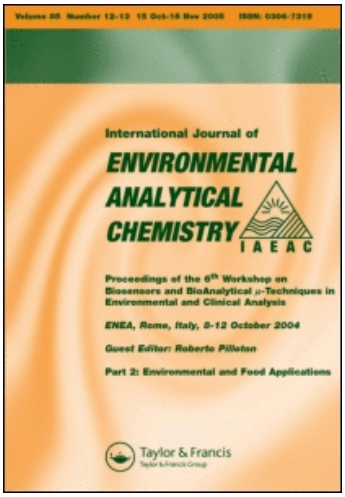

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CHARACTERIZATION OF TRIAZINE HERBICIDES BY ELECTROSPRAY AND TANDEM MASS SPECTROMETRY

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Electrospray mass spectrometry has aided the structural characterization of triazine herbicides standards. Possible fragmentation routes were first obtained by controlled collision-activated dissociation (CAD) initiated by cone voltage fragmentation. Low energy CAD MS-MS analyses of the protonated molecules $[M+H]^+$ confirmed the characteristic fingerprint patterns obtained by cone voltage fragmentation for all investigated triazine herbicides and also permitted differentiation of isomeric triazines. MS-MS analyses of selected intermediate fragments provided additional structural data, and established the fragmentation routes of their $[M+H]^+$ precursors. Electrospray MS has been proven to be a specific and very sensitive method for the detection and characterization of herbicides.

KEY WORDS: Herbicide, triazine, electrospray, mass spectrometry.

INTRODUCTION

Pesticides are a structurally diverse class of chemical compounds, utilized throughout the world which have had a tremendous impact on crop protection and hence on economic growth[1]. Modern agriculture relies on the use of pesticides to assist in the production of food. The U.S. Environmental Protection Agency has conducted a National Survey of Pesticides in Groundwater (NPS) and found that approximately 10% of the community water wells contain one or more pesticides[2]. The triazine herbicides, which are derivatives of substituted bis(alkylamino)-s-triazines, have been the most heavily used class of herbicides in North America during the last two decades[3]. These herbicides are effective plant growth inhibitors used for weed control in food crops and for inhibiting the photosynthesis of most plants, including freshwater algae[4]. They affect seasonally grown crops and appear to contaminate wells and streams by runoff[5]. The herbicide atrazine has even been detected in rainwater[6]. The morphological effects of acute and chronic exposure of atrazine on the kidney of rainbow trout (*Oncorrhynchus mykiss*) have been reported[7]. Simulation of the natural incidental runoff resulting from several atrazine applications on the total community of an enclosed ecosystem and the evaluation of these effects with respect to species interactions and impact on community stability have been described[8]. The indirect effects of triazine herbicides on fish have

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also been documented and it was shown that atrazine has an inhibitory effect on the macrophyte communities as a photosynthesis inhibitor which leads to a decline in the invertebrate fauna which are essential as prey for fish. Therefore, the diet and reproduction of fish are also affected[9]. There is a continuous impetus to develop new methods for the identification of these herbicides and their metabolites because of their increasing presence, persistence and potential threat to the environment.

Mass spectrometry has long been a useful technique for the analysis of triazine herbicides and their N-dealkylated degradation products[10,11]. Many modes of ionization have been employed including electron-impact (EI) and chemical ionization (CI)[11]. It has recently been shown that liquid chromatography (LC) may also be used for the separation of pesticides in ground water[5]. It may be the polar nature of most of these pesticides which makes them potential ground water pollutants. Consequently this property makes LC separation a more convenient technique than the more traditional gas chromatography (GC) methods. Although LC methods for monitoring pesticides, are either used or are under development, there is a significant shortage of LC methods followed by mass spectrometry for the precise identification of these analytes.

Thermospray (TSP) and particle beam (PB) are the most commonly used LC-MS interfaces for the identification of triazine herbicides[12,13]. The lack of structural information obtained by TSP-MS has required the use of tandem mass spectrometry (MS-MS) to provide diagnostic ion patterns which allowed the identification of the analytes[12]. The use of the PB-LC-MS technique gave electron impact spectra which permitted the identification of pesticide residues using multiple peak matching[13].

Electrospray ionization (ES) is well established as a robust LC-MS technique that allows rapid, accurate and sensitive analysis of a wide range of analytes from low molecular weight polar compounds (less than 200 Da) to biopolymers larger than 100 KDa. Although ESMS has been distinguished for its ability to produce intact multiple-charged ions proteins and other biopolymers[14–16], compounds of less than 1 KDa produce single-charged $[M+H]^+$ protonated molecules (in positive ion mode). Under appropriate experimental conditions, gas-phase fragmentations are minimized and the subsequent ions, which possess low internal energy, are sufficiently stable to pass from the ion source to the detector without dissociation. This is common for ions produced under "very soft" ionization processes.

Furthermore, dissociations may be induced or activated by collision. In this process a portion of the kinetic energy of the ion is converted to internal energy which collides with a neutral gas phase species, usually in the pressurized collision cell of a tandem MS-MS instrument[17,18]. Ions that have undergone this collisional excitation process may subsequently fragment. Thus, collision-activated dissociation CAD MS-MS, also known as low-energy CAD MS-MS, is a valuable method for generating structural information if the primary ionization process does not impart enough internal energy for spontaneous fragmentation to occur[19].

Another way to generate structural information by dissociation of the $[M+H]^+$ protonated molecular ion, can be induced by controlled adjustment of the accelerating voltage (0 ± 250 V) applied to the sampling cone or focus voltage (known as cone voltage fragmentation) of the electrospray source. This procedure is also known as CAD in the atmospheric pressure/vacuum interface region under mild conditions[20]. Unlike CAD experiments performed using tandem mass spectrometers, no mass filtering precedes ion-neutral collisions. Mass analysis of surviving precursor ions plus the decomposition products generated by the subtotal of all dissociations from all precursors contribute to the ions observed in the CAD spectrum.

As part of a programme aimed at the determination of trace levels of toxic chemical residues in the Newfoundland environment and as a continuation of our interest in the

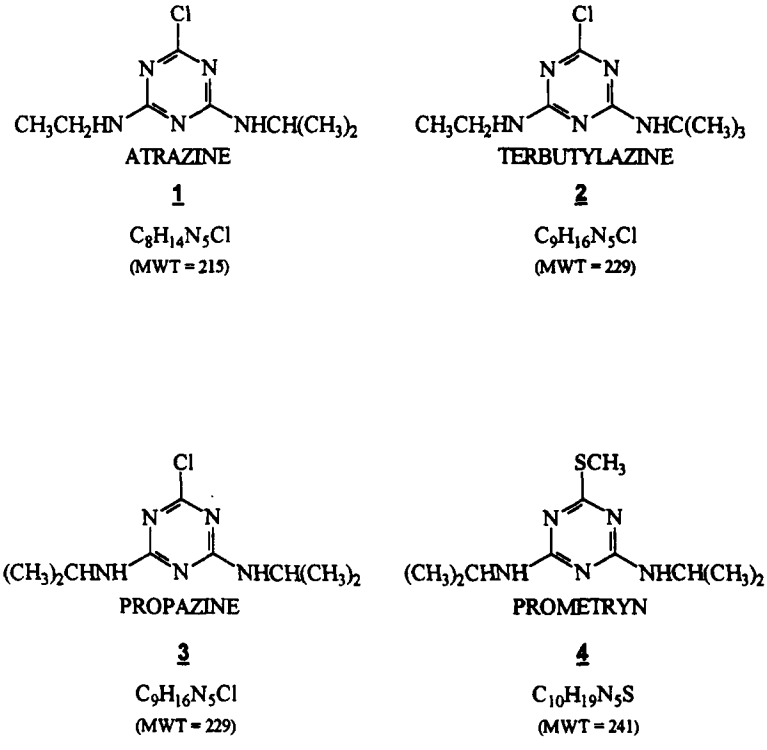

Figure 1 Chemical structures of chlorotriazine herbicides 1 – 3 and thioatrazine herbicide prometryn 4.

tandem mass spectrometry of bioactive molecules[21-25], we now report on the structural characterization and differentiation of triazine herbicides 1–4 (Figure 1) using electrospray mass spectrometry. Evidence of the possible fragmentation routes was first obtained by cone voltage fragmentation. Structural information was also derived from low energy tandem mass spectral analysis of the $[M+H]^+$ protonated molecules. Rationalization of the fragmentation routes was made by obtaining the product and precursor ion spectra of the various intermediate ions.

EXPERIMENTAL

Sample preparation

Samples of triazine herbicides were obtained from Ultra Scientific, North Kingstown, Rhode Island, U.S.A. The standard herbicide solutions used for LC-MS and LC-MS-MS were prepared with HPLC solvent grade methanol at concentrations of 50 p mol/ml. A 20 µl aliquot of sample was then introduced into the electrospray ion source by a continuous flow of acetonitrile:water (CH_3CN:H_2O, 1:1) at a flow rate of 10 µl/min using a PE series 4 pump connected to the Reodyne injector with a 20 µl loop. Sensitivity studies were done with concentrations varying from 1 µg/ml to 1 fg/ml.

Mass spectrometry conditions

The electrospray MS(positive ion mode) were measured with a Fisons VG-Quattro triple quadrupole mass spectrometer, equipped with an electrospray ionization source, capable of analyzing ions up to m/z 4000. A 486, 66 MHz personal computer equipped with Fisons MASSLYNX Mass Spectrometry Data System Software, was used for data acquisition and processing.

The temperature of the ES ionization source was maintained at 70°C. The operation voltage of the ES capillary was 3.08 KV and the HV lens was at 0.38 KV throughout the whole operation. ESMS were recorded with a focus setting varying from 50 to 100 volts. Generally, higher focus voltage induced fragmentation of lower molecular weight samples. The conventional ESMS were obtained by scanning in the Multichannel Analysis mode (MCA) with a scan time of 1 second 250 amu. Spectra are an average of 3–4 scans. The mass scale was calibrated in the positive ion mode using a polyethylene glycol mixture, and MS-MS experiments were conducted on the same instrument. Fragment ion spectra of mass-selected ions were induced by collision with argon in the second (RF only) hexapole. Argon collision gas was added in the enclosed chamber of the hexapole to give a pressure of 2 mTorr for collisional activation of the sample ions. The resulting fragments were analyzed by the third quadrupole. Collision energies of approximately 50 eV and a focus voltage of 75 V were used in all MS-MS experiments.

Precursor ion scans were obtained by scanning the first quadrupole while selecting a given m/z value with the third quadrupole.

RESULTS AND DISCUSSION

The electrospray mass spectrum (positive ion mode) of the chlorotriazine herbicide atrazine 1 was recorded with a lower focus voltage (50 V) and gave only the protonated molecular ions $[M+H]^+$ at m/z 216 and 218 with correct ratio in accordance with the isotopic abundance of chlorine (^{35}Cl and ^{37}Cl). However, this simple electrospray MS lacked substantial structural information. This problem was overcome by recording the electrospray MS with a higher focus voltage to induce the fragmentation of the $[M+H]^+$ protonated molecules which can provide structurally useful information. The electrospray mass spectra of atrazine 1 were recorded with focus voltages of 50, 60, 75 and 100 volts and are shown in Figure 2. The fragmentation route of the protonated molecule of this herbicide (Figure 3) has been tentatively rationalized using the scheme for systematic fragmentation of triazine herbicides by electron impact mass spectrometry proposed by Ross and Tweedy[26]. In this rationale the fragmentation of the $[M+H]^+$ protonated molecule which produces $[M+H\text{-}C_3H_6]^+$ ion at m/z 174 occurs by the loss of a neutral molecule of isopropylene by a McLafferty rearrangement. Similarly the fragmentation route yielding the $[M+H\text{-}C_3H_6\text{-}C_2H_4]^+$ ion at m/z 146 may arise either by double McLafferty rearrangements which cause the concerted losses of molecules of isopropylene and acetylene in a single step, or more likely by a two-step process involving the loss of a molecule of acetylene from the $[M+H\text{-}C_3H_6]^+$ ion at m/z 174. The $[M+H\text{-}C_3H_6\text{-}CH_2N_2]^+$ ion at m/z 132 was formed by ring opening of the triazine molecule with loss of a molecule of CH_2N_2. The $[M+H\text{-}C_3H_6\text{-}CH_2N_2\text{-}C_2H_4]^+$ and $[M+H\text{-}C_3H_6\text{-}CH_2N_2\text{-}HCl]^+$ ions at m/z 104 and 96 have been formed by the respective losses of molecules of acetylene and HCl from the ion at m/z 132. Similar fragment ions were obtained from the $[M+H]^+$ protonated molecular ion containing the ^{37}Cl isotope.

Low energy tandem mass spectrometric analyses were conducted to rationalize the fragmentation pathways leading to the various fragmentations obtained in the

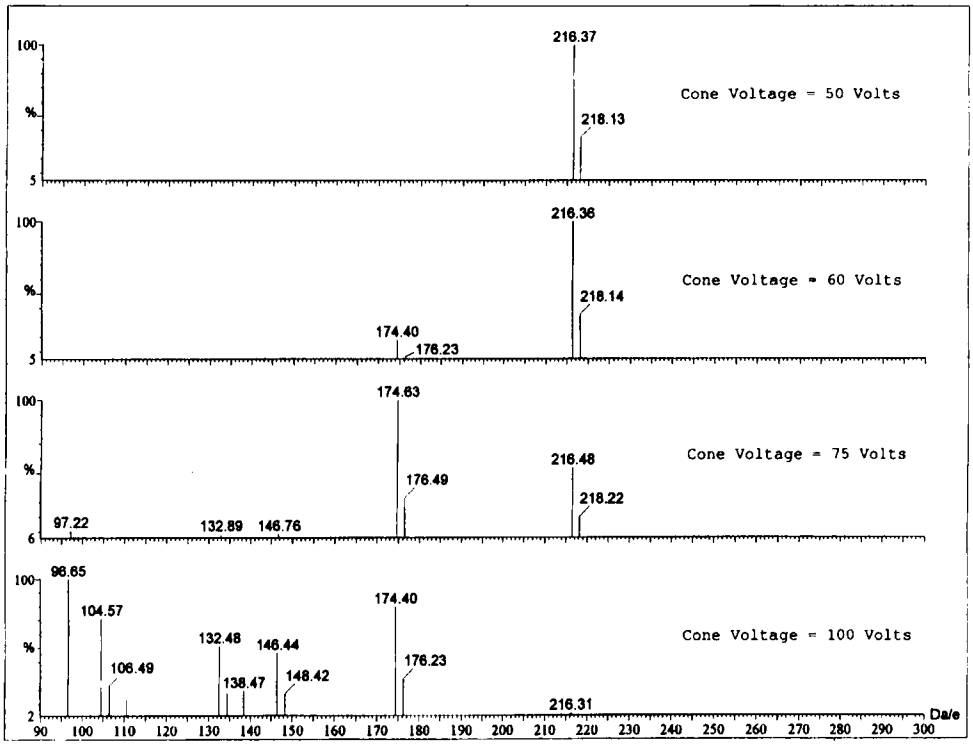

Figure 2 Electrospray mass spectra of atrazine (1) recorded with focus voltages of 50, 60, 75 and 100 volts.

conventional electrospray MS. Product ion spectrum (also called daughter ion spectrum) and precursor ion scan (also called parent ion spectrum) arising from fragmentation in the RF-only hexapole collision cell of the triple quadrupole instrument were obtained[19,21]. The $[M+H]^+$ ion at m/z 216 was selected for the recording of the unimolecular mass-analyzed ion kinetic energy (MIKE) and CAD MS-MS. One of the main benefits of the MS-MS technique is that all uncertainties concerning the origin of fragment ions are removed. The CAD MS-MS of the $[M+H]^+$ ion of atrazine 1 suggested the formation of the following product ions at m/z 174, 146, 132, 104 and 96 (Figure 4). Second generation product ions of the intermediate fragment ion at m/z 174, which was assigned as $[M+H\text{-}C_3H_6]^+$ (see Figure 3), were generated in an MS-MS experiment and afforded the product ions at m/z 146, 132, 104 and 96 as shown in Figure 5. Schematic representation of the different scan model is conveniently represented on all the MS-MS figures with symbols (filled circle indicates a fixed or preselected mass, open circle indicates a scanned or variable mass) described by Wysocki[19] and originally introduced by Cooks and co-workers[27].

In a different set of experiments, the precursors of the $[M+H\text{-}C_3H_6\text{-}C_2H_4]^+$ ion at m/z 146 were sought using the precursor ion scan technique and it was established that this ion originated from either the intermediate $[M+H\text{-}C_3H_6]^+$ ion at m/z 174 by loss of a molecule of ethylene or the protonated molecule $[M+H]^+$ at m/z 216 by the concerted loss of a molecule of propylene and a molecule of acetylene or vice-versa (Figure 6). Similarly, it was established that the $[M+H\text{-}C_3H_6\text{-}CH_2N_2]^+$ ion at m/z 132 originated from

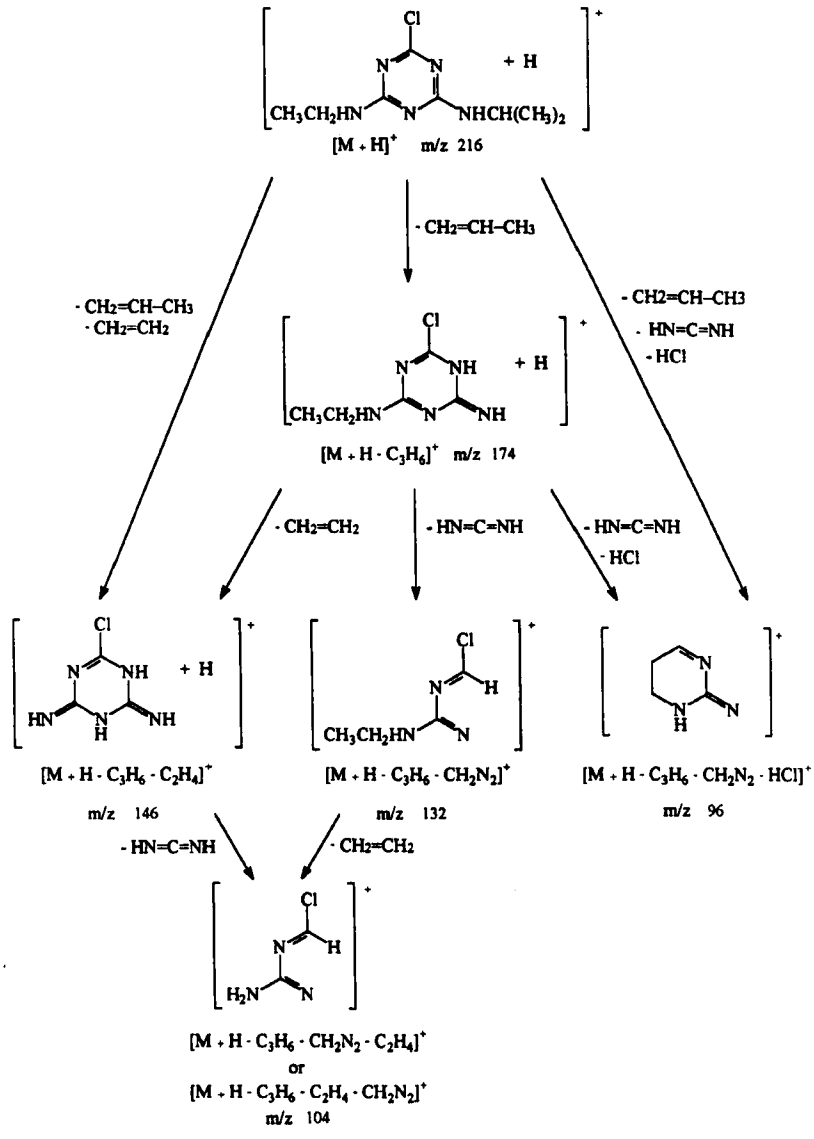

Figure 3 Major fragmentation routes of the $[M+H]^+$ ion of atrazine observed by ESMS and CAD MS-MS.

the $[M+H-C_3H_6]^+$ ion at m/z 174 by loss of a molecule of CH_2N_2 or the protonated molecule $[M+H]^+$ at m/z 216 by the concerted loss of a molecule of propylene and a molecule of CH_2N_2 or vice-versa (Figure 7). Precursor ion scan of the $[M+H-C_3H_6-CH_2N_2-HCl]^+$ ion at m/z 96 showed that this ion originated either from the $[M+H-C_3H_6]^+$ ion at m/z 174 by the concerted loss of a molecule of CH_2N_2 and a molecule of hydrochloric acid, or vice-versa, or from the protonated molecule [M+H] at m/z 216 by losses of molecules of propylene, CH_2N_2 and hydrochloric acid. The order of elimination

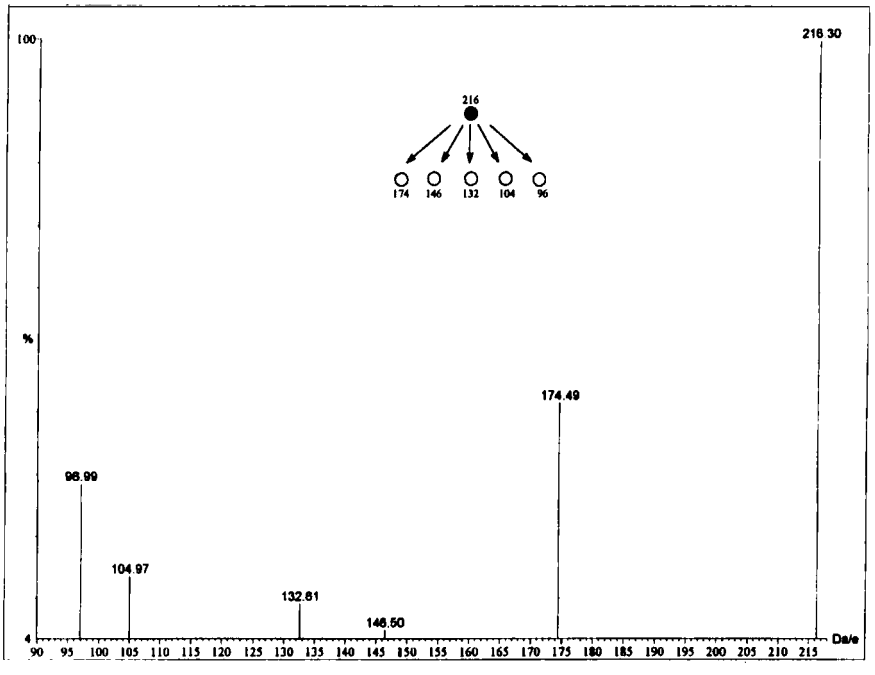

Figure 4 Low energy CAD MS-MS spectrum of the precursor ion $[M+H]^+$ at m/z 216.

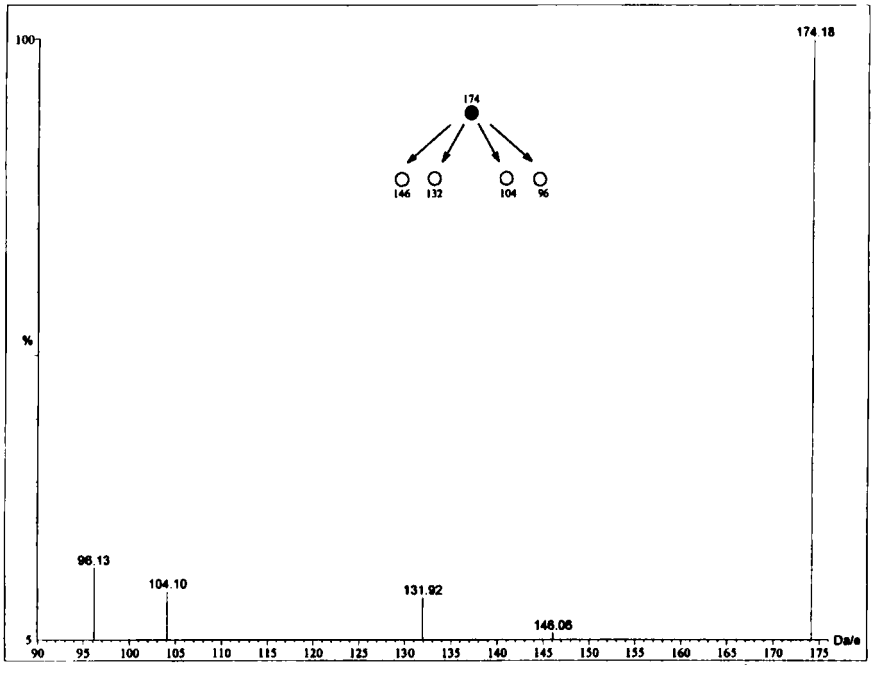

Figure 5 MS-MS spectrum of the intermediate ion m/z 174 from atrazine formed in the electrospray source.

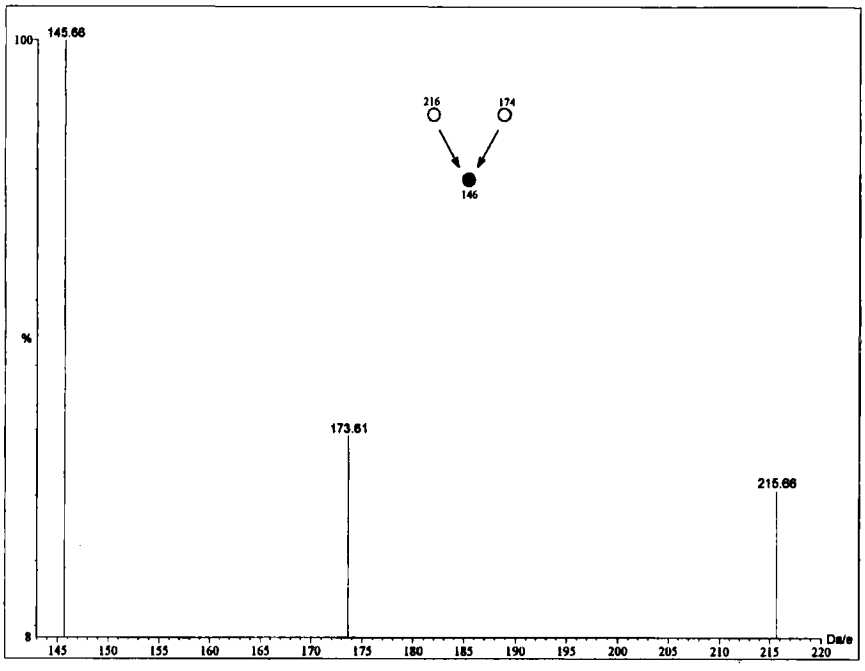

Figure 6 Parent ion scan of the intermediate ion m/z 146 from atrazine.

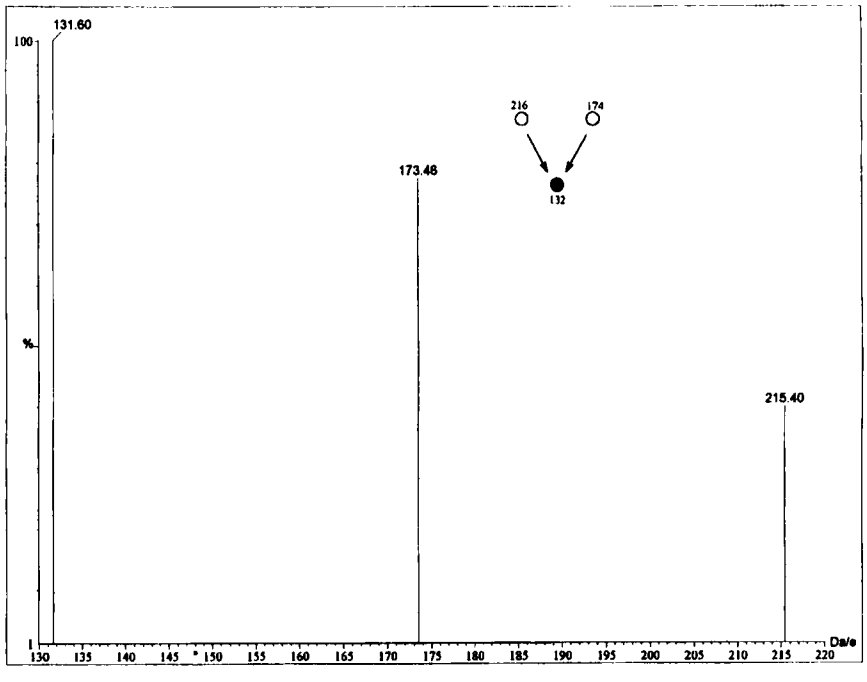

Figure 7 Parent ion scan of the intermediate ion m/z 132 from atrazine.

of the molecules has not been studied further and is beyond the scope of the present work. In this context, it should be noted that "concerted losses" of two (or three) molecules, in the MS-MS experiment, simply means that they are both lost within the time-window of the same reaction region within the tandem mass spectrometer. Precursor ion scan of the ion at m/z 104 showed that it originated from both intermediate ions at m/z 174 and 132 (Figure 8).

The electrospray mass spectra of terbutylazine 2 were recorded with focus voltages of 50, 60, 75 and 100 volts and are shown in Figure 9. The ESMS recorded with focus voltages of 50, 60, and 75 volts showed the protonated molecules $[M+H]^+$ at m/z 230 and 232 with correct ratio in accordance with the isotopic abundances of chlorine. The ESMS of terbutylazine recorded with a focus voltages of 100 volts shows a fragmentation similar to that of atrazine 1 and identical fragment ions at m/z 176, 174, 148, 146, 134, 132, 106, 104 and 96 were observed. CAD MS-MS of the protonated molecular ion $[M+H]^+$ at m/z 230 afforded only the $[M+H\text{-}C_4H_8]^+$ product ion at m/z 174 by a McLafferty rearrangement which was induced by the loss of a molecule of isobutylene.

Second generation product ions of the intermediate fragment ion at m/z 174 afforded product ions at m/z 146, 132, 104 and 96 similar to the one found for the CAD MS-MS of the ion at m/z 174 obtained for atrazine. As for the atrazine derived ions, the precursor scan for the ion at m/z 146 showed that it originated from ions at m/z 174 and 216. Similarly the ion at m/z 132 originated from ions at m/z 174 and 216. Also, the precursor ion scan of the ion at m/z 104 showed that it was produced by ions at m/z 146 and 132.

The electrospray mass spectra of propazine 3 were recorded with focus voltages of 50, 60, 75 and 100 volts and are shown in Figure 10. All the ESMS recorded with focus voltages of 50, 60 and 75 volts showed the protonated molecules $[M+H]^+$ at m/z 230 and 232. The fragmentation route of the protonated molecule $[M+H]^+$ at m/z 230 afforded the

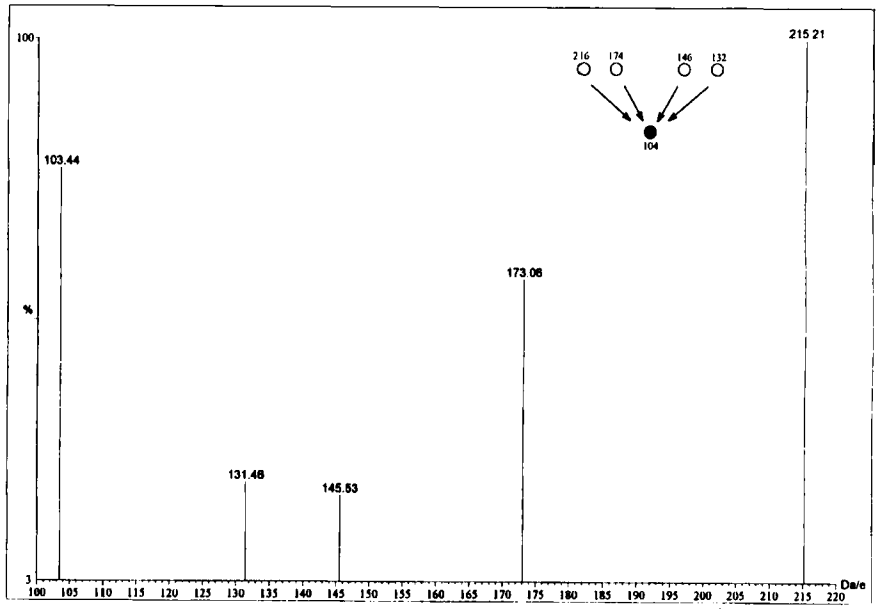

Figure 8 Parent ion scan of the intermediate ion m/z 104 from atrazine.

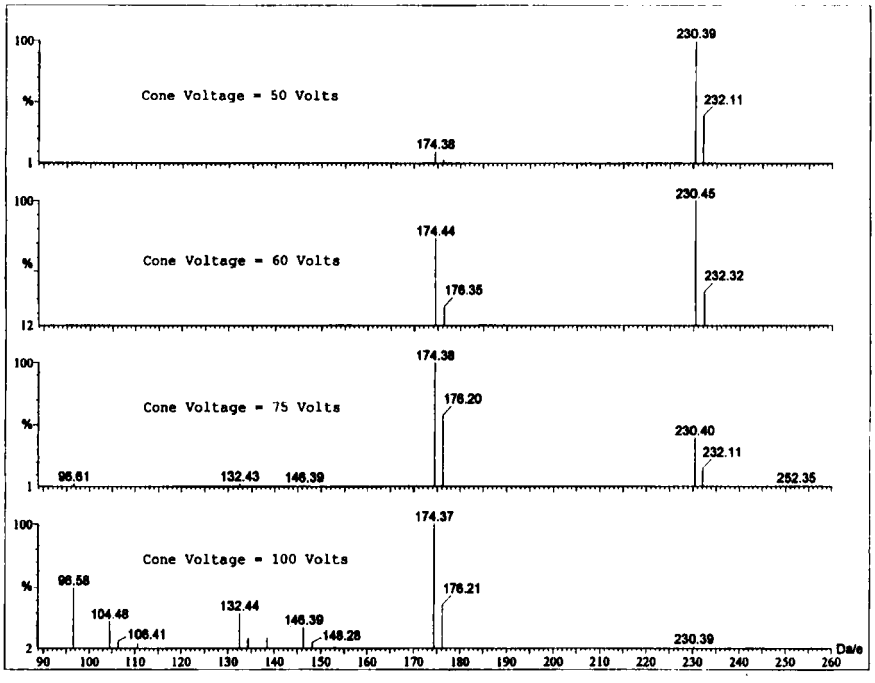

Figure 9 Electrospray mass spectra of terbuylazine (2) recorded with focus voltages of 50, 60, 75 and 100 volts.

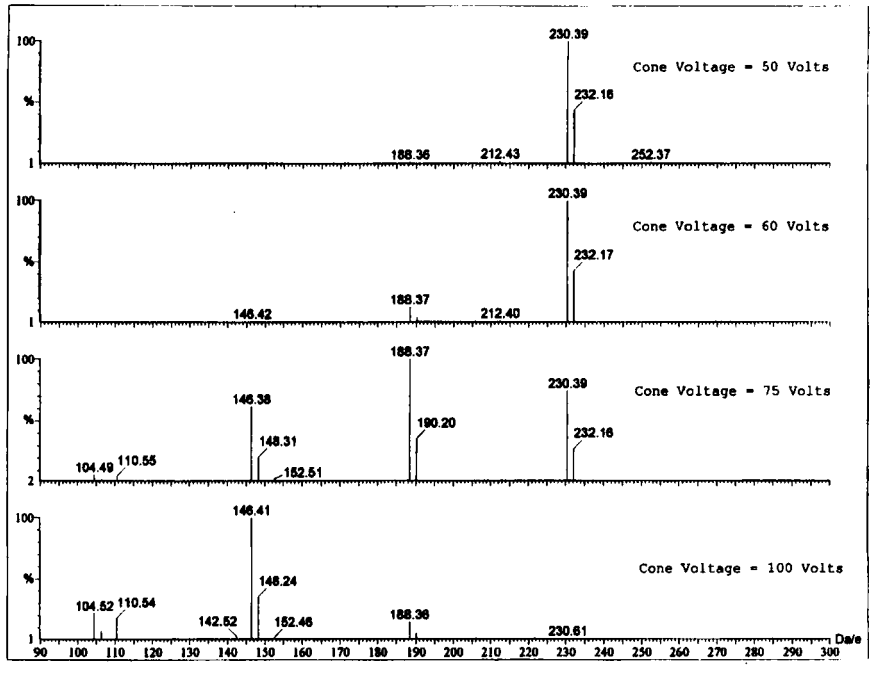

Figure 10 Electrospray mass spectra of propazine (3) recorded with focus voltages of 50, 60, 75 and 100 volts.

diagnostic fragment ion at m/z 188, which is formed by the loss of a molecule of propylene by a McLafferty rearrangement. CAD MS-MS of the protonated molecule $[M+H]^+$ at m/z 230 afforded only the $[M+H-C_3H_6]^+$ ion at m/z 188. Second generation product ions of the intermediate ion at m/z 188 afforded the $[M+H-2(C_3H_6)]^+$ ion at m/z 146 by loss of a molecule of propylene and the $[M+H-C_3H_6-CH_2N_2]^+$ ion at m/z 104.

The precursor ion of the $[M+H-2(C_3H_6)-CH_2N_2]^+$ ion at m/z 104 originated either from the $[M+H-C_3H_6]^+$ ion by losses of a molecule of CH_2N_2 and a molecule of propylene or from the $[M+H-2(C_3H_6)]^+$ ion at m/z 146 by loss of a molecule of CH_2N_2. The recording of the ESMS of a 50:50 mixture of terbutylazine 2 and propazine 3 (1:1, v/v) with focus voltages of 50, 60, 75 and 100 volts are shown in Figure 11. A quick perusal of these spectra will show that it is possible to distinguish between the substantially different diagnostic ions. Indeed we noticed the $[M+H-C_4H_8]^+$ ion at m/z 174 for terbutylazine 2 and the $[M+H-C_3H_6]^+$ ion at m/z 188 for propazine which permitted discrimination and identification of these two isomers in the mixture.

The electrospray mass spectra of the thioatrazine herbicide prometryn 4 were recorded with focus voltages of 50, 60, 75 and 100 volts and are shown in Figure 12. All ESMS showed the expected protonated molecular ion $[M+H]^+$ at m/z 242. The fragmentation route of the protonated molecule $[M+H]^+$ of prometryn is tentatively depicted in Figure 13. Cone voltage fragmentation ESMS of 4 (60, 75 and 100 volts) afforded a series of diagnostic fragment ions $[M+H-C_3H_6]^+$ at m/z 200, $[M+H-C_3H_6]^+$ at m/z 158 and $[M+H-2(C_3H_6)-CH_2N_2]^+$ at m/z 116, which permitted the structural characterization of 4.

Low energy tandem mass spectrometric analyses were conducted to rationalize the fragmentation pathways leading to the various fragment ions obtained in the

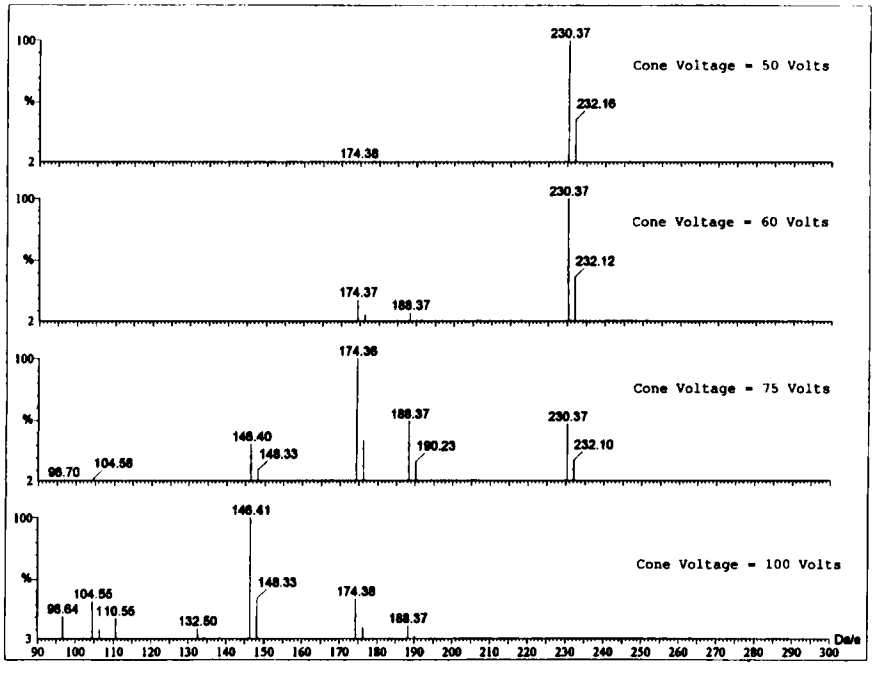

Figure 11 Electrospray mass spectra of a mixture of terbutylazine: propazine (1:1, v/v) recorded with focus voltages of 50, 60, 75 and 100 volts.

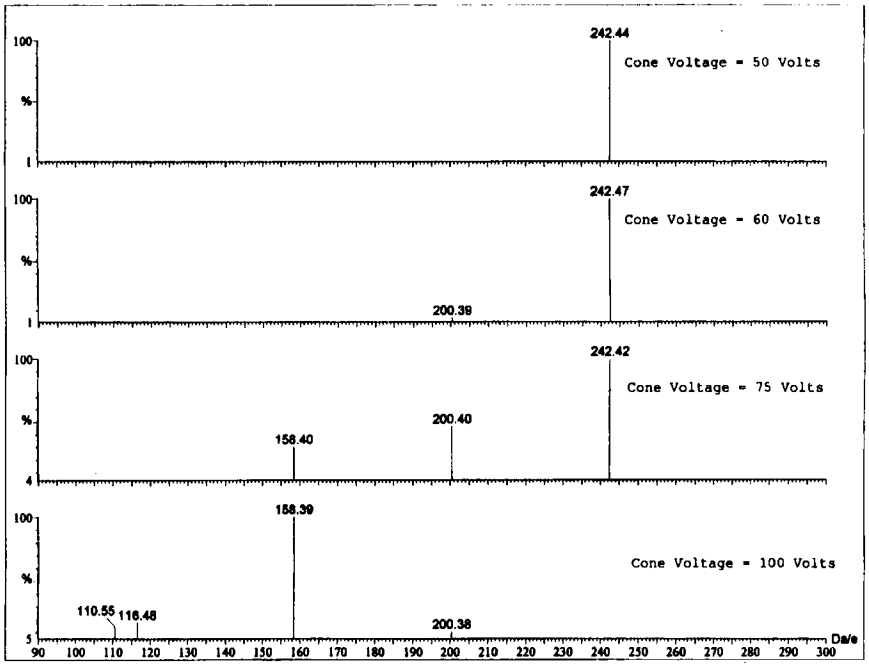

Figure 12 Electrospray mass spectra of prometryn (4) recorded with focus voltages of 50, 60, 75 and 100 volts.

conventional ESMS. The $[M+H]^+$ ion at m/z 242 was selected for the recording of the MIKE and CAD MS-MS. The low energy MIKE MS-MS of the protonated molecule at m/z 242 is shown in Figure 14a. The CAD MS-MS is shown in Figure 14b and suggests the formation of the product ions at m/z 200, 158 and 116. Second generation product ions of the intermediate fragment ion $[M+H-C_3H_6]^+$ at m/z 200 were sought in an MS-MS experiment and afford the product ions $[M+H-2(C_3H_6)]^+$ and $[M+H-2(C_3H_6)-CH_2N_2]^+$ at m/z 158 and 116 respectively.

In a different set of experiments, the precursors of the $[M+H-2(C_3H_6)]^+$ fragment ion at m/z 158 were sought using the precursor ion scan technique and it was established that this ion originated from both the precursor ion $[M+H-C_3H_6]^+$ and the protonated molecule $[M+H]^+$ at m/z 200 and 242 respectively (Figure 15). This means that the ion at m/z 158 is formed either by a concerted elimination of two molecules of propylene from the $[M+H]^+$ precursor protonated molecule or by elimination of one molecule of propylene from the intermediate product ion $[M+H-C_3H_6]^+$ at m/z 200.

Precursor ion scan of the ion at m/z 116 showed that it originated from the precursor ions $[M+H]^+$, $[M+H-C_3H_6]^+$ and $[M+H-2(C_3H_6)]^+$ at m/z 242, 200 and 158 respectively. The last finding indicates that the fragmentation of prometryn is essentially different from that of the chloroatrazines.

Detection limits for chlorotriazine herbicides have been reported to be in the 5–20 ng range for full scan data by TSP-LC-MS and PB-LC-MS[12,13]. In this rationale, electrospray MS was shown to be a more specific and sensitive method for the detection of triazine herbicides. The concentration detection limit of the studied chloro-and thio-atrazine herbicides by ESMS for a full scan spectrum was estimated to be in the range of

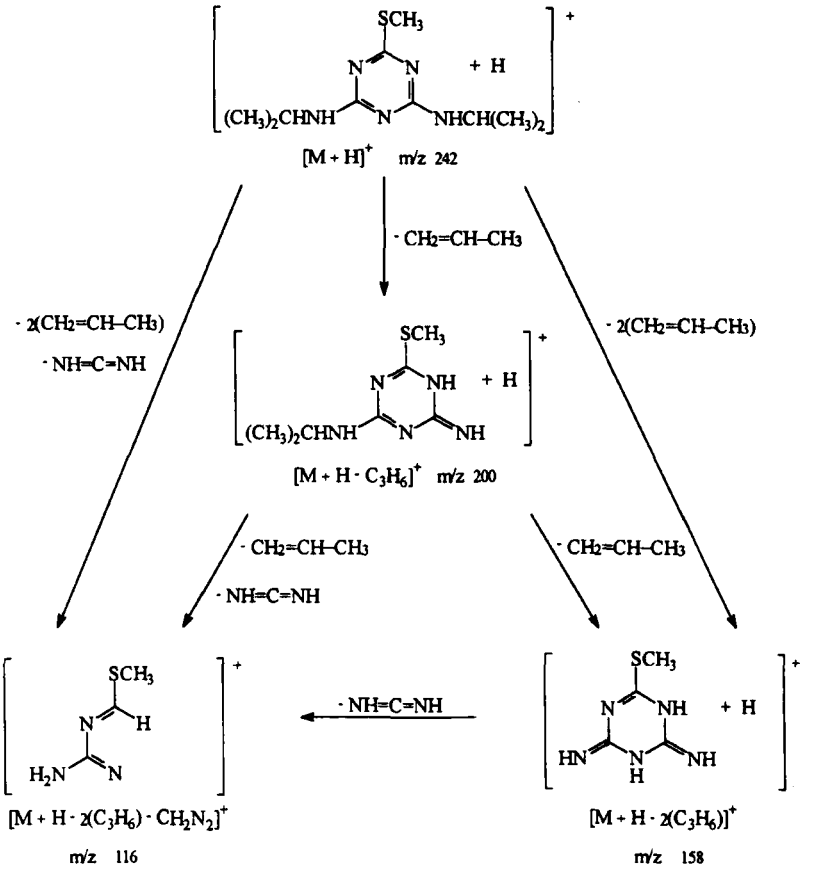

Figure 13 Major fragmentation routes of the [M+H]+ ion of prometryn observed by ESMS and CAD MS-MS.

100 pg and the mass detection limit was in the range of 20 pg (or 87.3 femtomoles) which is nearly 1000 times more sensitive than TSP-MS or PB-MS methods.

Signal to noise (S/N) measurements for one full ESMS scan for various injected quantities of atrazine were successfully recorded. The concentrations were: 1 ng (1 µl of a stock solution of 1 µg/ml), 100 pg (20 µl of a stock solution of 5 pg/µl) and 20 pg (4 µl of a stock solution of 5 pg/µl). The S/N ratios were found to be 42, 22 and 4 respectively.

CONCLUSIONS

The herbicides studied herein were characterized with certainty individually as well as in mixtures. This last aspect was of particular importance for the detection of chemicals originating from biological extracts. Indeed, the superior detection limits of these compounds by ESMS compared with more conventional methods allowed the detection of some of these chemicals from local lakes and sediments in the Newfoundland region[28]. These results will be published separately in due time. In conclusion, the absolute

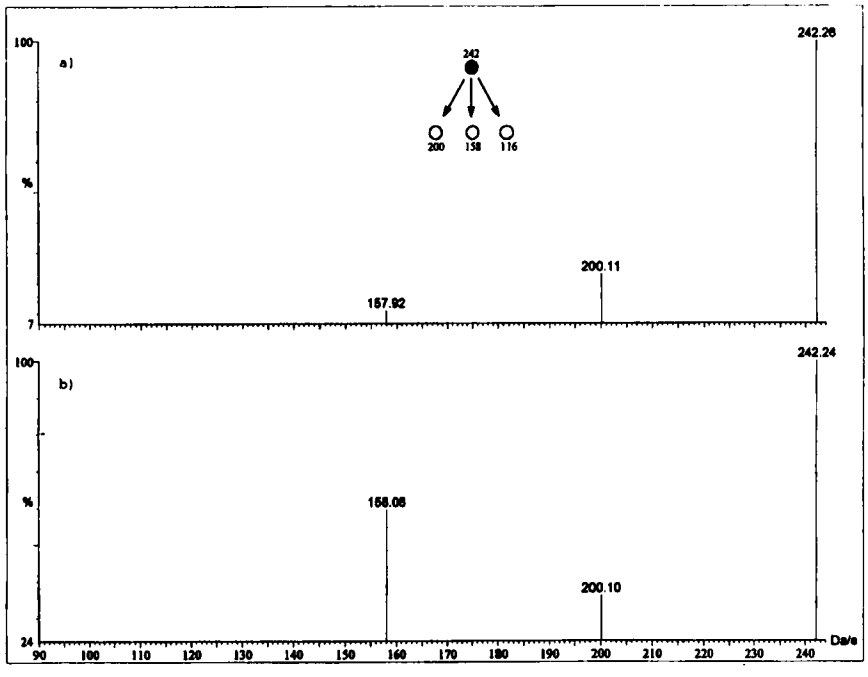

Figure 14 MIKE MS-MS spectrum (a) and CAD MS-MS spectrum (b) of the precursor ion $[M+H]^+$ at m/z 242.

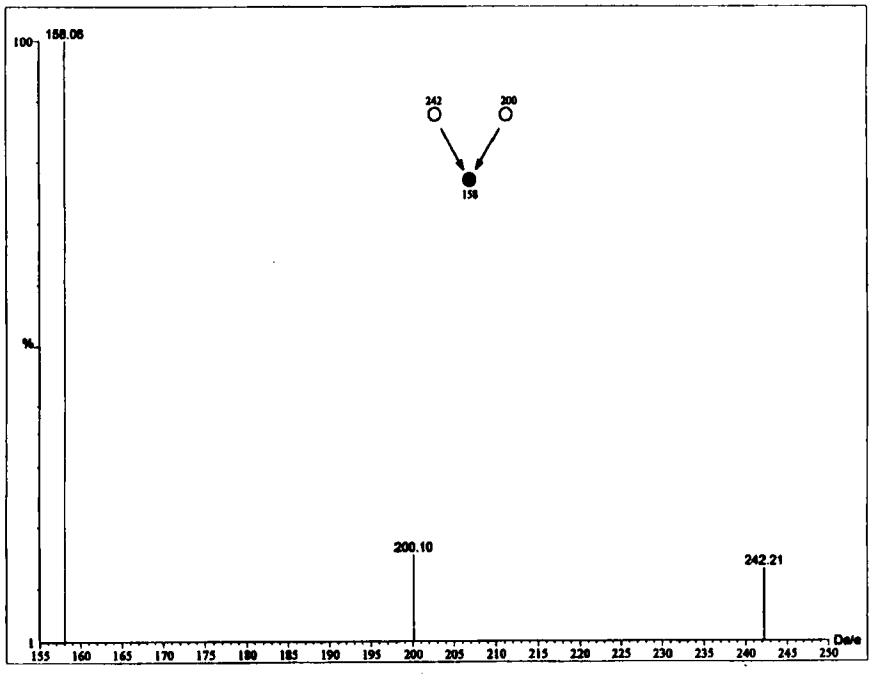

Figure 15 Parent ion scan of the intermediate ion m/z 158 from prometryn.

compatibility of ESMS with HPLC provides a valuable method for the quantitative and qualitative analyses of toxic chemicals.

Mass spectral analyses of triazine herbicides have been facilitated using electrospray ionization. Abundant signals corresponding to protonated herbicide molecules were observed in all cases using this ionization technique. Collision-activated dissociations in the atmospheric pressure/vacuum interface were promoted by increasing the accelerating voltages and generated a wealth of structural information on the dissociations of the formed protonated herbicide molecules and permitted the differentiation of isomeric herbicides. However it should be pointed out that CAD analyses, performed by changing the cone fragmentation voltage, do not permit the establishment of the different origins of fragmentation pathways or the fate of the fragment ions.

MS-MS spectra of the triazine herbicides obtained using low energy collisional activitation, permitted not only the rationalization of the fragmentation pathways but also confirmed the difference of the various isomers. Furthermore, parent ion and daughter ion series, and MS-MS spectra of selected intermediate ions formed during the cone voltage fragmentation of the ionized species, permitted rationalization of the fragmentation behaviour.

ESMS and ES MS-MS of triazine herbicides were shown to be valuable and very sensitive methods for the detection of triazine herbicides.

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