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British Standard Methods of analysis of

Wood preservatives and treated timber

Part 6. Quantitative analysis of preservative solutions and treated timber containing pentachlorophenol, pentachlorophenyl laurate, γ-hexachlorocyclohexane and dieldrin

Méthodes d'analyse des produits de préservation du bois et du bois traité
Partie 6. Analyse quantitative des solutions de préservation et des bois traités contenant du pentachlorophénol, du laurate de pentachlorophényle, du γ-hexachlorocyclohéxane et de la dieldrine

Verfahren zur Untersuchung von Holzschutzmitteln und imprägniertem Holz
Teil 6. Quantitative Analyse von Holzschutzmittellösungen und imprägniertem Holz, die Pentachlorphenol, Pentachlorphenyllaurat, γ-Hexachlorcyclohexan und Dieldrin enthalten

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

Contents

Compliance with a British Standard does not of itself confer immunity from legal obligations.

1. Scope and field of application

This Part of BS 5666 describes procedures for the quantitative determination of pentachlorophenol (PCP), pentachlorophenyl laurate (PCPL), γ-hexachlorocyclohexane (γ-HCH) and dieldrin present in preservative solutions and treated wood. Both colorimetric and gas-liquid chromatographic (GLC) methods are given for the determination of PCP and PCPL but only a GLC method is given for the determination of γ-HCH and dieldrin as no suitable specific chemical methods are available for these chlorinated hydrocarbon insecticides.

The GLC method is suitable for the determination of the total amount of PCP, PCPL, γ-HCH and dieldrin within a single sample of wood. It may be used to study the distribution of these components through such a sample. Since the preservative solution, or the solution obtained by extraction of treated timber, is diluted to a suitable concentration for analysis, a wide range of concentrations may be assessed. In treated timber, at the lower end of the range, loadings down to 0.001 % (*m*/*m*) have been determined by this method. However, at very low loadings, where little or no dilution is required, it is necessary to consider the possibility of interference from what are normally minor constituents of the system (e.g. wood extractives or solvent impurities).

The colorimetric method is suitable for the determination of PCP or PCPL in solutions or extracts from treated timber containing γ-HCH, dieldrin, tributyltin oxide (TBTO), copper naphthenate, zinc naphthenate, *di*sodium octaborate and wood extractives.

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

Caution. Attention is drawn to the general safety precautions mentioned in clause **4** of Part 1 of this British Standard and also to the specific hazard warnings given in **2.2.7**, **2.2.12** and **2.3.2** of this Part.

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2. Method I. Gas-liquid chromatographic method

2.1 Principle. PCP is extracted from treated wood with ethanol and preservative solutions containing PCP are diluted with ethanol before being methylated with diazomethane to produce pentachlorophenyl methyl ether. The resultant solutions are further diluted with hexane. γ-HCH and dieldrin are extracted from treated wood with ethanol and preservative solutions containing γ-HCH and dieldrin are diluted with ethanol before being further diluted with hexane.

Preservative solutions containing PCPL are saponified with morpholine and subsequently acidified to produce free PCP. For treated wood, the saponification is accomplished using morpholine as the extractant. The PCP is extracted into xylene and diluted with ethanol. Methylation and further dilution follow as for PCP.

The active components in all diluted solutions are determined using GLC with an electron-capture detector. Aldrin is used as an internal standard for PCP and γ-HCH, and 2,2-bis (3-chlorophenyl)-1,1-dichloroethylene (*p,p'*DDE) is similarly used for dieldrin.

2.2 Reagents. All reagents shall be of recognized analytical reagent quality and water complying with BS 3978 shall be used throughout.

Check the solvents for purity by passing samples through the chromatograph under the conditions of the determination. If a response is obtained on the chromatogram that is likely to cause significant errors in the determination on the test sample, redistil the solvent until a satisfactory response is obtained.

2.2.1 *Hexane.*

2.2.2 *Ethanol,* complying with BS 507 or *industrial methylated spirits,* complying with BS 3591*.

2.2.3 *Morpholine.*

2.2.4 *Xylene.*

2.2.5 *Hydrochloric acid,* concentrated (ρ = 1.18 g/mL).

2.2.6 *Sodium hydroxide solution,* c(NaOH) = 0.1 mol/L approximately. Dissolve 4 g of sodium hydroxide in 1 L of water.

2.2.7 *Diazomethane solution*†. Prepared as follows.

Dissolve 0.9 g of potassium hydroxide in 22 mL of ethanol (**2.2.2**) and add the solution slowly to a solution of 5 g of *N*-methyl-*N*-nitrosotoluene-4-sulphonamide in 70 mL of diethyl ether at 0 °C. Allow the resulting solution to stand for 5 min, transfer the flask containing the reaction mixture to a water bath and fit an efficient water-cooled condenser. Raise the temperature of the water bath to distil over the contents of the flask and collect the distillate in a flask cooled to below 30 °C. Continue the distillation until the reaction mixture appears colourless. The yellow distillate is an ethereal solution of diazomethane.

NOTE. Diazomethane can also be prepared from *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine and aqueous alkali. (See *Anal. Chem.*, 1973, **45**, 2302.)

Warning. Diazomethane is highly toxic and solutions may explode on contact with ground glass joints, sharp glass edges or in direct sunlight. It is imperative that all work involving diazomethane up to the final dilution is carried out behind a safety shield in an efficient fume cupboard. A diazomethane generator with smooth edges and joints throughout is commercially available and is recommended. It is essential that the preparation and use of diazomethane is carried out only by properly trained personnel.

2.2.8 *Standard aldrin solution,* 1 mg/L. Weigh 0.1000 g of aldrin into a 100 mL one-mark volumetric flask. Add approximately 50 mL of ethanol (**2.2.2**), shake well to dissolve and make up to the mark with ethanol. Dilute 5 mL of this solution to 100 mL in a one-mark volumetric flask with hexane (**2.2.1**). Shake well and similarly dilute 5 mL of this solution to 250 mL in a one-mark volumetric flask.

2.2.9 *Standard PCP solution,* 1 mg/L. Weigh 0.1000 g of PCP, 99 % pure‡, into a 100 mL one-mark volumetric flask. Add approximately 50 mL of ethanol (**2.2.2**), shake well to dissolve and make up to the mark with ethanol. Dilute 5 mL of this solution to 100 mL in a one-mark volumetric flask using the same solvent. Shake well and similarly dilute 5 mL of this solution to 250 mL in a one-mark volumetric flask.

2.2.10 *Standard γ-HCH solution,* 0.1 mg/L. Weigh 0.1250 g of γ-HCH and transfer quantitatively to a 500 mL one-mark volumetric flask, washing-in with ethanol (**2.2.2**), shake well to dissolve and make up to the mark with ethanol. Dilute 5 mL of this solution to 250 mL in a one-mark volumetric flask using hexane (**2.2.1**). Shake well and similarly dilute 5 mL of this solution to 250 mL in a one-mark volumetric flask.

2.2.11 *Standard p,p'-DDE solution,* 0.25 mg/L. Weigh 0.1250 g of *p,p'*-DDE into a 100 mL one-mark volumetric flask. Add approximately 50 mL of ethanol (**2.2.2**), shake well to dissolve and make up to the mark with ethanol. Dilute 5 mL of this solution to 250 mL with hexane (**2.2.1**) in a 250 mL one-mark volumetric flask. Shake well and similarly dilute 5 mL of this solution to 500 mL in a one-mark volumetric flask.

2.2.12 *Standard HEOD solution* (for dieldrin analysis), 0.1 mg/L. Weigh 0.1250 g of 1,2,3,4,10, 10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-exo-1,4,-endo-5,8,-dimethanonaphthalene, (HEOD)§ and transfer quantitatively to a 500 mL one-mark volumetric flask, washing in with ethanol (**2.2.2**), shake well to dissolve and make up to the mark with ethanol. Dilute 5 mL of this solution to 250 mL in a one-mark volumetric flask with hexane (**2.2.1**). Shake well and similarly dilute 5 mL of this solution to 250 mL in a one-mark volumetric flask.

Warning. All of the organochlorine compounds referred to in **2.2.8** to **2.2.12** are toxic and have to be handled with care to avoid ingestion or skin contact. *p,p'*-DDE is a suspected carcinogen.

2.3 Apparatus

2.3.1 *Volumetric glassware,* complying with the requirements for class A of BS 1583 or BS 1792, as appropriate.

2.3.2 *Electron-capture detector gas-liquid chromatograph* with the following characteristics:

(a) column temperature 170 °C;

(b) detector temperature 250 °C;

* The ethanol used as a reagent in this determination may be replaced for this purpose by industrial methylated spirits, 95 % (*V/V*), complying with BS 3591. It should be noted that the use of industrial methylated spirits is governed by the Methylated Spirits Regulations 1983 (S.I. 1983, No. 252). It is not permissible to use duty-free ethanol, received under the provisions of the Alcoholic Liquors Duties Act 1979, Section 10, for purposes for which industrial methylated spirits is an acceptable alternative to ethanol.

† For reference see A.I. Vogel *A textbook of practical organic chemistry,* p291, Longmans 1978.

‡ Technical PCP normally contains about 86 % pentachlorophenol.

§ Technical dieldrin contains a minimum of 85 % HEOD.

(c) glass-lined injector zone, with silicone rubber septum and maintained at 190 °C to 200 °C;

(d) glass column, approximately 1.5 m in length and 4 mm i.d., packed with 80-100 mesh (50 μm to 175 μm) chromosorb W AW/DMCS carrying 5 % of QF 1 and fitted with a silanized glass-wool plug at its head*;

(e) detector type, ^{63}Ni electron-capture detector, pulsed-mode or direct current type;

(f) suitable recorder.

Warning. The electron-capture detector contains radioactive material and it is essential that it is used in accordance with the manufacturer's instructions.

2.3.3 *Micro-pipette, syringe type,* suitable for accurately injecting 1 μL, and with a needle length so that on-column injection is avoided.

2.3.4 *Carrier gas,* nitrogen flowing at a rate of 75 mL/min, dried by passage through a molecular sieve before entering the column.

NOTE. An argon/methane mixture is also suitable for use with a pulsed mode detector.

2.3.5 *Soxhlet apparatus* complying with BS 2071.

2.4 Procedure

2.4.1 *Preparation of the column.* Condition the column using nitrogen as the carrier gas for about two days at a temperature of approximately 225 °C with the detector disconnected.

2.4.2 *Instrument setting and operation.* Operate the instrument in accordance with the requirements stated in **2.3.2.**

NOTE. Using these conditions the following retention times are typical of those obtained:

PCP methyl ether	1.9 min
γ-HCH	2.8 min
aldrin	3.5 min
p,p'-DDE	7.7 min
HEOD (dieldrin)	11.7 min

Changes in the oven temperature, gas flow rate and column dimensions may be made to vary the retention times according to the operator's requirements. However, it is important that complete resolution of the peaks is attained.

2.4.3 *Preparation of calibration solutions*

NOTE. The calibration solutions prepared as described in this clause are stable for limited periods only and it is recommended that working standards are freshly prepared.

2.4.3.1 *Methylation of the PCP standard solution.* Pipette 10 mL of PCP standard solution (**2.2.9**) into a 50 mL conical flask and add diazomethane solution (**2.2.7**) until the yellow colour persists. Leave for at least 2 h and, if the yellow diazomethane is still present, gently warm the solution in the fume cupboard until colourless. Transfer the solution quantitatively to a 100 mL one-mark volumetric flask and make up to the mark with hexane (**2.2.1**).

2.4.3.2 *PCP calibration solutions.* Pipette 1 mL, 2 mL, and 3 mL of the methylated standard PCP solution (**2.4.3.1**) into 10 mL one-mark volumetric flasks, add 1 mL of standard aldrin solution (**2.2.8**) (see note 1) to each and make up to the mark with hexane (**2.2.1**). These calibration solutions contain 0.01 mg/L, 0.02 mg/L and 0.03 mg/L PCP respectively.

NOTE 1. It is recommended that the same pipette should always be used for the addition of the solution used as the internal standard.

NOTE 2. These concentrations and others used in the determinations of γ-HCH and dieldrin have been found to be suitable for a pulsed-mode ^{63}Ni electron-capture detector. Instruments using direct current detectors may require the use of solutions about ten times more concentrated. It is important, however, that manufacturer's instructions regarding the maximum amount of organochlorine compounds to be injected are followed.

2.4.3.3 *γ-HCH calibration solutions.* Pipette 1 mL, 2 mL and 3 mL of standard γHCH solution (**2.2.10**) into 10 mL one-mark volumetric flasks, add 1 mL of standard aldrin solution (**2.2.8**) (see note 1 to **2.4.3.2**) to each and make up to the mark with hexane (**2.2.1**). These calibration solutions contain 0.01 mg/L, 0.02 mg/L and 0.03 mg/L γ-HCH respectively.

2.4.3.4 *HEOD calibration solutions* (for dieldrin analysis). Pipette 1 mL, 2 mL and 3 mL of standard HEOD solution (**2.2.12**) into 10 mL one-mark volumetric flasks, add to each 1 mL of standard *p,p'*-DDE solution (**2.2.11**) (see note 1 to **2.4.3.2**) and make up to the mark with hexane (**2.2.1**). These calibration solutions contain 0.01 mg/L, 0.02 mg/L and 0.03 mg/L HEOD respectively.

2.4.4 *Preparation of calibration graphs*

NOTE 1. It is important with this and all other determinations that the volumetric flasks are shaken immediately before the sample for injection is taken.

NOTE 2. It is important that the measurement of the test solution and the calibration solutions should be carried out with the same settings of the chromatograph. Treat the test solution and the calibration solutions in a single series of measurements.

2.4.4.1 *PCP or γ-HCH calibrations.* Inject 1 μL of one of the calibration solutions from **2.4.3.2** (PCP) or **2.4.3.3** (γ-HCH), as appropriate, into the chromatograph (**2.3.2**) and adjust the amplifier attenuation to obtain an aldrin peak height on the recorder chart of about 80 % full scale deflection and measure the peak height for the PCP or γ-HCH, as appropriate. Then inject, in succession, each of the remaining calibration solutions from either **2.4.3.2** or **2.4.3.3**, as appropriate, and measure the peak heights for PCP (or γ-HCH)†. Repeat the injections at least once.

Calculate the peak height ratio values‡ by expressing the peak height obtained for PCP (or γ-HCH) in each solution as a percentage of the corresponding aldrin peak height. Average the peak height ratio values for each concentration of calibration solution and plot a graph of concentration against the respective average peak height ratios for PCP (or γ-HCH).

2.4.4.2 *HEOD calibration.* Inject 1 μL of one of the calibration solutions from **2.4.3.4** into the chromatograph (**2.3.2**) and optimize the amplifier attenuation to give the best measurable peaks for *p,p'*-DDE and HEOD and measure the peak areas† for *p,p'*-DDE and HEOD. Then inject, in succession, each of the remaining calibration solutions from **2.4.3.4**. Repeat the injections at least once and measure the peak areas for *p,p'*-DDE and HEOD in each.

Calculate the peak area ratio values‡ by expressing the peak areas obtained for HEOD in each solution as a percentage of the corresponding *p,p'*-DDE peak area. Average the peak area ratio values for each concentration of calibration solution and plot a graph of concentration against the respective average peak area ratios for HEOD.

* This plug is fitted to absorb unmethylated PCP.

† For well-resolved peaks with a relatively narrow base, such as are obtained for PCP, γ-HCH, and aldrin, it is appropriate to use the peak height ratio as a means of expressing the chromatograph's response.

‡ For compounds with longer retention times, such as HEOD and *p,p'*-DDE the peaks will be broader and it is usually necessary to use peak area ratios. These can be calculated on the basis of the peak height multiplied by the peak width at half the peak height. If an integrator is being used peak areas will be obtained automatically for all compounds.