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On-line low-level screening of polar pesticides in drinking and surface waters by liquid chromatography–thermospray mass spectrometry

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ABSTRACT

Mass spectra of 39 carbamate, triazine, phenylurea and organophosphorus polar pesticides were obtained by liquid chromatography–mass spectrometry with a thermospray interface. The analytes generated $[M + H]^+$ or $[M + NH_4]^+$ as the base peak with methanol–0.1 *M* ammonium acetate as the mobile phase in the discharge positive-ion mode. Chlorophenols showed much better sensitivity in the negative-ion mode; their spectra were dominated by the deprotonated molecular ion. Trace enrichment of these pesticides on a 10 mm × 3.0 mm I.D. precolumn packed with C_{18}-bonded silica was coupled on-line with reversed-phase column liquid chromatography–thermospray mass spectrometry (LC–TSP-MS). The LC separation was carried out on a 250 × 4.6 mm I.D. C_{18}-bonded silica column using a linear methanol–aqueous ammonium acetate gradient [10:90 to 90:10 (v/v) in 45 min]. When optimized TSP-MS conditions and 50-ml water samples were used, the detection limits for the pollutants tested typically were in the 2–90 ng/l range with time-scheduled selected-ion monitoring; the repeatability was good and the LC–TSP-MS system was robust. Several surface and drinking water samples were analysed and low levels of simazine, atrazine, isoproturon and diuron were detected.

INTRODUCTION

Polar pollutants are of major interest in environmental water studies. In our laboratory, preliminary results on the determination of these pollutants using an on-line trace enrichment–column liquid chromatography (LC)–diode-array detection (DAD) system have been reported [1]. In order to establish whether or not the concentrations of polar pesticides exceed tolerance levels in surface water (1–3 μg/l) and drinking water (0.1 μg/l) samples, it is necessary to have a robust system that meets these low detection limit requirements.

In most instances, the determination of toxic organic compounds is still carried out by means of gas chromatography (GC) coupled with selective and/or mass spectrometric (MS) detection. However, for polar pollutants LC and especially reversed-phase LC (RPLC) is nowadays regarded as the separation technique of choice. RPLC has been used for the determination of organic pollutants with a variety of detectors [2–6]; however, the use of (RP)LC in conjunction with MS detection is becoming increasingly important. In the last decade, a variety of interfaces such as the direct liquid introduction [7], thermospray (TSP) [8] and particle beam [9,10] types have been designed and developed to solve the incompatibility of these two powerful analytical techniques. Whereas a particle beam interface provides electron impact (EI) spectra (suitable for identification), TSP, the most commonly used interface, offers better sensitivity. However, the limits of detection obtained by conventional LC–TSP-MS do not meet the tolerance levels for environmental pollutants (0.1 μg/l for drinking water and 1–3 μg/l for surface water) [8,11,12]. Trace enrich-

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ment prior to LC is therefore a necessary step. Trace enrichment is still mainly carried out by means of liquid–liquid extraction. These methods, however, are laborious and time consuming, large volumes of (toxic) organic solvents are used and sample losses can hardly be avoided. The use of off-line [13,14] or on-line [15–18] precolumn techniques is therefore to be preferred to obtain trace enrichment. In the on-line mode the compounds of interest are trapped on small (5–10 mm × 2.0–4.6 mm I.D.) precolumns packed with a suitable stationary phase (*e.g.*, alkyl-bonded silica, polymer-based materials, ion exchangers) or on so-called membrane extraction discs, which contain up to 90 mass% of such stationary phases in a PTFE mesh, and transferred to the analytical column. It is obvious that compared with off-line techniques, in which only part of the total sample is injected, the analyte detectability will be much better and the speed of analysis, of course, much higher in the on-line mode.

LC–TSP-MS coupled off-line with sample treatment has been used for the determination of different polar pesticides [19–23]. In a recent paper, the on-line trace enrichment of several phenylurea herbicides on a polymer-based precolumn and on membrane extraction discs (C_{18}-bonded silica) combined with this coupled set-up was reported [24]. Some of these compounds were identified in environmental samples at the low ng/l level. In this study, an attempt was made to extend this work and to develop a method that will allow the analysis of drinking and surface water for the simultaneous determination of several groups of pesticides, *e.g.*, carbamates, triazines, organophosphorus and phenylureas pesticides, in a single procedure.

EXPERIMENTAL

Chemicals

HPLC-grade water was prepared by purifying demineralized water in a Mili-Q filtration system (Millipore, Bedford, MA, USA). HPLC-grade methanol was obtained from J.T. Baker (Deventer, Netherlands) and ammonium acetate (99%) from Merck (Darmstadt, Germany). All pesticides were of 96–99% purity and were purchased from Riedel-de Haën (Seelze, Germany). Stock solutions (200 μg/ml) of the analytes were made by weighing and dissolution in methanol. Drinking and surface water samples were spiked with a standard mixture of 21 pesticides at levels ranging from 0.1 to 10 μg/l.

Instrumentation

The LC system consisted of a Kipp & Zonen (Delft, Netherlands) Model 4140 LC pump for delivering the aqueous sample (5 ml/min) and wetting of the precolumn, a Hewlett-Packard (Waldbronn, Germany) Model 1090 gradient pump for delivering the mobile phase (1 ml/min) and a six-port switching valve (Rheodyne, Berkeley, CA, USA). The analytical column was a 250 mm × 4.6 mm I.D. stainless-steel column packed with 5-μm base-deactivated C_{18} material (Supelchem, Leusden, Netherlands). The precolumn was a 10 × 3.0 mm I.D. stainless-steel column packed with 40-μm Bondesil-C_{18} (Analytichem, Harbor City, CA, USA).

A Hewlett-Packard (Palo Alto, CA, USA) Model 5989 A MS Engine was connected to the LC column outlet via a Hewlett-Packard TSP interface. All data were acquired on a Hewlett-Packard UX 98578 X data system. A solution of polypropylene glycol (PPG) (16.7 mg/ml) in methanol–0.1 *M* ammonium acetate (1:3, v/v), was used to calibrate the mass spectrometer for m/z 268.2, 442.3 and 558.4 ($[M + NH_4]^+$ ions of PPG oligomers with relatively equal intensity over the mass range 150–800 u) in the discharge positive-ion (PI) mode and for m/z 367.3, 715.3 and 889.6 ($[M + CH_3COO]^-$ ions of PPG oligomers) in the negative-ion (NI) mode using discharge ionization. The source block temperature was set at 200°C and that of the quadrupole analyser at 100°C.

The vaporization temperature of the TSP cartridge was optimized by a probe survey facility programme. A plot of stem temperature *vs.* tip temperature was made and the stem temperature required for complete vaporization of the mobile phase was determined by finding the inflection point and taking a *ca.* 5% lower temperature for the actual LC–TSP-MS operation [25]. Changing the composition of the mobile phase can affect the stem temperature. In

this study, the stem temperature was programmed from 120 to 110°C when altering the methanol–water composition from 10:90 to 90:10 (v/v) in 45 min.

Analytical procedures

The C_{18} precolumn was flushed at 5 ml/min with 5 ml of methanol and then 5 ml of HPLC-grade water prior to preconcentration. Subsequently, a 50-ml sample was preconcentrated (5 ml/min) on the precolumn. The analytes trapped on the precolumn were desorbed in the backflush mode with methanol–0.1 *M* ammonium acetate (10:90, v/v) and transferred on-line to the C_{18} analytical column. The actual separation of the analytes was carried out using a 45-min linear gradient to methanol–0.1 *M* ammonium acetate (90:10, v/v).

For all compounds calibration graphs were constructed over the range 0.1–10 μg/l; the analyses were done in duplicate (six data points). These calibration graphs were used as external standards for the analysis of real samples.

RESULTS AND DISCUSSION

Recently, we reported on the use of RPLC–TSP-MS for the determination of phenylurea herbicides in drinking and surface waters [24]. In order to test the general usefulness of the method, a large number of polar pollutants representing different classes of compounds were studied using essentially the same conditions as before, *viz.*, gradient elution with methanol–0.1 *M* ammonium acetate and TSP-MS in the discharge PI and, occasionally, the NI mode. Preliminary studies revealed that N-methylcarbamates, organophosphorus pesticides and triazines can be included in the chromatographic procedure developed for the phenylureas. Chlorophenols showed much better analyte detectability in the NI than in the PI mode. With the nitrophenols studied the breakthrough volumes generally were much smaller than the 50 ml recommended for the other classes of pesticides. Phenoxyacetic acids did not show a good TSP-MS response under the conditions used. The latter two classes of analytes were therefore not included in the present study.

Mass spectra

Table I shows that the TSP mass spectra (PI mode) of all but four of the pesticides selected are dominated by the protonated molecular ions. Aldicarb-sulphone, carbaryl and malation have $[M + NH_4]^+$ as the base peak and paration-ethyl ($M_r = 291$) has a base peak at m/z 262, which may be due to the formation of an $[M + H - NO]^+$ fragment ion [26]. Some further comments are as follows. Among the carbamates tested, aldicarb-sulphone showed fragment ions at m/z 165 and 183, corresponding to the loss of isocyanate from the protonated molecular ion, and the ammonia adduct ions, respectively (Fig. 1). The ammonia chemical ionization (CI) mass spectrum of this carbamate was also reported to show an ion at m/z 165 in capillary supercritical fluid chromatography–MS [27]. All phenylureas generated $[M + H]^+$ as the base peak; $[M + NH_4]^+$ was observed as adduct ion in some instances [28]. These results are in good agreement with literature data [29–31], although for, *e.g.*, monuron and diuron, $[M + NH_4]^+$ has sometimes been reported to be the base peak [29]. In LC–MS using a direct liquid introduction interface, the mass spectra of some phenylureas have been found to be dominated by quasi-molecular ions [32,33]. The mass spectra of the triazine herbicides were relatively simple and they all showed the protonated molecular ion as the base peak. A protonated methanol adduct ion was observed for both simazine and atrazine. Fragment ions at m/z 168 and 182 generated by simazine and atrazine, respectively, may well be due to the replacement of a chlorine by a hydrogen atom, taking place in the spray (see Fig. 7). Actually, with the phenylurea diuron the same phenomenum is observed, but as a two-step process for both chlorine atoms. For all organophosphorus compounds except parathion-ethyl and diazinon the ammonia adduct ions were either very intense fragments or the base peak, which is in agreement with previously reported results [29].

In contrast to the pesticides discussed above, chlorophenols show distinctly stronger signals in

TABLE I

RETENTION TIMES, MAJOR IONS AND LIMITS OF DETECTION OF 39 POLAR PESTICIDES IN LC–TSP-MS

No.	t_R (min)	Compound	Class[a]	M_r	Major ions, m/z (relative abundance, %)[b]	LOD[c] (ng/l)
1	10.6	Aldicarb-sulphone	CA	222	240(100), 165(51), 183(30), 223(10)	65
2	16.8	1-(3-Chloro-4-hydroxy-phenyl)-3,3-dimethylurea	PU	214	215(100), 217(22), 232(17), 181(15)	50
3	19.3	Dimethoate	OP	229	230(100), 247(50)	10
4	20.5	Desmethylmetoxuron	PU	200	201(100), 218(57), 203(32), 220(16)	25
5	21.8	Isocarbamid	CA	185	186(100), 203(20)	–
6	22.3	Carbendazim	CA	191	192(100)	–
7	23.1	Monomethylmetoxuron	PU	214	215(100), 217(33), 232(25)	10
8	24.5	Metoxuron	PU	228	229(100), 231(33), 201(18)	10
9	26.4	Cyanazine	TZ	240	241(100), 243(33), 207(13)	10
10	27.1	Monuron	PU	198	199(100), 201(32), 216(15)	10
11	28.5	Simazine	TZ	201	202(100), 204(40), 168(32)	2
12	29.9	Carbaryl	CA	201	219(100), 202(35), 220(13)	–
13	30.5	Monolinuron	PU	214	215(100), 232(50), 217(32)	–
14	31.3	Fluormeturon	PU	232	233(100), 250(30)	–
15	31.7	Atraton	TZ	211	212(100), 213(14)	10
16	32.0	Chlortoluron	PU	212	213(100), 215(25), 230(10)	–
17	32.0	Metobromuron	PU	258	259(100), 261(90), 276(53), 278(53)	–
18	32.2	Atrazine	TZ	215	216(100), 218(32), 182(22)	5
19	33.3	Isoproturon	PU	206	207(100), 208(15)	5
20	33.9	Diuron	PU	232	233(100), 235(65), 250(22), 165(17), 252(15), 199(15)	15
21	34.0	Difenoxuron	PU	286	287(100), 288(15)	–
22	35.1	Azinphos-methyl	OP	317	318(100), 335(78)	25
23	35.2	Terbutylazine	TZ	225	226(100), 227(14)	–
24	35.5	Promethon	TZ	225	226(100), 227(16)	–
25	35.7	Propazine	TZ	229	230(100), 232(50), 231(32)	5
26	36.0	Secbutylazine	TZ	229	230(100), 232(35), 231(12)	–
27	36.3	Linuron	PU	248	249(100), 266(76), 251(70), 268(50)	–
28	36.7	Terbutylazine	TZ	229	230(100), 232(35), 231(12)	–
29	36.7	Secbumeton	TZ	225	226(100), 201(2)	–
30	37.2	Chlorobromuron	PU	292	295[d](100), 312(80), 293(76), 310(53)	–
31	37.8	Malathion	OP	330	348(100), 331(50), 175(20), 192(20)	35
32	39.2	Terbutryne	TZ	241	242(100), 243(12)	–
33	39.3	Trietazine	TZ	229	230(100), 232(26)	15
34	39.8	Prometryn	TZ	241	242(100), 243(14)	15
35	41.2	Neburon	PU	274	275(100), 277(66)	–
36	41.2	Parathion-ethyl	OP	291	262(24), 263(11)	90
37	42.2	Diazinon	OP	304	305(100), 306(15)	30
38	43.8	Disulfoton	OP	274	275(100), 292(50)	30
39	47.8	Carbotuthion	OP	342	343(100), 345(35)	–

[a] CA = Carbamates; OP = organophosphorus pesticides; PU = phenylureas; TZ = triazines.
[b] LC eluent: methanol–0.1 *M* ammonium acetate [10:90 to 90:10 (v/v) in 45 min].
[c] Limits of detection (signal-to-noise ratio = 3:1) under time-scheduled SIM conditions.
[d] Highest peak of cluster starting at m/z 293.

TSP-MS in the NI mode [34,35]. As an example, Fig. 2 shows the mass spectra of 3,4-dichlorophenol, 2,3,4-trichlorophenol and 2,3,5,6-tetrachlorophenol. $[M-H]^-$ is the base peak in all instances; the adduct ion $[M+CH_3COO]^-$ for 3,4-dichlorophenol (m/z 221) is much more

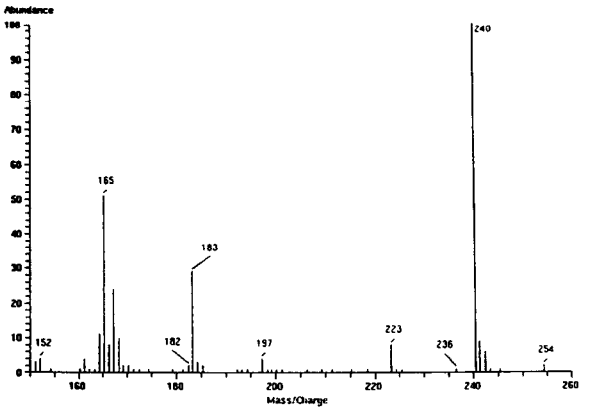

Fig. 1. TSP mass spectrum of aldicarb-sulphone in the discharge PI mode. For details, see text.

pronounced than the corresponding adducts of 2,3,4-trichlorophenol and 2,3,5,6-tetrachlorophenol at m/z 255 and 289, respectively. The cluster ions beginning at m/z 161 (Fig. 2B) and 195 (Fig. 2C) are due to the presence of $[M - Cl]^-$. The predominance of the deprotonated molecular ions in the mass spectra can be attributed to the lower gas-phase acidity of the chlorophenols compared with acetate.

RPLC–TSP-MS

In order to achieve good chromatographic resolution and efficient trace enrichment from 50–100-ml aqueous samples, it is necessary to use the same type of bonded-phase material, *i.e.*, C_{18}-bonded silica, in the precolumn and the analytical column, to select a sufficiently long, *i.e.*, 25 cm, analytical column, and to use a fairly large diameter, *i.e.*, 3.0–4.6 mm I.D., pre- and main columns. Under these conditions, the sample capacity will be high and the separation power of the analytical column will not be affected by band broadening caused during analyte transfer from the precolumn. Fig. 3 shows a full-scan RPLC–TSP-MS trace for a mixture of 21 pesticides (N-methylcarbamates, phenylureas, organophosphorus compounds and triazines) using a 45-min linear gradient of methanol–0.1 *M* ammonium acetate (10:90 to 90:10, v/v). All analytes except malathion and trietazine are well resolved. The last two pesticides can easily be distinguished on the basis of their base peaks, which are at m/z 348 and 230, respectively. The peak at 45.2 min is probably phthalate esters.

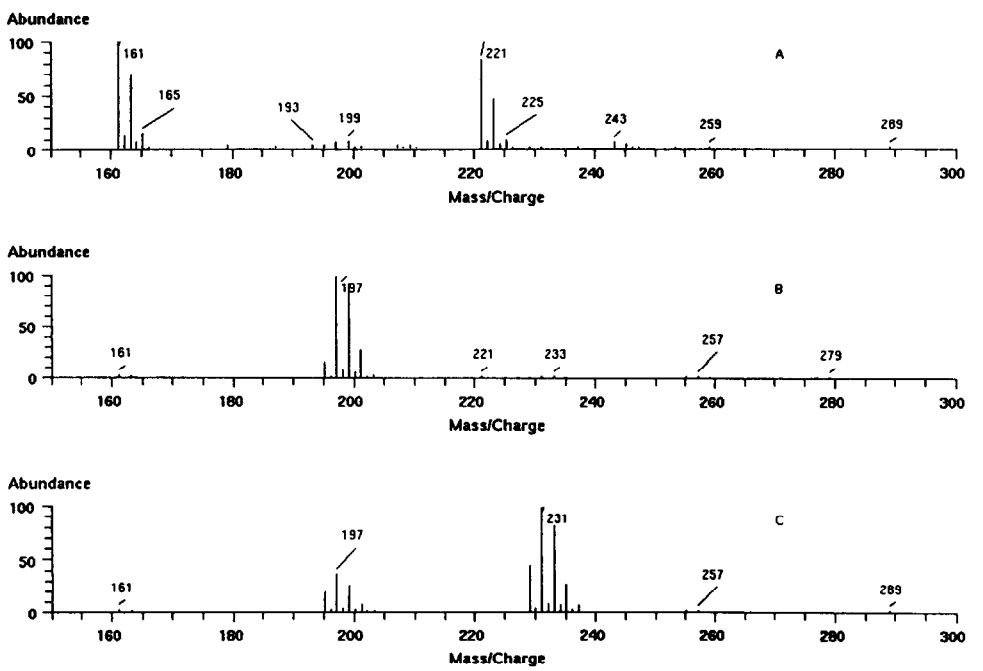

Fig. 2. TSP mass spectra of (A) 3,4-dichlorophenol, (B) 2,3,4-trichlorophenol and (C) 2,3,5,6-tetrachlorophenol in the discharge NI mode. For details, see text.

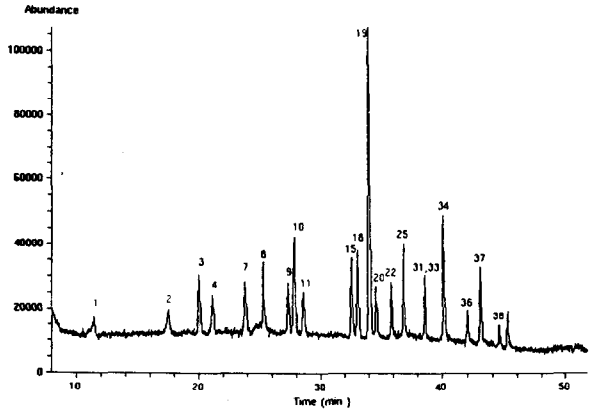

Fig. 3. RPLC–TSP-MS full-scan trace for 21 polar pesticides (150–350 u). Column, 250 mm × 4.6 mm I.D. stainless-steel containing 5-μm C_{18}-bonded silica; eluent, linear methanol–0.1 *M* ammonium acetate gradient [10:90 to 90:10 (v/v) in 45 min]; 25-μl loop injection. For peak designation, see Table I.

Fig. 4 shows on-line trace enrichment–RPLC–TSP-MS traces obtained after preconcentration of 50 ml of river Rhine water and 50 ml of river Rhine water spiked with the mixture of 21 pesticides at the 1 μg/l level. The chromatograms were recorded under time-scheduled selected-ion monitoring (SIM) conditions using the base peaks listed in Table I. As C_{18}-bonded silica rather than a more hydrophobic polymer is used as the packing material in the precolumn, the peak broadening is less than in our previous study [24]. On-line trace enrichment–RPLC–TSP-MS traces (NI mode) obtained after preconcentration of 50 ml of river Meuse water and 50 ml of the river water spiked with four chlorophenols at the 1 μg/l level are shown in Fig. 5.

The performance of the total trace enrichment–RPLC–TSP-MS system was tested by analysing river Rhine water spiked with the mixture of 21 pesticides at various levels ranging from 0.1 to 10 μg/l. Each experiment was carried out by preconcentrating 50 ml of water and using time-scheduled SIM. Over the concentration range tested, the correlation coefficients (R^2) were 0.97–0.998 for all analytes. The relative standard deviation (R.S.D.) was typically 5–15% ($n = 6$) using a river Rhine water sample spiked at the 1 μg/l level. The limits of detection for the 21 pesticides in the mixture were in the range 2–90 ng/l (signal-to-noise ratio = 3:1); they are included in Table I. The analytical data can be considered satisfactory.

Applications

Preliminary experiments indicated that at least three of the pesticides tested, *viz.*, simazine, atrazine and isoproturon, are present at low levels in the river Rhine water. In order to improve further both the sensitivity and selectivi-

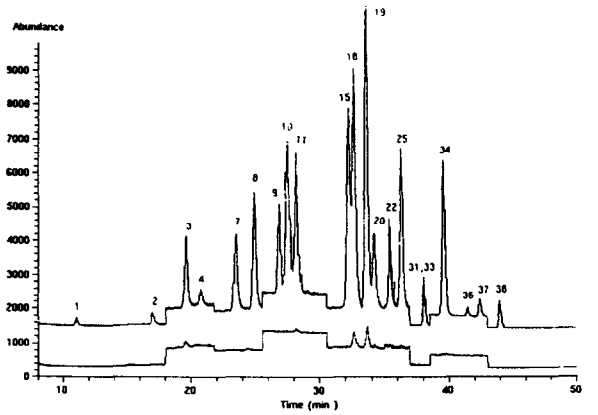

Fig. 4. On-line trace-enrichment RPLC–TSP-MS trace for 50 ml of (bottom) river Rhine water and (top) river Rhine water spiked with a mixture of 21 polar pesticides at 1 μg/l. Column, 250 mm × 4.6 mm I.D. stainless-steel containing 5-μm C_{18}-bonded silica; eluent, linear methanol–0.1 *M* ammonium acetate gradient [10:90 to 90:10 (v/v) in 45 min]; MS, discharge PI mode. For peak designation, see Table I.

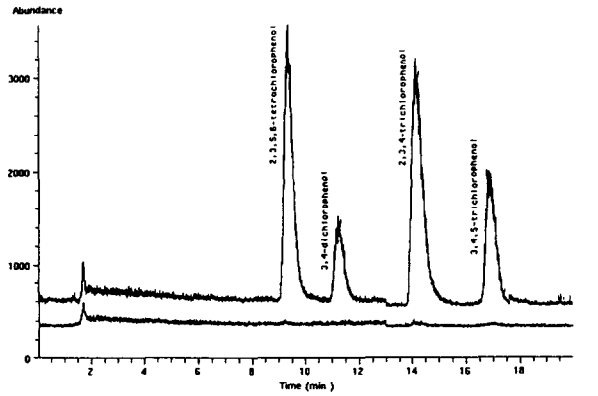

Fig. 5. On-line trace-enrichment RPLC–TSP-MS trace for 50 ml of (bottom) river Meuse water and (top) river Meuse water spiked with a mixture of four chlorophenols at 1 μg/l. Column, 150 mm × 4.6 mm I.D. stainless-steel containing 5-μm Rosil C_{18}-bonded silica; eluent, linear methanol–0.1 *M* ammonium acetate gradient [10:90 to 90:10 (v/v) in 45 min]; MS, discharge NI mode, For details, see text.

ty, the sample volume was increased to 200 ml (which may cause breakthrough of some early eluting analytes, but not of these target compounds) and carefully time-scheduled SIM was used. Fig. 6 compares trace enrichment–RPLC–TSP-MS traces (PI mode) for river Rhine water, Amsterdam drinking water, HPLC-grade water (each 200 ml of sample) and a blank (no preconcentration) recorded using the following SIM schedule: 8–30.5 min, m/z 202; 30.5–33.2 min, m/z 216; 33.2–50 min, m/z 207. The presence of simazine, atrazine and isoproturon in the river Rhine and drinking water samples can be clearly seen. The small and distinct peaks in the chromatogram for HPLC-grade water (Fig. 6D) were not caused by memory effects, but were intrinsically present in this sample. This is demonstrated by the absence of these peaks in the chromatogram shown as trace C, and by the fact that no such peaks were observed in several mineral water samples (data not shown). The peak at $t_R = 31.6$ min in trace D, showing an ion at m/z 216, is not caused by any of the pesticides in our test set.

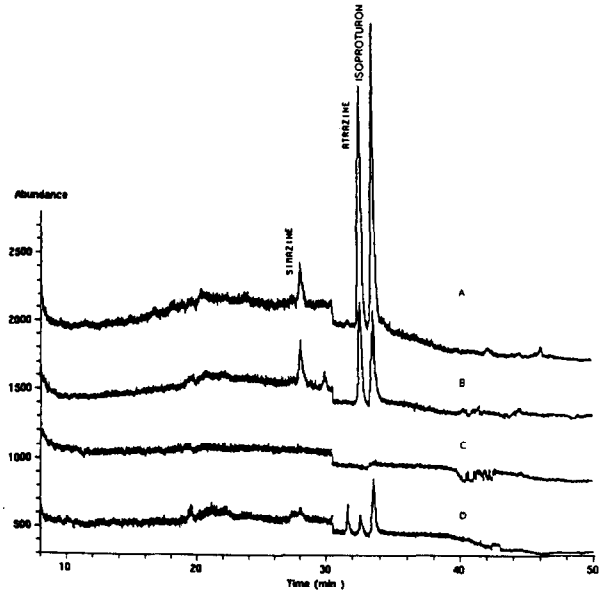

Fig. 6. On-line trace-enrichment RPLC–TSP-MS trace for 200 ml of (A) Rhine water, (B) Amsterdam drinking water, (C) blank without preconcentration and (D) HPLC-grade water. Column, 250 mm × 4.6 mm I.D. stainless-steel containing 5-μm C_{18}-bonded silica; eluent, linear methanol–0.1 M ammonium acetate gradient [10:90 to 90:10 (v/v) in 45 min]; MS, discharge PI mode. For details of time-scheduled SIM, see text.

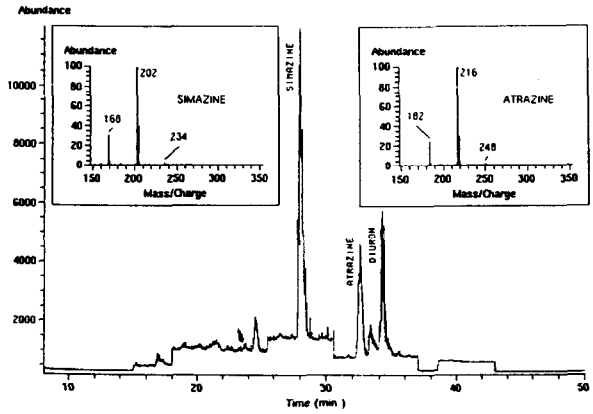

Fig. 7. On-line trace-enrichment RPLC–TSP-MS trace for river Mersey water (ions at m/z 202, 216, 207 and 233 monitored). Column, 250 mm × 4.6 mm I.D. stainless-steel containing 5-μm C_{18}-bonded silica; eluent, linear methanol–0.1 M ammonium acetate gradient [10:90 to 90:10 (v/v) in 45 min]; MS, discharge PI mode. For details, see text.

Analysis of 50 ml of water from the river Mersey (UK) and the river Meuse (Netherlands) gave the results shown in Figs. 7 and 8, respectively. As a further demonstration of the presence of the pesticides referred to above, mass spectra are included as insets. Table II summarizes the concentrations of simazine, atrazine,

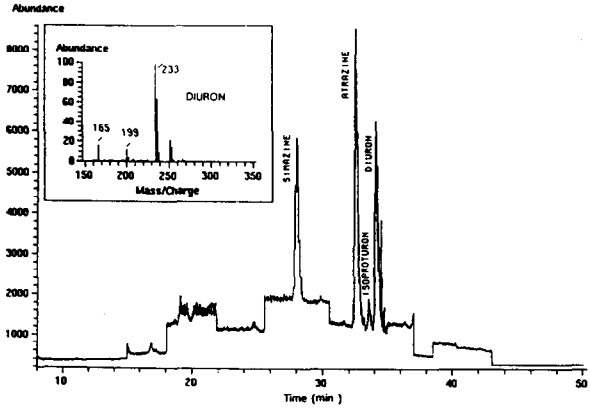

Fig. 8. On-line trace-enrichment RPLC–TSP-MS trace for river Meuse water (ions at m/z 202, 216, 207 and 233 monitored). Column, 250 mm × 4.6 mm I.D. stainless-steel containing 5-μm C_{18}-bonded silica; eluent, linear methanol–0.1 M ammonium acetate gradient [10:90 to 90:10 (v/v) in 45 min]; MS, discharge PI mode. For details, see text.

TABLE II

SURVEY OF SOME PESTICIDES DETECTED IN DRINKING AND SURFACE WATERS

Water source[a]	Concentration (μg/l)				Fig.
	Simazine	Atrazine	Isoproturon	Diuron	
Amsterdam drinking water	0.015	0.025	0.015	–	6A
River Rhine	0.030	0.070	0.065	0.030	–
River Mersey	3.2	0.9	–	2.1	7
River Meuse	1.2	1.0	0.070	2.0	8
HPLC-grade water	–	<0.006	<0.007	–	6D

[a] Sample size, 50 ml; for further details, see text.

isoproturon and diuron found in various water samples tested. With LC–TSP-MS under optimized conditions (PI mode) and 50-ml water samples, the detection limits for the four pollutants are in the 5–15 ng/l range for real samples. None of the other compounds listed in Table I was ever detected. In the drinking water samples tested, the observed levels for the polar pesticides in Table II invariably were below those permitted for drinking water (0.1 μg/l). As regards the surface water samples, high values (alert-alarm level, 1 and 3 μg/l, respectively) were occasionally found. It is interesting that the presence of 0.5–1.5 μg/l concentrations of diuron has recently been reported by another group from our laboratory using on-line trace enrichment–RPLC with diode-array UV detection [36].

As regards simazine and atrazine, the present results regarding Amsterdam drinking water and river Rhine water are consistent with our previous work using an off-line combination of LC and GC–MS [37]. Finally, the two chloro-*s*-triazines have also been detected at similar levels in drinking water from Paris using trace enrichment on a cation exchanger and LC with UV detection [38].

CONCLUSIONS

The mass spectra of 39 polar pesticides have been recorded in RPLC–TSP-MS using a C_{18} analytical column and a linear methanol–0.1 *M* ammonium acetate gradient under discharge PI conditions. The protonated molecular ion or an ammonia adduct ion appeared as the base peak for all N-methylcarbamates, triazines, organophosphorus pesticides and phenylureas tested except for parathion-ethyl. Proton abstraction was the dominant mechanism for a selected group of chlorophenols studied in the NI mode.

The on-line combination of trace enrichment of the pesticides from the four classes of compounds mentioned above from, typically, 50-ml water samples with RPLC–TSP-MS offers a fast, sensitive and selective method for the identification and determination of the target compounds down to the 5–100 ng/l level. This was demonstrated by analysing a series of surface and drinking water samples. Additional advantages are that the C_{18}-type precolumns can easily be reused for at least ten 50-ml runs, and that the consumption of organic solvents is extremely low. Current research is devoted to an extension of the programme to include an even larger number of environmental pollutants using both the PI and the NI modes, and to the use of a particle beam interface for the identification of unknown pollutants.

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