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# Rapid target analysis of microcontaminants in water by on-line single-short-column liquid chromatography combined with atmospheric pressure chemical ionization ion-trap mass spectrometry

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**Abstract**

The applicability of trace enrichment and separation of microcontaminants on a single 10×2 mm I.D. high-pressure-packed liquid chromatography (LC) column, combined on-line with an atmospheric pressure chemical ionization (APCI)–ion-trap tandem mass spectrometry (MS–MS) instrument was studied for the target analysis of herbicides in river water. The total analysis time was 15–20 min. With the on-line short-column LC–MS–MS method, detection limits of 0.1–1 μg/l can be achieved using only 4 ml of river water. However, the results obtained for a mixture of six triazines were considerably better than those for a mixture of eight phenylureas. An attempt is made to explain this difference on the basis of various processes that occur within the ion trap and the measurement procedure itself. © 1998 Elsevier Science B.V.

*Keywords:* Trace enrichment; Atmospheric pressure chemical ionization; Mass spectrometry; Ion-trap mass spectrometry; Triazines; Pesticides

## 1. Introduction

In recent years, several analytical methods have been developed for the monitoring and screening of organic microcontaminants in surface and ground water [1,2]. In order to detect compounds at the very low levels encountered in such samples, sample concentration prior to analysis is a necessity. Nowadays, the most popular method of preconcentration is to perform on-line solid-phase extraction (SPE). For identification or confirmation of the identity of compounds, mass spectrometry (MS) is frequently used [3–8]. The on-line combination of solid-phase extraction (SPE)–liquid chromatography (LC)–MS has successfully been applied for the confirmation and quantification of microcontaminants of widely different polarity in surface water [9–11]. When the goal of the analysis is to detect target compounds only, the conventional run times can be dramatically reduced, from approx. 60 min to about 15 min per sample, by taking advantage of the high selectivity that can be achieved by (tandem) MS procedures.

Reduction of the analysis time in on-line SPE–LC–MS was recently demonstrated by us using a single short (but high-pressure packed) LC column of 20, or even 10, mm in length for both SPE and analytical separation [12–14]. The single-short-column approach was found to enable the rapid target analysis of up to eight target compounds, some of which may even be isomers. MS detection was

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performed using either a thermospray (TSP) [15] or an atmospheric pressure chemical ionization (APCI) interface [16]. For the target analysis of six triazine and eight phenylurea herbicides in surface water at the 0.1 μg/l level, a total analysis time of only 10–15 min was required by optimally tuning the chromatographic resolution on the LC column and the selectivity of the MS–MS system in the selected reaction monitoring (SRM) mode. The ruggedness of the total procedure was demonstrated by a series of overnight runs.

The above experiments were performed on relatively expensive triple-stage quadrupole instruments (QqQ). Recently, a commercial LC–MS system based on ion-trap technology was introduced, i.e., the LCQ. The latter type of instrument is considerably less expensive than a triple quadrupole MS system and it would therefore be well suited for target-type screening procedures in environmental analysis. Both types of instruments can be used to perform MS–MS in product-ion mode and SRM mode. There are also differences between the instruments: The ion-trap instrument also allows multiple-stage MS–MS to be performed. In addition, it is important to note that the measurement procedures of both types of instruments in MS and MS–MS are quite different. This will be discussed in more detail in Section 3.

In this paper, the potential of combining the single-short-column approach and ion-trap-based LC–MS detection using an APCI interface is demonstrated. In order to be able to directly compare the results with previous data obtained using a triple quadrupole instrument, the same sampling and separation conditions, and the same type of analytes, were used. This allowed a true comparison of the scanning capabilities of the respective instruments.

## 2. Experimental

### 2.1. Chemicals and reagents

HPLC-gradient-grade methanol, acetonitrile and water were from J.T. Baker (Deventer, Netherlands). The triazine and phenylurea herbicide standards were obtained as analytical standards (over 95% purity) from Riedel-de Haën (Seelze, Germany). Stock solutions were prepared by dissolving 10 mg of each compound in 10 ml of acetonitrile; these were stored in the dark at −20°C. Because simazine was less soluble in acetonitrile, a standard stock solution of 200 μg/ml was prepared. Standard mixtures were prepared by diluting the stock solutions with HPLC-grade water to give concentrations ranging from 5 ng/ml to 5 μg/ml. The mixtures were used for standard injections and for spiking the surface water samples. The standard mixtures were stored at 4°C throughout the study.

Surface water was collected from the river Rhine at Watertransportbedrijf Rijn-Kennemerland (WRK) (Nieuwegein, Netherlands) in April 1997. Before use, 1 l was filtered over a 0.45-μm membrane filter (Schleicher and Schuell, Dassel, Germany). Spiking was done by adding an appropriate amount of a standard mixture to 100 ml samples.

### 2.2. Instrumentation and columns

#### 2.2.1. Short-column LC

Trace enrichment and separation were done on a short column (10×2 mm I.D.) packed with 8 μm $C_{18}$ bonded silica. These high-pressure-packed short columns were from batches that were kindly provided by Spark Holland (Emmen, Netherlands).

#### 2.2.2. LC set-up

The LC eluent was delivered by an HP 1050 LC system equipped with a quaternary solvent delivery system (Hewlett-Packard, Waldbronn, Germany). The eluent was degassed by bubbling helium through it. Automated sample handling, including conditioning and washing of the 10 mm column and loading of the water sample onto the column, was done by a Prospekt (Spark Holland) sample handling module equipped with three six-port switching valves and a solvent delivery unit (SDU) (for set-up, see Ref. [16]). The on-line analyses were carried out in an automated fashion. During trace enrichment, the LC and MS systems were in the ‘‘waiting’’ position. After the enrichment procedure had been completed, a contact closure signal was given to the HP 1050 to start the LC run. At the same time, the HP 1050 gave a contact closure signal to the LCQ.

#### 2.2.3. MS–MS

MS–MS was performed on a Finnigan MAT (San

Table 1
Gradient LC conditions

| Compounds | Linear gradient elution conditions[a] | Flow-rate (ml/min) |
|---|---|---|
| Triazines | A–B (80:20, v/v) to (50:50, v/v) in 5 min | 0.5 |
| Phenylureas | A–B (95:5, v/v) to (50:50, v/v) in 5 min, held at (50:50, v/v) for 2 min | 0.5 |

[a] Eluents: (A) Water–methanol (95:5, v/v) and (B) water–methanol (5:95, v/v).

José, CA, USA) LCQ ion-trap MS equipped with an APCI interface. The interface was operated with the heated capillary at a temperature of 165°C and a voltage of 45 V. The temperature of the vaporizer was set at 450°C and the nitrogen sheath and auxiliary gas flows were set at 26 and 3 (instrument settings in arbitrary units), respectively. For positive ions, the corona discharge current was maintained at 7.0 μA. The analyser temperature was held at 32°C. For all experiments, the multiplier voltage had to be increased by 300 V from its standard setting (700 V) and the pulse counting had to be decreased to 5000 to obtain optimum conditions.

### *2.3. Analytical conditions and procedures*

Gradient LC elution was performed using water–methanol mixtures, as is indicated in Table 1. The trace-enrichment procedure, which was similar to previous procedures, is summarized in Table 2. The linearity of the method was tested over the range of 0.1 to 10 μg/l, which is the relevant range in environmental analysis. However, as indicated below, the lower limits could not be detected in all cases.

In MS–MS, the collision energy, which with the LCQ is given as a percentage (see below), was optimized for each individual compound. The optimized collision energies are shown in Table 3. In quantitative analysis, MS–MS was performed by selecting $[M+H]^+$ as the precursor ion and, depending on the compound, either scanning the product-ion mass spectrum or performing SRM. The precursor and produced product-ions and abundances are included in Table 3. The ion injection time was set at 100 ms (see below).

In the LCQ, the collision energy is specified as a percentage. It must be emphasized that the collision energy in an LCQ experiment is defined in a completely different manner from that in a QqQ instrument. In the latter, the collision energy is derived from the direct-current potential offset of the collision cell. In the LCQ, the collisions are induced by a radio frequency (RF) potential applied to the

Table 2
Time schedule for the Prospekt sample preconcentration procedure

| SDU | | Prospekt | | | | | |
|---|---|---|---|---|---|---|---|
| Time (min:s) | Purge flow (ml/min) | Solvent | Event[a] | Valve | | | Auxiliary |
| | | | | 1 | 2 | 3 | 5 |
| 0:00 | 1.0 | Methanol | Condition column | Purge | Purge | Purge | |
| 2:00 | 1.0 | Water | Activate column | | | | |
| 4:00 | 1.0 | Sample | Load sample on column | | | | |
| 8:00 | 1.0 | Water | Wash column | | | | |
| 9:00 | 1.0 | | Start LC | Elute | | | On |
| 9:01 | 1.0 | | Desorb analytes with eluent to MS | | | | Off |
| 9:05 | 2.0 | Methanol | Flush/clean SDU lines | | | | |
| 11:05 | 0.0 | Off | | | | | |
| 15:00 | | | End of run | | | | |

[a] Wash column, remove inorganic salts from column. Start LC, contact closure to start LC programme.

Table 3
Protonated molecules and product ions (monitored in MS–MS experiments) using single-short-column LC–APCI–MS–MS (LCQ) of 100 ng loop injection experiments

| | Compound | CE | $[M+H]^+$ | Product ions in $MS^2$ | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Scanfilter | *p*1 | *p*2 | *p*3 | *p*4 |
| 1 | Simazine | 18 | 202.0 | 120–180 | 124.1(100) | 131.9 (55) | 174.1(35) | |
| 2 | Cyanazine | 18 | 241.1 | 213.5–214.5 | 214.1(100) | | | |
| 3 | Atrazine | 18 | 216.0 | 173.6–174.6 | 174.1(100) | | | |
| 4 | Propazine | 18 | 230.0 | 170–190 | 188.1(100) | | | |
| 5 | Sebutylazine | 18 | 230.0 | 170–190 | 174.1(100) | | | |
| 6 | Terbutylazine | 18 | 230.0 | 170–190 | 174.1(100) | | | |
| 7 | Desmethylmetoxuron | 16 | 201.0 | 157.5–158.5 | 158.0(100) | 183.9(34) | 123.1(17) | |
| 8 | Metoxuron | 15 | 229.1 | 71.6–72.6 | 72.0(100) | | | |
| 9 | Monuron | 18 | 199.1 | 71.6–72.6 | 72.1(100) | | | |
| 10 | Chlorotoluron | 17 | 213.0 | 71.6–72.6 | 72.0(100) | | | |
| 11 | Diuron | 18 | 233.0 | 71.6–72.6 | 72.0(100) | | | |
| 12 | Linuron | 18 | 249.0 | 155.0–225.0 | 182.2(100) | 160.0(48) | 192.0(10) | 187.9(8) |
| 13 | Chlorobromuron | 19 | 292.9 | 180.0–206.0 | 182.2(100) | 204.0(45) | 232.1(8) | 261.8(7) |
| 14 | Neburon | 19 | 275.3 | 80.0–120.0 | 88.1(100) | 113.9(66) | | |

[a] CE, collision energy (%); scan filter, product-ion scan range set during experiments; *p*1–4, product ions; numbers in brackets give relative abundances of the product ions.
For quantification, the response of the most abundant product ions was used.

endcap electrodes. The maximum voltage that can be applied is 5 V. The percentage collision energy refers to the percentage of the 5 V that is actually applied.

## 3. Results and discussion

### 3.1. Short column LC–APCI–MS–MS of triazines

For the on-line trace enrichment and separation of a series of triazines on a single short LC column with subsequent APCI–MS–MS detection, the sample pretreatment and set-up were identical to those used previously with a QqQ instrument (TSQ 7000 from Finnigan MAT). After preconcentration of 4 ml of surface water, the LC separation was performed using a steep linear gradient. This suffices to effect an almost complete separation of six triazine herbicides on a 10-mm long $C_{18}$ column. Initially, the analytical performance of the complete set-up was tested by using 10 μl loop injections of the standard mixture. The loop injections were performed to provide information about the sensitivity and selectivity of the procedure. When monitoring the six triazines simultaneously in the full-scan product-ion or SRM mode, detection limits were in the range of 100–200 pg (signal-to-noise ratio ($S/N$)=3).

Fig. 1 shows a chromatogram of the trace enrichment and separation of six triazines spiked at the 0.2 μg/l level in 4 ml of water from the river Rhine. The results at this concentration level are fully satisfactory and identification of the compounds of interest can easily be achieved. The detection limits of the six triazines in 4 ml of surface water were 100 ng/l, except for simazine for which it was 200 ng/l ($S/N$=3). The linearity of the procedure was evaluated by analysing 4 ml samples spiked at concentrations ranging from 0.2 to 10 μg/l. Peak integration was performed over the signal of the most intense product ions for each individual triazine. For all analytes, the calibration curves were linear, with $r^2$ values of over 0.95 (five data points in triplicate). This can be considered to be a satisfactory, but not an extremely good, result. The total time of analysis (trace enrichment, separation and detection) was 20 min.

The applicability of the single-short-column LC approach for the target analysis of triazines was demonstrated by the analysis of several surface water samples. Target analysis allowed the rapid detection

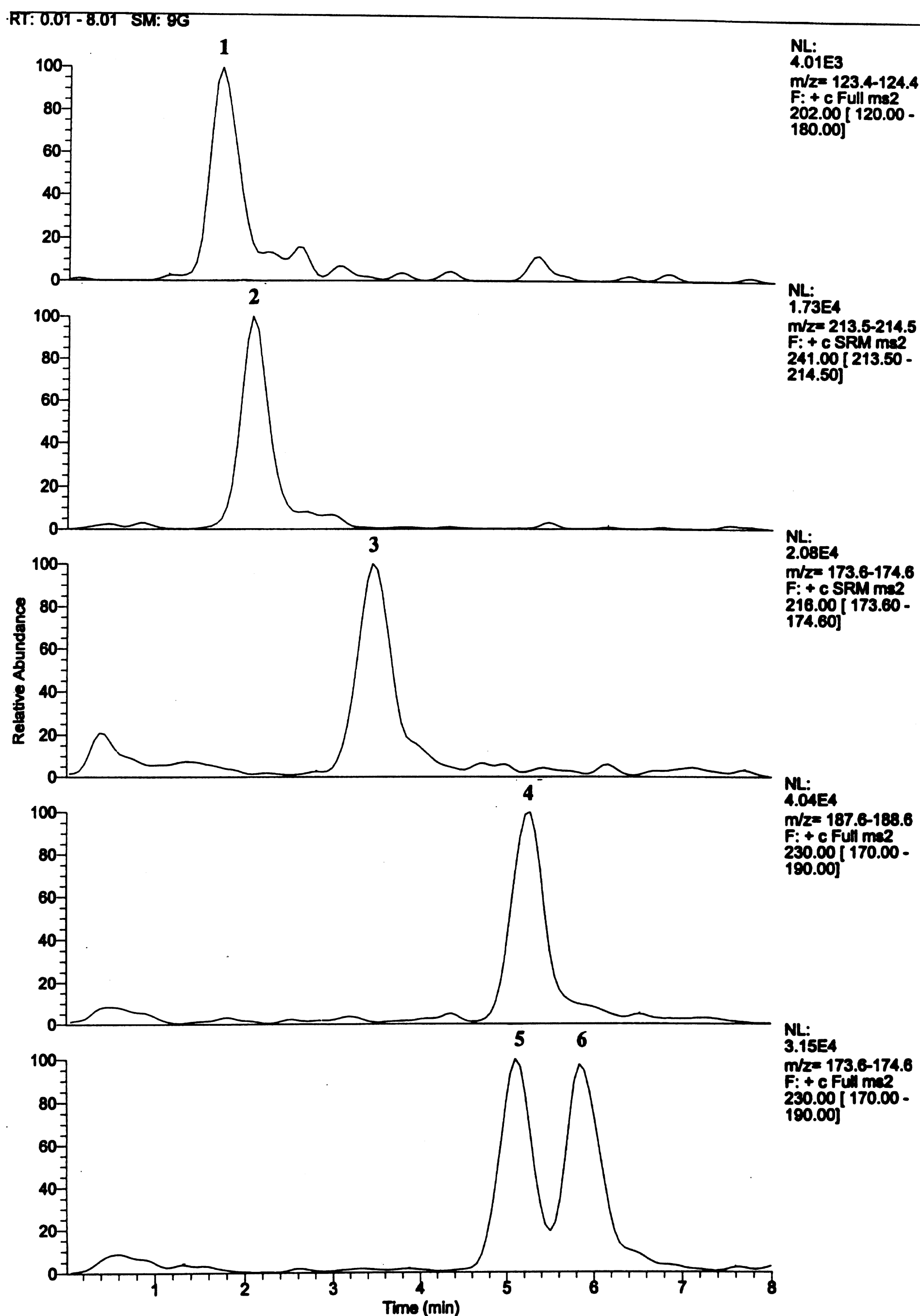


Fig. 1. Target analysis of six triazines at the 0.2 μg/l level in a 4-ml water sample on a 10×2 mm I.D. 8 μm $C_{18}$ bonded silica column. All sampling flow-rates were 1 ml/min. Conditioning was with 2 ml of methanol and 2 ml of water and clean-up was with 1 ml of water (Table 2). Linear gradient from A–B (80:20, v/v) to (40:60, v/v) in 5 min at a flow-rate of 0.5 ml/min (Table 1). For peak assignment and precursor and product ions selected for each analyte, see Table 3. SRM conditions: Ion injection time, 100 ms. For other conditions, see Section 2.

and identification of atrazine at levels of 80–100 ng/l.

### 3.2. Short-column LC–APCI–MS–MS of phenylurea herbicides

When using the same set-up as in Section 3.1 and the analytical conditions summarized in Table 1, a partial separation of the eight phenylurea herbicides was obtained on the 10-mm long $C_{18}$ bonded silica column. With 10 μl loop injections and detection in either the full-scan product-ion or SRM mode, the detection limits were in the range of 1–2 ng ($S/N=3$).

Typical results obtained after single-short-column LC–MS–MS analysis of 4 ml surface water samples spiked with the phenylurea mixture at the 2 μg/l level are shown in Fig. 2. It should be added that the present result could not be improved by performing time-scheduled product-ion monitoring, as will be explained below.

Triplicate analyses of spiked samples in the range of 0.5–10 μg/l showed linearity, with $r^2$ values of between 0.955 and 0.995. A repeatability study performed at the detection limit of the majority of the phenylurea herbicides, i.e. 1 μg/l, resulted in R.S.D. values of peak areas of 32–85% ($n=15$). These results are distinctly worse than in our earlier study with a triple quadrupole MS (4–5% at the 0.5 μg/l level). However, one has to bear in mind that they were obtained rather close to the detection limits of the phenylureas, which were in the range of 0.5–1 μg/l for 4 ml samples, while they were distinctly better (10–100 ng/l) in the quoted paper [16].

### 3.3. Comparison of ion-trap and QqQ data

The single-short-column approach used in this study was similar to that used in an earlier study with a QqQ as the mass spectrometer [16]. It will therefore be of interest to compare the data obtained with the two types of instrument. Detection limits with loop injections and the single-short-column approach using 4 ml samples as well as repeatabilities for ten consecutive analyses of 4 ml samples are compared in Table 4. From the manufacturer's specifications, it can be envisaged that the detection limits achievable with the ion trap system will be five–tenfold higher than with a QqQ. While the data for the triazines agree with these expectations, this is certainly not true for the phenylureas. The detection limits with the ion-trap system are 10–30-fold higher than those obtained on a QqQ [16]. These somewhat disappointing results can, to some extent, be explained by the operation of the ion-trap system.

The measurement procedures of QqQ and ion trap in MS and MS–MS are quite different. With a QqQ, the ions that are continuously generated in the APCI source are continuously transmitted to the first quadrupole for precursor-ion selection, to the octapole collision cell for collision-induced dissociation (CID) and to the third quadrupole for product-ion separation and detection. The various steps of the process take place simultaneously but are separated in space. With an ion trap, however, these steps are separated in time, with a sequence of events taking place in the same space. Given the single-short-column approach and the short analysis time, the time schedule of events in the MS–MS process is thus of major importance. The (deliberately) poor chromatographic resolution on the single short column prohibits the use of time-scheduled product-ion or SRM procedures, which, in turn, leads to somewhat poorer analyte detection limits. When comparing the triazines and phenylureas, this effect is enhanced by the fact that only five precursor–product ion transitions have to be monitored for the triazines, while eight have to be monitored for the phenylureas.

In the QqQ, the time schedule of events is determined by the acquisition time per ion as well as the time the instrument needs to change from monitoring one precursor product ion transition to another. From our optimization of the scan time [16], it was found that a sequence of eight precursor–product ion transitions can be monitored within 2.4 s. Some ten data points could then be acquired per chromatographic peak. With the ion trap, the time schedule of events is more complex. Each scan comprises a number of microscans. Each microscan consists of a number of steps. First, a pre-ionization time is taken to determine the optimum ion injection time in order to avoid saturation of the ion trap (and spectral distortion by space charging). Next, when

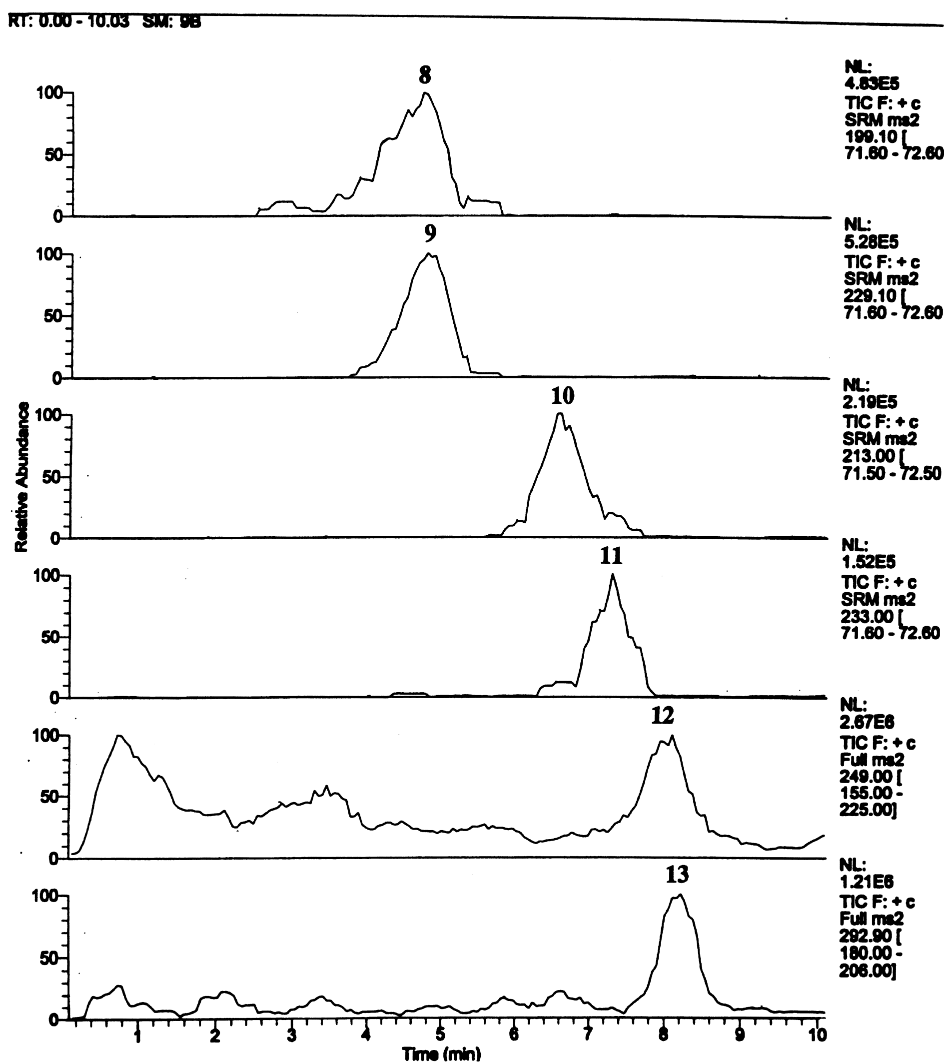


Fig. 2. Short-column LC–APCI–MS–MS SRM chromatogram of trace enrichment of 4 ml of water from the river Rhine spiked with a mixture of phenylurea herbicides at the 2 μg/l level on a 10×2 mm I.D. column. All sampling flow-rates were 1 ml/min; the elution flow-rate was 0.5 ml/min. Conditioning was with 2 ml of methanol and 2 ml of water, and clean-up was with 1 ml of water (Table 2). The linear gradient was from A–B (95:5, v/v) to (50:50, v/v) in 5 min and it was held at (50:50, v/v) for 2 min (Table 1). For peak assignment and precursor and product ions selected for each analyte, see Table 3. For other conditions, see Section 2.

the storage RF voltage at the ring electrode of the trap has been set, ions are sampled from the APCI source during the optimum ion injection time that has been determined. Then, the precursor ion is selected by applying appropriate ion isolation RF waveform voltages to the endcaps, while the RF storage voltage at the ring electrode is set at an appropriate value to trap both the precursor ion and its product ions. Next, a resonance excitation RF voltage is applied to the endcap electrodes to perform CID. The product ions are stored and subsequently scanned out of the trap to the detector in the usual way, i.e., by increasing the RF voltage at the ring electrode and applying a resonance ejection RF voltage to the endcaps. Finally, the instrument is prepared for the next microscan, which means re-

Table 4
Comparison of analytical data of short-column-QqQ and short-column-ion trap MS–MS

| | Triazines | | Phenylureas | |
|---|---|---|---|---|
| | QqQ | Ion trap | QqQ | Ion trap |
| Detection limits (pg; loop injections) | 30–100 | 100–200 | 30–200 | 1000–2000 |
| Detection limits (ng/l single short column; 4 ml sample) | 10–30 | 100–200 | 10–100 | 500–1000 |
| Repeatability (4 ml sample) | at 0.5 μg/l: R.S.D. values<5% ($n$=10) | Not tested | at 0.5 μg/l: R.S.D. values<4% ($n$=10) | at 1 μg/l: R.S.D. values 32–85% ($n$=15) |

moving all ions and setting the storage and gate lens voltages for the next pre-ionization scan. In practice, many of the time intervals of the various events cannot be influenced by the operator. For a given scan range, which is of course determined by the application, the most important parameter appears to be the ion injection time. For instance, it was found that the duration of a scan for one precursor product ion transition is 0.37 s when the ion injection time is 100 ms, and is 0.30 s when the ion injection time is 50 ms. For eight precursor–product ion transitions, this would result in total cycle times of 2.9 and 2.4 s with ion injection times of 100 and 50 ms, respectively. However, in practice, the total cycle times for eight transitions were found to be 4.0 and 3.4 s, respectively. As a result, often only six scans per chromatographic peak, or even less, could be acquired in the single-short-column procedure, which is generally not sufficient to adequately describe the chromatographic peak. In conclusion, it was found that the interscan time plays a significant role in the procedure with the LCQ.

Next to the unfavourable time schedule, another aspect is of importance as well. The version of the LCQ ion-trap system we used was limited with respect to the mass range of product ions that can be stored. Currently, only ions with an $m/z$ larger than ca. one-third of the precursor-ion $m/z$ can be efficiently stored for later detection. Furthermore, ions with $m/z$ values below 50 cannot be stored at all. For the phenylureas, these limitations are important. For metoxuron, monuron, chlorotoluron and diuron, only one product ion can be monitored. The most intense product ion is found at $m/z$ 72 [due to $(CH_3)_2-N=C=O^+$], while another product ion is present at $m/z$ 46 [due to $(CH_3)_2-NH_2^+$]. The latter is lost, while the $m/z$ 72 ion is relatively close to the one-third storage limit.

From the experimental results, we also learned that smoothing of the peaks, which is routinely applied in most data systems nowadays, should be performed with great care. As a result of the smoothing and the degree of smoothing applied, the effects described above are easily overlooked, because a smoothed peak appears to be wider than it actually is.

#### 3.3.1. MS$^n$ option

An additional feature of the LCQ ion-trap MS–MS instrument is that it allows multiple stages of MS–MS. Although this feature obviously is of more importance in structure elucidation than in quantitative target compound analysis, some experiments with multiple MS–MS were performed, i.e., with the triazines. It was found that, with the collision energies used (17–18%; cf. Table 3), all of the triazines tested, with the exception of simazine, yielded only one major product ion in the first stage of MS–MS. In that respect, the product-ion mass spectra from the ion trap differ from those obtained with a QqQ instrument. While this may be a (serious) disadvantage when a more general screening is pursued, it is not important in our target screening. In a second or third stage of MS–MS, additional structural information may be obtained by using a product ion from the previous stage as the precursor ion. As an example, a schematic diagram of the breakdown of propazine in each of the sequential MS–MS stages is given in Fig. 3 [17–19]. Some product ions observed for the triazines differed from those observed in QqQ product-ion mass spectra (see Table 5). In terms of information content, the same

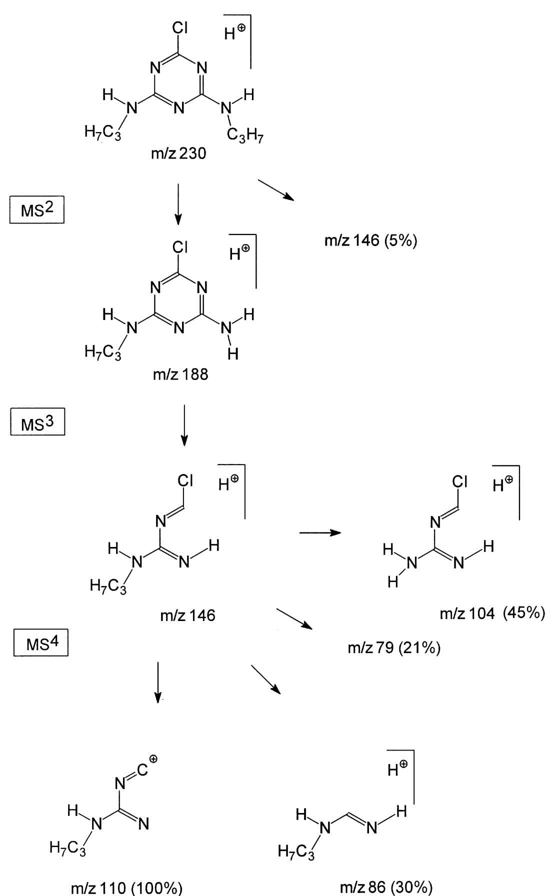


Fig. 3. Breakdown of propazine in multistage MS–MS in an ion-trap mass spectrometer. Ion identification is based on ref. [20].

structural information can be obtained, although in the ion trap, a multi-MS–MS procedure is required, which is more time-consuming within the time-frame of the narrow chromatographic peak from the single short column. The further possibility of the ion-trap system performing consecutive reaction monitoring, i.e., SRM over a number of MS–MS stages, in order to monitor for instance the precursor–product ion transition from $m/z$ 230 to 79 for propazine (cf. Fig. 3), has not yet been studied.

## 4. Conclusions

The applicability of an LCQ ion-trap MS–MS system for the rapid analysis of triazines and phenylureas in surface water using the single-short-column approach was studied. Whereas satisfactory results were obtained in terms of detection limits for the triazine herbicides when using 4 ml water samples, this was not true for the phenylureas. The poorer performance with the latter compound class can be attributed to several limitations in the current version of the LCQ ion-trap mass spectrometer. Primarily, these are the rather long interscan times required by the instrument between monitoring various precursor–product ion transitions, and the problems encountered if there are large differences in $m/z$ values between precursor ion and product ion (as is true for the phenylureas), which results in less efficient storage of product ions. Under these conditions,

Table 5
Comparison between protonated molecules and product ions (monitored in $MS^2$, $MS^3$ and $MS^4$ experiments) using single-short-column LC–APCI–MS–MS ion trap instrument and the QqQ instrument (monitored in $MS^2$) for propazine

| Compound | Precursor $MS^2$ | Precursor $MS^3$ | Precursor $MS^4$ | Product ions[a] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Product ions in $MS^2$ | | | | |
| Propazine | 230 | | | 188 (100) | 146 (5) | | | |
| | | | | Product ions in $MS^3$ | | | | |
| Propazine | | 188 | | 146 (100) | | | | |
| | | | | Product ions in $MS^4$ | | | | |
| Propazine | | | 146 | 110 (100) | 146 (50) | 104 (45) | 86 (30) | 79 (21) |
| TSQ | | | | Product ions in $MS^2$ | | | | |
| Propazine | 230 | | | 146 (100) | 188 (65) | 110 (14) | 230 (12) | 79 (6) |

[a] CE, collision energy 17% in ion trap and −25 eV for QqQ; numbers in brackets give relative abundances.

identifying eight ions obviously is too much to handle. Therefore, a careful selection of the target analytes combined in one run is to recommended. If this is done, single-short-column LC–MS can be performed with an ion-trap instrument at a considerably reduced cost compared with a QqQ-type instruments.

One way to improve analyte detectability would be to preconcentrate samples larger than 4 ml, such as the 15 ml samples that were used frequently in earlier work [12–14]. Another approach would of course be to combine a ''conventional'' on-line SPE–LC set-up with the ion-trap system, which will provide the relatively longer retention times needed to perform time-scheduled product-ion scanning or SRM and to preconcentrate up to 100 ml of surface water [11]. One has to keep in mind, however, that this procedure will significantly increase the total analysis time and decrease sample throughput and, consequently, cannot be considered as a suitable alternative within the scope of the present study.

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