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GAS–LIQUID CHROMATOGRAPHIC DETERMINATION OF ALDICARB, ALDICARB SULFOXIDE AND ALDICARB SULFONE IN SOILS AND WATER USING A HALL ELECTROLYTIC CONDUCTIVITY DETECTOR

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SUMMARY

A method is described for the determination of individual components of toxic aldicarb residues (aldicarb sulfoxide and aldicarb sulfone) in water and soils using a gas chromatographic method with the Hall electrolytic conductivity detector.

Aldicarb and its metabolites were extracted from water by chloroform and from soils by water–acetone and water–methanol mixtures. They were separated on a Florisil column and identified by GLC after conversion into aldicarb sulfone by peracetic acid oxidation.

The sensitivity of the method is *ca.* 0.05 ppm of aldicarb.

INTRODUCTION

Aldicarb, 2-methyl-2-(methylthio)propionaldehyde-O-(methylcarbamoyl) oxime, is a systemic insecticide manufactured by Union Carbide, under code U.C. 21149 and the trade mark Temik®.

Aldicarb was previously shown[1,2] to be metabolized in soils, plants and insects to aldicarb sulfoxide, aldicarb sulfone, aldicarb oxime, aldicarb sulfoxide oxime, aldicarb sulfone oxime and some other derivatives not fully identified yet. However, aldicarb, its sulfoxide and its sulfone are known to be the most toxic of these compounds. Aldicarb sulfoxide is a potent cholinesterase inhibitor and is responsible for the high systemic activity and the long-term persistence of the insecticidal activity in soil[1,3]. It was therefore interesting to develop a method for determining aldicarb and its toxic metabolites in soils and water.

In outline, the method consists of the simultaneous extraction of aldicarb and its metabolites from water with chloroform and from soils with water–acetone and water–methanol mixtures. The metabolites are separated on a Florisil column with diethyl ether–acetone mixtures and identified using a gas–liquid chromatographic (GLC) procedure and the Hall electrolytic conductivity detector. This detector is especially suited for the analysis of trace organic compounds containing chlorine, nitrogen or sulfur.

Because the retention times of aldicarb, aldicarb sulfoxide and solvent are very close, both compounds were identified as aldicarb sulfone after quantitative conversion by peracetic acid oxidation.

Fig. 1 shows the three oxidation states of aldicarb.

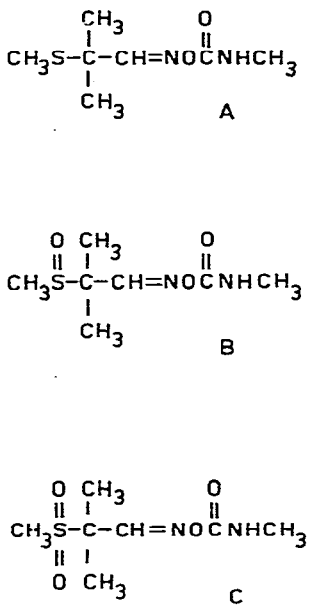

Fig. 1. The three oxidation states of aldicarb: (A) aldicarb, (B) aldicarb sulfoxide, (C) aldicarb sulfone.

EXPERIMENTAL

Reagents

All solvents were of chromatographic grade or for residue analysis and were checked by GLC before use. Aldicarb and its metabolites were kindly supplied by Union Carbide (New York, N.Y., U.S.A.). The 2.5-m nickel wire catalyst, wrapped in a 4-cm long bundle, and the strontium hydroxide-coated fiberfrax were supplied by Tracor (Austin, Texas, U.S.A.). Thiazafluron [1,3-dimethyl-1-(5-trifluoromethyl-1, 3,4-thiadiazol-2-yl)urea], used as internal standard, was from Ciba-Geigy (Basle, Switzerland).

Solvent mixtures. The mixtures used were (all v/v): acetone–water (40:60): acetone–diethyl ether (4:96); acetone–diethyl ether (25:75); acetone–diethyl ether (50:50); methanol–water (50:50); benzene–diethyl ether (50:50).

Adsorbent. P. R. Grade Florisil (BDH, Poole, Great Britain) 60–100 mesh for chromatographic analysis, activated at 105° for 24 h, was used.

Preparation of 15% peracetic acid. 0.5 ml of concentrated sulfuric acid was added, with stirring, to 50 ml of 30% aqueous hydrogen peroxide. After cooling, 50 ml of acetic anhydride was slowly added, with stirring, in a cool bath. The mixture was allowed to stand for 16 h at room temperature until equilibrium was reached (peracetic acid 15%). The mixture was prepared fresh every week and stored in a refrigerator (+ 4°).

Standard pesticide solutions. These were prepared by weighing 0.1500 g of pure aldicarb, aldicarb sulfoxide and aldicarb sulfone into individual 1000-ml volumetric flasks, and adding acetone to volume. They were stored in a refrigerator. From these stock solutions, the dilute standards (1–150 mg/l) in acetone were prepared as required.

The internal standard, thiazafluron, was used at 2 mg/l. A stock solution in acetone was prepared and kept in a refrigerator.

Apparatus

The GLC apparatus is a Tracor 560 instrument equipped with the Hall electrolytic conductivity detector Tracor 700. The detector has been described by Hall[4] and Pape *et al.*[5].

In the nitrogen-selective mode (the aldicarb molecule contains two nitrogen atoms), the detector works as follows. After catalytic reduction at high temperature, the nitrogen compounds of the column effluent produce ammonia, which is combined with a stream of deionized liquid in a gas–liquid contactor. The electrical conductivity of the liquid is continuously measured. A vent valve protects the catalyst and the furnace tube from contamination by repetitive injections of solvent. The valve, when open, allows all the carrier gas and some of the reaction gas to vent from the furnace.

A silanized glass column (180 cm × 4 mm I.D.) is packed with 4% Carbowax 20 M on 80–100 mesh Gas-Chrom Q AW DMCS.

The detector signal is measured in terms of peak area by an Hewlett-Packard integrator automation system 3385 A.

Chromatographic conditions

Good resolution of the aldicarb sulfone peak from the internal standard peak is obtained under the following conditions: injector temperature, 215°; oven temperature, 210°; transfer line temperature, 210° (between column and detector).

The carrier gas must be high purity helium with a flow-rate of 30 ml/min. Nitrogen cannot be used as the carrier because a small but significant percentage would be converted into ammonia in the furnace.

The catalytic reduction is conducted in a quartz combustion tube (19 cm × 6 mm O.D.) containing a nickel wire catalyst. The catalyst must be well centred in the hot zone of the furnace.

Strontium hydroxide-coated fiberfrax (1 cm long) is used to eliminate interference from acid gases. The scrubber is inserted in the quartz tube 0.5 cm inside the furnace. To maintain good reproducibility and sensitivity, the scrubber must be replaced after 100 injections. To avoid any contamination of the detector, catalyst and strontium hydroxide must not be touched by fingers.

The furnace temperature is fixed at 850° and hydrogen flow-rate adjusted to 10 ml/min. Figs. 2 and 3 show the furnace temperature (hydrogen flow-rate at 10 ml/min) and hydrogen flow-rate (furnace temperature at 850°) profiles for aldicarb sulfone and thiazafluron.

The vent valve is turned off 1 min after the injection; this produces a weak detector response due to an additional gas supply from the column. The valve must be open after each chromatographic analysis.

The electrolytic solution contains 40% 1-propanol in distilled water. When the

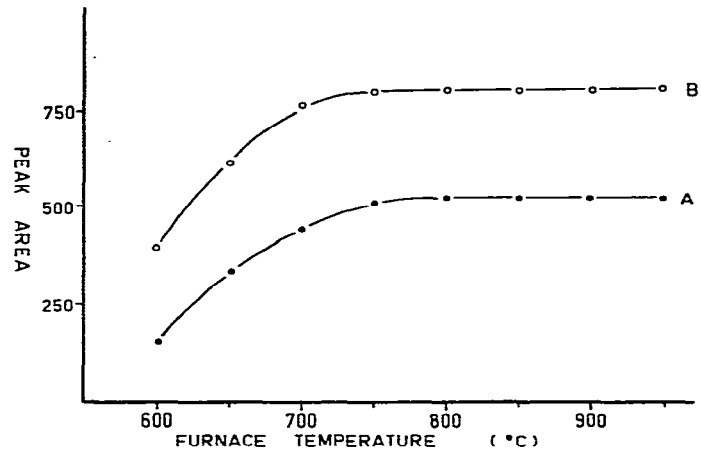

Fig. 2. Hall electrolytic conductivity detector furnace temperature profiles of aldicarb sulfone (A) and thiazafluron (B) in nitrogen-selective mode.

propanol concentration increases, the sensitivity decreases, but if the propanol concentration is too low (less than 30%) background conductivity is too high and low concentrations of aldicarb sulfone cannot be detected. The flow-rate of the electrolytic solution is fixed at 0.7 ml/min. Below 0.5 ml/min, the noise is too great; above 1 ml/min, the sensitivity is too low. Optimal working conditions are achieved when the stabilized chromatographic system shows a conductivity less than $0.5\,\mu\Omega^{-1}$.

Fig. 4 illustrates a typical chromatogram of aldicarb sulfone and thiazafluron under these conditions. Aldicarb sulfone and thiazafluron retention times are 2 min 5 sec and 3 min 45 sec, respectively.

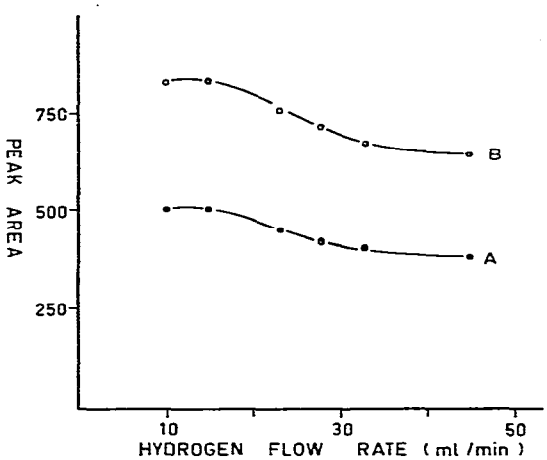

Fig. 3. Hydrogen flow-rate profiles of aldicarb sulfone (A) and thiazafluron (B) in nitrogen-selective mode.

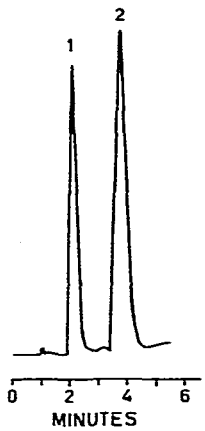

Fig. 4. Chromatogram of GLC–Hall detector analysis of aldicarb sulfone (1) and thiazafluron (2).

Methods

Soil extraction. The soil sample is dried in air at room temperature on aluminium foil, and passed through a 1-mm sieve. 50 g of the sieved soil is extracted with 50 ml of acetone–water (40:60) in a capped centrifuge tube, shaken for 30 min and centrifuged for 5 min at 3000 rpm (2960 *g*). The extract is transferred to a 250-ml separatory funnel. A second extraction is performed with 40 ml of methanol–water (50:50), and the two extracts are combined.

Three extractions with 50 ml of chloroform are then carried out, and the chloroform extracts are passed through a 5-cm bed of anhydrous sodium sulfate. The sodium sulfate is washed with chloroform.

Water extraction. 100 ml of the water sample is extracted in a separatory funnel with 4 × 50 ml of chloroform. After the layers separate, the chloroform layer is drained through a bed of anhydrous sodium sulfate in the same flask. After the fourth extraction, the sodium sulfate is washed with an additional portion of chloroform (*ca.* 25 ml).

Separation of aldicarb and its metabolites[6]. The extract is evaporated to a small volume in a vacuum rotary evaporator at 40° and then to dryness under a dry air stream. The residue is dissolved in 10 ml of benzene–diethyl ether (50:50) and poured onto a 12.5 cm × 1.1 cm I.D. column of activated P. R. Grade Florisil 60–100 mesh prewetted with 25 ml of benzene–diethyl ether (50:50). The flask is washed with 25 ml of diethyl ether, and the solvents are discarded.

Aldicarb is eluted with 150 ml of acetone in diethyl ether (4:96), aldicarb sulfone with 150 ml of acetone in diethyl ether (25:75) and aldicarb sulfoxide with 150 ml of acetone. The three eluates are collected in separate conical flasks and treated individually.

Oxidation to aldicarb sulfone. The eluate is evaporated to dryness in a vacuum rotary evaporator at 40°. 25 ml of water and 2 ml of the peracetic acid solution are added, and the solution is stirred for 15 min at room temperature in order to achieve complete oxidation. Excess of acid is neutralized with 40 ml of 10% sodium bicarbonate (w/v) and 30 min stirring. The solution is transferred to a separatory funnel and the sulfone extracted four times with 25 ml of chloroform.

The chloroform layers are drained through a 5-cm bed of anhydrous sodium sulfate in the same flask, and the bed is washed with 20 ml of chloroform.

Purification of aldicarb sulfone. The solution is evaporated to a volume of 25 ml in a vacuum rotary evaporator at 40°. It is then poured onto a 10 × 1.1 cm I.D. column of activated P. R. Grade Florisil 60–100 mesh prewetted with 50 ml of chloroform. The flask is washed with chloroform. 100 ml of acetone–diethyl ether (4:96) is passed through to remove aldicarb sulfone nitrile and aldicarb sulfone oxime if present. The aldicarb sulfone is eluted with 125 ml of acetone–diethyl ether (50:50). The eluate is evaporated, transferred to a 5-ml reaction vial and evaporated to dryness under a light stream of air. The vials are refrigerated (4°) until analysis by GLC.

At the time of injection, 1 ml of acetone containing thiazafluron as internal standard is added. The vials are kept at 0° to prevent evaporation. Any residue is dissolved by shaking, and 8 μl is injected into the gas chromatograph.

Interpretation of the results. The transformation factor of aldicarb and its sulfoxide to sulfone must be taken into account. During oxidation, 1 mg of aldicarb (MW 190.3) and 1 mg of aldicarb sulfoxide (MW 206.3) yield 1.1681 and 1.0775 mg, respectively, of aldicarb sulfone (MW 222.3).

RESULTS AND DISCUSSION

Choice of the column

Attempts have been made to improve the linearity of the calibration curve (Fig. 5). The curve was obtained from GLC analysis of aldicarb sulfone standards, dissolved in acetone at concentrations varying from 5 to 150 μg/ml.

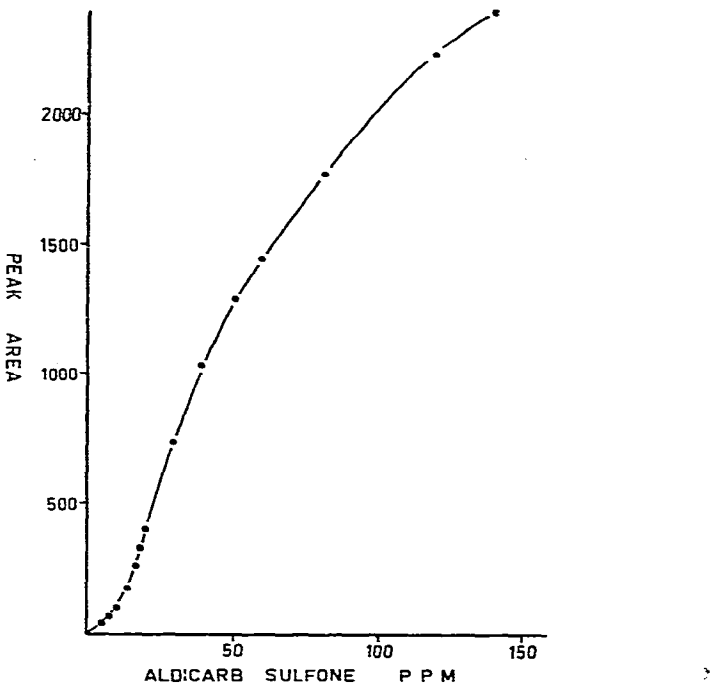

Fig. 5. Typical calibration curve of aldicarb sulfone in GLC using the Hall detector.

Different column packings tested included: 6%, 5%, and 2% Carbowax 20 M on 80–100 mesh Gas-Chrom Q AW DMCS; 4% Carbowax 20 M and 5% KOH on 80–100 mesh Gas-Chrom Q; 4% Carbowax 20 M and 10% OV-1 on 80–100 mesh Gas-Chrom Q; 4% Carbowax 20 M on 80–100 mesh Chromosorb 750. The length and internal diameter of the columns were also varied but without success.

It is generally recommended to inject solutions containing 25–70 μg/ml of aldicarb sulfone; however, we obtained a satisfactory response with solutions of 5 μg/ml.

Stability of aldicarb

The stability of aldicarb, its sulfoxide and its sulfone was tested in acetone, chloroform, methanol, diethyl ether, benzene and water as solvents. No degradation was observed after three weeks at room temperature or three months at 4°.

Recovery

Using the method detailed at length in this paper (extraction excepted), we recovered 99% of sulfone, 97% of sulfoxide and 98% of aldicarb.

Soil extraction

Extraction of aldicarb and its metabolites from a sandy loam soil containing 1.9% (w/w) of organic matter has been investigated. Different solvents (carbon tetrachloride, diethyl ether, chloroform, acetone, methanol and water) were tried for aldicarb-fortified soil extraction. Each sample (50 g) was extracted four times with 40 ml of solvent.

The results (see Table I) were unsatisfactory. Pesticide recovery was low, and in some cases emulsions were formed. Subsequently, soil samples were extracted by the solvent mixtures described in Table II. Recovery of added pesticide was achieved by two or more successive extractions. Acetone–water (40:60) for the first and methanol–water (50:50) for the second give the best results. The third is not necessary.

TABLE I

EXTRACTION BY VARIOUS SOLVENTS OF SOIL SAMPLES FORTIFIED WITH 1 PPM OF ALDICARB

Recovery of four extractions of 40 ml.

Solvent	*Recovery (%)*
Carbon tetrachloride	29.4
Diethyl ether	37.2
Chloroform	39.8
Acetone	49.1
Methanol	48.5
Water	48.9

Table III details the results obtained when the method described here was applied to soil samples fortified with 0.05, 0.10, 0.25, 0.50, 1.00, 1.50 mg/kg (ppm). The results presented are means of four determinations on separate samples. The coefficient of variation is less than 6%.

TABLE II

EXTRACTION BY VARIOUS SOLVENT MIXTURES OF SOIL SAMPLES FORTIFIED WITH 1 PPM OF ALDICARB

Total recovery from three different extractions.

Solvent			*Recovery (%)*
First extraction	*Second extraction*	*Third extraction*	
Acetone–water (50:50)	Acetone–water (50:50)	Acetone–water (50:50)	85.2
Acetone–water (50:50)	Acetone	Acetone	58.5
Acetone–water (50:50)	Methanol	Methanol	67.8
Acetone–water (50:50)	Methanol	—	69.4
Acetone–water (50:50)	Methanol–water (50:50)	Methanol–water (50:50)	86.8
Acetone–water (50:50)	Methanol–water (50:50)	—	89.4
Acetone–water (40:60)	Methanol–water (50:50)	Methanol–water (50:50)	90.4
Acetone–water (40:60)	Methanol–water (50:50)	—	91.2
Water	Acetone–water (50:50)	—	60.7
Water	Methanol–water (50:50)	—	64.0
Methanol–water (50:50)	Methanol–water (50:50)	—	84.3

TABLE III

DETERMINATION OF ALDICARB, ALDICARB SULFOXIDE AND ALDICARB SULFONE IN SOIL SAMPLES (SANDY LOAM) FORTIFIED AT VARIOUS LEVELS

N.D. = not detected.

Added (ppm)			*Recovery (%)*		
aldicarb	*aldicarb sulfoxide*	*aldicarb sulfone*	*aldicarb*	*aldicarb sulfoxide*	*aldicarb sulfone*
0	0	0	N.D.	N.D.	N.D.
1.50	1.50	1.50	89.7	91.2	86.8
1.00	1.00	1.00	89.8	91.5	87.1
0.50	0.50	0.50	90.7	90.4	86.1
0.25	0.25	0.25	91.6	92.7	87.9
0.10	0.10	0.10	92.9	93.6	89.2
0.05	0.05	0.05	90.3	92.6	85.3

TABLE IV

DETERMINATION OF ALDICARB, ALDICARB SULFOXIDE AND ALDICARB SULFONE IN WATER SAMPLES FORTIFIED AT VARIOUS LEVELS

N.D. = not detected.

Added (ppm)			*Recovery (%)*		
aldicarb	*aldicarb sulfoxide*	*aldicarb sulfone*	*aldicarb*	*aldicarb sulfoxide*	*aldicarb sulfone*
0	0	0	N.D.	N.D.	N.D.
1.50	1.50	1.50	94.7	91.2	93.9
1.00	1.00	1.00	94.5	93.7	95.4
0.50	0.50	0.50	86.9	95.2	90.8
0.25	0.25	0.25	94.8	91.3	94.4
0.10	0.10	0.10	94.2	92.3	94.6
0.05	0.05	0.05	92.1	93.0	93.7

Water extraction

Water samples fortified with 0.05–1.50 mg/l (ppm) of aldicarb and its metabolites were investigated. The results are given in Table IV. As in the case of soils, the recovery was very satisfactory.

CONCLUSIONS

The method described yields quite satisfactory results provided that the analytical conditions are carefully applied. The Hall electrolytic conductivity detector is highly sensitive. Even minimal variations in the analytical parameters can alter the chromatographic response. The high specificity of the detector allows the determination of aldicarb sulfone without any interference. The procedure suffers, however, from one drawback: it is time-consuming. However, if it is not necessary to distinguish between aldicarb and its metabolites, the separation step can be omitted. The total extract is oxidized to aldicarb sulfone and the result expressed as total aldicarb, including sulfoxide and sulfone metabolites.

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