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SOLID PHASE SAMPLE COLLECTION FOR THE ANALYSIS OF ALDICARB RESIDUES IN GROUNDWATER

by

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ABSTRACT

A new sample collection/preparation technique for the analysis of aldicarb residues in groundwater, using Supelco C-8 reverse phase cartridges, was developed. The method significantly reduces shipping costs and allows the conservation of samples for several months. It also serves as a sample preconcentration technique improving detection limits over the direct analysis method while retaining the advantages of automation.

RÉSUMÉ

Pour l'analyse des résidus d'aldicarbe des eaux souterraines, on a mis au point une nouvelle technique de prélèvement et de préparation des échantillons dans laquelle on utilise des cartouches à inversion de phase Supelco C-8. Avec cette méthode, les frais de transport sont réduits dans une mesure significative et les échantillons peuvent se conserver plusieurs mois. De plus, comme les échantillons sont pré-concentrés, les limites de détection sont meilleures que celles de la technique d'analyse directe et ce, avec tous les avantages de l'automatisation.

MANAGEMENT PERSPECTIVE

This paper describes a method for sample collection and presentation for the analysis of aldicarb residues in groundwater. It offers two main advantages: the reduction of shipping costs and problems, because currently samples have to be shipped frozen; and the automation of the analytical method, reducing direct laboratory costs. Water samples are concentrated on a small (3 mL) cartridge in the field, and then can be shipped in an envelope, since the pesticide is immobilized on the adsorbent, which simplifies the compliance to the Transport of Hazardous Materials Act.

PERSPECTIVE - GESTION

Dans cet article, on décrit une méthode de prélèvement et de préparation des échantillons qui peut servir dans l'analyse des résidus d'aldicarbe des eaux souterraines. Cette méthode présente deux grands avantages : le transport des échantillons est moins coûteux et pose moins de problèmes qu'avec les méthodes actuellement employées où les échantillons doivent être congelés; de plus, la technique d'analyse est automatisée, ce qui abaisse les frais directement liés au traitement en laboratoire. On concentre les échantillons d'eau sur le terrain au moyen d'une petite cartouche (3 mL), après quoi on peut les expédier dans une enveloppe, car le pesticide est retenu sur l'élément adsorbant; il est ainsi plus simple de se conformer à la réglementation concernant le transport des produits dangereux.

INTRODUCTION

The requirement for the analysis of a large number of samples for aldicarb toxic residues (sum of aldicarb, aldicarb sulfone and aldicarb sulfoxide) has arisen because of groundwater contamination in several agricultural areas (Long Island, Florida, Prince Edward Island, Canada) (1,2). This has led to the investigation of a sample collection and preservation technique that would be simple and inexpensive. At the moment, the recommended method of preservation is freezing (3), which is difficult as samples have to be shipped to the laboratories, often several hundred miles away. Not only is this expensive, but samples often thaw in transit, requiring resampling. Also, as drinking water guidelines are becoming more restrictive, the need for lower detection limits has become apparent. A sample collection technique that would allow for sample preconcentration would thus be highly desirable.

The use of solid phase sample collection system was therefore investigated, as it could not only serve as a convenient sample collecting and shipping device, but would allow the use of an automated analytical system.

EXPERIMENTAL

Solid phase extraction cartridges were obtained from Waters/Millipore (C-18 Sep-Pak) and from Supelco Canada Ltd. (LC-8, 1 mL and 3 mL cartridges).

Cartridges were prepared by eluting with 2 mL of methanol followed by 5 mL of distilled water. The samples (10 to 20 mLs) were loaded dropwise using a Supelco sample reservoir held onto a vacuum flask and evacuated with a hand-held vacuum pump. Alternately, the water could be drawn with a Luer tip syringe attached to the cartridge with a small piece of tubing. In the field, the cartridge was simply wrapped in aluminum foil for shipping in a cooler. Field samples were collected from a series of monitoring wells situated in an agricultural field where aldicarb had been applied.

Just prior to analysis, the cartridge was dried with a stream of pressurized air for 1 min., and then eluted sequentially with 0.4 mL of acetonitrile followed by 1.1 mL of 0.01 M HCL into an autosampler vial.

The HPLC analysis was done with a Spectra-Physics 8100 automated liquid chromatograph and a Kratos FS 950 fluorescence detector. The post-column derivatization system was as described by Krause (4). The analytical column was a Spherisorb ODS, 10 µm particles, 25 cm x 4.6 mm i.d., injection volume 250 µL. The eluting solvent was 28% acetonitrile, 72% water at 1.0 mL/min.

RESULTS AND DISCUSSION

In situ sample preconcentration for aldicarb, its sulfone and sulfoxide, has been demonstrated by Chaput (5). His method involved sample preconcentration on a 3 cm column installed in the loop

position of the injector, which is done manually using an external pump, since HPLC autosamplers are not generally designed to handle large (10 mL) volumes. Because of the large number of samples requiring aldicarb residue analysis, automation is essential.

The investigation was initiated using the C-18 Sep-Pak cartridges, but the results were disappointing as the recoveries of aldicarb sulfoxide (ASO) and sulfone (ASO_2) were 35 and 50% respectively for a 10 mL sample fortified at the 10 µg/L level. The lower retention of the sulfoxide could presumably be attributed to its higher solubility in water (43 g/L vs 7.8 g/L) (6). It was then decided to evaluate C-8 material since it had been found suitable for on-line preconcentration (5).

The initial experiment was carried out using the 1 mL cartridges available from Supelco and yielded recoveries of 60 and 73% for ASO and ASO_2. It was slightly lower than what had been reported by Chaput (5), but rather encouraging considering the difference in particle size (40 µm vs. 10 µm).

Since the eluting solvent organic strength cannot exceed that of the chromatographic system for proper separation, the strongest eluent that could be used was 28% acetonitrile. The eluting strength could be enhanced, however, by eluting the cartridge sequentially with 0.4 mL of acetonitrile and allowing it to equilibrate for one minute and then with 1.1 mL of 0.01M HCl, rather than doing a single elution with the premixed solvent. The analysis was done isocratically which was a distinct improvement over the previous methods, since they use

solvent programming which require extra time to get the system to reequilibrate. A typical chromatogram obtained at detection limit (1 µg/L) is shown in Figure 1.

The results obtained at three fortification levels are listed in Table 1. The levels were chosen to reflect current drinking water guidelines (9 µg/L total toxic residue). The replicates were from three separate cartridges and not triplicate analysis of the same elution. The response was linear for all three analytes (r values listed in Table 1) with the intercept going through the origin.

This sampling system was tried in the field where samples were collected in the normal manner, and using a cartridge; the results are listed in Table 2. No parent aldicarb data were available for comparison since none of the samples contained any. The samples were analysed using both the method of Chaput (5) which carries an inherent correction for recoveries because the standards are preconcentrated in the same manner as the samples, and by this method, by which cartridges are eluted first and the eluate analysed against a standard that was made up in mobile phase, but had not been passed through a cartridge, and is thus affected by recoveries.

The stability of the samples adsorbed to the cartridges was assessed. A second group of cartridges was analysed eight months after collection. The sample cartridges were simply kept in aluminum foil wrapping in a coldroom at 7°. The results are listed in Table 3. Most of the samples were at detection limit (1 µg/L), and the discrepancies between the on-line trace enrichment and the

cartridge methods were within the expected error for each method.

The aqueous samples were analysed within two weeks of collection, whereas the cartridges were stored. These results indicate that the samples can be kept for several months without significantly affecting the analytical results even at levels very close to detection limit.

CONCLUSION

The use of solid phase sample collection offers many advantages over the existing techniques. It greatly reduces shipping costs, provides a stable means of sample storage, allows up to a 20 fold concentration of the sample thus improving detection limit, is inexpensive and easily automated. Isocratic analysis also reduces analysis time.

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Table 1. Triplicate Analysis of Spiked Water Samples

Spiking Level	ASO	ASO_2	Aldicarb
1 µg/L	0.7 ± 0.2	0.8 ± 0.3	0.9 ± 0.5
5 µg/L	3.3 ± 0.4	3.4 ± 0.4	3.0 ± 0.5
10 µg/L	5.9 ± 0.5	6.4 ± 0.9	5.2 ± 0.9
r	1.0002	1.0001	0.997

Table 2. Comparison of Field Samples Using Solid-Phase Trace Enrichment vs. On-line Trace Enrichment

Sample	ASO		ASO_2	
	On-line	Cartridge	On-line	Cartridge
1	1.7	-	5.2	2.4
Duplicate	a	-		2.4
2	--	--	3.7	2.5
3	4.2	3.1	10.8	5.3
Duplicate	a	3.1		5.9
4	--	--	0.9	1.3

-- non detected
a duplicates available for cartridge only

Table 3. Effect of Sample Storage on C-8 Cartridges

Sample	ASO		ASO_2	
	On-line	Cartridge	On-line	Cartridge
1	0.8	1.4	0.7	1.2
2	0.6	1.4	0.5	1.3
3	0.5	1.0	0.9	1.3
4	0.7	1.0	0.7	1.5
5	2.4	1.7	3.5	2.1
6	1.5	0.9	2.2	0.9

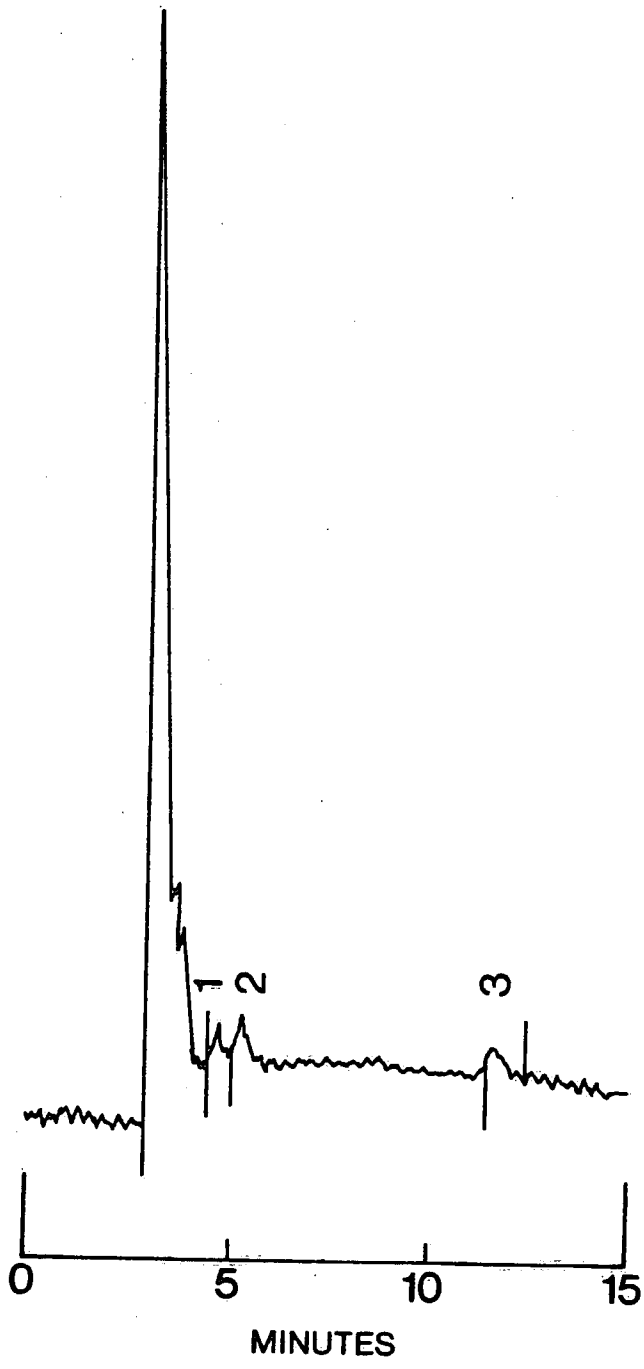

Figure 1. Chromatogram of water spiked with 1 µg/L of: (1) aldicarb sulfoxide; (2) aldicarb sulfone and (3) aldicarb. Concentration factor 10X, 250 µL injected.