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Note

Rapid two-step preconcentration procedure for Aldicarb determination in water by high-performance liquid chromatography using a 254-nm detector

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Quantitative determination of the food crop protectant carbamate pesticide Aldicarb at trace levels has been usually carried out by gas chromatography or by high-performance liquid chromatography (HPLC) following derivatization or prior oxidation of Aldicarb to its sulfone, respectively[1–6]. Recently Aldicarb and environmental metabolites of Aldicarb were found in Long Island ground water at concentrations exceeding the New York State Department of Health permitted level of 7 ppb*: in 1981 the Suffolk County Department of Health Services reported a mean concentration of 23.5 ppb in over 2000 wells drawing from the polluted aquifer[7]. (Some wells in three other states also contained low concentrations of Aldicarb.)

A simple analytical procedure was desired for use in a study of the feasibility and efficiency of a point-of-use water detoxification method currently being investigated by Janauer and co-workers[8,9] and for potential use in analysing drinking water directly for Aldicarb. The procedure described in this paper is straightforward and convenient. It offers good precision in the low ppb concentration range as demonstrated with Aldicarb-spiked tap water.

EXPERIMENTAL

Reagents

Aldicarb standards were obtained from the U.S. Environmental Protection Agency and from Union Carbide Corporation. HPLC-grade methanol was purchased from J. T. Baker. Water for dilutions was prepared by passing it through a Barnstead purification system consisting of an organic-removal (D8904), a high-capacity (D8901), and an ultra-pure mixed column (D8902). The mobile phase for HPLC was prepared using the above solvents and analytical grade acetic acid and

The third set of solutions prepared by dilution of standards 1000:1 and re-

* Throughout this article, the American billion (10^9) is meant.

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sodium acetate. Ordinary local tap water (≈40 ppm hardness, low in chlorinated hydrocarbons) was used for spiking as is. C_{18} SEP-PAK cartridges (Waters Assoc.) used in this investigation were all pretreated by passing through 5 ml of HPLC-grade methanol followed by an equal volume of pure water (see above).

Equipment and procedures

Analyses were performed using a Waters Model 6000A pump, a Model 440 absorbance detector, and a μBondapak C_{18} column. In most experiments the eluting solvent was methanol–water (25:75) with a small amount of acetic acid (4%) added to the solvent mixture. Flow-rate in HPLC runs was usually 1.0 ml/min. Peak heights (or areas) were used to quantify Aldicarb. Weighings were made on a Perkin-Elmer AD-2 digital balance. Delivery of samples was effected utilizing a custom-built peristaltic pump driven by an Integrand microcomputer so that precise flow-rates and volumes could be easily selected.

Preliminary HPLC experiments were performed to ascertain that detection and linearity could be achieved with aqueous solutions of A at the 1–30 ppm level. Chromatograms obtained were then used as standards for determining preconcentration efficiencies for low ppb level solutions.

Aldicarb stock solutions were prepared by weighing 0.5 mg Aldicarb to the nearest 0.1 μg into a 5-ml volumetric flask and diluting with methanol. Further dilutions with methanol were made as necessary to obtain standards with a range of concentrations from 1 ppm to 30 ppm. Three more sets of solution standards were prepared in order to check the individual and overall effectiveness of preconcentration steps. The original 1–30 ppm solutions were diluted 10:1 with methanol, and 100:1 and 1000:1 with water, respectively. Preconcentration was effected as follows: 200-ml aliquots of the 100:1 and 1000:1 dilutions were passed through C_{18} Sep-Paks and eluted with 2.00 ml of methanol. The 100:1 dilutions were analysed directly by HPLC using 25-μl injections. Eluates from the 1000:1 dilutions were concentrated further in micro Kuderna-Danish evaporators under a gentle stream of dried and filtered air. The 10:1 dilutions in methanol were evaporated directly before analysis. One drop of ethylene glycol was always added before evaporation.

RESULTS AND DISCUSSION

An extraction efficiency study was completed in which 50–500 ml aliquots of 100:1 dilution standards with a concentration of Aldicarb of 0.256 ppm were concentrated using Waters C_{18} Sep-Paks. Results of these experiments showed that excellent efficiencies are achieved with sample aliquots of 100–250 ml (Table I). These volumes gave directly a preconcentration factor of about 100, allowing analysis of samples down to the 10-ppb range. The standard sample volume of 200 ml used in all later work was chosen well within the limits of optimum retention of Aldicarb on the Sep-Paks under the conditions employed, and so as to ensure complete Aldicarb elution by 2 ml of methanol (a very convenient volume for the solvent evaporation step).

It may be worthwhile to mention also that the solvent pretreatment procedure for Sep-Paks (see Reagents) gave excellent reproducibilities —both in terms of preconcentration efficiency and in ensuring freedom from background trace impurities—

TABLE I

ALDICARB PRECONCENTRATION EFFICIENCY BY 100:1 EXTRACTION ON C_{18} SEP-PAKs

Triplicate experiments. Starting concentration was 0.258 ppm.

Volume (ml)	*Efficiency*				
	I	*II*	*III*	*Mean*	*Standard deviation*
50	0.94	0.95	1.08	0.99	0.08
100	1.00	0.95	1.03	0.99	0.04
150	0.99	0.95	1.05	1.00	0.05
200	0.99	0.99	0.98	0.99	0.01
250	0.96	0.93	0.97	0.95	0.02
300	0.85	0.86	0.85	0.85	0.01
350	0.55	0.55	0.83	0.64	0.16
400	0.72	0.66	0.68	0.69	0.03
450	0.55	0.68	0.64	0.62	0.07
500	0.57	0.52	0.62	0.57	0.05

with cartridges having the same *and* different lot numbers. Indeed it was found that the cartridges could be reused, again and again, as long as the solvent pretreatment was repeated in between runs. In this connection it may also be recalled that Sep-Paks have been applied successfully in the concentration of a variety of chemicals, *e.g.*, aromatic nitro compounds[10].

Aldicarb recovery efficiencies were determined by comparing chromatograms from diluted or spiked samples with results of HPLC runs obtained with standard solutions ranging from 1 ppm to 30 ppm initial Aldicarb concentrations. Fig. 1 shows a typical chromatogram for 18 ppm of Aldicarb, representative of many others obtained in the ppm range.

Preconcentration of the 10:1 dilution in methanol by evaporation with dry air (Kuderna-Danish, see Experimental) showed that enrichment by a factor of 10:1 could be accomplished with $\geqslant 90\%$ yields (Table II).

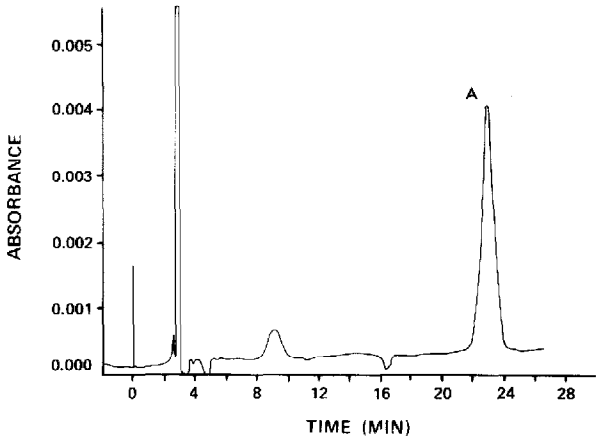

Fig. 1. Direct HPLC analysis of 18 ppm Aldicarb (A) (0.01 a.u.f.s.). Solvent: methanol–water (25:75) containing 4% acetic acid.

TABLE II

ALDICARB PRECONCENTRATION EFFICIENCY (% RECOVERY) BY 10:1 SOLVENT EVAPORATION

Starting concentration was 0.60 ppm Aldicarb. Ethylene glycol added before solvent evaporation in experiments represented in last column.

Trial series	*Nitrogen*	*Air*	*Air (ethylene glycol)*
1	93.4	40.0	93.6
2	92.3	74.0	96.1
3		81.9	94.0
4		75.2	92.8

concentrated by the same factor (using Sep-Paks plus the solvent evaporation step) gave recoveries of about 100% with good precision (Table III). The actual chromatogram of an 18 ppm solution concentrated from 18 ppb shows complete agreement (Figs. 1 and 2) with respect to the main peak (A), and no significant differences otherwise. Quite generally, chromatograms before and after preconcentration exhibited near perfect correlation.

TABLE III

OVERALL ALDICARB RECOVERY BY TWO-STEP PRECONCENTRATION PROCEDURE (1000:1)

Initial concentration (ppb)	*Per cent recovery in replicate analyses*	*Mean (%)*	*Standard deviation (%)*
10	104, 95, 114, 95, 97	101	8
6	101, 107, 104	104	3
6	100, 100, 97, 86, 101	97	6
3	120, 109, 111, 120	115	6

Figs. 3 and 4 show typical chromatograms of reconcentrates from 5 ppb Aldicarb-spiked pure water (see Experimental) and a sample of local tap water, respectively. Binghamton tap water is supplied from the Susquehanna River. It can be expected to have the following values for quality parameters (which will vary with the season): a hardness of 50–70 ppm, pH of 7.4–8.3, 0.1–0.2 ppm free Cl_2, ≈ 2 ppm chloride, ≈ 2 ppm dissolved oxygen, ≈ 2 ppm biological oxygen demand, and 2–3 ppm total organic carbon. Trihalomethanes were between 12 ppb (summer) and 55 ppb (winter).

Peaks due to unidentified impurities present in the tap water (and not removed by the Sep-Pak) never interfered with nor obscured the Aldicarb peak even at 0.005 a.u.f.s. (Fig. 4 is representative of a number of runs with tap water at different times).

The shorter retention times for Aldicarb (Figs. 3 and 4) are due mainly to the higher methanol content of the eluent (35%). Various different eluting mixtures were tried and further time savings found with other solvents/compositions. However, the elutrient mixture used in these experiments will ensure good resolution in the presence of impurities expected in tap or well waters.

In conclusion, it can be said that a fast and reliable analytical procedure for the

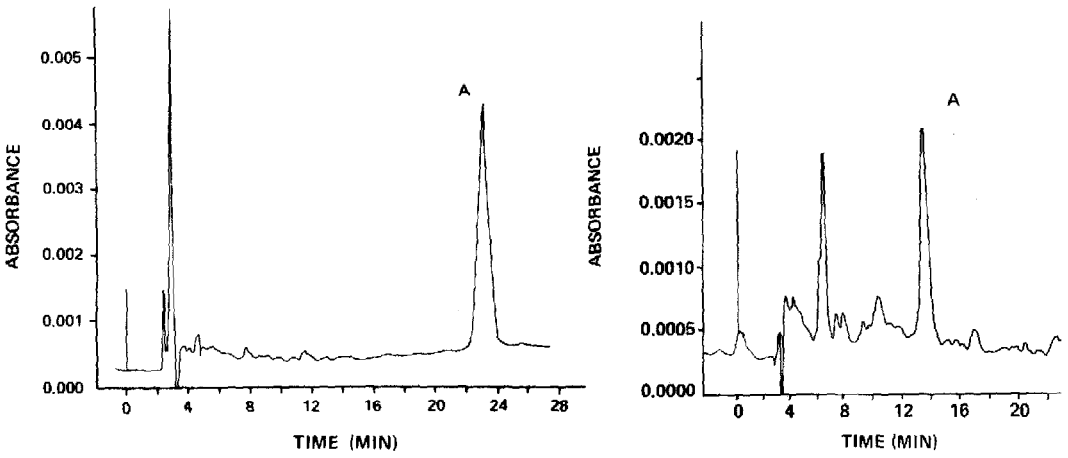

Fig. 2. Analysis of 18 ppb Aldicarb (A) by HPLC following 1000:1, two-step concentration (0.01 a.u.f.s.). Solvent as in Fig. 1.

Fig. 3. Analysis of 5 ppb Aldicarb (A) by HPLC following 1000-fold reconcentration (0.005 a.u.f.s.). Solvent: methanol–water (35:65) containing 1 % acetic acid– sodium acetate buffer.

direct determination of low Aldicarb concentrations in water has been developed. By combining HPLC with simple preconcentration steps, one can quickly determine if a drinking water is safe or requires treatment. The procedure may be extended to the quantitation of the environmental metabolites of Aldicarb and to other carbamate pesticides by the use of smaller particle sizes in column packings, by employing a more sensitive detector, and, possibly, by varying the eluting solvent to provide a spectral "window" at the lower wavelengths where the oxidation products of Aldicarb absorb strongly. The method has the advantage of not requiring bulk extraction or cleanup of water samples and requires but simple equipment.

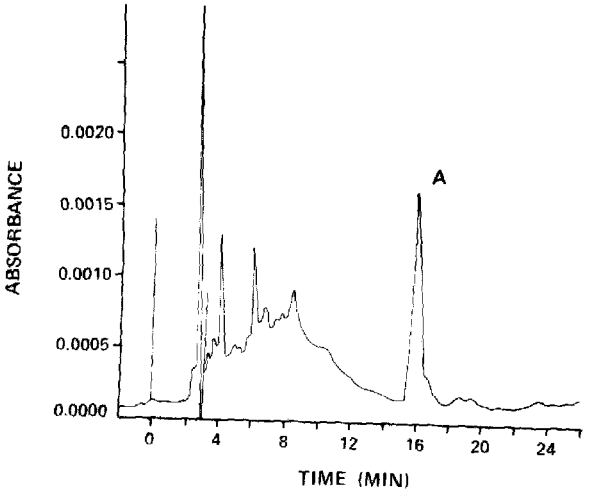

Fig. 4. Analysis of 5 ppb Aldicarb (A) by HPLC in reconcentrate (1000:1) from spiked Binghamton tap water (0.005 a.u.f.s.). Solvent as in Fig. 3.

ACKNOWLEDGEMENTS

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