Journal of Chromatography, 634 (1993) 87-100
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 774

Determination of phenylurea pesticides in water by derivatization with heptafluorobutyric anhydride and gas chromatography-mass spectrometry

Frank P.M. Karg

ENSP — École Nationale de la Santé Publique, LERES — Laboratoire d'Étude et de Recherche en Environnement et Santé, Avenue Prof. L. Bernard, F-35043 Rennes (France)

(First received May 4th, 1992; revised manuscript received September 29th, 1992)

ABSTRACT

The application of direct gas chromatographic methods to phenylurea pesticides is difficult because these compounds are thermally unstable and rapidly give isocyanates and amines when using standard gas chromatography. However, derivatixation to more thermally stable compounds can be used. Procedures for solid-liquid extraction, catalytic heptatluorobutyrylation, clean-up and determination by GC-MS of phenylurea pesticides in water samples are reported. Detection limits are of the order of 10-50 ng/l.

INTRODUCTION

Since the discovery in 1946 [1] of the herbicidal properties of phenyl-substituted ureas, these compounds have been extensively used in agriculture as selective herbicides, mainly for pre-crop emergence and for weed control by inhibiting photosynthesis. Residues of these compounds can be found in soils and surface, ground and sometimes drinking waters.

High-performance liquid chromatographic (HPLC) analysis of phenylurea herbicides has been developed [2–19], but the methods often lack specificity, sensitivity and selectivity [10,11,20–22].

Direct gas chromatographic (GC) analysis of phenylurea herbicides and detection of the thermal degradation products (isocyanates and amines) has been reported [23–37]. Unfortunately, direct determination often results in poor reproducibility owing to incomplete thermal degradation of the phenylureas. Thermal reactions of these compounds in the injector and column usually do not proceed quantitatively. Also, different phenylurea herbicides can form the same isocyanate as degradation products (Fig. 1).

Methods for the hydrolysis of the phenylureas to their corresponding anilines and subsequent derivatization for GC with electron-capture or mass specific detection have been described [21,33,38–46,70–73]. These procedures based on phenylurea hydrolysis have a distinct lack of selectivity because different ureas can form the same aniline as hydrolysis products, e.g., diuron, linuron and neburon form 3,4-dichloroaniline (Fig. 2). The anilines formed by the hydrolysis procedure cannot be distinguished from the same anilines present at background levels in the sample. Anilines can occur in the environment in a number of ways, such as from direct industrial disposal, (bio)degradation of phenylureas, phenylcarbamates, acylanilides and dye products, reduction of nitrobenzene or combustion of polyurethanes [21]. Another point is the time-consuming and sometimes ineffective quantitative

0021-9673/93/$06.00

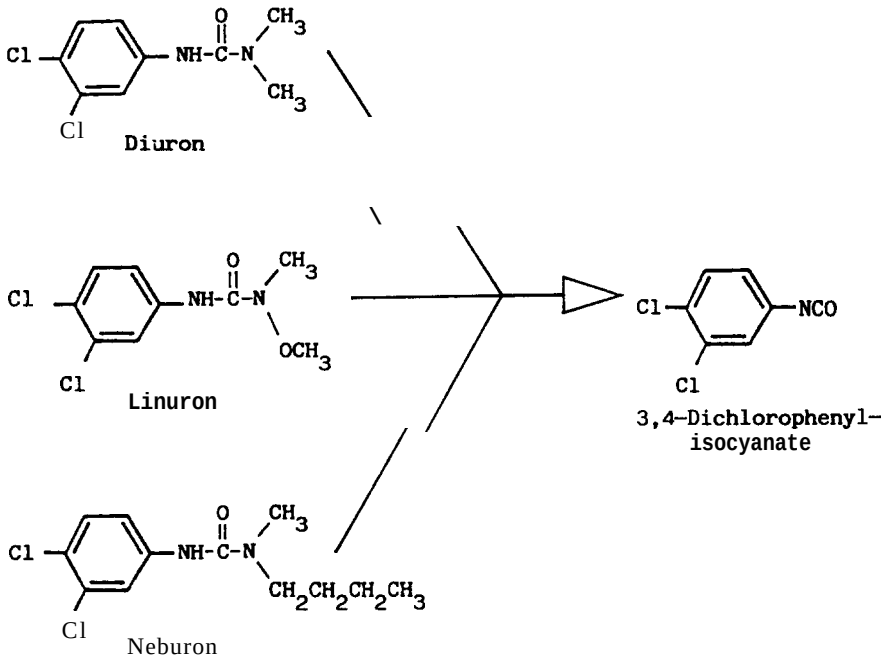


Fig. 1. Thermal degradation of diuron, linuron and neburon to 3,4-dichlorophenylisocyanate in the injector and capillary column.

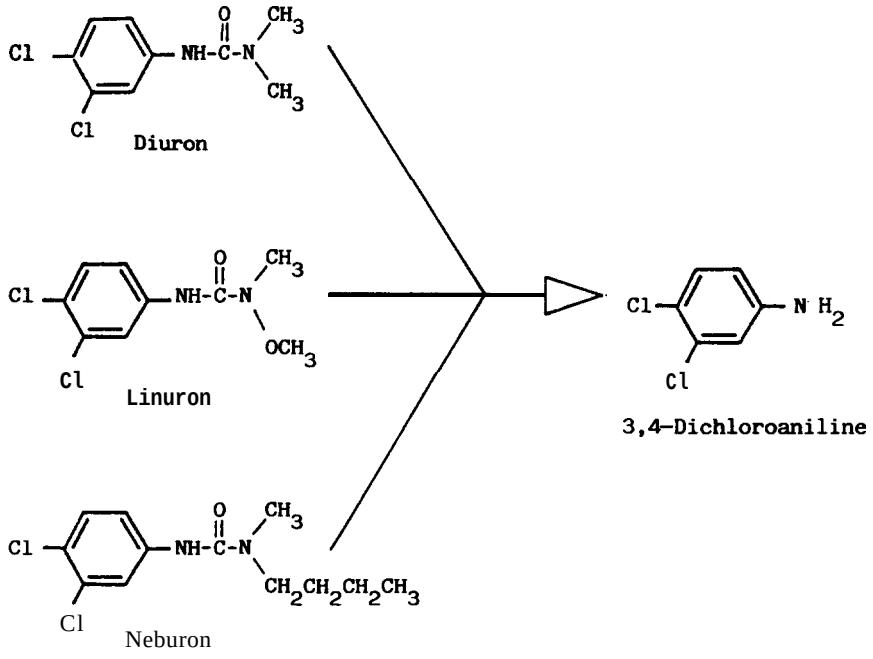


Fig. 2. Hydrolysis of diuron, linuron and neburon to 3,4-dichloroaniline.

conversion of phenylureas into their anilines.

Direct derivatization methods have been reported, including direct alkylation [35,47,48, 74–76]. Flash-heater methylation with trimethylanilinium hydroxide (methelute) was used to produce the N-methyl derivatives of several

phenylureas. In this on-column alkylation technique a minimum of 1 μg of the urea herbicide is required.

Alkylation of phenylureas with NaH-methyl iodide or NaH-ethyl iodide has been reported [5,8,23,34,49–55]. In all instances the alkylated products were far superior to the parent compounds for GC determination.

Fishbein and Zilinski [56] reported a silylation method for blocking the NH groups, which are the main contributor factor to the thermal decomposition of phenylurea molecules. Direct N-perfluoroacylation of the phenylurea herbicides has been achieved with trifluoroacetic anhydride (TFAA), heptafluorobutyric anhydride (HFBA), pentafluoropropionic anhydride (PFPA) and pentadecafluoroundecanoic anhydride (PFD) [20,22,34,52,55,57–66]. It has proved to be very useful for analysis by GC Perfluoro derivatization of compounds containing an OH or NH moiety.

This work is based on derivatization with heptafluorobutyric anhydride (HFBA) of phenylurea pesticides. The advantage of this method is that the phenylurea HFB derivatives are thermally stable and can be chromatographed over a wide temperature range without column decomposition. The described procedure of derivatization and capillary CC has some distinct advantages over HPLC for pesticide analysis. The higher resolution requires less clean-up of the sample as the by-products are more likely to be separated from the peaks of interest than by less efficient chromatographic methods (e.g., HPLC). The present work is based principally on reported procedures from [20,22,34,60,61,66] and the use of GC-MS. General information is given in refs. 77-79.

EXPERIMENTAL

The substances investigated were of certified purity purchased from Dr. Ehrenstorfer (Augsburg, Germany). The structures are given in Fig. 3. Stock solutions of these herbicides were prepared in toluene. For dilutions methanol and for cartridge elution acetone were usually employed. Dichloromethane was used for the derivatization procedure. All solvents were Pestipure products from SDS (Peypin, France).

HFBA was supplied by ICT (Regis 2708853). Bonded-phase cartridges were 6-ml Varian Mega Bond Elut C_{18} containing 1 g of octadecylsilane. J.T. Baker 3-ml cartridges containing 500 mg silica gel were used for the clean-up procedure. Standards were prepared in water and treated in the same way as samples.

Instrumentation

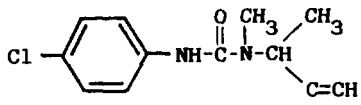
Capillary GC was carried out on an HP 5890 gas chromatograph fitted with a 25 m × 0.2 mm I.D. fused-silica column coated with a 0.25-μm film of OV-1 stationary phase. Mass spectrometric measurements were made with an HP 5970 mass-selective detector coupled directly to the capillary column. The mass-selective detector was operated in the electron impact (EI) mode and tuned by the autotune programme. Selected ion monitoring (SIM) was applied. The carrier gas was helium N55 (Alphagaz, Paris, France). The operating conditions were as follows: injector temperature, 250°C; oven temperature: initially 80°C for 0.5 min, increased at rate 30°C/min to 150°C, held for 10 min isothermal, increased at 5°C/min to 240°C, final hold for 10 min isothermal; detector temperature, 250°C; and GC-MSD interface temperature, 250°C.

Preparation of spiked water samples

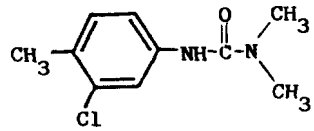
Calibration graphs were constructed for each phenylurea by using the internal standard method with fenuron as the internal standard. Distilled water (1 1) was spiked with 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1.0, 5.0 and 10.0 μg/l of each phenylurea.

Sample extraction

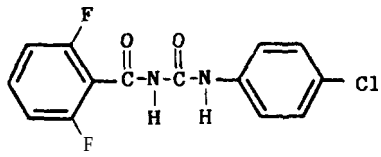
The RP-C,, cartridges were washed twice with one cartridge volume of acetone and twice with blank water for conditioning. Drying of the cartridges must be strictly avoided. The sample (1 1) was extracted under neutral or slightly alkaline conditions (pH 7-8). The pH was adjusted before extraction. The flow-rate for the aqueous sample was 20-25 ml/min over the carrier material. The flow-rate was regulated by altering the vacuum. After the enrichment the adhering water was removed under vacuum or with



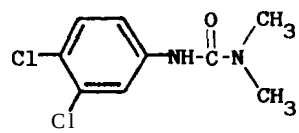
Buturon



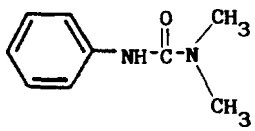
Cblortoluron



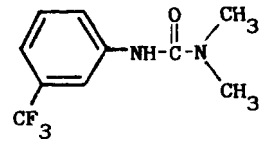
Diflubenzuron



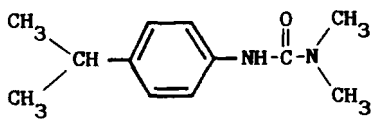
Diuron



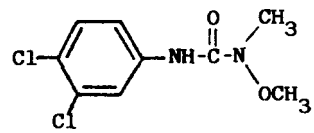
Fenuron



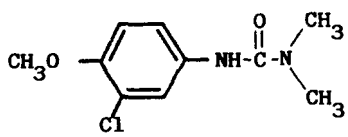
Fluometuron



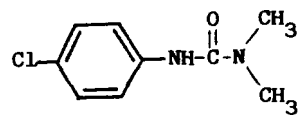
Isoproturon



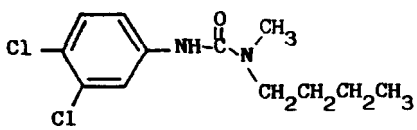
Linuron



Metoxuron



Monuron



Neburon

Fig. 3. Phenylurea pesticides investigated.

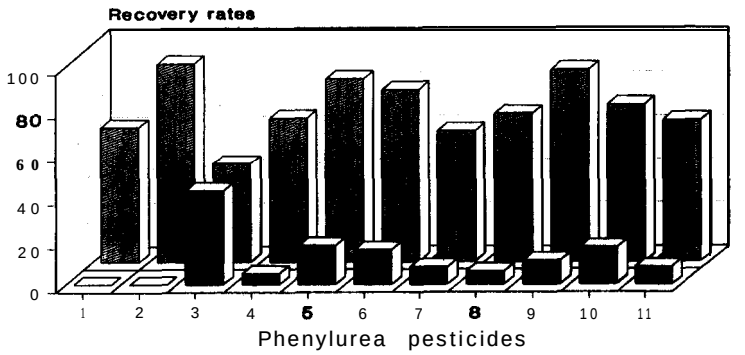


Fig. 4. Recoveries (%) of pesticides from water spiked with 0.5 μg/l of each compound. 1 = Buturon; 2 = chlortoluron; 3 = diflubenzuron; 4 = diuron; 5 = fenuron; 6 = fluometuron; 7 = isoproturon; 8 = linuron; 9 = metoxuron; 10 = monuron; 11 = neburon. Series 1 (black); liquid–liquid extraction with one 50-ml volume of dichloromethane. Series 2 (hatched): solid-liquid extraction with RP-C_{18} (1 g/6 ml).

gen. After this cartridge drying, elution was done twice with 2 ml of acetone. The solvent was transferred under pressure into volumetric flasks.

It should be noted that commercially available RP-C,, materials are sometimes of varying quality [SO] from batch to batch. The calibration and analysis should be performed with cartridges from the same batch and only by using an internal standard with the same chemical characteristics as the compounds under investigation.

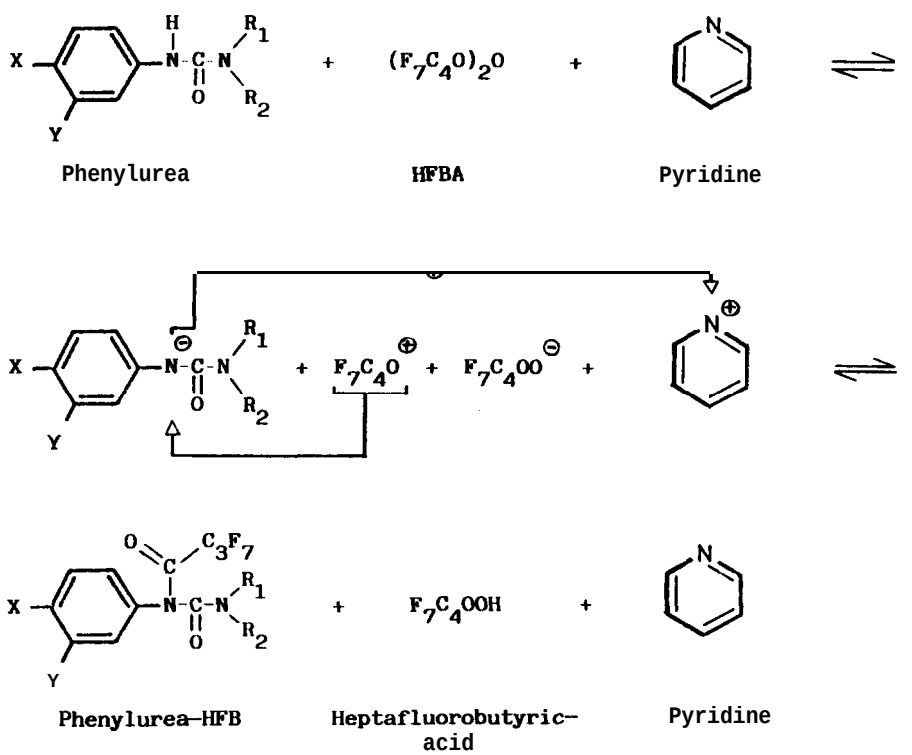


Fig. 5. Course of the derivatization.

Suspended matter in the sample (iron hydroxide, calcium carbonate, etc.) and increased concentrations of microorganism may clog the cartridge. In this event the water sample must be filtered through a glass filter before extraction.

Derivatization

The combined eluates from the cartridge enrichment were evaporated to dryness with a gentle stream of nitrogen. The dry residue was dissolved in 1 ml of dichloromethane using an ultrasonic bath for 5 min. To this solution 100 μl of HFBA and 100 μl of pyridine (catalyst) were added and the mixture was left at room temperature for 2 h. The excess of HFBA and pyridine was then separated by using a silica gel cartridge. The reaction mixture was placed on the cartridge and the phenylurea derivatives were eluted with 1 ml of dichloromethane directly into a vial. After closing the vial the eluate containing the phenylurea heptafluorobutyrates can be analysed directly by GC.

RESULTS AND DISCUSSION

Particularly for phenylurea pesticides, solid–liquid phase extraction using RP-C,, cartridges has several advantages over liquid-liquid extraction with dichloromethane. The recovery rates are better if RP-C,, cartridges for solid-liquid phase extraction is used than if liquid-liquid extraction of 1 1 water with 50 ml of dichloromethane is used (Fig. 4). Similar results were found by Klaffenbach [60]. The bad recoveries of buturon and chlortoluron and also of diuron, isoproturon, linuron, metoxuron and neburon with liquid-liquid extraction using dichlorome-

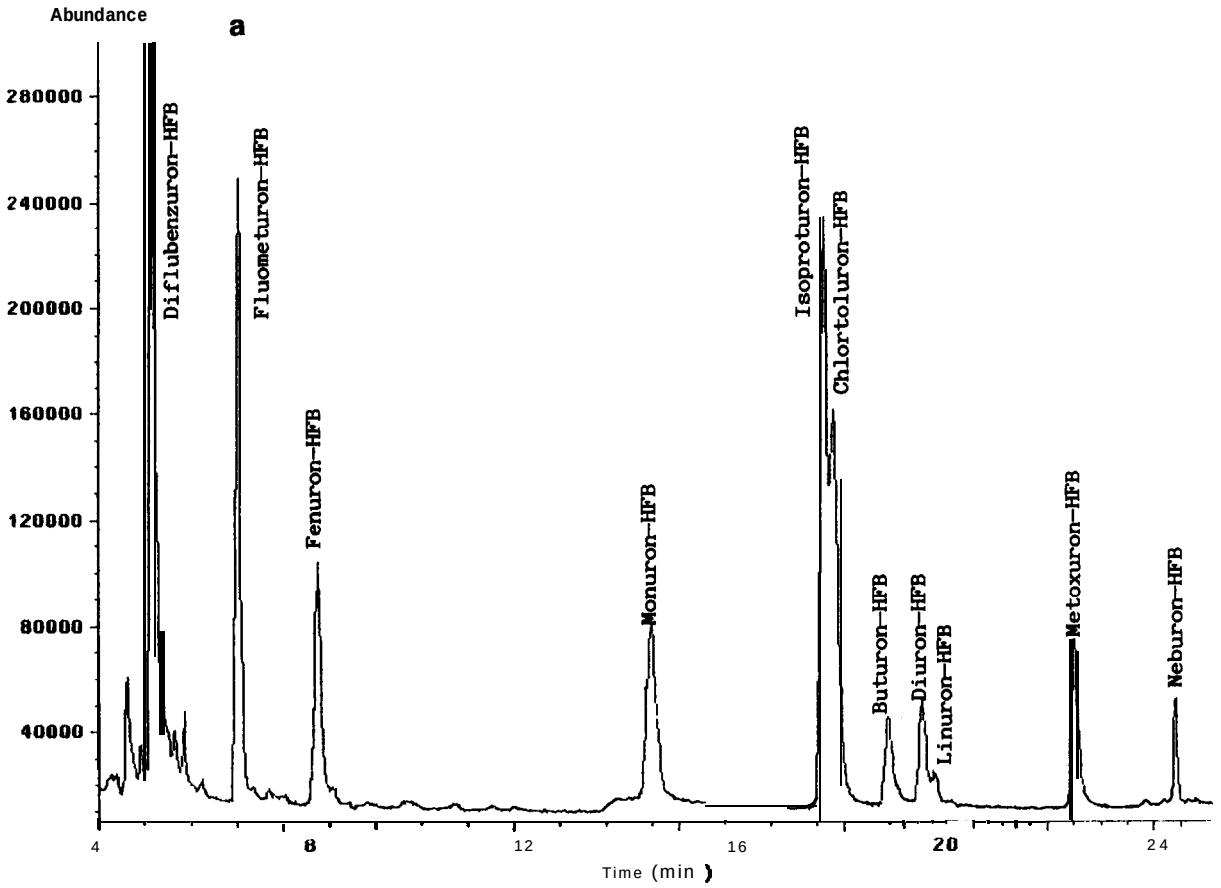


Fig. 6.

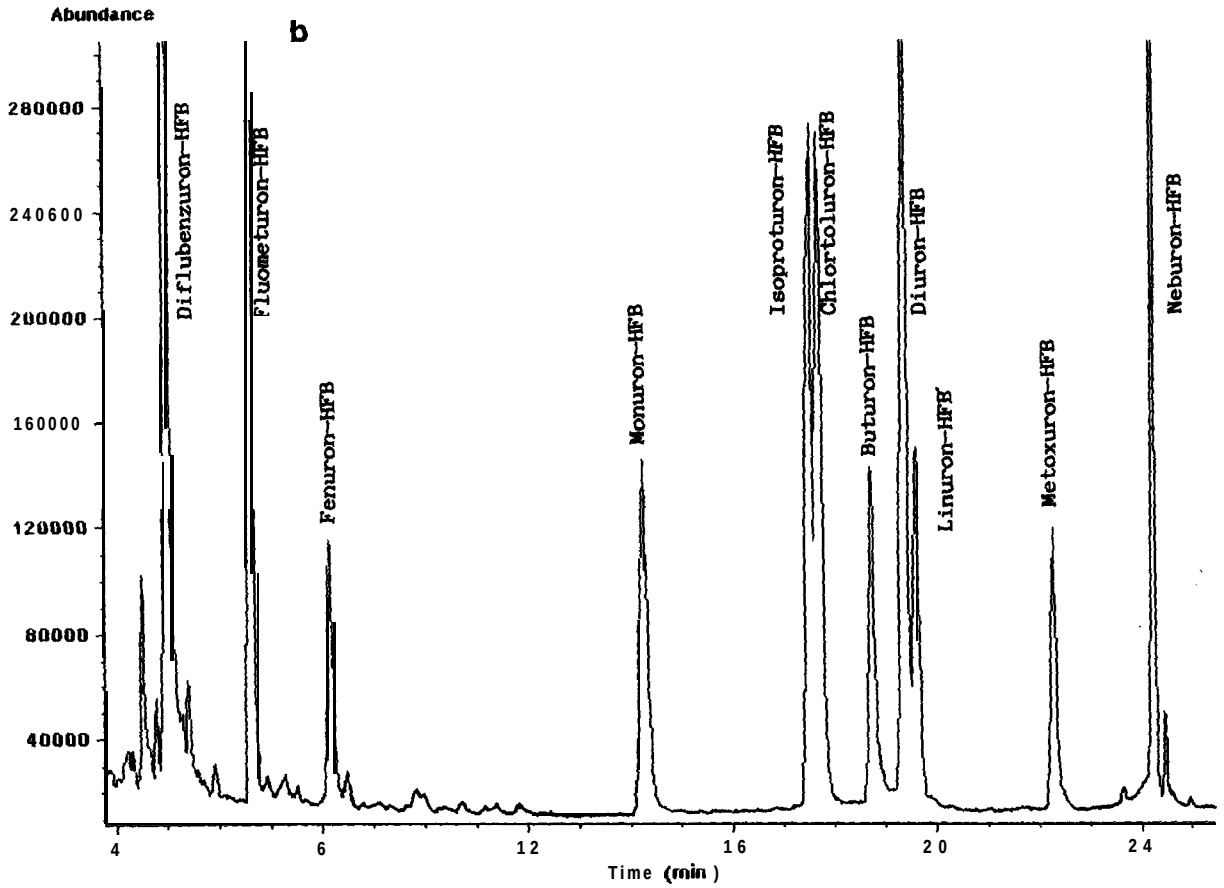


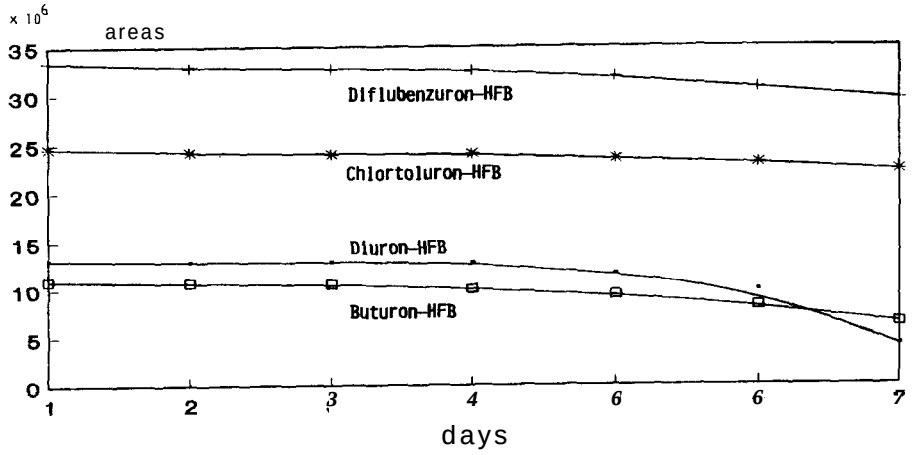
Fig. 6. Derivatization of phenylurea pesticides in spiked drinking water (1 μg/l) with HFBA. Reaction time: 2 h at room temperature. (a) Derivatization in toluene (method of Stan and Klaffenbach [22]); (b) derivatization in dry dichloromethane.

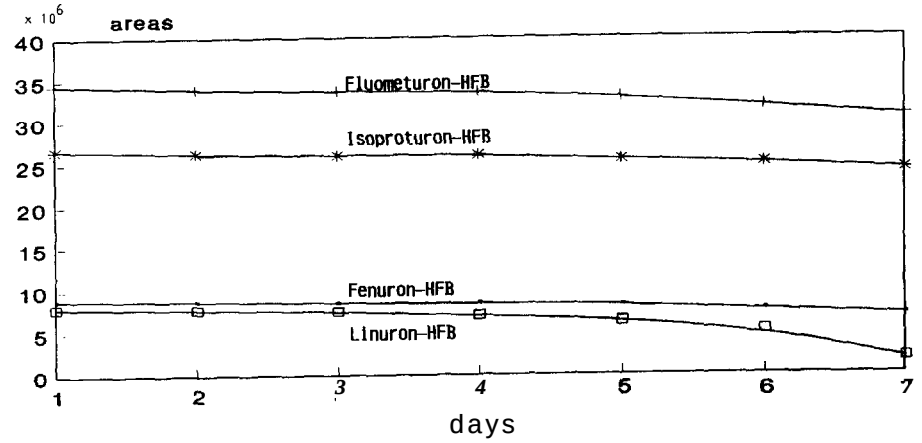
thane showed this very clearly. Only diflubenzuron shows a slightly better recovery with dichloromethane liquid-liquid extraction. Another problem is the emulsification that occurs when extracting surface waters with dichloromethane.

For the heptafluorobutyrylation of phenylurea pesticides a great variety of conditions (solvents, catalysts, etc.) can be used. Our aim was to find a simplified procedure with good derivatization results. The various conditions reported in the literature were tried, and the best solution for a rapid derivatization procedure was the use of dichloromethane as the derivatization medium, pyridine as catalyst (Fig. 5) and silica gel for clean-up. The derivatized reagent blank was free from interferences in the SIM mode. The rate of reaction of perfluorobutyrylation depends on the catalyst and the polarity of the solvent. Similar results have also been found by other workers [20,65–68]. Worobey [66] reported that the derivatization of toluene-based standards gave cu. 50% lower yields than that of standards prepared in acetonitrile. This well shows the influence of solvent polarity.

Other principle factors governing the rate of reaction, in addition to solvent polarity and temperature, are the catalyst and the purity of water. Fig. 6 shows the different derivatization results obtained using toluene (method of Stan and Klaffenbach [22]) and dichloromethane. The derivatization in dichloromethane gave significantly better yields of the heptafluorobutyrates for the same time and temperature. Heating of the reaction mixture is not required with dichloromethane.

A very important point is the protection of the derivatization mixture from water. The presence





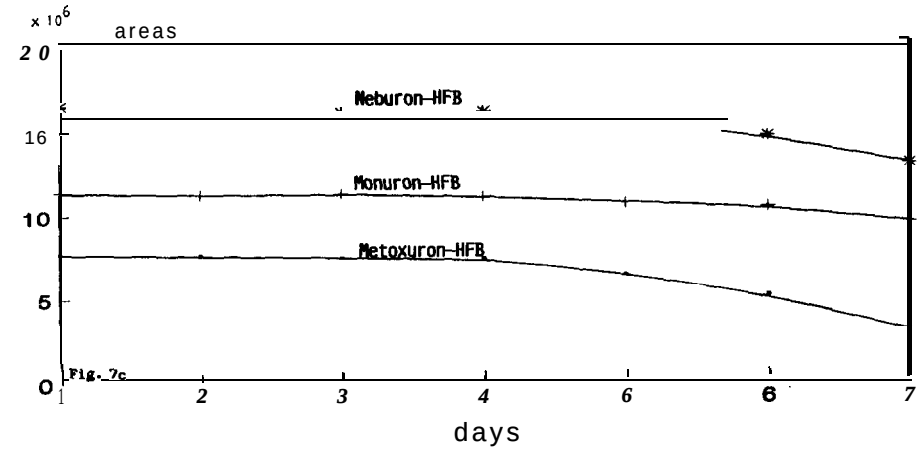


Fig. 7. Degradation of the phenylurea derivatives during seven days (peak area *versus* storage time). Storage under dry conditions at 4°C in the dark.

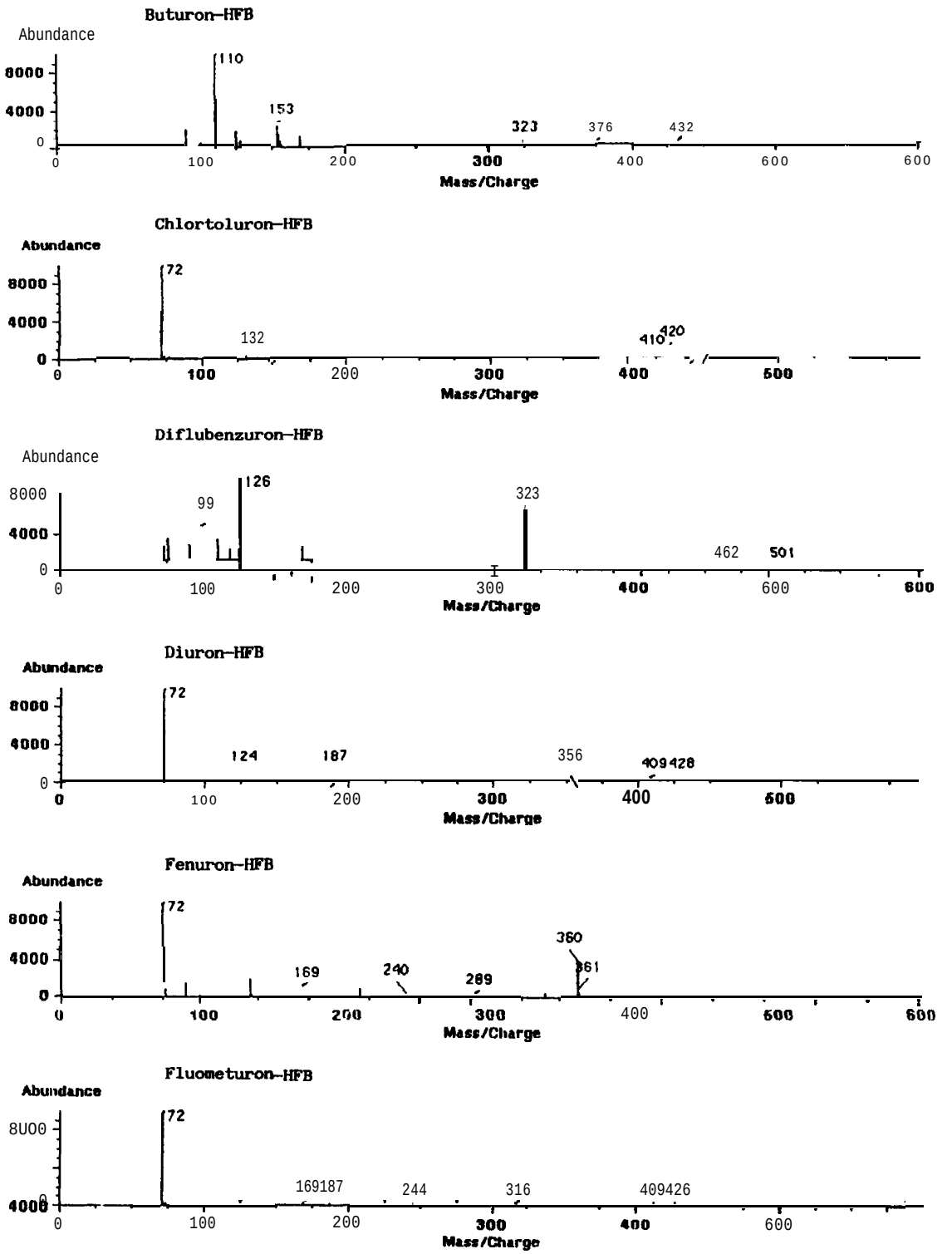


Fig. 8.

(Continued on p.96)

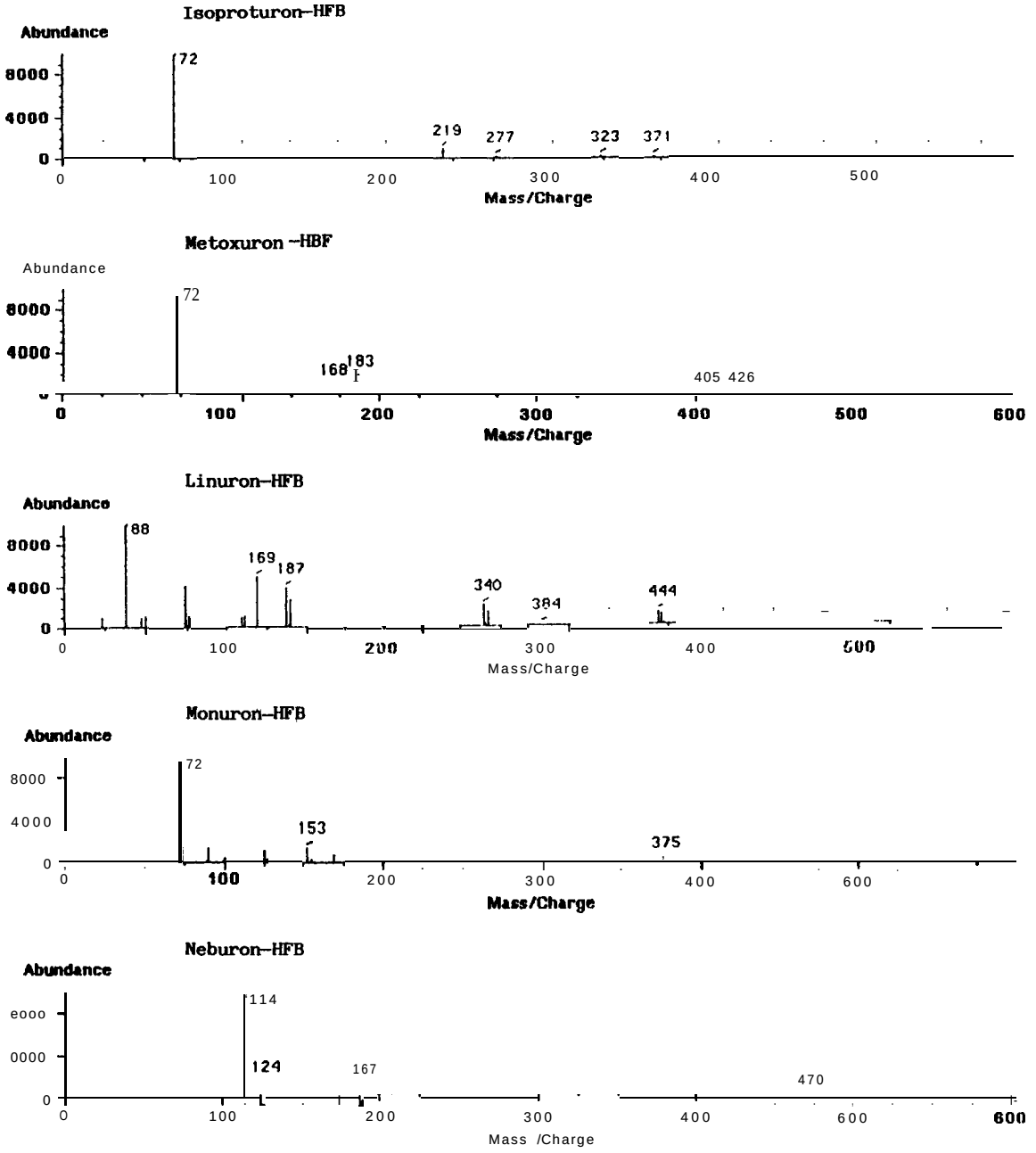


Fig. 8. Full scan mass spectra of phenylurea heptafluorobutyrates

of water can result in hydrolysis of the phenylurea heptafluorobutyrates. The use of sodium sulphate can eliminate such problems.

The derivatization with heptafluorobutyric anhydride and pyridine as catalyst in a solvent such as dichloromethane under dry conditions was found to give successful results for the compounds in Fig. 3 and also for chlorbromuron and metobromuron. The maximum yield of derivatization products was also found by Klaffenbach [60] at room temperature. Higher temperatures gave lower yields of the HFB-phenylureas. This may be the result of hydrolysis effects.

The degradation rates of the heptafluorobutyrates are shown in Fig. 7. No degradation was observed after 3 days of storage at 4°C in the dark.

All heptafluorobutyrates gave sharp peaks under the chromatographic conditions used. The HFB derivative of diflubenzuron is the heptafluorobutyrate of 4-chloroaniline [22,57,64,65].

TABLE I

MASS SPECTRAL DATA FOR THE PHENYLUREA HEPTAFLUOROBUTYRATES

HFB derivative	M_r	m/z (relative intensity, %)
Buturon	432.1	53 (100), 110 (51), 153 (24), 432 (3)
Chlortoluron	488.0	72 (100), 408 (8), 132 (4)
Diflubenzuron	323.0	323 (100), 126 (57), 154 (34), 325 (33)
Diuron	428.0	72 (100), 124 (5), 428 (4)
Fenuron	360.0	72 (100), 360 (10)
Fluometuron	428.1	72 (100), 168 (3), 428 (1)
Isoproturon	402.1	72 (100), 402 (19)
Linuron	444.0	340 (100), 88 (69), 60 (64), 342 (50)
Metoxuron	424.0	72 (100), 424 (9), 183 (8)
Monuron	394.0	72 (100), 394 (5), 153 (4)
Neburon	470.0	57 (100), 114 (82), 187 (13)

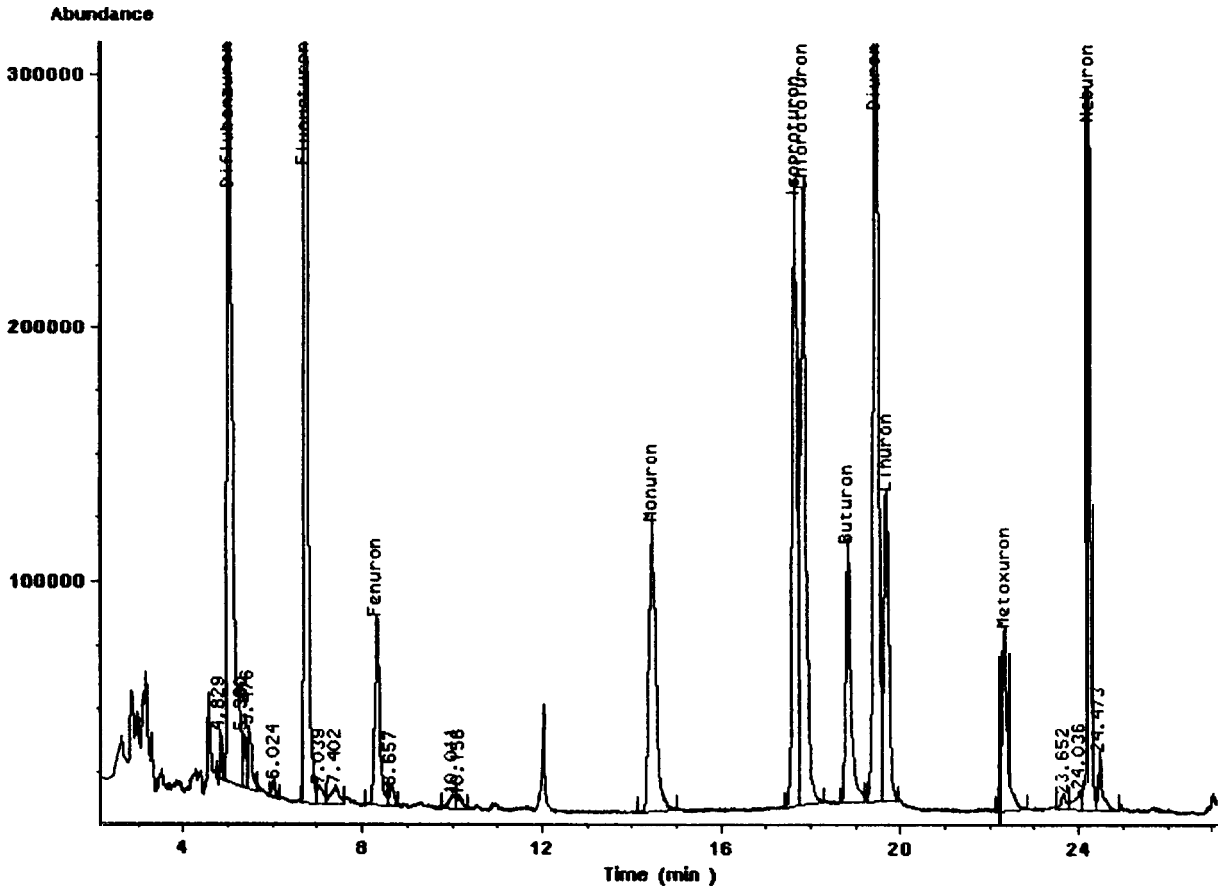


Fig. 9. SIM chromatogram of spiked surface water from the Vilaine river (400 ng/l of each phenylurea pesticide).

TABLE II

TIME PROGRAMME FOR SELECTED ION AQUISITION (SIM)

Ion group No.	HFB derivative	Ions (m/z)	Start time (min)	Dwell time (ms)
1	Diflubenzuron	154	3.8	200
		323		200
2	Fluometuron	72	6.0	100
	Fenuron	360		200
3	Monuron	72	13.0	200
		394		200
4	Isoproturon	72	16.5	100
	Chlortoluron	402		100
		408		200
5	Buturon	53	18.3	100
		110		100
6	Diuron	72	19.3	100
	Linuron	428		100
		88		100
		340		200
7	Metoxuron	72	20.5	100
		424		100
8	Neburon	114	23.0	100
		187		100

All other derivatives result from proton substitution (Fig. 5) of the NH moiety by a heptafluorobutyric acyl group.

The mass spectra of the derivatives are shown in Fig. 8 and mass spectral data are given in Table I. For the derivatives of the N,N-dimethylphenylureas the base peak always occurs at *m/z* 72 (dimethyl isocyanate). The derivatives of the N-methyl-N-methoxyphenylureas exhibit a peak at *m/z* 88 (methylmethoxy isocyanate).

The applicability of the method to surface waters is demonstrated in Fig. 9 for a sample from the Vilaine river spiked with phenylurea pesticides at the 400 ng/l level and analysed by GC-MS in the SIM acquisition mode with time programming. The selected ions and their time windows for the specific detection used are given in Table II.

CONCLUSIONS

The direct HFBA derivatization and determination by GC-MS of trace levels of phenylurea herbicides in water samples has been shown to be successful for all eleven compounds investigated. The heptafluorobutyrylation of the phenylureas provided high specificity for their parent compounds. Also, the phenylurea derivatives show good sensitivity when using SIM acquisition for GC-MS detection.

REFERENCES

1 H.E. Thompson, C.P. Swanson and A.C. Norman, *Bot. Gaz.*, 107 (1946) 476.
2 B. Berger and R. Heitefuss, *Fresenius'* Z. *Anal. Chem.*, 334 (1989) 360-362.
3 T.H. Byast, *J.* Chromatogr., 134 (1977) 216-218.
4 D.S. Farrington, R.G. Hopkins and J.H.A. Ruzicka, Analyst, 102 (1977) 337-381.
5 G. Glad, T. Popoff and 0. Theander, *J.* Chromatogr. *Sci.*, 16 (1978) 118-122.
6 J.H. Kennedy, *J.* Chromatogr. *Sci.*, 15 (1977) 79-81.
7 G. Kulshrestha and R. Khazanchi, *J.* Chromatogr., 318 (1985) 144-148.
8 J.F. Lawrence, *J. Chromatogr. Sci., 14 (1976) 557-559.*
9 J.F. Lawrence and D. Turton, *J. Chromatogr., 207 (1978) 159-163.*

10 H.A. Moye, ***Analysis of Pesticides Residues (Chemical Analysis Series,*** Vol. 58), Wiley, New York, 1981, pp. 157-198.
11 L. Muszkat and N. Aharonson in G. Zweig and J. Sherma (Editors), ***Analytical Methods for Pesticides and Plant Growth Regulators,*** Vol. XIV, Academic Press, Orlando, FL, 1986, pp. 95-132.
12 J. Pribyl and F. Herzel, ***J. Chromatogr., 125 (1976) 487-494.***
13 J. Pribyl and F. Herzel, ***J. Chromatogr.,*** 166 (1978) 272-278.
14 R. Reupert and E. Plöger, ***Fresenius' Z. Anal.*** Chem., 331 (1988) 503-509.
15 R. Reupert and E. Plöger, ***Wasser,*** 72 (1989) 211-233.
16 R. Reupert, E. Plöger and G. Brausen, ***Application Note,*** Hewlett-Packard, Avondale, PA, 1990.
17 J.A. Sidwell and J.H.A. Ruzicka, ***Analyst,*** 101 (1976) 111-121.
18 A.E. Smith and K.A. Lord, ***J. Chromatogr., 107 (1975) 407-410.***
19 C.M. Sparacino and J.W. Hines, ***J. Chromatogr. Sci., 14 (1976) 549-556.***
20 U.A.Th. Brinkman, A. de Kok and B. Geerdink, ***J. Chromatogr., 283 (1984) 113-126.***
21 A. de Kok, Y.J. Vos, C. van Gardenen, T. de Jong, M. van Opstal, R.W. Frei, B. Geerdink and U.A.Th. Brinkman, ***J. Chromatogr., 288 (1984) 71-89.***
22 H.J. Stan and P. Klaffenbach, ***Fresenius' J. Anal.*** Chem., 339 (1991) 40-45.
23 A. Biichert and H. Lokke, ***J. Chromatogr., 115 (1975) 682-686.***
24 R. Deleu and A. Copin, ***J. Chromatogr., 171 (1979) 263-268.***
25 K. Grob, ***J. Chromatogr., 208 (1981) 217-229.***
26 H.J. Jarczyk, ***Pflanzenschutz-Nachr., 28 (1975) 334-352.***
27 E. Katz and R.F. Strusz, ***J. Agric. Food*** Chem., 17 (1969) 140991411.
28 G.C. Mattern, G.-M. Singer, J. Louis, M. Robson and J.D. Rosen, ***J. Assoc. Off. Anal.*** Chem., 72 (1989) 970-974.
29 C.E. McKone, ***J. Chromatogr., 36*** (1968) 234-237.
30 C.E. McKone, ***J. Chromatogr., 44 (1969) 60-66.***
31 C. Parouchais, ***J. Assoc. Off. Anal. Chem., 56 (1973) 831-833.***
32 S. Perez, J.-M. Garcia-Baudi and J.L. Tadeo, in H. Frehse, E. Kessler-Schmitz and S. Conway (Editors), ***Book of Abstracts -7th International Congress of Pesticide Chemistry,*** Vol. 3, 1990, abstract no. 3.
33 K. Ramsteiner, ***DFG Deutsche Forschungsgemeinschaft, Riickstandsanalytik von Pflanzenschutzmitteln***, Band II, Verlag Chemie, Weinheim, 1977, p. 56-A1.
34 D.G. Saunders and L.E. Vanata, ***Anal.*** Chem., 46 (1974) 1319-1324.
35 D. Spengler and B. Hamroll, ***J. Chromatogr., 49 (1970)*** 205–214.
36 T. Tamani and S. Zitrin, ***Biomed. Mass Spectrom., 14 (1987) 39-42.***
37 M.J. Wimmer and R.R. Smith, ***J. Agron.*** Food Chem., 39 (1991) 280–186.
38 I. Baunok and H. Geissbühler, ***Bull. Environ. Contam. Toxicol., 3 (1968) 7-17.***
39 W.E. Bleidner, H.M. Baker, M. Levitzky and W.K. Lowen, ***J. Agric. Food*** Chem., 2 (1954) 476-479.
40 D.J. Caverly, ***Analyst, 103 (1978) 368-374.***
41 ***I.C.*** Cohen and B.B. Wheals, ***J. Chromatogr., 43*** (1969) ***233-240.***
42 A. de Kok, I.M. Roorda, R.W. Frei and U.A.Th. Brinkman, ***Chromatographia, 14 (1981) 579-586.***
43 W.H. Gutenman and D.J. Lisk, ***J. Agric. Food*** Chem., 12 (1964) 46-48.
44 H.-J. Müller, ***Thesis,*** Technische Universität Berlin, Berlin, 1989.
45 K. Ramsteiner, ***Analysis,*** Vol. I, Verlag Chemie, Weinheim, 1987, pp. 251-263.
46 M. Wisson, C. van Hoek and H.H. Sauer, in G. Zweig and J. Sherma (Editors), ***Analytical Methods for Pesticides and Plant Growth Regulators,*** Vol. III, Academic Press, New York, 1976, p. 417.
47 L. Ogierman, ***Fresenius' Z. Anal. Chem., 320 (1985) 365-368.***
48 F.S. Tanaka and R.G. Wien, ***J. Chromatogr., 87 (1973) 85-93.***
49 R. Greenhalgh and J. Kovacicova, ***J. Agric. Food Chem., 23 (1975) 325-329.***
50 W.P. Cochrane and R. Greenhalgh, presented at the ***166th National Meeting of the American Chemical Society, Chicago, IL, 1973.***
51 J.F. Lawrence, ***J. Assoc. Off. Anal. Chem., 59 (1976) 1061-1065.***
52 J.F. Lawrence, ***J. Agric.*** Food Chem., 24 (1976) 1236-1238.
53 J.F. Lawrence and G.W. Laver, ***J. Agric. Chem., 23 (1975)*** 1106-1109.
54 J.F. Lawrence, C. van Buuren, U.A.Th. Brinkman and R. Frei, ***J. Agric.*** Food Chem., 28 (1980) 630–632.
55 J.J. Ryan and J.F. Lawrence, ***J. Chromatogr., 135 (1977) 117-122.***
56 L. Fishbein and W.L. Zilinski, ***J.*** Chromatogr., 20 (1965) 9-14.
57 A.B. De Milo, P.H. Terry and D.M. Rains, ***J. Assoc. Off. Anal.*** Chem., 61 (1978) 629-635.
58 R.T. Evans, ***J. Chromatogr., 88 (1974)*** 398–402.
59 A.H. Hofberg, L.C. Heinrichs, M. Barringer, M. Tin and G.A. Gentry, ***J. Assoc. Off. Anal. Chem., 60 (1977) 716-719.***
60 P. Klaffenbach, ***Thesis,*** Technische Universität Berlin, Berlin, 1991.
61 D.R. Knapp, ***Handbook of Analytical Derivatization Reactions,*** Wiley, New York, 1979.
62 J.F. Lawrence, ***J. Chromatogr., 130 (1977) 97-102.***
63 S. Smith, G.H. Willis and L.L. McDowell, ***J. Agric. Food*** Chem., 31 (1983) 610-612.
64 B.L. Worobey and G.R.B. Webster, ***J. Assoc. Off. Anal. Chem., 60 (1977) 213-217.***
65 B.L. Worobey and G.R.B. Webster, ***J. Chromatogr., 153 (1978) 423-431.***
66 B.L. Worobey, ***J. Chromatogr., 262 (1983) 328-330.***
67 J.N. Seiber, ***J. Agric. Food*** Chem., 20 (1972) 443-446.
68 J.R. Bose, ***J. Agric.*** Food Chem., 25 (1977) 1209–1210.
69 K. Blau and G.S. King, ***Handbook of Derivatization for Chromatography,*** Heyden, London, 1977.

70 W.R. Benson and J.N. Damico, ***J. Assoc. Off.*** Agric. ***Chem.,*** 51 (1968) 347-365.
71 T.M. Ragab, C.F. Everett and A.C. DeMarco, ***J.*** Agric. Food ***Chem.,*** 31 (1983) 449-451.
72 R. Deleu, J.-P. Barthelemy and A. Copin, ***J. Chromatogr.***, 134 (1977) 483-488.
73 H.R. Schulten, ***Fresenius' Z. Anal.*** Chem., 293 (1978) 273-281.
74 J.F. Lawrence and K.M.S. Sundram, ***J. Assoc. Off. Anal. Chem.***, 59 (1976) 938-948.
75 J. Drozd, ***Chemical Derivatization in Gas Chromatography (Journal of Chromatography Library,*** Vol. 19), Elsevier, Amsterdam, 1981.
76 G. Voss, in ***DFG Deutsche Forschungsgemeinschaft Manual of Pesticide Residue Analysis,*** Vol. I, Verlag Chemie, Weinheim, 1987, pp. 241–250.
77 G.C. Milde and U. Müller Wegener (Editors), ***Pflanzenschutzmittel und Grundwasser***, Gustav Fischer, Stuttgart, New York, 1989.
78 H. Thieme and U. Kurzik-Dumke, ***Pharmazie, 36 (1981) 304.***
79 C.R. Worthing and R.J. Hance, ***The Pesticide Manual,*** British Crop Protection Council, London, 9th ed., 1990.
80 E. Chladez and R.S. Murano, ***J. Chromatogr. Sci., 22 (1984) 313-320.***