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Short communication

Preconcentration of triazine herbicides from water by an ion chromatography column and determination by gas chromatography–mass spectrometry

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Abstract

The efficiency of ion chromatography columns packed with styrene–divinylbenzene copolymer containing quaternary ammonium groups to preconcentrate triazine herbicides and their degradation products below μg/l levels has been established. Retention is studied for different types of water. Pure methanol was used in a one-step elution. Enrichment factors of at least 4000 are achieved. Determination was carried out by using gas chromatography–single-ion monitoring mass spectrometry. Recoveries for run-off agricultural water were between 67–100% and close to 100% for ground water. The maximun admissible concentration in drinking water (0.1 μg/l) and the alert and alarm threshold values in surface water (1 and 3 μg/l, respectively) dictated by the European Union can be measured.

Keywords: Water analysis; Environmental analysis; Sample preparation; Triazines; Pesticides

1. Introduction

Triazines are nowdays one of the most widely used class of herbicides. Because of their easy transport, they are common contaminants in surface and drinking water and they are likely to be found in ground water.

Water quality has received considerable attention and stringent regulations have been issued by legislation agencies. For example, the current European Union (EU) directive dictates that the concentration of, e.g., individual pesticides should not exceed a maximum admissible concentration of 0.1 μg/l in drinking water, the alert and alarm threshold values being typically 1 and 3 μg/l, respectively, in surface water [1].

Triazines have been determined using gas chromatography (GC) [2–5] and high-performance liquid chromatography [6,7], mainly for thermally unstable triazines. Although liquid–liquid extraction [8] is still used to preconcentrate, solid-phase extraction is becoming the technique of choice. The most commonly employed adsorbents are C_{18} bonded silica cartridges [2,9,10] or disks [4,11] and polymeric adsorbents, XAD type [6,7]; however, some drawbacks, including low breakthrough volumes and low sampling rate, still remain. Recently, a PRP X-100 ion chromatography (IC) column, which is a styrene–divinylbenzene copolymer with partially substituted quaternary ammonium groups, has been

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used [12] to retain phenols based on their non-ionic interactions with the copolymer in acidic medium. Since the preconcentration of triazines and their degradation products continue to be a problem, the aim of this research is to study the ability of a PRP X-100 ion chromatography column to retain triazines and some of their degradation products, as a method of enrichment of these residues for water analysis by gas chromatography–single-ion monitoring mass spectrometry (GC–SIM-MS).

2. Experimental

2.1. Equipment

Preconcentration was carried out with a medium pressure Metron 607 IC pump in a PRP X-100 125×4.0 mm IC column supplied by Hamilton. Evaluation of the recoveries was made with a Hewlett-Packard HP 8452-A diode array spectrophotometer interfaced to a HP Vectra AT computer and a HP Think Jet printer. The determination of triazines was carried out in a Hewlett-Packard 5989 A MS engine, equipped with an electron impact source in conjunction with a HP 5890 (series II) GC system and an Apolo series 400 HP data system. A 12 m×0.2 mm I.D. HP-1 (cross-linked methyl silicone gum, 0.33 μm film thickness), fused-silica capillary column was used.

2.2. Chemicals

All chemicals were of analytical grade. Atrazine (98% pure), simazine (99% pure), cyanazine (99% pure), ametryne (98% pure), propazine (99% pure), terbutylazine (99% pure), methoprotryn (97% pure), terbutryn (98% pure) and hydroxyatrazine (99% pure) (all from Riedel de Haën, Seelze, Germany) were used for preparing 100 mg/l stock solutions in methanol. For quantitation, 4,4′-dichlorobiphenyl (98% pure, Riedel de Haën) was used as the internal standard in GC–MS. Purified water was obtained using a Milli-Q apparatus.

2.3. Procedure

2.3.1. Preparation and storage of samples

The water samples were collected and the pH adjusted by adding hydrochloric acid or sodium hydroxide to obtain a pH of between 5 and 9. Samples were stored at 4°C [13].

2.3.2. Preconcentration

The IC PRP X-100 column was cleaned and regenerated by passing 30 ml of 60 m*M* nitric acid in 99% methanol at 0.5 ml/min. Evaluation of the column's efficiency at concentrating triazines was made by passing 100 ml of an aqueous solution containing 50 μg of each triazine through the column. The standards were treated as specified in Section 2.3.1. The retained triazines were eluted with 10 ml of methanol and tested with the diode array spectrophotometer. When water samples were studied, 2000 or 250 ml of the spiked water containing between 0.2 and 20 μg of triazines were first filtered through filter paper followed by a 0.45-μm nylon microfilter. Then the sample was passed through the column at 4.5 ml/min. Triazines were eluted with 10.0 ml of pure methanol at 1.5 ml/min.

2.3.3. Gas chromatography–mass spectrometry determination

The collected sample was evaporated under reduced pressure in a rotary evaporator to a final volume of 0.5 ml and 2 μg of internal standard were added before the injection of 2 μl into the GC–MS system. The injection was made in splitless mode (0.75 min). The column temperature was mantained at 80°C for 2 min and programmed from 80°C at 30°C/min to 160°C and then at 1°C/min to 180°C. The injector temperature was set at 250°C, the transfer line at 280°C and the ion source at 200°C. Helium was used as the carrier gas. The data acquisition was made in SIM mode, maintaining the quadrupole analyzer at 100°C. The ions monitored were *m/z* 200, 201, 214 and 222 between 7.50 and 11.00 min and *m/z* 214, 225, 226 and 227 up to 11.00 min.

3. Results and discussion

3.1. Selection of working conditions

Previous assays showed that the studied triazines were retained in the styrene–divinylbenzene column when water contained less than 30% methanol.

Moreover, when water contained more than 90% methanol, all triazines were eluted or not retained. Taking this behavior into account, pure methanol was used for elution.

Hydrodynamic variables affecting the preconcentration process were studied by UV spectrophotometry at the maximum wavelength of each triazine. Recoveries of triazines were determined by comparing the spectra of the recovered triazines with those of the standard solutions. The influence of flow-rate on the retention of the triazines was evaluated in the 1.5 to 4.5 ml/min range. In all cases, the recoveries found were around 100%, except for terbutylazine, which was between 70 and 75%, for which no conclusive explanation can be given at present, although steric hindrance might be involved. The flow-rate of 4.5 ml/min was chosen as a compromise between sample throughput and suitable performance for the pump. Elution was carried out at a flow-rate of 1.5 ml/min and, in spite of the size of the column, 10 ml of methanol were enough to obtain good recoveries.

Regarding the capacity, the maximum amount of each triazine retained by the column was evaluated using solutions containing different amounts of each triazine (between 100 and 1000 μg in 100 ml of water). The recoveries were, in all cases, around 100%, again with the exception of terbutylazine.

The breakthrough volume was determined by studying the recovery of 50 μg of each triazine in volumes between 250 and 2000 ml (Table 1). As can be seen, recoveries remained similar for all volumes studied, so we can state that breakthrough volumes were larger than 2000 ml, except for cyanazine whose breakthrough volume was around 1000 ml. Under these conditions, a preconcentration factor of 4000 was achieved since the analytical volume was 0.5 ml.

The reproducibility of the preconcentration process (expressed as relative standard deviation for 50 μg of each triazine in 100 ml and five determinations) is shown in Table 2. For all triazines studied with the exception of terbutylazine, recoveries were close to 100%.

The high retention capacity and large breakthrough volume of the column suggests that the retention mechanism is non-ionic, based on interactions between aromatic rings, which could confirm the retention mechanism previously reported for phenols [12].

3.2. Determination of triazines in water samples

Whenever possible, triazines are determined by GC. Due to the complexity of water samples, GC–MS has been used to identify and to quantify the analytes. This technique is very suitable for the determination of simazine, atrazine, cyanazine, ametryne, propazine, terbutylazine and terbutryn; however, methoprotryn and hydroxytriazine are thermally unstable under GC conditions. Therefore, the last two compounds mentioned were not included in the chromatographic study. The study was carried out by preconcentration of spiked purified water, agricultural run-off water and ground water samples. The chromatographic method used is based on a method proposed by Bagheri et al. [14]. Slight changes were made, as shown in the procedure to

Table 1
Breakthrough volumes of triazines

Triazine	Volume (ml)			
	250	500	1000	2000
Hydroxyatrazine	98(4)	100(4)	95(5)	91(16)
Simazine	102(4)	103(5)	99(4)	98(12)
Atrazine	100(6)	98(6)	100(4)	98(18)
Cyanazine	100(8)	99(5)	97(5)	5(2)
Ametryne	98(6)	99(3)	103(6)	87(24)
Propazine	100(4)	96(4)	95(5)	84(27)
Terbutylazine	72(8)	70(4)	74(5)	89(21)
Methoprotryn	94(4)	102(6)	100(4)	108(12)
Terbutryn	102(2)	100(5)	101(4)	102(24)

Sample concentration, 50 μg. Recoveries[a], % (s_r, %).
[a] Mean of three determinations.

Table 2
Reproducibility of the preconcentration process

Triazine	Recovery[a] (%)	s_r (%)
Hydroxyatrazine	94	6
Simazine	102	8
Atrazine	101	3
Cyanazine	101	3
Ametryne	103	6
Propazine	101	3
Terbutylazine	72	8
Methoprotryn	103	4
Terbutryn	100	4

Sample concentration 50 μg. Sample volume, 100 ml.
[a] Mean of five determinations.

resolve the terbutylazine peak, which was not studied by the authors referred to. Two internal standards proposed in several US Environmental Protection Agency methods were tested, i.e., triphenylphosphate and 4,4′-dichlorobiphenyl. Because of overlapping of the triphenylphosphate and the terbutylazine peaks, 4,4′-dichlorobiphenyl was chosen as the internal standard (Fig. 1).

In order to evaluate the influence of organic matter present in a real sample on the preconcentration step, pure, agricultural run-off and ground water samples were studied. By following the proposed procedure, no triazines were detected in these samples. Samples containing 250 ml of the agricultural run-off water were spiked with between 4 and 6 μg of each triazine, except for cyanazine, where amounts of between 10 and 20 μg were used. The recoveries found are shown in Table 3 and are similar to those obtained from purified water, except for propazine; the altered recovery of which may be due to some unknown matrix effect. When ground water was studied, 2000 ml of water were spiked with between 0.2–5.0 μg of each triazine. The results obtained are shown in Table 4; for all triazines (except cyanazine), the recoveries were higher than 89%, but the reproducibilities were lower than those obtained for purified and run-off water. As can be seen, the recovery of propazine is higher than that obtained in agricultural run-off water and is similar to that of pure water. This confirms the influence of organic matter on the recovery of propazine.

4. Conclusions

The proposed preconcentration method using commercially available ion chromatography columns based on styrene–divinylbenzene copolymer is useful for partially polar compounds with aromatic rings. It is possible to preconcentrate small amounts

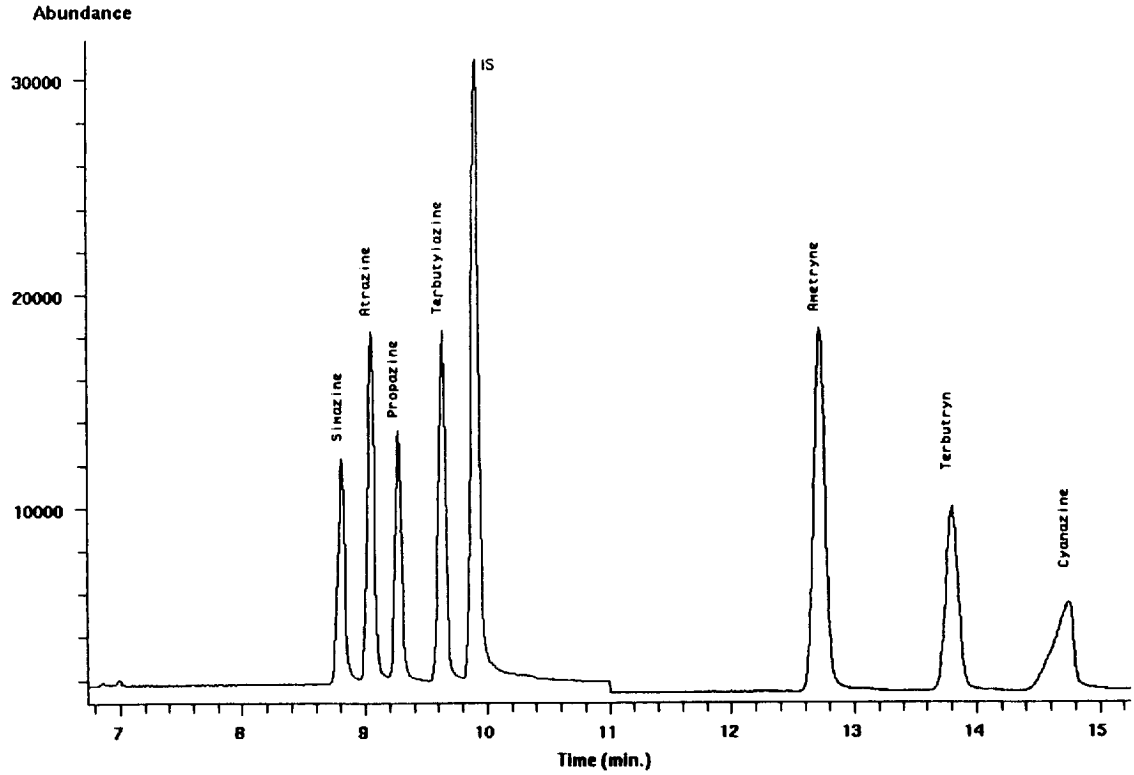

Fig. 1. GC–SIM-MS of a spiked sample of run-off agricultural water treated as described in Section 2.3.

Table 3
Recovery of triazines from spiked water

Triazine	Amount spiked (μg)	Purified water		Agriculture run-off water	
		Recovery[a] (%)	s_r (%)	Recovery[a] (%)	s_r (%)
Simazine	4–6	104	6	105	3
Atrazine	4–6	102	6	98	8
Propazine	4–6	92	8	67	5
Terbutylazine	4–6	77	13	73	7
Ametryne	4–6	87	5	84	10
Terbutryn	4–6	87	2	89	10
Cyanazine	10–20	95	9	96	7

Sample volume, 250 ml.
[a] Mean of four determinations.

Table 4
Recoveries of triazines from spiked ground water

Triazine	Amount spiked (μg)	Recovery[a] (%)	s_r (%)
Simazine	0.2–1.8	97	31
Atrazine	0.2–1.5	100	28
Propazine	0.2–1.5	92	32
Terbutylazine	0.2–1.4	89	33
Ametryne	0.2–1.5	93	28
Terbutryn	0.2–1.5	108	33
Cyanazine	0.4–5.0	8	5

Sample volume, 2000 ml.
[a] Mean of five determinations.

of triazines in high volumes due to the high capacity and breakthrough volumes of the column. The proposed method has been used to determine seven triazines in agricultural run-off water at levels of between 16 and 80 μg/l, and six triazines in ground water at levels of between 0.1 and 0.9 μg/l.

Acknowledgments

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