Journal of Chromatography A, 660 (1994) 231–248
Elsevier Science B.V., Amsterdam

CHROMSYMP. 2932

Thermospray liquid chromatographic–mass spectrometric multi-residue determination of 128 polar pesticides in aqueous environmental samples

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ABSTRACT

Thermospray (TSP) ionization was evaluated with respect to its suitability in the LC–MS determination of a broad range of pesticides. The sensitivity and the selectivity of this method for the determination of 128 pesticides having a wide range of structures and polarities were investigated. An LC separation in combination with postcolumn addition of a volatile salt solution was developed, which permits the analysis of 95 pesticides with a single LC–MS method using reversed-phase gradient elution. The retention data and TSP mass spectra of these compounds are presented. The advantages of TSP postcolumn techniques in comparison with conventional systems are discussed. The application of this method to the analysis of an environmental sample (river water) spiked with eight phenylureas is demonstrated. The method was evaluated with respect to detection limit, linearity and reproducibility. In addition, a simple method for enhancing the structural information from TSP spectra is reported, which makes use of specific instabilities found with many pesticides. As an example, possibilities for the confirmatory analysis of carbamates are described.

INTRODUCTION

The common European Community (EC) market and thus the anticipated large number of different pesticides used within the EC necessitate the development of rapid screening multi-purpose methods for as many as possible of the most relevant agents. Further, the EC drinking water guidelines demand analytical methods that allow the verification of the concentration limit of 100 ng l^{-1} for individual pesticide species [1]. Therefore, universal, specific, sensitive and reliable methods are required that with permit the determination of a broad variety of target and non-target compounds, preferable both volatile and non-volatile compounds.

Gas chromatography is still the most popular method for the determination of pesticides. GC–MS allows the identification and determination of a wide variety of pesticides in several matrices. However, owing to their thermal instability and polarity, many pesticides are not amenable to GC analysis. In many instances they can, however, be measured by column liquid chromatographic methods, which can be applied equally well to most typical "GC compounds". Conventional detection in HPLC is usually achieved with UV or diode-array detection (DAD). UV detection often provides adequate sensitivity. In combination with a diode-array detector, an unambiguous identification in en-

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0021-9673/94/$07.00
SSDI 0021-9673(93)E0939-R

vironmental samples is sometimes possible for certain compound classes, *e.g.*, nitrophenols [2]. However, structural information is lacking for most pesticide compound classes, because the UV spectra of one compound class are often almost identical and differences between compound classes are frequently small. Further, several pesticides have a low UV absorbance as they lack a strong chromophore in the UV region for sensitive detection. Hence UV detection and DAD are not well suited for universal application.

The potential of combined LC–MS for the determination of both thermally labile and nonvolatile compounds has been demonstrated [3]. Further, typical "GC pesticides" are also amenable to LC–MS, which makes LC–MS an ideal method for the determination of a broad range of pesticides. Different types of LC–MS interfaces have been applied to pesticide analysis such as a moving belt [4,5], direct liquid introduction [6,7], fast atom bombardment (FAB) [8], thermospray (TSP) [9,10] and particle beam [11]. The applicability of atmospheric pressure chemical ionization (APCI) and ionspray (ISP) compared with TSP and particle beam for trace-level determinations of pesticides has been demonstrated recently [12]. Among the different interfaces, TSP is the one most widely used today. As TSP mass spectra often show little fragmentation and thus lack structural information, several techniques are available to overcome these limitations, *e.g.*, the variation of the gas-phase and vaporizer temperature to induce controlled chemical reactions during TSP vaporization and ionization [13], the use of external ionization media and tandem MS techniques [14,15], repeller-induced fragmentation [16] and additional cluster ions with solvent or additive molecules and additional information gained from the complementary interpretation of positive- and negative-ion spectra [13,17,18]. By applying these techniques, LC–TSP-MS can be used as an ideal confirmatory method.

TSP has been employed in analyses for large variety of pesticides such as carbamates [12], organophosphorus [19,20] and quaternary ammonium compounds [21], phenylureas [22,23], phenoxy acids [22,24], triazines [25,26] and some other classes. However, so far applications of TSP only to special groups or compound classes of pesticides have been reported. Only a few workers, *e.g.*, Bellar and Budde [26] and Vreeken *et al.* [18], have reported methods applicable to a broad range of compounds with large differences in polarities and structures.

We have developed an LC–TSP-MS method for the extraction, separation and determination of *ca.* 130 pesticides from aqueous environmental samples including anilides, carbamates, phenylureas, phenoxy acids, oximes, organophosphorus and quaternary ammonium compounds, triazines and other N-heterocyclic compounds and some other classes. Special attention has been paid on the one hand to compounds with low UV absorbance and on the other to pesticides produced in the former German Democratic Republic ("GDR-specific" pesticides). Although the production of most "GDR-specific" pesticides was prohibited in Germany at the beginning of 1993, further application is still allowed for many of these compounds because the disposal of the large remainder as waste is too expensive. For many of these compounds, no methods for determination at trace levels are available. Trace enrichment from aqueous samples is achieved by means of a conventional off-line on an on-line preconcentration procedure using solid-phase extraction. A more detailed description of the extraction procedure will be presented in a subsequent paper.

The purpose of this work was to demonstrate the applicability of LC–TSP-MS as a rapid screening method for the identification and determination of pesticides. One objective was to develop a single method with a set of identical experimental parameters that allow the determination of a broad range of pesticides having widely differing structures and polarities. Moreover, a detection limit of 100 ng l^{-1} was sought. This required the ability to detect at least 2–5 ng of each compound after extraction and enrichment of the aqueous sample using both off-line or on-line preconcentration techniques. Further requirements were a precision of at least 15% (relative standard deviation) for determination and a linear dynamic range of $>10^3$ in order to allow external determination.

EXPERIMENTAL

Materials

Pesticide standards were purchased from Riedel-de Haën (Seelze-Hannover, Germany) and Promochem (Wesel, Germany). They were of purity >98% and were used as received. Buminafos and butonate were gifts from Dr. J. Efer (University of Leipzig, Leipzig, Germany). Methanol was purchased from Riedel-de Haën (Chromasolv HPLC grade) and reagent water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). The solvents were passed through a 0.45-μm filter (Sartorius, Göttingen, Germany) before use. Ammonium acetate (Gold Label grade) was obtained from Aldrich (Steinheim, Germany). PEG-300, PEG-400 and caffeine were purchased from Fluka (Buchs, Switzerland).

Sample extraction

The pesticides were extracted from water (1 l, 10 ml min^{-1}) using solid-phase extraction cartridges filled with 2 g of C_{18} material (Amchro, Sulzbach-Taunus, Germany). Four 1-ml methanol washes carried the pesticides trapped on the cartridge to a sample vial. Thereafter, the volume was reduced to 1 ml using a gentle stream of nitrogen.

Liquid chromatography

Details of the experimental set-up have been described elsewhere [13]. Briefly, a postcolumn technique was employed in order to allow the separate optimization of the HPLC separation and the TSP ionization (see Results and Discussion).

The best results were obtained with narrow-bore (3 mm I.D.) columns, a column flow-rate of 0.6 ml min^{-1} and an additional buffer flow-rate of 0.4 ml min^{-1} (175 m*M* ammonium acetate). LiChrospher 60 RP-select B (5 μm) columns (125 × 3 mm I.D.) (Merck, Darmstadt, Germany) were used. Gradient elution was performed with methanol–water mixtures. The solvents were degassed in an ultrasonic bath and continuously purged with *ca.* 25 ml min^{-1} of helium to maintain very low levels of dissolved air. The methanol–water eluent composition was linearly programmed from 20 to 95% methanol in 45 min and then held for 15 min at 95% methanol. A Model 7125 injection valve equipped with a 20-μl loop from Rheodyne (Cotati, CA, USA) was used to introduce the samples. In order to avoid peak broadening of early-eluting compounds, it was necessary to inject sample solutions with a high water content (≥80%).

For comparative studies, normal-bore LiChrospher 100 RP-18 columns (250 × 4 mm I.D.) (Merck) were used. A postcolumn addition of 0.2 ml min^{-1} of 450 m*M* aqueous ammonium acetate solution was employed. A slightly different methanol–water gradient programme was used within these experiments, from 10 to 90% methanol in 45 min, the latter composition being held for 15 min.

Thermospray mass spectrometry

The experiments described here were performed using a Finnigan MAT (San José, CA, USA) Model 4500 mass spectrometer equipped with a Vestec (Houston, TX, USA) thermospray source. Typical operating conditions of the TSP interface were as follows: vaporizer control temperature $T_1 \approx 135$–150°C; vaporizer temperature $T_v \approx 190$–220°C; tip heater temperature $T_3 = 270$°C; source jet temperature $T_g \approx 230$–240°C; source temperature $T_s = 250$°C and exit line pressure $p_g \approx 2$–4 Torr (1 Torr = 133.322 Pa). The mass spectrometer was operated in the positive-ion (PI) and negative-ion (NI) modes and was scanned at a rate of 1 s per scan over the range m/z 130–450 (PI) and m/z 185–500 (NI). The vaporizer temperature was optimized before each analysis to obtain a stable maximum ion intensity of the solvent cluster ions in the range m/z 18–139. In order to keep the vaporizer fraction of the carrier stream constant during gradient operation, the vaporizer temperature was adjusted by means of automatic gradient compensation control of the interface as the solvent composition changed. The mass scale was calibrated with an aqueous solution of caffeine, PEG-300 and PEG-400 containing 100 m*M* ammonium acetate where the solution was continuously pumped into the TSP ion source.

The polyethylene glycol–ammonium cluster ions were also used to tune the instrument.

In all experiments discharge-assisted buffer ionization (1000 V) was used, because the absolute signal intensities are approximately three times higher in this mode than with buffer ionization alone and at least 1.5 times higher than in the filament-assisted buffer ionization mode. The actual gain in sensitivity was lower, because a slight increase in noise was observed when using additional external ionization media.

Direct flow-injection experiments were performed using a carrier stream of methanol–water (50:50, v/v) with a salt concentration c_s (ammonium acetate) of 50 m*M* and a flow-rate of 1.0 ml min^{-1}. The samples were introduced via a sample loop of 50 μl.

LC–TSP-MS–MS was carried out on a Finnigan MAT TSQ 70 triple-stage quadrupole mass spectrometer (Q1, Q2, Q3). In these MS–MS experiments, the $[MH]^+$ or $[MHNH_3]^+$ ions were chosen as precursor ions and selectively transmitted by Q1 for further collisional dissociation to Q2. Argon was used as the collision gas with a collision chamber pressure of $1.3 \cdot 10^{-3}$ Torr. A collision offset (COFF) of 10 V was applied to Q2. The collision-activated dissociation (CAD) daughter ions thus obtained were then analysed by scanning with the third quadrupole (Q3) over the mass range 20–500. For the LC–MS–MS studies, direct flow injection was used to introduce the samples into the mass spectrometer. The TSP vaporizer control temperature was set to 90°C and the aerosol temperature was kept at 240°C.

RESULTS AND DISCUSSION

The 128 compounds listed in Table I were successfully determined by means of LC–TSP-MS, although not all of them are thermally labile, typical "HPLC compounds". Many typical "GC compounds" are also amenable to TSP and HPLC, hence the latter compounds were also included. Special compound classes such as quaternary ammonium compounds are not included here because their determination required specific HPLC or TSP conditions. The determination of these compounds will be described in a subsequent paper.

Improving selectivity and sensitivity via postcolumn techniques

Improvements in selectivity and sensitivity in the determination of pesticides by means of TSP can be achieved by postcolumn addition of aqueous buffer solution and the use of external ionization media as described under Experimental.

The TSP response is directly related to the water fraction, x_w, in the final TSP carrier stream and the dielectric constant of the mixed solvent, ε_{solv}. Fig. 1 shows a typical LC–MS trace obtained with a conventional 4 mm I.D. C_{18} column. Postcolumn addition of 0.2 ml min^{-1} of 450 m*M* aqueous ammonium acetate solution was employed in this instance. The sensitivity is much higher for early-eluting compounds than for compounds with longer retention times. This is probably due to changes in the fraction of water in the carrier stream during gradient elution. In Fig. 2a the dependence of the absolute ion intensities of two pesticides (carbofuran, m/z 222 and 239, and desmetryn, m/z 214) are plotted against ε_{solv}, which is approximately proportional to x_w (the salt concentration, c_s, was 50 m*M* in each instance). A factor of at least two in sensitivity can be gained if x_w is increased from 50% to 80% (ε_{solv} changes almost linearly with x_w when using methanol–water; ε_{solv} values were taken from ref. 27). However, one should note that the noise increases slightly with increasing x_w, so the actual increase in the signal-to-noise ratio for most pesticides is slightly lower.

It is interesting that this behaviour can be correlated with variations of the reagent gas ion intensities as x_w is changed. This is demonstrated in Fig. 2b, where the dependence of the integrated solvent ion current (m/z 18–139) on ε_{solv} and thus x_w is shown [$c_s = 50$ m*M* in all instances; carrier stream flow-rate 1.0 ml min^{-1}; T_v was adjusted to 3°C below the point of complete vaporization ("take-off" temperature) for each solvent composition]. A further correlation is possible with eqn. 4 in ref. 28. As shown there,

TABLE I

PESTICIDES INVESTIGATED IN THIS STUDY

No.	Compound	Chemical class	No.	Compound	Chemical class
1	Ametryn	Triazine	67	Aldicarb	Carbamate
2	Anilazine	Traizine	68	Aldicarb sulfone	Carbamate
3	Atraton	Triazine	69	Aldicarb sulfoxide	Carbamate
4	Atrazine	Triazine	70	Asulam	Carbamate
5	Atrazine-desethyl	Triazine	71	Barban	Carbamate
6	Atrazine-desisopropyl	Triazine	72	Benomyl	Carbamate
7	Cyanazine	Triazine	73	Cartap	Carbamate
8	Hexazinone	Triazine	74	Carbaryl	Carbamate
9	Desmetryn	Triazine	75	Carbendazim	Carbamate
10	Prometryn	Triazine	76	Carbetamide	Carbamate
11	Propazine	Triazine	77	Carbofuran	Carbamate
12	Secbumeton	Triazine	78	Chloropropham	Carbamate
13	Sebutylazine	Triazine	79	Desmedipham	Carbamate
14	Simazine	Triazine	80	Methiocarb	Carbamate
15	Terbutryn	Triazine	81	Methomyl	Carbamate
16	Terbutylazine	Triazine	82	Oxamyl	Carbamate
17	Bromacil	Pyrimidine	83	Phenmedipham	Carbamate
18	Chloridazon	Pyrimidine	84	Pirimicarb	Carbamate
19	Crimidine	Pyrimidine	85	Promecarb	Carbamate
20	Terbacil	Pyrimidine	86	Propham	Carbamate
21	Amitrole	Triazole	87	Propoxur	Carbamate
22	Terbuconazole	Triazole	88	Triallate	Carbamate
23	Triadimefon	Triazole	89	Prosulfocarb	Thiocarbamate
24	Metamitron	Pyridine	90	Thiodicarb	Thiocarbamate
25	Metribuzin	Pyridine	91	Chlorobromuron	Phenylurea
26	Aldimorph	Morpholine	92	Chloroxuron	Phenylurea
27	Fenpropimorph	Morpholine	93	Chlorotoluron	Phenylurea
28	Tridemorph	Morpholine	94	Difenoxuron	Phenylurea
29	Allidochlor	N-Substituted amide	95	Diuron	Phenylurea
30	Alachlor	Anilide	96	Fenuron	Phenylurea
31	Butachlor	Anilide	97	Fluometuron	Phenylurea
32	Dimethachlor	Anilide	98	Isoproturon	Phenylurea
33	Metalaxyl	Anilide	99	Linuron	Phenylurea
34	Metazachlor	Anilide	100	Methabenzthiazuron	Phenylurea
35	Methfuroxam	Anilide	101	Metobromuron	Phenylurea
36	Metolachlor	Anilide	102	Metoxuron	Phenylurea
37	Monalide	Anilide	103	Metsulfuron-methyl	Phenylurea
38	Pentanochlor	Anilide	104	Monolinuron	Phenylurea
39	Propachlor	Anilide	105	Monuron	Phenylurea
40	Propanil	Anilide	106	Isocarbamide	Thiourea
41	Prochloraz	Anilide	107	Benazolin	Carboxylic acid
42	Pendimetalin	Dinitroaniline	108	Chloramben	Carboxylic acid
43	Azinphos-ethyl	Organophosphorus	109	Dalapon	Carboxylic acid
44	Buminafos	Organophosphorus	110	Dicamba	Carboxylic acid
45	Butonate	Organophosphorus	111	TCA	Carboxylic acid
46	Chlorfenvinphos	Organophosphorus	112	2,4-D	Phenoxy acid
47	Demeton	Organophosphorus	113	2,4-DB	Phenoxy acid
48	Demeton-S-methyl	Organophosphorus	114	Dichlorprop	Phenoxy acid
49	Diazinone	Organophosphorus	115	MCPA	Phenoxy acid
50	Dichlorvos	Organophosphorus	116	MCPB	Phenoxy acid
51	Dimethoate	Organophosphorus	117	Mecoprop (MCPP)	Phenoxy acid
52	Disulfoton	Organophosphorus	118	Silvex (2,4,5-TP)	Phenoxy acid
53	Fenamiphos	Organophosphorus	119	2,4,5-T	Phenoxy acid
54	Fenithrotion	Organophosphorus	120	Bifenox	Carboxylic ester
55	Mecarbam	Organophosphorus	121	Chlorfenvinprop	Carboxylic ester
56	Merphos	Organophosphorus	122	Fluazifop-butyl	Carboxylic ester
57	Methamidophos	Organophosphorus	123	Haloxyfop-ethyl	Carboxylic ester
58	Monocrotophos	Organophosphorus	124	Naphthyl acetate	Carboxylic ester
59	Naled	Organophosphorus	125	Benzalkonium chloride	Quaternary ammonium
60	Oxydemeton-methyl	Organophosphorus	126	Chlormequat	Quaternary ammonium
61	Parathion-methyl	Organophosphorus	127	Diquat	Quaternary ammonium
62	Phosalone	Organophosphorus	128	Paraquat	Quaternary ammonium
63	Phosmet	Organophosphorus			
64	Prothiofos	Organophosphorus			
65	Triazinone	Organophosphorus			
66	Trichlorfon	Organophosphorus			

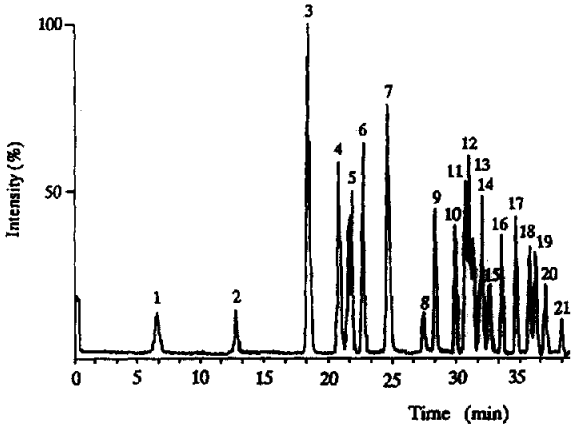

Fig. 1. LC–TSP-MS separation of 21 pesticides (180 ng each). Conditions: column, 250 × 4 mm I.D. LiChrospher 100 RP-18 (5 μm); mobile phase, methanol–water at a column flow-rate of 1.0 ml min^{-1}; gradient profile, from 10% methanol linearly to 90% methanol in 45 min and held for 10 min; postcolumn addition of 0.2 ml min^{-1} of 450 m*M* ammonium acetate. TSP: discharge ionization; T_s = 250°C; $T_g \approx$ 235°C; T_v = 210→195°C. Peak assignment: 1 = asulam; 2 = aldicarb sulfone; 3 = atrazine-desisopropyl; 4 = fenuron; 5 = dimethoate; 6 = chloridazone; 7 = atrazine-desethyl; 8 = aldicarb; 9 = metoxuron; 10 = cyanazine; 11 = terbacil; 12 = monuron; 13 = carbofuran; 14 = simazine; 15 = hexazinon; 16 = carbaryl; 17 = monolinuron; 18 = chlorotoluron; 19 = atrazine; 20 = isoproturon; 21 = diuron.

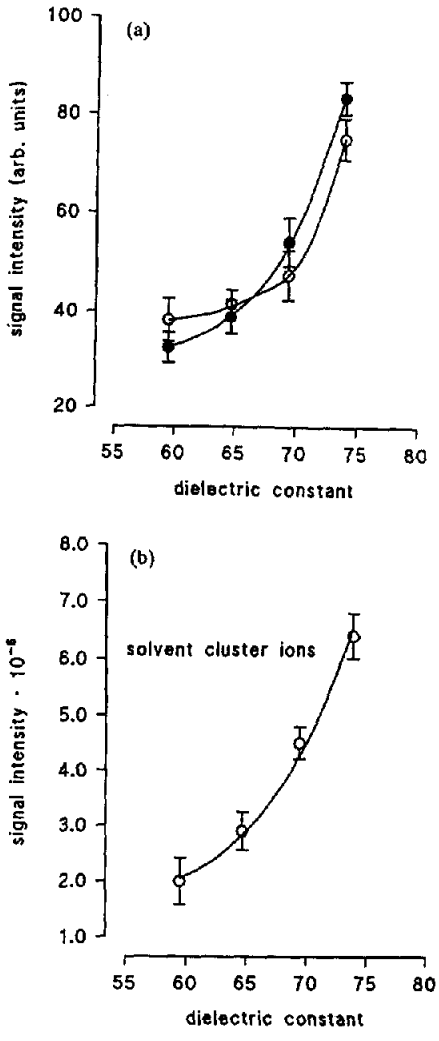

Fig. 2. Absolute ion intensities as a function of the bulk solvent dielectric constant ε_{solv} of the carrier stream (mixed solvent methanol–water; c_s = constant) for (a) ○ = carbofuran (*m/z* 222 and 239) and ● = desmetryn (*m/z* 214) and (b) the integrated solvent ion current (*m/z* 18–139).

the dependence is directly related to the ammonium acetate ionic activity in the mixed solvent. Hence the Debye–Hückel theory can be used for the description of this dependence.

Fig. 2b demonstrates that the ion current of the solvent cluster ions directly reflects the dependence of the analyte signal intensities on the amount of water in the carrier stream. This is the expected behaviour as these solvent cluster ions act as ionizing reagents. However, the gain in sensitivity is higher for the solvent cluster ions compared with those obtained with both pesticides. As shown by Voyksner *et al.* [29], a postcolumn addition of a buffer salt can be used to enhance the sensitivity. In order to avoid dilution of the samples, one has to find an optimum ratio of the buffer flow-rate relative to the column flow-rate. A further parameter affects this ratio, namely the absolute flow-rate of the TSP carrier stream. For the varporization of high carrier stream flows, very high vaporizer temperatures are necessary and, as a consequence, chemical dissociations of the sample [13,30–32] and fragmentations of the quasi-molecular ions are enhanced [preliminary experiments with postcolumn addition of the buffer salt in combination with normal-bore 4 mm I.D. columns revealed that in the case of the Vestec source the vaporization of the resulting flow (*ca.* 1.5 ml min^{-1}) often requires vaporizer temperatures higher than 250°C]. In this study, in most instances 3 mm I.D. narrow-bore columns were

TABLE II

LIQUID CHROMATOGRAPHIC RELATIVE RETENTION TIMES, MOLECULAR MASSES (M_r) AND IONS OBSERVED FOR THE INVESTIGATED PESTICIDES

Relative retention time, $\alpha_i = t_i/t_{caffeine}$. Experimental conditions: $T_v = 205 \rightarrow 195°C$; $T_g \approx 235°C$; discharge-assisted buffer ionization; $c_s = 70$ mM ammonium acetate (carrier stream).

α_i	Compound	M_r[a]	Main ions (PI): m/z (RA, %)[b]	No.[c]
0.107	Asulam	230	190 (100), 173 (5), 231 (5), 248 (10)	1d
0.259	Methamidophos	141	159 (100), 142 (15)	1f
0.548	Aldicarb sulfone	222	240 (100), 150 (42), 165 (70), 223 (14)	2d
0.638	Oxamyl	219	237 (100), 163 (33), 180 (13), 220 (4)	3d
0.744	Oxydemeton-methyl	246	247 (100), 264 (5)	2f
0.775	Methomyl	162	163 (100), 180 (12), 194 (10)	4d
0.832	Demeton-S-methyl sulfone	262	280 (100), 263 (52)	3f
0.993	Monocrotophos	223	241 (100), 224 (39)	4f
1.000	Caffeine	194	195 (100)	I.S.[e]
1.136	Atrazine-desisopropyl	174	175 (100)	2b
1.202	Trichlorfon	256	274 (100), 238 (12), 257 (23)	6f
1.243	Fenuron	164	165 (100), 182 (40)	2c
1.265	Metamitron	202	203 (100)	2a
1.392	Dimethoate	229	230 (100), 247 (38)	7f
1.544	Chloridazon	221	222 (100), 239 (20)	3a
1.697	Atrazine-desethyl	187	188 (100)	3b
1.746	Benomyl	290	192 (100), 134 (90), 149 (55)	6d
1.764	Isocarbamid[d]	185	186 (100), 146 (5)	
1.887	Aldicarb	190	208 (100), 148 (30), 191 (30), 222 (15)	7d
1.935	Allidochlor	173	174 (100), 191 (15)	2e
2.017	Metoxuron	228	229 (100), 201 (8)	3c
2.031	Crimidin	171	172 (100)	4a
2.241	Carbetamide	236	237 (100), 177 (28)	8d
2.294	Metribuzin	214	215 (100), 200 (10)	5a
2.315	Monuron	198	199 (100), 171 (5), 216 (5)	4c
2.362	Dichlorvos	220	238 (100), 221 (15)	8f
2.409	Propoxur	209	227 (100), 210 (20)	9d
2.444	Demeton-S-methyl	230	231 (100), 248 (15)	9f
2.468	Cyanazin	240	241 (100)	4b
2.476	Hexazinon	252	253 (100)	5b
2.502	Carbofuran	221	222 (100), 182 (15), 239 (35)	10d
2.521	Bromacil	260	261 (100), 183 (73)	6a
2.588	Simazin	201	202 (100), 168 (3)	6b
2.614	Terbacil	216	178 (100), 161 (23), 217 (1)	7a
2.751	Carbaryl	201	219 (100), 145 (7), 202 (18)	11d
2.754	Monolinuron	214	215 (100), 185 (10), 232 (10)	5c
2.762	Fluometuron	232	233 (100), 222 (10)	5c
2.852	Pirimicarb	238	239 (100)	12d
2.872	Metsulfuron-methyl	381	233 (100), 167 (13), 184 (89), 199 (78)	6c
2.877	Chlorotoluron	212	213 (100), 185 (5), 230 (5)	7c
2.900	Metobromuron	258	259 (100), 151 (15), 229 (5), 276 (10)	8c
2.949	Propham	179	197 (100), 180 (90)	13d
3.000	Methabenzthiazuron	221	222 (100), 165 (17)	9c
3.031	Naled	380	398 (100), 221 (2), 238 (3), 381 (7)	2g
3.035	Isoproturon	206	207 (100), 179 (12), 224 (8)	10c
3.065	Fensulfothion	308	309 (100), 326 (23)	3g
3.069	Atrazine	215	216 (100), 182 (5)	7b
3.127	Diuron	232	233 (100), 199 (4), 205 (5), 250 (10)	11c
3.162	Metazachlor	277	278 (100)	3e
3.185	Difenoxuron	286	287 (100), 216 (68), 259 (10)	12c
3.192	Propachlor	211	212 (100), 229 (10)	4e
3.222	Metalaxyl	279	280 (100), 256 (5)	5e
3.232	Phosmet	317	335 (100), 209 (30), 237 (40), 318 (35)	4g

(Continued on p. 238)

TABLE II (*continued*)

α_i	Compound	M_r [a]	Main ions (PI): *m/z* (RA, %)[b]	No.[c]
3.254	Dibutyl phosphite	194	212 (100), 195 (30)	10f
3.281	Desmetryn	213	214 (100)	8a
3.285	Dimethachlor	255	256 (100), 193 (5), 222 (25)	6e
3.293	Desmedipham	300	199 (100), 137 (60), 169 (45), 182 (50)	14d
3.326	Phenmedipham	300	185 (100), 151 (40), 168 (45), 210 (10)	15d
3.333	Thiodicarb	354	355 (5), 142 (10), 149 (10), 163 (100), 180 (25), 224 (85)	16d
3.355	Butonate	326	344 (100), 308 (70), 327 (30)	11f
3.386	Methfuroxam	229	230 (100)	7e
3.420	Linuron	248	249 (100), 219 (10), 266 (18)	13c
3.427	Parathion-methyl	263	281 (100), 264 (13)	5g
3.455	Secbumeton	225	226 (100)	9b
3.480	Chloropropham	213	231 (100), 214 (20)	17d
3.489	Anilazine	274	275 (100), 241 (15), 256 (10)	9a
3.508	Chlorobromuron	292	293 (100), 310 (5)	14c
3.549	Fenithrothion	277	295 (100), 278 (4)	6g
3.549	Ametryn	227	228 (100)	10a
3.582	Propazine	229	230 (100), 196 (3)	10b
3.632	Terbutylazine	229	230 (100), 196 (4)	11b
3.636	Propanil	217	218 (100), 184 (10), 235 (65), 250 (5)	8e
3.641	Methiocarb	225	243 (100), 226 (65)	18d
3.655	Mecarbam	329	330 (100), 347 (20)	7g
3.684	Azinphos-ethyl	345	160 (100), 346 (65), 363 (33)	8g
3.687	Barban	257	275 (100), 239 (10), 258 (10)	19d
3.716	Chloroxuron	290	291 (100), 220 (20)	15c
3.728	Triadimefon	293	294 (100), 168 (60)	11a
3.848	Fenamiphos	303	304 (100), 258 (10), 321 (5)	9g
3.875	Prometryn	241	242 (100)	12b
3.987	Terbutryn	241	242 (100)	13b
3.992	Alachlor	269	270 (100), 226 (65), 238 (20), 243 (36)	9e
3.999	Chlorfenvinphos	359	377 (100), 360 (55)	10g
4.048	Metolachlor	283	284 (100), 250 (22)	10e
4.073	Phosalone	367	385 (100), 368 (20)	11g
4.111	Disulfoton	274	275 (100), 292 (14)	12g
4.141	Monalide	239	240 (100)	11e
4.167	Prochloraz	375	376 (100), 342 (15), 180 (90)	12a
4.227	Tebuconazol	307	308 (100), 274 (5)	13a
4.319	Pentanochlor	239	240 (100), 257 (5)	12e
4.501	Prosulfocarb	251	252 (100)	20d
4.749	Triallate	303	304 (100), 162 (20)	21d
4.762	Prothiophos	344	345 (100), 362 (5)	13g
4.781	Merphos	298	315 (100), 299 (7)	14g
4.982	Butachlor	311	226 (100), 192 (10), 204 (38), 238 (78), 270 (60), 312 (30)	13e
5.092	Buminafos	347	212 (100), 154 (10), 195 (30)	12f

[a] Monoisotopic molecular mass calculated from the atomic masses of the isotopes with smallest masses.
[b] Relative abundance (in parentheses).
[c] Number of peak in Fig. 3a–g.
[d] Not shown in chromatogram in Fig. 3c.
[e] Internal standard.

used for the separation with typical flow-rates in the range *ca.* 0.5–0.6 ml min^{-1}. They are ideally suited for postcolumn addition, because the buffer flow can be varied over a wide range and the final carrier stream does not exceed critical values >1.5 ml min^{-1}. There are further advantages of this technique: the buffer salt concentration in the carrier stream is constant during gradient operation (c_s = 70 m*M* for all chromatographic experiments) and a negative influence of the buffer salt on the chromatographic separation is avoided [29,33].

The postcolumn techniques can also be used for the addition of reagent compounds to form

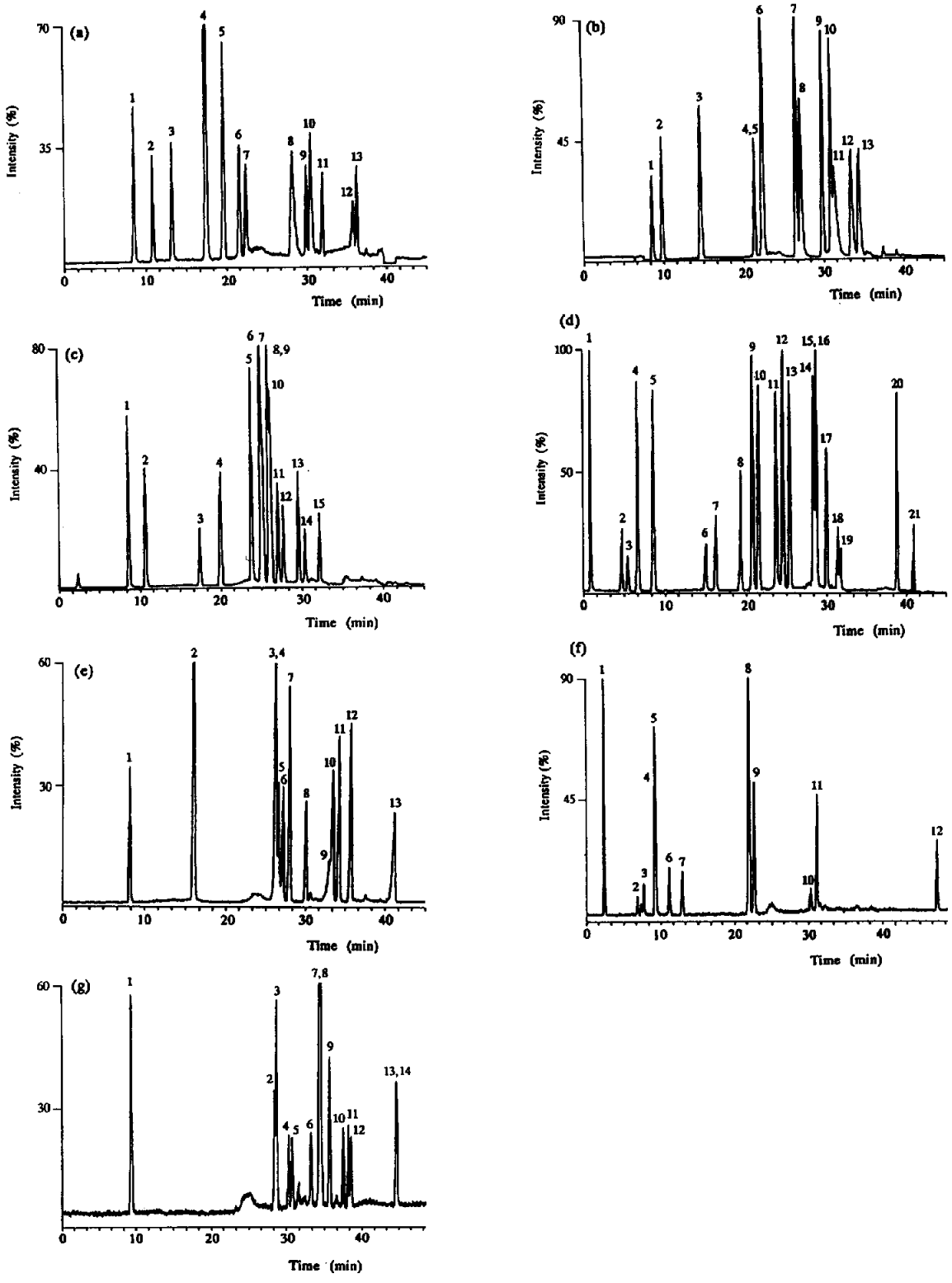

Fig. 3. LC–TSP-MS separation (full scan, m/z 130–450) of 95 pesticides. Conditions: column, narrow-bore 125 × 3 mm I.D. LiChrospher 60 RP-select B; column flow-rate, 0.6 ml min^{-1} methanol–water; postcolumn flow-rate 0.4 ml min^{-1} 175 m*M* ammonium acetate (for details, see Experimental). (a) N-Heterocyclic compounds; (b) N-heterocyclic compounds; (c) phenylureas and thioureas; (d) carbamates and thiocarbamates; (e) anilides and N-substituted amines; (f) "GDR-specific" [illegible] compounds; (g) organophosphorus compounds. For peak assignments, see Table II.

cluster ions with the analytes or to induce derivatization reactions [14]. These additional ions are expected to be useful for an unambiguous identification of pesticides in real environmental samples.

Chromatography, detection limits, linear range and reproducibility

Of the 128 pesticides in Table I, 95 were chosen as target compounds for the development of a common method with identical experimental parameters for all compounds. These compounds were selected because they are priority pollutant pesticides. As mentioned in the Introduction, special attention was paid to compounds with low UV absorbance such as aldicarb, methomyl, oxamyl, triallate, allidochlor and several organophosphorus compounds. In this section all chromatographic and TSP mass spectrometric experiments were performed with the experimental set-up described under Experimental, *i.e.*, gradient elution with methanol–water on narrow-bore 3 mm I.D. columns in combination with postcolumn addition of buffer salt.

Table II shows the relative retention times, α_i, the molecular masses and the main ions and their abundances under typical operating conditions, *i.e.*, discharge-assisted buffer ionization with ammonium acetate ($c_s = 70$ mM). Most compounds produce only few fragment ions under the experimental conditions chosen, *i.e.*, the cationized molecular ions are observed, although some compound classes produce characteristic fragment ions owing to their chemical reactivity. In addition, in some instances "chemical dissociations" of the neutral precursors in the vaporizer probe or in the gas phase prior to ionization led to additional ions, *e.g.*, with organophosphorus compounds, carbamates and anilides. The usefulness of such reactions is explained in more detail later.

Liquid chromatography. A complete LC separation of 95 pesticides with only one set of identical experimental parameters is not possible and not necessarily required in combination with mass spectrometry. When two compounds do co-elute, LC–MS allows the identification and determination of both if each has different characteristic ions. Fig. 3 shows total ion current chromatograms of all pesticides obtained by injecting standard solutions of equal amounts (180 ng per compound). The arrangement of the pesticides in seven chromatograms according to their compound classes is arbitrary and has only practical reasons. Table II lists all the pesticides together with their relative retention times and their main TSP positive ions and abundances.

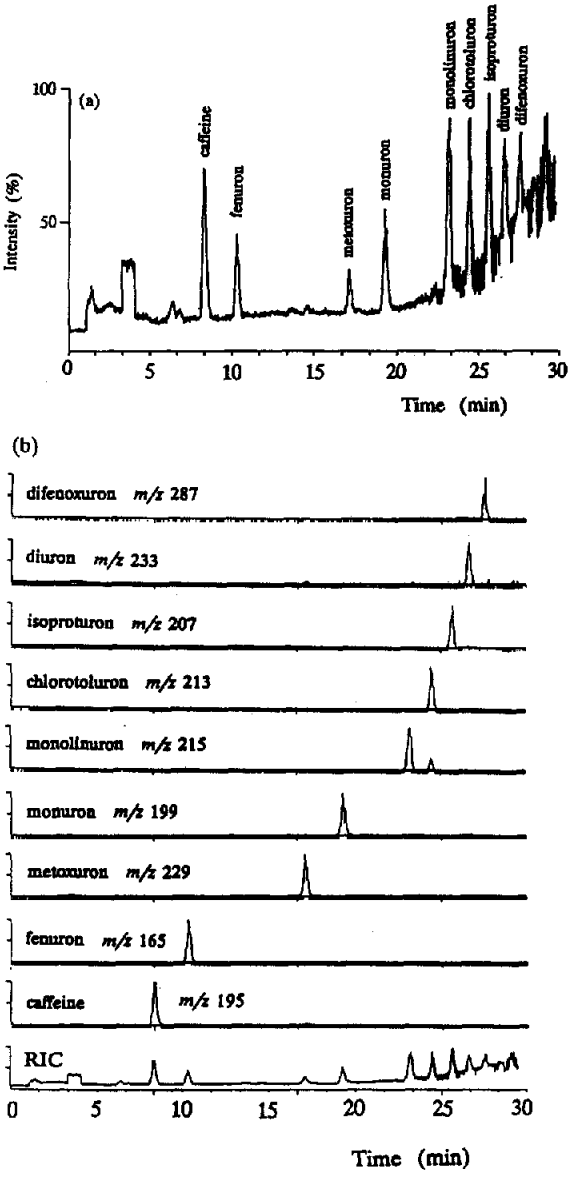

Fig. 4. Analysis of a water sample from the river Leine (Hannover) spiked with eight phenylureas at the 2 ppb level. (a) Full-scan TIC and (b) ion traces of the $[MH]^+$ ions.

This table also contains the peak assignments for Fig. 3. As can be seen, no co-elution of compounds with identical molecular masses occurs. In critical cases it is possible to distinguish between analytes by means of one of the confirmatory methods described later.

During all chromatographic experiments, caffeine was added to each standard and sample solution. This standard was used for several purposes. Caffeine was used as an internal standard for determinations in combination with off-line preconcentration. Further, slight changes of the retention times with temperature were compensated for by using relative retention times [relative to cafeine (Table II)]. With the exception of monocrotophos, caffeine does not co-elute with any of the compounds investigated (it was attempted to avoid co-elution of the chromatographic standard with one of the pesticides; this allows the comparison of the chromatogram with that obtained with a UV detector). Finally, we used caffeine as a standard for mass calibration and TSP performance tests and for the compensation of long-term reproducibility deviations (see explanations below).

To evaluate the performance of the LC–MS interface for the determination of these compounds in aqueous environmental samples, a water sample from the river Leine (Hannover) was spiked with eight phenylureas at the 2 ppb level. The spiked water sample was extracted (see Experimental) and the extract analysed by LC–TSP-MS (Fig. 4). At higher retention times a strong baseline drift and noise were observed, probably owing to matrix effects, which makes identification and quantification from the total ion chromatogram (TIC) difficult (Fig. 4a). However, as can be seen from the ion chromatograms of the $[MH]^+$ ions of all phenylureas, extracted from the full-scan TIC, the quality of these chromatograms is much better than that of the TIC and the identification, confirmation and determination of all compounds are readily possible (Fig. 4b).

Detection limits. The full-scan limits of detection (LOD) obtained for the different compound classes investigated are summarized in Table III. These LODs are very similar to those presented by other workers [17]. The LODs were calculated by either selecting a concentration of a standard solution that gave a signal-to-noise ratio of *ca.* 3:1 or by calculating the $S/N = 3$ values from the calibration data for at least three concentrations beginning near the detection limit. Exact full-scan and selected-ion monitoring (SIM) detection limits for typical pesticides and

TABLE III

INSTRUMENTAL DETECTION LIMITS FOR THE DIFFERENT PESTICIDE COMPOUND CLASSES INVESTIGATED

Experimental conditions: full-scan (m/z 130–450) detection limits (signal-to-noise ratio = 3); methanol–water gradient in combination with narrow-bore HPLC columns + postcolumn addition of aqueous volatile salt solution as described under Experimental; discharge-assisted buffer ionization (ammonium acetate).

Compound class	Positive ions (ng)	Negative ions (ng)
Triazines	0.5–5	n.d.[a]
Anilides	2–10	n.d.
Carbamates + thiocarbamates	0.1–5	5–20
Phenylureas + thioureas	2–10	20–50
Organophosphorus compounds, phosphates	1–5	50–100
Organophosphorus compounds, phosphorothioates and phosphorodithioates	10–100	>100
Organophosphorus compounds, phosphonates	2–10	>100
Carboxylic acids, phenoxy acids	>500	2–10
Carboxylic esters	5–15	>500
Quaternary ammonium compounds	5–20	n.d.

[a] Not determined.

the corresponding calibration data are presented in Table IV.

The EC drinking water guidelines demand a limit of 100 ng l^{-1} for pesticides. Assuming a 1000-fold concentration step (1 l to 1 ml) and an injection volume of 20 μl into the HPLC system, this requires the detection of at least 2 ng of the individual pesticides. However, by using higher injection volumes (50 μl) or higher concentration factors, this value can be increased to *ca.* 5–10 ng. Further, preliminary experiments with on-line preconcentration revealed higher preconcentration factors, while background signals were suppressed as compared with off-line solid-phase extraction. Unfortunately, Tables III and IV show that only some compound classes reach this criterion when performing full-scan experiments. However, for target analyte screening, time-scheduled SIM experiments may be used. This allows the detection limits to be lowered by a factor of 8–100 (Table IV). As an example, Fig. 5 shows SIM traces for repetitive injections

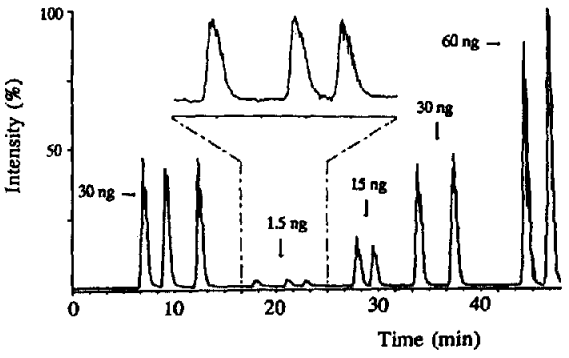

Fig. 5. SIM trace of the protonated molecule (*m/z* 222) for repetitive injections of different amounts of methabenzthiazuron under isocratic elution with methanol–water (50:50, v/v).

TABLE IV

LINEARITIES, FULL-SCAN AND SIM DETECTION LIMITS OBTAINED FOR SEVERAL PESTICIDES

Experimental conditions: full-scan (*m/z* 130–450) and SIM detection limits (signal-to-noise ratio = 3); linearity: $\log s_i = a_i \log m + b_i$, s_i = ion current of the analyte ion i, m = amount injected; r = correlation coefficient.

Compound	Linearity[a]			Detection limit (ng)	
	a_i	b_i	r	Scan	SIM
Aldicarb	0.923	2.167	0.998	4.0	0.220
Ametryn	0.973	2.535	0.999	2.4	
Atrazine	0.971	2.830	0.999	1.2	
Carbaryl	0.955	2.490	0.999	5.0	0.080
Carbofuran	0.981	2.918	0.999	0.3	0.065
Chlorobromuron	0.897	2.273	0.999	8.2	
Chlorotoluron	1.133	2.358	0.999	3.6	0.035
Desmetryn	0.969	2.861	0.999	1.0	0.080
Difenoxuron	0.890	2.134	0.996	9.0	0.175
Diuron	0.991	2.389	0.999	5.0	0.140
Fenuron	0.915	2.792	0.999	3.2	0.380
Isoproturon	0.984	2.358	0.999	4.8	
Methabenzthiazuron	1.120	2.600	0.998	2.0	0.150
Methiocarb	1.042	2.057	0.999	2.7	
Metobromuron	1.001	2.499	0.999	3.9	0.190
Metoxuron	0.973	2.012	0.998	10.7	0.310
Monuron	1.052	2.543	0.999	2.3	0.100
Prometryn	0.863	2.782	0.999	4.9	
Propazine	1.032	2.467	0.992	1.9	
Simazine	0.971	2.773	0.999	1.2	
Trichlorfon	0.809	1.981	0.998	15.0	

[a] Data from three to five repetitive injections for at least three different amounts injected in the range 3–3000 ng.

of different amounts of methabenzthiazuron using isocratic elution with methanol–water (50:50, v/v). As expected, the detection limit observed is much lower than in the full-scan mode.

Linearity. The parameters derived from calibration graphs for several pesticides, obtained from three to five repetitive injections over a range of 3–3000 ng, are presented in Table IV. The quality of the linear relationships in the log–log diagrams was evaluated by calculating the slope of the regression lines and the correlation coefficients. As can be seen from these values, a linear range of at least 10^3 beginning from the detection limits was observed. This allows an external quantification in combination with on-line preconcentration.

Reproducibility. The inability of TSP to provide sufficiently stable and reproducible ion currents over extended periods is a serious problem. Whereas the reproducibility during one-day experiments is often excellent to satisfactory, it is often poorer if determined over longer periods. Typical reproducibilities for several pesticides from standard injections obtained during 8-h periods are presented in Table V. The R.S.D.s for different sample amounts range from 1.2 to 11.8%. The long-term reproducibility often exceeds 20%. To some extent, these reproducibilities can be improved if relative intensities or peak areas are used, *e.g.*, relative to caffeine as a TSP standard. However, the long-term variations of the sensitivity remain a major problem of TSP ionization.

Enhancing structural information from TSP mass spectra. Confirmation of pesticide residues in environmental samples

Ammonium acetate TSP mass spectra of pesticides usually show only quasi-molecular ions such as $[MH]^+$ and $[MHNH_3]^+$, which limits their specificity, while structural information is lacking. Several techniques are available to overcome these limitations: (1) the variation of interface temperatures, (2) the use of external ionization media (filament, discharge), (3) MS–MS techniques, (4) repeller-induced spectral changes [16], (5) additional cluster ions with solvent or additive molecules and (6) additional information gained from the complementary positive- and negative-ion spectra. As mentioned above, "chemical dissociations" of neutral precursors in the vaporizer probe or in the gas phase, *e.g.*, with asulam, carbendazim, alachlor, butachlor, metolachlor and several sul-

TABLE V

MEAN RESPONSES AND INTRA-DAY REPRODUCIBILITIES FOR SOME OF THE PESTICIDES

Data from three to five repetitive injections.

Compound	Amount injected (ng)					
	300		30		15	
	Area/ng[a]	R.S.D. (%)	Area/ng	R.S.D. (%)	Area/ng	R.S.D. (%)
Ametryn	11 623	7.4	13 001	5.2	13 583	1.2
Carbofuran	16 140	4.2	14 509	7.4	15 276	5.1
Chlortoluron	13 206	9.8	12 974	5.5	13 378	7.2
Desmetryn	15 650	5.0	13 545	8.2	17 613[b]	2.2
Methabenzthiazuron	16 889	3.5	17 007	8.3	19 040[b]	9.3
Metoxuron	10 376	6.3	11 199	4.2	10 912	7.7
Prometryn	12 641	2.4	12 910	5.0	11 488	8.2
Propazine	11 181	3.4	13 509	7.4	15 485[b]	7.2
Trichlorfon	3877	6.4	5136	5.2	6188	11.8

[a] Quantification ion abundances integrated over the LC peak.
[b] 3-ng injections.

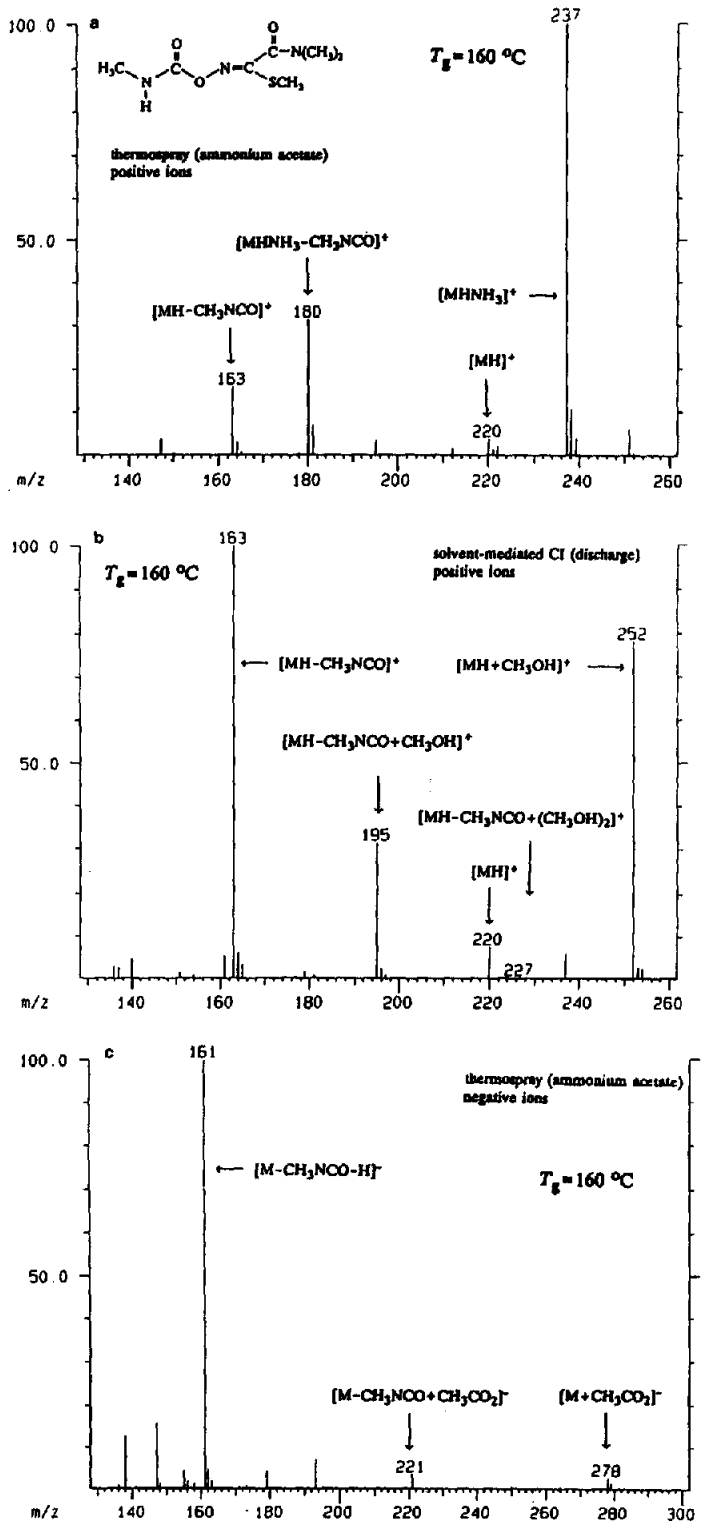

Fig. 6. TSP mass spectra of oxamyl under different ionization conditions (T_g, T_v = constant). (a) Discharge-assisted buffer ionization (ammonium acetate), positive ions; (b) solvent-mediated chemical ionization (discharge), positive ions; (c) discharge-assisted buffer ionization (ammonium acetate), negative ions.

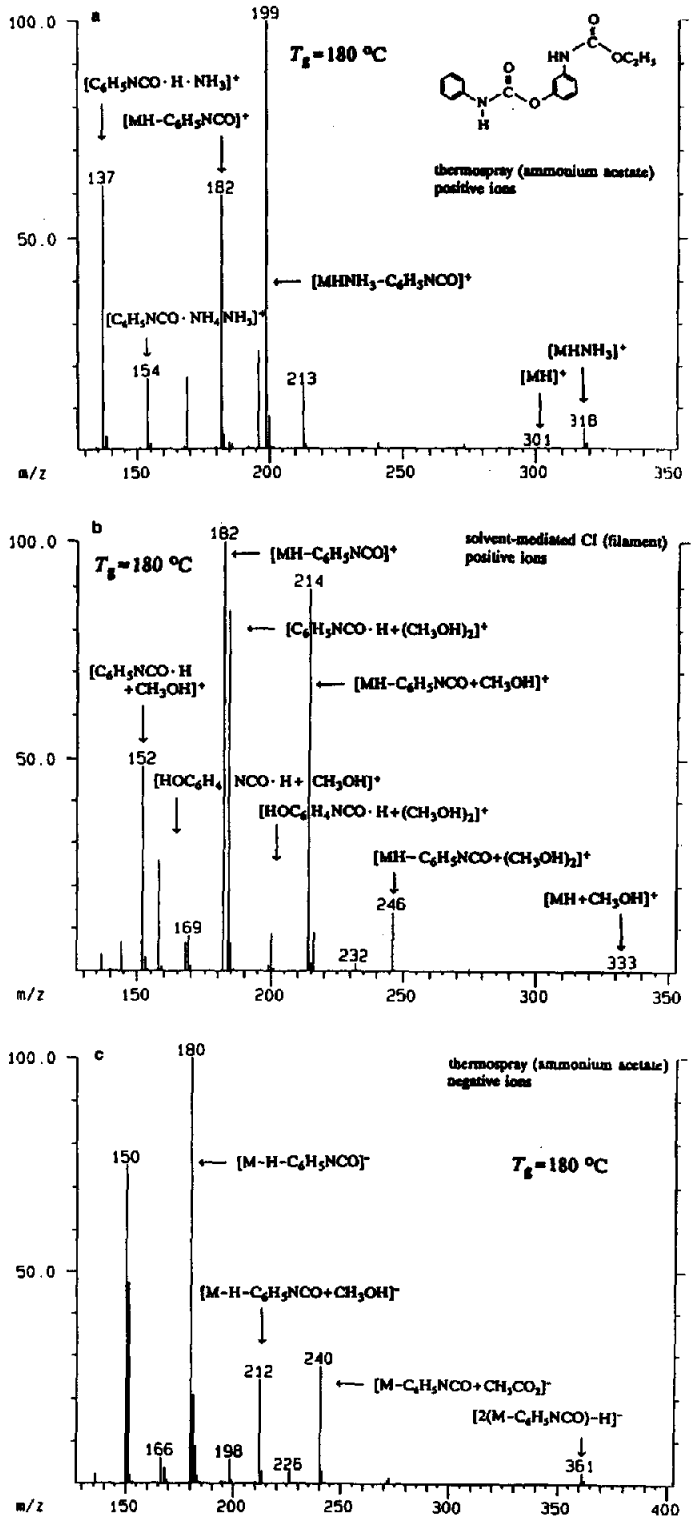

Fig. 7. TSP mass spectra of desmedipham under different ionization conditions (T_g, T_v = constant). (a) Filament-assisted buffer ionization (ammonium acetate), positive ions; (b) solvent-mediated chemical ionization (filament), positive ions; (c) filament-assisted buffer ionization (ammonium acetate), negative ions.

phonylurea and organophosphorus pesticides, were observed. This degradation is predominantly followed by ionization with, sometimes, successive fragmentation. These dissociations are strongly dependent on temperature, both T_g and T_v, and may be of value in the confirmation of pesticides in environmental samples. The usefulness of varying the interface temperatures is demonstrated in more detail elsewhere [13].

In this section, a simple example is shown which makes use of specific instabilities found in many pesticides and which can be used to enhance structural information. The confirmatory analysis can be done by using the postcolumn technique described above either with or without ammonium acetate and without changing the experimental set-up.

For example, with most carbamates and thiocarbamates no significant loss in sensitivity occurs when one switches from discharge-assisted buffer ionization with ammonium acetate to solvent-mediated chemical ionization (CI) with discharge or filament without ammonium acetate. Ionizing a compound with protonated methanol [proton affinity (PA) = 180 kcal mol^{-1} (1 kcal = 4.184 kJ)] is more exothermic than ionizing it with the ammonium ion (PA = 204 kcal mol^{-1}), that is, fragmentation is strongly enhanced. Further, in comparison with ammonia very intense solvent cluster ions $[MH(CH_3OH)_x]^+$ of the quasi-molecular and fragment ions are observed as the clustering depends strongly on the proton affinity of the solvent and the ionizing plasma [34]. For this reason, fewer water cluster ions than methanol cluster ions are observed with methanol–water mixtures. Further, carbamates, phenylureas, organophosphorus compounds and some other

TABLE VI

MAIN POSITIVE IONS AND THEIR RELATIVE ABUNDANCES OBTAINED FROM THE TSP, CI AND CAD MASS SPECTRA OF OXAMYL

Experimental conditions: flow-injection, amount injected = 300 ng; carrier stream, methanol–water (50:50, v/v); flow-rate 1.0 ml min^{-1}; CAD conditions, collision-offset 10 V, collision cell pressure = $1.3 \cdot 10^{-3}$ Torr (argon); T_g = 160°C, T_v = 190°C, p_g = 3.4 Torr. Ionization: TSP = discharge-assisted buffer ionization, c_s = 50 mM; CI = solvent-mediated CI with either discharge (D) or filament (F); discharge voltage = 1 kV; filament = 1 keV.

m/z	Tentative structure assignment	Relative abundance (%)[a]			
		TSP	CI(D)	CI(F)	CAD[b]
72	$[MH - CH_3NCO - CH_3SCH{=}NOH]^+$	+	+	+	100
90	$[MH - CH_3NCO - (CH_3)_2NC(O)H]^+$	+	+	+	58
104	$[MH - CH_3NCO - CH_3SCH{=}NOH + CH_3OH]^+$	+	+	+	
122	$[MH - CH_3NCO - (CH_3)_2NC(O)H + CH_3OH]^+$	+	+	+	
136	$[MH - CH_3NCO - CH_3SCH{=}NOH + (CH_3OH)_2]^+$		3	2	
154	$[MH - CH_3NCO - (CH_3)_2NC(O)H + (CH_3OH)_2]^+$		2	5	
163	$[MH - CH_3NCO]^+$	17	100	100	3
180	$[MHNH_3 - CH_3NCO]^+$	31			
194	$[MHNH_3 - CH_3NCO - H_2O + CH_3OH]^+$		3	3	
195	$[MH - CH_3NCO + CH_3OH]^+$	5	30	28	
220	$[MH]^+$	5	10	14	
227	$[MH - CH_3NCO + (CH_3OH)_2]^+$		1	3	
237	$[MHNH_3]^+$	100			
251	$[MHNH_3 - H_2O + CH_3OH]^+$	8			
252	$[MH + CH_3OH]^+$		79	85	
278	$[MHNH_3 + CH_3CO_2NH_4 - 2H_2O]^+$	19			
325	$[M_2H - 2CH_3NCO]^+$	<1	3	2	

[a] + = This ion was observed in SIM experiments.
[b] Precursor ion m/z 237 (=$[MHNH_3]^+$).

compound classes are detected very sensitively as negative ions, at least under solvent-mediated CI conditions. Therefore, the combination of discharge-assisted buffer ionization with either positive- or negative-ion discharge solvent-mediated CI offers valuable additional structural information for characterizing the pesticides.

This is demonstrated in Figs. 6 and 7, where the direct-flow injection TSP mass spectra of the carbamates oxamyl and desmedipham under different ionization conditions but with identical solvent composition and temperatures are presented. Both compounds show characteristic fragment ions especially under solvent-mediated CI conditions, which can be attributed to the alcohol and the isocyanate formed. In the case of aryl-N-alkyl carbamates such as desmedipham, the formation of the phenol is favoured and the $[MH\text{-}RNCO]^+$ ion often dominates the spectrum. In addition, very intense solvent clusters of both the quasi-molecular and the fragment ions were observed. Tables VI and VII summarize these ions and the CAD spectra of the compounds.

CONCLUSIONS

LC–TSP-MS is a sensitive, specific and versatile technique for the determination of pesticides in aqueous environmental samples. A reversed-phase gradient LC separation was developed which permits the determination of 95

TABLE VII

MAIN POSITIVE IONS AND THEIR RELATIVE ABUNDANCES OBTAINED FROM THE TSP, CI AND CAD MASS SPECTRA OF DESMEDIPHAM

Experimental conditions as in Table VI, expect T_s = 180°C.

m/z	Tentative structure assignment	Relative abundance (%)[a]			
		TSP	CI(D)	CI(F)	CAD[b]
94	$[C_6H_5NH_2 \cdot H]^+$	+	+	+	1
120	$[C_6H_5NCO \cdot H]^+$	10	15	13	<1
136	$[MH - C_6H_5NCO - C_2H_5OH]^+$	1	1		<1
137	$[C_6H_5NCO \cdot H \cdot NH_3]^+$	62			100
152	$[C_6H_5NCO \cdot H + CH_3OH]^+$		49	45	
154	$[C_6H_5NCO \cdot NH_4NH_3]^+$	17	<1	<1	<1
158	?		27	25	
168	$[MH - C_6H_5NCO - C_2H_5OH + CH_3OH]^+$	8			<1
169	?	10	24	20	<1
182	$[MH - C_6H_5NCO]^+$	60	100	100	5
184	$[C_6H_5NCO \cdot H + (CH_3OH)_2]^+$		84	89	
196	?	23			
199	$[MHNH_3 - C_6H_5NCO]^+$	100			
200	$[MH - C_6H_5NCO - C_2H_5OH + (CH_3OH)_2]^+$		10	10	
213	?	18			
214	$[MH - C_6H_5NCO + CH_3OH]^+$		90	85	
232	$[MH - C_6H_5NCO - C_2H_5OH + (CH_3OH)_3]^+$		5	5	
241	$[MH - C_6H_5NCO + CH_3CO_2NH_4 - H_2O]^+$	3			
246	$[MH - C_6H_5NCO + (CH_3OH)_2]^+$		16	20	
301	$[MH]^+$	<1			<1
318	$[MHNH_3]^+$	6			
332	$[M + CH_3NH_3]^+$	<1			
333	$[MH + CH_3OH]^+$		<1	<1	

[a] + = This ion was observed in SIM experiments.
[b] Precursor ion *m/z* 318 (=$[MHNH_3]^+$).

pesticides with one common LC–MS method. The TSP interface is operated under discharge-assisted buffer ionization conditions as the sensitivities obtained in this mode are much higher than those in the filament-on mode or with volatile salt ionization without external ionization media. The reproducibilities, linearities and instrumental detection limits obtained are adequate for environmental monitoring of a broad range of pesticides and will, in many instances, allow the verification of the EC drinking water guidelines even in the full-scan mode. In combination with time-scheduled SIM, the method should permit the detection of all pesticides down to the 10–100 ppt level in combination with conventional off-line solid-phase extraction or on-line preconcentration. By combining the retention data and TSP mass spectra of all the pesticides presented in this paper, LC–TSP-MS can be used as an ideal confirmatory method for the identification of almost all pesticides investigated in environmental samples. Further confirmation can readily be achieved by using either positive- or negative-ion solvent-mediated CI with discharge or filament operation.

ACKNOWLEDGEMENT

This study was carried out with funds provided by the Bundesministerium für Forschung und Technologie, Bonn.

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