Journal of Chromatography, 260 (1983) 502–506
Elsevier Science Publishers B.V., Amsterdam — Printed in the Netherlands

CHROM. 15,703

Note

Direct determination of some carbamate pesticides in water and soil by high-performance liquid chromatography

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(First received August 2nd, 1982; revised manuscript received January 18th, 1983)

The number and amount of carbamate pesticides used in agriculture continue to increase, replacing the more environmentally stable organohalogen pesticides. Direct gas chromatographic (GC) determination of carbamate pesticides is difficult because they have a tendency to break down to the corresponding phenol on GC columns, and most carbamates are unstable under common GC conditions[1–3]. The methods based on derivatization of carbamates to thermally stable products have several limitations that often reduce their sensitivity andv ersatility[4–11].

More recently, high-performance liquid chromatography (HPLC) has been increasingly applied to the separation and direct determination of carbamates[12–16]. In order to attain maximum efficiency in the determination of carbamate residues in environmental components, it is desirable to use a single analytical method that selectively determines the individual residues.

An HPLC method for the simultaneous detection of ten carbamate pesticides (Baygon, carbaryl, 2-isopropylphenyl-N-methylcarbamate (MIPC), 2-*sec*-butylphenyl methylcarbamate (BPMC), isopropyl-3-chlorophenylcarbamate (CIPC), *m*-tolyl-N-methylcarbamate (MTMC), carbofuran, hydroxycarboruan, aldicarb and methomyl) in water and soil is presented in this paper.

EXPERIMENTAL

Apparatus and operating conditions

A Hewlett-Packard 1084 B high-pressure liquid chromatograph equipped with a UV detector (254 nm) was used. The stainless-steel column (25 cm × 4.6 mm I.D.) was packed with 10-μm LiChrosorb RP-18 (E. Merck, Darmstadt, G.F.R.).

Elution was carried out during the first 16 min with 40% methanol in water, between 16 and 17 min a step gradient was introduced from 40 to 60% methanol in water, then the elution was continued with 60% methanol in water at a flow-rate of 1.2 ml/min.

Extraction

Water. To a 250-ml sample in a 500-ml separating funnel, dilute sulphuric acid

0021-9673/83/$03.00

(50%) is added until the pH reches 3 (indicator paper) and then 10 g of sodium chloride is dissolved in the solution.

Extraction is carried out with 50 ml of methylene chloride and then with 2 × 25 ml of methylene chloride. The extract is dried by passing it through a column containing 15–20 g of anhydrous sodium sulphate and the eluate is collected in a round-bottomed flask and evaporated to dryness in rotary vacuum evaporator. For analysis by HPLC, the residue is dissolved in 1 ml of methanol.

Soil. The procedure described by Caro *et al.*[11] for the extraction of carbofuran from soil was used. A 50-g soil sample is homogenized at 60°C for 1 h with 150 ml of acidic ammonium acetate. The homogenate is filtered by suction through a Büchner funnel containing filter-paper. The total filtrate is transferred into a 500-ml separating funnel, 10 g of sodium chloride are added and the separating funnel is shaken until the sodium chloride is dissolved. This solution is extracted as described under *Water.*

Cleanup procedure

When the soil sample contains more than 3% of organic matter, the soil sample must be purified. A chromatographic column (I.D. 1.8 cm) containing (from bottom to top) glass-wool, 7 g of Florisil (2% deactivated) and 1–2 g of anhydrous sodium sulphate is prepared. The column is washed with 50 ml of methylene chloride–light petroleum (b.p. 36–40°C). The concentrated methylene chloride extract is added to the column, is washed with 50 ml of methylene chloride–light petroleum (1:1) and the eluate is discarded. The column is eluted with 125 ml of 15% acetone in methylene chloride. The eluate is collected in a 250-ml flask and evaporated to dryness in rotary vacuum evaporator.

The residue is dissolved in 1 ml methanol for analysis by HPLC. All carbamates were totally recovered from the Florisil column except aldicarb (64%).

Determination

A 10-μl methanolic sample solution is injected on to the chromatographic column. The carbamate peaks are identified on the basis of retention times. The amounts of the residues are determined by comparison with peak areas obtained from known amounts of reference substances of appropriate concentration.

RESULTS AND DISCUSSION

A good separation on an ODS reversed-phase column with 40–60% methanol in water as the mobile phase and with a step gradient between 16 and 17 min for the carbamates (except Baygon and carbofuran) was possible.

Fig. 1 shows that under the above conditions, the ten carbamate compounds could be resolved within less than 24 min. Retention data expressed as capacity ratios (k') relative to methanol (t_0 = 69 sec) and detection limits are listed in Table I. A good separation between Baygon and carbofuran was obtained with isocratic elution with 35% methanol in water, but the analysis time was long.

Recoveries of ten carbamates from water fortified at 0.10 μg/g and from soil fortified at 0.50 μg/g are listed in Table II. The average recovery from water was over 80%, except for aldicarb (62%), and from soil over 80%, except for aldicarb (59%) and CIPC (71%).

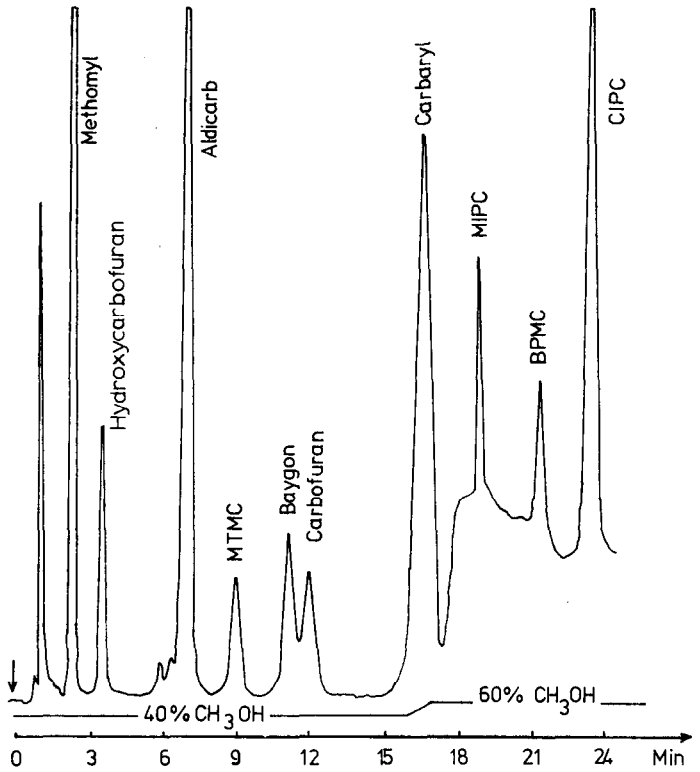

Fig. 1. Chromatogram of standard mixtures of carbamates in methanol (10 ng/μl).

Fig. 2 shows the chromatogram of carbamates extracted from water fortified at 0.10 μg/g and Fig. 3 presents the chromatogram of carbamates extracted from soil fortified at 0.50 μg/g and purified on the Florisil column.

Detection limits of 0.005–0.010 μg/g were obtained for carbamates in water and 0.050–0.10 μg/g for carbamates in soil.

TABLE I

RETENTION DATA AND DETECTION LIMITS OF CARBAMATE PESTICIDES

Compound	*k'*	*Detection limit (ng)*
Methomyl	1.12	0.2
Hydroxycarbofuran	2.14	5.0
Aldicarb	5.07	2.0
MTMC	6.77	10.0
Baygon	8.71	7.0
Carbofuran	9.38	7.0
Carbaryl	12.94	0.5
MIPC	15.86	5.0
BPMC	18.03	5.0
CIPC	19.74	1.0

TABLE II

RECOVERY OF CARBAMATE PESTICIDES FROM FORTIFIED WATER AT 0.10 μg/g AND FROM FORTIFIED SOIL AT 0.50 μg/g

Results are means ± standard deviation (n = 4).

Compound	*Recovery (%)*	
	From water	*From soil*
Methomyl	82.8 ± 2.1	100.2 ± 2.6
Hydroxy-carbofuran	83.5 ± 3.0	96.2 ± 2.6
Aldicarb	62.3 ± 2.1	59.0 ± 2.5
MTMC	88.8 ± 2.4	94.7 ± 1.7
Baygon	91.0 ± 3.2	93.5 ± 3.8
Carbofuran	89.8 ± 4.3	94.7 ± 3.4
Carbaryl	109.2 ± 2.2	96.0 ± 4.1
MIPC	100.0 ± 4.3	99.2 ± 2.5
BPMC	95.2 ± 4.4	83.8 ± 2.6
CIPC	108.5 ± 2.6	71.0 ± 2.6

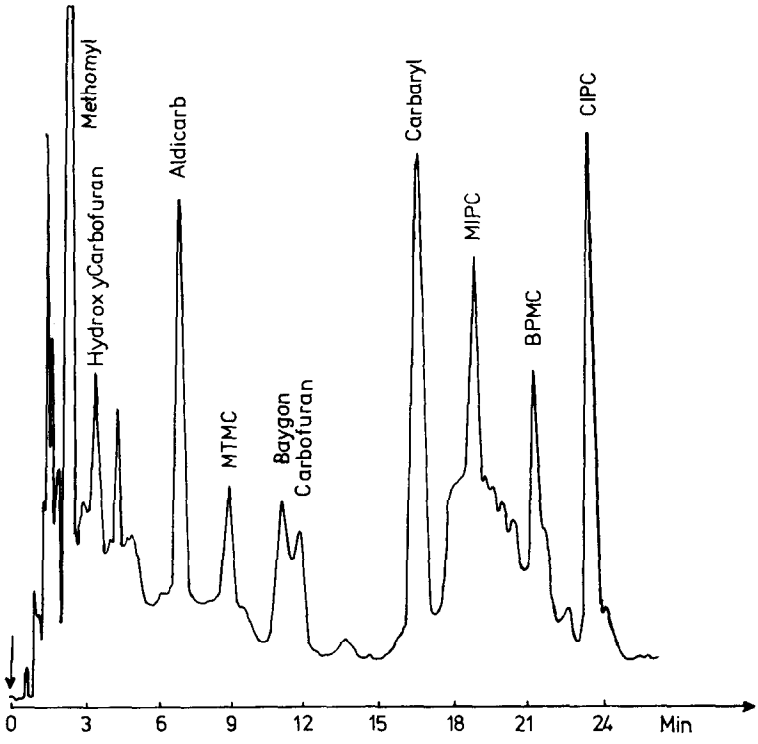

Fig. 2. Chromatogram of carbamates extracted from water fortified at 0.10 μg/g (without cleanup).

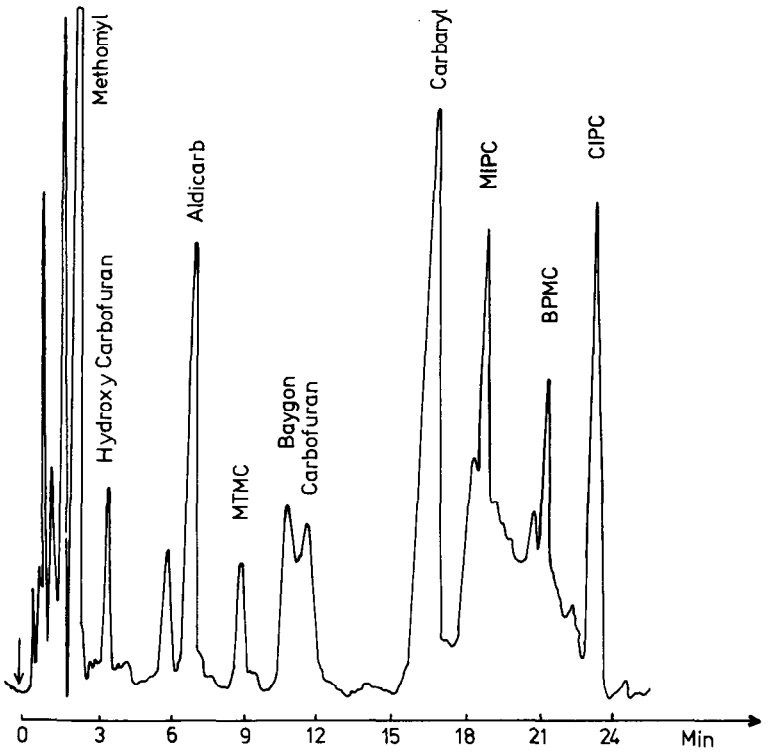

Fig. 3. Chromatogram of carbamates extracted from soil fortified at 0.50 μg/g (cleanup on Florisil).

CONCLUSIONS

The method gives good recoveries of carbamate residues from water and soil samples, and it is highly selective for determining residues of some oximes, N-methylcarbamates, phenyl-N-methylcarbamates and N-phenylcarbamates.

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