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Short Communication

Gas chromatographic determination of aldicarb and its metabolites in urine

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ABSTRACT

A method is described for the determination of aldicarb and its metabolites (the sulphoxide and sulphone) in urine by gas chromatography with flame photometric detection (GC–FPD). The sample was concentrated with a column containing activated charcoal and Florisil, and then eluted with dichloromethane–acetone (1:1, v/v). The aldicarb and aldicarb sulphoxide in the eluate solution were oxidized to aldicarb sulphone and the total sulphone concentration was determined by GC–FPD after extraction with dichloromethane and clean-up with an activated charcoal column. The detection limit was 0.0024 mg/l. The mean recoveries from spiked urine in the range 0.04–0.12 mg/l were 90.9%, 86.6%, 92.6% for aldicarb, aldicarb sulphoxide and aldicarb sulphone, respectively.

INTRODUCTION

Aldicarb [2-methyl-2-(methylthio)propionaldehyde-O-(methylcarbamoyl)-oxime] is a highly effective and highly poisonous broad-spectrum N-methylcarbamate insecticide. It can be degraded by oxidation into aldicarb sulphoxide and sulphone in human and animal body tissue. Wagner [1] reported that 80% of aldicarb and its metabolites are excreted in the urine by 24 h after external exposure. Because aldicarb and the sulphoxide and sulphone are toxic with potential risks for human health, it is important to be able to determine the levels of all three compounds in urine for biological monitoring of workers' exposure to aldicarb.

A number of methods have been reported for the determination of aldicarb residues but there have been few papers on its determination in urine. On the basis of published work [2–4], we developed an method for the determination of aldicarb and its metabolites in urine by gas chromatography with flame photometric detection (GC–FPD). This method involves determining aldicarb sulphone in urine from rats dosed with aldicarb orally. The results showed that the method is an efficient technique for biological monitoring of exposure to aldicarb.

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EXPERIMENTAL

Equipment

A Shimadzu GC-RIA gas chromatograph equipped with a flame photometric detector and a sulphur filter was used. The glass column (2.1 m × 2.7 mm I.D.) was packed with 3% polyethylene glycol 20M–Gas-Chrom Q (80–100 mesh). A glass chromatographic column (20 cm × 1.0 cm I.D.) with a stopcock was also used.

Reagents

Acetone and dichloromethane (analytical-reagent grade) were glass distilled. Florisil (pure reagent grade, 60–80 mesh) was heated in an oven at 400°C for 4 h prior to use. Activated charcoal (60–80 mesh) was obtained from the Berjing Guang Hua Wood Factory.

The oxidizing reagent was prepared by mixing 0.1 ml of concentrated sulphuric acid with 10 ml of 30% hydrogen peroxide and 10 ml of glacial acetic acid. The mixture was placed in a refrigerator and allowed to stand overnight. This solution could be used for 1 week.

A standard solution was prepared by dissolving appropriate amounts of aldicarb, aldicarb sulphoxide and aldicarb sulphone (Union Carbide Agricultural Products) in methanol.

Procedure

Concentration. The column was prepared by insterting glass-wool at the bottom, adding 1.0 g of activated charcoal and 1.0 g of Florisil, tapping it gently, then plugging with glass-wool at the top of the column. The column was washed with 30 ml of distilled water. A 50-ml urine sample was passed through the column at a flow-rate of 1 ml/min and the eluate was discarded. The column was then cleaned up with 40 ml of acetone–water (1:30). Finally, the analyte on the column was eluted with 20 ml of acetone–dichloromethane (1:1) and collected in a 50-ml beaker. The eluate was evaporated to dryness on a water-bath (40°C). The residue was then ready for oxidation.

Oxidation. A beaker containing 20 ml of distilled water was placed on a magnetic stirrer, then 25 ml of oxidizing reagent were added. The reaction mixture was stirred for 30 min, then the pH was adjusted to 6–7 with 10% sodium hydrogencarbonate solution and the mixture was stirred for a further 20 min. The mixture was transferred into a 150-ml separating funnel and aldicarb sulphone was extracted with three 30-ml portions of dichloromethane. The dichloromethane extracts were combined and evaporated to dryness and the residue was dissolved in 10 ml of distilled water.

Clean-up. The chromatographic column was prepared by adding 1.0 g of activated charcoal and pretreated by passing 20 ml distilled water through the column. The sample extract from the oxidation step was then passed through the column at flow-rate of 1 ml/min and eluted with 10 ml of acetone–dichloromethane (1:1). The eluate was evaporated to dryness and the residue was dissolved in and diluted to 1.0 ml with methanol. The solution was then ready for GC analysis.

GC analysis. Quantitative analysis was performed according to the external standard method. A calibration graph was prepared in the range 2 ng–10 ng. The GC conditions were as follows: injector temperature, 220°C; detector temperature, 220°C;

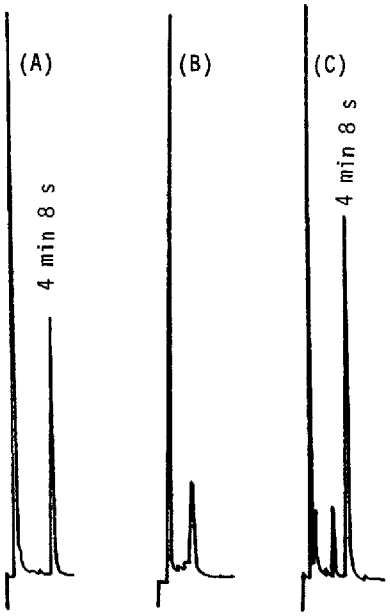

Fig. 1. Gas chromatograms of standard and urine samples spiked with aldicarb. (A) Aldicarb sulphone standard; (B) urine blank; (C) urine from rats dosed with aldicarb.

column temperature, 160°C; flow-rates, hydrogen 50 ml/min, air 52 ml/min and nitrogen 45 ml/min; and injection volume, 5 μl.

RESULTS AND DISCUSSION

Because some co-extracted impurities in the dichloromethane extract interfere in the determination of aldicarb sulphone it is necessary for the extract to be cleaned up with an activated charcoal column. After treatment with this column, the peaks of both aldicarb sulphone and the impurities can be separated at the baseline (see Fig. 1). The retention time for aldicarb sulphone was 4 min 8 s.

TABLE I

PRECISION OF THE METHOD [RELATIVE STANDARD DEVIATION (R.S.D.) ($n=6$)]

Parameter	Spiking level (μg per 50 ml)		
	2	4	6
Single day			
S.D. (μg per 50 ml)	0.08	0.14	0.23
R.S.D. (%)	4.0	3.5	3.8
Different days			
S.D. (μg per 50 ml)	0.15	0.30	0.35
R.S.D. (%)	7.5	7.5	5.8

TABLE II

RECOVERIES OF ALDICARB, ALDICARB SULPHOXIDE AND ALDICARB SULPHONE FROM SPIKED URINE SAMPLES

Pesticide	Amount added (μg per 50 ml)	Amount found (μg per 5 ml)	Mean recovery (%) ($n=6$)	R.S.D. (%)
Aldicarb	2	1.82	91.0	4.5
	4	3.71	92.8	3.5
	6	5.34	89.0	5.3
Aldicarb sulphoxide	2	1.72	86.0	3.0
	4	3.57	89.3	3.3
	6	5.11	85.1	5.5
Aldicarb sulphone	2	1.87	93.5	2.5
	4	3.76	94.0	4.3
	6	5.44	90.7	4.3

The relative standard deviations obtained with the method were 4.0–3.5% for analyses on a single day and 5.8–7.5% for analyses on different days for urine spiked with aldicarb sulphone in the range 2–6 μg per 50 ml (Table I). The detection limit was 0.0024 mg/l.

The recoveries of aldicarb, aldicarb sulphoxide and aldicarb sulphone spiked in urine at three levels (2 μg, 4 μg and 6 μg per 50 ml) were determined and the results are given in Table II. The recoveries ranged from 89% to 92.8% for aldicarb, 85.1% to 89.3% for aldicarb sulphoxide and 90.7% to 94% for aldicarb sulphone, with relative standard deviations of 3.5–5.3%, 3.0–5.5% and 2.5–4.3%, respectively.

Urine samples were collected from rats dosed with aldicarb orally at 0–24 h and 24–48 h after dosing and after oxidation the total amount of aldicarb sulphone was determined. The results are given Table III.

TABLE III

RESULTS FOR DETERMINATION OF ALDICARB SULPHONE IN RAT URINE

Dose (μg)	No. of rats	Found (μg)	
		0–24 h	24–48 h
0.168	3	35.3	2.3
0.125	3	25.8	1.8
0.080	4	15.5	1.2
0.050	4	9.9	1.1
0.000	2	0.0	0.0

CONCLUSION

The method described is sensitive, inexpensive and efficient. It has potential use for biological monitoring of aldicarb and its metabolites in the urine of workers who are exposed to aldicarb for estimating occupational exposure levels.

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