrochloric acid solution (**4.2.2**). Add 10 ml of the zinc dibenzyldithiocarbamate solution (**4.2.5**) and vigorously shake the separating funnel for 90 s. Allow the two phases to separate. Run off the carbon tetrachloride layer through a dry 70 mm filter paper[8], after discarding the first runnings, into one of the spectrophotometer cells. Measure the absorbance of the yellow complex against a reagent blank, prepared in a similar way, at a wavelength of 435 nm. Determine the copper content, by comparing the absorbance value with the calibration curve (see **4.4.1**).

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[5] A Whatman no. 1 filter paper has been found to be suitable.

[6] For solutions complying with the requirements of BS 5056, 0.800 g is suitable.

[7] A Whatman no. 42 filter paper has been found to be suitable.

[8] A Whatman no. 1 filter paper has been found to be suitable.

4.4.3 *Analysis of treated wood.* Accurately weigh approximately 0.1 g[9] of the wood sample into a 50 ml conical flask. Add 10 ml of hydrochloric acid solution (**4.2.1**) and stand the flask in a water bath at a temperature of 55 °C to 60 °C for 30 min with occasional swirling. Remove the flask from the water bath, cool to room temperature, and filter the flask contents through a filter paper[10] into a 50 ml one-mark volumetric flask. Wash the residue and the filter paper thoroughly with water, adding the washings to the filtrate in the one-mark volumetric flask. Make up to the mark with water and mix to give the test solution.

Transfer 4 ml of the test solution to a 250 ml separating funnel and dilute to approximately 100 ml with the hydrochloric acid solution (**4.2.2**). Add 10 ml of the zinc dibenzyldithiocarbamate solution (**4.2.5**) and shake vigorously the separating funnel for 90 s. Allow the two phases to separate. Run off the carbon tetrachloride layer through a dry 70 mm filter paper[11], discarding the first runnings, into one of the spectrophotometer cells. Measure the absorbance of the yellow complex against a reagent blank, prepared in a similar way, at a wavelength of 435 nm. Determine the copper content, by comparing the absorbance value with the calibration graph (see **4.4.1**).

4.4.4 ***Calculations***

4.4.4.1 *The percentage of copper in a preservative solution.* The percentage, by mass, of copper in the preservative is given by the formula:

$$\frac{m_3}{10m_4}$$

where

m_3 is the amount in micrograms of copper found in the carbon tetrachloride solution;

m_4 is the mass in grams of copper naphthenate preservative solution taken.

4.4.4.2 *The percentage of copper in treated wood.* The percentage, by mass, of copper in the dry wood is given by the formula:

$$\frac{m_5}{800m_6}$$

where

m_5 is the amount in micrograms of copper found in the carbon tetrachloride solution;

m_6 is the oven-dry equivalent mass in grams of the wood sample taken.

To calculate the oven-dry equivalent mass, determine the moisture content (see Part 1) of a similar sample of wood to that used for the analysis.

5 Test report

The test report shall include the following particulars:

a) full identification of the sample tested and details of its preparation for analysis;

b) a reference to this British Standard and the method used e.g. BS 5666-4:Method 2;

c) any deviation from the method described e.g. the use of a different sample mass;

d) the results of the analysis and the method of expression used e.g. 2.0 % by mass of copper, expressed as Cu;

e) any unusual features noted during the analysis.

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[9] See clause **1**.

[10] A Whatman no. 44 filter paper has been found to be suitable.

[11] A Whatman no. 1 filter paper has been found to be suitable.

Publications referred to

BS 245, *Specification for mineral solvents (white spirit and related hydrocarbon solvents) for paints and other purposes.*

BS 700, *Specification for graduated pipettes (including blowout pipettes).*

BS 846, *Burettes and bulb burettes.*

BS 1583, *One-mark pipettes.*

BS 1792, *One-mark volumetric flasks.*

BS 3978, *Water for laboratory use.*

BS 5056, *Copper naphthenate wood preservatives.*

BS 5666, *Methods of analysis of wood preservatives and treated timber.*

BS 5666-1, *General considerations and sampling and preparation of materials for analysis.*

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