Journal of Chromatography, 603 (1992) 175–184
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 993

Comparison of gas chromatographic–mass spectrometric methods for screening of chlorotriazine pesticides in soil☆

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(First received September 18th, 1991; revised manuscript received January 3rd, 1992)

ABSTRACT

The performance of a coupled technique resulting from the combination of gas chromatography with a selective mass spectrometric technique (tandem mass spectrometry) (GC–MS–MS) with collisionally activated dissociation (CAD) and multi-reaction monitoring (MRM) was compared with that of GC–low resolution MS (GC–LRMS) at a resolving power of 1000 and GC–high-resolution MS (GC–HRMS) at resolving powers of 5000 and 10 000 for the determination of atrazine, simazine, cyanazine, deethylatrazine and deisopropylatrazine in polluted soil samples. GC–MS–MS daughter ion spectra for the parent ions $[M]^{+\cdot}$ and $[M - CH_3]^+$ were generated using collisionally activated dissociation and studied. Also, by optimizing the collision energy for maximum sensitivity a method for screening chlorotriazines by MRM was developed. Analyses of soil sample extracts showed that GC–MS–MS overcomes interferences from other chlorotriazines and interfering compounds that could not be removed by GC–HRMS or GC–LRMS at resolving powers of 10 000 and 1000, respectively. The limits of detection for GC–MS–MS and GC–HRMS at a signal-to-noise ratio of 10 ranged between 1 and 24 pg, with a mean relative standard deviation of 25–30%. Soil samples known to contain chlorotriazines and their degradation products were analysed by GC–MS–MS and the results obtained were compared with those given by GC–HRMS at resolving powers of 5000 and 10 000, with quantification differences of 25–30%.

INTRODUCTION

Chlorotriazines are broad-spectrum residual herbicides used widely for pre-and post-emergency weed control in corn, wheat, barley and sorghum, and also on railways and roadside verges [1]. Microbial degradation and volatility are two of the main degradation processes affecting their persistence in soil [2] and yielding dealkylated metabolites which have been detected in different types of soil [3,4]. These studies on the fate of chlorotriazine pesticides in the environment have prompted the need for sensitive, specific methods for their determination.

The gas chromatographic–mass spectrometric (GC–MS) determination of chlorotriazine pesticides using a variety of ionization techniques has been approached in a number of ways. Applications reported so far include GC–MS with electron im-

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☆ Presented at the *12th International Mass Spectrometry Conference, Amsterdam, August 26–30, 1991.*

0021-9673/92/$05.00

pact (EI) [3–5] and with positive- and negative-ion chemical ionization (PCI and NCI, respectively) [5,6]. Confirmation of pesticide residues is accomplished by using two or three diagnostic ions in the selected ion monitoring (SIM) mode. When higher selectivity is needed, *e.g.* to avoid false-positive identifications in environmental samples, GC–high-resolution MS (GC–HRMS) and GC–tandem MS (GS–MS–MS) are highly recommended.

Collisionally activated dissociation (CAD) MS–MS has rarely been applied to pesticide analysis. Most work reported in this respect involves the use of a triple quadrupole mass spectrometer in combination or not with GC, and with EI [7–9] or chemical ionization [10–12]. This approach has been used to confirm of a variety of organic compounds [7–9] and chlorotriazine [10], organophosphorus [11,12] and carbamate [12] insecticides. In the last few years, liquid chromatography (LC)–MS–MS, also with quadrupole systems, has been applied to the determination of chlorotriazine pesticides [13,14] and organophosphorus [15] and carbamate insecticides [16], all of which testify to an increasing use of tandem MS for screening different groups of pesticides in environmental matrices. However, GC–MS–MS hybrid instruments have rarely been used in analysis for organic compounds of environmental interest [8] and only a few applications to specific compounds (*e.g.*, dioxins [17,18]) have been reported so far. By using this type of instrumentation, the high selectivity of capillary GC is enhanced as a result of the increased mass resolution of parent ions. This can be accomplished by coupling a high-resolution, double-focusing mass spectrometer in series with a quadrupole collision cell and a second quadrupole mass filter.

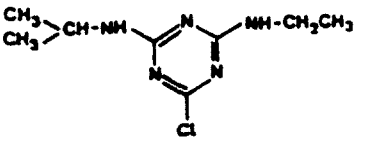
The lack of reports on the application of GC–MS–MS hybrid instruments to pesticide analyses prompted us to carry out a study of this nature. Thus, the aim of this work was to study the use of GC–MS–MS hybrid instruments by using CAD and different parent ions, to compare the selectivity and sensitivity of GC–MS–MS with that of GC–low-resolution MS (GC–LRMS) and GC–HRMS at resolving powers of 1000 and 10 000, respectively, and to assess the performance of different MS methods for the determination of the chlorotriazine pesticides atrazine, simazine and cyanazine and their dealkylated degradation products deethylatrazine and deisopropylatrazine in polluted soil samples.

EXPERIMENTAL

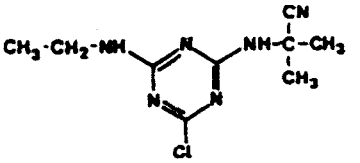
Chemicals

The structures of the pesticides studied are given in Fig. 1. Pesticide-grade ethyl acetate, *n*-hexane, diethyl ether and dichloromethane supplied by Mallinckrodt (Paris, KY, USA) were used as solvents. Florisil (100–200 mesh) was purchased from

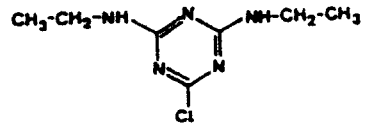
Atrazine



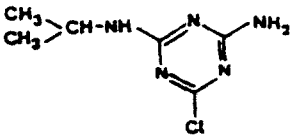
Cyanazine



Simazine



Deethylatrazine



Deisopropylatrazine

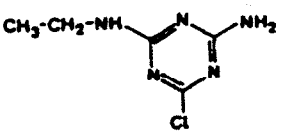


Fig. 1. Structures of the compounds.

Merck (Darmstadt, Germany). Cyanazine was supplied by Riedel-de Haën (Seelze-Hannover, Germany) and atrazine and simazine by Polyscience (Niles, IL, USA). Deethylatrazine and deisopropylatrazine were donated by Ciba-Geigy (Basle, Switzerland). Labelled atrazine (ethylamine-d_5) was purchased from Cambridge Isotope Instruments (Innerberg, Switzerland).

Sample preparation

Soil samples from the Ebro Delta (Tarragona, Spain) were pretreated by using a modification of a procedure commonly used at our laboratory for the residue analysis of chlorotriazine pesticides [3,5]. Thus, 10 g of soil sample were freeze-dried and sieved through a 120-μm mesh and Soxhlet extracted with methanol for 12 h. The extracts were concentrated in a rotary evaporator to *ca.* 20–25 ml carefully evaporated to dryness and the residue was dissolved in 400 μl of *n*-hexane.

Clean-up was carried out in glass columns (150 mm × 5 mm I.D.) filled with *ca.* 2 g of Florisil previously activated at 300°C overnight, cooled and deactivated with 2% of water. The packing material was mixed with *n*-hexane and placed on the glass column. The soil extracts in *n*-hexane (400 μl) were placed on top of the column and eluted with diethyl ether–*n*-hexane (1:1) according to a clean-up procedure reported elsewhere [3,5]. The fractions were evaporated nearly to dryness and the residue was dissolved in 500 μl of ethyl acetate. The volume injected into the gas chromatograph was generally 1 μl.

Instrumental methods

GC. A Hewlett-Packard Model (Palo Alto, CA, USA) Model 5890 gas chromatograph coupled to a VG (Manchester, UK) Model 70-250-SQ mass spectrometer was used. A GC column of 15 m × 0.25 mm I.D. consisting of a fused-silica capillary coated with chemically bonded cyanopropylphenyl DB 225 (J&W Scientific, Folsom, CA, USA) with a film thickness of 0.15 mm was used for chlorotriazines and their dealkylated metabolites. Such a column was used in previous work [5] to achieve complete separation of chlorotriazines and their degradation products. Helium was used as the carrier gas at a flow-rate of 50 cm/s. The temperature of the injector was kept at 260°C and the column temperature was programmed from 70 to 220°C at 6°C/min.

GC–LRMS and GC–HRMS. Experiments were performed on a VG Model 70-250-SQ mass spectrometer working in the Selected Ion Recording (SIR) mode at a resolving power of 1000. HRMS experiments were performed on a VG Model 70-250-SQ mass spectrometer working in the SIR mode at resolving powers of 5000 and 10 000. The source temperature was kept at 200°C, the electron energy was 70 eV, the filament emission current was 0.2 mA and the accelerating voltage was 8 kV. The ions monitored were *m/z* 215.0938 and 217.0908 for atrazine, 201.0781 and 203.0752 for simazine, 240.0890 and 242.0861 for cyanazine, 173.0468 and 175.0439 for deisopropylatrazine, 187.0625 and 189.0595 for deethylatrazine and 220.0938 and 222.0908 for labelled atrazine (ethylamine-d_5). Labelled atrazine, used to measure the detection sensitivity, was eluted before atrazine under the GC conditions used.

GC-MS–MS. A VG Model 70-250-SQ (EBqQ configuration) hybrid mass spectrometer was used for the MS–MS analyses. The monitored transitions using multi-reaction monitoring of the loss of $CH_3^{\bullet}$ from $M^{+\bullet}$ are listed in Table I. Argon was used as the collision gas and its pressure was optimized at $3 \cdot 10^{-6}$ mbar in the ion gauge, which resulted in a pressure of *ca.* $4 \cdot 10^{-4}$ mbar in the collision cell.

TABLE I

IONS AND TRANSITIONS MONITORED IN COLLISION ENERGY EXPERIMENTS

Pesticide	$M^{+\bullet}$ ion (*m/z*)	Transition monitored
Deisopropylatrazine	173	$173^+ \rightarrow 158^+ + CH_3$
	175	$175^+ \rightarrow 160^+ + CH_3$
Deethylatrazine	187	$187^+ \rightarrow 172^+ + CH_3$
	189	$189^+ \rightarrow 174^+ + CH_3$
Simazine	201	$201^+ \rightarrow 186^+ + CH_3$
	203	$203^+ \rightarrow 188^+ + CH_3$
Atrazine	215	$215^+ \rightarrow 200^+ + CH_3$
	217	$217^+ \rightarrow 202^+ + CH_3$
Atrazine	220	$220^+ \rightarrow 205^+ + CH_3$
(ethylamine-d_5)	222	$222^+ \rightarrow 207^+ + CH_3$
Cyanazine	240	$240^+ \rightarrow 225^+ + CH_3$
	242	$242^+ \rightarrow 227^+ + CH_3$

Optimization of GC–MS–MS

The collision energy was optimized for each chlorotriazine studied. Argon was used as the collision gas at the pressure given above. The results obtained are shown in Fig. 2A for atrazine, simazine and cyanazine and in Fig. 2B for deethylatrazine and deisopropylatrazine. The collision energy was varied from 20 to 100 eV (Fig. 2A) and from 20 to 170 eV (Fig. 2B). The collision energy in Fig. 2B was varied up to 170 eV, as above 80 eV the response was found to increase and give rise to a second, lower maximum between 100 and 105 eV. The optimum collision energies were found to be 50 eV for atrazine, deethylatrazine and deisopropylatrazine, 40 eV for cyanazine and 35 eV for simazine. They were optimized for each pesticide by using GC–MS–MS with MRM and monitoring of the transitions listed in Table I.

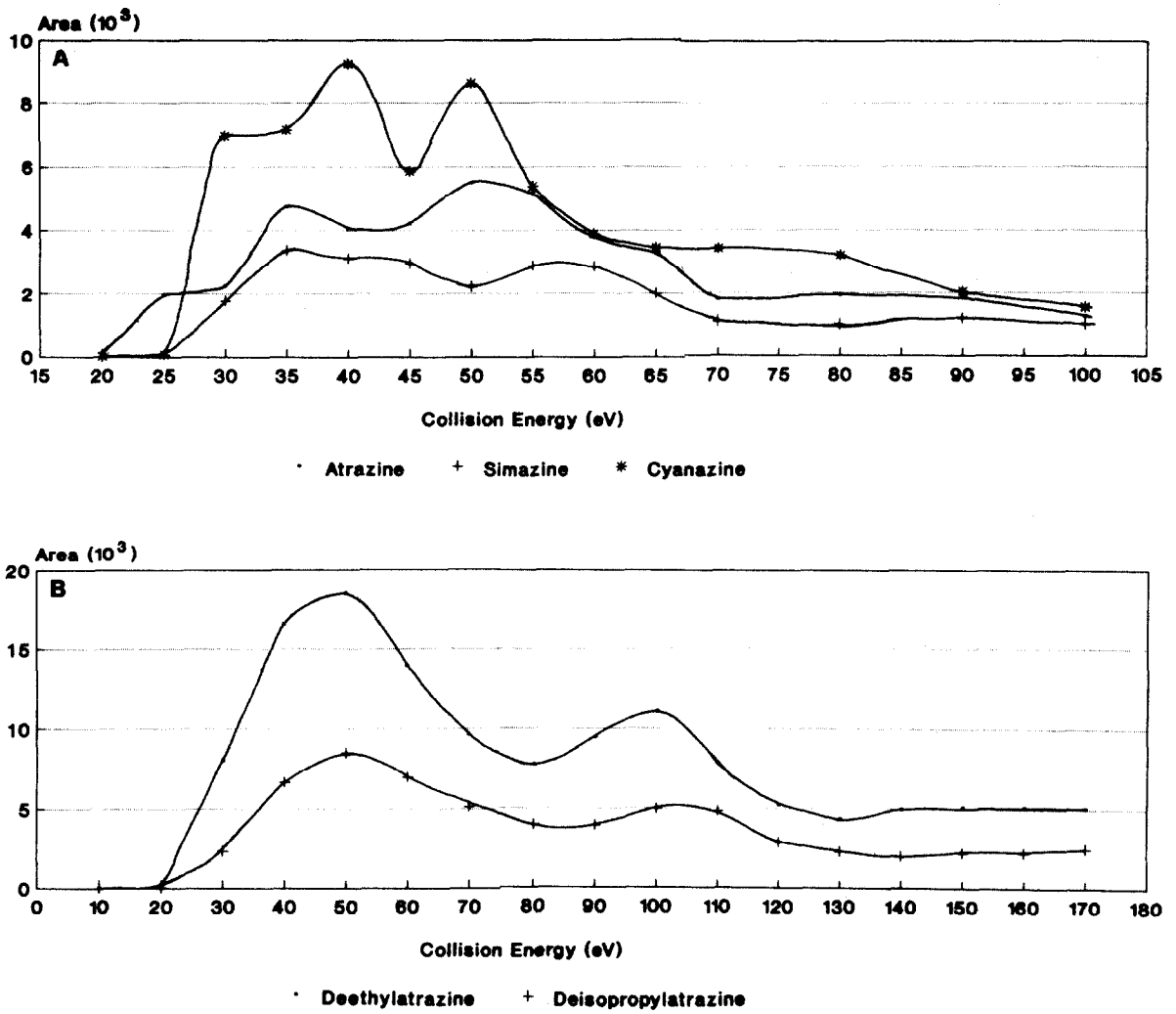


Fig. 2. Effect of the collision energy on formation of $[M - CH_3]^+$ using GC–MS–MS with MRM for (A) · = atrazine, + = simazine and * = cyanazine and (B) · = deethyaltrazine and + = deisopropylatrazine.

RESULTS AND DISCUSSION

Tandem mass spectrometry

Table II lists the major ions (relative abundance >10%) in the CAD mass spectra of the chlorotriazine pesticides studied. Daughter ion spectra from the parent ion corresponding to $[M]^{+\cdot}$ were obtained for all the compounds. Deethylatrazine, atrazine and cyanazine yielded additional daughter ions as their base peaks in their EI spectra corresponded to $[M - CH_3]^+$ ions. All the CAD spectra show characteristic ions of the structure or class of compound. It should be noted that the CAD spectra for deethylatrazine, atrazine and cyanazine for the two different parent ions, $[M]^{+\cdot}$ and $[M - CH_3]^+$, are completely different.

When $[M]^{+\cdot}$ is used as the parent ion, the daughter ion formed resembles the fragments obtained by conventional GC–MS in the EI mode [4,5,18]. Thus, CH_3 loss is observed with all compounds.

TABLE II

CAD DAUGHTER IONS FROM CHLOROTRIAZINE PESTICIDES AND THEIR DEALKYLATED DEGRADATION PRODUCTS

MW	Compound	Parent ion (*m/z*)	Daughter ion (*m/z*), identification and relative abundance (%)
173	Deisopropylatrazine	173	173, $[M]^{+\cdot}$ (100)
			158, $[M - CH_3]^+$ (20)
			145, $(M - C_2H_4]^+$ (45)
			69, $[M - NCNH - C_2H_4 - Cl]^+$ (10)
			44, $[C_2H_5NH]^+$ (20)
187	Deethylatrazine	172	172, $[M - CH_3]^+$ (100)
			104, $[M - HCN - C_3H_7]^+$ (20)
			79, $[M - CH_3 - C_3H_6 - HCl]^+$ (10)
			69, $[M - NCNH - C3H_6 - Cl]^+$ (10)
		187	187, $[M]^{+\cdot}$ (100)
			172, $[M - CH_3]^+$ (30)
			145, $[M - C_3H_6]^+$ (10)
			58, $[C_3H_7NH]^+$ (20)
201	Simazine	201	201, $[M]^{+\cdot}$ (100)
			186, $[M - CH_3]^+$ (10)
			173, $[M - C_2H_4]^+$ (70)
			158, $[186 - C_2H_4]^+$ (20)
215	Atrazine	200	200, $[M - CH_3]^+$ (100)
			158, $[M - C_3H_6 - CH_3]^+$ (15)
			132, $[M - NCNH - C_3H_6]^+$ (45)
			122, $[158 - HCl]^+$ (50)
			104, $[132 - C_2H_4]^+$ (45)
			96, $[132 - HCl]^+$ (20)
			71, $[C_2H_5 - NH - CNH]^+$ (60)
		215	215, $[M]^{+\cdot}$ (100)
			200, $[M - CH_3]^+$ (25)
			173, $[M - C_3H_6]^+$ (40)
			158, $[M - C_3H_6 - CH_3]^+$ (15)
			58, $[C_3H_7NH]^+$ (15)
240	Cyanazine	225	225, $[M - CH_3]^+$ (100)
			198, $[M - HCN - CH_3]^+$ (25)
			189, $[M - HCl - CH_3]^+$ (30)
		240	240, $[M]^{+\cdot}$ (100)
			225, $[M - CH_3]^+$ (50)
			213, $[M - HCN]^+$ (30)
			173, $[M - C(CN) - CH_3 - CH_3 + H]^+$ (15)

whereas C_2H_4 loss is observed with deisopropylatrazine and simazine and C_3H_6 loss with deethylatrazine and atrazine. Other fragments correspond to typical diagnostic ions with $[C_2H_5NH]^{+\cdot}$ loss (*e.g.*, deisopropylatrazine) or $[C_3H_7NH]^{+\cdot}$ loss (*e.g.*, deethylatrazine and atrazine) [4,5,19].

Other daughter ions obtained correspond to ring-opening reactions resulting in a signal at *m/z* 132, 104 and 96 for atrazine and at *m/z* 104 for deethylatrazine, indicating the presence of a C_2H_5 group. For atrazine, this can lose a C_2H_4 group to yield the fragment at *m/z* 104. The daughter ions at *m/z* 69 for deethylatrazine and deisopropylatrazine also correspond to the same ring-opening reactions, with an additional Cl loss for both compounds and C_3H_6 and C_2H_5 loss for deisopropylatrazine. The ion at *m/z* 158 from atrazine corresponds to a loss of C_3H_6 and CH_3 groups, while the fragment ion at *m/z* 71 confirms the presence of the C_2H_5 group and a secondary amine structure.

The different fragmentation pattern observed for atrazine in GC–MS–MS is partly consistent with data obtained by GC–MS–MS with PCI [10], and also by other techniques such as LC–thermospray MS–MS [13] and LC–particle beam EI-MS [14]. The ions at *m/z* 79 and 122 from deethylatrazine and atrazine, respectively, corresponding to CH_3, C_3H_6 and HCl losses, have also been observed by GC–MS with ion-trap detection [4].

The losses of HCN–CH_3 and HCl–CH_3 from cyanazine are consistent with results obtained by GC–EI-MS reported elsewhere [4,19]. The ion obtained at *m/z* 173 was also observed by LC–thermospray-MS–MS [13] and corresponds to the loss of nitrile and a CH_3–C–CH_3 group from cyanazine.

As triazines include a chlorine atom in their structure, the metastable transition from $[M]^{+\cdot}$ to $[M - CH_3]^+$ was monitored for each analyte by GC–MS–MS. This allowed us to use a common transition for all the chlorotriazines, which provided excellent responses and avoided the interferences between the chlorotriazines typical of other transitions (*e.g.*, $[M]^{+\cdot}$ to $[M^+ - C_3H_6]$ for atrazine).

Selectivity

The selectivity of the different MS techniques studied was assessed by analysing a soil sample containing 37 ng/g of simazine and trace amounts of the other chlorotriazines. Fig. 3 shows the different chromatograms obtained using (A) GC–LRMS, (B) GC–HRMS and (C) GC–MS–MS with MRM. The amount injected corresponds to *ca.* 700 pg of simazine.

As can be seen in Fig. 3A, several compounds yield the ions at *m/z* 201.078 and 203.075, which do not allow the presence of simazine to be confirmed. Using GC–HRMS at a resolving power of 10 000 diminishes interferences from GC–HRMS traces, even though two main peaks corresponding to simazine are still obtained in the traces of the *m/z*

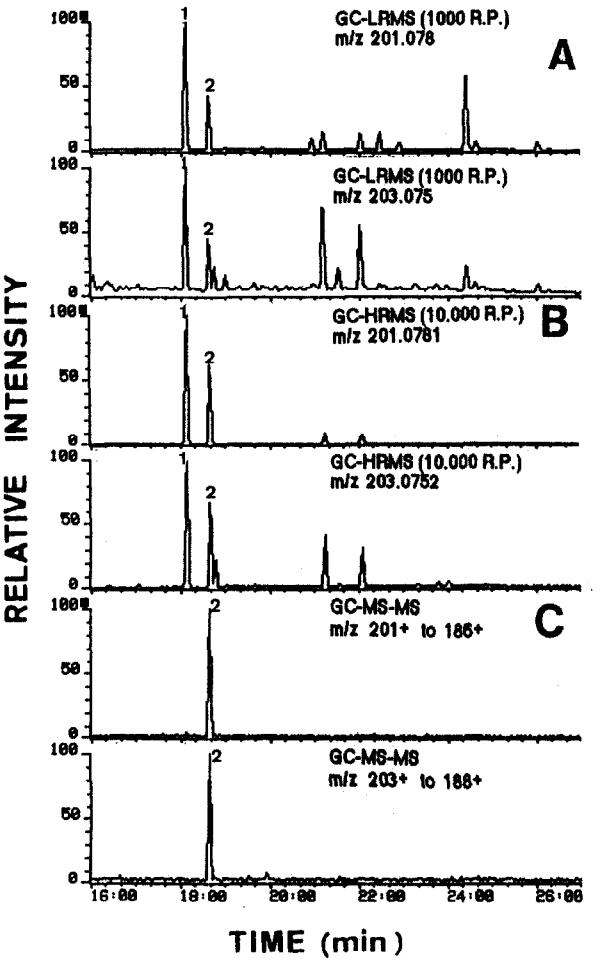


Fig. 3. Comparison of (A) GC–LRMS at a resolving power of 1000 (SIR of *m/z* 201.078 and 203.075), (B) GC–HRMS at a resolving power of 10 000 (SIR of *m/z* 201.0781 and 203.0752), (C) GC–MS–MS (MRM of transitions *m/z* 201^+ to 186^+ and 203^+ to 188^+) on a soil sample containing 270 ng/g of atrazine (peak 1) and 28 ng/g of simazine (peak 2).

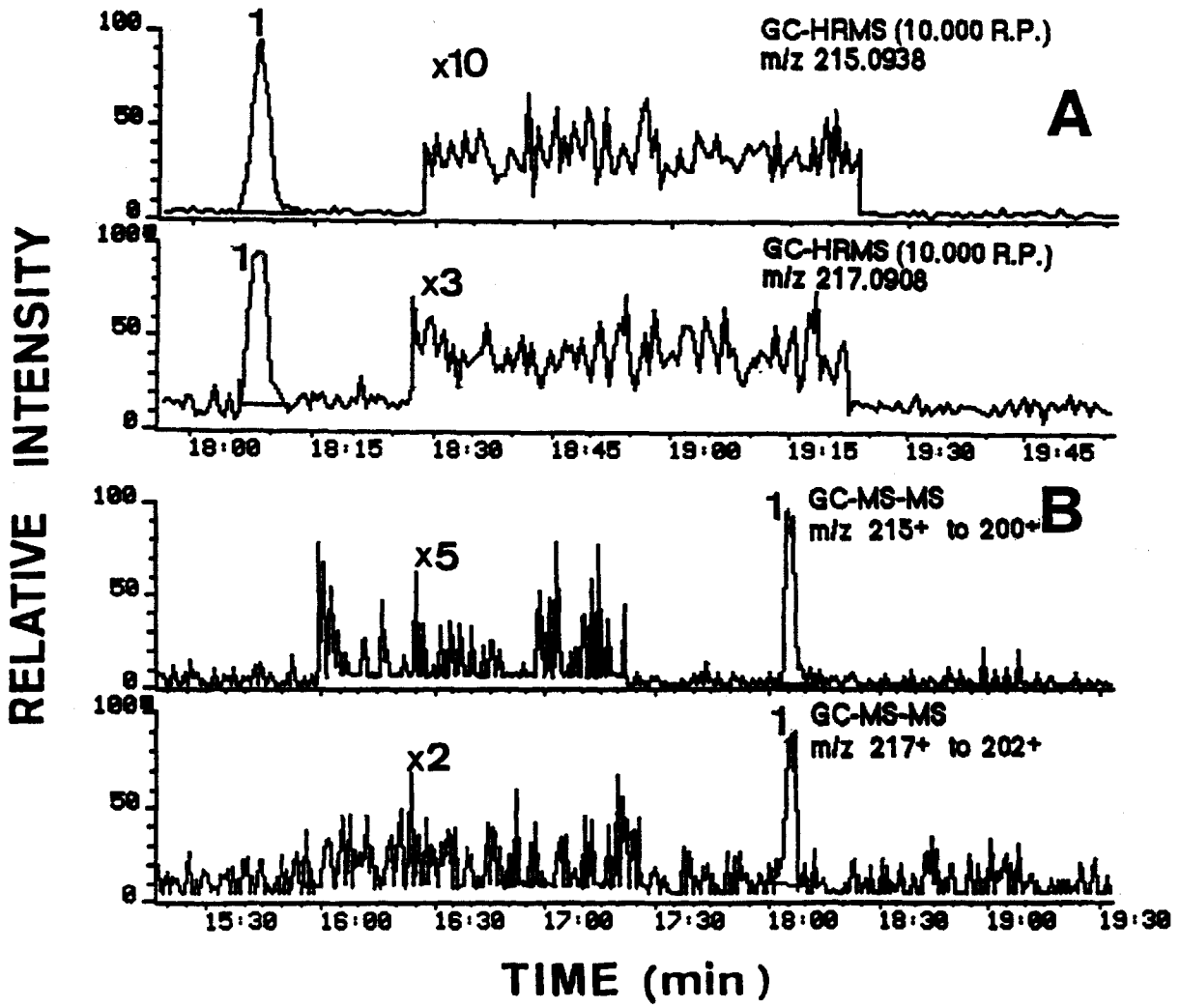


Fig. 4. Comparison of sensitivity for a 20-pg injection of atrazine using (A) GC–HRMS at a resolving power of 10 000 (SIR of m/z 215.0938 and 217.0908) and (B) GC–MS–MS (MRM of transitions m/z 215^+ to 200^+ and 217^+ to 202^+). Time scale in min:s.

201.0781 and 203.0752 ions. Only GC–MS–MS provides the confirmation of simazine in soil samples with a high degree of certainty.

The problems encountered in both GC–LRMS and GC–HRMS arise from interferences from the other chlorotriazines, namely atrazine (peak 1) in the traces in Fig. 3A and B. In this example, the concentration of atrazine in the soil sample was *ca.* ten times higher than that of simazine. The appearance of the atrazine peak is to be expected when analysing for simazine residues as most formulations based on chlorotriazines contain a mixture of the two compounds. Hence atrazine and simazine co-occur in many environmental matrices [4,5]. A second problem arises from the fact that the interference of atrazine on the simazine trace obtained by GC–HRMS at a resolving power of 10 000 is still significant. This is a result of the fragmentation of atrazine always causing CH_3 loss and hence yielding traces of a compound with the same m/z as simazine, even at such a high resolving power. Therefore, GC–MS–MS is to be preferred to confirm the occurrence of different chlorotriazines in soil samples.

TABLE III

COMPARISON OF LIMITS OF DETECTION FOR THE CHLOROTRIAZINES BY GC–HRMS AND GC–MS–MS (MEAN RELATIVE STANDARD DEVIATION 25–30 %)

Pesticide	Quantitation ion (*m/z*)	L.O.D. (pg)		
		GC–HRMS[a]	GC–MS–MS[b]	Ref. 10[c]
Deisopropylatrazine	173.0468, 175.0439	1		5000
	173→158, 175→160		6	
Deethylatrazine	187.0625, 189.0595	2		100
	187→172, 189→174		5	
Simazine	201.0781, 203.0752	4		100
	201→186, 203→188		15	
Atrazine	215.0938, 217.0908	4		100
	215→200, 217→202		20	
Cyanazine	240.0890, 241.0861	13		n.r.[d]
	240→225, 242→227		24	

[a] Resolving power 10 000; S/N = 10.
[b] MRM; *S/N* = 10.
[c] Ref. 10: obtained with GC–MS–MS and PCI; S/N = 3.
[d] Not reported.

Sensitivity

Fig. 4 shows the GC–HRMS traces obtained by using the SIR of *m/z* 215.0703 and 217.0908 (Fig. 4A) and GC–MS–MS with the MRM mode of the transitions from 215 to 200 and from 217 to 202 (Fig. 4B). The amount injected corresponds to 15–20 pg of atrazine in both instances. The limits of detection (L.O.D.) at a signal-to-noise ratio (S/N) of 10 for all the chlorotriazines are listed in Table III.

As can be seen from the chromatograms in Fig. 4, GC–HRMS and GC–MS–MS traces obtained by using ^{37}Cl are subject to higher noise levels than those obtained with ^{35}Cl because the isotope abundance of ^{37}Cl is about one third of the ^{35}Cl transition, and GC–HRMS features a slightly lower noise

TABLE IV

CONCENTRATIONS OF CHLOROTRIAZINE PESTICIDES AND THEIR DEALKYLATED DEGRADATION PRODUCTS FOUND IN SOIL SAMPLES

Pesticide	Quantitation ion (*m/z*)	Concentration (ng/g)	
		GC–HRMS[a]	GC–MS–MS
Deisopropylatrazine	173.0468, 175.0439	18	
	173→158, 175→160		23
Deethylatrazine	187.0625, 189.0595	109	
	187→172, 189→174		100
Simazine	201.0781, 203.0752	37	
	201→186, 203→188		56
Atrazine	215.0938, 217.0908	710	
	215→200, 217→202		1000
Cyanazine	240.0890, 241.0861	30	
	240→225, 242→227		26

[a] Resolving power 5000 or 10 000.

level than GC–MS–MS at approximately the same response level. Hence the L.O.D. will be slightly better for GC–HRMS with SIR than for GC–MS–MS with MRM. This can be ascribed to the fact that, although MS–MS provides enhanced selectivity, as shown in Fig. 3, the chemical noise level decreases more gradually than the signal with decreasing absolute signal and noise levels, so a net reduction in S/N is observed.

GC–MS–MS is about five times less sensitive than GC–HRMS. The sensitivities are in the low picogram range (1–20 pg) S/N = 10, *i.e.*, they are better than those achieved with an L.O.D. of 100 pg at S/N = 3 using GC–MS–MS with PCI [10]. The mean relative standard deviation (R.S.D.) varied between 25 and 30%, *i.e.*, over a common range for these techniques at levels close to the L.O.D. As the two L.O.D.s were calculated at different S/N, it should be noted that the L.O.D. reported here is enhanced with respect to those obtained by GC–MS–MS with PCI by 1.5–2 orders of magnitude [10]. This increased sensitivity may be ascribed to the use of hybrid instruments rather than a triple quadrupole, the work reported in ref. 10 involved PCI with methane rather than EI and we achieved complete separation between deethylatrazine and deisopropylatrazine rather than the co-elution accomplished in ref. 10. In relation to this last point, we have reported [5] that the complete separation of atrazine, simazine and their delakylated degradation products requires a polar, short (15 m) GC column with elution profiles of increasing polarity rather than increasing molecular weight.

We analysed a soil sample by GC–HRMS at resolving powers of 5000 and 10 000 and by GC–MS–MS. The results obtained are summarized in Table IV as averages of triplicate injections, with a precision consistent to within ± 10%. The chlorotriazine pesticide standards yielded linear responses from 50 pg up to 10 ng. The differences in the concentrations obtained by the various techniques were between 25 and 30%, *i.e.* reasonably acceptable when compared to with determinations using coupled MS systems [15,20].

CONCLUSIONS

GC–MS–MS with MRM and GC–HRMS at a resolving power of 10 000 are useful techniques for the determination of chlorotriazines in polluted soil samples. GC–MS–MS has been shown to be even more selective than GC–HRMS at a resolving power of 10 000 for monitoring compounds of a given group (*e.g.*, chlorotriazines) yielding fragments of identical molecular weights. In addition, GC–MS–MS with MRM completely overcomes interferences from the polluted soil matrices containing chlorotriazines.

The L.O.D.s achieved by using either GC–HRMS with SIR or GC–MS–MS with MRM for the determination of chlorotriazines and their dealkylated degradation products are a few picograms *i.e.*, 1.5–2 orders of magnitude lower than those afforded by triple quadrupole and conventional GC–MS with a single quadrupole instrument.

As all the triazines feature a common metastable transition in GC–MS–MS, namely from $[M]^{+\cdot}$ to $[M - CH_3]^+$, this can be used as a common monitoring technique for screening chlorotriazines in environmental samples and provides an alternative to other GC–MS methods. In addition, unlike other MS techniques, GC–MS–MS offers two information levels for deethylatrazine, atrazine and cyanazine, which depend on the parent ion used ($[M]^{+\cdot}$ or $[M - CH_3]^+$). In each instance, completely different daughter ion spectra are obtained which can be used as complementary structural information for the identification of unknown chlorotriazine metabolites in environmental samples.

ACKNOWLEDGEMENTS

Financial support from the BCR, Community Bureau of Reference of the Commission of The European Communities, is gratefully acknowledged. G. D. also acknowledges the award of a fellowship by the Commission of the European Communities (Contract ST2*-0488).

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