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Screening and identification of unknown contaminants in water with liquid chromatography and quadrupole-orthogonal acceleration-time-of-flight tandem mass spectrometry

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Abstract

In order to assess and maintain the quality of surface waters, target compound monitoring is often not sufficient. Many unknown micro-contaminants are present in water, originating in municipal, industrial or agricultural effluents. Some of these might pose a risk to drinking water production and consequently to human health. The possibilities of screening surface water and identification of these non-target water pollutants with modern data acquisition possibilities of hybrid quadrupole-orthogonal acceleration time of flight mass spectrometers (Q-TOF), such as data-dependent MS to MS/MS switching were investigated. Using model compounds, a procedure for the liquid chromatography–tandem mass spectrometry (LC–MS/MS) screening of water extracts was developed, enabling the detection and identification of compounds at levels ≤ 0.25 μg/l in surface water. Based on the accurate mass the elemental compositions for the precursor and product ions are calculated. The calculated chemical formulae are searched against the Merck index, the NIST library, an own database containing about 2500 water pollutants (pesticides and other contaminants) as well as a CI-CID library containing tandem MS spectra of about 100 water contaminants. The developed approach was applied for the identification of unknown compounds, present in native surface water extract. For three of these compounds, structures were proposed. Confirmation of the proposed structures with standards was beyond the scope of this study.

Keywords: Water analysis; Mass spectrometry

1. Introduction

In many countries surface water is one of the main sources for drinking water production. The quality of this source is influenced by many factors, such as agricultural and industrial effluents, and has to be monitored regularly. Within regular monitoring programs modern techniques such as gas and liquid chromatography combined with different types of detection are used in order to detect and quantify known (target) pollutants. There are however many (as yet) unknown compounds present in water, of which some may pose a health risk, if not removed by water treatment. Screening for unknown apolar contaminants is performed by gas chromatography–mass spectrometry (GC–MS) [1]. Identification of

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unknown compounds is then based on comparison of the mass spectra of the peaks in the sample with mass spectral libraries or interpretation of the fragmentation patterns.

For semi-polar and polar compounds, LC–MS/MS in the multiple reaction monitoring (MRM) mode has already proven its applicability in target determinations [2–4]. Although the sensitivity, selectivity and efficiency of the MRM approach are excellent, qualitative information needed to support the recognition and structural elucidation of compounds other than the target compounds is lost. In full scan mode, this information can be obtained, but in addition to the decrease of sensitivity with conventional equipment [5], the lack of large libraries of LC–MS/MS spectra prevents the identification of real unknowns. Within the recent advances in mass spectrometry, a new powerful identification tool has become available, the Q-TOF mass spectrometer [6]. Although environmental applications are still scarce [7], these types of instruments are often used for the identification of small molecules (<1000 Da) due to the advantages of the ion separation and detection principle of a TOF compared to the one of a quadrupole [8,9].

In this paper, we explored the possibilities of a Q-TOF mass spectrometer in a LC–MS/MS screening and identification approach. Test samples were prepared by the fortification of surface water extracts with several model compounds at different concentration levels. The study was limited to positive electrospray ionisation. In addition to accurate mass determination [10], extensive structural information was obtained by applying automated MS to MS/MS function switching, that is data dependent scanning. ''Full scan'' product-ion spectra were then obtained for each compound eluting above a certain threshold. Based on the determined exact mass and the fragmentation, the model compounds could be identified. The identification procedure was applied to unknown compounds present in a native surface water extract. Within this study, the analysis of the selected samples was limited to a single measurement (per ionisation mode) in order to mimic the usual screening approach with GC–MS. Evaluation of the extraction procedure, as well as confirmation of the proposed structures with a standard compound, were beyond the scope of this paper.

2. Experimental

2.1. Chemicals

The HPLC-grade water is obtained from a Milli-Q system (Millipore, Bedford, MA, USA). Gradient grade acetonitrile is used as the organic modifier (Riedel-de Haën, Seelze, Germany). The eluent is de-aerated using helium (99.999% pure) and placed under a constant pressure of 0.2 bar. The model compounds were obtained from Riedel-de Haën. Polyethylene glycol (PEG) was from Sigma (St. Louis, MO, USA).

2.2. Surface water extraction

The samples are filtered over 0.2 μm regenerated cellulose material RC 58 (Schleicher and Schuell, Dassel, Germany). A 500 ml sample of filtered surface water sample is extracted using Oasis™ (Waters, Milford, MA, USA) solid-phase sorbent. Oasis™ is a porous co-polymer [poly(divinyl–benzene–co-*N*-vinylpyrrolidone)] with an adsorption capacity for both lipophilic and hydrophilic compounds, HLB, 25–35 μm, 73–89 Å pores, 800 m^2/g. Experiments have shown that this material can extract compounds with a broad range of polarities. The phase is conditioned with 6 ml of methanol twice and 6 ml of ultra-pure water twice; the sample is loaded onto the column at approximately 2 ml/min, in order to keep the extraction comparable to the on-line methods in our laboratory [17]. Higher flow-rates can be used if required. After a rinse step with 1 ml of 5% solution of acetonitrile in water and 30 min drying time with nitrogen, the column is eluted with 2 ml of acetonitrile four times. The solvent is evaporated under nitrogen to a final volume of 0.5 ml (1000-fold concentration factor).

2.3. Samples

The selected compounds were added to the surface water extract in two concentrations, i.e. 0.25 and 0.5 mg/l, corresponding to 0.25 and 0.5 μg/l in the original water samples (1000-fold concentration factor). An additional sample was prepared by diluting the extract fortified with 0.5 mg/l of each compound further with acetonitrile. This results

again in a concentration of approximately 0.25 mg/l of each analyte, but now with a more favourable matrix:analyte ratio. Names, structural formulae and elemental composition of the model compounds are shown in Table 1. All these compounds can be analysed by means of positive electrospray ionisation. In order to limit the data processing to relevant peaks, a procedure blank covering the filtration and extraction step is treated as an individual sample.

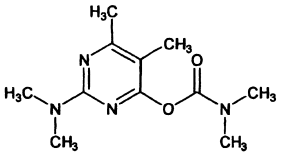
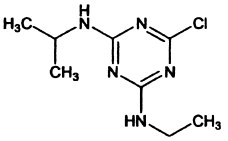
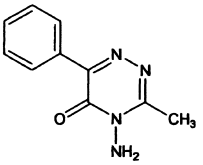
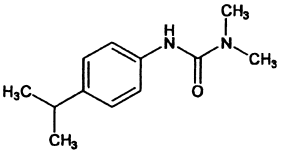
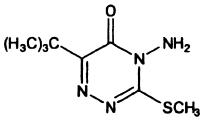
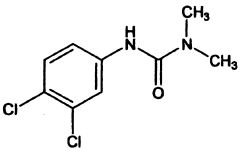
2.4. Apparatus

The analysis is performed using a 2690 solvent delivery/sample handling system (Waters) equipped with a 20 μl sample loop and a 250×4 mm I.D. Inertsil ODS-2, 5 μm material analytical column (GL Sciences, Tokyo, Japan). The guard column is 10×2 mm I.D. packed with pellicular C_{18} material, 25–35 μm (Varian-Chrompack, Middelburg, The Netherlands). The LC is interfaced to a Q-TOF2 mass spectrometer (Micromass, Manchester, UK) equipped with a Z-spray ionisation source.

2.5. Analysis

The sample is injected through a 20 μl sample loop onto the analytical column. The compounds are eluted with a flow of 0.7 ml/min using a gradient of 0.1% of formic acid in Ultrapure water and 0.1% of formic acid in acetonitrile. A linear gradient from 10 to 80% (in 40 min) and from 80 to 100% in 2 min) of acetonitrile was applied. The column was rinsed at a flow of 1 ml/min with 100% of acetonitrile for 10 min and then brought to 10% of acetonitrile in 2 min. A lock mass is added post-column at a flow-rate of 1–2 μl/min in order to allow for internal mass calibration. For this purpose sulfadimethoxine is used, which ionises well in both positive (m/z 311.0814) and negative (m/z 309.0658) electrospray ionisation mode. The electrospray source conditions are: capillary voltage 3 kV, cone voltage 24 V, source temperature 120°C and the desolvation temperature is set at 450°C. The LC column effluent was introduced into the source of the mass spectrometer without applying any post-column splitting. Hence, 0.7 ml/min of aqueous solvent was continuously

Table 1
Model compounds used for fortification experiments

Compound	Formula	Compound	Formula
Pirimicarb-I	$C_{11}H_{18}N_4O_2$	Atrazin-IV	$C_8H_{14}ClN_5$
			
Metamitron-II	$C_{10}H_{10}N_4O$	Isoproturon-V	$C_{12}H_{18}N_2O$
			
Metribuzin-III	$C_8H_{14}N_4OS$	Diuron-VI	$C_9H_{10}Cl_2N_2O$
			

introduced into the source of the mass spectrometer. The desolvation gas temperature had to be set at 450°C to prevent droplet formation at the probe tip. No thermal degradation or fragmentation was observed applying these settings for the various model compounds during initial experiments and the conditions were therefore applied throughout the complete study. Pusher frequencies and cycle times are selected automatically. The resolution of the TOF was set to 7000, in order to enhance sensitivity (in general, the operating resolution of the Q-TOF2 is 11 000–12 000).

During the completion of this paper, a new source type became available, which allows for the continuous introduction of a lock mass via a second sprayer, which provides exact mass information in both the MS and MS/MS mode [11,12]. A separate optimised lock mass sprayer may also overcome practical constraints such as ion suppression for compounds which are more difficult to ionize in ESI-MS. Furthermore, lock mass ions might interfere with analyte ions or might be suppressed themselves by mobile phase gradient composition alteration. Details on the use of lock mass spray in identification studies with the Q-TOF will be published elsewhere [12].

Calibration in positive electrospray mode was conducted with a PEG mixture containing PEG200, PEG400 and PEG600 in equimolar quantities.

In order to obtain maximum structural information, the samples are analysed with the MS/MS automatic function switching conditions in centroid mode. In these experiments the survey scan (single MS) was performed in the mass range of 190–500 Da. Above a certain threshold value (in this case 60) the most abundant ion in the spectrum is automatically selected as the precursor ion and the acquisition is automatically switched from MS to MS/MS. Due to the continuous addition of sulfadimethoxine, the nominal m/z values of both the protonated and sodiated molecules are excluded from MS/MS analysis. The loss of MS/MS information for ions with the same nominal m/z value as the protonated and sodiated ions of the lock mass, can be assessed by checking the survey scan data. This approach can be used for any other known interference, as well as be applied in experiments with samples where compounds of interest co-elute with interferences. The maximum number of excluded masses that can be programmed is not limited.

In the MS/MS mode, product ion spectra are generated at four collision energies, 15, 20, 25 and 30 eV consecutively, and acquired in the mass range of 50–500 Da. Argon was used as the collision gas and the gas cell pressure in the collision cell was $6 \cdot 10^{-5}$ mbar. Acquisition and data processing was performed with MassLynx 3.4 software.

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2.6. Data processing

Generally, for the determination of accurate mass, the experiments are performed in the continuum mode and then converted to centroid data in order to implement lock mass correction and obtain accurately mass measured spectra [10]. No TDC dead time correction is applied during acquisition. Centroiding of the data is applied with and without applying the dead time correction model to ensure that the exact masses are not biased. In instances where mass deviations are expected (e.g. abundant peaks) data are taken from the peak tail, i.e. at lower concentration, hence, lower signal intensity.

For data, obtained in the centroid mode – as described here for the automated MS/MS switching experiments – this correction can either be applied automatically to all MS and MS/MS function or performed separately for each spectrum of interest. The latter was applied in this study.

Based on the accurate mass, the (possible) elemental composition of the peaks of interest is calculated using the elemental composition tool within the MassLynx software. Parameter settings are: C 1–50, H 0–100, N 0–10, O 0–10, P 0–2, (S 0–4), even electron ions (for the precursor ions), odd and even electron ions (for the product ions). The appropriate numbers of Cl and Br are determined from the isotopic pattern and added if required. The double bond equivalent (DBE) parameter is set in the default values (−5 to 50) and is not used as a identification criterion. In this study, the calculated elemental composition possibilities with a maximum deviation of 5 mDa from the measured exact mass are considered. The search is performed in the Merck index, NIST mass spectra library, InfoSpec® GC–MS database [13] supervised by Kiwa and the CI-CID mass spectra library of the Institute for Inland Water Management and Wastewater Treatment in the Netherlands (RIZA) [14]. In addition to various

compound information, InfoSpec® contains about 3000 EI spectra of known and unknown water pollutants. The CI-CID database contains about 100 LC–MS/MS spectra of water pollutants.

3. Results and discussion

3.1. General

The evaluation and performance of the single MS oa-TOF instrument for the determination of target compounds has been described elsewhere and includes the combination of exact mass determination and the diode array UV-spectra for identification of unknown (non-target) pesticides [10]. Our effort was directed to the applications of the hybrid quadrupole-oa-TOF instrument. For screening purposes with LC–MS/MS, preferably as much structural information as possible should be generated with each experiment. Therefore, the exact mass determination and structural elucidation based on fragmentation at different collision energies were combined in one single experiment. In the experiments described here, the scan range in the survey scan was limited to m/z 190–500. However, due to the ''scanning principle'' of the TOF mass spectrometer, if required, the mass range can be broadened without effecting the sensitivity. One should note that for complex matrices, a broader mass range during the survey scan results in more ''peaks'', making the acquisition of automated product-ion spectra of unknown trace contaminants more complex and difficult.

The fortified surface water extracts with two different concentration levels of the selected compounds and different matrix:analyte ratio's were analysed using the automated MS to MS/MS switching. In Fig. 1 the LC–MS survey scan of the extract (1000-fold concentration factor) fortified with 0.25 mg/l of each of the model compounds is shown (Fig. 1A). Even though this is the least favourable situation investigated, with the exception of diuron (VI),

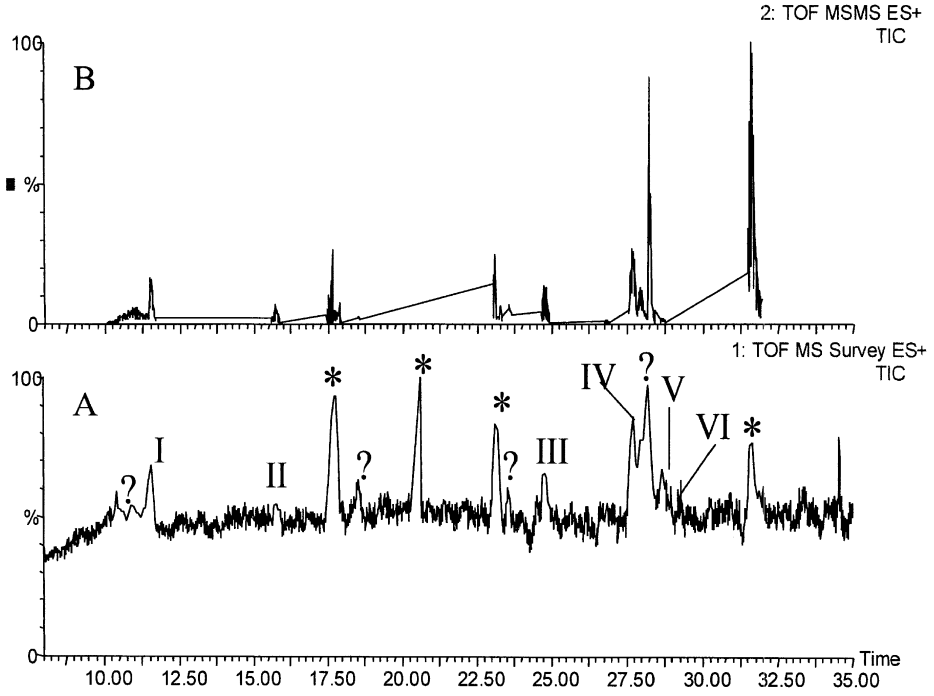

Fig. 1. Total ion chromatograms of the survey scan (A) and automated MS to MS/MS switching (B) of a surface water extract fortified with 0.25 mg/l (corresponding to 0.25 μg/l in the surface water) of selected compounds. A base peak chromatogram (BPI) does not necessarily result in a better signal-to-noise of the peaks with lower intensity as the lock mass is in most cases the most abundant fragment. The numbering of the peaks corresponds with Table 1, peaks marked with * are also present in the procedure blank, peaks marked with ? are investigated unknown contaminants.

Table 2
Exact mass determination of the protonated model compounds

Compound	Elemental composition $[M+H]^+$	Retention time (min)	Theoretical mass	Measured mass	Δ mDa	Δ ppm
Metribuzin	$C_8H_{15}N_4OS$	25.18	215.0967	215.0969	0.2	1.1
Pirimicarb	$C_{11}H_{19}N_4O_2$	11.43	239.1508	239.1501	−0.7	−2.7
Diuron	$C_9H_{11}Cl_2N_2O$	30.20	233.0265	233.0260	−0.5	−2.3
Isoproturon	$C_{12}H_{19}N_2O$	29.33	207.1497	207.1509	1.1	5.5
Metamitron	$C_{10}H_{11}N_4O$	15.77	203.0933	203.0951	1.8	8.8
Atrazine	$C_8H_{15}N_5Cl$	28.83	216.1016	216.1021	0.5	2.5

all model compounds are visible in the TIC chromatogram, and this matrix:analyte ratio is sufficient for triggering the MS to MS/MS switching and acquisition of MS/MS spectra of the proton adducts of each model compound except diuron, Fig. 1B. As can be expected, even better results (not shown) were obtained in the sample with higher fortification level and the more favourable matrix:analyte ratio and automated MS to MS/MS switching resulted in data for all model compounds. We believe that with this approach it is possible to identify contaminants in surface waters even at lower concentrations (0.1 μg/l) by adjusting the concentration factor or the injection volume.

In the surface water extract, in addition to the model compounds, several unknown compounds, present in the surface water extract can be observed in both the survey scan and in the MS/MS data (see further).

3.2. Survey scan

For all the model compounds, the exact mass of the protonated molecules was determined based on the averaged spectra obtained in the survey scan, no background subtraction was performed. The results in Table 2 are in agreement with the results obtained with comparable experiments on a single MS oa-TOF instrument [10]. In addition to the exact mass, isotope patterns can be determined in order to facilitate the identification and structural elucidation, as is in this case for atrazine and diuron. Based on the determined exact mass, possible elemental compositions were calculated using the elemental composition program. It should be noted that all the model compounds were treated as real unknowns, therefore all possible elemental composition hits were searched against the available compound and mass spectra databases. As can be concluded from Table 3, for unknown compounds, exact mass alone is not sufficient for unambiguous identification of contaminants in surface water. With the exception of the halogenated compounds, where the isotope distribution observed with the survey scan limits the number of possible hits, the used approach still results in several structural formulae that have to be evaluated for identification. Combination with additional information such as retention time of standards

Table 3
Elemental composition hits

Compound	Elemental composition $[M+H]^+$	Calculated Elecomp hits	NIST search hits	InfoSpec search Hits	Total structures evaluated
Metribuzin	$C_8H_{15}N_4OS$	9	4	1	4
Pirimicarb	$C_{11}H_{19}N_4O_2$	6	14	1	14
Diuron	$C_9H_{11}Cl_2N_2O$	2	2	2	2
Isoproturon	$C_{12}H_{19}N_2O$	3	20	1	20
Metamitron	$C_{10}H_{11}N_4O$	4	27	2	27
Atrazine	$C_8H_{15}N_5Cl$	1	1	1	1

(if available), UV spectra, fragmentation upon CID, or in-source fragmentation is required [11,12,15].

3.3. MS to MS/MS switching

Although useful structural information can be obtained also by in-source fragmentation on a single TOF instrument, the advantage of the automated MS to MS/MS switching becomes evident especially when analysing complex matrices, such as some surface waters and waste waters in particular.

As mentioned above, by applying automated MS to MS/MS switching, full scan product ion spectra were obtained for all model compounds. Extra information on the stability of the precursor can be obtained by comparing the spectra obtained at different collision energies. An example for pirimicarb is shown in Fig. 2. In this particular case, it can be concluded that the ''unknown'' structure contains several functional groups as the precursor fragments readily already at the lowest collision energy applied, 10 eV. At 25 eV only the fragment ions are present in the spectrum. Exact mass of the fragment ions (and consequently calculation of their possible elemental compositions) can be determined if spectra, obtained at different collision energies, are summed and exact mass calibration is performed using the determined exact mass of the precursor ion, as shown in Table 4.

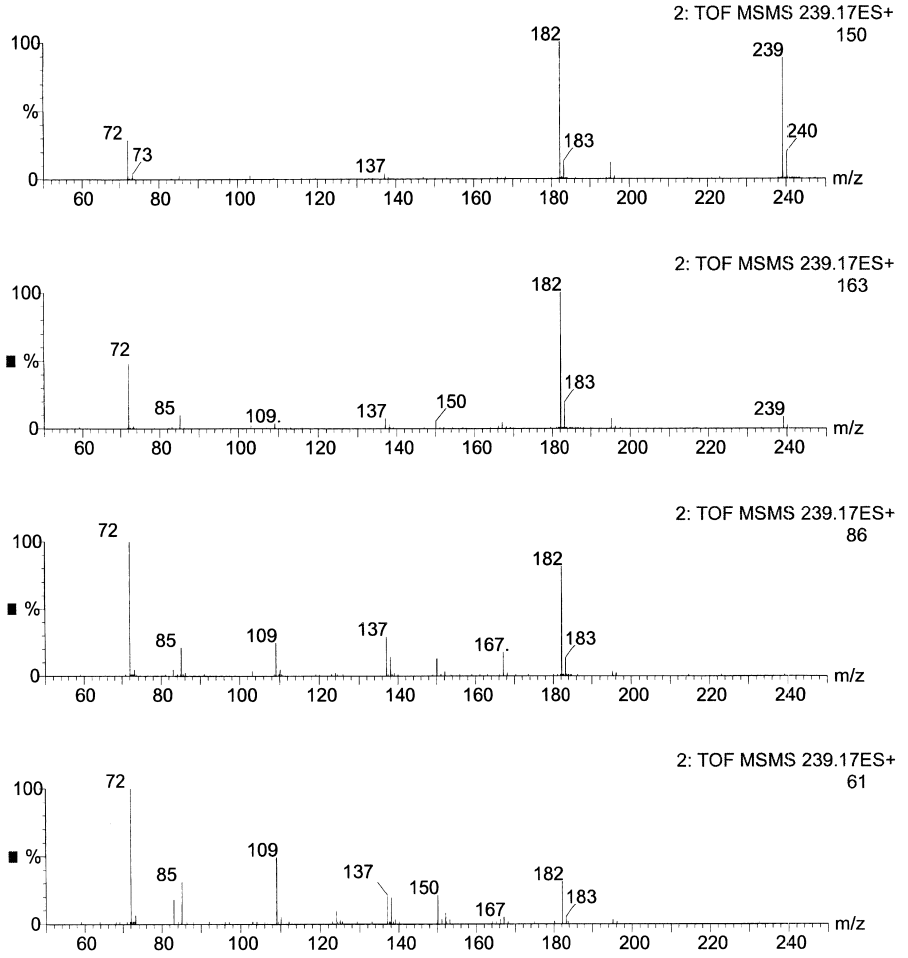

Fig. 2. Product ion spectra of pirimicarb, obtained at different collision energies: (from top to bottom) 15, 20, 25 and 30 eV. For elemental composition of the fragments, see Table 4.

Table 4
Elemental composition of the main product ions of the selected model compounds

Compound	Elemental composition ions	Theoretical mass	Measured mass	Δ mDa	Δ ppm
Metribuzin	$C_3H_7N_4S$	131.0391	131.0383	−0.8	−6.4
	$C_7H_{15}N_4S$	187.1017	187.1033	1.6	8.3
	$C_8H_{15}N_4OS$[a]	215.0967	***215.0969***	0.2	1.1
Pirimicarb	C_3H_6NO	72.0449	72.0465	1.6	21.7
	$C_9H_{16}N_3O$	182.1293	182.1306	1.3	6.9
	$C_{10}H_{19}N_4$	195.1610	195.1627	1.7	8.9
	$C_{11}H_{19}N_4O_2$[a]	239.1508	***239.1501***	−0.7	−2.9
Diuron	C_3H_6NO	72.0449	72.0456	0.7	9.2
	$C_9H_{11}Cl_2N_2O$[a]	233.0248	***233.0260***	1.1	4.8
Isoproturon	C_3H_6NO	72.0449	72.0461	1.2	16.1
	$C_9H_{13}N_2O$	165.1028	165.1035	0.7	4.3
	$C_{12}H_{19}N_2O$[a]	207.1497	***207.1509***	1.1	5.5
Metamitron	C_7H_6N	104.0500	104.0524	2.4	22.8
	$C_9H_{11}N_4$	175.0984	175.0989	0.5	3.0
	$C_{10}H_{11}N_4O$[a]	203.0949	***203.0893***	1.8	8.8
Atrazine	$C_5H_9N_5Cl$	174.0546	174.0563	1.7	9.5
	$C_8H_{15}N_5Cl$[a]	216.1016	***216.1021***	0.5	2.5

In bold: The measured accurate mass of the precursor (determined in the survey scan) was used as the lock mass for accurate mass determination of the product ions.
[a] Precursor ions.

As a complementary tool, exact mass of the neutral losses (and their elemental composition) can be determined, not shown. This information was used to evaluate the most plausible structures obtained by the searches of the libraries, as described above. With the exception of diuron, all the model compounds selected for this study could be identified based on the available information. For diuron, two isomers 3,4-dichloro-*N*,*N*-dimethylphenylurea (diuron itself) and 3,5-dichloro-*N*,*N*-dimethylphenylurea) were found as the most plausible structures. Based on the fragments in the MS/MS spectrum (*m*/*z* 72), it is not possible to distinguish between these two compounds. It should be noted that the MS/MS spectra of all the model compounds were in agreement with the CI-CID library.

3.4. Identification of unknown contaminants in surface water

The developed procedure was applied to the identification of four unknown peaks present in the chromatogram of the fortified surface water extract. The determined exact mass of the unknown protonated molecule at 10.9 min is 196.2057 Da. Within the set limits, the calculation of the possible elemental composition results in only one formula, $C_{13}H_{26}N$ (−0.9 mDa). Search of the databases results in eight structures with this elemental composition. Based on the product ion spectra of precursor *m*/*z* 196, the unknown compound is proposed to be *N*,*N*-di-cyclohexyl-*N*-methyl-amine (Fig. 3). Even though not found in the NIST library, this compound is listed in the Infospec database [13] and is often found in GC–MS chromatograms of neutral extracts of surface waters.

Based on the survey scan, the exact mass of an unknown compound with retention time 18.6 min was determined to be 239.1245 Da. The calculated elemental compositions were searched against the available databases, the precursor composition $C_9H_{15}N_6O_2$ (−1.1 mDa) resulted in three possible

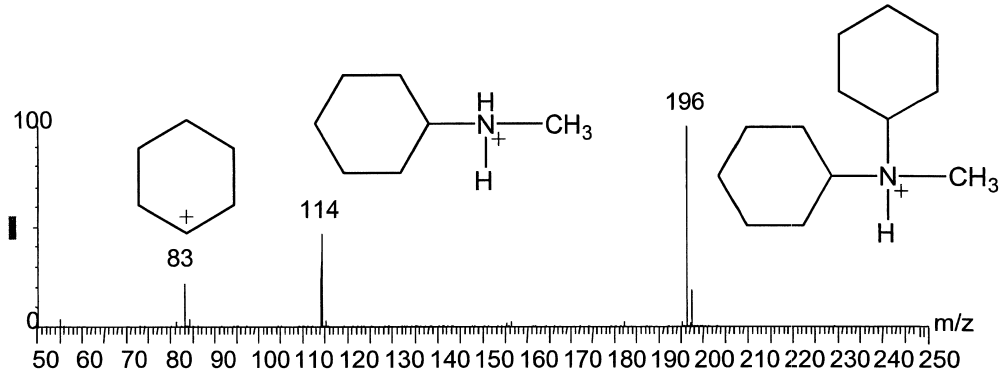

Fig. 3. Summed product ion spectrum (across all collision energies) of an unknown compound found in the surface water extract. Proposed structures of the precursor ion (m/z 196) and the product ions.

structures, precursor composition $C_{13}H_{19}O_4$ (−3.8 mDa) in 32. Only three fragments were observed in the product ion spectrum of the precursor 239, even at the highest collision energy applied: m/z 163 (100%), 177 (20%) and 209 (5%). Based on this information, we did not succeed in proposing one of the found structures as the structure of the unknown compound.

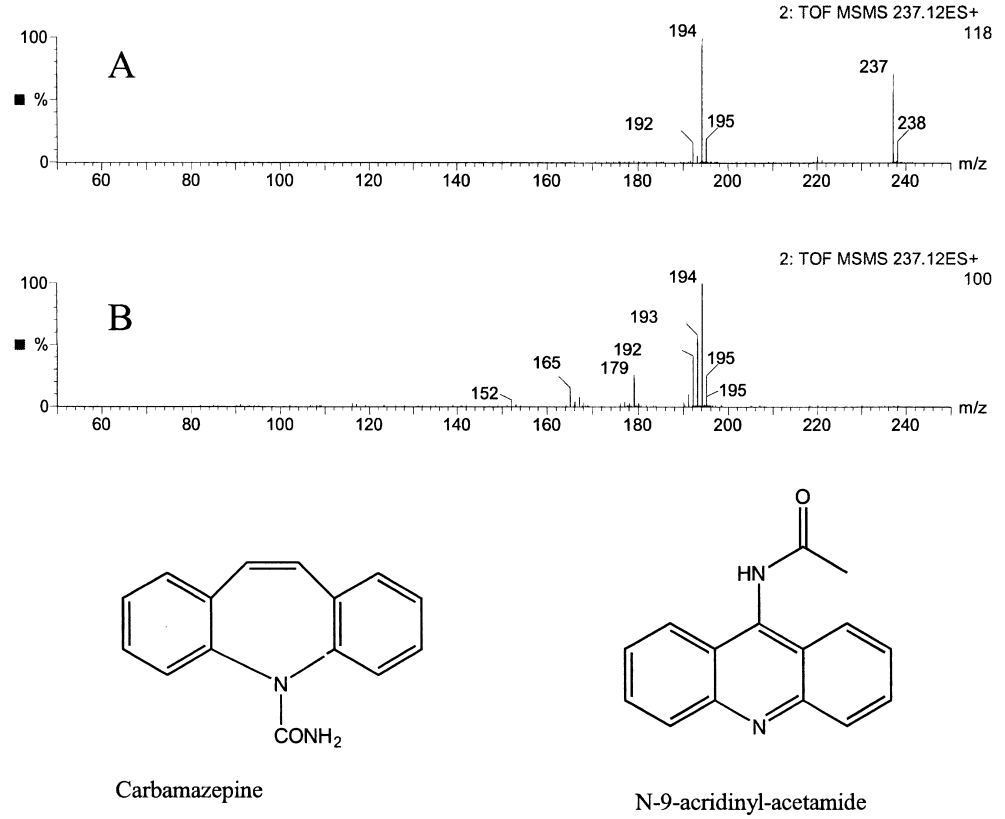

Fig. 4. Product ion mass spectra of an unknown compound with retention time 23.6 min found in surface water extract and the two most plausible structures. Collision energy: 15 eV (A) and 30 eV (B).

The exact mass of an unknown compound with retention time of 23.7 min was determined to be 237.1041 Da. Calculation of possible elemental compositions resulted in 11 formulae within the set limits, which were searched against the available libraries. Consequently, 24 possible structures were evaluated and matched with the fragmentation pattern observed in the product ion spectra, Fig. 4A and B. Two isomeric compounds, carbamazepine and *N*-9-acridinyl-acetamide (Fig. 4) were selected as most likely. All the fragments observed match very well with the entry of carbamazepine in the CI-CID MS/MS library. Furthermore, both fragments m/z 179 and m/z 165 are unlikely to be formed from the acridine structure. Proposed structures of the product ions are shown in Fig. 5. Carbamazepine (theoretical mass 237.1028, Δ=1.3 mDa), is a widely used pharmaceutical, often observed in waste and surface waters [16,17].

The determined exact mass of an unknown compound with retention time 28.3 min is 279.0941 Da. Calculation of the possible elemental composition provides 15 hits within the set limits, which were searched against the available databases. Only two elemental compositions, $C_{18}H_{16}OP$ (Δ=0.2 mDa) and $C_{13}H_{15}N_2O_5$ (Δ=−4.0 mDa) resulted in total five possible structures (Fig. 6A–E). In the MS/MS spectra, three main fragment ions are observed. Even at high collision energies, only one ion, formed by the loss of a benzene ring (concluded from the exact mass of this neutral loss) is predominant, Fig. 7D. This rules out structures 6B, D and E. As structure 6C contains several functional groups, it is unlikely, that the most intense fragment ion would result from a benzene ring, e.g. a fragment with m/z 105 formed upon cleavage of the amide bond is more plausible. The obtained MS/MS spectrum was compared to spectrum of triphenylphosphine oxide (Fig. 6A, TPPO) in the CI-CID library [14] and shows a good agreement. TPPO is toxic and is often found in surface waters [17].

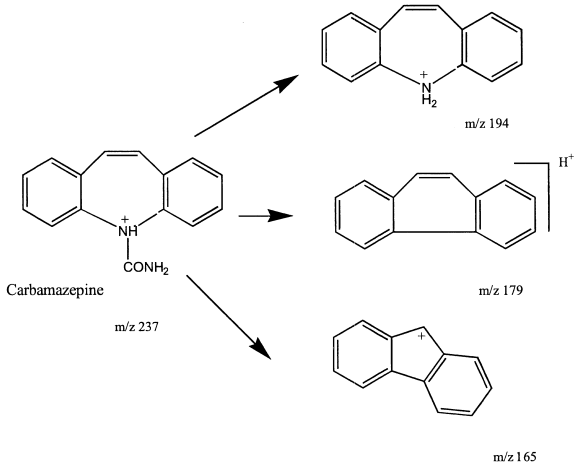

Fig. 5. Proposed structures of the observed product ions of carbamazepine.

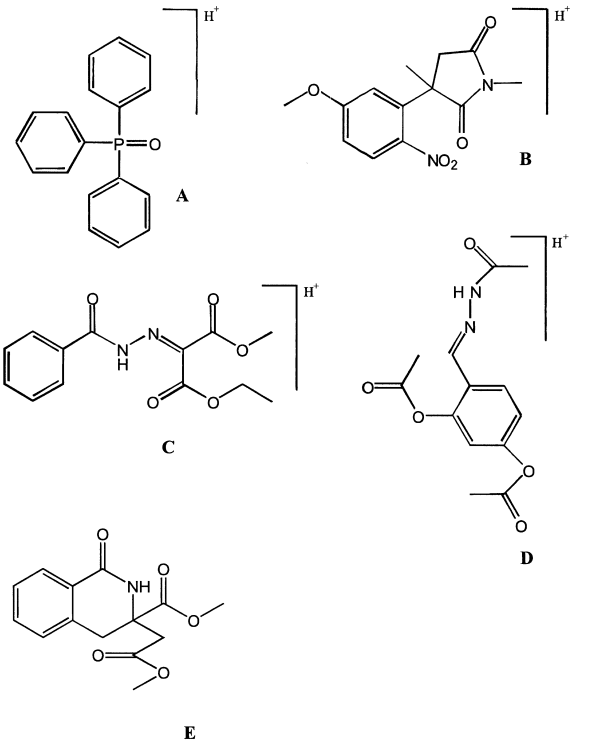

Fig. 6. Possible structural hits for the elemental compositions calculated for the determined exact mass (279.0971 Da) of an unknown compound with retention time 28.3 min, present in surface water extract.

4. Conclusions

An LC screening procedure for unknown contaminants in water has been developed, using the modern tandem, quadrupole-time of flight mass

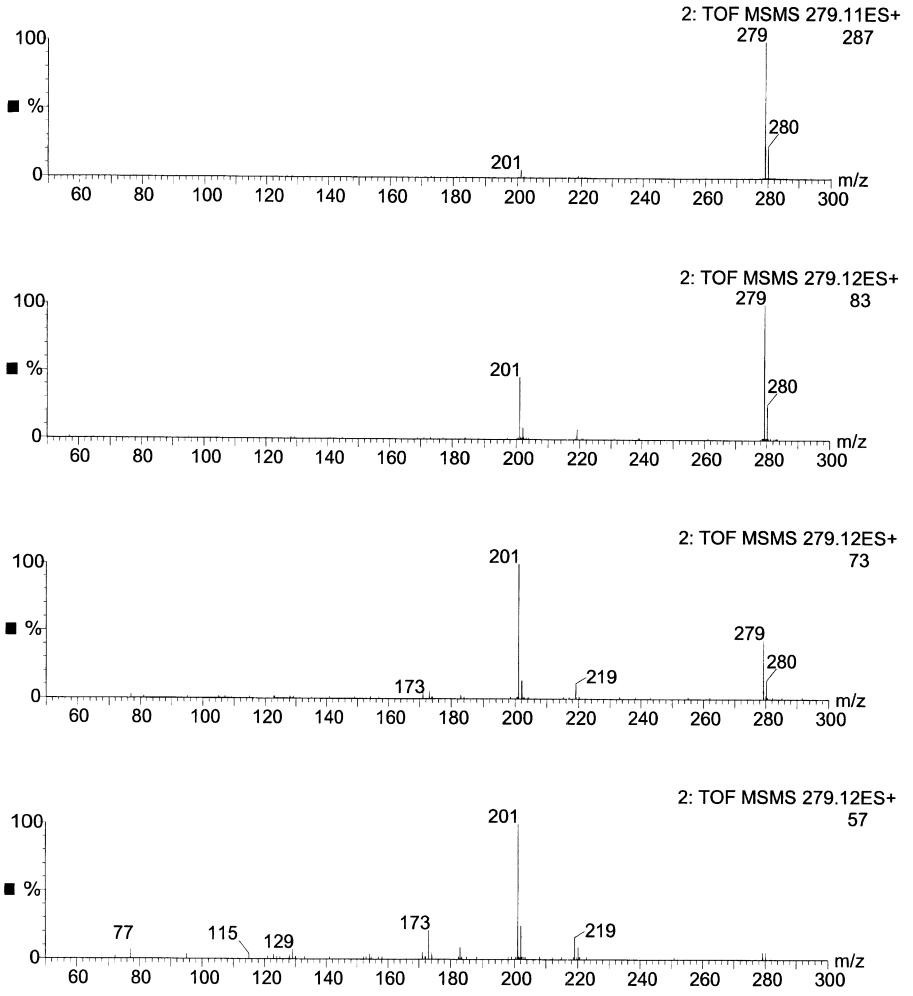

Fig. 7. Product ion spectra of an unknown compound with retention time 28.3 min, obtained at different collision energies (from top to bottom): 15, 20, 25 and 30 eV.

spectrometers. By applying the automated MS to MS/MS switching, maximum structural information can be obtained for both selected model compounds as well as unknown contaminants, present in surface water extracts. Based on the exact mass determination and consequently the calculated elemental composition, in combination with product ion spectra, all the selected model compounds could be identified in surface water extracts to which they were added in relevant concentrations (corresponding to 0.25 μg/l in the surface water). Furthermore, four unknown compounds were observed in both the survey scan and the MS to MS/MS automated switching. By applying the developed data processing procedure, the structure of three of the unknown compounds was elucidated: carbamazepine, TPPO and *N*,*N*-dicyclohexyl-*N*-methyl amine. The structure of the fourth compound remained unresolved within this study.

The success of the approach described in this paper is dependent on the availability of compound databases and mass spectra libraries, which can be searched. However, the availability of exact mass (elemental composition) of the unknown compound in combination with the fragmentation pattern brings the environmental analytical chemist a big step

closer to a screening approach for (polar) unknown contaminants. The approach described in this paper was applied in both positive and negative ionisation mode for structural elucidation of harmful compounds in wastewater and will be described elsewhere.

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