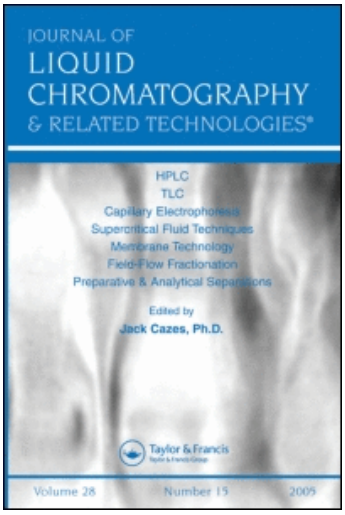

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Determination of Carbamate Insecticides in Water by C-18 Solid Phase Extraction and Quantitative HPTLC

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DETERMINATION OF CARBAMATE INSECTICIDES IN WATER BY C-18 SOLID PHASE EXTRACTION AND QUANTITATIVE HPTLC

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ABSTRACT

N-Methylcarbamate insecticides were extracted from water using solid phase extraction with a C-18 column. The column eluate was chromatographed on a high performance preadsorbent silica gel plate, the pesticides were detected with p-nitrobenzenediazonium fluoborate reagent, and quantification was performed by densitometric scanning. Recoveries of carbaryl, carbofuran, methiocarb, and propoxur at 0.5 to 5 ppm fortification concentrations averaged 96.8% with a range of 82.5 to 112% and an average standard deviation of 7.5% for triplicate determinations.

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), organochlorine insecticides (2), and organophosphorus insecticides (3). Earlier TLC analyses of water for N-methylcarbamate insecticides used conventional sequential solvent extraction methods (4) and were often based on visual estimation of spot area (5). This paper extends the SPE/quantitative TLC methodology to

four N-methylcarbamate insecticides. C-18 SPE columns were used for extraction, preadsorbent high performance silica gel layers for separation, and p-nitrobenzenediazonium fluoborate reagent for detection prior to densitometric scanning.

EXPERIMENTAL

Standards

Standards of carbaryl (Sevin), carbofuran (Furadan), methiocarb (Mesurol), and propoxur (Baygon) were obtained from the EPA Pesticide and Industrial Chemicals Repository (Las Vegas, NV). Individual stock standard solutions were prepared with concentrations of 5.00 mg/ml in ethyl acetate. These solutions were diluted 1:50 with ethyl acetate to prepare TLC standards with concentrations of 100 ng/ul. Stock solutions were stored in a freezer and TLC standards in a refrigerator when not in use.

Thin Layer Chromatography

TLC was carried out on 10 x 10 cm Whatman LHPKDF laned, high performance preadsorbent silica gel plates. Standards and samples from the C-18 SPE column were applied to the preadsorbent using a Drummond (Broomall, PA) digital microdispenser, and plates were developed for a distance of 7 cm beyond the preadsorbent in a paper-lined, vapor saturated Camag (Wilmington, NC) HPTLC twin-trough chamber with toluene-acetone (4:1) for carbaryl, carbofuran, and methiocarb or hexane-acetone-chloroform (75:15:10) for propoxur. After drying with warm air from a hair drier for ca. 5 min., pesticide zones were detected by dipping the plate into 1.0 M KOH in methanol held in a Desaga (Whatman, Clifton, NJ) dipping chamber, drying again with the hair drier, and dipping into freshly prepared chromogenic reagent, prepared by dissolving 25 mg of p-

nitrobenzenediazonium fluoborate in 90 ml of acetone plus 10 ml of diethylene glycol (4). Zone areas were measured by scanning with a Shimadzu (Columbia, MD) CS-930 densitometer in the single beam, reflectance mode at the wavelength of maximum absorption for each compound, as determined from the in situ spectra recorded between 400 and 700 nm with the spectral mode of the densitometer. Percent recovery was determined by comparing the areas of samples with standards representing 100% recovery.

Analysis of Samples

Samples were analyzed by use of J.T. Baker (Phillipsburg, NJ) 6 ml Bakerbond light loaded octadecyl SPE columns (no. 7189-07) and a J.T. Baker glass manifold no. 7018-00 operated with a vacuum of 15-20 mm of mercury to produce a flow rate of ca. 8 ml/min.. Each column was prewashed with two column volumes of ethyl acetate, one of methanol, and one of deionized water. The manifold stopcock below the column was adjusted to prevent the column from becoming dry during or after the conditioning stages. Sample was added through a 75 ml plastic reservoir attached to the column, followed by 1 column volume of deionized water. The column was dried by drawing vacuum for 15 minutes, and removed from the manifold. Pesticides were eluted into a 4 or 5 ml graduated vial with a tapered bottom by forcing 2 ml of ethyl acetate through the column with gentle pressure from a rubber bulb. The vial was placed in a 30-50°C water bath, and the ethyl acetate was evaporated within 10 min. by a flow of nitrogen gas. The residue was reconstituted in 2.00 ml of ethyl acetate, and three 2.00 ul aliquots of sample (representing 500 ng if recovery is 100%) and three 5.00 ul aliquots of standard (containing 500 ug of pesticide) were spotted

for TLC. The averages of the two closest standard and sample areas were compared to calculate percent recovery.

Initial recovery studies were carried out by analyzing deionized water fortified with the pesticides, and the applicability of the method to a real sample was tested by spiking a pond water sample that was preanalyzed and found not to contain any of the carbamate pesticides. Water was fortified at concentration levels of 5.00, 2.00, 1.00, and 0.50 ug/ml (ppm) by adding 100 ul of the stock pesticide solution (500 ug) from a 100 ul Drummond digital microdispenser to 100, 250, 500, and 1000 ml, respectively.

RESULTS AND DISCUSSION

Carbaryl, carbofuran and methiocarb appeared as flat, compact bands with respective R_f values of 0.55, 0.49, and 0.52 in toluene-acetone (4:1), while the propoxur band had a value of 0.30 in hexane-acetone-chloroform (75:15:10). Visible zone colors and wavelengths of maximum absorption from in situ spectra were as follow: carbaryl-blue, 610 nm; carbofuran and propoxur-purple, 550 nm; and methiocarb-pink, 510 nm. The plate background ranged from white to pale yellow. The variation in R_f values and zone colors aid in identifying unknown carbamates.

Aliquots of 3.00, 5.00, and 7.00 ul of carbaryl standard solution (containing 300, 500, and 700 ng) were spotted and developed, and the calibration equation of scan area versus weight, calculated using a linear regression program on a personal computer, had a linear regression coefficient of 0.999. This relationship permitted the use of a quantification method for determination of recovery based on area comparison between samples

and standards within this linear range on each plate. Areas of duplicate aliquots typically agreed within 3-5%. Plates were normally scanned immediately after zone detection. They could be stored if wrapped in aluminum foil, but colors faded within a few hours if exposed to light. To quantify unknown samples, apply extract samples and standards in the range of 1.00-10.0 ul on each plate, and compare the areas of the sample and standard zones that compare most closely, preferably within +/-25%.

Ethyl acetate was found to be a superior eluting solvent for a range of pesticides by Junk and Richard (6). The ethyl acetate column eluate contained 0.1 to 0.3 ml of water as a second phase. This water remained in the vial after nitrogen blowdown and reconstitution but was of no concern. Water could not be completely eliminated by prolonged vacuum drying nor by passing hexane through the column prior to the ethyl acetate eluent.

Recovery tests for the four carbamates in deionized water were carried out in triplicate. Respective average percent recovery values for carbaryl, carbofuran, methiocarb, and propoxur were 99.2, 97.1, 82.5, and 100.6 at 5 ppm and 96.5, 90.3, 94.6, and 112 at 2 ppm. Recovery of carbaryl at 1 ppm averaged 99.4%, and at 0.5 ppm 95.5%. Standard deviations ranged from 2.0 to 12%, with a mean of 7.5%. These recovery and precision values are acceptable for trace residue analysis at the low ppm level (7).

Separate 250 ml samples of pond water from a local farm, which was shown to contain no carbamate pesticides by prior analysis, were spiked with 1 ppm of carbaryl and carbofuran and analyzed in duplicate by the SPE/HPTLC method. Recoveries averaged 95.0 and 91.5 %, respectively. There were no interfering zones detected in the chromatograms of this sample. The selectivity of the detection

reagent was further demonstrated by chromatographing the related pesticides BPMC (fenocarb), aminocarb, aldicarb, and methomyl. None of these compounds was detected at the at the 1 ug level.

The purpose of this research was to demonstrate with a limited number of pesticides and samples that the SPE/HPTLC approach can be utilized successfully for determination of carbamate insecticides in water samples. Extraction efficiency, accuracy, and precision are adequate for routine use in water analysis. The method combines the convenience and low solvent consumption of SPE with the simplicity and high sample throughput of preadsorbent quantitative HPTLC. It will be applicable to the analysis of any water sample not containing co-extractable impurities that interfere with the chromatography, detection, or scanning of the analyte. It can be used to analyze lower concentrations of pesticides by passing greater volumes of water through the SPE column.

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