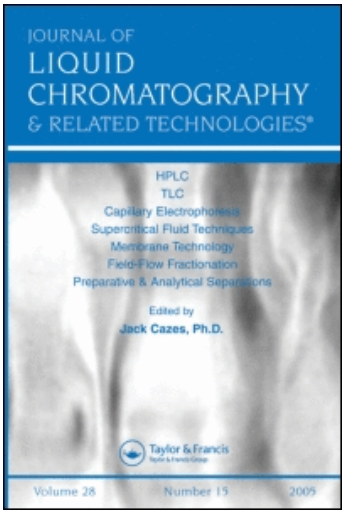

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Determination of Pentachlorophenol and Cymiazole in Water and Honey by C-18 Solid Phase Extraction and Quantitative HPTLC

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DETERMINATION OF PENTACHLOROPHENOL AND CYMIAZOLE IN WATER AND HONEY BY C-18 SOLID PHASE EXTRACTION AND QUANTITATIVE HPTLC

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ABSTRACT

Pentachlorophenol and cymiazole were extracted from water and honey using C-18 solid phase extraction, column eluates were chromatographed on a high performance preadsorbent silica gel plate containing a fluorescent phosphor, and the pesticides were quantified by densitometric scanning of fluorescence quenching. Recoveries from water at concentrations of 0.25-5 ppm ranged from 97.7 to 100% for PCP and 89.5-94.9 for cymiazole. Recoveries from honey at 10 and 50 ppm ranged from 94.0-96.1% for PCP and 91.9-93.7 for cymiazole.

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), organophosphorus insecticides (3), and carbamate insecticides

(4) in environmental water samples. Pentachlorophenol (PCP) is a widely used fungicide and molluscicide that is employed as a wood preservative in beehives, while cymiazole is an acaricide that is applied to the control of a honeybee parasitic mite among other applications. Because of the possibility of contamination of honey in apiculture as well as drinking and environmental waters through other uses of these pesticides, methods are needed for residue analysis. Previously published determinations of PCP in water involved conventional solvent extraction combined GC/MS (5), while PCP was determined in honey by C-18 SPE and GC/MS (6). The determination of the acaricide cymiazole in honey was reported using hexane extraction and HPLC (7). Methods have not been published for TLC analysis of water for these pesticides, nor for the solid phase extraction of cymiazole. This paper extends the SPE/quantitative TLC methodology to the determination of PCP and cymiazole in water and honey, using C-18 SPE columns for extraction, preadsorbent high performance silica gel plates for separation, and densitometric scanning of quenched zones for quantification.

EXPERIMENTAL

Standards

Standard PCP was obtained from the EPA Pesticide and Industrial Chemicals Repository (Las Vegas, NV) and standard cymiazole was supplied by Ciba-Geigy AG, Muenchwilen, Switzerland. Stock standard solutions were prepared with

concentrations of 5.00 mg/ml and were diluted 1:50 to prepare TLC standards with concentrations of 100 ng/ul. Toluene was the solvent used for PCP solutions and acetonitrile for cymiazole.

Thin Layer Chromatography

TLC was carried out on 10 x 10 cm Whatman laned, high performance preadsorbent silica gel plates with fluorescent indicator (catalog no. 4806-711) that were precleaned by development with methylene chloride-methanol (1:1) before use. Standards and samples from the SPE column were applied to the preadsorbent using a 10 ul Drummond digital microdispenser, and plates were developed in a Camag twin-trough chamber as described earlier (4) with toluene-methanol (9:1) for PCP or hexane-acetone-methanol-glacial acetic acid (35:10:5:0.1) for cymiazole. Pesticide zones were detected, after drying the mobile phase with warm air from a hair drier for 5 min, by fluorescence quenching under 254 nm UV light in a viewing box. Zone areas were measured by scanning with a Shimadzu CS-930 densitometer in the single beam, reflectance mode at 215 nm for PCP or 265 nm for cymiazole. Percent recovery was calculated by comparing the areas of samples with standards representing 100% recovery.

Analysis of Samples

Samples were analyzed by use of Supelco 6 ml solid phase extraction tubes containing 1 g C-18 sorbent (catalog no. 5-7055) and a J.T. Baker glass manifold no. 7018-00 that was

generally operated as described earlier (4). The flow rate of sample through the columns was 8-10 ml/min, and columns were dried by drawing vacuum for 10-15 min before elution of the pesticides into a graduated vial. For determination of PCP, water samples were initially adjusted to pH 2 with concentrated HCl and honey samples were dissolved in acidified water (10 g of honey per 100 ml of water containing 0.4 ml of 4 M HCl), the sample container and column reservoir were rinsed with pH 2 water, the column was washed with two column volumes of water after passing the sample and before drying, and PCP was eluted with two 3 ml portions of methanol using gentle pressure from a rubber bulb. For determination of cymiazole, water was initially adjusted to pH 9 with 1 M NaOH and honey was dissolved in pH 9 water (10 g per 100 ml), the sample container and column reservoir were rinsed with pH 9 water, the column was washed with 2 column volumes of pH 9 water after passing the sample and before drying, and cymiazole was eluted with two 3 ml portions of hexane. Eluates were evaporated just to dryness under nitrogen in a water bath at 40° C and reconstituted in 2.00 ml of the eluting solvent. Vacuum drying did not remove all of the water from the column, and 0.1 to 0.3 ml of water was eluted with the organic solvent and remained in the vial after drying under nitrogen. This water did not interfere with subsequent TLC analysis of the reconstituted samples. Two 2.00 ul aliquots of sample (representing 500 ng of pesticide if recovery is 100%) and two 5.00 ul aliquot of the TLC standard (containing 500 ng of pesticide) were spotted on each plate, and the average sample

and standard areas were compared to determine percent recovery.

Initial SPE recovery studies were carried out by analyzing deionized water spiked with the pesticides, and then the method was extended to spiked river water and honey samples that were preanalyzed and found not to contain either pesticide. Water was fortified at concentration levels of 5.00, 1.00, 0.50, and 0.25 ug/ml (ppm) by adding 100 ul of stock pesticide solution (500 ug) to 100, 500, 1000, and 2000 ml, respectively. Honey was fortified at 50.0 and 10.0 ppm by spiking 10.0 and 50.0 g samples with 100 ul of pesticide stock solution.

RESULTS AND DISCUSSION

PCP and cymiazole formed compact bands with R_f values of 0.52 and 0.64 in their respective mobile phases described above. The sensitivity of detection of each pesticide was ca. 200 ng by fluorescence quenching under 254 nm UV light. Calibration curves relating zone area and weight spotted between 300 and 500 ng typically had linear regression coefficients of ca. 0.98, which permitted the reliable determination of recovery based on area comparison between samples and a single standard within this linear range spotted on each plate.

Samples containing PCP were adjusted to pH 2 so that the acid was unionized and would be retained by the C-18 column. Samples to be analyzed for cymiazole were alkalinized to pH

9 because its solubility in aqueous solutions is reduced and extraction into hexane is quantitative at this pH (7).

Recovery tests for the pesticides from spiked deionized water were carried out in duplicate at various concentrations, and percent recoveries of PCP were 99.5 and 98.5 at 5 ppm, 98.3 and 98.8 at 1 ppm, 97.7 and 100.0 at 0.5 ppm, and 98.0 and 99.5 at 0.25 ppm. Percent recoveries of cymiazole from deionized water were 93.8 and 94.4 at 5 ppm, 91.5 and 92.8 at 1 ppm, 89.5 and 91.6 at 0.5 ppm, and 90.9 and 92.6 at 0.25 ppm. Water from a local river was spiked at 0.5 ppm, and the recoveries for duplicate analyses by the SPE/TLC method were 98.4 and 99.2 for PCP and 93.3 and 94.9 for cymiazole. There were no zones detected by fluorescence quenching in the chromatograms of these samples that interfered with the scanning of the analyte zones. Spiked honey samples were analyzed in duplicate and respective recoveries were 95.4 and 96.1% for PCP and 91.9 and 92.4% for cymiazole at 50.0 ppm, and 94.0 and 95.5% for PCP and 92.1 and 93.7% for cymiazole at 10.0 ppm. Again, no interfering zones were present in sample chromatograms.

The recovery and repeatability data presented above for spiked samples demonstrate that the SPE/HPTLC approach can be successfully applied for routine analyses of PCP and cymiazole in water and honey samples at the concentration levels specified. Recoveries of both compounds from water were at least 89% for all concentrations tested. Recoveries of PCP from honey were in the same range as reported earlier by Sep-Pak SPE and GC/MS (6). Recoveries of cymiazole from honey were

somewhat lower than by conventional solvent extraction and HPLC (7) but were acceptable (>90%) considering the advantages of SPE. The SPE/HPTLC 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 any water or honey samples not containing co-extractable impurities that interfere with the chromatography, detection, or scanning of the pesticide analytes. The limits of determination can be lowered by passing more sample through the SPE column, reconstituting the column eluate with a smaller volume of solvent and/or spotting a larger aliquot of sample, or scanning zones containing weights of analyte close to the 300 ng lower end of the calibration curve.

REFERENCES

1. J. Sherma, J. Liq. Chromatogr. 9, 3423 (1986)

2. J. Sherma, J. Liq. Chromatogr. 11, 2121 (1988)

3. J. Sherma and W. Bretschneider, J. Liq. Chromatogr. 13, 1983 (1990)

4. S.C. McGinnis and J. Sherma, J. Liq. Chromatogr. 17, 151 (1994)

5. M.A. Fernandez Muino, J. Simal Gandara, and J. Simal Lozano, Chromatographia 32, 238 (1991)

6. M.A. Fernandez Muino and J. Simal Lozano, Anal. Chim. Acta 247, 121 (1991)

7. P. Cabras, M. Melis, and L. Spanedda, J. AOAC Int. 76, 92 (1993)

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