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Determination of herbicides, including thermally labile phenylureas, by solid-phase microextraction and gas chromatography–mass spectrometry

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Abstract

A method for the determination of 10 herbicides, including thermally unstable compounds, has been developed. The method uses solid-phase microextraction (SPME) with a polyacrylate fibre. Separation, identification and quantification were accomplished with gas chromatography–mass spectrometry. The herbicides chosen belong to different chemical groups and were alachlor, atrazine, chlorotoluron, diclofop, diflufenicam, ethofumesate, isoproturon, linuron, terbutryn and trifluralin. In the present work we studied the chromatographic behaviour of three phenylureas as a function of the medium and injection mode employed. The compounds generated as a function of the solvent used in direct injection of the phenylureas (ethyl acetate, methanol and methanol–water) and those obtained when injection was accomplished using the polyacrylate fibre were determined. The results allow us to propose a method for the determination of stable and thermally unstable herbicides as long as a preconcentration step involving SPME is carried out. In the proposed method, the limits of detection varied between 0.02 μg/l for ethofumesate and 0.11 μg/l for chlorotoluron. The method was applied to the determination of these herbicides in surface and ground water samples, performing quantification by standard addition calibration. The contents of chlorotoluron and atrazine found were significantly equal to those obtained using HPLC after a preconcentration step with styrene–divinylbenzene sorbents.

Keywords: Solid-phase microextraction; Environmental analysis; Water analysis; Pesticides; Phenylureas

1. Introduction

Solid-phase microextraction (SPME) is currently one of the methods used for the isolation and/or preconcentration of analytes in different matrices and is a previous step to their analysis. The basic concepts of SPME were first reported by Belardi and Pawliszyn [1] and are based on the distribution of analytes between the extractant phase immobilized on the fibre and the matrix (water, air, soils, foodstuffs, etc.).

The first studies addressing SPME refer only to the determination of analytes by SPME–GC coupling. In 1995, a report was made by Chen and Pawliszyn [2] of the first interface for SPME–HPLC

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coupling. Today, the analytical instrumentation includes complete automatization of SPME–GC [3], and SPME–HPLC [4] systems.

The fibres most commonly used for SPME are polymethylsiloxane (PDMS) and polyacrylate (PA). However, fibres with an octadecyl (C_{18}), octyl (C_8) or phenyl extractant phase, and also with two extractant phases (polymethylsiloxane–divinylbenzene, PDMS–DVB, polymethylsiloxane–carboxen, PDMS–CAR, and carbowax–divinylbenzene, CW–DVB) have been used.

The application of SPME for the preconcentration of analytes of different chemical nature in aqueous environmental samples is widespread. This extraction technique has been applied to the determination of benzene, toluene, ethylbenzene, xylenes and aromatic polycyclic hydrocarbons [5]; alkanes, benzene and alkylbenzene [6]; petroleum hydrocarbons [7]; organic Hg, Pb and Sn compounds [8], polychlorobiphenyls [9]; phenols [10]; polar and non-polar compounds (alcohols, anilines, chlorobenzenes, nitrocompounds) [11]; iodinated disinfection sub-products [12] and aliphatic hydrocarbons, aldehydes, alcohols and ketones [13].

The applications of SPME in sample preparation for the analysis of pesticides by gas chromatography and high-performance liquid chromatography have been reviewed by Beltran et al. [14]. This review includes the different applications classified as a function of the different families of pesticides (organochlorine, organophosphorus, triazines, thiocarbamates, uracils, urea derivatives and dinitroanalines) and the samples analysed include water, soils, foods and biological fluids.

Among the 10 herbicides determined here, three of them were phenylureas (chlorotoluron, linuron and isoproturon), whose analysis by direct GC is not recommended owing to their thermal instability. To avoid the thermal degradation of phenylureas in the injector and in the column, derivatization methods able to convert the phenylureas into thermally stable compounds have been used [15–17]. Despite this, derivatization involves longer analysis times and affords low reproducibility. Gerecke et al. [18] determined phenylureas (diuron, isoproturon and chlorotoluron) by solid-phase extraction of the analytes, later derivatization and, finally, extraction and injection by SPME. The combination of these three steps, SPE–derivatization–SPME, allows one to obtain detection limits between 0.3 and 1.0 ng/l such that the method is highly suitable for the determination of these analytes in aqueous samples.

Through careful control of the experimental conditions, Gennaro et al. [19] were able to use direct GC to determine four phenylureas (fenuron, monuron, isoproturon and linuron) since they minimized the thermal decomposition of the compounds or determined them indirectly by converting the phenylureas into the corresponding isocyanates.

Berrada et al. [20] described a procedure for the SPME determination of six ureas (chlorsulfuron, fluometuron, isoproturon, linuron, metabromuron and monuron). Two of the fibres used were of PDMS, one was of PA, and analysis was accomplished by GC with a nitrogen–phosphorus detector. The determination of phenylureas is indirect since the compounds detected and quantified are the aniline derivatives.

Here we studied the chromatographic behaviour of three phenylureas and propose a method for the determination of these and another seven herbicides using SPME and later separation and quantification by GC–MS. The herbicides selected for study are widely used in an agricultural area close to the city of Salamanca (Spain) and hence the method developed was applied to the determination of these herbicides in samples of surface and ground waters.

2. Experimental

2.1. Materials

The SPME holder and PA fibre (85 μm thickness) were supplied by Supelco (Bellefonte, CA, USA). The fibre was conditioned prior to use by placing it in the injector of the gas chromatograph for 3 h at 300 °C. Following this, a series of blank assays was performed until no chromatographic signals were obtained.

An SBS immersion thermostat from Selecta (Barcelona, Spain) was used to maintain a constant temperature during the SPME extraction. The magnetic stirrer used was a Jenway 1000 model from Selecta. Vials of 10-ml capacity were used throughout the study.

Sodium chloride at a purity of 99.8%, RA quality, was purchased from Panreac (Barcelona, Spain). Methanol of HPLC-grade was supplied by BDH (Poole, UK). Ultra-high-quality water was obtained with an Elgastat UHQ water purification system.

2.2. Standards

The herbicides were obtained from Riedel-de Haën (Seelze-Hannover, Germany) and were used without further purification (minimum percent purity greater than 98%). The herbicides studied were as follows: alachlor, 2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl) acetamide, CAS RN [15972-60-8]; atrazine, 6-chloro-*N*-ethyl-*N′*-(1-methylethyl)-1,3,5-triazine-2,4-diamine, CAS RN [1912-24-9]; chlorotoluron, *N′*-(3-chloro-4-methylphenyl)-*N*,*N*-dimethylurea, CAS RN [15545-48-9]; diclofop-methyl, (±)-2-[4-(2,4-dichlorophenoxy)phenoxy] propanoic acid, CAS RN [40843-25-2]; diflufenican, *N*-(2,4-difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]-3-pyridinecarboxamide, CAS RN [83164-33-4]; ethofumesate, (±)-2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranylmethanesulfonate, CAS RN [26225-79-6]; isoproturon, *N*,*N*-dimethyl-*N′*[4-(1-methylethyl)phenyl]urea, CAS RN [34123-59-6]; linuron, *N′*-(3,4-dichlorophenyl)-*N*-methoxy-*N*-methylurea, CAS RN [330-55-2]; terbutryn, *N*-(1,1-dimethylethyl)-*N′*-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine, CAS RN [886-50-0], and trifluralin, 2,6-dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)-benzenamine, CAS RN [1582-09-8].

Standard stock solutions of the herbicides (200 mg/l) were prepared by weighing and dissolving the compounds in methanol. These stock solutions were stored at 4 °C and diluted daily with methanol to prepare a multicomponent solution with an approximate concentration of 80 μg/l of each herbicide, which served for the preparation of the working solutions.

2.3. GC–MS chromatographic conditions

The GC–MS system consisted of a gas chromatograph GC-17A (Shimadzu, Kyoto, Japan) coupled with a quadrupole mass spectrometer QP 5000 (Shimadzu). A capillary column, DB-5, poly-(5% diphenyl–95% dimethylsiloxane) 30 m×0.25 mm I.D. and 0.25 μm film thickness (J&W Scientific, Folsom, CA, USA) was used. The chromatographic conditions were as follows: injector temperature, 270 °C; oven temperature program, 50 °C (5 min) to 180 °C at a rate of 40 °C/min, to 190 °C at 5 °C/min and then to 270 °C (12 min) at 20 °C/min. The carrier gas was helium at a column flow-rate of 1.2 ml/min. The temperature of the interface was 280 °C. A mass interval of 100.0 to 400.0 a.m.u. and a scanning interval of 0.5 s were used. Spectra were obtained at 70 eV and sample injection was accomplished in splitless mode. The ions selected to quantify the response in SIM mode are shown in Table 1.

2.4. SPME procedure

A 2.0-ml volume of a saturated solution of NaCl was added to a suitable aliquot of the multicomponent solution of herbicides for the desired final concentration to be reached, and volume was brought up to 10.0 ml with ultrapure water. A 5.0-ml aliquot of this solution was placed in a 12-ml vial, sealed with hole-caps and PTFE-lined septa. This was placed in a magnetic stirrer and the whole system was thermostated at 25 °C. While the solution was being stirred magnetically, the fibre was inserted into the vial and exposed to the solution for an appropriate time period of 75 min. After this preconcentration time, the polymeric phase was retracted inside the protective needle and then conveyed to the injector of the gas chromatograph, where the analytes were desorbed for 5 min at a temperature of 270 °C.

2.5. Analysis of herbicides in water samples

The water samples were taken from two rivers and six wells. The sampling zone includes the basin of the River Guareña, a tributary of the River Duero, and the lower part of the Almar basin, a tributary of the River Tormes. Most of the zone studied belongs to the province of Salamanca (Spain).

Samples were collected directly in 1-l glass bottles, stored at 4 °C in the dark, and analysed within 24 h after collection.

In this type of analysis, the water sample does not require previous filtration. To a volume of 5 ml of

Table 1
GC–MS parameters for the determination of the herbicides investigated

No.	Herbicide	Molecular mass	Retention time (min)	SIM ions m/z (% relative abundance)
1	Isoproturon[a]	206	10.52	120 (100)
2	Chlorotoluron[b]	212	11.31	140 (100)
3	Linuron[c]	249	12.75	161 (100)
4	Trifluralin[d]	335	14.30	306 (86)
5	Atrazine[d]	215	15.15	200 (100)
6	Alachlor[d]	269	16.39	188 (79)
7	Terbutryn[d]	241	16.62	226 (98)
8	Ethofumesate[d]	286	16.69	161 (100)
9	Diflufenicam[d]	394	22.81	266 (100)
10	Diclofop[d]	341	22.90	253 (100)

Identified compounds (molecular mass): [a]$[M-CON(CH_3)_2]^+$ (134); [b]$[M-CON(CH_3)_2]^+$ (140); [c]$[M-CON(CH_3)OCH_3]^+$ (161); [d]$[M^+]$.

the sample to be analysed, 0.3 g of sodium chloride was added, and then, preconcentration by SPME was achieved as described above. When the presence of some herbicide was detected in the samples analysed, quantification was carried out by the standard addition method. To do so, 0.3 g of sodium chloride was added to aliquots of the sample, then adding concentrations of 0, 0.3, 0.6, 0.9, 1.2 and 1.5 μg/l of the herbicide to be determined.

3. Results and discussion

3.1. Chromatographic behaviour of the phenylureas

The analysis of phenylureas by GC is problematic because owing to the temperature of the injector these compounds give rise to different decomposition products the nature of which also varies as a function of the solvent used to inject the phenylurea [21].

Fig. 1 shows the results obtained on injecting a solution of linuron in ethyl acetate, in methanol and in a methanol–water (6:1, v/v) mixture. In ethyl acetate, the main product of the decomposition of this phenylurea was an aromatic isocyanate. Injection in methanol generated an ester of carbamic acid and, although in lower amounts, the derived aniline was also obtained. In methanol–water as solvent, mainly the derived aniline was obtained, with the ester of carbamic acid as a minor product. The same behaviour was observed for the herbicide chlorotoluron. The different types of behaviour found for these two phenylureas with methanol and methanol–water mixtures were due to the fact that water is more reactive and less volatile than methanol and is hence in contact with the isocyanate in the chromatographic system for longer, favouring the hydrolysis of the isocyanate to give the corresponding aniline. It should be noted that in ethyl acetate and methanol a small amount of derived aniline is produced owing to the small amount of water contained in the solvents.

Scheme 1 shows the behaviour of the phenylureas, linuron and chlorotoluron. It may be seen that the thermal degradation of these compounds generated the aromatic isocyanate, which may undergo different chemical reactions in the solvent used in the injection.

A slightly different behaviour was observed for isoproturon. Firstly, when a 6:1 (v/v) mixture of methanol–water was used as solvent for direct injection into the GC system, mainly an ester of carbamic acid was obtained, and the derived aniline from isoproturon as a minor product. Secondly, the aromatic isocyanate derived from isoproturon was also obtained as a minor product in all three solvents tested. The presence of the isocyanate derived from isoproturon may be due to its higher stability because of the lack of the electron-withdrawing chlorine atoms in the isoproturon aromatic ring.

Also, when the phenylurea isoproturon was analysed by direct injection into the GC device, two peaks were obtained. One of them was narrow (peak A) and was due to the isocyanate; this was followed

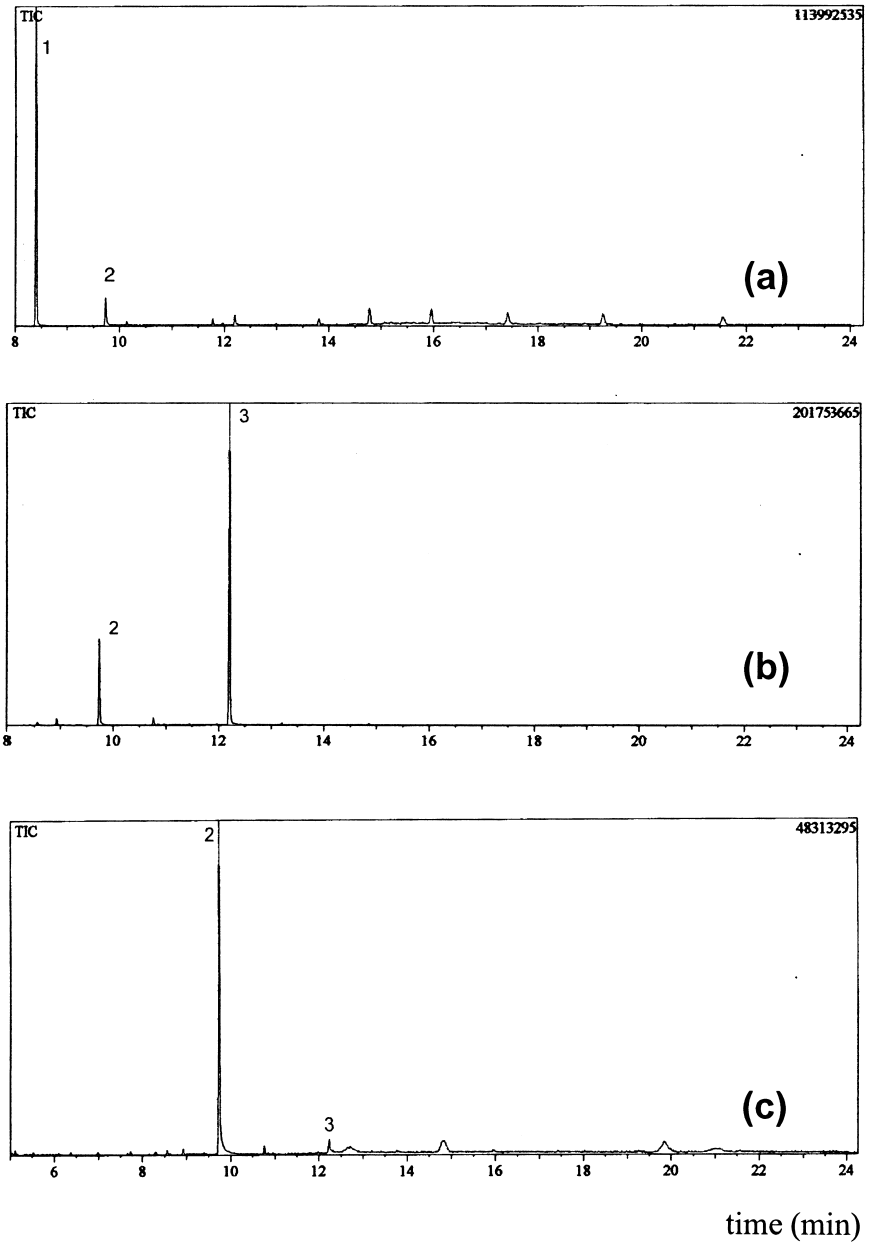
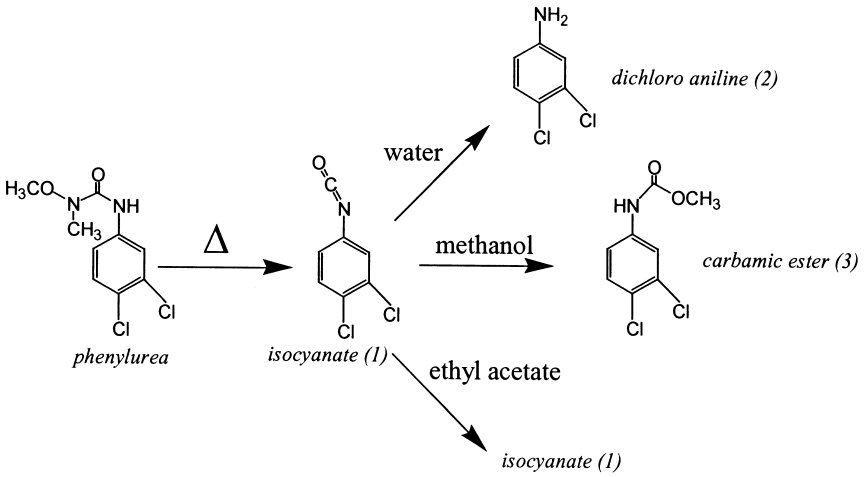


Fig. 1. Chromatograms obtained on performing direct injection of linuron dissolved in (a) ethyl acetate, (b) methanol and (c) methanol–water (6:1, v/v). Peaks: (1) *m-p*-dichlorophenyl isocyanate, (2) *m-p*-dichloroaniline, (3) carbamic acid ester.

by a second blunt peak, which lasted for several minutes (peak B) and has the same mass spectrum as the narrow peak. Fig. 2 shows the chromatogram obtained upon injecting a solution of isoproturon dissolved in ethyl acetate. The mass spectra show that both signals (peaks A and B) are due to the derived isocyanate from isoproturon. This type of behaviour indicates that in direct injection not all the isoproturon decomposes in the same zone; instead, some of it decomposes in the injector, giving rise to



Scheme 1.

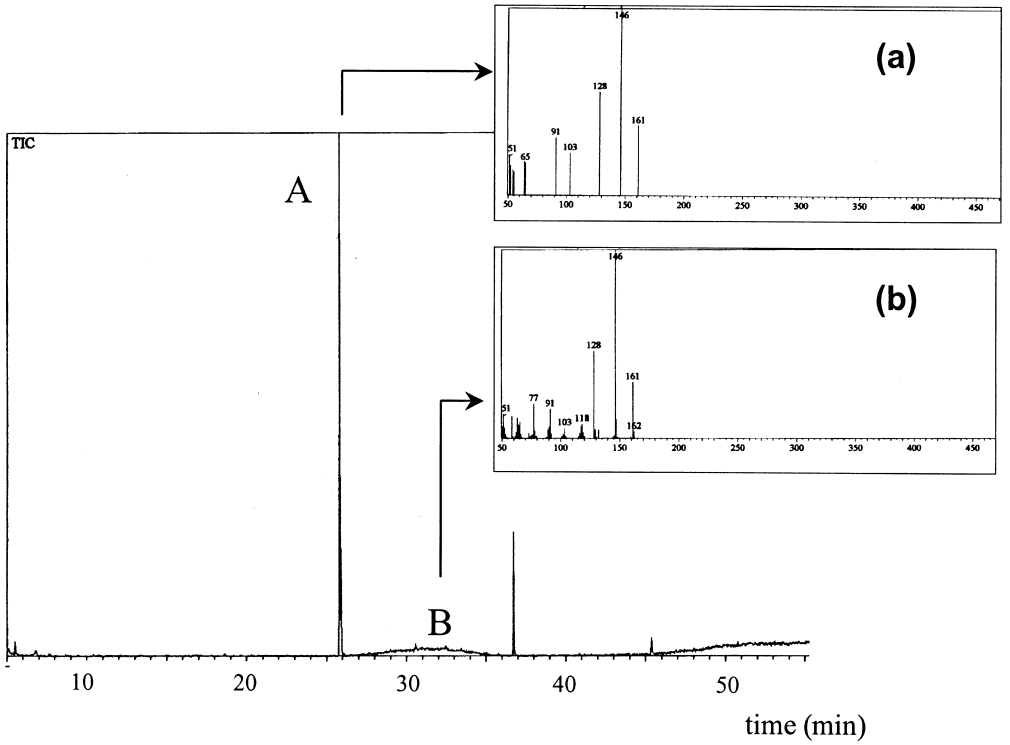


Fig. 2. GC–MS chromatogram of the direct injection of isoproturon dissolved in ethyl acetate; (a) mass spectrum of peak A (4-(isopropyl)-phenyl isocyanate); (b) mass spectrum of peak B (4-(isopropyl)-phenyl isocyanate).

the narrow peak, while the other part of it degrades along the chromatographic column, giving rise to a considerable broadening of the band.

It should be noted that when injection of the phenylureas is carried out after SPME preconcentration, a single chromatographic peak of the derived anilines is obtained. This is because, over a given time, the desorption of the analytes from the fibre generates the isocyanate and this then gives rise to the derived aniline.

From the above observations it may be inferred that as long as a preconcentration step with SPME is carried out it is possible to analyse phenylureas by GC since under these conditions a single peak corresponding to the derived aniline is obtained.

3.2. Choice of the polymeric phase of the fibre and chromatographic behaviour

In the choice of the fibre to be used, both the physico-chemical properties of the analytes and the characteristics of the fibre (thickness, polarity and porosity of the polymeric phase) must be taken into account. Considering that in the present work a relatively large number of herbicides belonging to different chemical groups were analysed, the choice of a suitable fibre was difficult.

Two types of fibre were assayed: PDMS fibre, with a thickness of 100 μm, and PA fibre, with a thickness of 85 μm. For most of the herbicides studied, extraction yield was higher with the PA fibre and this was therefore used for the SPME process. This choice is consistent with the observations of Pawliszyn [22], who recommends use of an 85-μm PA fibre for the extraction of polar and non-polar compounds.

Using the SPME preconcentration step, the chromatographic separation of the herbicides studied was optimised. Table 1 shows the retention times, the compounds identified, and the ions chosen for carrying out quantification in the selected ion monitoring (SIM) mode.

3.3. Optimisation of the SPME process

SPME is an equilibrium process that involves the partition of analytes from a liquid sample to the polymeric phase in accordance with a distribution coefficient [23]. The amount of analyte extracted and the range of linearity depend on the distribution coefficient and the volume of the stationary phase. Accordingly, optimisation of the parameters affecting the distribution coefficient and the choice of an appropriate stationary phase are of considerable importance.

The variation in the amount of herbicide extracted as a function of the preconcentration time is shown in Fig. 3 for some of the herbicides studied. On the basis of these data, an optimum extraction time of 75 min—the time at which nearly all the analytes had reached equilibrium—was chosen.

The presence of organic solvents in the sample decreases yield in solid-phase microextraction. The reason for this is the increase in the hydrophobic character of the sample solution, which involves a smaller difference in hydrophobicity between the polymeric coating of the fibre and the sample solution, and hence the coefficient of distribution between both phases decreases. Eisert [24] and Urruty [25] have reported that the presence of methanol decreases pesticide recovery in water samples. However, for the herbicides studied here, the variation in the percentage of methanol between 2 and 10% methanol did not significantly affect the yield of solid-phase microextraction of the 10 herbicides.

One very important variable in extraction is the

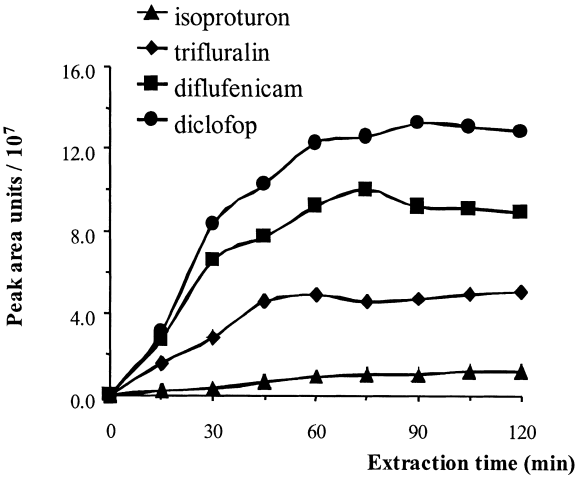


Fig. 3. Extraction time profiles for selected herbicides. Temperature and desorption time: 280 °C and 10 min.

ionic strength of the solution. Accordingly, a study was carried out in which the concentration of NaCl was varied between 20 and 60% (v/v) of a saturated NaCl solution. From the results obtained it was deduced that ionic strength affects the yield of SPME in different ways and that yield depends on the nature of the herbicide. Herbicides can thus be classified on the basis of their behaviour as a function of ionic strength.

The first group includes the herbicides for which the extraction yield decreased with the increase in the NaCl concentration. This group is made up of the less polar herbicides, trifluralin, diflufenicam and diclofop, whose log K_{OW} values were 4.83, 4.90 and 4.58, respectively. The second group comprises herbicides for which the extraction yield increased with the ionic strength until a given value was reached after which it decreased. This kind of behaviour corresponds to the model that considers that there is an initial decrease in the solvatation of the analyte, which is therefore more amenable to extraction by the fibre. However, as the concentration of NaCl increases, the interaction between the salt ions and the analytes predominates, and hence the capacity of the latter to approach the fibre decreases. This group includes ethofumesate, linuron and terbutryn, which are of intermediate polarity: log K_{OW} values of 2.70, 3.00 and 3.65, respectively. Finally, the most polar herbicides increased extraction yield with the increase in the NaCl concentration (salting-out effect). This third group contains alachlor, atrazine, chlorotoluron and isoproturon, whose log K_{OW} values were 3.09 for alachlor, and 2.50 for the other three. Fig. 4 shows the effect of ionic strength on the analytical signal for a characteristic herbicide from each group. It is recommended that preconcentration be carried out in a medium containing 20% (v/v) of a saturated solution of NaCl.

The desorption step was optimised by varying the temperature of the injector between 250 and 280 °C. For each temperature, the desorption times were 2, 5 and 10 min. After each analysis, assays were made to determine whether there was a ''memory effect''. It was seen that this occurred for all the temperatures studied when the desorption time was 2 min and also when it was 5 min at 250 °C. The analytes displaying the most marked memory effect were the phenylureas. This is because such compounds are the most

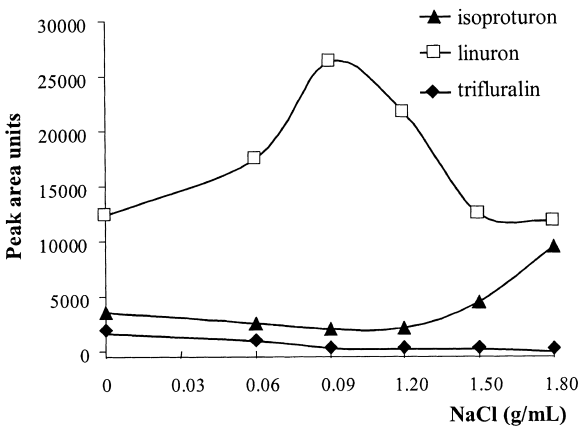


Fig. 4. Effect of sample salt percentage on the extraction efficiency of trifluralin, isoproturon and linuron. Preconcentration time, 75 min. Temperature and desorption time: 280 °C and 10 min.

polar of those studied and hence the most volatile. Fig. 5 shows the results obtained for all the herbicides for the different desorption temperatures and for times of 5 and 10 min. It may be seen that the desorption of the analytes did not follow a homogeneous trend and compromise conditions of 270 °C and 5 min desorption time were chosen.

3.4. Analytical data

Linear relationships were found between peak area and the concentration of herbicides in the 0.05 to 2.0 μg/l range. The precision of the method was determined for a concentration of each of the herbicides of 0.3 μg/l. The relative standard deviations (RSD) were lower than 20%, except in the case of trifluralin (23.8%), atrazine (25.6%) and alachlor (20.2%). These values are acceptable for the concentration level used. The detection limits calculated when the signal-to-noise ratio (S/N) was 3 were lower than the maximum concentration acceptable for individual pesticides in drinking water according to current legislation (0.1 μg/l), except for chlorotoluron (Table 2).

3.5. Environmental water analysis

Samples of ground and river waters were analysed to evaluate the presence of these herbicides. The

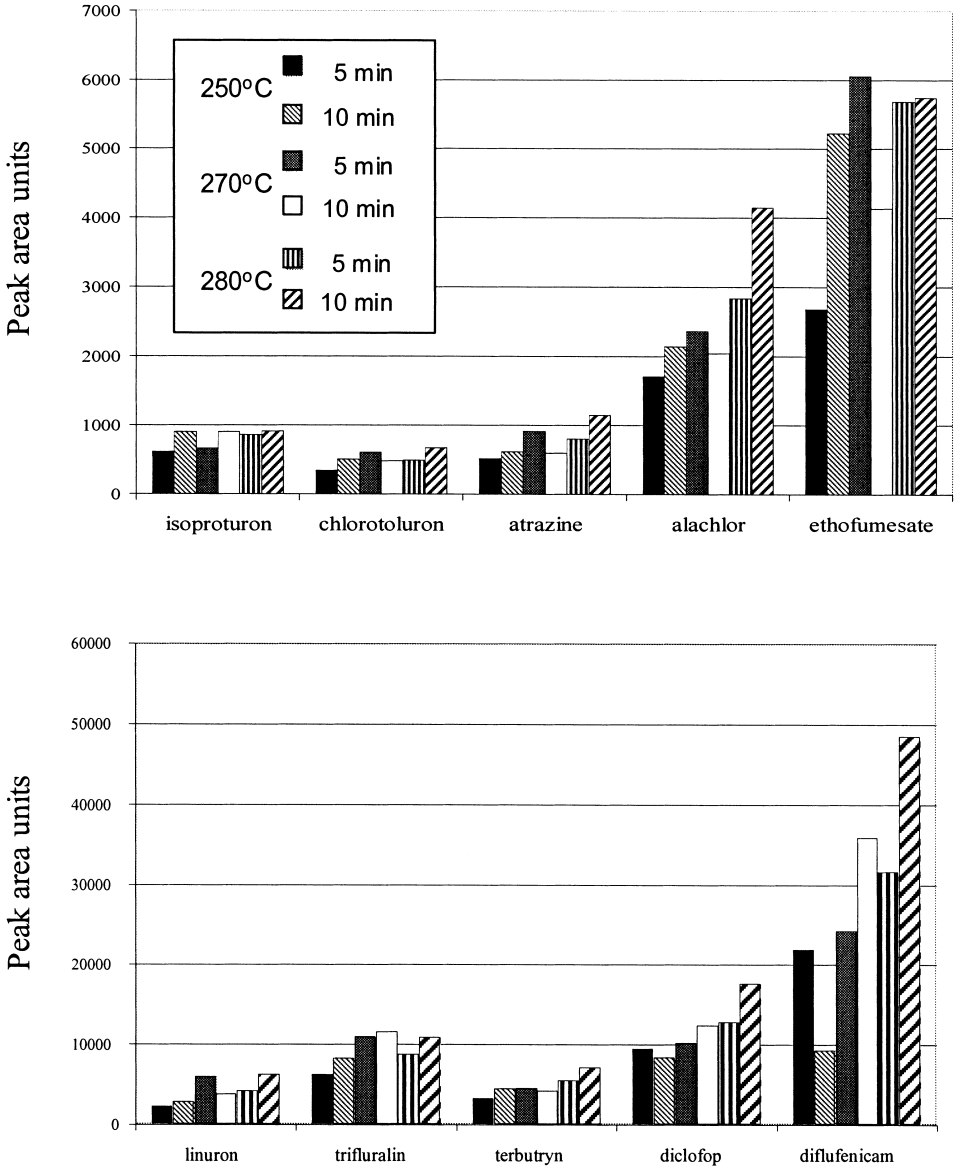


Fig. 5. Effect of temperature and desorption time. Preconcentration time, 75 min. Sample salt percentage of 20% (v/v) NaCl.

sampling zone has been described in a previous work [26]. Nine samples were analysed, six of them (marked ''P-1'' to ''P-6'') were ground water samples from wells and the other three were surface waters (marked ''R-1'' to ''R-3'').

The contents in herbicides of the samples, applying calibration by external standard, proved to be significantly lower than those obtained with another method using solid-phase extraction prior to HPLC with diode array detection [27]. This suggests the existence of matrix effects that would in particular affect the fibre preconcentration step, which is highly susceptible to the presence of salts or other organic compounds able to modify the behaviour of the analytes, either by hindering their incorporation to the fibre or by altering the desorption process.

Table 2
Analytical characteristics of the GC–MS method after SPME

Herbicide	Intercept	Slope (area units/μg l^{-1})	r^2	RSD[a] (%)	LOD[b] (μg/l)
Isoproturon	$(2.1\pm0.8)\times10^2$	$(30.0\pm0.8)\times10^2$	0.9947	18.6	0.02
Chlorotoluron	$(3.7\pm0.7)\times10^2$	$(11.0\pm0.7)\times10^2$	0.9742	11.6	0.11
Linuron	$(3.7\pm0.5)\times10^3$	$(14.4\pm0.5)\times10^3$	0.9916	15.5	0.07
Trifluralin	$-(5\pm2)\times10^3$	$(39.3\pm0.2)\times10^3$	0.9802	23.8	0.01
Atrazine	$(4.6\pm0.9)\times10^2$	$(32.5\pm0.9)\times10^2$	0.9953	25.6	0.02
Alachlor	$(4\pm3)\times10^2$	$(9.9\pm0.3)\times10^3$	0.9951	20.2	0.03
Terbutryn	$-(1\pm1)\times10^3$	$(2.4\pm0.1)\times10^4$	0.9892	18.3	0.01
Ethofumesate	$(6\pm2)\times10^3$	$(3.5\pm0.2)\times10^4$	0.9784	18.4	0.02
Diflufenicam	$-(3\pm4)\times10^3$	$(7.6\pm0.4)\times10^4$	0.9816	16.0	0.02
Diclofop	$(2\pm1)\times10^3$	$(3.2\pm0.1)\times10^4$	0.9902	18.1	0.06

[a] RSD, relative standard deviation, $n=8$, at a concentration level of 0.3 μg/l of each herbicide.
[b] LOD, limit of detection for a signal/noise ratio of 3.

Similar results have been reported in the literature [28]. As a result, it was decided to perform the quantification in natural water samples using the method of standard additions.

Table 3 shows the contents in herbicides found in the nine samples analysed. The results concerning atrazine and chlorotoluron were not significantly different, confirming the applicability of the proposed method for the analysis of ground and surface waters. In the samples of ground water, the herbicides ethofumesate, atrazine, linuron and chlorotoluron were detected, while in the surface water samples ethofumesate, linuron and chlorotoluron were detected.

A river water sample not containing the herbicides (sample R-1) was spiked at 0.3 μg/l and used in the recovery study. The concentration was determined using the standard addition method. The recovery values obtained (Table 4) were in the 94–107% range and the standard deviations varied between

Table 3
Results obtained for the analysis of herbicides in ground (P-1 to P-6) and river (R-1 to R-3) waters using the proposed SPME–GC–MS method. Comparison of contents for atrazine and chlorotoluron using SPE–HPLC–DAD

Water sample	SPME–GC–MS[a]	SPE–HPLC–DAD
P-1	Ethofumesate: 0.23±0.02 μg/l	
	Atrazine: 0.99±0.02 μg/l	Atrazine: 1.03±0.08 μg/l
P-2	Ethofumesate: 0.54±0.07 μg/l	
	Atrazine: 0.74±0.07 μg/l	Atrazine: 0.76±0.08 μg/l
P-3	Linuron: below LOD	
	Ethofumesate: 0.38±0.04 μg/l	
P-4	Chlorotoluron: 0.4±0.1 μg/l	Chlorotoluron: 0.4±0.2 μg/l
P-5	Linuron: 0.13±0.04 μg/l	
P-6	Chlorotoluron: below LOD	Chlorotoluron: below LOD
R-1	–	–
R-2	Chlorotoluron: 1.1±0.2 μg/l	Chlorotoluron: 1.3±0.2 μg/l
	Linuron: 0.22±0.08 μg/l	
	Ethofumesate: 0.35±0.04 μg/l	
R-3	Chlorotoluron: 0.6±0.1 μg/l	Chlorotoluron: 0.6±0.2 μg/l
	Linuron: 0.24±0.09 μg/l	
	Ethofumesate: 0.12±0.03 μg/l	

[a] Values obtained by the standard addition method.

Table 4
Recoveries obtained for the analysis of herbicides in river waters[a] using the proposed SPME–GC–MS method

Herbicide	Recovery±SD[b] (%)	Herbicide	Recovery±SD[b] (%)
Isoproturon	98±15	Alachlor	105±10
Chlorotoluron	96±12	Terbutryn	94±16
Linuron	98±8	Ethofumesate	98±7
Trifluralin	107±12	Diflufenicam	103±16
Atrazine	104±16	Diclofop	102±12

[a] Sample R-1, spiked at a concentration level of 0.3 μg/l of each herbicide.
[b] Values correspond to analyses carried out in triplicate.

16% for terbutryn and 7% for ethofumesate. The values obtained confirm the reliability of the proposed method.

4. Conclusions

The observed chromatographic behaviour of the phenylureas reveals that the corresponding derived isocyanate is generated in the injector; that compound reacts in the different solvents used in the injection to generate carbamic acids or anilines. Also, degradation may occur in the injector or in the actual chromatographic column. All these drawbacks can be circumvented if extraction is performed by SPME. By controlling the time and temperature of desorption of the fibre, the phenylureas decompose to originate an analytical signal due to the derived anilines.

When a fibre coated with PA polymer is used, SPME is a sensitive and reproducible technique for the determination of herbicide residues, including phenylureas, in aqueous environmental samples of both surface and ground waters. The small sample volume (5.0 ml) allows the method to be applied when the sample volume is limited.

The proposed method is simple, rapid and economic and the detection limits are much lower than those permitted by current legislation for surface water destined for the production of drinking water [29]. Quantification should be accomplished using the standard addition method with a view to avoiding the matrix effects that occur when analysing natural water samples by SPME preconcentration. The contents in chlorotoluron and atrazine found in the samples analysed here are significantly equal to those obtained using HPLC after preconcentration with styrene–divinylbenzene sorbents [27].

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