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Determination of phenylurea herbicides in water samples using on-line sorptive preconcentration and high-performance liquid chromatography with UV or electrospray mass spectrometric detection

Erik Baltussen*, Henri Snijders, Hans-Gerd Janssen, Pat Sandra, Carel A. Cramers

Eindhoven University of Technology, Laboratory of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven, Netherlands

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Abstract

A recently developed method for the extraction of organic micropollutants from aqueous samples based on sorptive enrichment in columns packed with 100% polydimethylsiloxane (PDMS) particles was coupled on-line with HPLC analysis. The sorptive enrichment procedure originally developed for relatively nonpolar analytes was used to preconcentrate polar phenylurea herbicides from aqueous samples. PDMS extraction columns of 5, 10 and 25 cm were used to extract the herbicides from distilled, tap and river water samples. A model that allows prediction of retention and breakthrough volumes is presented. Despite the essentially apolar nature of the PDMS material, it is possible to concentrate sample volumes up to 10 ml on PDMS cartridges without losses of the most polar analyte under investigation, fenuron. For less polar analytes significantly larger sample volumes can be applied. Since standard UV detection does not provide adequate selectivity for river water samples, an electrospray (ES)-MS instrument was used to determine phenylurea herbicides in a water sample from the river Dommel. Methoxuron was present at a level of 80 ng/l. The detection limit of the current set-up, using 10 ml water samples and ES-MS detection is 10 ng/l in river water samples. Strategies for further improvement of the detection limits are identified. © 1998 Elsevier Science B.V.

Keywords: Water analysis; Electrospray ionisation; Preconcentration methods; Mass spectrometry; Pesticides; Phenylureas

1. Introduction

Phenylurea herbicides are widely used for agricultural purposes both in Europe and in the US. At present, regulations limit the concentration of these compounds in drinking water to 0.1 μg/l for individual components and to 0.5 μg/l for the total pesticide content [1]. Analytical techniques available today do not exhibit adequate sensitivity for direct analysis of these components in water samples, i.e. the solutes have to be enriched prior to the actual analysis. Also, at the concentration level of 0.1 μg/l and lower a massive number of analytes is present, imposing high demands on the chromatographic separation step. For phenylurea herbicides, efficient separations can be realized by either gas chromatography (GC) or liquid chromatography (LC).

GC analysis of underivatized phenylurea herbicides has been described in the literature [2].

*Corresponding author.

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Unfortunately, most of these compounds are thermally labile and therefore thermal degradation products are often detected instead of the molecular herbicides. This renders quantification difficult. Moreover, identification of the individual herbicides originally present is often impossible since several different solutes generate identical degradation products [3]. To overcome these problems derivatization procedures were developed to prevent thermal degradation of the phenylurea herbicides [3,4]. The derivatized compounds can be reasonably well chromatographed but since the derivatization process itself is composed of several steps this methodology is rather time-consuming. Moreover, every sample preparation step is a possible source of errors and therefore sample preparation should be kept as simple as possible. For these reasons we considered GC to be unsuitable for the routine analysis of phenylurea herbicides.

Liquid chromatography is widely used for the determination of phenylurea herbicides in aqueous samples [5–7]. In LC, the pesticides in question can be analyzed without the risk of thermal degradation. Unfortunately, however, due to the low resolution of LC compared to GC, complete separation of all solutes is often difficult to achieve.

Classically, the analytes are preconcentrated from the aqueous sample by liquid–liquid extraction (LLE). Because this technique is laborious, uses vast amounts of expensive and toxic organic solvents, is difficult to automate and requires additional concentration steps it has largely been replaced by solid-phase extraction (SPE) [8,9]. Numerous SPE methods have been developed over recent years. The difference between these SPE methods mainly lies in the adsorbent used to isolate the analytes from the water matrix. Many different materials are used such as, octadecylsilica [8,10,11], styrene–divinylbenzene (S–DVB) [12] and many others [10]. Although these methods generally show adequate performance the extraction selectivity is usually poor, though this is not a problem in those cases where it is desired to detect as much solute as possible (e.g. screening procedures) it can be a problem in low-level target compound analysis. Also, more polar analytes can be partially lost, e.g. chlortoluron is partially lost on S–DVB cartridges [12]. Lack of retention is a problem that can basically only be overcome by either changing the solid-phase material or increasing the amount of the retaining phase. Selectivity, on the other hand, can only be enhanced by a change in the solid-phase material. In order to increase the selectivity of the preconcentration step, Pichon et al. [13] used an immunosorbent containing anti-isoproturon antibodies. This phase showed a highly improved selectivity and a high affinity for the target solute isoproturon. However, the material exhibits a poor selectivity for the other phenylurea herbicides, these solutes were partially or totally lost, resulting in recoveries ranging from only 0 to 40%. More successfully, an on-line SPE–LC–thermospray-MS procedure was developed by Bagheri et al. [14] for the preconcentration and analysis of a range of phenylurea herbicides from surface and drinking water samples.

In recent years, some emphasis has been on the use of short, e.g. 1-cm long preconcentration columns [15]. Such small columns provide several advantages, such as rapid desorption and a need for a small sample volume. Such small extraction columns can easily be coupled on-line with LC analysis and it was recently shown by Hoogenboom et al. that it is possible to do both sample preconcentration and the analytical separation on the same 2-cm column [16].

Retention in all of the above methods occurs by adsorption of the analytes on active sites on the adsorbent surface (e.g. antibodies). In this contribution an alternative type of solid-phase is evaluated. Here, 100% polydimethylsiloxane (PDMS), known as e.g. OV-1, SE-30, DB-1 etc. in GC, is used as the retaining phase. The main difference of the PDMS phase compared to the aforementioned adsorbents is that the analytes are not retained on the surface, rather they are retained in the bulk of the PDMS phase which essentially behaves as a liquid phase. Retention of solutes on the PDMS phase thus occurs by dissolution (sorption) of the analytes into this polymeric phase. The retaining power of the PDMS phase for a certain solute is therefore not dependent on its concentration or on the concentration of matrix compounds. The extraction selectivity of the PDMS phase is comparable to that of ODS and S–DVB materials, as the extraction efficiencies are essentially only determined by the polarity of the analytes. The use of the PDMS phase, in an SPE like set-up, was recently demonstrated for the analysis of

organochlorine pesticides (OCPs) and PAHs from water samples followed by GC–MS analysis [17].

The PDMS-based extraction technique described here shows resemblances with other techniques such as SPME [18] and open tubular trapping [19]. However, compared to these techniques it poses several advantages such as easier quantitation, better detection limits and others [20]. In this paper, the possibilities are explored to couple the sorptive extraction procedure on-line with LC analysis for the trace analysis of phenylurea herbicides in water samples. At first, a UV detector was used but in order to improve the selectivity of the analytical procedure an electrospray MS instrument was coupled in series with the UV detector. This combination was recently shown by Molina et al. [21] to be suitable for the analysis of phenylurea herbicides. Additionally, a theory model is described which allows calculation of retention and breakthrough volumes from octanol–water partitioning coefficients.

2. Theory

In previous work a model was developed for the calculation of retention and breakthrough volumes of solutes on packed PDMS traps [20]. This model was originally derived and evaluated for air sampling and is here applied to water sampling. The basic equations in the model are listed below. The breakthrough volume can be calculated from the equations derived by Lövkvist and Jönsson [22]:

5% breakthrough:

$$V_b^5 = V_r f(N) = V_0(1+k)\left(0.9025 + \frac{5.360}{N} + \frac{4.603}{N^2}\right)^{-\frac{1}{2}} \quad (1)$$

10% breakthrough:

$$V_b^{10} = V_r f(N) = V_0(1+k)\left(0.81 + \frac{2.878}{N} + \frac{1.941}{N^2}\right)^{-\frac{1}{2}} \quad (2)$$

where V_b is the breakthrough volume, V_r is the retention volume, V_0 is the trap dead volume, k is the retention factor and N is the number of theoretical plates. In air sampling, k can be directly calculated from GC retention indices. When sampling water, this is no longer possible. Fortunately, Pawliszyn et al. [23,24] found good correlation in solid-phase micro-extraction between log $K_{PDMS/w}$ and log $K_{o/w}$, where $K_{PDMS/w}$ and $K_{o/w}$ are the PDMS–water and octanol–water partitioning coefficients respectively. Therefore log $K_{o/w}$ values were used to estimate k by:

$$k = \frac{K_{PDMS/w}}{\beta} = \frac{K_{o/w}}{\beta} \quad (3)$$

where β is the phase ratio of the PDMS trap. Plate numbers were calculated by the Knox equation [25,26]:

$$h_r = 3\nu^{1/3} + \frac{1.5}{\nu} + 0.05\nu \quad (4)$$

with:

$$h_r = \frac{H}{d_p} = \frac{L}{Nd_p} \quad (5)$$

$$\nu = \frac{ud_p}{D_m} \quad (6)$$

After the choice of the sampling velocity (u, m/s) and trap parameters (d_p and L, m), the diffusivity of the analyte (D_m, m^2/s) in the mobile phase has to be obtained from published data sets [27] or calculated using approximation techniques [28]. Then N can be calculated directly from Eqs. (4)–(6). Log $K_{o/w}$ values can be found for many compounds in literature [29,30] and allows calculation of retention and breakthrough volumes on the PDMS traps.

In practice the recovery of the analytes as a function of the volume sampled through the cartridge is an important feature of the sample pretreatment procedure. It can be useful to know the maximum recovery that can be expected under real-life sampling conditions. Maximum recovery (R_m) occurs at an infinite number of plates and can be expressed as:

$$R_m = \frac{V_r}{V_s}100\% \; V_r < V_s$$
$$R_m = 100\% \; V_r \geq V_s \quad (7)$$

where V_s is the sample volume.

3. Experimental

3.1. Phenylurea herbicides

In this investigation emphasis is on the characteristics of the PDMS extraction phase. Therefore, only five phenylurea herbicides were selected from the priority list to facilitate the chromatographic separation on the analytical LC column. The selected phenylurea herbicides ranged from the most polar one, fenuron, to the most apolar one, chloroxuron. All nonincluded phenylureas are of a polarity in between these extremes. It is therefore assumed that if this procedure shows adequate performance for the five analytes under investigation, it will be viable for all phenylureas. Structural formulas and physical properties of the analytes used, are listed in Table 1. Standard solutions were prepared in acetonitrile.

3.2. Extraction cartridges

The PDMS particles were made by the cryogenic grinding method described previously [17,20]. The starting material was Silastic silicone laboratory tubing obtained from Dow Corning (Midland, MI, USA). The obtained particles were sieved in the range 240–400 μm (average $d_p = 320$ μm).

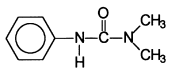
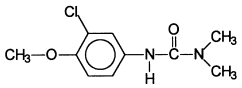
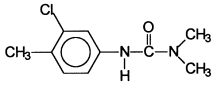
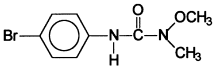
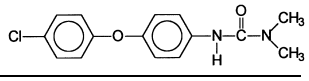
An empty HPLC column ($L = 25$ cm, I.D. = 4.6 mm) (Chrompack, Middelburg, Netherlands) was cut into five pieces of 5 cm. The outlets and inlets were fitted with female 1/16‘ valco zero dead volume connectors. The five short columns were slurry packed with the PDMS particles and 0.45-μm filters were placed on the inlet and outlet of all five columns. By connecting either 1, 2 or 5 columns in series, extraction columns of 5-, 10- and 25-cm length were obtained. Although extraction cartridges are generally required to be shorter than 1.5 cm for successful application in on-line SPE–LC [13], the long PDMS tubes were used for direct coupling to the LC.

3.3. Experimental set-up

A standard LC gradient system with UV detection was used. It consisted of a Shimadzu AT-10 low pressure gradient pump (Shimadzu, Tokyo, Japan), a Rheodyne six-port injection valve (Rheodyne, Berkeley, CA, USA) equipped with a 20-μl injection loop and an Applied Biosystems UV detector (Applied Biosystems, Foster City, CA, USA). The analytical column was a Zorbax ODS column (MacMod Analytical, Chadds Ford, PA, USA) with an I.D. of 4.6 mm and a length of 25 cm. The column flow-rate was 1 ml/min during all experiments. The composition of the mobile phase is discussed below.

The extraction columns were built around a six-way valve (Valco, Houston, TX, USA) inserted between the gradient pump and the sample injection valve. A schematic overview of the system is given

Table 1
Structural formulas and physical properties of the selected phenylurea herbicides

No.	Herbicide	M_r	log $K_{O/W}$ [30]	Structure
1	Fenuron	164	0.87	
2	Methoxuron	228	1.68	
3	Chlorotoluron	212	2.53	
4	Metobromuron	259	2.46	
5	Chloroxuron	290	4.00	

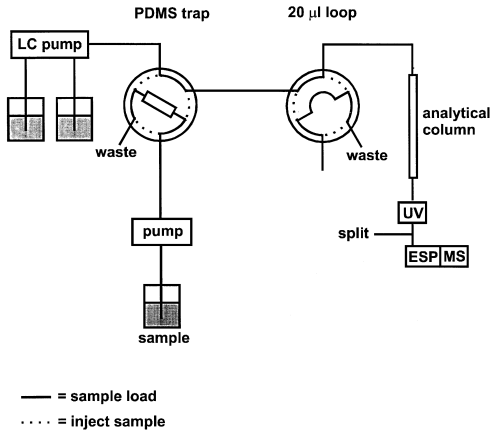


Fig. 1. Diagram of the on-line SPE–HPLC–MS system. For injection of a water sample, the PDMS trap is used (left valve). For injection of a standard, the 20-μl injection loop (right valve) is used. ESP = electrospray interface.

in Fig. 1. All water samples were filtered through a 0.45-μm filter prior to analysis. An LKB 2150 (LKB-Produkter, Bromma, Sweden) HPLC pump was used to pump the water sample through the extraction cartridge. For all water extraction experiments, a sample volume of 10 ml was used which was pumped at a flow-rate of 1 ml/min through the extraction column. With the present set-up it is possible to inject 20 μl of standard solutions as well as to perform on-line SPE–HPLC of aqueous samples.

LC–MS experiments were carried out with a PE-SCIEX API300 LC–MS–MS instrument (Perkin-Elmer SCIEX Instruments, Thornhill, Canada), equipped with a pneumatically assisted electrospray (ion spray) interface. Since the optimal flow-rate for this interface is 40 μl/min, the column effluent was split after the UV detector, allowing only 40 μl/min to enter the MS. The mass spectrometer was set to the following parameters: ion spray voltage, 5.4 kV; orifice voltage, 35 V. The nebulizer gas (air) and curtain gas (nitrogen) were adjusted to 1.23 l/min and 0.95 l/min respectively. During all experiments, the instrument was operated in the positive ion mode.

Initial experiments showed that single stage MS in the selected ion monitoring (SIM) mode provided adequate selectivity and sensitivity. Hence, the superior selectivity of the MS–MS mode was not required for the analysis of phenylurea herbicides in river water samples. Maximum sensitivity was determined by testing the four eluent systems listed in Table 2. To the aqueous phase, trifluoroacetic acid (TFA) or formic acid (FA) was added to promote protonation of the analytes in the ion source of the MS. Also, the applicability of adding ammonium acetate (AA) the aqueous phase for the formation of NH_4-adducts in the electrospray interface was tested. For all eluent systems, the gradient program started at 5% B which was held for 5 min. The eluent composition was then programmed with a linear gradient to 100% B at 35 min. After 40 min the run was stopped and the gradient composition was programmed back to 5% B in 10 min.

Table 2
Eluent systems

System	Eluent A	Eluent B
1	H_2O	Acetonitrile
2	H_2O + 0.1% (v/v) trifluoroacetic acid	Acetonitrile
3	H_2O + 0.1% (v/v) formic acid	Acetonitrile
4	H_2O + 5 m*M* NH_4COOCH_3	Acetonitrile

4. Results and discussion

4.1. Extraction

Retention and breakthrough volumes were calculated with the equations described in Section 2. The diffusivity in the mobile phase, D_m, was assumed to be 10^{-9} m^2/s for all analytes, log $K_{o/w}$ values were used from Table 1. The parameters of the prepared traps are listed in Table 3. The calculated retention volumes (V_r), maximum recoveries (R_m) and the 5% and 10% breakthrough volumes (V_b^5 and V_b^{10}) are listed in Table 4.

For fenuron, a retention volume of 14.3 ml is calculated for the 25-cm trap. The corresponding 5%

Table 3
Properties of the prepared traps

Trap	*L* (m)	V_0 (ml)	β	*N*
A	0.05	0.289	0.851	3.57
B	0.1	0.577	0.851	7.14
C	0.25	1.443	0.851	17.86

Table 4
Calculated retention data (further details as in text)

	A	B	C
V_r (ml)			
Fenuron	2.86	5.71	14.3
Methoxuron	16.6	33.2	82.9
Chlortoluron	115	230	577
Metobromuron	98.4	196	491
Chloroxuron	$3.40 \cdot 10^3$	$6.79 \cdot 10^3$	$1.70 \cdot 10^4$
R_m (%)			
Fenuron	28.6	57.1	100
Methoxuron	100	100	100
Chlortoluron	100	100	100
Metobromuron	100	100	100
Chloroxuron	100	100	100
V_b^5 (ml)			
Fenuron	1.72	4.32	12.9
Methoxuron	9.99	25.1	75.2
Chlortoluron	69.5	175	523
Metobromuron	59.2	149	445
Chloroxuron	$2.04 \cdot 10^3$	$5.1 \cdot 10^3$	$1.53 \cdot 10^4$
V_b^{10} (ml)			
Fenuron	2.15	5.10	14.4
Methoxuron	12.5	29.6	83.9
Chlortoluron	86.9	206	584
Metobromuron	74.0	176	497
Chloroxuron	$2.56 \cdot 10^3$	$6.07 \cdot 10^3$	$1.72 \cdot 10^4$

breakthrough volume is 12.9 ml. Since the aim of this paper is the quantitative determination of the components, a sample volume (V_s) of 10 ml was selected for further use. Using a sample volume of 10 ml losses are anticipated for fenuron on the 5- and 10-cm traps but all other components should be quantitatively retained on all traps.

In Table 5 the experimental recoveries obtained at a sample volume of 10 ml are listed. For the determination of these recoveries a concentration of 40 μg/l of the analytes spiked in distilled water was used. This relatively high spiking level was chosen, since initially only UV detection was available. However, retention on the PDMS phase is based on a partitioning mechanism rather than on an adsorption mechanism. Recoveries do therefore, to a large extent, not depend on the concentration levels used [17,20]. Recoveries were calculated by comparison to a direct injection of a 20 mg/l standard (20 μl) which contains the same amount of analyte. As was expected, fenuron is partially lost on the 5- and 10-cm columns and in fact the recovery is very close to the calculated maximum recovery (i.e. 32 vs. 28.6 and 56 vs. 57.1) indicating that $K_{o/w}$ is indeed a good approximation for $K_{PDMS/w}$. There is a slight loss of methoxuron on the 5- and 10-cm columns but since the recovery is above 70% this is considered to be satisfactory for quantitative determinations. Reproducibility is between 10–15% ($n=3$) for all compounds under investigation.

Table 5
Experimental recoveries ($V_s=10$ ml)

Recovery (%)	A	B	C
Fenuron	32	56	110
Methoxuron	76	84	113
Chlortoluron	93	109	95
Metobromuron	106	116	114
Chloroxuron	98	108	112

As an illustration of the performance of the system, Fig. 2 shows the analysis of the five phenylurea herbicides spiked at a level of 4 μg/l in tap water. A 25-cm PDMS column was used to concentrate 10 ml of the sample. It is clear that the PDMS column despite its relatively large dimensions does not result in additional band broadening. This is probably caused by the much lower retention of PDMS compared to the C_{18} material in the analytical column, i.e. the analytes are efficiently focused on the analytical column under the applied mobile phase composition and gradient. Moreover, it was confirmed that the recoveries of the solutes at this level (4 μg/l) are identical as those listed in Table 5 (40 μg/l).

4.2. Environmental samples/LC–MS

For the LC–MS experiments a new LC column was used. This resulted in somewhat increased retention times and an improved peak shape of the target solutes. To identify the mobile phase composition that yields maximum sensitivity for the combined LC–UV–MS set-up, four eluent systems (see Table 2) were used to analyze a 20 mg/l standard of the five phenylurea herbicides. The MS was operated in the full scan mode, scanning from 150 to 350 amu at a scanning speed of 2 scans/s. The four chromatograms obtained are shown in Fig.

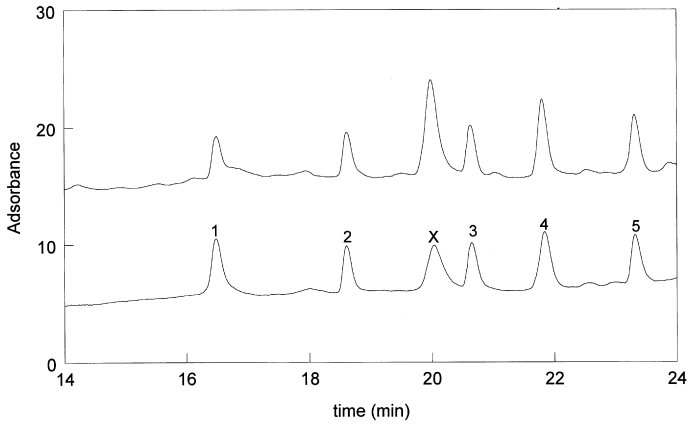


Fig. 2. Analysis of phenylurea herbicides spiked in tap water at a concentration of 4 μg/l. Standard is a 20-μl injection of a 20 mg/l solution in acetonitrile containing an equal amount of the analytes. Peak assignment, see Table 1, X=unknown impurity. Gradient: acetonitrile–water (10:90, v/v) for 5 min, then a linear program to 100% acetonitrile in 35 min.

3A to D. It is clear that maximum sensitivity (S/N) is obtained with systems 3 and 4. For several solutes (e.g. chloroxuron) a slightly better sensitivity is obtained using eluent system 4 where ammonium acetate was added to the mobile phase. However, this additive generates a more complicated background than formic acid (system 3) and therefore the formic acid system was chosen for all further experiments.

In Fig. 4, a chromatogram is shown for the on-line preconcentration and LC–UV–MS analysis of the five phenylureas at a level of 40 μg/l in tap water. The MS was operated in the SIM mode monitoring ions of protonated molecules $(MH)^+$. These were the only ions generated by the herbicides under the experimental conditions used. For maximum sensitivity a time program was set-up such that only one ion was monitored corresponding to that of the eluting component. From this chromatogram, the detection limit can be estimated to be approximately 10 ng/l (ppt). Fig. 5A shows a chromatogram of the analytes spiked at a level of 40 ng/l in distilled water and Fig. 5B shows a chromatogram of 10 ml of a water sample taken from the river Dommel. In this sample methoxuron was identified and found to be present at a level of 80 ng/l. An interesting feature of the method described here is that there are very few interferences observed in the chromatogram. Hence, identification of the target solutes is relatively straightforward.

5. Conclusions

A method for sorptive enrichment of water samples coupled on-line with HPLC analysis is described. It is based on sorption of the analytes in pure 100% polydimethylsiloxane (PDMS) particles. A set of equations is presented that allows estimation of retention and breakthrough volumes using $K_{o/w}$ values from the literature. The theoretically calculated breakthrough volumes were in excellent agreement with the experimental results. This allows selection of PDMS trap parameters, i.e. length and diameter, for proper retention of the analytes without a need for preliminary experiments. For the polar phenylurea herbicides a relatively long trap of 25 cm was necessary but this did not pose any problems in the on-line coupling to LC.

Since the selectivity of the PDMS phase is not very high, i.e. comparable to C_{18} and S–DVB, the selectivity of an electrospray-MS instrument was used for the determination of phenylurea herbicides in river water samples. Methoxuron was detected at a level of 80 ng/l in a water sample taken from the river Dommel. The detection limit of the current set-up using electrospray MS detection and sample volumes of 10 ml is 10 ng/l. Due to the relatively low retention of the PDMS phase for the most polar solutes, compared to other more strong adsorbents (e.g. S–DVB), the sample volume is here restricted

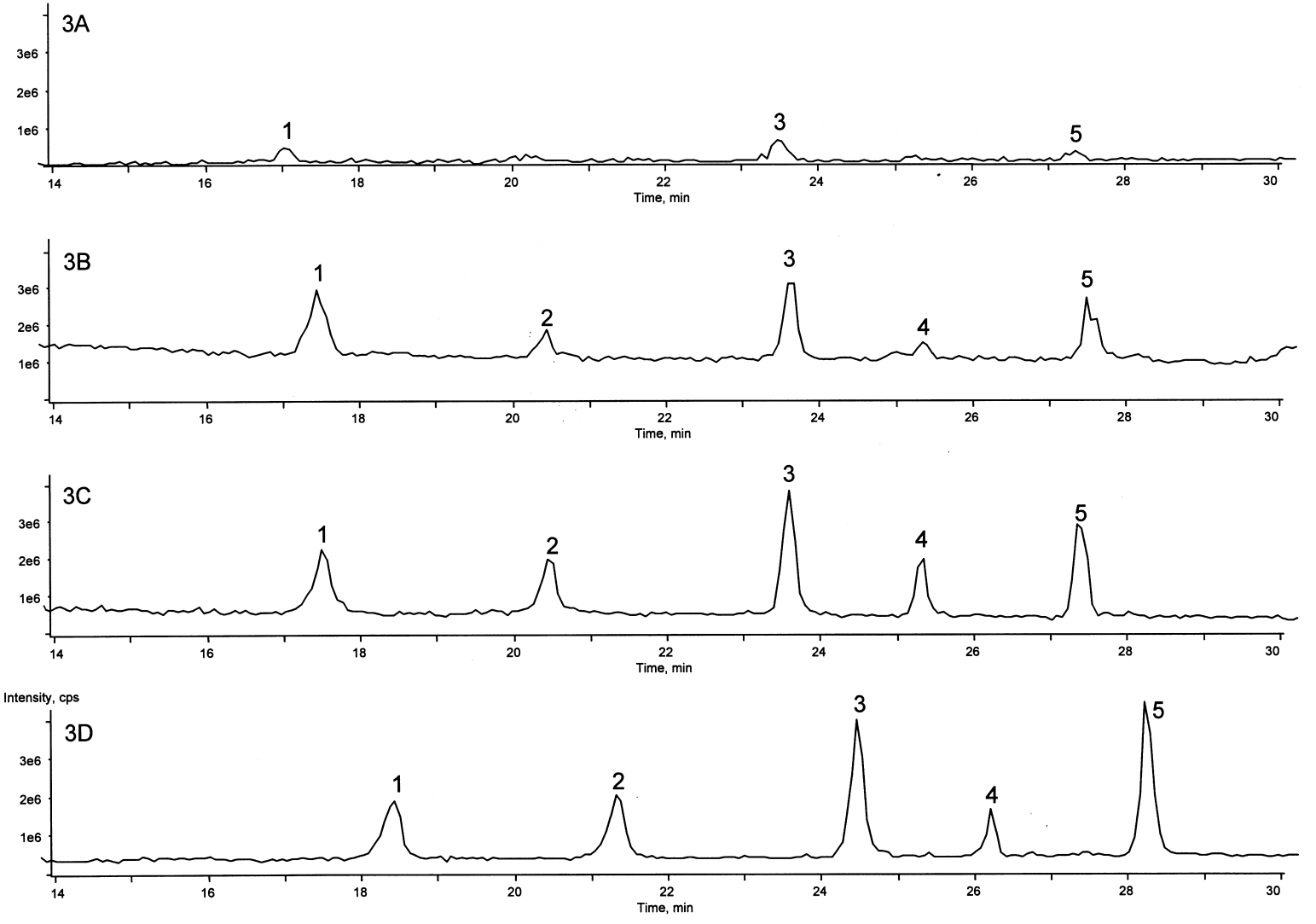


Fig. 3. Comparison of the different eluent systems listed in Table 2. Chromatograms are the result of a direct injection of a standard solution (20 mg/l), Gradient conditions as in Table 2: (A) system 1; (B) system 2; (C) system 3, (D) system 4. For peak assignment, see Table 1.

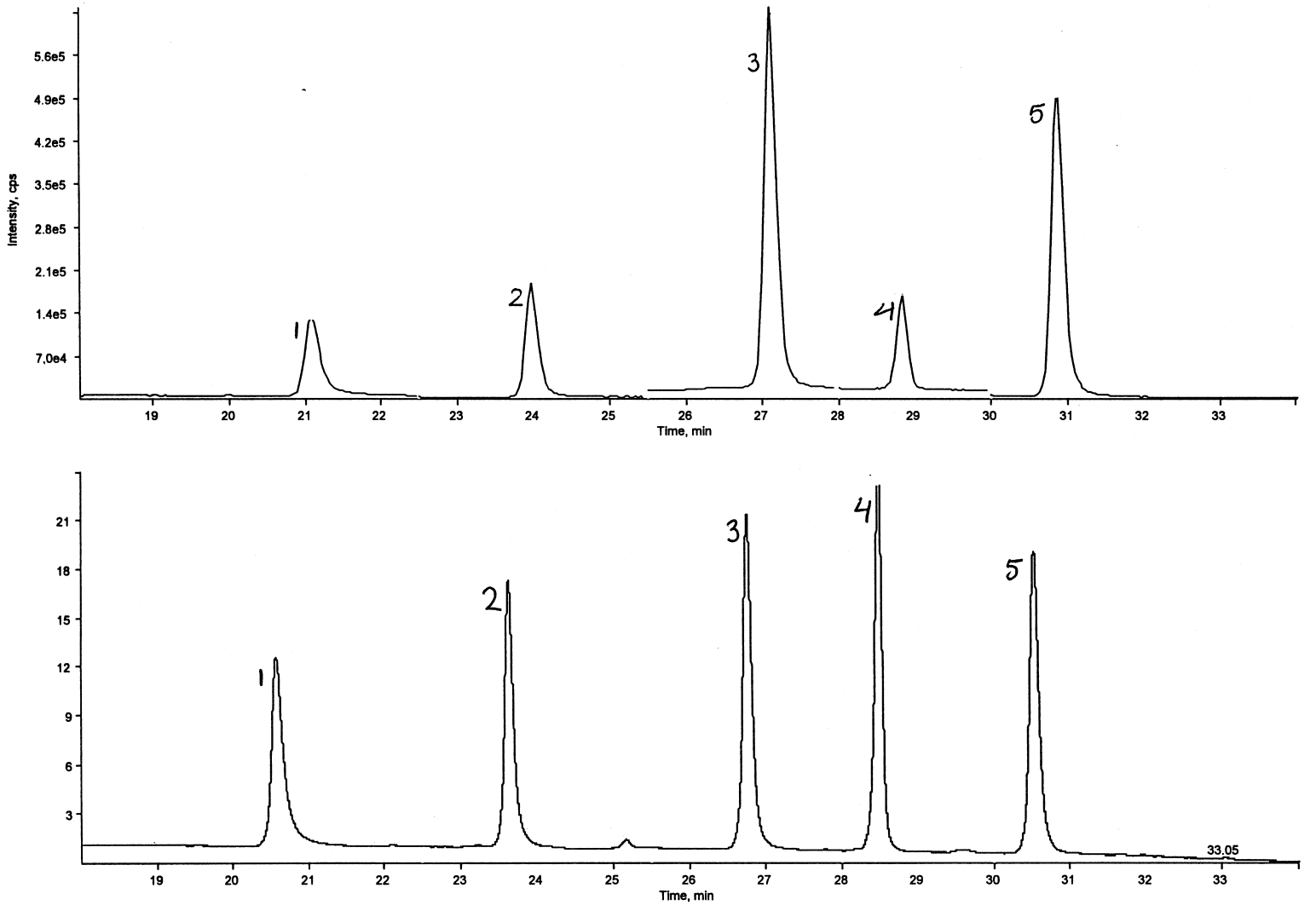


Fig. 4. Preconcentration of 10 ml of a distilled water sample spiked to a level of 40 μg/l with five phenylurea herbicides. Upper trace, mass spectrometric detection; lower trace, UV detection. Peak assignment, see Table 1.

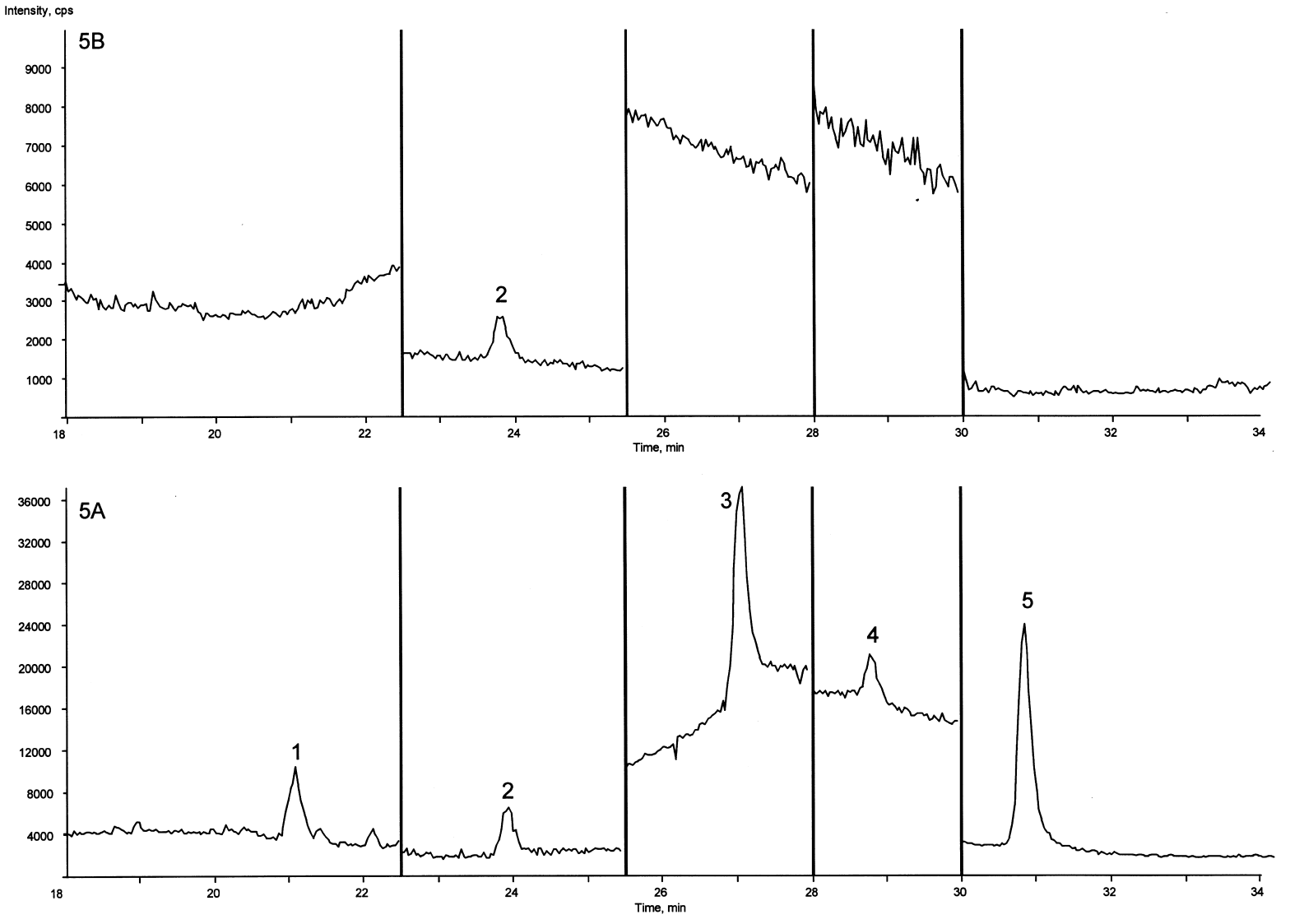


Fig. 5. Standard (40 ng/l, 10 ml) of phenylurea herbicides in distilled water (A) and a 10-ml water sample from the river Dommel (B). Peak assignment, see Table 1. The vertical stripes indicate the switch points in the MS time program. Detected solute (2, methoxuron) was found at a concentration of 80 ng/l.

to 10 ml. In future, the sample volume might be increased by the use of more polar sorbents (e.g. substituted silicones, acrylics) which have a higher affinity for polar species. The detection limits can be even further enhanced using ES-MS–MS.

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