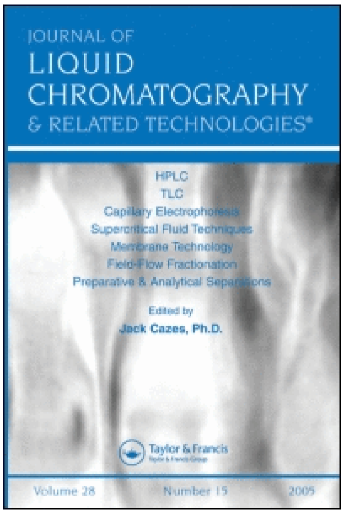

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Determination of Organophosphorus Insecticides in Water by C-18 Solid Phase Extraction and Quantitative TLC

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DETERMINATION OF ORGANOPHOSPHORUS INSECTICIDES IN WATER BY C-18 SOLID PHASE EXTRACTION AND QUANTITATIVE TLC

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ABSTRACT

Organophosphorus insecticides were extracted from water using a C-18 solid phase extraction cartridge. The concentrated extract was spotted directly for silica gel TLC separation, followed by detection with TCQ reagent and quantification by densitometric scanning. When removal of interfering coextractives was required, the extract was chromatographed on an acetic acid-conditioned silica gel column. Recoveries of ethyl parathion and azinphos-ethyl at fortification concentrations of 4 ppb and carbophenothion at 0.4 ppb were 90% or greater from waters not requiribg silica gel cleanup, and 76-93 % for ethyl parathion, diazinon, and malathion when this step was included.

INTRODUCTION

In previous papers, methods based on solid phase extraction (SPE) and quantitative silica gel TLC were reported for the determination of chlorophenoxy acid and triazine herbicides (1) and organochlorine insecticides (2) in water. Earlier TLC analyses of water for organophosphorus (OP) insececticides used conventional sequential solvent extraction methods (3,4) and were often only suitable for qualitative screening (5, 6). This paper extends the SPE/quantitative TLC methodology to a series of seven OP insecticides. C-18 SPE columns were used for extraction, preadsorbent HP silica gel layers for separation, and TCQ reagent for detection prior to densitometric scanning.

EXPERIMENTAL

Standards

Pesticide standards were obtained from the EPA Pesticide Repository (Research Triangle Park, NC), commercial suppliers, or the manufacturer. Stock standard solutions at a concentration of 1.00 mg/ml were prepared in ethyl acetate. These solutions were diluted appropriately with ethyl acetate to prepare TLC standards with a concentration of 100 ng/ul and spiking solutions at 400 ng/100 ul.

Thin layer chromatography

TLC was carried out on 10 x 20 cm Whatman LHPK laned, high performance preadsorbent silica gel plates. Standards and samples from C-18 SPE or silica gel cleanup columns were applied using a 10 ul Drummond digital microdispenser, and plates were developed in a paper-lined, vapor-saturated glass TLC tank with hexane-acetone (4:1) mobile phase. After air drying in a hood, pesticide zones were detected by dipping for 5 seconds into a 5% methanolic solution of magnesium chloride, air drying, dipping into a hexane solution of 0.3% N,2,6-trichlorobenzoquinoneimine (TCQ), and heating in an oven at 110^{o} C until maximum contrast between the red-orange spots and white plate background was achieved (10-15 minutes). Zones were scanned and calibration curves and sample concentrations determined as previously described (2).

Analysis of samples

Samples were analyzed using J.T. Baker C-18 SPE columns as previously described (2), except that the column was more thoroughly dried by drawing vacuum for 15 minutes rather than 5 minutes, and two 0.5 ml portions of ethyl acetate were used to elute pesticides from the column. Initial recovery studies were carried out by analyzing 100 ml of distilled water fortified separately with 100 ul (400 ng) of spiking solution of each pesticide (4.0 ppb). The applicability of the method to actual samples was tested by spiking surface and river water samples, which were preanalyzed and found not to contain OP pesticides, at the same concentration. Extracts requiring cleanup prior to TLC were evaporated to ca. 25 ul with a gentle stream of dry nitrogen at room temperature, dissolved in several ml of hexane, and chromatographed on a 3.5 g acetic acid-treated silica gel column eluted succesively with 20 ml each of 5% and 10% ethyl ether in hexane (7). The column fraction containing the pesticide of interest was evaporated to ca. 20 ul and spotted on the TLC plate with several ethyl acetate rinsings.

RESULTS AND DISCUSSION

The pesticides that were studied and their R_f values in hexane-acetone (4:1) mobile phase were as follow: azinphos-ethyl (0.31), diazinon (0.54), ethyl parathion (0.47), fonofos (0.62), malathion (0.33), carbophenothion (trithion) (0.63), and methyl parathion (0.38). Other mobile phases for silica gel that are useful alternatives for possibly improved separations of a particular OP pesticide from other pesticides or matrix constituents, or for confirmation of identity based on R_f values, include hexane-ethyl acetate (3:1), cyclohexane-chloroform (7:3), cyclohexane-acetone-acetonitrile (17:2:1), cyclohexane-acetone-ethanol (95:1:4), diethyl ether-methanol (3:1), and carbon tetrachloride-ethyl acetate (3:2).

The preadsorbent plates produced flat, compact pesticide zones across the lanes. The zones were detected with a red-orange color by the TCQ reagent, with sensitivity level of ca. 100 ng for visual detection and ca. 200 ng for reliable scanning. Calibration curves between 200 and 900 ng of pesticide consistently had linearity correlation coefficients of 0.98 or greater. Standards were chromatographed on each plate with samples to correct for variations in slope and intercept values of the calibration plots.

Recovery tests for the seven OP pesticides were carried out in duplicate using 100 ml of distilled water fortified at a concentration level of 4 ppb. Average recovery values ranged from 83.5% for diazinon to 96% for fonofos. The percentage difference between duplicates was no greater than 5% (relative). Samples of surface water were spiked separately at 4 ppb with ethyl parathion and azinphos-ethyl, and analysis of the C-18 column eluates gave recoveries of 95% and 91%, respectively.

Extracts of spiked samples of a local river water required cleanup using the acetic-acid treated silica gel column. Overall recoveries of ethyl parathion (fraction 1) and diazinon and malathion (fraction 2) from spiked samples were 93%, 76%, and 80%, respectively. This supplemental cleanup method is recommended for C-18 column eluates that contain co-extracted compounds that cause streaking zones or have the same R_f value as the analyte and are visualized by the TCQ reagent.

The purpose of this research was to demonstrate with a limited number of compounds and samples that the SPE/quantitative HPTLC approach can be utilized successfully for determinations of OP pesticides in waters. The method combines the convenience, speed, safety, and low solvent consumption of solid phase extraction with the simplicity, accuracy, precision, and high sample throughput of preadsorbent quantitative HPTLC. Other pesticides that chromatograph successfully on silica gel and react with TCQ reagent, and can most likely be determined in water as described above, include mecarbam, ethion, fenthion, fensulfothion, and phorate. Other detection reagents that could be used as alternatives for densitometric quantification or confirmation of residue identity based on zone color include 2,6-dibromoquinone-4-chlorimide (Gibbs' reagent), 4-(4-nitrobenzyl)pyridine, and palladium chloride (8).

Samples containing a high concentration of impurities that can be co-extracted on the SPE column, such as certain river and industrial wastewater samples, require cleanup prior to TLC. The method involving acid-treated alumina was successful for our river water sample. Extracts from less impure samples, such as ground, surface, pond, lake, and tap water, can be often be analyzed directly. To test extraction efficiency at a lower concentration, 1 liter of tap water spiked with 400 ng (0.4 ppb) of carbophenpthion was passed through the C-18 column. Recovery was found to be 90%, and coextractives did not interfere with the analysis. Reports in the literature indicate that as much as 10 liters of some water samples have been analyzed successfully for certain analytes by SPE, but concentrations this low were not tested in the present study.

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