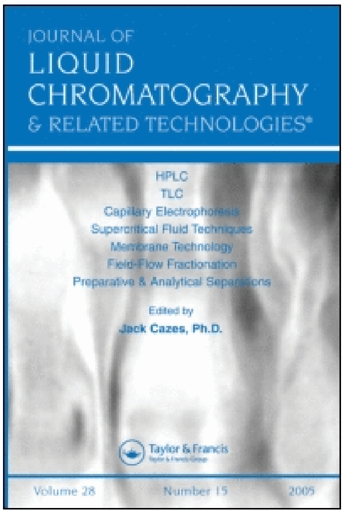

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Determination of Triazine and Chlorophenoxy Acid Herbicides in Natural Water Samples By Solid Phase Extraction and Quantitative Thin Layer Chromatography

Joseph Sherma[a]
[a] Department of Chemistry, Lafayette College, Easton, Pennsylvania

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DETERMINATION OF TRIAZINE AND CHLOROPHENOXY ACID HERBICIDES IN NATURAL WATER SAMPLES BY SOLID PHASE EXTRACTION AND QUANTITATIVE THIN LAYER CHROMATOGRAPHY

Joseph Sherma
Department of Chemistry
Lafayette College
Easton, Pennsylvania 18042

ABSTRACT

Atrazine, simazine, 2,4-D, silvex, and 2,4,5-T, were determined in natural water samples at 10 ppb levels by solid phase extraction on disposable C_{18} columns and TLC on preadsorbent silica gel layers impregnated with $AgNO_3$, exposure to UV light, and densitometric scanning. Recoveries ranged from 70 to 88% for the triazines and 93 to 100% for chlorphenoxy acid herbicides, with average CV values of 7 to 8%. Solid phase extraction proved to be an advantageous alternative to classical liquid-liquid partition for the analysis of water for these compounds by quantitative TLC.

INTRODUCTION

In earlier papers, determinations of triazine (1) and chlorophenoxy acid (2) herbicides in natural water samples were reported using liquid-liquid partitioning in a separatory funnel followed by

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silica gel TLC, detection with silver nitrate reagent, and quantification by scanning densitometry. The present paper describes procedures for the extraction and concentration of these pesticides on disposable columns containing C_{18} bonded silica gel. Analyses using solid phase extraction were much simpler and faster and had adequate recovery and precision for routine residue screening.

EXPERIMENTAL

TLC was carried out on Analtech silica gel GF plates containing a preadsorbent spotting area and 19 scored lanes using procedures already described (1,2). Sample and standard solutions were applied with a 25 μl Drummond Dialamatic micropipet (1). Plates were preimpregnated with ammoniacal silver nitrate reagent prior to spotting, and the herbicides were detected by exposure to UV light. Zones were scanned with a Kontes Chromaflex densitometer, and the amounts of pesticides in samples were interpolated from calibration lines relating peak areas to weights of standards spotted along with samples on the same plate.

Analysis was carried out using J. T. Baker 6 ml C_{18} extraction columns in combination with the Baker-10 solid phase extraction (SPE) vacuum manifold apparatus. Columns were prewashed with two column volumes of reagent-grade methanol followed by two column volumes of distilled water. Samples of local creek, river, and pond water (250 ml), fortified separately with the triazine herbicides atrazine and simazine at a concentration of 10 ppb, were passed through 75 ml reservoirs into the columns at a flow rate of ca. 25 ml per minute. Each column was washed with distilled water, dried by drawing vacuum for 5 minutes, and the herbicide then eluted into a 4 ml screw-top vial by passing three one-ml portions of methanol through the column with gentle pressure from a pipet bulb rather than vacuum. The solution in the vial was evaporated just to dryness under a gentle stream of nitrogen on a warm hotplate. The residue was dissolved in 100 µl of chloroform, and duplicate 20 µl aliquots (equivalent to 500 ng for 100% recovery) were chromatographed adjacent to 300 ng, 500 ng, and 700 ng amounts of the appropriate standard with chloroform-acetone (9:1) as the mobile phase. Recoveries were calculated as already described (1).

Analyses of 250 ml water samples fortified separately with the chlorophenoxy acid herbicides 2,4-D, silvex, and 2,4,5-T at 10 ppb were performed in a similar manner. Water samples were acidified to pH 2 with conc. HCl, and herbicides were eluted with three one-ml portions of methanol. The columns were preconditioned with acidified water and methanol, and were washed with acidified water after passing the samples through. The TLC mobile phase was hexane-glacial acetic acid-diethyl ether (72:30:18) (2). Other steps in the procedure for solid-phase extraction and TLC were as described above for the triazines.

RESULTS AND DISCUSSION

Solid phase extraction proved to be an attractive alternative to classical liquid-liquid partition for the isolation and concentration of triazine and chlorophenoxy acid herbicides from natural waters prior to quantitative TLC determination as reported earlier (1,2). Analyses were much faster, multiple samples were easily processed at one time, and a considerable savings in solvent usage resulted. Eluates were suitable for direct analysis by densitometry after detection with silver nitrate reagent for all water samples. Chromatograms were free of interfering spots in the vicinity of the herbicides spiked into the samples. Additional zones noted in some of the sample chromatograms above or below the pesticide zones were proven by blank runs to be caused by interferences that were co-extracted from the water samples rather than impurities present in the column packing itself.

Recoveries by solid phase extraction were found to be adequate for residue analysis although they were somewhat lower than those obtained earlier by conventional extraction. Recoveries of atrazine from creek, river, and pond water averaged 78.3, 80.4, and 85.0, respectively, for triplicate determinations, while results for simazine were 87.9, 70.5, and 75.5%. Coefficients of variation ranged from 5.5 to 13%, with a mean of 8.5%, Recoveries of 2,4-D, silvex, and 2,4,5-T in creek, river, and pond water averaged between 92.6 and 99.7% in all cases (triplicate determinations), with CV values averaging 7.4%.

Recoveries and reproducibilities obtained for a limited number of experiments with C_8 columns in place of C_{18} were very similar. These results differed from two earlier studies in which C_8 columns were somewhat superior compared to C_{18} for determinations of chlorinated insecticides (3) and neutral pollutants such as phthalates (4). There appears to be no reason why a C_{18} packing should sorb organics less strongly than C_8, and it is likely that lower recovery on a C_{18} column may be due to incomplete elution.

Water samples that were collected were clear enough not to require filtration. If necessary, residual particulates can be removed from water samples by placing a 6 ml Baker filtration column and adaptor between the extraction column and the reservoir. Recovery studies using a filtration column proved that its presence in the system did not lower the recovery of simazine or 2,4-D from fortified creek water.

The water samples used in this study did not require additional cleanup in order to produce chromatograms that were clean enough to allow reliable identification and quantification of the herbicides present. It is likely that other water types will require solvent partitioning (2) or column adsorption (1) purification of extracts prior to TLC. Even so, the use of solid phase cartridges as described above is the preferred first step for extraction and concentration of these herbicides.

The TLC determinative procedures, densitometric scans, and calibration curves were essentially the same as reported and illustrated in our earlier papers (1,2). Silver nitrate detection reagent can be incorporated in the layer prior to chromatography as done here, or it can be applied by spraying or dipping after TLC development (5). An advantage of TLC for determination of chlorophenoxy acid herbicides is that the usual derivatization step prior to gas chromatography (6) is not required.

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