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THE DETECTION OF ORGANIC SOLVENT PRESERVATIVES IN WOOD BY THIN-LAYER CHROMATOGRAPHY

B. G. HENSHAW, J. W. W. MORGAN and N. WILLIAMS

Department of the Environment, Building Research Establishment, Princes Risborough Laboratory, Aylesbury, Bucks. HP17 9PX (Great Britain)

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SUMMARY

A simple and rapid method for the detection of common organic solvent wood preservative materials is described. The method uses thin-layer chromatography after leaching of the preservative from sections of timber with chloroform. R_F values and the sensitivity of the method are discussed and a routine procedure for identification of the organic and organometallic preservatives is proposed. Methods of achieving greater sensitivity for particular applications are also described.

INTRODUCTION

A number of thin-layer chromatographic (TLC) methods have been developed in recent years for the detection of various fungicides and insecticides in a range of matrices. Methods have been suggested for the determination of chlorinated pesticides[1–4], organophosphorus and carbamate insecticides[5,6] and organomercury fungicides[7].

Challen and Kučera[8] devised a method which was applicable to PCP, OPP, PCN, TBTO and γ-BHC*, but the limits of detection which they found (50 μg) were too high for detection of preservative in small sections of wood. They used a four hour Soxhlet extraction to dissolve the preservative, a lengthy procedure which is unsuitable for routine work. They also encountered considerable problems associated with extractives in the wood and inconsistent R_F values were obtained. Specific TLC methods for PCP, MCN and γ-BHC have been published[9].

The present paper describes a routine TLC method for the determination of the fungicides and insecticides commonly used in wood preservative formulations. Despite the plethora of commercial preservatives which are available today, the basic components of the organic and organo-metallic preservatives are relatively few. The

* Abbreviations used: BHC = benzenehexachloride; CuN = copper naphthenate; LPCP = pentachlorophenyl laurate; MCN = monochloronaphthalene; OPP = *o*-phenylphenol; PCN = polychloronaphthalene; PCP = pentachlorophenol; TBTO = tributyl tin oxide; ZnN = zinc naphthenate.

method was therefore oriented towards detection of the following ten preservative materials: PCP, OPP, LPCP, MCN, PCN, γ-BHC, dieldrin, ZnN, CuN and TBTO.

These preservatives are usually applied as solutions in hydrocarbon solvents by brushing, spraying or immersion, and in some cases by special plant (*e.g.*, double vacuum process). They are often present in small amounts located at or close to the surface of the timber to which they are applied, and methods of detection need to be sensitive and applicable to small samples. It must also be remembered that some of the chemicals used as wood preservatives are mixtures rather than pure compounds. In some cases this may lead to several spots for one ingredient, and to streaking, and it is important to compare the chromatograms with those for known materials.

Despite an exhaustive search it was found impossible to separate all ten preservatives using one solvent/plate system, and a two-plate/two-solvent system was therefore employed.

APPARATUS AND REAGENTS

Apparatus

Chromatographic tanks: Shandon Chromatanks 25 cm × 10 cm × 20 cm lined with Whatman No. 1 chromatography paper. TLC plates: Merck (Darmstadt, G.F.R.) pre-coated chromatography plates, cellulose F (0.1 mm) and silica gel 60 (0.25 mm) without fluorescent indicator. Two plate sizes (20 × 20 cm and 5 × 20 cm) were used. Disposable micro pipettes: Drummond Microcaps (1 μl and 5 μl). Spray units: Pulvérisateur Armand Vaast from Etab^{TS} Vaast (Paris, France). Ultraviolet (UV) lamp: Hanovia.

Reagents

Silver nitrate solution: 0.25 g of silver nitrate in 100 ml of 66% acetone. Catechol violet solution: 0.05 g catechol violet in 100 ml ethanol. Chrome azurol solution: 0.5 g of chrome azurol S and 5.0 g of anhydrous sodium acetate in 100 ml ethanol. Dithizone solution: 0.01 g of dithizone in 100 ml of chloroform. Brentamine solution: 0.5 g of brentamine fast red G in 100 ml of 50% acetone. Sodium acetate–carbonate solution: 12.5 g of anhydrous sodium acetate and 5 g anhydrous sodium carbonate in 100 ml water. Standard solutions: 0.5 g preservative in 100 ml chloroform (ten separate solutions, store away from direct sunlight). Developing solvent 1: cyclohexane–acetone–liquid paraffin 15:3:2. Developing solvent 2: ethyl acetate–glacial acetic acid (2:1).

NORMAL DETECTION PROCEDURE

Extraction

A chloroform extract of the wood was prepared by removal of the surface millimetre of the sample with a chisel, rasp or microtome and saturation of the shavings with analytical-reagent grade chloroform in a 50 ml beaker covered with a watch glass: the mixture was heated on a hot plate at 50° for ten minutes, care being taken that the wood remained saturated with chloroform but the volume of the extract being kept to a minimum to achieve maximum sensitivity. The extract was then allowed to cool to room temperature and divided into two portions, before application to

TABLE I

R_F VALUES

Compound	*Plate*	*Developing solvent*	R_F *values*	
			Unwashed plate	*Washed plate*
OPP	Silica gel	1	0.21	0.37
PCP	Silica gel	1	0.25	0.32
γ-BHC	Silica gel	1	0.50	0.69
Dieldrin	Silica gel	1	0.61	0.76
MCN	Silica gel	1	0.68	0.85
PCN	Silica gel	1	0.78	0.94
LPCP	Silica gel	1	0.87	0.96
TBTO	Cellulose	2	0.98	1.00
CuN	Cellulose	2	0.89	0.80
ZnN	Cellulose	2	0.75	0.30

the TLC plates. If the presence of the anti-stain agent sodium pentachlorophenate is being investigated then the extractions must be carried out using methanol.

Organic preservatives

PCP, OPP, LPCP, PCN, MCN, γ-BHC and dieldrin were separated on silica gel plates using developing solvent 1. 1–5 μl of the chloroform extract was spotted on to the start line of the chromatographic plate (2 cm from the bottom edge of the plate). 1-μl volumes of suitable standards were also spotted at 1-cm intervals along the start line. After drying in an air stream for 10 sec the plates were developed using developing solvent 1 in a Shandon Chromatank. The solvent front was allowed to travel 14–16 cm for maximum separation (approx. 1½ h). The plate was allowed to air-dry for 5 min and exposed to unfiltered UV light for 30 min. Then the plate was sprayed uniformly with silver nitrate solution and irradiated for a further period of 30 min using filtered UV light. The preservatives were then visible as dark brown spots on a light brown background. The R_F values obtained using this system are shown in Table I.

It was necessary to carry out a specific test for OPP as this compound is not made visible using the above spray reagent. If OPP was present, a purple-brown spot was observed after the first exposure period. Although this provides an identification of the compound by comparison with a standard, a confirmatory test should be applied. By spraying the immediate area of the spot with brentamine solution, a bright yellow spot is obtained which on further spraying with sodium acetate–carbonate solution after drying of the plate produces a purple spot. The use of this spray is worthwhile to avoid masking of the spot by wood extractives which travel between 1/5 and 1/4 of the distance moved by the solvent up the plate. The detection limits using this system for organic preservatives are shown in Table II. The sensitivities obtained thus are adequate for most routine determinations of preservatives in wood, but a more sensitive technique is described later.

Organometallic preservatives

TBTO, ZnN and CuN were separated on cellulose plates using developing

TABLE II

DETECTION LIMITS

Compound	*Detection limit (μg), unwashed plates*	*Detection limit (μg), washed plates*
OPP	0.70	0.40
PCP	0.06	0.025
γ-BHC	1.0	0.40
Dieldrin	0.45	0.20
MCN	0.2	0.2
PCN	0.85	0.10
LPCP	0.30	0.30
TBTO	0.04	0.015
CuN	0.07	0.03
ZnN	0.05	0.01

solvent 2. 1–5 μl of the chloroform extract was spotted on to the start line of the chromatographic plate. 1-μl volumes of suitable standards were also spotted at 1-cm intervals along the start line. After drying in an air stream the plate was developed in a Shandon Chromatank. The solvent front was allowed to travel 14–16 cm (1 h). The plate was allowed to air-dry for 5 min and exposed to unfiltered UV light for 30 min. The plate was divided into three approximately equal parts by two pencil lines parallel to the base line. The top third was sprayed with catechol violet solution. If tin was present it was visualised as a sky blue spot on a light yellow background. The central portion of the plate was sprayed either with chrome azurol S solution or with catechol violet solution to visualise the copper. Catechol violet was the most sensitive of the two reagents, but chrome azurol S solution should be used if a high concentration of tin is present in the sample. The lower portion of the plate was sprayed with dithizone solution to visualise the zinc, as a pink streak on a blue background. The R_F values obtained using this system are shown in Table I. Both copper and zinc produce a streak rather than a discrete spot presumably due to the diversity of naphthenic compounds present in commercial preparations. R_F values for the leading edge are given as an indication of position on the plate, rather than a definitive value for these two preservatives, as the R_F tends to change by up to 20% depending on the concentration and composition of the naphthenate mixtures. The detection limits obtained for the organometallic preservatives were generally better than for the organic preservatives and are shown in Table II.

Spray reagents for copper and zinc can be applied directly to treated wood but this method does not distinguish between salt and organic solvent type preservatives.

HIGHER-SENSITIVITY TECHNIQUE

The method as described so far is adequate for most routine procedures. However, in some cases greater sensitivity may be required and this can be achieved by use of a more elaborate procedure. The main factors which are significant for the improvement of sensitivity are:

(a) Use of pre-washed plates: by allowing a solution of 80% acetone to traverse the full length of the plate in a Chromatank a considerable amount of the background

colouration of the plate can be removed. The plate should be allowed to air-dry before use after washing. Removal of the impurities from the plate causes a considerable change in R_F values and the R_F values found using a washed plate are shown in Table 1.

(b) Longer irradiation time: for the organic preservatives the lengthening of the second period of exposure to UV light from 30 to 60 min improves sensitivity.

(c) Use of back-light viewer: in some cases, particularly on washed plates the use of a back-light viewer was found to improve sensitivity slightly.

(d) Use of Stahl (TAS) oven[10]: for small samples (10–15 mg) where extraction would be difficult, the use of a Stahl (TAS) oven is recommended. All the volatile preservatives can be transferred directly from sample to the plate by this procedure (but not CuN or ZnN) and direct spotting onto the plate is an obvious concentration factor. The method avoids contamination by most wood extractives but separate tests are necessary if the presence of copper or zinc naphthenates is suspected.

INTERFERENCES

Wherever possible samples should be taken from sapwood areas. The sapwood usually contains more preservative than the heartwood and causes little problem with extractives. However, identification is still adequate when heartwood samples are used. Care must be taken when paint or other finishes have been applied to the timber since these often contain both copper and zinc, but again identification is not seriously affected. Commercial preparations of PCP often contain lower chlorophenols as impurities; these will resolve themselves on the plate as a series of decreasing shadow spots directly ahead of the pentachlorophenol spot.

SCOPE OF THE METHOD

The method has been applied over a period of several years in this laboratory to a variety of timber samples. It has been found to be rapid, efficient and reproducible. The technique has been applied to the detection of anti-staining agents at very low level, and to establishing of the composition of preservative formulations.

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