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Note

Determination of aldicarb and its derivatives in groundwater by high-performance liquid chromatography with UV detection

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Aldicarb (2-methyl-2(methylthio)propionaldehyde O-(methylcarbamoyl)oxime, marketed as Temik®) is a toxic pesticide widely used in Florida on citrus, potato, and peanut crops to control nematodes. It is highly soluble in water (6000 ppm, w/w[1]). In soil, it is oxidized to aldicarb sulfoxide and aldicarb sulfone[1,2]. Due to the porous nature of Florida's soils, these compounds have been detected in groundwater. As a result of the heavy usage of this pesticide, we felt it necessary to predict the fate of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in the Floridan Aquifer using groundwater microcosms in the laboratory. Since each of these carbamoyl oximes degrades to the corresponding oximes and nitriles, we required an analytical method that could rapidly identify and quantitate these nine compounds in aqueous samples at low concentrations.

Several methods have been developed for analysis of aldicarb and degradation products in environmental samples but most have been developed for aldicarb, aldicarb sulfoxide, and aldicarb sulfone (often called total toxic residue, TTR)[2–14]. Gas chromatogrpahic procedures are difficult because (a) many of these compounds are thermally unstable, (b) samples must be extracted and treated before analysis, and (c) speciation of the TTR requires an additional liquid chromatographic clean-up step[2–7]. Trehy *et al.*[5] reported a gas chromatographic–mass spectrometric method that is rapid and sensitive for aldicarb, aldicarb oxime, and aldicarb nitrile, but did not include aldicarb sulfoxide, aldicarb sulfone, and their oximes and nitriles. Thin-layer chromatography is also a very useful technique for monitoring pesticide degradation but usually requires radiolabelled compounds for sensitive detection[9].

High-performance liquid chromatography (HPLC) offers a simple and rapid method for determination of aldicarb and its derivatives. HPLC with post-column reaction and fluorescence detection is a widely accepted method for the determination of very low concentrations of aldicarb, aldicarb sulfoxide, and aldicarb sulfone (all carbamoyl oximes)[9,10]. Although this technique is sensitive and selective for these compounds, it does not respond to the non-carbamoyl oxime derivatives such as the oximes and nitriles. HPLC with mass spectrometric detection is also a sensitive method that provides qualitative as well as quantitative information, but the high cost of this instrumentation precludes its use for routine analysis[11].

HPLC with UV detection has been used for the determination of aldicarb in vegetation but crop interferences limited its usefulness[12]. Cochrane *et al.*[13] used

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HPLC with UV detection for the determination of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in water down to levels as low as 1 μg/l but solvent extraction (1-l sample) and silica gel clean-up were employed before HPLC analysis. Since we investigated groundwater that was low in organic matter, we chose to evaluate HPLC with UV detection for groundwater analysis. We present here a method that allows rapid and precise determination of aldicarb and several of its derivatives in groundwater down to the μg/l or nanogram level without sample pretreatment.

EXPERIMENTAL

UV spectra were recorded on a Perkin-Elmer Model 552 UV–VIS spectrophotometer with a Perkin-Elmer/Hitachi Model 057 *x–y* recorder. Matched quartz cuvettes and acetonitrile (HPLC grade, Fisher) allowed spectra to be scanned from 190 to 300 nm. All analytical separations were performed with a Perkin-Elmer Series 2 solvent delivery system (1.0 ml/min), Rheodyne Model 7125 injector (200-μl loop), DuPont Zorbax C_8 column (5 μm, 15 × 0.4 cm I.D.), a Perkin-Elmer LC 100 column oven maintained at 30°C, and a Perkin-Elmer LC 75 variable-wavelength UV detector (set at 200 nm). A strip chart recorder (Fisher Recordall) was used to measure peak heights. The heights of external standards were compared with those of the unknowns.

Mobile phase was prepared from acetonitrile and water that was obtained from a laboratory reagent water system (Millipore Milli-Q). Phosphate buffer was prepared from analytical grade phosphate salts (Fisher). Aldicarb, aldicarb sulfone, aldicarb oxime, and aldicarb sulfoxide oxime were obtained from USEPA (Research Triangle Park, NC, U.S.A.). Aldicarb sulfone oxime, aldicarb sulfone nitrile, aldicarb sulfoxide, and aldicarb sulfoxide nitrile were provided by Union Carbide. Aldicarb nitrile was synthesized by Trehy *et al.*[5]. Groundwater was obtained from the raw water intake line of the Murphree Water Treatment Plant in Gainesville, FL, U.S.A. and limestone was collected from an outcrop of the Floridan Aquifer in Ocala, FL, U.S.A.

RESULTS AND DISCUSSION

UV spectra of aldicarb and its derivatives showed the maximum absorption wavelengths to range from 197 to 203 nm with the exception of aldicarb sulfone nitrile (see Table I). Thus a wavelength of 200 nm was chosen for maximum sensitivity of a mixture of these compounds. The wavelength maxima for aldicarb, aldicarb sulfoxide, and aldicarb sulfone compare well with a similar study performed by Sparacino and Hines[14]. They also reported extinction coefficients of 40,800, 27,900, and 11,000 for aldicarb, aldicarb sulfoxide, and aldicarb sulfone at their respective wavelength maxima and noted that the extinction coefficients were about 2 to 3 orders of magnitude larger than the corresponding coefficients at 254 nm or 280 nm. Therefore UV absorption offers a sensitive mode of detection of these compounds provided that interferences are minimal.

Initially, we screened the experimental groundwater for interferences and found no significant peaks that co-eluted with any of the standards. This was fortuitous since most organics and many inorganics absorb strongly in the low UV

TABLE I

UV ABSORPTION MAXIMA (190–300 nm) FOR ALDICARB AND DERIVATIVES

Compound	*Maximum wavelength (nm)*	*Secondary peak (nm)*
Aldicarb	193	247
Aldicarb sulfoxide	195	245
Aldicarb sulfone	201	–
Aldicarb oxime	192	238
Aldicarb sulfoxide oxime	202	238
Aldicarb sulfone oxime	203	–
Aldicarb nitrile	195	236
Aldicarb sulfoxide nitrile	200	223
Aldicarb sulfone nitrile	< 190	–

region. Apparently, most of the potential interferences in Floridan Aquifer groundwater were very polar and eluted at or near the void volume of the column.

Aldicarb and many of its derivatives can be readily separated by reversed-phase HPLC[10]. A chromatogram of four aldicarb derivatives separated isocratically with a mobile phase of acetonitrile–water (12:88) on a Zorbax octyl (C_8) stationary phase is shown in Fig. 1a. Aldicarb sulfone nitrile is also well resolved within 8 min but aldicarb sulfone oxime is only partially resolved from aldicarb sulfoxide. In the groundwater experiments, aldicarb sulfoxide and aldicarb sulfone oxime were not present concurrently, so no improvement in separation was necessary. At one point in our experiments, a mobile phase consisting of acetonitrile–0.02 *M* phosphate buffer pH 7 (12:88) was used to prevent column damage as a result of injecting alkaline samples. No significant change in retention times was observed from that shown in Fig. 1a. Cochrane and Lanouette[12] found that using acetonitrile–water as the mobile phase resulted in non-reproducible retention times for aldicarb sulfoxide on a C_{18} column. Conversely, we observed very reproducible retention times for all compounds studied. This difference could be the result of the different types of stationary phases or the complete coverage of silica on the Zorbax column by end-capping. Cochrane and Lanouette[12] also found that a pH change from 7.6 to 8.4 affected retention of aldicarb sulfoxide on a C_{18} column. Therefore, changes in pH or electrolyte composition offer possible routes to complete resolution of these compounds.

With the acetonitrile–water (12:88) mobile phase, aldicarb, aldicarb oxime, and aldicarb nitrile were retained too long for reasonable analysis times (*ca.* 1 h). With a higher percentage of acetonitrile (40%), these three compounds could be easily separated within 8 min (see Fig. 1b), but the other derivatives eluted too early to be resolved. Obviously the solution to this problem of complete separation in a single run is gradient elution HPLC, but the lack of this capability in our laboratory at the time of this work required us to perform two separate isocratic runs. Nevertheless, when experimental goals and column re-equilibration time are considered as a part of the total analysis time, the two isocratic runs approached the efficiency of a solvent-programmed run.

Standard curves for the the compounds tested were linear over the range exam-

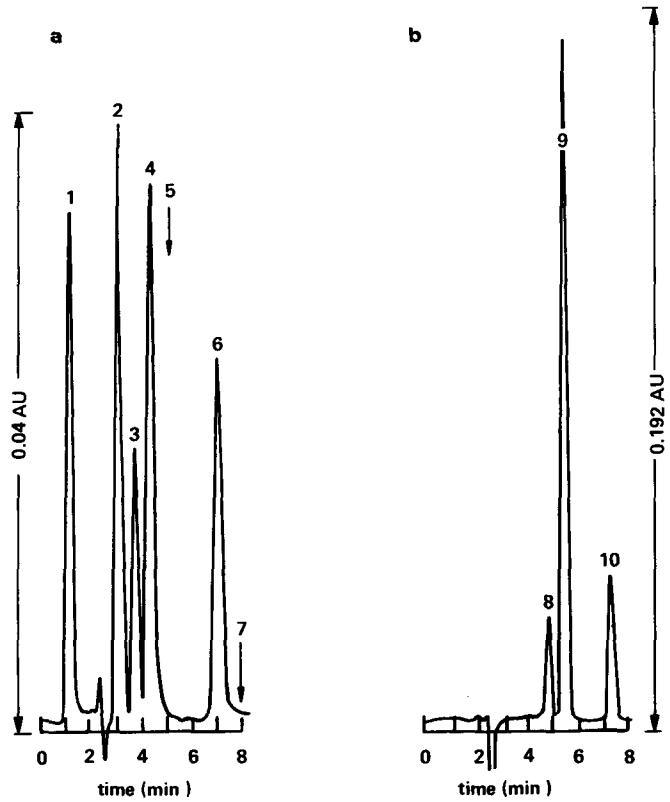

Fig. 1. Liquid chromatograms of standard mixtures of aldicarb and its derivatives analyzed under the following conditions. Detection, UV (200 nm); column, 15 × 0.4 cm I.D., 5-μm C_8 Zorbax (30°C); mobile phase, (a) acetonitrile–water (12:88), (b) acetonitrile–water (40:60); flow-rate, 1.0 ml/min. Peaks: 1 = unknown; 2 = aldicarb sulfoxide oxime (150 ng); 3 = aldicarb sulfoxide nitrile (220 ng), 4 = aldicarb sulfoxide (200 ng); 5 = aldicarb sulfone oxime; 6 = aldicarb sulfone (200 ng); 7 = aldicarb sulfone nitrile; 8 = aldicarb oxime (64 ng); 9 = aldicarb (500 ng); 10 = aldicarb nitrile (590 ng).

ined and squares of the correlation coefficients (r^2) for four-point standard curves were very good (see Table II). Limits of detection [signal-to-noise ratio (S/N) = 5] for the three carbamoyl oximes and their oximes were approximately 10 μg/l or 2 ng each. The nitriles were relatively poor chromophores at 200 nm and subsequently had higher detection limits. Detection of aldicarb sulfone nitrile can be vastly improved by decreasing the wavelength of detection but increased absorption of interferences and mobile phase limit the usefulness of this modification. Also, lower detection limits for many of the compounds studied could be improved by sample concentration with either solvent extraction[13] or adsorption to solids such as XAD resins.

Since we could detect concentrations down to about 10 μg/l, we started our degradation experiments at about 2 mg/l to be able to observe at least a 100-fold change in concentrations and work in a region of higher precision. A typical chromatogram of groundwater samples spiked with aldicarb sulfoxide shortly after fortification and 19 days later is shown in Fig. 2. Hydrolysis of the sulfoxide to the

TABLE II

LINEARITY OF STANDARD CURVES AND DETECTION LIMITS FOR ALDICARB AND ITS DERIVATIVES

Compound	*Range* (mg/l)*	r^2	*Limits of detection***	
			µg/l	*ng*
Aldicarb	0.36–2.49	0.9998	6	1.2
Aldicarb sulfoxide	0.20–2.00	0.9999	11	2.2
Aldicarb sulfone	0.25–2.50	0.9996	10	2.0
Aldicarb oxime	0.032–0.32	0.9991	5	1.0
Aldicarb sulfoxide oxime	0.038–0.38	0.9975	6	1.2
Aldicarb sulfone oxime	0.078–0.78	0.9970	9	1.8
Aldicarb nitrile			31	6.1
Aldicarb sulfoxide nitrile	0.22–2.20	0.9999	20	4.0
Aldicarb sulfone nitrile			6600	1300

* Four-point standard curves.
** S/N = 5.

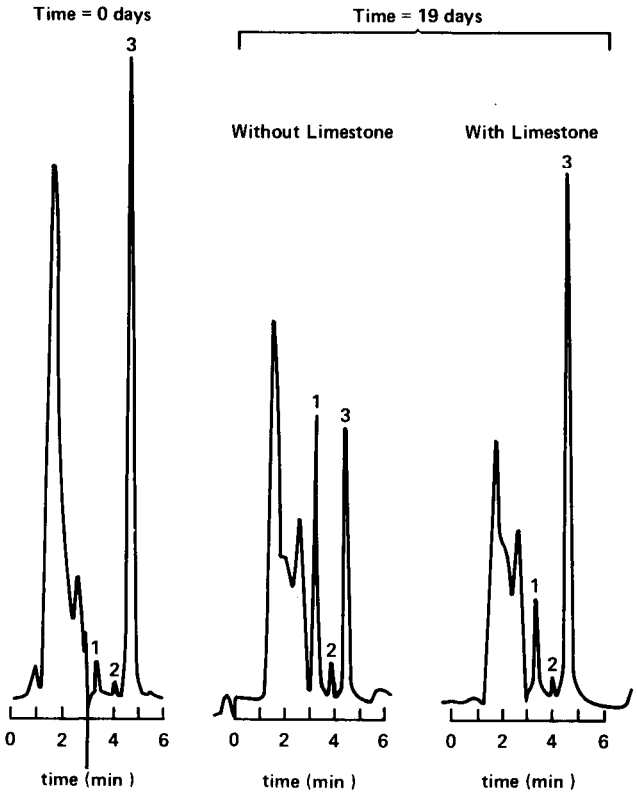

Fig. 2. Liquid chromatograms of aerobic groundwater microcosms (pH 8.5, 20°C) spiked with aldicarb sulfoxide (peak 3) showing degradation to sulfoxide oxime (peak 1) and sulfoxide nitrile (peak 2).

oxime was observed by following both the decrease in sulfoxide concentration and a subsequent increase in the oxime level. No sample preparation was necessary prior to injection which increased the precision of this determination over other methods where extraction or other sample preparation steps can cause spurious results. The simplicity, speed, and sensitivity of this method has allowed us to collect kinetic data for hydrolysis reaction with half-lives on the order of 30 min. We have performed degradation experiments with each of these carbamoyl oximes in groundwater microcosms under both aerobic and anaerobic conditions, with and without limestone (limestone was added to simulate aquifer conditions), and in the presence and absence of the native microorganisms. The results of these experiments will be reported elsewhere.

In conclusion, we have demonstrated that reversed-phase HPLC with UV detection is a useful method for the rapid determination of aldicarb and its derivatives in aqueous samples down to the μg/l or nanogram level. Two isocratic runs were used to separate all the aldicarb compounds in a reasonable time, although solvent programming could decrease total analysis time. No sample pretreatment was necessary which allowed rapid and precise measurements of degradation of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in groundwater microcosms.

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