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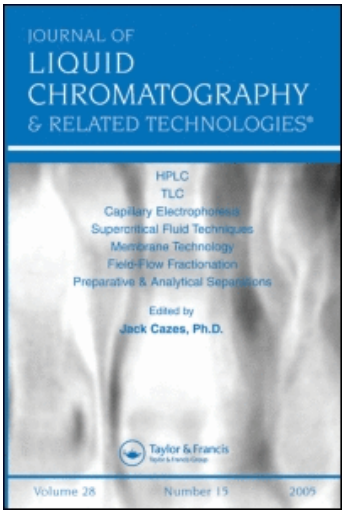

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DETERMINATION OF ORGANOCHLORINE INSECTICIDES IN WATERS BY QUANTITATIVE TLC AND C-18 SOLID PHASE EXTRACTION

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ABSTRACT

Organochlorine insecticides were extracted from water using a C-18 solid phase extraction cartridge. The concentrated pesticide residues were spotted directly for silica gel TLC separation, followed by detection with ammoniacal $AgNO_3$ solution and quantification by densitometric scanning. When removal of interfering constituents was required, the extract was chromatographed on a water-deactivated silica gel column. Recoveries of methoxychlor and p,p'-DDT were greater than 90% at fortification concentrations of 2.5 and 0.25 ppb for waters not requiring silica gel cleanup and greater than 85% when this step was included.

INTRODUCTION

In previous papers, quantitative silica gel TLC methods were reported for the determination of chlorophenoxy acid herbicides (1) and triazine herbicides (2) in potable and environmental water samples. This paper reports an extension of these studies to a series of organochlorine (OC) insecticides. Residues were

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extracted with C-18 solid phase extraction (SPE) cartridges, and extracts cleaned up, when necessary, using columns of water-deactivated silica gel. Separation was carried out on preadsorbent silica gel layers with detection by silver nitrate reagent and quantification by densitometric scanning.

EXPERIMENTAL

Standards

Pesticide standards were obtained from the EPA Pesticide Repository (Research Triangle Park, NC). Solutions were prepared in ethyl acetate at concentrations of 50, 100, and 500 ng/µl for TLC standards and 250 ng/100 µl for the spiking standard solution.

Thin layer chromatography

TLC was carried out on channeled 20 x 20 cm Analtech Uniplates containing a preadsorbent sample application strip below the analytical layer of siica gel G. Plates were pre-developed with methylene chloride-methanol (1:1) and dried before use. Pesticide standards (50-1000 ng) and SPE or cleanup column eluates were applied using a 25 µl Drummond digital mircodispenser, and plates were developed in a paper-lined, vapor saturated glass TLC chamber with hexane- methanol (9:1) or one of the other solvents listed below. Halogen- containing zones were detected on air-dried chromatograms by dipping into a 0.5% ethanolic solution of silver nitrate containing 5% concentrated ammonium hydroxide. After

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drying the plate in air, it was irradiated with a germicidal ultraviolet lamp until maximum contrast developed between the purple, grey, or brown spots and white background (10-30 minutes).

Zones were scanned with a Kontes Model 800 fiber optics densitometer in the single beam transmission mode using the 8 mm light beam across the 9 mm plate channels, and the white source phosphor (440 nm peak, 300 nm band width). Peaks were recorded and areas calculated by an attached Hewlett-Packard Model 3390A recorder/integrator. Calibration equations relating peak areas and nanograms of pesticide standards spotted were calculated with a linear regression computer program. Concentrations in samples were calculated from the calibration equation and scan areas of pesticide zones, and recoveries were determined by comparing theoretical and experimental amounts of pesticides.

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Analysis of samples

Pesticides were extracted from water samples on J. T. Baker octadecyl (C-18) 500 mg, 6 ml SPE cartridges (part number 7020-6) fitted with 75 ml reservoirs and held in a Baker-10 vacuum manifold operated at 15 inches of Hg. Cartridges were washed with 2 column volumes of ethyl acetate followed by 1 column volume each of methanol and deionized water. A glass wool plug was placed on top of the reservoir when necessary to filter any solid particles. The water sample was added to the column through the reservoir, and the column was then washed with 1 column volume of distilled water. The column was dried by drawing vacuum for 5 minutes. The cartridge was taken from the manifold and the reservoir removed,

and pesticides were eluted into a 1 ml conical sample vial with 0.5 ml of ethyl acetate, using gentle pressure from a rubber bulb. The eluate was evaporated to about 25 µl under a gentle stream of nitrogen in a 40°C water bath. The entire sample was spotted for TLC, including several 10 µl ethyl acetate rinses of the vial walls. For higher concentrations of pesticides, the eluate can be taken just to dryness, reconstituted in a known microliter volume of ethyl acetate, and an aliquot spotted on the layer.

Waters of different types were fortified by addition of 100 µl of spiking solution to 100 ml or 1 liter of water (resulting concentrations 2.5 ppb and 0.25 ppb, respectively). Blank (unfortified) samples were analyzed in parallel with spiked samples and recovery values corrected as necessary.

When required, extract cleanup was carried out on 1 g columns of activity grade I Woelm silica gel deactivated with water (1.0 ml water per 5 g of silica gel) packed in Kontes size 22 Chromaflex tubes. About 1 ml of hexane was added to the concentrated C-18 column eluate. The column was prewashed with 10 ml of hexane, the extract solution was transferred quantitatively, and the column was eluted with a total of 10 ml of hexane (including vial rinsings), collected in a 15 ml centrifuge tube. A second fraction was collected in another centrifuge tube by passing 15 ml of benzene-hexane (6:4) through the column. The fraction containing the pesticide was evaporated to near dryness, reconstituted with ethyl acetate, and applied to a TLC plate.

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Results

The organochlorine insecticides studied are shown in Table 1, along with their R_F values in the mobile phase hexane-methanol (9:1). This mobile phase provided R_F values within the range of 0.3-0.7, which is ideal for densitometry (3). The following mobile phases are useful as alternatives for possibly improved separation of any particular OC insecticide from other pesticides and matrix constituents: hexane-acetone (9:1), hexane-butanone (39:1), hexane-dioxane (49:1), cyclohexane-acetone (99:1), cyclohexane-dimethyl formamide (19:1), cyclohexane-methylene chloride (9:1), light petrolem ether-chloroform (97:3), light petroleum ether-acetic acid (19:1), hexane-methanol (99:1), and benzene-hexane (1:1).

The visual detection sensitivity of the silver nitrate/UV reagent ranged from 50 ng (e.g., for methoxychlor, lindane, endrin, and DDT) to 100 ng (for aldrin, dieldrin, and heptachlor), with a 100-200 ng limit for precise densitometric measurement. Calibration curves were generally linear (correlation coefficient >0.99) for zones containing amounts between the quantification limit and five times that level. Slope and intercept values of the calibration plots differed somewhat for each pesticide, so standards were always chromatographed together with samples on each plate.

Recovery of pesticides with the C-18 column extraction was tested using reagent grade deionized water fortified separately at a concentration of 500 ng pesticide/100 ml water (5.0 ppb). For the 12 pesticides shown in Table 1 recoveries ranged from a low of

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TABLE I

R_F Values of Organochlorine Insecticides on Silica Gel G Developed with Hexane-Methanol (9:1) Mobile Phase

Aldrin	0.69
p,p'-DDE	0.64
o,p'-DDT	0.58
p,p'-DDT	0.58
Dieldrin	0.52
Endosulfan I	0.56
Endosulfan II	0.32
Endrin	0.57
Heptachlor	0.65
Heptachlor Epoxide	0.56
Lindane	0.45
p,p'-Methoxychlor	0.49

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85% (for p,p'-DDE and aldrin) to 100% (for endrin), with an average recovery of 92%.

Methoxychlor and p,p'-DDT were used as model compounds to study recovery from samples of natural (lake, creek, river, surface, ground) water, drinking water, and industrial wastewater. C-18 column eluates from relatively pure samples, such as some natural waters, could be spotted directly without addition of a

cleanup step. Recoveries of methoxychlor and p,p'-DDT from these samples at 2.5 ppb (100 ml sample) and 0.25 ppb (1000 ml sample) were between 90 and 95%. Fortified (2.5 ppb) surface water samples were analyzed five times each, and the relative standard deviations were 7 and 9%, respectively.

Samples with more impurities, such as untreated and treated drinking water and industrial wastewater, gave chromatograms with inteferring halogen-containing zones or distorted pesticide zones. To minimize the sample co-extractives causing these anomalous chromatograms, the C-18 column eluate containing methoxychlor or p,p'-DDT was cleaned up on a water-deactivated silica gel column, as described originally for analysis of pesticides in air by Sherma and Shafik (4,5). p,p'-DDT eluted completely in the first (hexane) fraction and methyoxychlor in the benzene-hexane fraction. Average recoveries of these pesticides from duplicate fortified wastewater samples carried through the two-column system were 89 and 87%, respectively, at the 2.5 ppb level (100 ml sample) and 86 and 85% at 0.25 ppb (1000 ml sample).

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RESULTS AND DISCUSSION

Ethyl acetate proved to be the best solvent among those tested for the elution of a variety of organochlorine insecticides from the C-18 SPE cartridge, and it was also an excellent solvent from which to apply samples to TLC plates. Other eluents that gave good recovery for most of the pesticides tested were hexane-benzene

(1:1) and hexane-ethyl ether (1:1). The flow rate of water samples through the SPE column was varied between about 5 and 30 ml/min with no significant effect on recovery of the pesticides. These results were consistent with those of Junk and Richard (6) for 5 chlorinated pesticides on C-18 columns.

Both the electron capture (EC) GC detector and the $AgNO_3$ TLC reagent detect halogen-containing compounds selectively, and as a first approximation, similar cleanup is required for the two detection systems. Some compounds to which the EC detector responds, such as the ubiquitous phthalate esters, are not detected by $AgNO_3$ reagent. However, more vigorous cleanup may be required for TLC than for GC with the EC detector if streaked zones due to co-extracted material are to be avoided.

For samples requiring cleanup, the deactivated silica gel system is convenient and reliable. In addition to removing co-extracted impurities, the elution of a pesticide in a certain fraction helps confirm the identity of that residue. For cleanup of extracts for determination of methoxychlor residues, Fraction I (10 ml hexane) is discarded and the pesticide is recovered completely in Fraction II (15 ml benzene-hexane, 6:4). p,p'-DDT and many other OC pesticides are recovered completely in Fraction I, while some compounds, such as endosulfan, split between Fractions I and II. Two additional solvents are included in the silica gel cleanup system, 15 ml of acetonitrile-benzene (5:95) (Fraction III) and 15 ml of acetone-methylene chloride (Fraction IV). The more polar organochlorine pesticides, such as atrazine,

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gamma-BHC, and 2,4-D esters, are recovered in Fraction III, organophosphorus pesticides in Fractions II, III, and IV, and carbamate insecticides in II and III. Reference (5) describes the procedure in detail and the elution pattern of 87 pesticides, including 42 organochlorines, from the silica gel column. A similar silica gel column cleanup method after liquid-liquid extraction was described by Ambrus et al. (7) for the qualitative detection of pesticide residues in foods, soil, and water.

Recovery studies were performed at 2.5 and 0.25 ppb levels to demonstrate the applicability of the TLC method to real water samples. Given the TLC detection sensitivity limit of 50 ng and quantification limit of 100 ng for methoxychlor and p,p'-DDT and assuming 80% recovery, the limit of detection in 1000 ml of water is approximately 0.06 ppb for visual determination and 0.13 ppb for quantification. Detection limits are proportionately higher for those pesticides that are less sensitively visualized on the layer. If lower limits of detection are required, a method providing lower sensitivity limits, such as electron capture GC, or the ability to process larger samples must be used. If these limits of detection are adequate, the recognized advantages (8) of quantitative TLC can be realized by use of the analyses described in this paper.

The reported method uses a solid phase extraction column instead of conventional liquid-liquid extraction, as reported in some earlier TLC procedures for the determination of OC pesticides in water (e.g., reference 9). Solid phase extraction is faster and more convenient, and because it requires much less solvent, it is

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cheaper and safer. The described method has the additional advantage of being quantitative, through use of preadsorbent TLC plates and a scanning densitometer.

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