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Optimization of an analytical procedure for the determination of triazine herbicides in environmental samples☆

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Abstract

A clean-up procedure and high-performance liquid chromatographic conditions were optimized for the determination of triazines in drinking and surface water. Two extraction systems were tested: off-line solid-phase extraction (SPE) with C_{18}-bonded silica gel cartridges and on-line SPE with PLRP-S (styrene–divinylbenzene copolymer) preconcentration cartridges. The on-line SPE procedure was chosen for further work. Chromatographic conditions were optimized for UV absorbance and particle beam (PB) MS detection. The LC–UV analytical system with on-line preconcentration showed excellent linearity over the concentration range tested and low detection limits (below 0.05 μg/l) for drinking water. With preconcentration from large volumes of water, some triazines and other pesticide pollutants could be detected in drinking and river water by PB-MS. Quantification was achieved by means of the standard addition method. For soil samples, the extraction procedure was off-line and more elaborate.

1. Introduction

Environmental pollution with pesticides is of major public concern and maximum allowable concentrations have been set for drinking water and for surface water, which is often a source of drinking water. In the European Community, the upper limit for the presence of an individual pesticide in drinking water is set at 0.1 and at 0.5 μg/l for the total pesticide content [1]. In surface water, these limits are about an order of magnitude higher (1–3 μg/l). Such strict limits imply lower limits of detection for analytical methods used for pesticide determination in waters. Recommended limits of detection for drinking water are in the 0.01–0.02 μg/l range [1].

Although capillary gas chromatography (GC) is the method most often used for pesticide determinations in environmental samples, it is not a suitable technique for some analytes because of their thermal lability or polarity. Therefore, liquid chromatography (LC) is becoming a method of choice in many instances, particularly for the determination of polar compounds and for screening purposes [2]. The most common mode of detection is with a UV–visible absorbance detector, preferably a diode-array detector, which offers the advantage of recording the UV spectrum of each compound and comparing it with those from a library [2,3].

Unfortunately, LC cannot be as easily coupled

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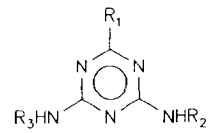
as GC with MS. There are various different LC–MS interfaces available, but so far three types have proved to be the most useful in environmental analysis: thermospray (TSP), particle beam (PB) and atmospheric pressure ionization (API) [1]. Among these, only PB offers the advantage of both the electron impact (EI) and chemical ionization (CI) modes, and therefore the possibility of direct comparison of the recorded spectrum with library spectra, as is commonly accomplished in GC–MS analysis. Although there are some drawbacks to the use of PB, such as its reported non-linearity, matrix effects and lack of sensitivity, procedures employing LC–PB-MS analysis have recently been included in US Environmental Protection Agency (EPA) analytical protocols for pesticide analysis [4].

Another important advantage of LC determination of water contaminants is the ease of coupling with on-line preconcentration techniques for water samples [5]. These techniques have gained in popularity in the last few years because they can readily be automated [6] and offer greater sensitivity, less contamination and analyte loss than off-line solid-phase extraction techniques or even classical liquid–liquid extraction of water samples [7]. Although most of the papers dealing with on-line SPE–LC analysis use UV absorbance detection for pesticides, recently there have appeared several applications using PB-MS [8] or TSP-MS detection [9].

In this work, the target compounds were triazines, which are well known herbicides. Their structures together with some chemical constants important for their behaviour are shown in Fig. 1. Some of them, especially atrazine, have become major pollutants of ubiquitous presence owing to their widespread use in agriculture and for other purposes [2]. Besides environmental waters, most pollution with triazines occurs in soil. The higher residual concentrations in soils after spraying of crops prevent crop rotation in successive years [10], and also represent a threat to ground waters. Atrazine especially has a high leaching potential [2]. Triazines are sufficiently volatile and thermally stable enough to be determined by GC, but LC has also proved to be equally applicable [11]. Some papers have been published dealing with the determination of triazines in water with on-line preconcentration coupled to LC and with UV absorbance [12,13] and TSP detection [14,15], whereas the possibility of detecting triazines by PB-MS has been only partially examined [16, 17].



Name	R_1	R_2	R_3	M_w	pK_a	P_{ow}
atrazine	—Cl	$-CH(CH_3)_2$	$-CH_2CH_3$	215.7	1.7	2.57
simazine	—Cl	$-CH_2CH_3$	$-CH_2CH_3$	201.7	1.7	2.00
cyanazine	—Cl	$-C(CH_3)_2$ | CN	$-CH_2CH_3$	240.7	1.0	1.73
terbutylazine	—Cl	$-C(CH_3)_3$	$-CH_2CH_3$	229.7	2.0	3.04
ametryn	$-SCH_3$	$-CH_2CH_3$	$-CH(CH_3)_2$	227.3	4.1	3.07
prometryn	$-SCH_3$	$-CH(CH_3)_2$	$-CH(CH_3)_2$	241.4	4.1	3.41
dipropetryn	$-SC_2H_5$	$-CH(CH_3)_2$	$-CH(CH_3)_2$	255.4	NA	NA

Fig. 1. Structures, molecular masses, ionization constants (pK_a) and *n*-octanol–water partition coefficients (P_{ow}) for target triazine herbicides.

The aim of this work was to compare the off-line and on-line SPE of triazines from water samples and to optimize the extraction procedure for soil samples. Subsequent analysis was performed by LC with UV absorbance detection and PB-MS detection was also tested. Combining these two modes of detection is useful because of the low detection limits that can be achieved with UV absorbance detection, while PB-MS detection offers confirmation of the presence of a pesticide in unknown samples.

2. Experimental

2.1. Materials

Triazine standards of 98–99% purity were obtained from Riedel-de Haën (Seelze, Germany). A stock standard solution of a mixture of triazines was prepared in acetonitrile at a con-

centration of 50 mg/l every 2 months and kept in a refrigerator. No decomposition of triazines was observed during that time. Methanol and acetonitrile were of LC-gradient grade from Merck (Darmstadt, Germany). Ethyl acetate was 99.5% pure from Carlo Erba (Milan, Italy). Acetone was ≥99.7% pure "Baker analysed" HPLC reagent grade from J.T. Baker (Deventer, Netherlands). LC-grade water was obtained by purifying distilled water with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Other reagents used, such as ammonium acetate, sodium sulphate, dilute ammonia solution and dilute hydrochloric acid solution, were of analytical-reagent or prepared from analytical-reagent grade reagents.

Solid-phase extraction cartridges used for off-line extraction were Bakerbond disposable cartridges from J.T. Baker packed with 3 g of C_{18} Polar Plus silica gel. SP extraction precolumns for on-line use were 10 × 2.0 mm I.D. cartridges packed with styrene–divinylbenzene (PLRP-S) copolymer of 15–25-μm particle size from the Prospekt method development set from Spark Holland (Emmen, Netherlands). The cartridge holder was purchased from Spark Holland. Anion-exchange cartridges were 3-ml Supelclean LC-SAX SPE tubes (Supelco, Bellefonte, PA, USA).

The LC analytical column was 150 × 3.0 mm I.D., laboratory packed with 5-μm particle size Hypersil ODS from Hewlett-Packard (Palo Alto, CA, USA). Helium used for PB operation was 99.996% pure from Messer Griesheim (Gumpoldskirchen, Austria).

For calibration a tap water sample and weakly polluted river water were spiked with triazines. River water was filtered before extraction through a dense-pore laboratory filter-paper.

2.2. Off-line SPE sample preparation

The SPE cartridge was preconditioned with 10 ml of methanol and 10 ml of LC-grade water. A 250-ml volume of water sample was loaded on the cartridge. The pH of the sample was adjusted before extraction with dilute HCl or dilute ammonia solution. After sample loading, the cartridge was rinsed with 10 ml of LC-grade water and partially dried by passing air through it. Analytes were eluted with 10 ml of ethyl acetate. Residual water in the eluate was removed by drying with sodium sulphate. The ethyl acetate eluate was evaporated under a stream of nitrogen on a water-bath (ca. 50°C). The analytes were redissolved in 0.1 ml of acetonitrile and injected into the LC system.

2.3. On-line SPE sample preparation

The experimental set-up used for on-line SPE was comparable to similar systems [2,7,8]. The cartridge was conditioned with 10 ml of acetonitrile and rinsed with the mobile phase prior to preconcentration in order to avoid initial loss of analytes. The sample delivery pump and attached tubes were first rinsed with sample and then 200 ml of sample were passed through the cartridge at a flow-rate of 6 ml/min. After preconcentration, the analytes were eluted from the cartridge to the analytical column with mobile phase in the backflush mode.

2.4. Chromatographic conditions

The mobile phase pump and sample delivery system consisted of a ConstaMetric III pump from LDC Analytical, Milton Roy (Riviera Beach, FL, USA). The mobile phase was acetonitrile–0.1 *M* ammonium acetate solution (pH 7) (1:1) and the flow-rate was set to 0.4 ml/min. The variable-wavelength UV–visible absorbance detector was a SpectroMonitor 3100 from LDC Analytical, Milton Roy and was set to 240 nm. The manual injection valve equipped with a 20-μl sample loop and a six-port switching valve were obtained from Rheodyne (Cotati, CA, USA). Chromatograms were recorded with a computing integrator (Model 4100, Milton Roy). For quantification, peak areas were used.

2.5. Particle beam and mass spectrometer conditions

For coupling of LC with MS, a particle beam interface was used (Model 59980B, Hewlett-

Packard). Its operating conditions were optimized by flow injection of 1 μg of atrazine and monitoring the response with a mass spectrometer in the electron impact (EI) ionization mode and selected-ion monitoring (SIM) at m/z 200. Parameters optimized were helium pressure, nebulizer position, desolvation chamber temperature and ion source temperature. Their values were set to 50 psi (345 kPa), position 9, 60°C and 250°C, respectively.

The mass spectrometer was an HP 5989A MS-Engine (Hewlett-Packard). The instrument was operated in the EI ionization mode at a filament emission of 300 mA and an electron energy of 70 eV. Spectra of triazines were recorded in the scan mode from m/z 50 to 400. For quantification, areas of the base peaks in the extracted ion chromatograms were measured.

2.6. Soil extraction procedure

All soil samples were provided by the Agricultural Institute, Ljubljana. Soils were air-dried, finely ground and homogenized.

Uncontaminated soil from the Slovenian Alps was suspended in an acetone solution of an appropriate amount of triazines. The suspension was then allowed to air-dry for ca. 24 h.

A 10-g amount of soil (spiked or sample) was mixed with 20 ml of LC-grade water and extracted on an ultrasonic bath for 15 min. To the suspension, 20 ml of acetone were added and the mixture was ultrasonically extracted for 15 min. The suspension was centrifuged for 10 min. The clear, brown-yellow supernatant was evaporated under a stream of nitrogen until less than 20 ml of aqueous solution was left (partial adsorption of water on the soil particles). The residual aqueous solution was loaded on a preconditioned C_{18} disposable SPE cartridge. The cartridge was rinsed with 10 ml of LC-grade water and partially dried. Triazines were eluted with 10 ml of ethyl acetate. Part of the brown substances (presumably humic acids) retained on the cartridge was also eluted. The eluate was dried with sodium sulphate and cleaned on an SAX disposable SPE cartridge, preconditioned with 2 ml of LC-grade water, 2 ml of methanol and 2 ml of ethyl acetate. Coloured ionic substances were retained, while triazines passed through the cartridge. The colourless eluate was evaporated under a stream of nitrogen on a water-bath (ca. 50°C) and the residue was dissolved in 0.1 ml of acetonitrile and injected into the LC system.

3. Results and discussion

3.1. Chromatographic conditions

The target compounds were triazines differing minimally in chemical structure and properties, as shown in Fig. 1. It was necessary to find a suitable isocratic mobile phase for their separation, recommended also for the PB interface to the MS system.

Recently, the RP chromatographic behaviour of triazines was investigated [11]. It was stated that a mobile phase with an ion-pairing reagent (sodium dodecyl sulphate) gave a better separation than a buffer–organic solvent mobile phase. Owing to its insufficient volatility for use with the PB, an ion-pairing reagent could not be used, but we found a much better separation of almost the same set of triazines with an acetonitrile–buffer system. If no buffer was added to the mobile phase, the compounds were less well separated.

Ammonium acetate solution was added to the mobile phase because it reportedly increased the transport of analytes through the PB interface [18]. In previous work [17], the addition of ammonium acetate did not significantly contribute to the noise in MS-generated chromatograms when an EI scan was performed above m/z 64. In our case, the noise was very high, thus increasing the limits of detection, whereas the noise was significantly lower when using LC-grade water–acetonitrile as the mobile phase. The pH of the mobile phase did not have any significant impact on the separation of compounds and was set to neutrality.

3.2. Optimization of off-line SPE conditions

The initial off-line SPE conditions were those recommended by the cartridge producer. The elution solvent was methanol and the cartridge

Table 1
Triazine recoveries from tap water: influence of sample pH and NaCl addition (2 g/l)

Compound	Recovery (%)						
	Off-line SPE			On-line SPE			
	pH 3–4	pH 6–7	pH 9–10	pH 3–4	pH 6–7	pH 9–10	Salt added
Atrazine	89	87	93	50	68	96	83
Ametryn	36	79	140	60	79	77	80
Terbutylazin	90	126	133	89	110	94	93

Off-line SPE: C_{18} cartridge, theoretical amount on analytical column 100 ng. On-line SPE: PLRP-S cartridge, theoretical amount on analytical column 200 ng.

was to be thoroughly dried prior to elution. However, we found drying of the cartridge to be very time consuming and not entirely successful. The elution solvent was therefore changed to ethyl acetate, which is immiscible in water and thus amenable to drying of residual water by means of sodium sulphate addition. A similar procedure has already been used by other workers [10,19].

The influence of the sample pH on the analyte recovery was also tested. The pH of the samples was adjusted to ca. 3, 7 and 9. The recoveries at neutral and basic pH were essentially the same, but those from acidic samples were lower for certain triazines, as shown in Table 1. This implies decreased retention of protonated species on the C_{18}-bonded silica gel material. Breakthrough of compounds was also tested with up to 500 ml of sample and no loss of analytes at this volume was found. Breakthrough volumes for simazine and atrazine on a C_{18} cartridge have been reported to be more than 1 l [10]. The usual volume of sample preconcentrated was set to 250 ml as a compromise between time and sensitivity.

3.3. Optimization of on-line SPE conditions

The conditions for on-line SPE are strongly influenced by the chromatographic conditions previously adjusted. In our case, the recoveries of less polar analytes such as prometryn and dipropetryn were lower than those using off-line SPE cartridges, as can be seen from Table 2. Although a different sorbent was used, we explain these lower recoveries by incomplete elution of these less polar analytes from the cartridge owing to an insufficient percentage of organic solvent in the mobile phase. If the same on-line SPE cartridge was used several times, a

Table 2
Comparison of extraction recoveries and repeatabilities for target triazines in tap water using off-line and on-line SPE ($n = 4$).

Compound	Off-line SPE		On-line SPE	
	Recovery (%)	Repeatability (%)	Recovery (%)	Repeatability (%)
Cyanazine	86	±7	102	±6
Simazine	102	±6	93	±9
Atrazine	124	±10	96	±10
Ametryn	85	±14	82	±6
Terbutylazin	128	±18	97	±2
Prometryn	113	±21	74	±3
Dipropetryn	100	±8	74	±6

Sample volume: 250 ml off-line SPE, 200 ml on-line SPE. Triazine concentration in sample: 1 μg/l.

regeneration step following the elution with mobile phase was necessary. Pure acetonitrile was passed through the cartridge before the next preconcentration in order to ensure complete removal of residual substances.

The influence of the sample pH and the addition of a neutral salt (sodium chloride) to the sample before extraction was also studied. There was a decrease in recoveries for some compounds at acidic sample pH, while NaCl addition had no significant effect on the recoveries, as shown in Table 1. Neutral pH was chosen for further work, as it was also advisable in order to avoid interferences from humic substances [20].

No breakthrough of analytes was observed up to a volume of 500 ml, and 200 ml of sample were found to be sufficient for quantification purposes with a UV absorbance detector.

3.4. Comparison of off-line and on-line sample preparation procedures

The two most commonly used sorbent materials for both types of extraction were compared. Although C_{18}-bonded silica gel is sometimes used in on-line SPE, its use has been widely superseded by styrene–divinylbenzene copolymer material, mainly because of its higher breakthrough volumes for more polar compounds [20]. In off-line extraction procedures, this polymer is less often used and has only recently gained in popularity [1].

The recoveries and repeatabilities for both types of extraction are compared in Table 2. The recoveries for prometryn and dipropetryn are lower with PLRP-S cartridges for the reasons discussed above but, in general, the recoveries are higher for PLRP-S cartridges and also the repeatability is better, as there is less sample manipulation in the on-line process. Triazines are moderately volatile compounds and some loss may occur during the evaporation step in the off-line SPE procedure.

In order to reach the same detection limit with both sample preparation methods, higher volumes of water sample should be preconcentrated in the off-line SPE procedure, as only part of the final extract is injected on to the LC column, which implies a longer sample preparation process. Even with very similar sample volumes for preconcentration (250 ml off-line and 200 ml on-line), the off-line procedure was found to be more time consuming and tedious, as it required the attention of the operator, which was not necessary in the on-line process, although it was not automated. Ease of automation is one of the main advantages of on-line SPE [7], although off-line SPE can also be automated by means of robotization [10]. The advantage of off-line SPE is its greater flexibility in the choice of elution solvents and in impurity removal [7].

Owing to its inherent simplicity of operation and better repeatability, on-line SP extraction was used for further work. However, the modified off-line procedure was applied for isolation and clean-up of triazines from soil samples, which will be discussed later.

3.5. UV detection of triazines in water

The performance of the method was checked by analysing spiked tap water. Fig. 2a shows a typical chromatogram of tap water spiked with triazines. The linearity was very good ($r^2 = 0.9986–1.000$) and the limits of detection (signal-to-noise ratio = 3) were below 0.05 μg/l and most of them were in the range recommended [1].

For river water, the interference peak at the beginning of the chromatogram was much higher and therefore strongly interfered with the determination of cyanazine and simazine, which elute first, as can be seen from Fig. 2b. Other triazines also showed higher limits of detection, while dipropetryn could not be determined in river water because of its co-elution with an impurity present in the water. Better limits of detection could be achieved by including an additional clean-up step in the preconcentration procedure, but this implied a much more complicated system with additional pumps and valves.

3.6. Particle beam-mass spectrometric results

Although it has been reported that some triazines can be determined by PB-MS [16,17], in our case the performance of the PB-MS system for the detection of triazines was not satisfactory.

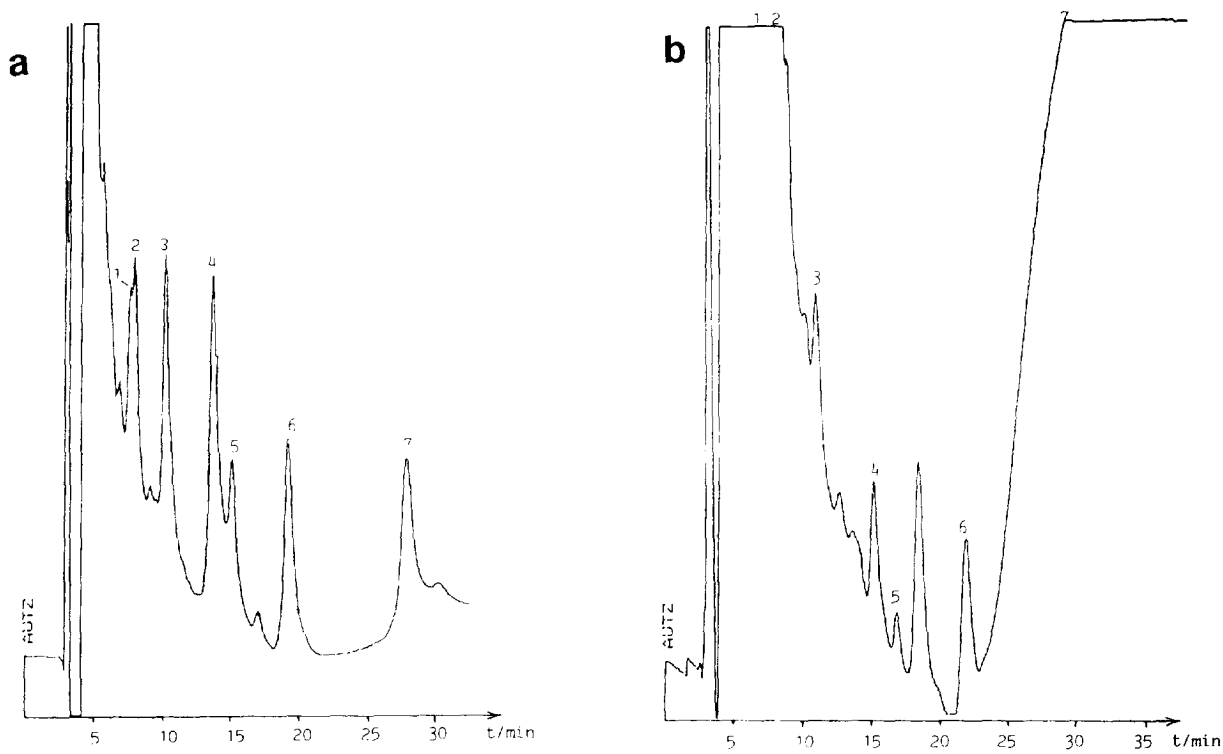


Fig. 2. UV absorbance chromatograms of preconcentrated spiked water samples. (a) Tap water, 0.2 μg/l triazines, 200 ml; sensitivity 0.005 AUFS, detector attenuation 6. (b) River water, 0.2 μg/l triazines, 200 ml; sensitivity 0.02 AUFS, detector attenuation 6. Peaks: 1 = cyanazine; 2 = simazine; 3 = atrazine; 4 = ametryn; 5 = terbutylazin; 6 = prometryn; 7 = dipropetryn.

There was significant peak broadening, as can be observed in Fig. 3, for an injected standard solution compared with the chromatograms in Fig. 2a and b recorded with a UV absorbance detector. The sensitivity was low, typical limits of detection when injecting standard solutions being in the range 2–5 mg/l. Addition of ammonium acetate to the mobile phase did not significantly improve the transport of analytes through the PB interface.

However, when analyses were performed with on-line SPE–LC connected to the PB-MS system, a significant matrix effect could be observed when processing preconcentrated water samples. Quantification was thus best achieved by the standard addition method.

River and drinking water samples were analysed with the on-line SPE–HPLC–PB-MS coupled system. In Table 3, calibration parameters, ranges of linearity and limits of detection are given for the target compounds in drinking water. It is evident that because of high limits of detection, higher volumes of water, typically 300–600 ml, had to be preconcentrated in order to achieve sufficient sensitivity with PB-MS detection for real samples.

In water from a highly polluted stream flowing through an agricultural area, atrazine was detected at the level of 0.3 ± 0.1 μg/l.

In drinking water, an unknown peak was detected, which was subsequently identified as the herbicide bromacil. In Fig. 4, an extracted ion chromatogram of bromacil and a comparison of spectra are shown. The presence of this compound was further confirmed with a bromacil standard. The concentration measured was 0.2 ± 0.1 μg/l.

3.7. Soil analysis results

For pesticide separation from soil before clean-up procedures (including SPE), Soxhlet

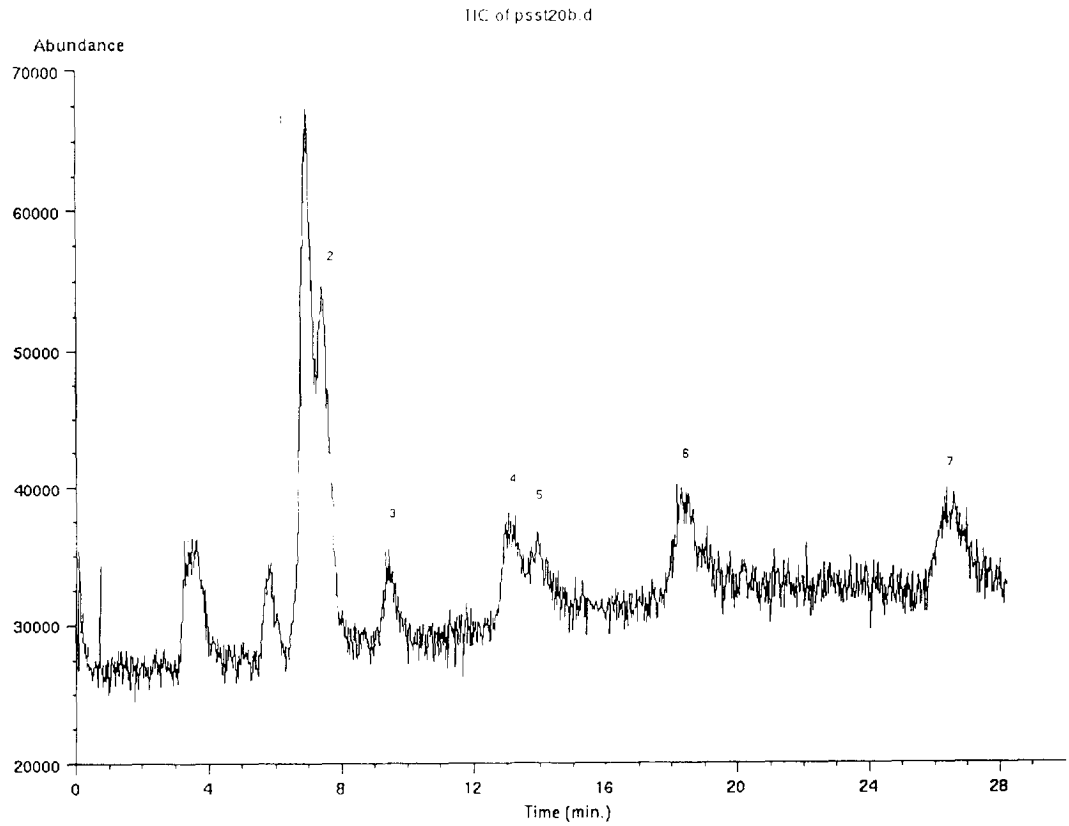


Fig. 3. Total ion chromatogram (scan range from m/z 50 to 400) of a standard solution of pesticides in acetonitrile, 400 ng injected. Peaks as in Fig. 2.

extraction, ultrasonic extraction and supercritical fluid extraction are mostly used. They were found to be comparable in recoveries, while the repeatability was best with supercritical fluid extraction [21]. However, in Soxhlet and ultrasonic extraction, the choice of solvent is very

Table 3
Calibration parameters, ranges of linearity and limits of detection (LOD) (signal-to-noise ratio = 3) for the determination of target triazines by LC–PB-MS

Compound	m/z for quantification	Calibration graph[a]	r	Linearity range (μg/l)	LOD (μg/l)
Cyanazine	225	$y = 39.8x - 1.6$	0.9987	0.2–5.0	0.2
Simazine	201	$y = 160.2x - 49.2$	0.9906	0.2–2.0	0.4
Atrazine	200	$y = 29.9x - 10.4$	0.9866	0.2–5.0	0.7
Ametryn	227	$y = 21.9x + 6.1$	0.9995	0.5–5.0	0.2
Terbutylazin	214	$y = 15.0x - 2.7$	0.9996	0.2–5.0	0.2
Prometryn	184	$y = 26.4x - 1.7$	0.9877	0.2–5.0	0.7
Dipropetryn	255	$y = 23.3x - 4.5$	0.9625	0.2–5.0	1.2

On-line preconcentration of 200 ml of spiked drinking water. Full-scan conditions (m/z from 50 to 400), base peak quantification.
[a] y = in arbitrary units; x = in μg/l.

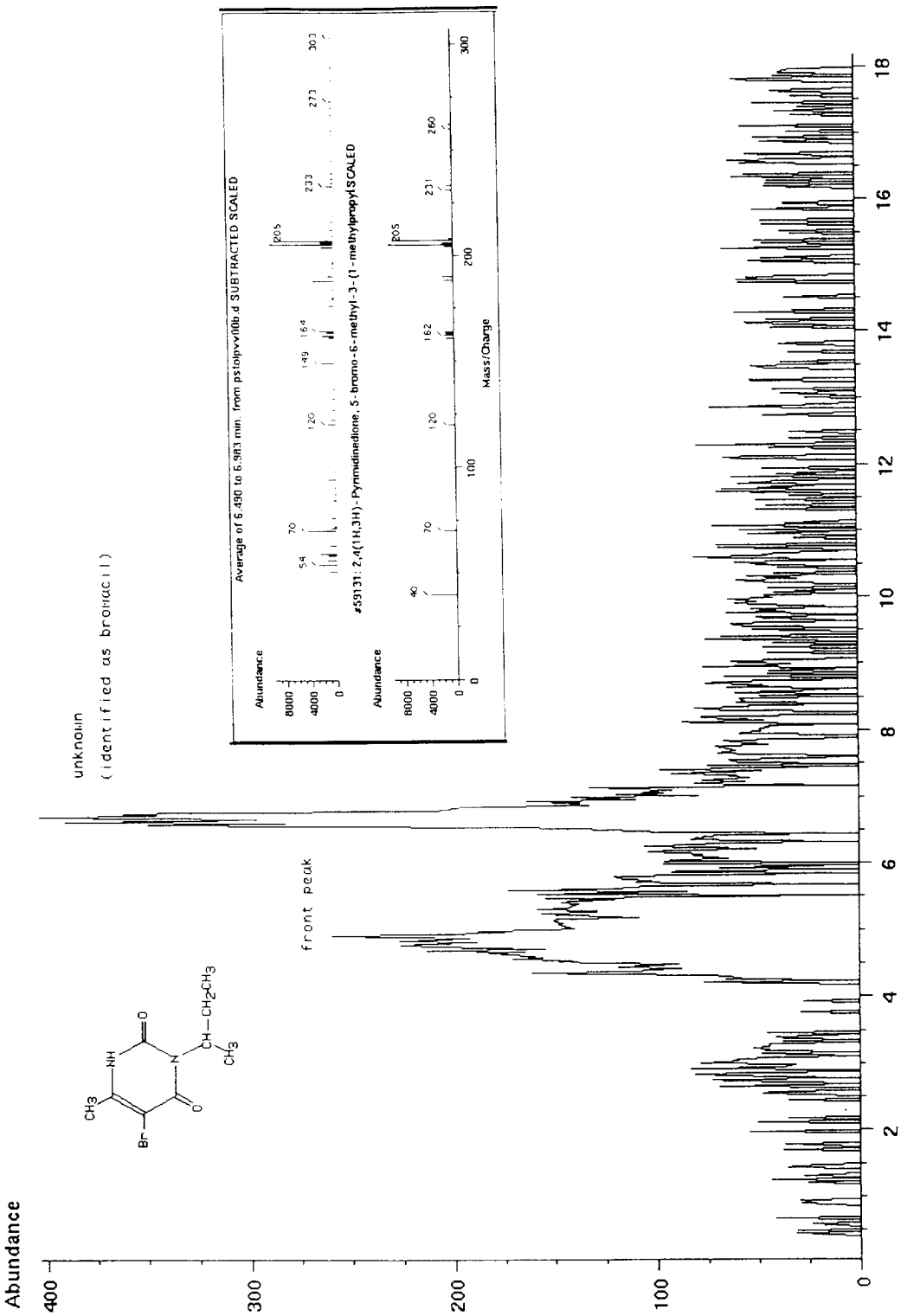


Fig. 4. Extracted ion chromatogram (m/z 207) of an on-line preconcentrated 500-ml sample of drinking water. Inset: comparison of unknown peak spectrum (scan range from m/z 50 to 400) with the spectrum of the herbicide bromacil from a library.

important. As we decided to use C_{18} SPE cartridges for further clean-up of the sample extract, the percentage of organic solvent in the extract applied to the cartridge should be as low as possible in order to allow complete retention of analytes on the C_{18} cartridge [10]. Therefore, all traces of organic solvent should be evaporated before the SPE procedure.

Methanol is the solvent most frequently used for soil extraction, either alone or in mixtures with other solvents or water. However, we decided to use acetone–water, which has been reported to be successful when extracting soil by sonication [19]. The main advantage of acetone over methanol is its greater volatility.

The SPE procedure was the same as for water samples. The ethyl acetate eluate was light brown, indicating a moderate content of other soil components, presumably humic acids. These compounds were removed by passing the ethyl acetate eluate through a strong anion-exchange cartridge, where triazines were not retained.

In spite of several clean-up steps, many interferences were still present in the UV absorbance chromatogram, and therefore some of the triazines could not be quantified in this way. In the PB-MS analysis, the detection limits were too high to detect triazines in soil extracts. Recoveries of the overall extraction procedure ranged from 45% (terbutylazine) to 120% (atrazine).

In the PB-MS analysis of cornfield soil samples, we were not able to detect any triazines, but some other pesticides were identified, e.g., chloromethylaniline and the herbicide chlorotoluron.

4. Conclusions

On-line solid-phase extraction demands less sample manipulation and is simpler than off-line SPE. It is more convenient for the analysis of water samples, while soil samples are better processed using off-line SPE. UV absorbance detection of triazines is sensitive enough, but lacks confirmation, while PB-MS detection lacks sensitivity for triazines, as typical limits of detection for drinking water samples are in the 0.2–1.2 μg/l range. This can be overcome by preconcentrating higher volumes of sample or, alternatively, by using SIM. However, this implies losing information about other pollutants present in environmental samples, as the LC–PB-MS system serves also as a powerful tool for the detection and identification of unknown contaminants.

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