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DETERMINATION OF PHENYLUREA HERBICIDES VIA DIRECT DERIVATISATION WITH HEPTAFLUOROBUTYRIC ANHYDRIDE*

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SUMMARY

Direct derivatisation of fifteen phenylurea herbicides with heptafluorobutyric anhydride (HFBA) has been studied. Quantitative conversion is obtained within 1 h at 60°C, using hexane as solvent. The nuclear magnetic resonance and mass spectrometric characteristics of the HFB-herbicides are reported, as well as their behaviour in adsorption high-performance liquid chromatography and capillary gas chromatography; detection limits are of the order of 50 pg and 1 pg, respectively, using electron-capture detection. Applications to water and crop samples are reported.

INTRODUCTION

Substituted phenylurea herbicides are widely used in agriculture as selective herbicides[1] and, consequently, can give rise to residues in crops, soil and surface water, for example. For these sample types knowledge of the residue tolerances is required, and selective and sensitive methods of analysis must, therefore, be evaluated. Table I shows the general structure and names of the fifteen major phenylurea herbicides.

In recent years increasing attention has been given to direct determination of phenylureas by means of high-performance liquid chromatography (HPLC[2–5]; however, lack of adequate sensitivity often makes HPLC unsuitable for trace-analytical work. Direct gas chromatography (GC) of the herbicides has also been reported[6–11]. Difficulties frequently arise because of the rapid thermal decomposition of some of these compounds into their isocyanates. A favoured alternative GC technique is based on the hydrolysis of the phenylureas to their corresponding anilines[12–15], which are then derivatised for sensitive electron-capture detection (ECD) and analysed by GC–ECD. Hydrolysis of phenylureas is time-consuming, however, and recent research[16–18] has been directed to optimisation of the reaction conditions, *viz.* by using catalytic hydrolysis on a solid silica surface. Still, it should be realised that all procedures based on hydrolysis have an inherent lack of selectivity, because they cannot distinguish between anilines initially present in the sample to be analysed, and those originating from phenylurea hydrolysis.

* This work forms part of the thesis of A. de Kok.

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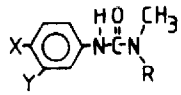
TABLE I

NAMES AND STRUCTURES OF THE FIFTEEN MAJOR PHENYLUREA HERBICIDES



Herbicide	*Code**	*M.W.*	*Substituents*		
			X	*Y*	*R*
Fenuron	Fe	164	H	H	CH_3
Isoproturon	Ip	206	$(CH_3)_2CH$	H	CH_3
Fluometuron	Fm	232	H	CF_3	CH_3
Monuron	Mo	198	Cl	H	CH_3
Chlortoluron	Ct	212	CH_3	Cl	CH_3
Diuron	Di	233	Cl	Cl	CH_3
Metoxuron	Mx	228	OCH_3	Cl	CH_3
Chloroxuron	Cx	290	4-Cl-C_6H_4O	H	CH_3
Difenoxuron	Dx	286	4-CH_3O-C_6H_4O	H	CH_3
Buturon	Bu	236	Cl	H	$CH(CH_3)C{\equiv}CH$
Neburon	Nb	275	Cl	Cl	C_4H_9
Monolinuron	Ml	214	Cl	H	OCH_3
Linuron	Li	249	Cl	Cl	OCH_3
Metobromuron	Mb	259	Br	H	OCH_3
Chlorbromuron	Cb	293	Br	Cl	OCH_3

* Used in figures.

Recently, our group has attempted to overcome the selectivity problem in two different ways, *viz.* by elaborating an analysis scheme for phenylureas and anilines based on the combined use of HPLC and GC (*cf.* ref. 18) and by direct derivatisation of the intact herbicides with the same reagents as are used for the anilines. The latter approach is discussed in this paper.

EXPERIMENTAL

Materials

Linuron, diuron and metoxuron were obtained as gifts from Sandoz (Basle, Switzerland). All the other herbicides were gifts from the Food Inspection Service (Amsterdam, the Netherlands). Stock solutions of herbicides were made in toluene, ethyl acetate or acetone. For dilutions hexane and dichloromethane were mostly used.

All solvents were analytical-grade products from Baker (Deventer, The Netherlands). They were distilled before use. Heptafluorobutyric anhydride (HFBA) from Merck (Darmstadt, F.R.G.) was used as received.

Apparatus

Capillary GC was done on a Pye-Unicam (Philips, Eindhoven, The Netherlands) or a Packard-Becker Model 427 or 433 gas chromatograph equipped with a ^{63}Ni electron-capture detector. Injections (1 μl) were done with a solid injector or via a septum injector (splitless, according to Grob). The stationary phase on the 25 m × 0.22 mm I.D. wall-coated open-tubular (WCOT) fused-silica column was CP-Sil 5. The standard column temperature programme was from 110°C (5 min isothermal) to 250°C at a rate

of 6°C min^{-1}. The injector and detector temperatures were 240 and 300°C, respectively. The nitrogen carrier and purge-gas flow-rates were 1 and 30 ml min^{-1}, respectively.

Gas chromatography–mass spectrometry (GC–MS) was performed on a Finnigan (Sunnyvale, CA, U.S.A.) 4000-series quadrupole GC–MS system interfaced with an INCOS 2000-series data system with electron impact at 70 eV and an ion-source temperature of 230°C. GC conditions were the same as those given above, except that helium was used as carrier gas.

Thin-layer chromatography (TLC) was carried out in Hellendahl staining jars, using precoated silica gel F_{254} (Merck) and apolar chemically bonded KC_{18} (Whatman, Springfield Mills, U.K.) thin-layer plates. Spots were visualised by inspection under UV light. ^1H NMR spectra were recorded with a Bruker WH 90 F.T. spectrometer (Bruker Physics, Karlsruhe, F.R.G.). ^1H chemical shifts were measured with C^2HCl_3 as solvent.

The HPLC system consisted of an Orlita (Giessen, F.R.G.) Model AE 1044 or TW 1515 reciprocating pump, a Valco (Houston, TX, U.S.A.) six-port injection valve with a 100-μl loop, and a Pye-Unicam (Philips) Model LC 3, or a Zeiss (Oberkochen, F.R.G.) Model PM2 DLC variable-wavelength UV detector.

HPLC was carried out on 25 cm × 4.6 mm I.D. stainless-steel columns packed with 5-μm LiChrosorb SI-60 silica (Merck) or 10-μm LiChrosorb NH_2 chemically bonded phase. Mixtures of hexane with dioxane or dichloromethane were used as mobile phases.

For HPLC–ECD, the HPLC column was connected with a Pye-Unicam (Philips) ^{63}Ni electron-capture detector via an evaporisation interface, which is a modification of a former commercially available design. The interface essentially consists of a 75 cm × 0.25 mm I.D. capillary enclosed in a massive stainless-steel tube and kept at a temperature of 250–300°C[19,20].

Methods

Details of the derivatisation and sample pretreatment procedures are given in the appropriate sections below.

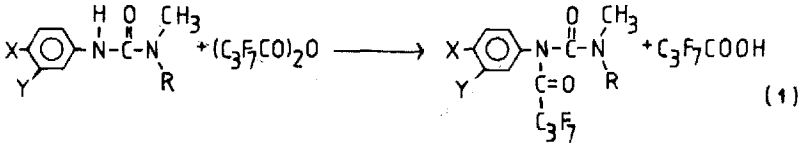
RESULTS AND DISCUSSION

Initial derivatisation studies

Direct derivatives of phenylurea herbicides have been prepared with alkylating reagents[21–24], such as methyl or ethyl iodide, and with silylating reagents[25]. These alkyl or silyl derivatives improve the thermal stability and chromatographic properties of the phenylureas, but sensitivity towards ECD is not increased. Acylation with electrophilic anhydrides, such as heptafluorobutyric (HFBA), pentafluoropropionic (PFPA) or trifluoroacetic (TFAA) anhydride should, therefore, be advantageous. Unfortunately, however, acylation of the intact herbicides is not as easy as that of the corresponding anilines, and has not attracted much attention. Saunders and Vanatta[26] studied the direct derivatisation of fenuron, monuron and diuron with TFAA in chloroform for 2–16 h at 52°C. Derivatives of fenuron and monuron, in low yield, were identified from GC chromatograms; no derivative of diuron was observed. Ryan and Lawrence[27] reported the preparation of perfluoro derivatives of linuron. The reaction was carried out in 0.1 *M* triethylamine in benzene for 1.5 h at 70°C. Hofberg *et al.*[28] prepared the TFA

derivative of milligram amounts of fluometuron by shaking the reactants for 15 min at room temperature and keeping the mixture at 55°C for a further 30 min.

In the present work, in early experiments on the direct derivatisation of the herbicides standard conditions, *i.e.* those used for anilines[17], were used. These involve: (1) mixing 5 ml of a sample solution with 20 μl of HFBA in a centrifuge tube, shaking for 1 min after stoppering the tube, and waiting for a further 5 min; (2) washing with 3 ml of an aqueous 1 *M* sodium hydroxide solution, separation of the layers, and drying of the organic phase over anhydrous sodium sulphate. Under these conditions, distinct peaks were observed for the HFB-herbicides of fenuron, isoproturon, fluometuron, monuron, chlortoluron and metoxuron, and a less pronounced one for diuron. The structures of the derivatives, formed according to eqn. 1, were confirmed by GC–MS (see below). It is interesting that, apparently, acylation with HFBA is successful with the trisubstituted phenylureas, whereas reaction of HFBA with mono- and di-substituted phenylureas[29] invariably results in the formation of N-perfluoroacylated cleavage products.



(1)

NMR spectroscopy

The fact that only herbicides with two alkyl groups attached to the N^1 atom yielded to direct derivatisation prompted us to carry out a short NMR study to establish whether a relationship exists between herbicide structure and ease of direct derivatisation. To this end NMR spectra were recorded for all herbicides, in the absence and presence of HFBA, with C^2HCL_3 as solvent. The herbicides containing an N,N-dimethylamino group showed similar results which were, however, totally different from those obtained for the four herbicides with an N-methyl-N-methoxyamino group. As an example, Table II lists the ^1H NMR data for fluometuron and metobromuron, which have R = CH_3 and OCH_3, respectively.

From the disappearance of the –NH signal, the appearance of a doublet signal due to $-N(CH_3)_2$ and the pattern change of the aryl protons it can be concluded that the herbicides with an N,N-dimethylamino group all form direct derivatives according to eqn. 1 on reaction with HFBA. The close identity of the NMR spectra of the remaining four herbicides in the absence and presence of HFBA, on the other hand, strongly suggests that no reaction takes place at all. Derivatisation is probably prevented by intramolecular hydrogen bonding between the proton on the N^3 atom and the oxygen atom of the methoxy group:

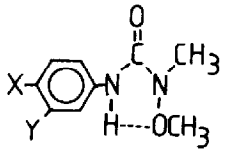


TABLE II

COMPARISON OF THE ^1H NMR DATA FOR FLUOMETURON AND METOBROMURON IN THE ABSENCE AND PRESENCE OF HFBA

	*Chemical shift**	*Remarks*
Fluometuron	3.07	6 H; *s*, $-N(CH_3)_2$
	6.47	1 H; *s*, –NH
	7.28–7.77	4 H; *m*, aryl H
Fluometuron + HFBA	3.09–3.18	6 H; *m*, $-N(CH_3)_2$
	7.43–7.83	4 H; *m*, aryl H
Metobromuron	3.17	3 H; *s*, $-N-CH_3$
	3.78	3 H; *s*, $-N-OCH_3$
	7.13–7.47	4 H; *m*, aryl H
	7.80	1 H; *s*, –NH
Metobromuron + HFBA	Identical with metobromuron	

* In ppm relative to tetramethylsilane.

This also explains the shift of the –NH signal towards lower field, relative to the signal of the herbicides with R = CH_3. Lastly we note that derivatisation of the latter type of herbicide is often incomplete in C^2HCl_3 at room temperature, as can be deduced from the asymmetry of the $-N(CH_3)_2$ signal.

Mass spectrometry

The formation of the HFB derivatives of the herbicides detected with GC–ECD was confirmed with GC–MS. Contrary to the findings[17] with the HFB-amides, the peaks conferring structure-relevant information in the mass spectra of the HFB-herbicides are of low intensity, *e.g.* for the N,N-dimethylamino phenylureas the base peak always occurs at *m/z* 72 or 73, originating from the $[(CO)N(CH_3)_2]^+$ or $[(CO)NH(CH_3)_2]^{+\cdot}$ ion, respectively. These are due to an α-cleavage with expulsion of the heavier part of the molecular ion, in the latter case accompanied by a proton transfer. The molecular ion peak is weak and often can be observed only after enhancement.

Another prominent fragmentation pathway that can be derived from the mass spectra, *e.g.* Fig. 1, involves the successive loss of $(CO)N(CH_3)_2$, C_3F_7 and CO, followed by the predictable loss of the phenyl substituent(s) and/or cleavage of the phenyl ring. With all derivatives, a remarkable peak is observed at *m/z* 241; it is caused by an α-cleavage and simultaneous C_3F_7 transfer yielding a $[C_3F_7(CO)N(CH_3)_2]^{+\cdot}$ peak. In the absence of the molecular ion peak, the formation of the direct derivatives can be deduced from the characteristic $[M - (CO)N(CH_3)_2 - C_3F_7]^{+\cdot}$ peak, and the $C_3F_7^+$ peak at *m/z* 169.

It should be kept in mind that, probably, chemical ionisation is more suitable for the detection of the HFB-herbicides, and also the HFB-amides, than is electron impact. Promising results may especially be expected in the negative-ion mode. This aspect will be important for definite confirmation of low levels of HFB derivatives as well as for detection with a sensitivity comparable with that of GC–ECD and HPLC–ECD.

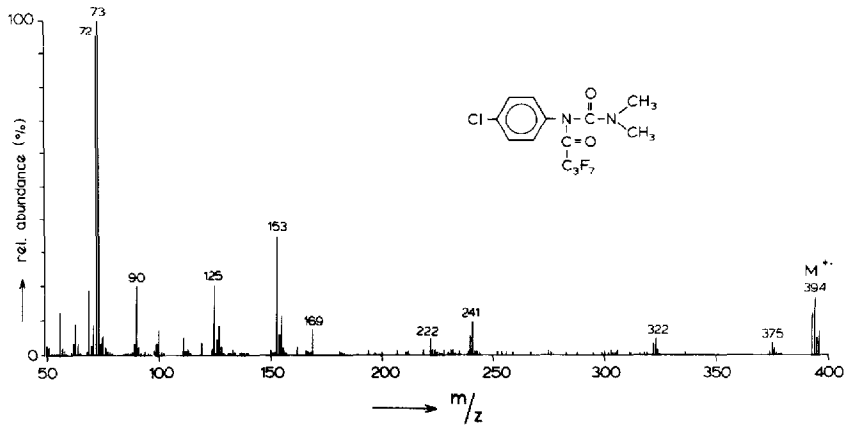


Fig. 1. Mass spectrum of the HFB derivative of monuron.

Optimisation of reaction conditions

The results of the NMR study unequivocally showed the formation of HFB derivatives for all herbicides with R = CH_3. Since in GC no such derivatives were observed for chloroxuron and difenoxuron, thermal decomposition was thought to play a role here. Varying the injection port temperature indeed revealed a distinct dependence on temperature of the peak heights of the derivatives of, *e.g.*, neburon and buturon. Increasing the injection port temperature from 200 to 270°C resulted in some 30% lower peak heights of their HFB derivatives, while (tailing) peaks due to the parent herbicides or their isocyanates started to show up in the initial part of the GC chromatogram. (The simultaneous detection of derivative and parent herbicide with GC–ECD, in order to determine the percentage conversion, was inconvenient in most cases because of the relatively low electron-capture response and thermal instability of most of the herbicides.)

For further studies on the efficiency of the direct derivatisation and the stability of the HFB derivatives, HPLC and thin-layer chromatography (TLC) were substituted for GC; both normal- and reversed-phase systems were used. The major advantages of HPLC over GC are: (1) analysis at room temperature, which should eliminate the problem of thermal instability; (2) determination of both derivatives and parent compounds in a single run, which allows a rapid assessment of percentage conversion. As for the HPLC and TLC systems used, chromatography on C_{18}-bonded phases was successfully employed to detect the HFB derivatives; it appeared, however, that storage of the derivatives in the methanol–water (70:30) mixture used as mobile phase invariably caused rapid hydrolysis (*cf.* Fig. 2). Normal-phase systems such as silica with hexane–dioxane (94:6) were therefore preferred for most experimental work.

TLC and HPLC studies indicated that direct derivatives are formed with all fifteen herbicides. The percentage of conversion for the herbicides chlorbromuron, linuron, metobromuron and monolinuron, which contain a methoxy group, and did not show up in the NMR study, was, however, at best some 10%. All the other herbicides, which have R = alkyl, showed over 95% conversion (except diuron). These recoveries were obtained using the standard derivatisation conditions quoted before. The modi-

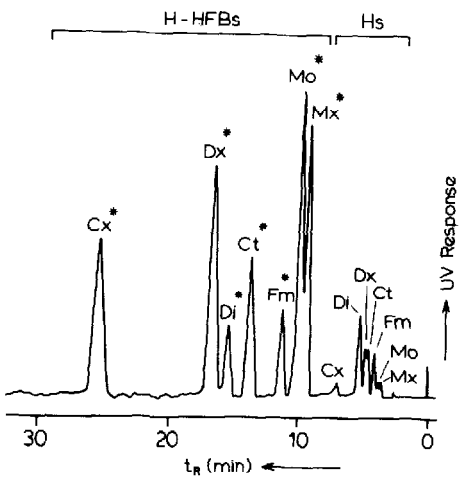


Fig. 2. Reversed-phase HPLC of seven HFB-herbicides (H-HFBs) and their corresponding parent herbicides (Hs). System: LiChrosorb RP-18 with methanol–water (70:30); UV detection at 245 nm. Presence of parent herbicides due to partial hydrolysis of H-HFBs in methanol–water sample solution.

fications introduced in order to obtain complete, *i.e.* at least 95%, conversion for all fifteen herbicides were as follows.

(1) After derivatisation, the excess of reagent is destroyed by shaking the organic solution with a phosphate buffer of pH 8, since shaking with 1 *M* sodium hydroxide effects nearly complete hydrolysis of the direct derivatives of the herbicides with R = OCH_3.

(2) Derivatisation is carried out at 60°C for 1 h to obtain optimum yields.

(3) Derivatisation is done in hexane, which allows a better separation after shaking with the buffer solution and dissolves less water than, *e.g.*, ethyl acetate or dichloromethane. Reaction also takes place, however, in the latter two solvents.

The stability of the HFB-herbicides is distinctly less than that of HFB-amides which can, for example, withstand heating for 20 min at 165°C (see ref. 18). Consequently, after derivatisation, which is executed in a PTFE-lined screw-capped reaction tube in an oven, shaking with buffer and phase separation, the hexane layer is transferred to another tube and the organic solvent evaporated to near dryness under a gentle stream of nitrogen. The residue is immediately dissolved in hexane, and some anhydrous sodium sulphate is added. If kept under these conditions, the derivatives are stable at room temperature for 6–16 h, the actual time being dependent on the herbicide structure. For more prolonged storage, the HFB-herbicides must be kept at a temperature of –24°C.

Contrary to the HFB-amides, the HFB-herbicides can be hydrolysed to the corresponding anilines when they are applied to a silica column and subjected to the catalytic hydrolysis conditions for the parent herbicides, *i.e.* 20 min heating at 165°C. This fact has been used to advantage in one of the schemes for discrimination between phenylurea herbicides and corresponding anilines discussed in ref. 18.

GC analysis

Initial work on the GC analysis of the HFB-herbicides was carried out on packed

columns with OV-210 as stationary phase. Peak shapes were excellent, even better than those for the corresponding HFB-amides, which are known[17] to show good behaviour on packed columns. For all further work, capillary GC was used. Retention times for all HFB-herbicides, and the corresponding HFB-amides, on a fused-silica column wall-coated with CP-Sil 5 are reported in Table III. The retention time data show a surprisingly good resolution for each pair of corresponding HFB-amide and HFB-herbicide, with relative retention values of between 1.4 and 2.8. More interestingly, even with the total group of 24 herbicides and anilines, and including three potential internal standards, separation is highly efficient. Serious overlap occurs with two compounds only, *viz.* the derivatives of monuron and the arbitrary internal standard 3,4,5-trichloroaniline. A typical chromatogram for a standard mixture of the derivatized anilines and herbicides is shown in Fig. 3.

TABLE III

GC RETENTION TIMES* OF HFB DERIVATIVES OF FIFTEEN PHENYLUREA HERBICIDES AND THE CORRESPONDING SUBSTITUTED ANILINES ON A CAPILLARY (CP-Sil 5) COLUMN

Herbicide	t_R *(min)*	*Aniline***	t_R *(min)*
Fenuron	9.50	Aniline (1)	3.45
Fluometuron	8.15	3-CF_3 (2)	3.60
		3-Cl (3)	5.75
Monuron	12.65	4-Cl (4)	5.90
Monolinuron	12.90		
Buturon	14.95		
Isoproturon	14.30	iso-C_3H_7 (5)	7.40
Metobromuron	14.60	4-Br (6)	7.60
Chlortoluron	14.40	3-Cl-4-CH_3 (7)	7.90
		3,5-di-Cl (8)	8.70
Diuron	15.35	3,4-di-Cl (9)	9.50
Linuron	15.45		
Neburon	18.65		
Metoxuron	17.15	3-Cl-4-OCH_3 (10)	11.15
Chlorbromuron	17.00	3-Cl-4-Br (11)	11.30
		3,4,5-tri-Cl (12)	12.80
Chloroxuron	n.d.***	4-[4-Cl-C_6H_4O] (13)	19.85
Difenoxuron	n.d.	4-[4-CH_3O-C_6H_4O] (14)	20.70

* For temperature programme and further conditions, see Experimental.

** Peak numbers used in Fig. 3 are given in brackets; 3-chloro-, 3,5-dichloro- and 3,4,5-trichloroanilines are arbitrarily chosen internal standards.

*** n.d., not detected due to thermal instability.

Contrary to the HFB-amides, the HFB-herbicides show mutual response differences during ECD, with a ratio of *ca.* 5:1 between the most (buturon) and the least (diuron) sensitive derivative. The absolute detection limits of the HFB-herbicides were in the 0.4–2.0 pg range, as against a 0.2–0.3 pg range for the HFB-amides[17]. Good linearity (r = 0.999) was obtained for injected amounts of up to 250–500 pg.

TLC analysis

TLC was mainly used for preliminary work, *e.g.*, in establishing the formation of the HFB-herbicides for all phenylureas tested and in studying their decomposition

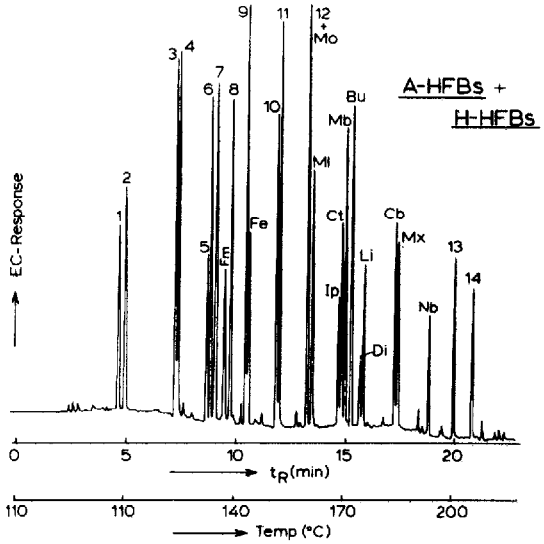


Fig. 3. Capillary GC on CP-Sil 5 of a mixture of HFB derivatives of fifteen phenylurea herbicides and of the corresponding substituted anilines and arbitrary internal standards (peaks 3, 8 and 12). For codes of herbicides and peak numbers of anilines, see Tables I and III, respectively.

upon storage. hR_F data for a typical reversed-phase and normal-phase system are recorded in Table IV.

HPLC analysis

In a previous paper[20] the potential of ECD in the system silica/hexane–dioxane has been discussed. Elution of phenylurea herbicides (and their anilines) generally requires a percentage of dioxane that is hardly compatible with ECD. Derivatisation with,

TABLE IV

hR_F VALUES OF ELEVEN PHENYLUREA HERBICIDES (H) AND THEIR HFB DERIVATIVES (H-HFB) IN TWO TLC SYSTEMS

Herbicide	*hR_F in NP-TLC**		*hR_F in RP-TLC***	
	H	*H-HFB*	*H*	*H-HFB*
Chlorbromuron	31	61	21	5
Linuron	30	61	24	6
Monolinuron	27	58	38	11
Metobromuron	25	59	34	9
Diuron	10	55	30	7
Fluometuron	10	61	38	13
Chlortoluron	9	52	35	9
Monuron	8	56	44	14
Chloroxuron	7	49	47	13
Metoxuron	5	39	51	13
Difenoxuron	5	43	32	5

* Normal-phase system: silica with dichloromethane–methanol (99:1).

** Reversed-phase system: C_{18}-bonded silica with methanol–water (70:30).

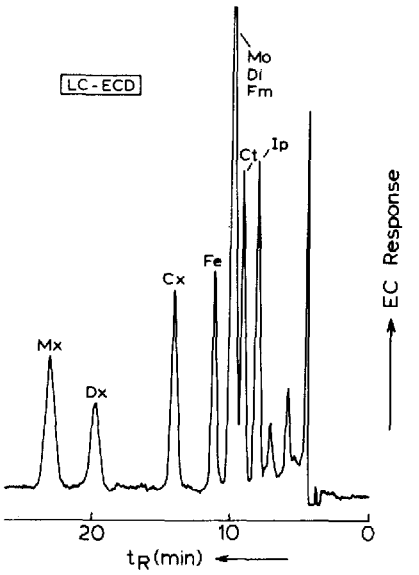


Fig. 4. HPLC–ECD of HFB derivatives of nine phenylurea herbicides (with R = CH_3) on LiChrosorb NH_2 with hexane–dioxane (90:10). Flow-rate, 1.0 ml min^{-1}; 0.5 ml min^{-1} directed to the electron-capture detector. Detector current, $1 \cdot 10^{-10}$ A; attenuation, × 128.

e.g. HFBA therefore serves a dual purpose: it decreases polarity, and thus the percentage of modifier required for elution, and it distinctly increases sensitivity.

The HFB-herbicides were analyzed[20] using hexane with 6% of dioxane as mobile phase, the latter being about the maximum allowable percentage of modifier. Analysis under these conditions was rather time-consuming. Recently, the use of a purer brand of dioxane from Baker has allowed us to use 10–20% of dioxane without deleterious effects on ECD performance. As an illustration, Fig. 4 shows a chromatogram for the nine HFB-herbicides having R = CH_3. Separation took place on a NH_2-bonded stationary phase with hexane–dioxane (90:10) as the eluent. The retention times for all HFB-herbicides, using a slightly different mobile phase composition, are recorded in Table V. It is noteworthy that HPLC–ECD allows the detection of the thermolabile direct derivatives of chloroxuron and difenoxuron which cannot be performed via GC-ECD (see above). Detection limits for the HFB-herbicides were in the 40–100 pg range.

TABLE V

RETENTION TIMES OF THE HFB DERIVATIVES OF FIFTEEN PHENYLUREA HERBICIDES

HPLC system: LiChrosorb NH_2 with hexane–dioxane (95:5); flow-rate, 1 ml min^{-1}.

Herbicide	t_R(min)	*Herbicide*	t_R(min)	*Herbicide*	t_R(min)
Neburon	9.2	Monolinuron	14.3	Fluometuron	15.6
Buturon	11.6	Chlorbromuron	14.6	Fenuron	16.8
Isoproturon	11.8	Metobromuron	15.0	Chloroxuron	25.2
Linuron	13.5	Diuron	15.1	Difenoxuron	36.3
Chlortoluron	13.7	Monuron	15.5	Metoxuron	40.4

Applications

In principle, discrimination between, and determination of all phenylureas and the corresponding anilines can be done via direct derivatisation with HFBA and subsequent GC–ECD, using the experimental conditions recorded above. Still, the problem of determining 20 or 30 relatively closely related compounds in a complex matrix, with the pre-chromatographic derivatisation with HFBA no doubt adding to the complexity of the final chromatogram, should not be underestimated. Generally speaking, direct derivatisation of a complete sample will therefore be most valuable for mixtures containing a restricted number of herbicides and anilines; an example of this is included below. Further applications deal with the analysis of herbicide-containing mixtures, since detailed results for the anilines will be presented elsewhere[18].

As a first example, 20-ml Bosbaan river water (Amsterdam) samples spiked with 1, 10 or 100 ppb of each of the fifteen phenylureas, were extracted with dichloromethane, the extract evaporated, redissolved in hexane and then subjected to derivatisation with HFBA, and analysed by means of HPLC–ECD or GC–ECD. Average recoveries for all herbicides were between 75 and 95%. Capillary GC has the advantage that separation and determination of all herbicides, except the thermolabile chloroxuron and difenoxuron, is obtained. An illustrative example (1-ppb spike) is shown in Fig. 5.

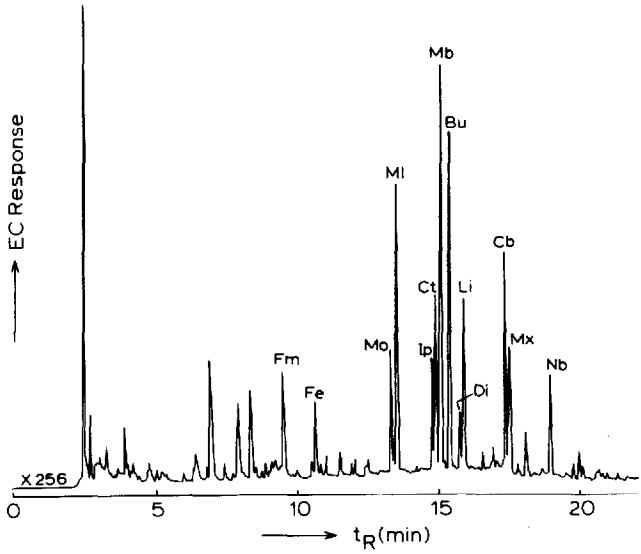


Fig. 5. Capillary GC on CP-Sil 5 of HFB derivatives of thirteen phenylurea herbicides obtained after extraction of a Bosbaan river water sample spiked at the 1-ppb level, and direct derivatisation with HFBA. Injected amount corresponds to 100 pg of each herbicide. For further details, see text.

In another example, a surface water sample spiked with herbicides and anilines at the 1-ppb level was extracted with dichloromethane and subjected to HPLC fractionation on silica with dichloromethane–hexane–triethylamine–ethanol (90:10:0.01:0.45). Next, the fraction containing the herbicides with R = CH_3 was evaporated, dissolved

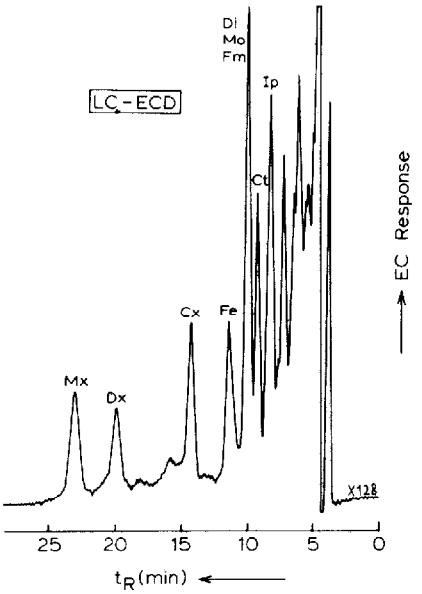


Fig. 6. HPLC–ECD of HFB derivatives of nine phenylurea herbicides obtained after extraction of a surface water sample (spiked at the 1-ppb level), HPLC fractionation and derivatisation of the fraction containing the R = CH_3 herbicides with HFBA. HPLC system: LiChrosorb NH_2 with hexane–dioxane (90:10); flow-rate, 1 ml min^{-1} directed to the electron-capture detector. Detector current, $1 \cdot 10^{-10}$ A; attenuation, × 128. For further details, see text.

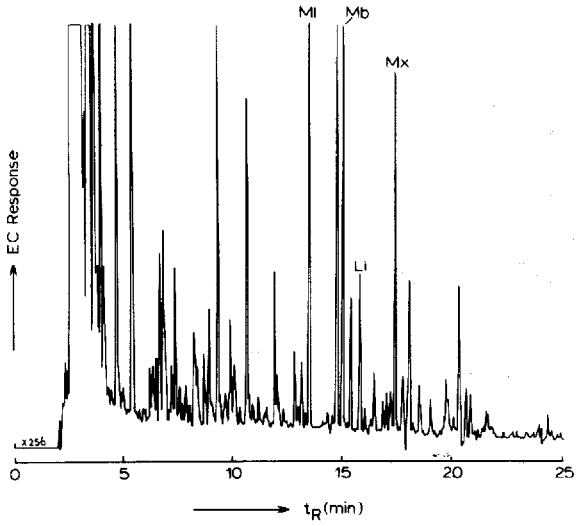


Fig. 7. Capillary GC on CP-Sil 5 of HFB derivatives of monolinuron (Ml), metobromuron (Mb), linuron (Li) and metoxuron (Mx) obtained after extraction of a potato sample spiked at the 0.1-ppm level, and direct derivatisation with HFBA. Injected amount corresponds to 150 pg of each herbicide.

in hexane, treated with HFBA and analysed by HPLC–ECD (Fig. 6). Note the peaks due to chloroxuron and difenoxuron, which do not show up in GC–ECD.

Results for a sample of potato spiked with 0.1 ppm of metobromuron, monolinuron, linuron and metoxuron are shown in Fig. 7. Pretreatment was limited[30] to sample extraction with acetone and back-extraction into dichloromethane. Recoveries were in the 70–110% range and detection limits, under optimised conditions, were of the order of 10 ppb.

Finally, a detailed study on the determination of metoxuron in water samples via direct derivatisation will be published shortly[31].

CONCLUSION

The direct derivatisation of the phenylurea herbicides with HFBA has been shown to be successful with all fifteen compounds studied. The HFB-herbicides, the majority of which have never been described in the literature, have been detected by means of NMR, MS, GC–ECD and HPLC–ECD. With capillary GC–ECD thirteen derivatives can be determined, those of chloroxuron and difenoxuron probably being lost because of thermal instability. HPLC–ECD allows the separation and detection of all HFB-herbicides, though with detection limits inferior to those in GC–ECD, *i.e. ca.* 50 *versus* 1 pg.

Direct derivatisation of the phenylureas with HFBA provides good sensitivity and adequate selectivity, as is apparent from the applications described above. Detection limits in surface water and crop samples are of the order of 0.1 ppb and 20 ppb, respectively.

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