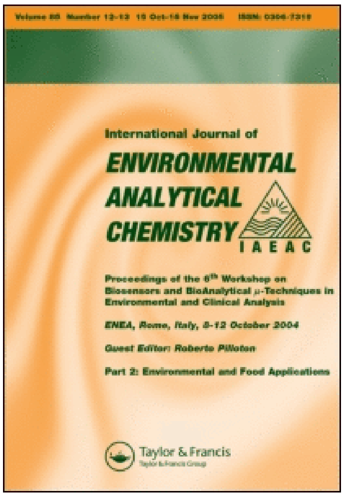

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S. M. Waliszewski[a]; V. T. Pardio Sedas[b]
[a] Institute of Forensic Medicine University of Veracruz Framboyanes esq, Veracruz, Ver, México [b] Environmental Health Laboratory Department of Health, Veracruz, Ver., México

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THE USE OF SILAR 10 CP FOR THE PACKED COLUMN GAS CHROMATOGRAPHIC DETERMINATION OF CHLOROPHENOXYACETIC ACID HERBICIDES IN WATER AND SEDIMENTS

S. M. WALISZEWSKI

Institute of Forensic Medicine University of Veracruz Framboyanes esq. Reyes Heroles
91950 - Veracruz, Ver. México

V. T. PARDIO SEDAS

Environmental Health Laboratory Department of Health 20 de Noviembre 1074,
91700 - Veracruz, Ver. México

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The determination of chlorophenoxyacetic acid herbicide residues was done with GC-ECD as pentafluorobenzyl derivatives. The herbicides were separated on a 3% Silar 10 CP column, which permits better resolution from interfering organic acids of environmental origin. The fortification study provides an 84 – 91% recovery for the water and sediment samples. The detection limits were established as 0.1 μg/l for the water and 1.0–1.5 ng/g for the sediment samples. The use of a 3%Silar 10 CP packed column in the monitoring study as compared with a 1.5% OV–17 + 1.95% QF–1 one, shows the very small amount of contamination of the samples with these herbicide classes.

KEY WORDS : Chlorophenoxyacetic acid, water, sediments, GC-ECD.

INTRODUCTION

Chlorophenoxyacetic acid herbicides are widely used in agriculture to control grass and broad-leaf weeds. They are considered an important group of commercial herbicides used for crop protection. As they are highly soluble in water, they can easily enter and pollute all agricultural ecosystems. The kinetics of its disappearance in water reservoirs show a slow decline and an accumulation in sediments[1,2,3,4]. Toxicologically, chlorophenoxyacetic acid herbicides constitute a danger to human health as they are considered to be a factor in causing soft tissue sarcoma in man[5,6] and embryotoxicity in pregnant animals[7,8]. The determination of their residues through gas chromatography and electron capture detection requires derivatization to increase volatility. The pentafluorobenzyl derivatives significantly increase the sensitivity of the GC-ECD making it possible to determine ppb levels of these herbicides in water and sediment samples.

The monitoring study initiated on chlorophenoxyacetic acid herbicide residues (Mecoprop, MCPA, 2.4-D) in water and sediments, showed a widespread contamination of water reservoirs, rivers and sediments, caused by the use of these herbicides in agriculture. The aim of this work is to make certain observations, which could help prevent analysts from misinterpreting gas chromatographic peaks of substances which, during the GC-ECD determination, overlap chlorophenoxyacetic acid herbicides but are not herbicides.

MATERIALS AND METHODS

The following reagents were purchased from Baker S.A. de C.V. and Técnica Química S.A.: distilled petroleum ether (boiling temp. 40–50°C), distilled acetone, distilled dichloromethane, distilled peroxide - free ethyl ether containing 2% of 96% ethyl alcohol, anhydrous sodium sulfate heated overnight at 650°C, Florisil activated overnight at 130°C. Before analysis, all reagents were tested for the presence of impurities. If such compounds were detected, the reagents were futher cleaned through fractional distillation and chemical purification to get a gas chromatogram without the peaks of impurities.

Glassware equipment was of a type appropriate for a pesticide residues laboratory. All equipment was glass to prevent contamination with undesirable common substances. The glassware was washed with concentrated KOH solution and then with concentrated sulfuric acid. It was rinsed with distilled water, distilled acetone and distilled petroleum ether.

The gas liquid chromatograph, Varian Model 2100, was equipped with a ^{63}Ni electron capture detector and 185 cm × 2 mm id. glass column, packed with 3% Silar 10 CP on Gas Chrom Q 100–120 mesh. Operating conditions were: nitrogen carrier gas at 15 ml/min; temperatures: column 200°C, injector 250°C, detector 250°C. Injection volume 1 μl.

The water or sediment samples were acidified to pH = 1 with 25% (v/v) sulfuric acid (9). Then residues of chlorophenoxyacetic herbicides were extracted with dichloromethane and the extracts rotary evaporated to dryness. The dry residues were dissolved in 1 ml of acetone and quantitatively transferred to a test tube. The derivatization was performed by adding 50 ul (3 drops) of 1% solution in acetone of 2,3,4,5,6-pentafluorobenzylbromide and the contents of the tube were mixed and left in a dark place for 90 minutes. Thereafter, 30 μl (2 drops) of 30% water solution of K_2CO_3 were added and the contents were mixed and left in the dark until the following day.

Twenty mililiters of distilled water were added to a tube containing the sample extract. The pentafluorobenzyl esters of chlorophenoxyacetic acid herbicides were extracted with three 10 ml portions of petroleum ether. The extracts were passed through a layer of sodium sulfate into a 100 ml round-bottomed flask and the combined extracts and rinses were rotary evaporated to a small volume. The concentrated extract was transferred to the top of a column filled with 5 g of Florisil previously deactivated by washing it with 12 ml of a mixture of 30% ethyl ether in petroleum ether and then with 15 ml of petroleum ether. The herbicide

Table 1 Statistical evaluation of results obtained from the recovery study (n=10).

	Compounds	*Fortification levels (ppb)*	x ± *SD*	*v%*
WATER	Mecoprop	0.5	88.3 ± 5.1	5.3
	MCPA	0.5	88.4 ± 5.6	5.6
	2.4–D	1.0	91.7 ± 5.9	6.4
SEDIMENT	Mecoprop	15	86.1 ± 6.7	7.4
	MCPA	12	84.7 ± 9.0	9.6
	2.4–D	25	87.3 ± 7.8	8.5

residues were eluted with 80 ml of a mixture of 6% ethyl ether in petroleum ether. The eluate was rotary evaporated to a small volume and quantitatively transferred to a calibrated tube with the end volume adjusted to 5.0 ml. The qualitative and quantitative determinations were made through gas chromatography with electron capture detection.

RESULTS AND DISCUSSION

The recovery study was done on ten replicate water and sediment samples. The recovery values obtained and their statistical evaluation are presented in Table 1. The mean values ranged from 84.7 to 91.7%, and the standard deviation (SD) and coefficient of variation (v%) were below 10, indicating excellent repeatability of the analytical procedure.

In beginning to monitor water and sediment samples according to the previously described method[9], peaks corresponding to the chlorophenoxyacetic acid herbicides were frequently observed. These observations led to a questioning of the analytical method. The confirmation with a GC-MS Hewlett Packard Model 5992B of those residues in the water samples which presented the largest peaks of herbicides gave quite different results, indicating an absence of pentafluorobenzyl derivatives of chlorophenoxyacetic acid herbicides. The GC peaks of herbicides obtained correspond to the pentafluorobenzyl derivatives of other organic acids, which overlap certain peaks of herbicides. On investigating the different GC packed columns in order to obtain a good separation of the herbicides studied from interfering compounds, it came down to a 3% Silar 10 CP column, which presented a quite different gas chromatographic pattern, one which permitted a better determination of these classes of herbicides in water and sediment samples. The use of packed columns, as compared to capillary ones, was justified in that the packed column makes possible the analysis of extracts with less clean-up. In capillary columns a great amount of saturation of the gas chromatographic image, which does not permit ECD determination, was observed. For this reason and so as not to increase the cost of analysis by introducing additional clean-up steps or other adsorbents, the study was done to seek a better separation of the herbicides studied from interfering substances in the sample. To illustrate the difference in results a comparative determination of the same 26 water and 28 sediment samples was conducted, using the previously recommended 1.5% OV–17 + 1.95% QF–1 on a Gas Chrom Q 80–100 mesh column and the 3% Silar 10 CP on a Gas Chrom Q 100–120 mesh one. The

Table 2 Comparison of results of chlorophenoxyacetic acid herbicides obtained from samples studied.

		1.5% OV-17+ 1.95% QF-1			*Silar 10 CP*		
		Mecoprop	*MCPA*	*2.4-D*	*Mecoprop*	*MCPA*	*2.4-D*
Water 26	% of positive samples	100	100	100	0	4	27
	ranges µg/l	0.1–08	0.1–06	0.1–1.1	n.d.	0.1	0.1–1.0
	averages µg/l	0.5	0.4	0.7	n.d.	0.1	0.5
	detection limits µgl	0.1	0.1	0.1	0.1	0.1	0.1
Sediments 28	% of positive samples	89	89	50	0	0	11
	ranges ng/g	n.d.–9.8	n.d.–14.5	n.d.–7.0	0	0	n.d.–3.8
	averages ng/g	3.0	4.2	3.7	0	0	2.6
	detection limits ng/g	0.5	0.5	1.0	1.0	1.0	1.5

n.d. = not detected

results of the analyses are presented in Table 2, which shows the percentage of positive samples, ranges, averages of results obtained and detection limits of studied herbicides for water and sediment samples.

Examples of gas chromatograms of the same sediment sample analyzed on both columns are shown in Figures 1 and 2. The results obtained from the Silar 10 CP column indicate the very small amounts of contamination in the monitored samples with these classes of herbicides. To confirm their identity, the samples which showed the herbicide residues were submitted to a spiking study which showed a rise in their peak areas. Due to the low residue contents, it was difficult to confirm these residues through GC-MS. The derivatization of chlorophenoxy acetic herbicide molecules with pentafluorobenzyl bromide increased the ECD response significantly, thus lowering the detection limits to sub-ppb levels. An example of a gas chromatogram of a sediment sample spiked with the herbicides studied can be seen in Figure 3.

Under the sponsorship of CONACYT and the University of Veracruz, the described method has been introduced for monitoring the contamination of water and sediments with chlorophenoxyacetic acid herbicides.

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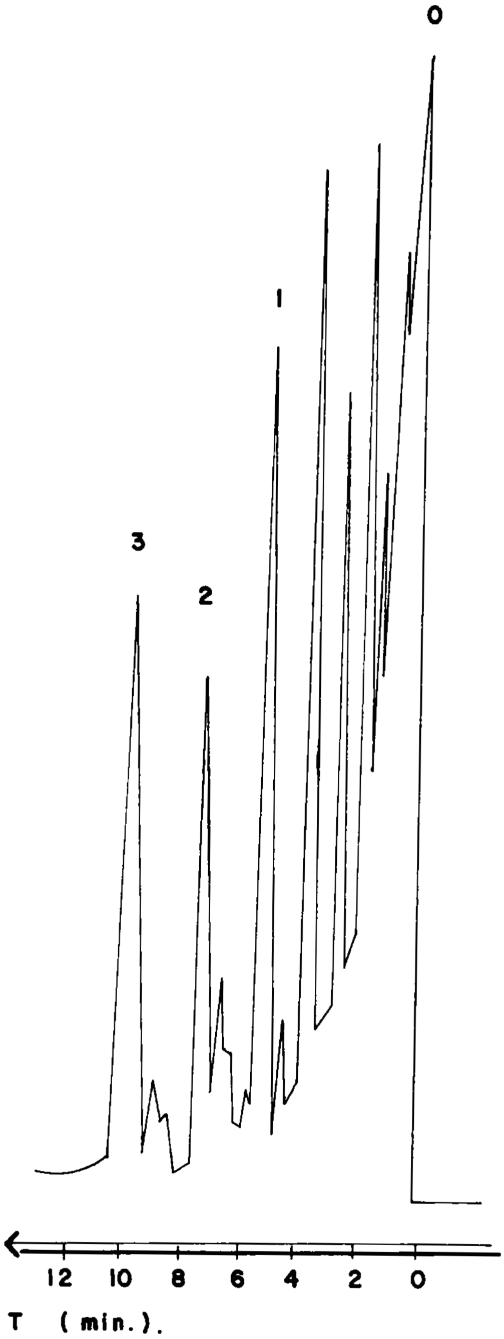

Figure 1 Gas chromatogram of a sediment sample analyzed on 1.5% OV-17 + 1.95% QF-1 column (0. solvent, 1. Mecoprop 12.8 ng/g, 2. MCPA 8.0 ng/g, 3. 2.4-D 13.8 ng/g).

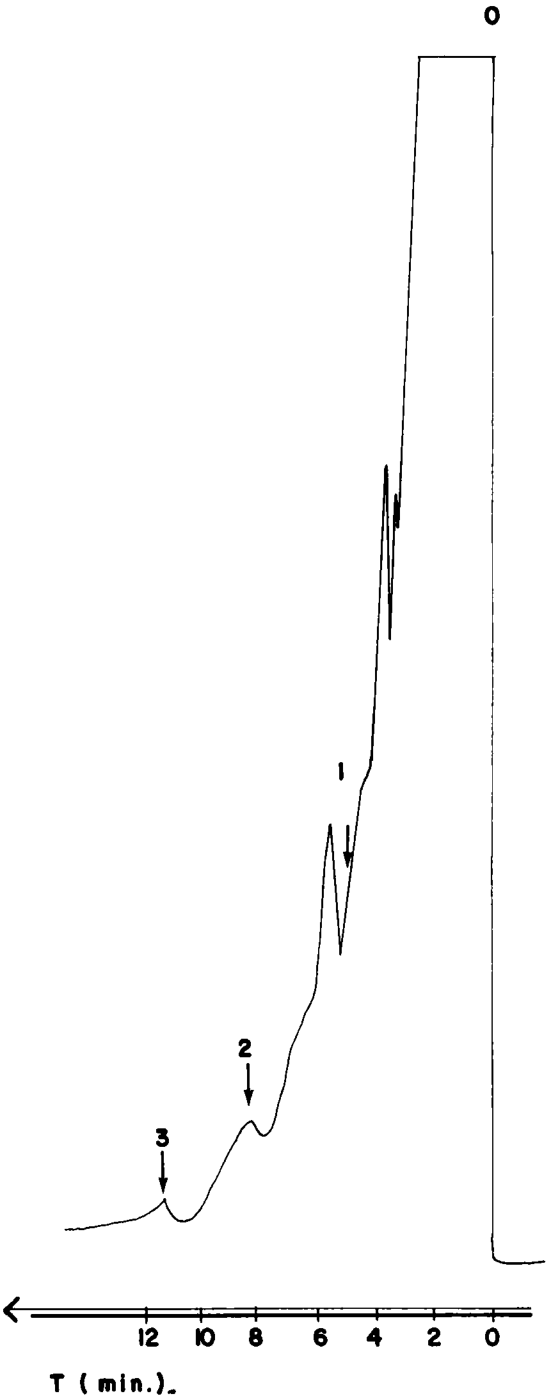

Figure 2 Gas chromatogram of the same sediment sample analyzed on 3% Silar 10 CP column (0. solvent, 1. Mecoprop 2. MCPA - traces, 3. 2.4–D—traces).

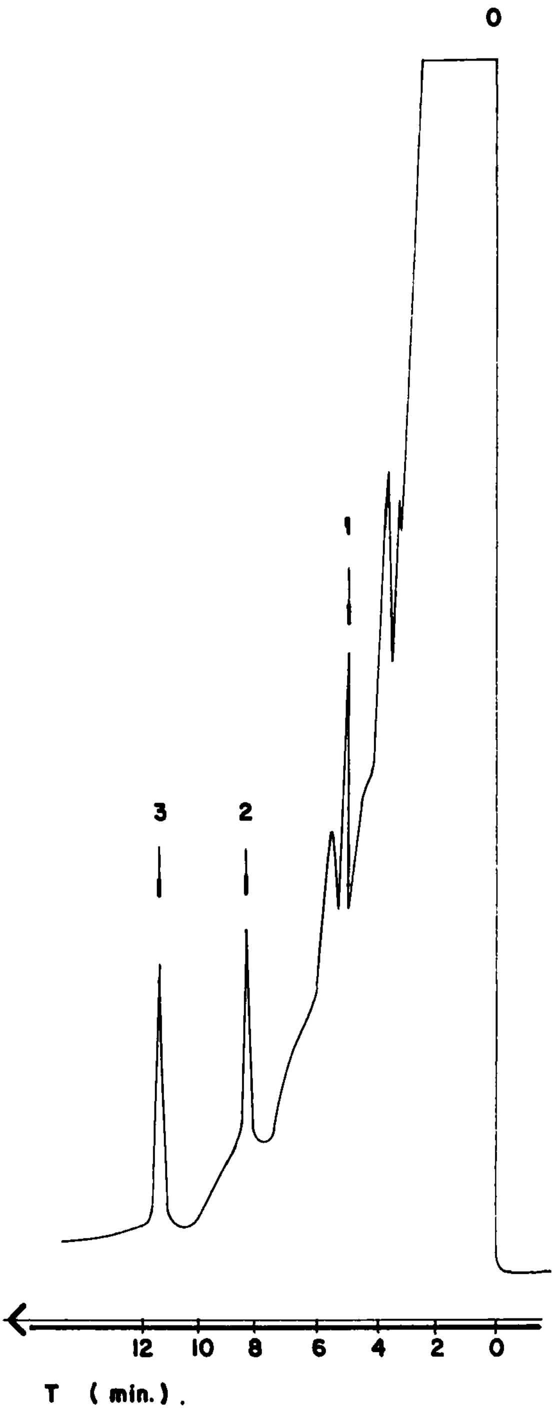

Figure 3 Gas chromatogram of the sediment spiked sample analyzed on 3% Silar 10 CP column (0. solvent, 1. Mecoprop 5.1 ng/g, 2. MCPA 4.0 ng/g, 3. 2.4–D 7.4 ng/g).

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