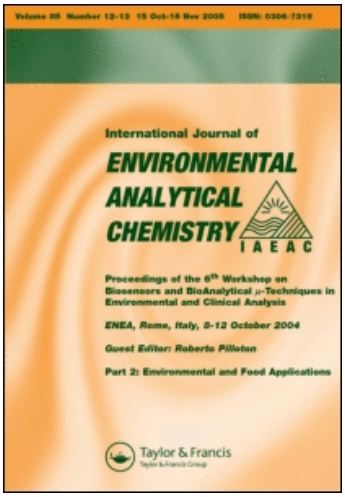

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Flow-Injection Analysis-Thermospray Tandem Mass Spectrometry of Triazine Herbicides and Some of Their Degradation Products in Surface Water

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FLOW-INJECTION ANALYSIS-THERMOSPRAY TANDEM MASS SPECTROMETRY OF TRIAZINE HERBICIDES AND SOME OF THEIR DEGRADATION PRODUCTS IN SURFACE WATER

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A rapid procedure to determine twelve triazines and eleven of their degradation products in water samples by means of flow-injection analysis with thermospray tandem mass spectrometry (FIA-MS-MS) is described. After solid-phase extraction (SPE) of a 30 mL sample on a C18 cartridge which also effects salt removal, elution with 5 mL methanol, evaporation of the eluate to 1 mL and dilution with 0.11 M ammonium acetate solution to a final volume of 10 mL, 2–5 mL are directly injected by means of FIA into the ion source of a tandem MS. Samples are first analysed with a target screening procedure in which only one characteristic product ion is acquired per compound and used to quantify. The identity of compounds in suspected samples is confirmed with a multiple reaction monitoring (MRM) procedure in which typically four product ions are analysed. All compounds show good linearity over the concentration range studied (0.05–1 µg/L). Recoveries of the triazines are over 82% while the recoveries of the degradation products are over 60% except for hydroxy-desethyl-desisopropyl-atrazine (47%). For most compounds the repeatability of the procedure is good (RSDs < 10%) at the 0.5 µg/L level. $^{2}H_{5}$-ethylamine-atrazine is used as an internal standard to check the reproducibility of the procedure and the ionization efficiency of the compounds. Detection limits are 0.05–0.15 µg/L for triazines and 0.20–0.45 µg/L for degradation products. The practicability of the method is tested by the analysis of samples from a national survey on atrazine and simazine. Even with seawater samples no problems are encountered as long as solid phase extraction is applied. The results obtained from two interlaboratory studies show that data obtained with FIA-MS-MS are fully comparable to those found by means of conventional chromatographic procedures.

KEY WORDS: Triazines, degradation products, rapid screening procedure, MS-MS, solid-phase extraction, multiple reaction monitoring.

INTRODUCTION

Flow-injection analysis (FIA) in combination with thermospray tandem mass spectrometry (MS-MS) is a fast and powerful technique to analyse a broad range of compounds[1-2]. Once the optimization for a group of compounds has been performed with

regard to optimum sensitivity[2], these compounds can be analysed in a mixture within one large-volume injection. In this way samples containing eight phenoxy acid herbicides and bentazone were analysed within a few minutes[1] down to 0.5–1 μg/L without any preconcentration of the sample.

One class of compounds which is widely used as herbicides in agriculture are the triazines. Due to leaching and run-off, these compounds and their (bio)degradation products are often found in surface, ground and tap water in concentrations exceeding the Netherlands' surface water quality objectives, i.e. 0.05–2.4 μg/L[3,4]. Despite the banning of atrazine in Germany, transboundary fluxes are still observed which indicates that the emission to surface water continues. Analytical procedures for the determination of these compounds are based on solid-phase or liquid-liquid extraction (SPE and LLE, respectively)[5–16] as sample pretreatment step. Because the (bio)degradation products of triazines are more polar than the parent compounds, they are more difficult to isolate from the sample, i.e. lower recoveries are usually obtained. For LLE with dichloromethane, the recoveries of desethylatrazine, desisopropyl-atrazine[5,6] and desethyl-desisopropyl-atrazine[6] are below 50%, but they can be improved considerably by using dichloromethane-ethyl acetate containing 0.2 M ammonium acetate[6]. As is to be expected, low breakthrough volumes have been reported for these compounds in SPE[7–10].

In this paper, FIA-MS-MS is used to analyse 12 triazines and 11 of their (bio)degradation products in surface water. In a first step a target screening of the samples is performed in which only one precursor ion and one characteristic product ion are selected for each relevant m/z value (cf. Table 1). Next, confirmation of the presence of suspected triazines is done by means of a MRM procedure using at least three product ions. In this way all 23 compounds can be detected and confirmed within a few minutes. The ionization conditions have been optimized for all compounds to give maximum sensitivity. $^{2}H_{5}$-ethylamine-atrazine, added to all samples, is used as an internal standard to guarantee the integrity of the final analytical procedure. For a series of 75 surface water samples, which have been analysed in the framework of a national survey, FIA-MS-MS results for two compounds, atrazine and simazine, are compared to those obtained by means of gas chromatography with nitrogen-phosphorus detection (GC-NPD). The reliability of the procedure is further demonstrated by the results of two interlaboratory studies for several triazines and degradation products.

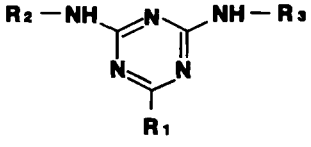
EXPERIMENTAL

Apparatus

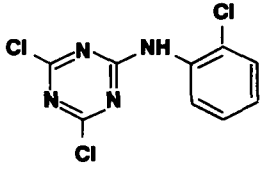
An LKB (Bromma, Sweden) Model 2150 pump was used to deliver the FIA carrier stream at a flowrate of 1.5 mL/min. An ASPEC (Gilson, Villiers-le-Bel, France) was used for automated sample concentration and to inject samples into the carrier stream by means of a 2 or 5 mL loop. After every injection, an injection with the carrier stream solvent was performed to clean the total system.

A Finnigan MAT TSQ-700 mass spectrometer (Finnigan MAT, San José, CA, USA) equipped with a Finnigan MAT thermospray interface (TSP-2) and a DEC 5000 data system computer was used. Typical instrument parameters used as default were: source temperature, 200°C; source pressure, 12×10^{-3} Pa; vaporizer temperature, 115°C; scan time, 0.5–1 s; repeller, 20 V; discharge, 2000 V. The conversion dynode was set at –20 kV, the electron multiplier at 2.7 kV and the electrometer amplifier gain at 10^{-9} A/V. Argon (quality 5.0, Hoekloos, Schiedam, The Netherlands) was used as collision gas

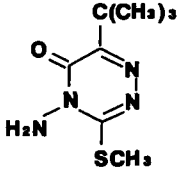
Table 1 Name and structures of triazine herbicides. Parent (PSM) and daughter (DAU) ions generated in MRM procedure at 0.4 Pa collision gas pressure and at optimum collision offset voltages (in brackets).



TRIAZINE



ANILAZINE



METRIBUZIN

Analyte	*R1*	*R2*	*R3*	*Mol Weight*	*PSM1*	*PSM2*	*DAU (COFF [-V])*			
Atrazine	Cl	C_2H_5	C_3H_7	215	216	218	104 (23)	132 (23)	**174 (16)**	176 (16)*
Cyanazine	Cl	C_2H_5	C_4H_6N	240	241	243	96 (26)	132 (26)	**214 (15)**	216 (15)*
Propazine	Cl	C_3H_7	C_3H_7	229	230	232	**146 (20)**	148 (20)*	188 (20)	190 (20)*
Simazine	Cl	C_2H_5	C_2H_5	201	202		96 (20)	104 (20)	**124 (20)**	132 (20)
Terbutylazine	Cl	C_2H_5	C_4H_9	229	230	232	132 (26)	146 (26)	**174 (16)**	176 (16)*
Ametryn	SCH_3	C_2H_5	C_3H_7	227	228		68 (26)	91 (26)	96 (26)	**186 (17)**
Desmetryn	SCH_3	CH_3	C_3H_7	213	214		82 (22)	91 (22)	124 (22)	**172 (22)**
Prometryn	SCH_3	C_3H_7	C_3H_7	241	242		68 (27)	85 (27)	**158 (20)**	200 (20)
Simetryn	SCH_3	C_2H_5	C_2H_5	213	214		**124 (17)**	144 (17)	166 (17)	186 (17)
Terbutryn	SCH_3	C_2H_5	C_4H_9	241	242		68 (26)	91 (26)	96 (26)	**186 (17)**
Anilazine				274	256	258	79 (22)	153 (22)	**178 (22)**	180 (22)*
Metribuzin				214	215		84 (18)	131 (18)	145 (18)	**187 (18)**
Desethyl-atrazine	Cl	H	C_3H_7	187	188	190	79 (24)	110 (24)	**146 (16)**	148 (14)*
Desisopropyl-atrazine	Cl	C_2H_5	H	173	174		79 (15)	96 (15)	**104 (21)**	132 (15)
Desethyl-desisopropyl-atrazine	Cl	H	H	145	146		68 (16)	79 (16)	**104 (16)**	110 (16)
Hydroxy-atrazine	OH	C_2H_5	C_3H_7	197	198		86 (22)	97 (22)	114 (22)	**156 (16)**
Hydroxy-desethyl-atrazine	OH	H	C_3H_7	169	170		43 (26)	69 (26)	86 (26)	**128 (14)**
Hydroxy-desisopropyl-atrazine	OH	C_2H_5	H	155	156		**69 (24)**	86 (16)	97 (16)	114 (16)
Hydroxy-desethyl-desisopropyl-atrazine	OH	H	H	127	128		43 (29)	69 (29)	**86 (16)**	
Hydroxy-propazine	OH	C_3H_7	C_3H_7	211	212		69 (29)	86 (29)	**128 (19)**	170 (19)
Hydroxy-simazine	OH	C_2H_5	C_2H_5	183	184		69 (24)	97 (24)	**114 (17)**	
Desethyl-terbutylazine	Cl	H	C_4H_9	201	202	204	104 (24)	110 (24)	**146 (16)**	148 (14)*
Hydroxy-terbutylazine	OH	C_2H_5	C_4H_9	211	212		86 (24)	97 (24)	114 (24)	**156 (14)**
$^2H_5$-ethylamine-atrazine	Cl	C_2D_5	C_3H_7	220	221	223	101 (23)	137 (23)	**179 (16)**	181 (16)*

Bold : base peak
* : PSM2

during MRM analysis at 0.4 Pa. All optimization procedures were written in Finnigan MAT instrument control language. A printout of the procedures is available from the authors upon request. The resolution of both mass analysers was adjusted to 30% valley, according to a procedure described in reference 2 using atrazine.

Reagents

Ultrapure water was delivered by a Barnstead system (Barnstead, Dubuque, IA, USA). All solvents and chemicals were of analytical-grade quality. Acetonitrile, methanol, ammonium hydroxide, formic acid, glacial acetic acid and ammonium acetate were obtained from J. T. Baker (Deventer, The Netherlands). All compounds were obtained from Riedel-de Haën (Hannover, Germany) or Promochem (Wesel, Germany).

Stock solutions of the compounds were prepared by dissolving 25 mg of each compound in 100 mL methanol or methanol/water (50:50, v:v); the hydroxy metabolites only dissolve after adding three droplets of formic acid. Stock solutions were kept at −20°C. From the stock solutions standard mixtures were prepared and diluted with water and aqueous 0.01, 0.1 or 0.5 M ammonium acetate to obtain a series of solutions which contained 10 vol. % methanol and 100 µg/L (to be used in optimization procedures), and 100, 50, 25, 10, 5, 2, 1, 0.5, 0.25, 0.1, 0.05, 0.02 or 0.01 µg/L (to be used for calibration graphs) of each analyte. These solutions were kept at +4°C

The stock solution of $^{2}H_{5}$-ethylamine-atrazine (Cambridge Isotope Laboratories, Andover, MA, USA) was prepared by dissolving 5 mg in 100 mL methanol/water (50:50, v:v). This solution was diluted to 100 ng/mL in methanol/water (10:90, v:v).

Extraction procedure

To every 100 mL water sample were added 7.8 g ammonium acetate (1 M) and 1 mL of $^{2}H_{5}$-ethylamine-atrazine (100 ng/mL); next the pH was adjusted to 7± 0.5 with ammonium hydroxide or glacial acetic acid.

The 1000 mg C18 and PolarPlus SPE cartridges (J. T. Baker) were conditioned by passing 5 mL of methanol and 5 mL of water. The 100 mg and 500 mg C18 SPE cartridges were conditioned by passing 2 mL of methanol and 2 mL of water. Samples (30 mL) were concentrated at a flow-rate of 3 mL/min. Next, the SPE cartridges were washed with 3 mL water and the compounds were eluted with 2 × 2.5 mL methanol (1000 mg cartridges) or 2 mL methanol (100 and 500 mg cartridges). The solution was evaporated to 1 (± 0.1) mL. Finally, each sample was diluted to 10 mL with a 0.11 M ammonium acetate solution and 2 or 5 mL were injected into the FIA carrier stream.

Target screening and confirmation procedure

The analysis of 24 compounds by means of FIA-MS-MS using one or two precursor ions and three to four product ions per compound, requires a large loop volume or a short scan time. With a loop volume of 5 mL, a flow rate of 1.5 mL/min and a scan time of 0.5 s, only four scans can be generated per compound. Therefore, in the target screening procedure the signal for only one characteristic production is acquired per compound. This signal (about 16 scans) is used for quantification. If no signal is detected for a particular m/z value, than m/z value is removed from the second, the confirmation,

procedure. In the latter procedure the signals of at least three product ions are acquired for each precursor m/z value selected. In this way at least 8–10 scans are always generated per compound and used for confirmation. Each product ion is analysed at the optimum collision offset voltage as described in ref. 2 (see also Table 1).

For isomeric compounds, e.g. simazine and desethyl-terbutylazine, the same precursor ion and one common product ion (out of four) is selected. If both compounds are present in a sample, the spectral features differ from those of the individual standards and only three out of four m/z values can be used to confirm the presence of a compound. More advanced procedures are currently under investigation.

RESULTS AND DISCUSSION

Optimization of analytical procedure

Optimum settings of all instrumental parameters as well as the ionization conditions (solvent, salt and flow) are required to obtain the highest response for a compound in thermospray MS-MS. With FIA, when using a large sample loop, all compounds in the mixture are introduced continuously and at a constant concentration. In previous reports, we described the development of two automated procedures to determine the optimum instrumental conditions and carrier stream composition[1-2]. Using these procedures we now designed a method to analyse triazines and their breakdown products at the 0.1 μg/L level, which enables one to meet the quality objective for surface water of 0.05–2.4 μg/L in the Netherlands[4].

The first procedure was used in both the positive and negative ionization mode (POS and NEG, respectively) to determine optimum ionization conditions for the generation of precursor ions for the individual compounds in the mixtures. In this procedure the vaporizer temperature, discharge voltage and repeller voltage were optimized in the ranges 85–135°C (5°C/step), 0–2000 V (250 V/step) and 0–200 V (20 V/step), respectively, while the samples were dissolved in 0, 0.01, 0.1 or 0.5 M ammonium acetate-methanol (or acetonitrile) (90:10, v/v). The experiments showed that POS gives much higher precursor ion signals than NEG. For all atrazine related compounds the precursor ions were, with one exception (see below), $[M+1]^+$ ions; the signal intensities with 10% methanol or acetonitrile were essentially the same. The responses for almost all triazines and breakdown products were about 25% higher in 0.5 M than in 0.1 M ammonium acetate. However, due to the chemical background generated by 0.5 M ammonium acetate, signal-to-noise ratios observed in 0.1 M and 0.5 M ammonium acetate were essentially the same. Therefore, all samples and standard solutions were prepared in aqueous 0.1 M ammonium acetate-methanol (90:10, v/v).

For one of the test compounds, anilazine, substitution of one (of the three) chlorine atom by ammonium ($R–Cl + NH_4^+ \rightarrow R–NH_3^+ + HCl$) was observed in the presence of 0.1 or 0.5 M ammonium acetate. This resulted in precursor ions at m/z 256 and 258 (isotope ratio, 100:66).

The optimum vaporizer temperature, discharge voltage and repeller voltage were found to be 115°C, 2000 V and 20 V, respectively. Figure 1 shows typical data from part of the optimization procedure. From the figure it is clear that the influence of the repeller was negligible at low discharge values (left part) but at high discharge voltages a low repeller voltage favoured precursor ion formation. The optimum conditions were used in the second procedure in which the collision gas pressure and the collision offset voltages

were optimized to generate high product ion intensities. From these results an argon pressure of 0.4 Pa turned out to be optimum. This optimum pressure was also found for the phenoxy acid herbicides in the NEG mode[1]. Table 1 summarizes the optimum collision offset voltages for the relevant product ion of all test compounds.

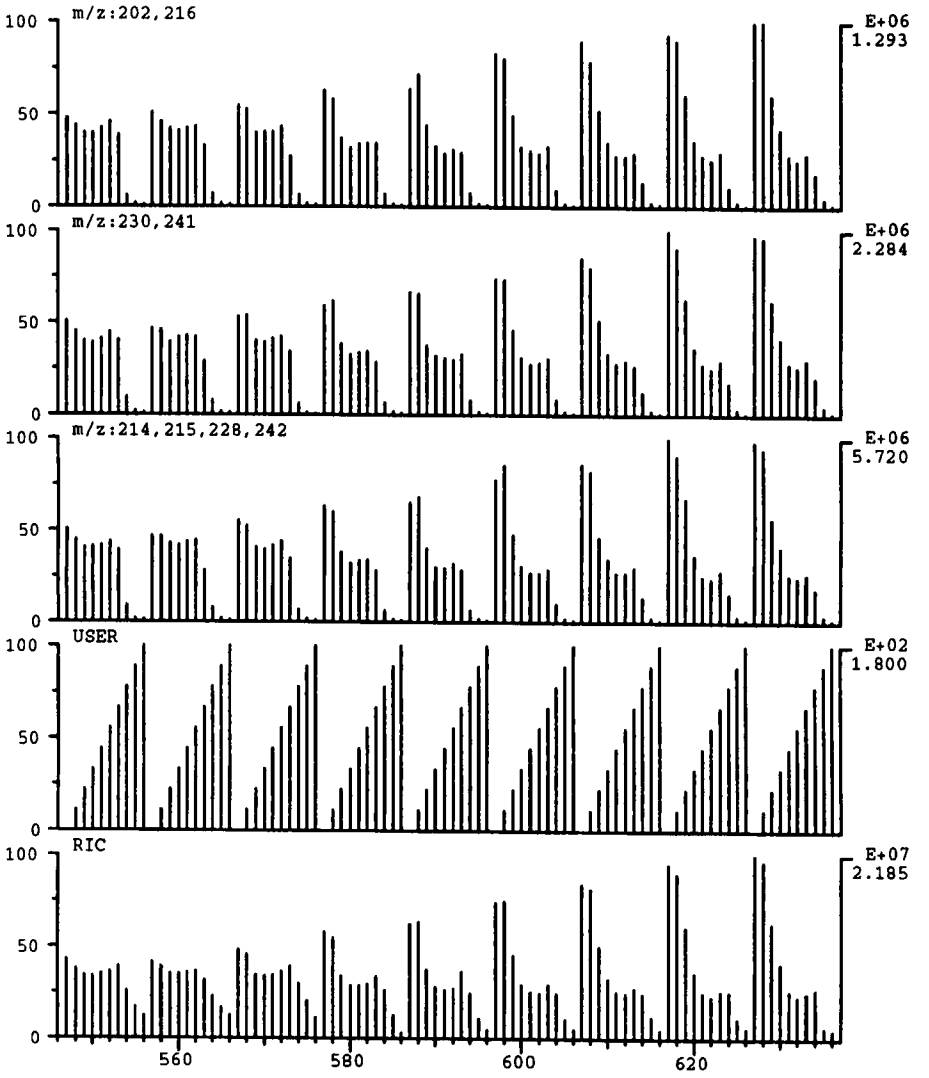


Figure 1 Part of the data generated with the first optimization procedure. The m/z 202, 216 trace represents the combined precursor ion masses of simazine and atrazine, respectively. The m/z 230, 241 trace represents the combined precursor ion masses of propazine and terbutylazine, and cyanazine, respectively. The m/z 214, 215, 228, 242 trace represents the combined precursor ion masses of desmetryn, metribuzine, ametryn and terbutryn, and prometryn, respectively. The user trace serves to read out the repeller voltage settings during the optimization procedure at the discharge settings applied; the discharge voltage was changed from 0 to 2000 V at 250 V/step and the repeller voltage from 0 to 180 V at 20 V/step.

The electron multiplier (EM) and conversion dynode voltages as well as the electrometer amplifier gain (ELGAIN) were optimized for maximum S/N ratios. This resulted in 2700 V (EM), –20 kV (conversion dynode) and 10^{-9} A/V (ELGAIN). Setting the mass analyser resolution at 30% valley instead of 10% valley resulted in a 3-fold gain in response, while adequate selectivity for compounds that differ only 1 Da was maintained. These settings in POS are comparable to the settings earlier reported for the NEG mode[2].

Electrometer amplifier gain

The effect of ELGAIN on the relative intensities of some product ions of terbutylazine, as a function of the analyte concentration is plotted in Figure 2. At an ELGAIN of 10^{-8} A/V the relative intensities at concentrations below 1 µg/L deteriorate considerably due to increased noise. At ELGAIN 10^{-9} A/V, however, the ratio is constant down to a concentration level of 0.05 µg/L, indicating better S/N ratios for this compound at the latter ELGAIN. All other test analytes were found to show the same behaviour. As adequate confirmation of the presence of a triazine (or its degradation product) is only possible if the relative intensities of the product ions are constant (to within a 20% intensity ratio), an ELGAIN of 10^{-9} A/V was used for trace level analysis (0.05–1 µg/L), while an ELGAIN of 10^{-8} A/V was used in the analysis of higher levels.

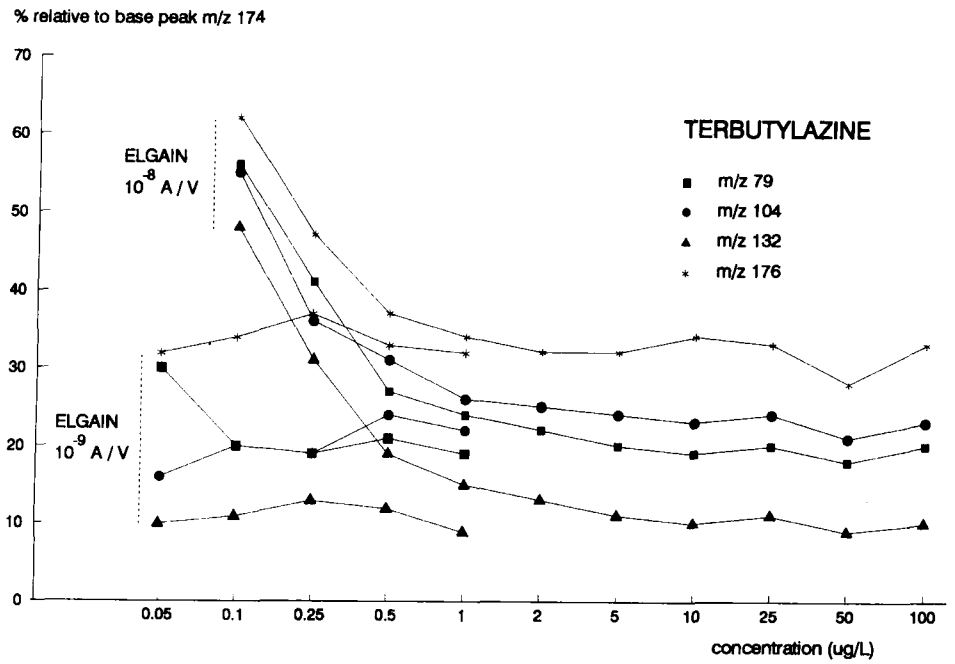


Figure 2 Ratio of product ion masses of terbutylazine relative to the base peak at ELGAIN 10^{-8} A/V and ELGAIN 10^{-9} A/V versus analyte concentration.
Note: m/z 176 is ^{37}Cl product ion mass with about 33% relative intensity of ^{35}Cl base peak of m/z 174.

Solid-phase extraction

In the present study Bakerbond SPE C18 cartridges containing 100, 500 or 1000 mg of sorbent and a Baker PolarPlus cartridge containing 1000 mg sorbent were tested. SPE was used to concentrate the sample and at the same time to remove salts from the surface and sea water samples, which can clog the thermospray interface. Recoveries and breakthrough volumes were determined for all test compounds. The recoveries on the Baker PolarPlus cartridges were comparable to or higher than those on the C18 cartridges (data not shown). Therefore, Baker PolarPlus cartridges were selected for this study. Relevant analytical data are provided in Table 2. With these cartridges complete desorption of all test compounds required 3–4 mL methanol. The breakthrough volumes on Baker PolarPlus were 50 mL or higher for all analytes with one exception, hydroxy-desethyldesisopropyl-atrazine (30 mL). In order to adsorb anilazine it was necessary to add 1 M ammonium acetate to the sample. Anilazine then had a breakthrough volume of 80 mL while the breakthrough volumes of the other analytes remained the same. Therefore, 1 M ammonium acetate was added to all samples prior to SPE.

It is interesting to add that when 3–4 mL of acetonitrile instead of methanol was used for desorption, some hydroxy degradation products were not desorbed at all. This indicates the possibility to desorb the hydroxy degradation products separately from the other compounds. Moreover, because most of the matrix constituents are eluted by acetonitrile, the fraction containing the hydroxy degradation products is relatively clean.

Table 2 Relevant breakthrough (mL), recovery (%), detection limit (μg/L) and relative standard deviation (RSD) data for the triazines and triazine degradation products using a 1000 mg PolarPlus cartridge and the target screening procedure (one product ion).

Analyte	*Breakthrough (mL)*	*LOD* (μg/L)*	*Recovery** (%)*	*RSD** (%)*
Atrazine	80	0.05	93	4
Cyanazine	90	0.15	84	9
Propazine	80	0.10	93	6
Simazine	>100	0.05	100	4
Terbutylazine	80	0.05	89	4
Ametryn	80	0.10	88	5
Desmetryn	60	0.10	85	6
Prometryn	80	0.10	90	7
Simetryn	100	0.10	102	8
Terbutryn	50	0.10	82	7
Anilazine	80	0.15	122	11
Metribuzine	>100	0.10	101	7
Desethyl-atrazine	50	0.10	95	5
Desisopropyl-atrazine	>100	0.10	105	8
Desethyl-desisopropyl-atrazine	60	0.15	60	8
Hydroxy-atrazine	>100	0.25	78	15
Hydroxy-desethyl-atrazine	>100	0.25	64	17
Hydroxy-desisopropyl-atrazine	60	0.30	64	19
Hydroxy-desethyl-desisopropyl-atrazine	30	0.45	47	29
Hydroxy-propazine	>100	0.20	74	13
Hydroxy-simazine	>100	0.30	68	20
Desethyl-terbutylazine	50	0.10	91	6
Hydroxy-terbutylazine	>100	0.30	71	20

* LOD = 3 * RSD/100 * C; C = 0.5 μg/L

** sample volume 30 mL; N = 10.

Validation and linearity

Calibration graphs constructed for standard solutions using the target screening procedure showed good linearity over the ranges studied with correlation coefficients, r, of over 0.99 for all compounds. To determine the limit of detection (LOD) with the complete procedure, i.e. including the SPE step, ten standard solutions of 30 mL containing all test analytes at 0.5 µg/L were analysed. For most compounds the repeatability (N = 10) of the procedure, expressed as an RSD, is better than 10% (Table 2). The higher RSDs found for the hydroxy as compared to the parent compounds were probably caused by the lower recoveries during SPE. The LODs were determined using the equation LOD = 3 * RSD/100 * C, cf. references 19–20, where C is the concentration of the analytes (0.5 µg/L) in the standard solution. Analyte detectability was found to be good with LODs of 0.05–0.10 µg/L for most compounds, except for the hydroxy compounds (0.20–0.45 µg/L).

Applications

Typical mass chromatograms for atrazine, simazine, desethyl-desisopropyl-atrazine and anilazine, recorded using the target screening procedure, of suspected water samples are shown in Figure 3. Each trace shows three replicate injections of the external standard mixture and single injections of five different surface water samples. A mass chromatogram of the internal standard is also shown.

Good recoveries, i.e. >85%, were found for this compound, which indicates the reliability of the SPE procedure and the proper ionization efficiency in the sample matrix. Quantitation was performed by comparing the signal of the sample product ion to that of the external standard product ion (one-point calibration). For the present samples, concentrations of typically 0.1–0.4 µg/L were calculated. In all instances, the presence of the suspected compounds was confirmed using the confirmation procedure.

In most cases, the product ion mass spectra obtained for surface water samples agreed well with those obtained from standards. Our criterion was that good agreement is achieved when the intensity ratios of at least three peaks in the analyte spectrum from a surface water sample are within ± 20% of the intensity ratios of the corresponding peaks in the spectrum from a standard. However, in some cases deviations between sample and standard product ion spectra were observed. As an example, three sample spectra of atrazine are compared with the standard spectrum in Figure 4. In the sample spectrum in Figure 4B all four peaks meet the ratio criterion, while in the sample spectra of Figures 4C and 4D only three peaks and two peaks, respectively, meet the ratio criterion. The spectrum in Figure 4C is still considered acceptable for confirmation, but the spectrum in Figure 4D is not.

In another study, GC-NPD analyses of 75 surface water samples indicated the presence of atrazine and simazine in ca. 80% of the samples. With FIA-MS-MS, LODs are higher (0.05 µg/L) than with GC-NPD (0.01 µg/L). Table 3 shows a comparison of FIA-MS-MS and GC-NPD results for a random selection out of the 75 samples. For most samples containing ≥ 0.05 µg/L of atrazine and/or simazine, the two procedures gave comparable results. Although some samples were brackish, due to the use of SPE no problems with clogging of the termospray vaporizer due to sodium chloride, were encountered.

In the framework of two interlaboratory studies, some triazines and the degradation product desisopropyl-atrazine and desethyl-atrazine were determined in tap and surface

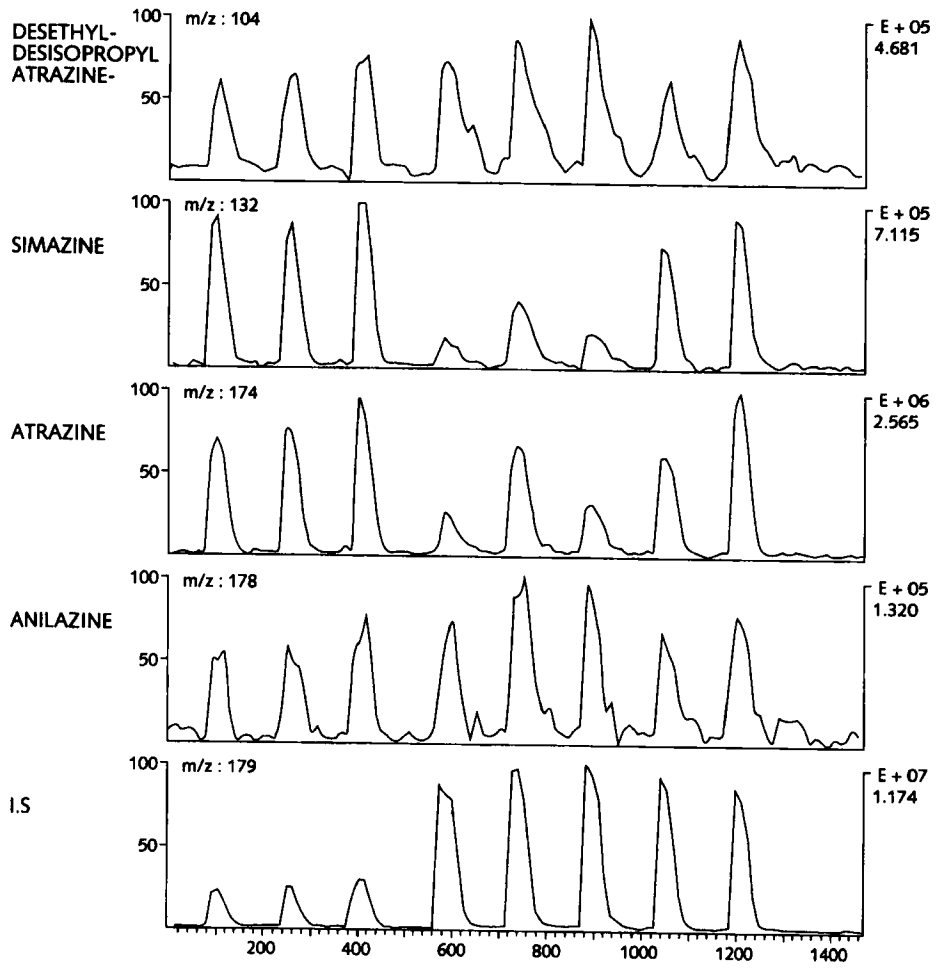


Figure 3 FIA-MS-MS chromatograms of product ion masses of several triazine herbicides using the target screening procedure. First three injections, 1 µg/L standard solution (including I.S.); latter five injections, five different surface water samples spiked at 1 µg/L (including I.S.), enriched three-fold with SPE. Bottom mass chromatogram, $^{2}H_{5}$-ethylamine-atrazine used as internal standard (I.S.).

water samples with or without spiking at the 0.1–1.0 µg/L level. Table 4 summarizes the FIA-MS-MS results and compares them with the results (range and median) of other (about 20) laboratories obtained by GC-MS and GC-NPD. In most instances, the FIA-MS-MS results are rather close to the spiking value. Agreement with the range of values found by the other laboratories, and often the median, is quite satisfactory. One exception is terbutryn, with which analyte too low results were obtained in one sample series. Since the range of data generated in the interlaboratory study also was much too low, errors made during sample preparation is not an unlikely explanation.

The presence of all analytes detected in Table 4 by means of FIA-MS-MS was confirmed by the confirmation procedure. The only exception was desethyl-atrazine which was detected with the target screening procedure in all tap and surface water samples, although no spike had been added. The low levels of 0.1–0.3 µg/L could,

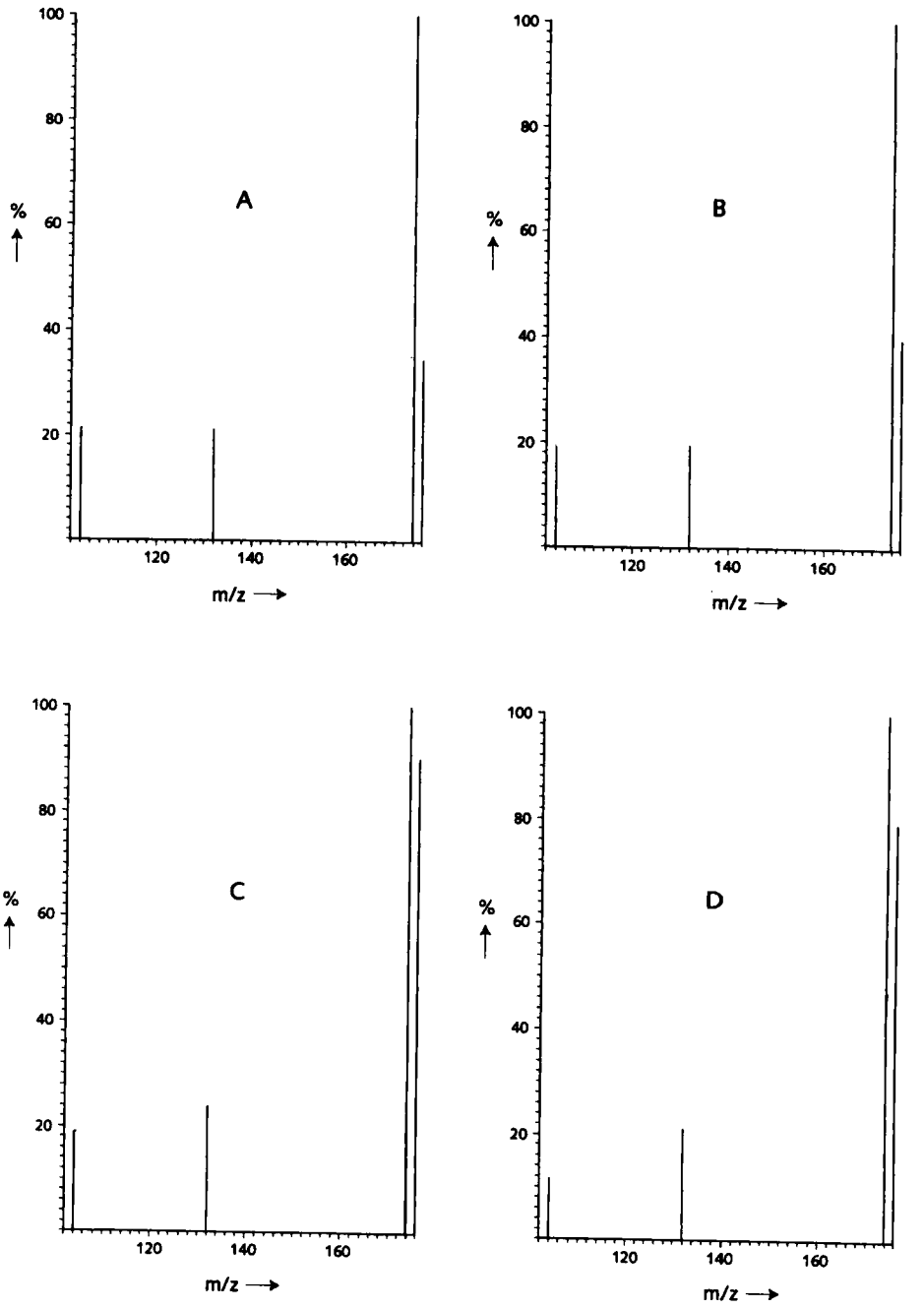


Figure 4 Relative intensities of m/z 104, 132, 174 and 176 (product ion spectrum) of atrazine in standard solution (A) compared with product ion spectra of atrazine in surface water samples (B–D). Example B meets the ratio criterion (± 20%) for all (four) product ions, in example C three product ions and in example D only two product ions meet the ratio criterion. The spectrum in example C is considered acceptable for confirmation, but the spectrum is example D is not.

Table 3 Concentrations (μg/L) of atrazine and simazine in a random selection of surface water samples determined by FIA-MS-MS and GC-NPD.

Atrazine		*Simazine*	
FIA-MS-MS	*GC-NPD*	*FIA-MS-MS*	*GC-NPD*
–	0.01	–	0.01
–	0.02	–	0.01
–	0.04	–	0.02
–	0.04	–	0.02
–	0.04	–	0.03
–	0.05	–	0.03
–	0.07	–	0.03
–	0.07	–	0.04
–	0.13	–	0.05
0.06	0.04	–	0.06
0.06	0.02	–	0.08
0.08	0.04	–	0.08
0.08	0.10	–	0.09
0.09	0.11	–	0.09
0.10	0.08	0.06	0.04
0.12	0.08	0.06	0.05
0.15	0.10	0.08	0.05
0.16	0.11	0.08	0.07
0.21	0.13	0.09	0.08
0.24	0.22	0.12	0.16
0.27	0.21	0.13	0.11
0.36	0.38	0.21	0.27

–, not detected; single analysis data

however, not be confirmed: the spectral criteria discussed above were not met for any of the samples.

CONCLUSIONS

In the present paper, a rapid FIA-tandem MS screening procedure is described for 12 triazines and 11 of their breakdown products. Most of the analytes can be detected in water samples down to 0.05–0.15 μg/L levels. For the hydroxy degradation products, however, the limits of detection are 0.20–0.45 μg/L. The procedure shows acceptable analytical characteristics with regard to linearity, repeatability and analyte recoveries. In the latter instance, there is a marked difference, however, between the triazines (recoveries >82%) and the more polar degradation products (recoveries >60%). From results obtained in several comparative studies, it can be concluded that FIA-MS-MS data for tap and surface water analyses are closely similar to those obtained by means of chromatographic procedures; this illustrates the reliability of the procedure. As regards the confirmation procedure used, essentially no problems were encountered with the parent compounds. However, at the low analyte levels problems did sometimes occur with some of the triazine degradation products. More advanced sample pretreatment procedures are now being studied in order to improve the selectivity of the total procedure. It is expected that this will help to improve the quality of the mass spectra for, especially, the degradation products.

Table 4 FIA-MS-MS and interlaboratory results (μg/L) for some triazines and degradation products in tap and surface water samples.*

	Tap water			*Surface water*		
Analyte	*Spike*	*FIA-MS-MS*	*Interlaboratory study range (median)*	*Spike*	*FIA-MS-MS*	*Interlaboratory study range (median)*
Atrazine	0.20	0.2	0.10–0.25 (0.19)	0.10	0.1	0.02–0.20 (0.14)
	0.40	0.4	0.17–0.50 (0.37)	0.25	0.2	0.11–0.42 (0.28)
	0.79	0.7	0.25–0.94 (0.68)	0.39	0.3	0.16–0.57 (0.38)
				0.99	0.9	0.50–1.19 (0.95)
Simazine	0.15	0.2	0.06–0.21 (0.15)	0.20	0.2	0.09–0.40 (0.22)
	0.20	0.2	0.06–0.25 (0.18)	0.30	0.3	0.08–0.41 (0.29)
	0.78	0.7	0.21–1.08 (0.68)	0.39	0.4	0.14–0.58 (0.34)
				0.98	1.0	0.33–1.17 (0.85)
Terbutryn	0.10	0.2	0.03–0.12 (0.07)	0.40	0.3	0.02–0.44 (0.31)
	0.20	0.2	0.04–0.23 (0.16)	0.50	0.4	0.02–0.51 (0.42)
	0.80	0.4	0.16–0.98 (0.54)	0.40	0.2	0.07–0.48 (0.33)
				1.01	0.5	0.22–0.10 (0.83)
Prometryn	0.20	0.2	0.07–0.27 (0.20)	0.10	0.1	0.03–0.12 (0.09)
	0.30	0.3	0.08–0.37 (0.26)	0.15	0.2	0.02–0.18 (0.14)
Propazine	0.81	0.7	0.26–1.07 (0.62)	0.40	0.3	0.18–0.50 (0.34)
				1.01	0.9	0.68–1.14 (0.84)
Desisopropyl-atrazine	0.35	0.5	0.02–0.24 (0.18)	0.16	0.2	0.01–0.20 (0.05)
	0.55	0.7	0.11–0.63 (0.20)	0.20	0.2	0.01–0.20 (0.06)
Desethyl-atrazine	0	0.2**		0	0.3**	
	0	0.2**		0	0.3**	
	0	0.1**		0	0.3**	

* All results are mean values of data obtained for two separate but identical samples. If necessary, experimental results were corrected for blank values which typically were 0.15 μg/L or less.

** Presence not confirmed by confirmation procedure; cf. text.

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