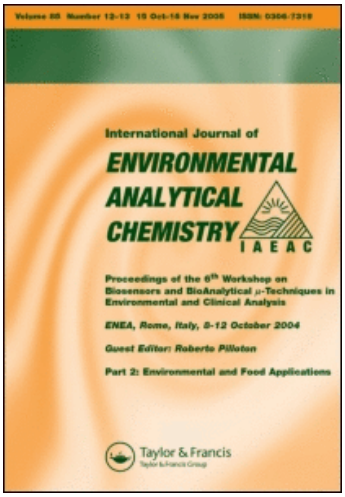

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Determination of atrazine and its deethylated degradation product in water and sediment by using gas chromatography/ion trap mass spectrometry

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A gas chromatography/ion trap mass spectrometry method was used for the trace analysis of atrazine and its deethylated degradation product deethylatrazine in environmental water and sediment samples. The isotope dilution technique was applied for the quantitative analysis of atrazine at parts-per-trillion levels. Water samples were pre-concentrated by solid-phase extraction using a C_{18} cartridge while the sediment samples were extracted by sonication with methanol. The concentrated extracts were analysed by a GC/ion trap MS operated in the MS/MS method. The extraction recoveries for the analytes were better than 83% when 1 L of water or 10 g of sediment was analysed. The method detection limits were 0.75 ng/L and 0.13 ng/g for atrazine and deethylatrazine detected in water and sediment, respectively. The precisions of the method represented by the relative standard deviation were in the range of 3.2–16.1%. The method was successfully applied to analyse surface water and sediment samples collected from Beijing Guanting reservoir. Trace levels of atrazine at 35.9–217.3 ng/L and 2.4–8.4 ng/g were detected in the water and sediment samples, respectively. The levels of deethylatrazine were five to 20 times lower that those of atrazine.

Keywords: Atrazine; Deethylatrazine; GC/MS/MS; Sediment; Water

1. Introduction

The development and use of pesticides and herbicides have played an important role in increasing agricultural productivity. Most of the agricultural chemicals are directly applied to soil or sprayed over crops fields. As a consequence of a high degree of production and field application, the chemicals are released directly into the environment. They can enter as contaminants into streams, rives, or lakes directly from drainage of agricultural lands [1]. Contamination of natural waters by the pesticides and herbicides has become a major concern.

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Atrazine (ATR) is one of the most widely used herbicides for a broad spectrum of crops. It helps to control the growth of weeds through the inhibition of photosynthetic reactions [2]. ATR degrades slowly in soil through hydrolysis and N-dealkylation under a wide range of environmental conditions. Typical degradation products of ATR include deethylatrazine (DEA), deisopropylatraine, didealkatrazine, and hydroxyatrazine. The herbicide has a relatively low adsorption in soil and easily migrates through soil into water [3–7]. Because of the potential toxicity of atrazine and its degradation products, a highly sensitive analytical method is compulsory for environmental monitoring [8, 9]. Gas chromatography (GC) with electron capture [10] and nitrogen–phosphorus detection [11–13] have been previously reported for the determination of this agrochemical in the environment. The identification was solely based on retention time, which cannot totally eliminate false identification. Mass spectrometry (MS) [14–22] has recently become a common detection technique for atrazine and its degradation products. GC/MS provides mass spectral information, in addition to the efficient chromatographic separation. LC/MS, on the other hand, has become an attractive alternative for the analysis of atrazine, especially for its polar degradation products [23–27]. In particular, LC/MS with a quadrupole mass analyser provides a good sensitivity and wide dynamic ranges for the quantitative analysis.

MS is a powerful tool for the identification and quantification of organic compounds in complex sample matrices. GC/MS operated in selected ion monitoring mode (SIM) provides an improved sensitivity for quantitative purposes. Recently, tandem mass spectrometry detection (MS/MS) is becoming more important for environmental analysis [1, 10, 28–34]. Compared with the single-stage MS mode, MS/MS offers a higher degree of selectivity and sensitivity. MS/MS enables the analysis of pesticides in trace levels in the presence of interfering compounds without reducing the identification capability due to a drastic reduction in the background [28–34]. The technique gives a high degree of confidence in compound identification. The controlled fragmentation generates cleaner chromatograms, improving the signal-to-noise ratio and thus decreasing detection limits. An ion trap mass spectrometry (ITMS) detector is the most commonly used mass analyser for MS/MS analysis.

The increased demand for analytical accuracy in trace environmental analysis has enhanced the importance of the use of isotope dilution procedure involving isotopically labelled standard and MS. The isotopically labelled internal standard is added to the sample prior to analysis for compensating for analyte losses during the procedures of sample preparation and instrumental analysis. MS/MS combined with isotope dilution method may significantly improve the selectivity as well as the accuracy and precision [20–22]. This paper describes the application of a previously developed GC/MS/MS method for the determination of atrazine and deethylatrazine in surface water and sediment samples collected in Guanting reservoir located in Beijing, China. A validation of the developed procedure for sediment sample preparation is also discussed.

2. Experimental

2.1 *Reagents and chemicals*

Authentic standards of ATR and ATR-d_5 were purchased from Crescent Chemical Co. (Augsburg, Germany) and Dr. Ehrenstorfer GmBH (Augsburg, Germany), respectively.

Native DEA was from Riedel-de Haen (Seeize, Germany). HPLC-grade organic solvents were obtained from Acros Organics (Morris Plains, NJ) and Labscan Analytical Science (Patumwan, Bangkok). An environmental Sep-Pak C_{18} cartridge (1 g) was purchased from Waters (Milford, MA). Each stock solution was prepared by dissolving 1.0 mg of DEA, ATR, and ATR-d_5 in 10 mL of ethyl acetate. Calibration standard solutions containing the analytes and internal standard were prepared for the determination of relative response factor (RRF) by diluting the corresponding stock solutions in ethyl acetate. Organic-free water was obtained from Milli-Q water purification system (Millipore).

Spiked water samples used for the determination of recovery as well as the method accuracy and precision were prepared by adding the analytes into 1 L organic-free water at various concentrations. A sediment matrix collected from a river located closed to Guanting reservoir in Beijing, China was used for preparing spiked sediment samples because the sediment contains no detectable ATR and DEA. The spiked sediment samples were prepared by adding known amounts of ATR and DEA into 10 g of sediment matrix.

2.2 *Optimization of GC/ion trap MS conditions*

A DB-5 GC column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was directly interfaced with a Polaris Q ion trap mass spectrometer (Thermo Finnigan, Austin, TX). Xcalibur software from Finnigan was used to set the instrument parameters and for data analysis. One microlitre of sample extract or standard calibration solution was manually injected for analysis in splitless injection mode, and the split valve was activated 1 min after injection. The temperature of the injector and transfer line was kept constant at 280 and 300°C, respectively. Helium was used as a carrier gas at a flow rate of 1.5 mL/min in a constant flow mode with vacuum compensation. The temperature of the oven was ramped from 90°C (for 0.5 min) to 160°C (for 3.7 min) at a rate of 15°C/min, and then increased to 280°C at the rate of 25°C/min and held for 5 min. The mass spectrometer was operated with electron impact ionization (EI), and the solvent delay was set to 8 min to avoid damaging the MS filament and to avoid contaminating the ion source. Development of the GC/MS and MS/MS method has been reported previously [29] with the original default values of the ITMS operating parameters set as follows: ion source temperature (IST) 200°C, electron energy (EE) 70 eV, and emission current 250 mA, isolation width 1.0 μm, isolation time (IT) 8 ms, excitation time (ET) 15 ms, resonance excitation voltage (REV) 1.0 V, and q value 0.45.

Calibration standard solutions contained ATR and DEA at concentrations ranging from 25 to 2000 pg/μL and the internal standard was kept at 800 pg/μL. With an injection volume of 1 μL, the corresponding column amount of the calibration standards range from 25 to 2000 pg and for the internal standard, 800 pg. The peak area ratios of the analytes to the internal standard were calculated to establish the calibration curve.

2.3 *Accuracy and precision*

Spiked matrix standard samples were analysed to obtain accuracy and precision data. The procedure for determining the method accuracy and precision of ATR and DEA in water has been reported previously [29]. For a sediment, two spiked concentrations of

ATR and DEA at 0.25 ng/L and 1 ng/g were used to determine the accuracy and precision. The relative errors and relative standard deviation (RSD) of the results obtained from six determinations were used to evaluate the accuracy and precision of the analytical method.

2.4 *Water-sample preparation*

Water samples were collected from Guanting reservoir in Beijing, China. Three litres of surface water were directly collected into amber glass bottles that had been pre-cleaned in series with detergent water, tap water, distilled water, methanol, ethyl acetate, methanol, and distilled water. After sample collection, the glass bottles were threaded with caps lined with Teflon and placed in an ice-filling cooler. The samples were then immediately delivered to the analytical laboratory and stored at 4°C in a refrigerator until sample analysis. Prior to the SPE extraction, 1 L of water sample was spiked with 24 ng of atrazine-d_5 internal standard. The SPE extraction was conducted according to the protocol published previously [29] except that a different C_{18} cartridge was used for achieving better recovery of DEA. 1 μL of sample extract was injected for the GC/ITMS analysis. The obtained peak area ratios of the analytes and the added internal standard were determined.

2.5 *Sediment-sample preparation*

Surface sediment samples ($\sim$50 g each) were collected with a hollow-stem auger equipped with a split tube core barrel from the Guanting reservoir. The samples, collected at a core depth range of 0–60 cm, were stored in glass bottles and allowed to air-dry at room temperature. Ten grams of the spiked matrix or field sediment sample was spiked with 40 ng of atrazine-d_5 internal standard prior to extraction. The samples were extracted with 50 mL of methanol twice by sonication for 30 min. The extracts were combined and filtered through a 0.45 μm filter. The filtered extract was finally concentrated to 50 μL. One microlitre of the extract was injected for the GC/ITMS analysis.

Identification of the analytes was performed with the following criteria: retention-time comparison with the corresponding authentic standards, detection of selected characteristic ions in MS/MS spectra with a signal-to-noise ratio greater than 3.

3. Results and discussion

3.1 *GC/ion trap MS method for ATR and DEA*

Full scan EI-MS spectra of ATR and DEA were obtained to select the most abundant ion as the precursor ions. The peak resulting from the loss of methyl group $[M\text{-}CH_3]^+$ was the most abundant ion for the analytes. The $[M\text{-}CH_3]^+$ ions at m/z 172 for DEA, m/z 200 for ATR and m/z 205 for ATR-d_5 were selected as the precursor ions for the subsequent tandem mass spectrometric analysis. The MS/MS analysis was conducted initially with the default parameters described in section 2. The MS/MS spectra of the targeted analytes were published previously [29]. Based on the MS/MS results, characteristic ions including the quantitation and confirmation ions were selected.

Table 1. Retention time, precursor ions and fragment ions of atrazine and deethylatrazine under the MS/MS conditions.

Compounds	Retention time (min)	Precursor ion (m/z)	Quantitation ion (m/z)	Confirmation ion (m/z)
DEA	9.54	172	105	130
ATR	10.52	200	122	132
ATR-d_5	10.50	205	127	–

The criteria for selecting quantitation ions included peak intensity and ion specificity as well as the separation from potential interference from other compounds. Consideration was given primarily to the most abundant ion to achieve the best sensitivity. The GC retention time and the selected characteristic ions of the analytes and the internal standard are listed in table 1.

The optimized values for the ion trap MS operation were mainly achieved by tuning up the q excitation time, isolation time, electron energy, and ion-source temperature value to 0.3, 15 ms, 8 ms, 60 eV, and 250°C, respectively. The optimized parameters were found to be similar to all analytes and the internal standard. The analytes were baseline separated by the established chromatographic and spectrometric conditions. The retention time of the analytes was 9.54 min, 10.50 min, and 10.52 min for DEA, ATR-d_5, and ATR, respectively. The calibration curve was obtained for each analyte by plotting the ratios of the ion peak responses of the native compound to that of the labelled internal standard vs. the corresponding concentration ratios of the native to labelled compound. The calibration curves for ATR and DEA were linear for the calibration range with $R^2 > 0.99$.

3.2 *Recovery and detection limit*

For the water-sample analysis, the C_{18} SPE extraction provided recoveries of 91 and 83% for ATR and DEA, respectively, when the spiked level of each analyte was 10 ng/L and when 1 L of water sample was extracted. The DEA recovery was poor in the previously published method [29]. Better recovery of DEA in water, however, was achieved by selecting a different C_{18} cartridge with a larger capacity (Environmental Sep-Pak C_{18} cartridge (1 g) from Waters). The instrument detection limit defined as a signal-to-noise ratio ≥ 3 for ATR and DEA was 25 pg per injection, corresponding to a method detection limit of 0.75 ng/L when the water sample volume was 1 L and the injection volume was 1 μL out of the final 30 μL extract. For the sediment sample analysis, sonication with methanol gave quantitative recoveries of 96 and 89% for ATR and DEA at a concentration of 0.5 ng/g. The limits of detection for sediment were 0.13 ng/g.

3.3 *Accuracy and precision*

The use of ATR-d_5 as internal standard resulted in a better accuracy and precision for the analysis of ATR and its degradation product because errors in the analytical process were reduced. A good method accuracy represented by the relative errors and precision expressed as the relative standard deviation (RSD) of the analytes was achieved for water-sample analysis and was reported previously [29]. In general, a better

accuracy was achieved for ATR when compared with DEA owing to the use of the corresponding isotopically labelled compound (ATR-d_5) as the internal standard. The accuracy and precision of ATR and DEA were determined by analysing six spiked sediment samples with levels at 0.25 ng/g and 1 ng/g each. The relative errors with RSD in brackets were 14.1% (RSD 9.6%) and 11.4% (RSD 5.9%) for the ATR spiked levels of 0.25 ng/g and 1 ng/g, respectively. The relative error was 17.5%, and the RSD was 12.7% ($n = 6$) for samples containing DEA at 0.25 ng/g. For DEA with a higher concentration at 1 ng/g in the sediment, a better accuracy (8.2%) and precision (10.1%, $n = 6$) were achieved.

3.4 *Determination of ATR and DEA in environmental samples*

Surface water and sediment samples were collected from Guanting reservoir in Beijing, China and analysed for ATR and DEA. Guanting reservoir has an area of 230 km^2 and was an important municipal water supply source in Beijing before 1997. However, it was reported that the water was being contaminated by the surrounding industrial factories and agrochemical manufacturers in recent years. As a result, the reservoir ceased providing municipal water after 1997. Because of the water-shortage problem in Beijing, however, the government has recently been urged to consider reusing it as a municipal water source. Therefore, there is now an important and urgent need to monitor the water quality and investigate the contamination of agricultural chemicals in the reservoir.

The GC/MS/MS method developed had been used successfully for analysing field samples collected in Guanting reservoir. Water and sediment samples were analysed together with field blank, method blank, and QC samples, including spiked matrix and duplicated samples. Both field and method blanks showed negative detection of ATR and DEA. Good accuracy and precision were achieved for the spiked and duplicated samples (table 2). ATR and DEA were identified in water and sediment samples based on criteria of retention time and selected characteristic ions in the GC/MS/MS

Table 2. Levels of atrazine and deethylatrazine detected in surface water and sediment samples collected from Guanting reservoir.

	Water (ng/L)		Sediment (ng/g)	
Sample	Atrazine	Deethylatrazine	Atrazine	Deethylatrazine
1	35.9	7.9	nd[a]	nd
2	170.9	21.9	4.9	0.91
3	217.3	30.5	Nd	nd
4	201.9	26.2	2.4	nd
5	207.2	25.9	8.4	0.52
5-duplicated	194.8	24.2	8.0	0.54
6	185.8	28.3	Nd	nd
FB[b]	nd	Nd	Nd	nd
MB[c]	nd	Nd	Nd	nd
SM[d]	10.8	11.3	0.95	0.89

[a]nd: not detected. The detection limits of atrazine and deethylatrazine were 0.75 ng/L and 0.13 ng/g for water and sediment, respectively.
[b]FB: field blank.
[c]MB: method blank.
[d]SM: spiked matrix. The spiked levels of ATR and DEA were 10 ng/L for water and 1 ng/g for sediment analyses.

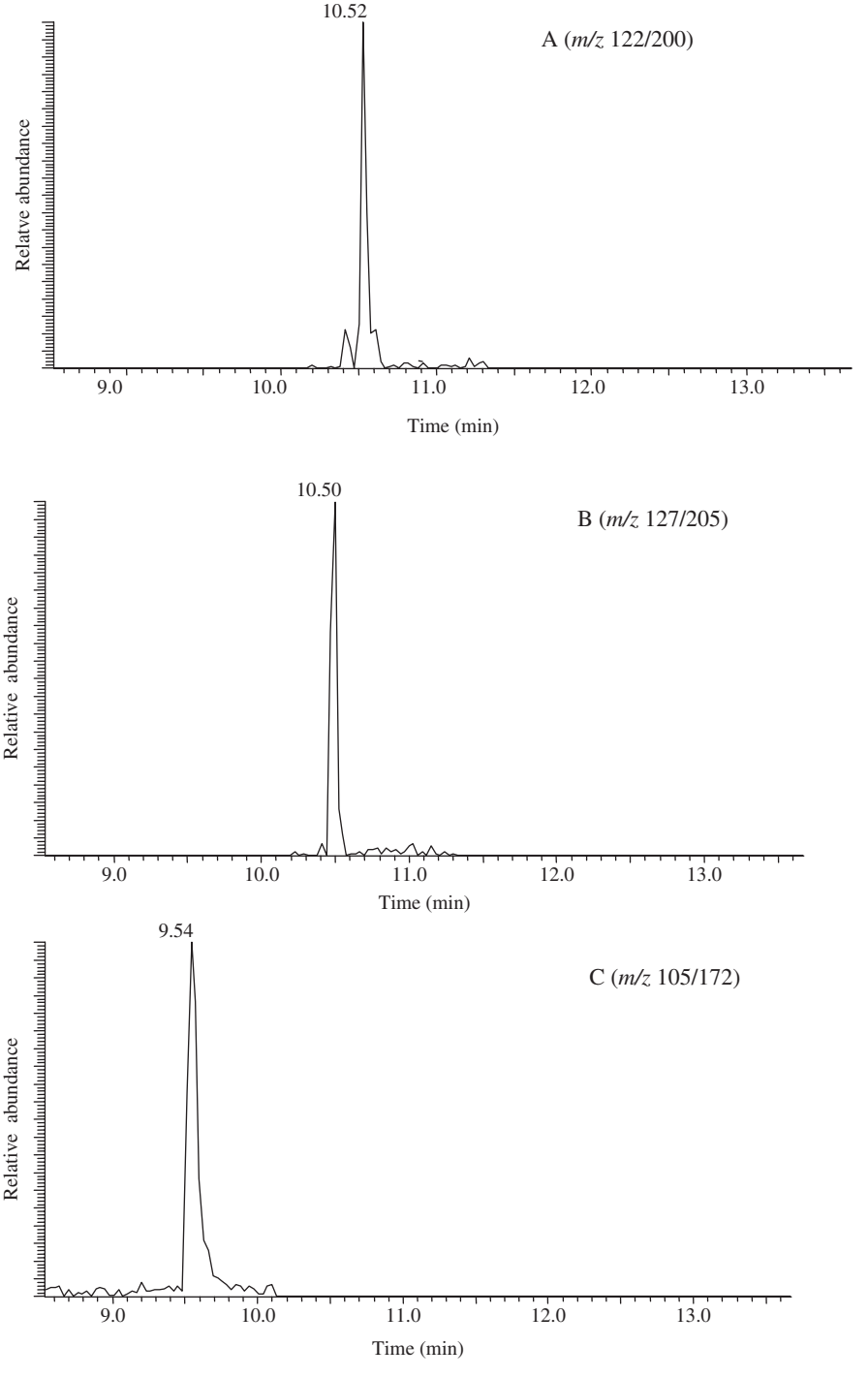

Figure 1. Extracted MS/MS chromatograms of (A) atrazine at m/z 122/200, (B) atrazine-d_5 at m/z 127/205 and (C) deethylatrazine at m/z 105/172 obtained from the analysis of a water sample collected from Guanting reservoir, Beijing, China.

analysis. The quantitative results obtained demonstrated that trace levels of ATR and DEA existed in both water and sediment. The analytical data obtained are listed in table 2. Levels of ATR were found to be five to 20 times higher than those of DEA, but the difference varied from sample to sample, depending on the location of the sample collection site. The concentration ranged from 35.9 to 217.3 ng/L and from 7.9 to 30.5 ng/L for atrazine and DEA detected in water, respectively. The extracted MS/MS chromatograms shown in figure 1 illustrate the detection of ATR and DEA in a water sample from Guanting reservoir when ATR-d_5 was used as internal standard. In the sediment samples containing detectable levels of the analytes, the ATR concentration ranged from 2.4 to 8.4 ng/g, and the DEA concentration ranged from 0.52 to 0.91 ng/g. The data indicated that atrazine contamination in the water of Guanting reservoir was lower than the upper limit for surface water (3 μg/L) regulated by the Chinese Environmental Protection Department. However, cleanup procedures to remove atrazine and its degradation products are strongly suggested when the water from Guanting reservoir is used as the source for municipal drinking water.

4. Conclusion

A method of GC/ion trap MS was applied for determining atrazine and its deethylated degradation product in environmental water and sediment samples. Atrazine and deethylatrazine were identified and quantitated in the samples collected from Guanting reservoir in Beijing, China. Solid-phase extraction with a 1 g C_{18} cartridge and sonication with methanol provided quantitative recovery for atrazine and the deethylated degradation product in water and sediment, respectively. The GC/MS/MS combined with the isotope internal standard method provided good accuracy and precision for the analysis at trace levels.

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