Journal of Chromatography, 455 (1988) 391–395
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 902

Note

Gas chromatographic determination of chloroacetamide herbicides in plants and soil*

ANNA BALINOVA
Institute for Plant Protection, Kostinbrod 2230, P.O.B. 238, Sofia (Bulgaria)
(First received October 12th, 1987; revised manuscript received June 15th, 1988)

Alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide], acetochlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(ethoxymethyl)acetamide], metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide] and propachlor [2-chloro-N-(1-methylethyl)-N-phenylacetamide] are some of the currently most widely used herbicides.

The methods of analysis of alachlor, propachlor and metolachlor in the literature are based mainly on gas chromatography (GC) with flame ionization detection (FID)[1–6]. With a non-specific detector, the sensitivity of the determination is relatively low (0.05 mg/kg), and laborious purification of samples is needed. GC determination with nitrogen–phosphorus detection (NPD) has been applied to the analysis of acetochlor residues after hydrolysis to the corresponding aniline (sensitivity of the method 0.02–0.05 mg/kg)[7], as well as in the analysis of alachlor, propachlor and butachlor in water[8].

Electron-capture detection (ECD) is a highly sensitive method for these compounds. I have used it in the analysis of alachlor and propachlor residues[9]. Ammann *et al.*[10] also determined alachlor by ECD. Other authors have used ECD in the analysis of alachlor after derivatization to the heptafluorobutyryl derivative[11]. This method is highly sensitive, but chemical derivatization complicates the analysis.

The method offered here is comparatively easy and less time-consuming than derivatization. It is highly sensitive and accurate, providing the separation, identification and quantitation of four of the most common chloroacetamide herbicides.

EXPERIMENTAL

The clean-up column was a 300 mm × 10 mm I.D. glass column. The gas chromatograph was a Model Sigma 300 (Perkin-Elmer, Norwalk, CT, U.S.A.), equipped with a ^{63}Ni electron-capture detector and glass columns (183 cm × 2 mm I.D.) packed with 5% QF-1 + 2.5% DC-200 or 10% Apiezon L on Chromosorb W AW DMCS 80–100 mesh. The operating conditions were: injector, 220°C; column, 200°; detector, 300°; carrier gas (nitrogen) flow-rate 30 ml/min when a column with

* Presented at the *6th Danube Symposium on Chromatography, Varna, October 12–17, 1987*. The majority of the papers presented at this symposium has been published in *J. Chromatogr.*, 446 (1988).

0021-9673/88/$03.50

5% QF-1 + 2.5% DC-200 was used and 60 ml/min when a column with 10% Apiezon L was used.

All reagents and solvents were of reagent grade. Chloroform, *n*-hexane and benzene were also distilled in glass. Florisil (Fluka, Buchs, Switzerland), 60–100 mesh, was heated at 135°C for 24 h, and deactivated with 10% (w/v) water. Since Florisil is not a perfectly standardized product, the elution characteristics of each batch should be determined before use.

All reagents were tested for impurities by GC–ECD.

The sample (50 g) was weighed out in the cup of a blender and then thoroughly homogenized with 100 ml acetonitrile for 2–3 min at high speed. Wet samples (fruit, vegetables) were filtered with suction through a buchner funnel or centrifuged. The blender jar and the cake were washed with 2 × 25 ml acetonitrile. The volume of the filtrates was measured. The extract was mixed thoroughly and an aliquot, corresponding to 25 g of sample, was taken. Dry samples (less than 10% water content) were blended with 100 ml acetonitrile–water (9:1) and filtered or centrifuged. A 50-ml volume of the filtrate (corresponding to 25 g of sample) was taken for analysis.

For clean-up, the extract was transferred to a 250-ml separatory funnel and extracted with two 20-ml portions of *n*-hexane. The hexane layers were discarded and the acetonitrile layer was transferred to a vacuum evaporator. The acetonitrile was removed at 50°C under vacuum. In the case of dry samples the extracts were evaporated to about 5 ml. The watery remainder was transferred to a 250-ml separatory funnel, using 20 ml of chloroform and 50 ml of saturated sodium chloride solution for rinsing, shaken for 2 min and the phases allowed to separate. The chloroform layer was collected and the extraction was repeated with two 20-ml portions of chloroform. The chloroform layers were pooled and dried over anhydrous sodium sulphate. After evaporation of the chloroform under vacuum at 40°C, the residue was dissolved in 1 ml hexane–diethyl ether (1:1).

The clean-up column was packed with 1 g Florisil in hexane–diethyl ether (1:1) and a 1-cm layer of anhydrous sodium sulphate on top. The residue was transferred to the column using four 1-ml portions of hexane–diethyl ether (1:1) and the column was eluted with the same solvent. The first 1-ml portion of the eluate was discarded, the following 7 ml were collected and evaporated under a gentle stream of air or nitrogen, about to dryness. The volume of the residue was adjusted to 2.0 ml with benzene. When necessary the samples were diluted to an higher volume.

For the GC determination, samples were injected with a 1-μl syringe and interspersed with standards, prepared by dissolving the analytical standards alachlor, acetochlor, propachlor (obtainable from Monsanto) and metolachlor (from Ciba-Geigy) in benzene to suitable concentrations. For quantitation, the detector response (peak height) was plotted against the amount of each standard compound. The samples were identified by comparing the retention times of the chromatographic peaks of the sample and standard compounds.

RESULTS AND DISCUSSION

The minimum detectable amounts of the compounds tested were between 0.02 and 0.05 ng (Table I). The relative retention times on two GC columns are presented in Table II. The chromatographic separation of the four compounds is complete

TABLE I

MINIMUM DETECTABLE AMOUNTS

Compound	*Amount (ng)*
Propachlor	0.05
Acetochlor	0.02
Alachlor	0.02
Metolachlor	0.05

TABLE II

RELATIVE RETENTION TIMES (RRT), BASED ON ALDRIN, FOR FOUR CHLOROACETAMIDE HERBICIDES ON TWO GC COLUMNS

Compound	*RRT*	
	5% QF-1 + 2.5% DC-200	*10% Apiezon L*
Propachlor	0.54	0.20
Acetochlor	1.06	0.53
Alachlor	1.13	0.57
Metolachlor	1.44	0.77
Aldrin	1.00	1.00

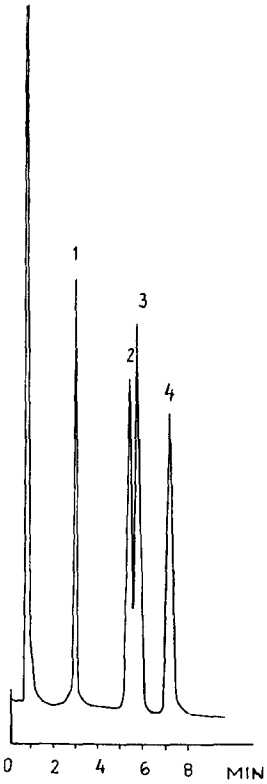

Fig. 1. Gas chromatogram of 0.4 ng propachlor (1), 0.2 ng acetochlor (2), 0.2 ng alachlor (3) and 0.4 ng metolachlor (4). A 183-cm column packed with 5% QF-1 + 2.5 % DC-200 on Chromosorb W AW DMCS (80–100 mesh) operated at 200°C and ECD were used.

TABLE III

RECOVERIES OF THE HERBICIDES TESTED FROM SPIKED SOIL AND POTATO SAMPLES

(Average of 11 fortifications).

Compound	*Spiking levels (mg/kg)*	*Recovery (%) and coefficient of variation (%)*	
		Soil	*Potatoes*
Propachlor	0.1	85.1 ± 9.3	82.5 ± 6.1
	0.02	69.5 ± 8.1	64.8 ± 7.4
Acetochlor	0.1	80.6 ± 7.1	84.0 ± 5.2
	0.02	71.3 ± 6.9	73.2 ± 8.6
Alachlor	0.1	83.2 ± 6.5	84.3 ± 4.9
	0.02	70.7 ± 7.3	68.2 ± 6.1
Metolachlor	0.1	86.7 ± 8.8	85.3 ± 7.4
	0.02	66.2 ± 5.8	65.6 ± 6.5

(Table II, Fig. 1), except for acetochlor and alachlor, which are isomeric. Their chromatographic separation proved to be difficult. Among the numerous columns tested, two (10% Apiezon L and 5% QF-1 + 2.5% DC-200) gave the best results.

The accuracy of the method developed is given in Table III. Since derivatization is avoided, a higher precentage recovery is obtained. The application of ECD, distinguished by an higher sensitivity than that of NPD and a greater specificity than that of FID, makes the method highly sensitive (Tables I and IV).

The method was applied to the determination of residues of the four herbicides in soil and plants (potatoes, tomatoes, grains and leaves of maize). Impurities in the extracts did not interfere with the determination of the compounds.

TABLE IV

LIMIT OF DETERMINATION OF THE METHOD

Compound	*Limit (mg/kg)*	
	Soil	*Potatoes*
Propachlor	0.005	0.01
Acetochlor	0.002	0.004
Alachlor	0.002	0.004
Metolachlor	0.005	0.01

REFERENCES

1 K. D. Wenzel, M. Monke and R. Grahl, *Fresenius' Z. Anal. Chem.*, 322 (1985) 423.
2 A. Krause, W. G. Hancock, R. D. Minard, A. J. Freyer, R. C. Honeycutt, H.M. LeBaron, D. L. Paulson, S. Y. Lin and J. M. Bollag, *J. Agric. Food Chem.*, 22 (1985) 584.
3 G. T. Gale and A. H. Hofberg, *J. Assoc. Off. Anal. Chem.*, 68 (1985) 570.
4 *Pesticide Analytical Manual*, Vol. II, U.S. Dept. of Health, Education and Welfare, Food and Drug Administration, 1974.

5 *Information to Support Label Registration Request*, Lasso, Book 2, Monsanto, St. Louis, MO, 1971.
6 *Information to Support Label Registration Request*, Analytical Section, 2-chloro-N-isopropylacetanilide, Monsanto, St. Louis, MO, 1968.
7 *Analytical Residue Method for Acetochlor*, Lab 7127, Monsanto, St. Louis, MO, 1982.
8 J. W. Worley, M. L. Rueppel and F. L. Rupel, *Anal. Chem.*, 52 (1980) 1845.
9 A. Balinova, *Materiali Symposiuma "Ostatochnie Kolichestva Gerbicidov v Rastenijach i v Pochve", Wroclaw, 1973*, SEV, Poznan, 1975, 111.
10 B. D. Ammann, D. J. Call and H. A. Draayer, *J. Assoc. Off. Anal. Chem.*, 859 (1976) 859.
11 W. H. Newsome, P. Collins and D. Lewis, *J. Assoc. Off. Anal. Chem.*, 69 (1986) 591.