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# Surface Ionization Organic Mass Spectrometry of *s*-Triazine Herbicides

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**Surface ionization organic mass spectrometry (SIOMS) was applied to some *s*-triazine herbicides (simazine, atrazine, simetryne, ametryne and prometryne) by using quadrupole mass spectrometry in which the thermal ion source has a rhenium oxide emitter. The mass spectra were interpreted in a purely empirical way by means of evidence from previous investigations, and then compared with conventional electron impact ionization techniques. Sensitivity and selectivity were also studied, demonstrating that (i) these herbicides are efficiently surface ionized, (ii) in the SI mass spectra all *s*-triazines exhibited the $M^+$ molecular ion as the base peak with only relatively minor fragment species, with the exception of prometryne, (iii) the experimental results rationalized the high sensitivity of surface ionization detection (SID) in gas chromatography (GC) for the herbicides examined and (iv) GC/SIOMS coupling can be used for the sensitive and selective detection of these herbicides in the water. An approach to the detection of these herbicides in water by GC/SIOMS and GC/SID is described. The characteristics of both methods provide a reliable, sensitive and selective method which is needed for low concentration level measurements in complex mixtures.** © **1997 by John Wiley & Sons, Ltd.**

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## INTRODUCTION

*s*-Triazine derivatives are important compounds in agriculture and industry because of their herbicidal properties and triazine herbicides are some of the most widely applied pesticides in the USA and Europe. The most common member of this class, atrazine, was the most heavily used pesticide in recent years. However, triazines can cause environmental poisoning[1] and analysis is often needed for low-level concentrations in environmental media. Recent studies indicate a relationship between water levels of these pesticides and environmental response.[2] Water levels are very low, even in fatal impact.

Considerable interest has prompted the development of several analytical methods for triazines,[3–19] such as radioimmunoassay,[3–5] gas chromatography (GC)[6–10] and liquid chromatography (LC).[11–14] GC with electric conductivity[8] or nitrogen-specific detectors[6–10] has been used, as has LC,[11–14] but these methods are prone to problems with sensitivity and/or lack of specificity, mainly due to interference from co-eluting compounds. A stringent clean-up procedure is required since N-containing compounds are ubiquitous in environmental media.

A number of papers[15,17,18] have appeared describing the use of GC/mass spectrometry (MS) and LC/MS for pesticide analysis. Selected ion monitoring brought the sensitivity for *s*-triazine substances in water to the 0.1 ppb level using an internal standard for quantitation.[19]

Among many MS schemes, electron impact (EI) ionization has been widely used[15,16,18] as a versatile and sensitive technique with a powerful means of molecular identification and structural analysis. However, despite the number of MS procedures available, the determination of the concentrations of *s*-triazines encountered in environmental waters receiving small discharges remains difficult in some cases.[20]

Surface ionization (SI) has proved to be a useful technique for MS[21] and GC.[22] With SI, some organic molecules can be ionized with high efficiency. In general, soft ionization, where only the molecular ion or the molecular ion with very few fragments are generated, can be achieved. In addition, high selectivity can be achieved by SI on the basis of the thermal characteristics and ionization energy of chemical species.

An area where SI can be successfully applied to complement conventional techniques is in the characterization of moderately polar and relatively small biomolecules and drugs.[23,24] Hence we are in the process of evaluating SI techniques, combined with GC and MS, for the determination of pesticides. As examples, the *s*-triazine pesticides simazine, atrazine, simetryne, ametryne and prometryne are selected here because relevant information was obtained by preliminary surface ionization detection (SID) studies. Knowledge about the exact identification of charged species being formed from these compounds in SID is limited partly owing to the lack of MS studies.

This paper describes a highly selective and sensitive method for the determination of *s*-triazines in water at

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levels as low as $<1$ ng ml$^{-1}$, utilizing GC/SID and GC/surface ionization organic mass spectrometry (SIOMS). The analytical power of the SI technique was demonstrated by studying its sensitivity and selectivity. The basis of the present assay is rationalized through the SI mass spectra obtained by SIOMS.

## EXPERIMENTAL

### Instrumentation

The experimental set-up for GC/SIOMS has been reported in detail elsewhere.[25] Briefly, a Finnigan Model 3300 dual EI/SI mass spectrometer coupled to a gas chromatograph was used. The SI source assembly was laboratory made so that the rhenium oxide emitter could be fitted in the center of the EI ion source chamber when the assembly was inserted. Analysis was carried out in the SI mode with $O_2$ added continuously through the gas flow line to allow the preparation of rhenium oxide and an increase in the work function at the emitter surface.

The GC/SID system[26] consisted of a gas chromatograph (Shimadzu GC-14BPF) fitted with a split and splitless injector (SPL-14) and a surface ionization detector with an electrically heated Pt emitter (Shimadzu SID-14/15).

### Analytical conditions

For all gas GC separations (both GC/SID and GC/SIOMS), a 30 m $\times$ 0.25 mm i.d. 0.25 μm DB-17 (chemically bonded 50% phenyl–polydimethylsiloxane) fused-silica capillary column was used. The column temperature was maintained initially at 50 °C for 10 min and then increased at 5 °C min$^{-1}$ to 270 °C. The flow rate of the helium carrier gas was 2.7 ml min$^{-1}$.

The other instrumental parameters were as follows: for GC/SID, air flow rate 150 ml min$^{-1}$ and detector temperature 300 °C, and for GC/SIOMS, separator-room temperature 260 °C and surface temperature of the rhenium oxide emitter 850 °C.

### Samples

The structures of the *s*-triazine samples investigated are shown in Fig. 1. All chemicals were products of Ciba-Geigy, purchased from Sigma Chemical (Tokyo, Japan) and used without further purification. To obtain reference data and to permit standardization of analysis, a series of *s*-triazine solutions (concentration 1–1000 μg ml$^{-1}$) were prepared in dichloromethane for GC/SID and GC/SIOMS.

### Water extraction procedure

For the determination of the five *s*-triazines in water, a simple and rapid extraction procedure was employed, which could be completed in less than 30 min: to 50 ml water samples add 0.3 ml of 1 M KOH, to each add 50 ml of dichloromethane, shake for 5 min and centrifuge at 12 000 rev min$^{-1}$ for 5 min. Aspirate off the upper aqueous layers, filter the dichloromethane layers (extracted) into a single 50 ml conical tube and concentrate them 100-fold. Finally, inject 2 μl of the concentrated sample solution into the GC port with a syringe.

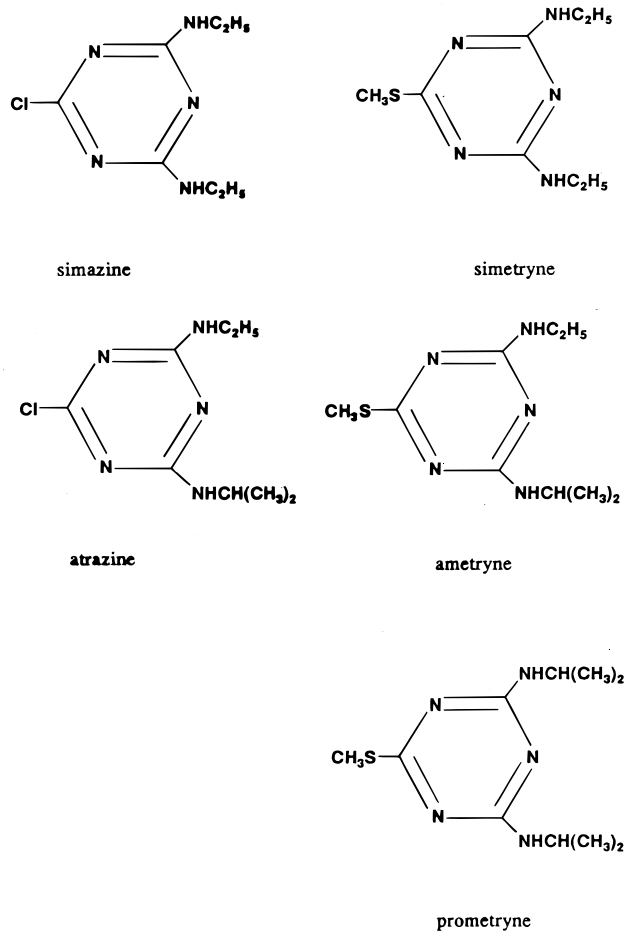


**Figure 1.** Structures of the *s*-triazines studied.

### Analytical procedures

EI and SI mass spectra were generated from the pesticide samples and were analyzed individually. About 100 μg of solid samples were placed in a glass sample holder which was located in the GC oven about 20 cm away from the ion chamber of the EI source. The desired amount of the sample was controlled by varying the GC oven temperature. Full mass spectra were acquired by scanning over the mass range $m/z$ 300–40 approximately once per 10 s.

The recovery was tested with water samples prepared by adding the samples to water to give final concentrations ranging from 1 to 3.4 μg ml$^{-1}$.

## RESULTS AND DISCUSSION

### Mass spectrometric considerations

We measured the mass spectra of the five *s*-triazine compounds using two ionization techniques, SI and EI.

The SI mass spectra are presented in Fig. 2. These were interpreted in a conventional way, characterized and compared with conventional EI mass spectra in order to illustrate the potential and limitations of the SI technique for this application. These full mass spectra also make it possible to choose suitable ions for selected ion monitoring and to ensure maximum sensitivity for quantitative purposes.

**EI *vs.* SI.** All the EI mass spectra are comparable to those reported in the literature[15,27] with a slight difference in intensity. The SI mass spectra of all the *s*-triazine samples are characterized by thermal dissociation on the hot emitter surface, followed by surface ionization of thermally dissociated products. The structural interpretation of the signals in SIOMS is based on this mechanism.[28,29]

Important points common to all the spectra are as follows: (i) the SI mass spectra exhibit a parent $M^+$ ion as a base peak, with the exception of prometryne; (ii) EI also yields $M^+$ ions, not as a base peak for all the pesticides examined; (iii) EI yields many fragment ions over the entire mass range, whereas SI shows abundant fragment ions only in the higher mass region and (iv) the SI mass spectra are basically different (unfamiliar) from the EI mass spectra.

Next we considered the ionization efficiency of the SI method. Since the present ion source is a combination type,[21] it is very easy to compare the relative ionization efficiencies in the SI and EI modes. To obtain an estimate of the efficiency of this method, the ion yield of the base peak ions from SI was compared with that from EI in terms of SI/EI, the ratio of the base peak intensity obtained in the SI mode to that in the EI mode. The values are given in Fig. 2. SI proved to give much higher yields than EI in all cases. The result for ametryne is striking, as it yields a peak which is 26.6 times higher in the SI mode. This result demonstrates that GC/SIOMS and GC/SID can be useful for the trace analysis of certain kinds of pesticide compounds. However, it should be noted that our comparisons were limited to the SI and EI sources we used and may have only a qualitative meaning.

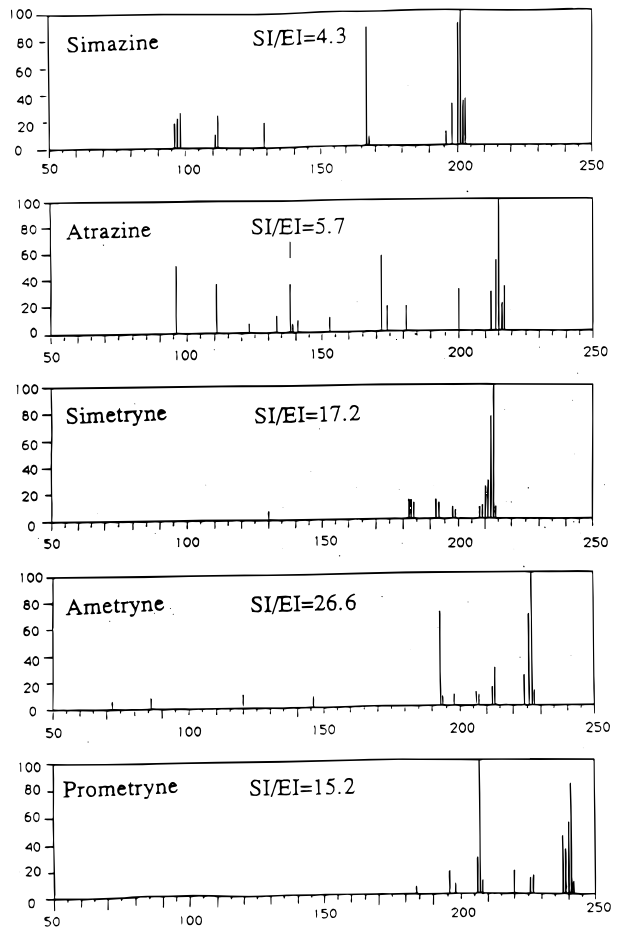


**Figure 2.** Surface ionization mass spectra of *s*-triazines. Mass spectral intensity is plotted as a normalized percentage scale.

Only a few signals of the higher mass range SI peaks can be reasonably assigned. For instance, the peaks at *m/z* 200, 198 and 196 in the simazine spectrum are due to the products arising from a simple hydrogen atom loss from the side-chain in the thermal dissociation process. For many other peaks, however, establishment of a link with the structure is more difficult, which is partly due to the tendency of the molecules to undergo complex thermal dissociation processes with skeletal rearrangement. In this respect, the SI results for the *s*-triazines are not useful for diagnostic analysis. This result was not expected since previous investigations on some biomolecules[23] and drug compounds[24] had revealed that many signals correspond to structure-specific losses and interpretation is fairly straightforward.

## Determination of *s*-triazines in water by GC/SID

The SIOMS studies revealed that SI gives greater ionic currents than EI for the *s*-triazines, hence SID appears to have greater potential for use in the routine analysis in laboratories which require sensitive, selective and rapid positive identifications and determinations. From the use of the SID, two advantages may be expected: first, because of the high specificity, the possibility of interferences is greatly reduced and clean-up procedures are usually unnecessary, and second, owing to the detector's increased sensitivity, a better detection capability is achieved.

Figure 3 shows a typical SID chromatogram obtained from the analysis of a dichloromethane extract of a river water sample (from the Katsura river, Kyoto) to which equal amounts of the five pesticides had been added. The major points of interest concern the relative sensitivity, the detection limit and the presence of interfering peaks. As can be seen from the Fig. 3, the relative sensitivity between the five pesticides differs by up to an order of magnitude. No interfering peaks were observed in the GC profiles of water extracts, demonstrating the specificity of SID.

The analytical results for all the pesticides tested are summarized in Table 1. After confirming the linearity of response, the overall detection limit was examined. The determination of atrazine in water at concentrations as low as 0.41 ng $ml^{-1}$ (at a signal-to-noise ratio of 3) can be achieved with the 100-fold concentration process. The accuracy and precision of the assay procedure were

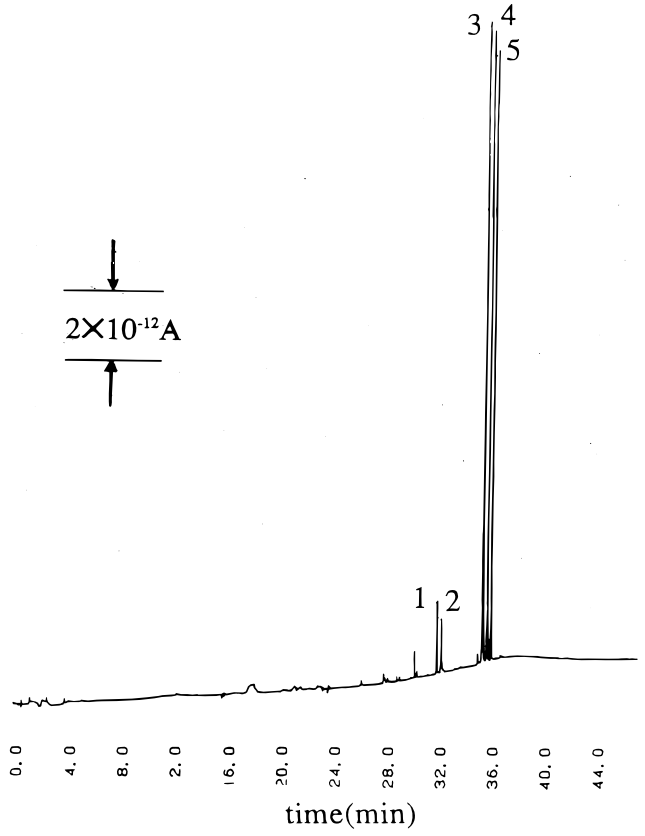


**Figure 3.** GC/SID of a river water sample supplemented with the five pesticides. Peaks: 1 = atrazine (4 ng); 2 = simazine (4 ng); 3 = prometryne (0.3 ng); 4 = simetryne (0.25 ng); 5 = ametryne (0.4 ng).

determined by measuring five different water samples, each spiked with simazine, atrazine, simetryne, ametryne and prometryne. The relative standard deviations (RSDs) for these assays were 12.5, 6.8, 3.5, 4.0 and 3.6%, respectively. The good reproducibility of the method is due to the reliability of SID and to the minimal handling of samples. The average recovery from five analyses ranges from 72.2 to 101.0%. No difficulties were encountered with the method in these analyses, confirming its validity for routine analysis. Full details of the study will be described elsewhere.

**Table 1. Analytical results for the determination of *s*-triazines in river water samples spiked at levels ranging from 1 to 3.4 μg ml$^{-1}$**

| Pesticide | Detection limit (ng ml$^{-1}$) This work[a] | Literature[b] | Added (μg ml$^{-1}$) | Found (%) (mean) | RSD (%) |
|---|---|---|---|---|---|
| Simazine | 0.5 | 0.025 | 3.4 | 101.0 | 12.5 |
| Atrazine | 0.41 | 0.025 | 3.0 | 94.0 | 6.8 |
| Simetryne | 0.025 | 0.025 | 1.0 | 72.2 | 3.5 |
| Ametryne | 0.041 | 0.025 | 1.0 | 89.1 | 4.0 |
| Prometryne | 0.017 | 0.025 | 1.0 | 100.6 | 3.6 |

[a] The detection limit for the overall method (a 2 μl injection of the concentrated (100-fold) extract from a 50 ml spiked water sample), which is given as the sample concentration (ng) in water (ml) at a signal-to-noise ratio of 3, provided that no other substance in the water interferes with each peak.
[b] Obtained using a 1 l water sample and NPD. The injection size of the 100-fold concentrated extract and the signal-to-noise ratio are unknown.[6]

A comparison of the use of SID with nitrogen–phosphorus detection (NPD) in GC in terms of the overall detection limit of *s*-triazines in water revealed that SID provides exactly the same detection limit for ametryne as the well established NPD.[6] There was a significant difference in relative sensitivity.

### Determination of *s*-triazines in river water by GC/SIOMS

GC/SIOMS also seems to be a promising method for the detection of *s*-triazines and was applied to the five compounds in water. Figure 4 shows the GC/SIOMS results obtained by (A) total ion monitoring (TIM) and (B) selected ion (*m/z* 213) monitoring (SIM). The sample in the TIM profile was a 10 μl extract solution (concentrated 100-fold) of river water samples supplemented with the five *s*-triazines at a concentration of 0.8 μg ml$^{-1}$ each. Interestingly, both chromatograms in the SI mode show little interference from compounds associated with river water, in which a large variety of normal constituents usually give interfering peaks.

The study showed that the GC/SIOMS results are comparable to those given by GC/SID with regard to accuracy and precision. TIM yields an easily identified mass spectrum, which, as expected, is almost identical with that obtained from the direct introduction of pure *s*-triazine samples.

Comparison with the EI mode revealed that the GC/SIOMS does not give rise to peak broadening, tailing and baseline drift in the TIM profiles, owing to its fast response characteristics. Hence SI is compatible with capillary column techniques.

Another important aspect of using the SI technique is its high sensitivity. The detection procedure for choosing the ions such as the base peak at *m/z* 213, in the light of the SI mass spectrum of simetryne, by selected ion monitoring allows the determination of much lower concentrations. If a spiked sample of water was treated (concentrated 100-fold) and a 10 μl injection of the water extract was made, a simetryne concentration in water of 22 pg ml$^{-1}$ was calculated as the detection limit at a signal-to-noise ratio of 3 from the SIM profile obtained with the SI technique. This value is at or below those typically present in environmentally important samples. It should be possible to improve on this value using more refined instruments, but an extensive study on the ultimate detection limit was not made here because of instrumental limitations.

## CONCLUSION

This is the first study on the use of SIOMS for the characterization of pesticides as an alternative, at least a complement, to conventional EIMS. It has been shown that a better idea of the possibilities and limitations of the SI technique, which allows the production of a few abundant specific ions, could be obtained and, in this

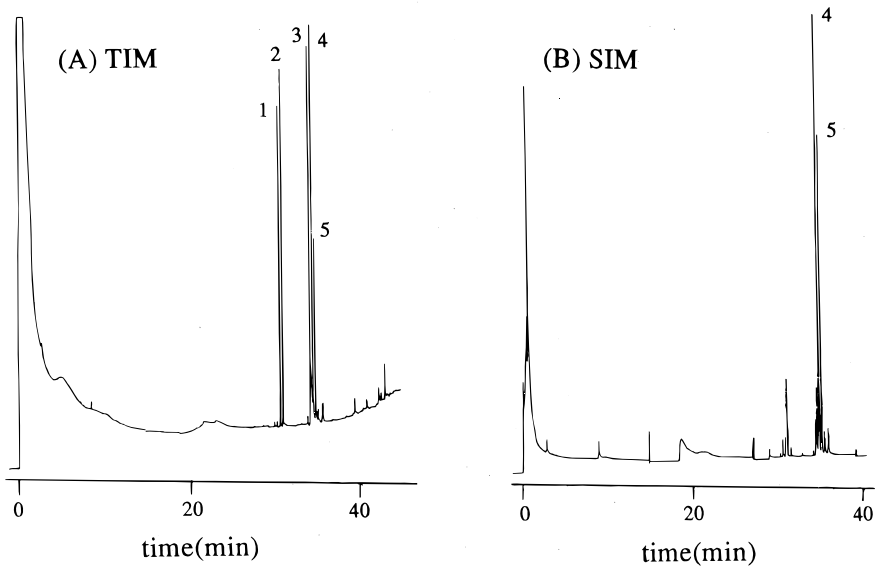


**Figure 4.** Gas chromatograms of a spiked river water sample obtained by (A) TIM and (B) SIM. Peaks: 1 = atrazine; 2 = simazine; 3 = prometryne; 4 = simetryne; 5 = ametryne. On the assumption that the extraction efficiency is 100%, each peak in the TIM profile corresponds to 0.8 μg, and the simetryne peak in the SIM profile corresponds to 28 ng.

respect, the GC/SID and GC/SIOMS methods associated with the SI technique should result in new opportunities in the field of agriculture.

The principal features of these methods are as follows: (i) GC/SID is a valuable and important tool in pesticide analysis and the simplicity, specificity and sensitivity of this method, provided by detecting abundant ions formed upon SI on a refractory metal surface, make possible the sensitive and selective determination of pesticide levels in water; (ii) GC/SIOMS allows the identification of *s*-triazines with certainty as a complement to conventional EIMS and offers a reliable basis for the GC/SID method; (iii) GC/SIOMS may detect a large number of pesticide metabolites if an extensive SI mass spectral library is established and (iv) to make full use of the advantages of GC/SID, an SI mass spectral library is also essential.

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