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Solid-phase microextraction of nitrogen-containing herbicides

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Abstract

A solid-phase microextraction (SPME) method, coupled with GC–MS, GC–NPD and GC–FID has been developed for the analysis of 22 nitrogen-containing herbicides in water. A polar poly(acrylate) coated fiber was used to extract the analytes directly from the samples over the concentration range 0.1 to 1000 ng/ml. Limits of detection with each of the detectors were determined to be in the ng/l, to sub ng/l levels. Some applications of the method have been demonstrated for soil samples and wine samples with GC–MS and the latter was quantified by standard addition.

1. Introduction

The analysis of herbicides and pesticides in natural waters is an area of increasing importance not only because of their potential toxicity, persistence and water solubility but also because of their universal application. This paper focuses on the analysis of nitrogen-containing herbicides which are currently investigated by US EPA methods 507 and 508, and some other related herbicides. These herbicides are widely used as pre- and post-emergent weed control agents for a wide variety of crops, including corn, sorghum, wheat, rice and sugar cane, and for fruits, vegetables and vineyards. Consequently they are found in river water [1–5], ground water [6,7] and soils [8–10] in Europe, the United States and Canada. A 1988 survey of pesticide residues in Ontario drinking water found that atrazine (one of the herbicides under investigation) was the most common pesticide detected [11]. It has also been identified as one of the most widely used herbicides, over $90 \cdot 10^6$ kg was consumed in 1980 alone [2].

Current methods of analysis for aqueous or solid samples involve either liquid–liquid extraction [1–3,11], solid-phase extraction (SPE) [2,3,7,12–14] or supercritical fluid extraction (SFE) [8]. The disadvantages of liquid–liquid extraction are the use of large quantities of often toxic and environmentally unfriendly solvents, the time consuming procedures and the need for concentration of analytes before analysis. SPE methods have eliminated many of these disadvantages by decreasing the amount of solvent required and shortening, somewhat, the extraction process. However, there are still disadvantages to SPE: the presence of particulate matter in samples can cause plugging of the cartridges, breakthrough is sometimes experienced for highly concentrated samples and dedicated instruments are required for subsequent analysis. SFE

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methods are generally non-portable and require large quantities of high purity CO_2.

An alternative technique is solid-phase microextraction (SPME), a solvent-free analytical process which overcomes most of the disadvantages of the conventional methods while maintaining the advantages [15]. It involves direct extraction of the analytes with the use of a small diameter optical fiber that has been coated with a polymeric stationary phase and housed in a syringe assembly for protection. Analytes in an aqueous sample, or the headspace above a sample, partition into the polymeric phase according to their distribution coefficient. They are subsequently thermally desorbed in the injection port of a gas chromatograph (GC) for analysis. The polymeric phase essentially behaves in the same way as the organic solvent in the liquid–liquid extraction process but has the advantage of being bonded to the fiber so that after desorption of the analytes, it is ready for the next extraction.

SPME has already been successfully applied to the analysis of a variety of analytes in solid, liquid and gas phases [16]. The method has been shown to be applicable to both polar and non-polar analytes, including, volatile organic compounds [17–19], phenols [20], and PAHs/PCBs [21]. This paper presents the first application of SPME to this important class of herbicides, the nitrogen-containing herbicides. A polar poly(acrylate) coated fiber was used to extract analytes from aqueous and soil samples.

2. Experimental

2.1. Fiber preparation

The coated fiber selected for the analysis of the nitrogen-containing herbicides was fused silica coated to a thickness of 95 μm with poly(acrylate) and 1 cm in length. Preliminary experiments were conducted to compare a 15 μm poly(dimethylsiloxane) coated fiber, a 55 μm poly(dimethylsiloxane) coated fiber and the 95 μm poly(acrylate) coated fiber. The poly(dimethylsiloxane) fibers were conditioned in the injection port of the GC for 3 hours at 250°C. However, to obtain consistent analytical results with the poly(acrylate) coated fiber, it must be conditioned before initial application by the procedure described in detail by Buchholz and Pawliszyn [22] and briefly outlined here. The coated fibers are placed inside a stainless-steel tube through which a stream of helium flows. The stainless-steel tube is then placed inside a muffle furnace and held at 300°C for four hours. After mounting the fibers in the needle assembly, further conditioning under He at 250°C in the injection port of a GC was required to remove impurities which may be present from the epoxy.

2.2. Reagents

Two separate standard mixtures of herbicides (herbicide mix 1 and herbicide mix 2, Supelco, Canada, catalogue numbers 4-9136 and 4-9138, respectively, 100 μg/ml) were purchased. The herbicides present were Atrazine, Benfluralin, Bromacil, Metolachlor, EPTC, Oxyfluorofen, Hexazinone, Molinate, Oxadiazon, Isopropalin, Propachlor, Propazine, Pendimethalin, Cycloate, Metribuzin, Simazine, Butylate, Terbacil, Pebulate, Profluralin, Trifluralin and Vernolate. The stock standards were used to prepare 50-ml aqueous solutions containing 0.1 mg/l of each analyte. Stock solutions were freshly prepared every two weeks and used to prepare 4-ml standards at the required concentration.

All solutions were prepared with NANOpure water (Barnstead ultrapure water system). Blank analyses were performed regularly to ensure that no herbicides were present in laboratory reagents, or fibers.

2.3. Instrumentation

Initial analysis was performed using both a Varian 3500 gas chromatograph (GC) equipped with a septum programmable injector (SPI) and a flame ionisation detector (FID) and a Varian 3400CX GC with an FID and a nitrogen–phosphorous detector (TSD or NPD). Analytes were separated with a Supelco PTE-5 column, 30 m × 0.25 mm with a phase thickness of 0.25 μm. The temperature program used for the analysis of

each herbicide mixture was: 100°C, hold for 5 min, then to 300°C at 10°C/min, and hold for 5 min. The carrier gas was ECD grade helium, maintained at a flow-rate of 1.0 ml/min. The SPI injector was isothermally programmed at 250°C for SPME extractions and direct solvent injections. The FID was held at 300°C, with a nitrogen make-up flow of 23.0 ml/min, hydrogen at 30.0 ml/min, and air at 280 ml/min.

Subsequent analysis was performed with a Varian Saturn ion trap mass spectrometric detector. The same column was used but the temperature profile was modified to enable separation of all 22 herbicides. The modified program was: 40°C, hold for 5 min, then to 100°C at 30°C/min, then to 300°C at 5°C/min. The ion-trap manifold was held at 250°C, as was the transfer line. The mass spectrometer was tuned to FC-43 (perfluorotributylamine). The electron multiplier and automatic gain control target were set automatically. The mass range scanned was 45–400 a.m.u. The detector was turned off for the first 300 s to prevent overloading the electron multiplier from the solvent used in preparation of the herbicide standards (ethyl acetate).

The responses of the FID, NPD and MS detectors were calculated for each analyte by injection of the standard herbicide mixture at a minimum of five different concentrations. For the FID and NPD, area counts were plotted against the amount injected (ng) to produce a calibration curve. For the MS, the most abundant mass peak above 100 a.m.u. was chosen for quantification and calibration. The masses chosen were: EPTC, 128; Butylate, 146; Vernolate, 128; Pebulate, 204; Molinate, 126; Propachlor, 212; Cycloate, 154; Trifluralin, 306; Benfluralin, 292; Simazine, 202; Atrazine, 216; Propazine, 214; Profluralin, 318; Terbacil, 161; Metribuzin, 198; Bromacil, 207; Metolachlor, 162; Isopropalin, 280; Pendimethalin, 252; Oxadiazon, 258; Oxyfluorofen, 361; Hexazinone, 171.

2.4. Analytical procedure

Aliquots (4 ml) of standard solutions or samples were extracted from 4.6-ml vials sealed with hole-caps and Teflon lined septa. After addition of 4 ml to the vials and a stirrer bar, approximately 0.5 ml of headspace is left into which the needle is placed to prevent wicking of the sample during extraction. The fiber is then exposed to the aqueous phase for an appropriate time period with stirring and at room temperature. After extraction, the fiber is directly exposed to the hot injector of the GC for analysis.

2.5. Optimisation

Initial experiments focused on determining the time at which equilibrium was established between the analytes in the stationary and aqueous phases. Triplicate solutions were extracted for periods of time ranging from 10–120 min. The amount extracted at each time was then calculated and graphed against time. The equilibration times were determined by inspection and are listed in Table 1.

Optimisation of the desorption temperature and time was investigated by considering the amount desorbed from fibers after extraction of analytes from a solution of known concentration and the subsequent carryover at a range of temperatures and time periods. The optimised conditions were 5 min desorption at 230°C.

The linearity of the method was tested by analysing triplicate solutions over the range 0.1–1000 ng/ml, on the NPD, MS and FID. Each set of replicates was one tenth the concentration of the previous one. Amounts extracted were calculated by comparison with calibration curves and plotted against the initial concentration of the solution. The precision of the method was determined with the NPD and MS by extracting a minimum of seven replicate samples of 50 ng/ml and 10 ng/ml, respectively. The relative standard deviation (% R.S.D.) was calculated by dividing the standard deviation by the mean and multiplying by 100.

As a means of enhancing the extraction of analytes, the effect of ionic strength and pH was investigated. 4-ml solutions were analysed over the pH range 4–10 by addition of buffers. The low pH buffer was acetic acid–sodium acetate and the high pH buffer, sodium hydroxide–boric acid; both prepared according to Perrin and

Table 1
Selected nitrogen containing herbicides

Herbicide		Molecular formula	Solubility in water (mg/l)	Equilibration time (min)	*K* value
Class	Name				
Triazines	Atrazine	$C_8H_{14}ClN_5$	70	90	2000[a]
	Hexazinone	$C_{12}H_{20}N_4O_2$	330 000	10	300[a]
	Propazine	$C_9H_{16}ClN_5$	8.6	90–120	3000[a]
	Metribuzin	$C_8H_{14}N_4OS$	1200	50–90	200[a]
	Simazine	$C_7H_{12}ClN_5$	3.5	10	300[a]
Nitroanilines	Benfluralin	$C_{13}H_{16}F_3N_3O_4$	< 1	50–90	7000[b]
	Isopropalin	$C_{15}H_{23}N_3O_4$	0.1	50	5000[b]
	Pendimethalin	$C_{13}H_{14}N_3O_4$	0.3	50	20 000[b]
	Profluralin	$C_{14}H_{16}F_3N_3O_4$	0.1	30	7000[b]
	Trifluralin	$C_{13}H_{16}F_3N_3O_4$	20	50	8000[b]
Substituted Uracils	Bromacil	$C_9H_{13}BrN_2O_2$	815	30	400[a]
	Terbacil	$C_9H_{13}CN_2O_2$	710	50–90	200[a]
Thiocarbamates	EPTC	$C_9H_{19}NOS$	365	90	4000[a]
	Molinate	$C_9H_{17}NOS$	800	50–90	2000[a]
	Cycloate	$C_{11}H_{21}NOS$	85	90	7000[a]
	Butylate	$C_{11}H_{23}NOS$	45	90	3000[a]
	Pebulate	$C_{10}H_{21}NOS$	60	90	4000[a]
	Vernolate	$C_{10}H_{21}NOS$	107	90	10 000[a]
Others	Metolachlor	$C_{15}H_{22}ClNO_2$	530	50	4000[a]
	Oxyfluorofen	$C_{15}H_{11}ClF_3NO_4$	0.1	30	3000[b]
	Oxadiazon	$C_{15}H_{18}Cl_2N_2O_3$	0.7	50	20 000[b]
	Propachlor	$C_{11}H_{14}ClNO$	700	50	1000[a]

[a,b] *K* values determined under optimum conditions; overnight extraction, 4 M NaCl ([a]) or unsalted ([b]).

Dempsey [23]. Subsequently, pH 2 and pH 11 were tested by simply using appropriate concentrations of acetic acid (1 *M*) and NaOH (0.01 *M*) respectively. Ionic strength was tested by addition of NaCl (2 *M*, 4 *M*, and supersaturated) to triplicate solutions. The effect of a combination of salt and pH was investigated by combining pH 2 and 4 *M* NaCl. In all cases triplicates were analysed together with triplicate neutral control solutions with which comparisons were made.

Detection limits are defined as the concentration of an analyte in a sample which gives rise to a peak with a signal-to-noise ratio (S/N) of 3. Solutions were analysed at subsequently lower levels until they approached the limit of quantification, at which point the limits of detection were calculated. For mass spectral analysis, the ratio of the quantification mass peak to the noise was used. If lower detection limits are required, analysis of more than one characteristic mass peak can be used to improve the signal-to-noise ratio at low concentrations. For the FID analysis, an area count of 1000 was chosen as a conservative estimate of the smallest detectable peak. This area count corresponds to three times the typical noise reading, which ranges from 400 to 600. For the NPD, the noise was measured before each run and was typically equivalent to a signal of 13 area counts, therefore the lowest detectable peak was defined as having an area greater than 40 area counts.

2.6. Sample analysis

Soil samples were analysed qualitatively by taking 0.3 g soil and adding approximately 4 ml of water, to ensure that the sample could be stirred. Wine samples were directly analysed by taking 4-ml aliquots. The standard addition method was used to quantify the amount of any herbicide present in real samples analysed with the MS. Samples were first analysed and herbicides identified if their mass spectrum and retention times were the same as those found for standards. Subsequently, triplicate real samples, together with triplicate spiked samples were analysed and the results calculated for those herbicides previously identified. Spike concentrations were 10 and 20 ng/ml.

3. Results and discussion

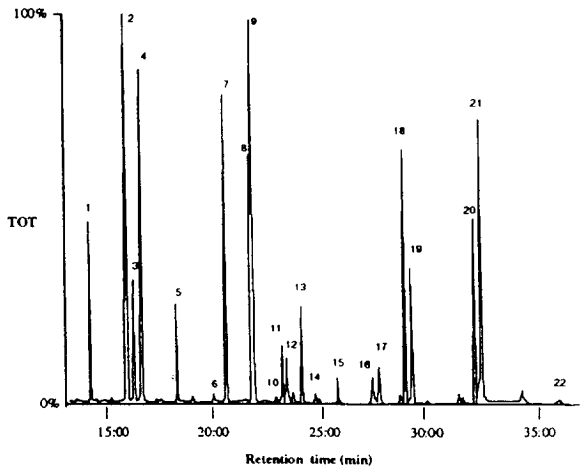
Solid-phase microextraction involves the partitioning of analytes between the sample matrix and a polymeric stationary phase according to their partition coefficients, K. This process can be defined by the following equation [16]

$$n_s = \frac{K V_s V_{aq} C^o_{aq}}{K V_s + V_{aq}} \quad (1)$$

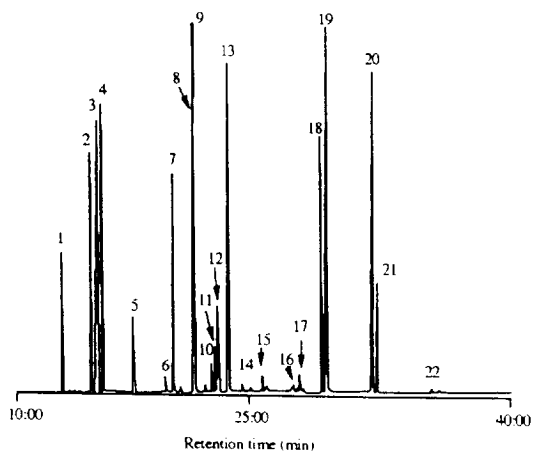
where n_s is the amount extracted by the fiber coating, K is the partition coefficient, V_{aq} and V_s are the volumes of the aqueous and stationary phases, respectively and C^o_{aq} is the initial concentration of analytes in the aqueous phase. It can be seen from Eq. 1 that the sensitivity of the method and the linear range are dependent upon the volume of the stationary phase and the partition coefficient. The choice of an appropriate stationary phase is thus extremely important. Currently two coated fibers are available commercially, the poly(dimethylsiloxane) and poly(acrylate). The herbicides analysed here are predominantly polar analytes with small octanol–water partition coefficients (log P_{ow}) [24], and generally high solubility in water. These analytes should therefore partition more favourably into a polar stationary phase than a non-polar one. This is exemplified by the analysis of phenols, a group of polar analytes which are poorly extracted from water by the poly(dimethylsiloxane) fiber but which are successfully extracted with the poly(acrylate) [20]. Preliminary experiments, conducted to compare the two coatings, indicated that the poly(acrylate) was capable of extracting all the analytes, whilst the poly(dimethylsiloxane) was not.

The rate at which the extraction process reaches equilibrium is primarily dependent upon the rate of mass transfer in the aqueous phase [25], and is improved by stirring. Therefore, all extractions were performed under stirred conditions. The time profiles obtained for the target herbicides enabled determination of the equilibration times shown in Table 1. Equilibration times ranged from 10 to 120 min with more than half of the analytes reaching equilibrium by 50 min. The optimised GC separation is also 50 min in duration, thus a 50-min extraction time ensures optimal time efficiency for the SPME method. The two factors which have the potential to be affected by choosing an extraction time that is less than the time required for equilibrium are precision and sensitivity. The former could be adversely affected if the extraction time is not carefully monitored since slight deviations in the extraction time imply large deviations in the amount extracted when equilibrium has not been established. Therefore extractions were performed for 50 ± 2 min. The latter is only likely to be affected if the K values are small and equilibrium has not been reached. Fortunately, the analytes with smaller K values generally have equilibration times less than 50 min thus the overall sensitivity of the method will not be affected. Fig. 1 shows a chromatogram obtained from extraction of a 100 ng/ml sample of the 22 herbicides using these conditions, with MS (a) and NPD (b) detection.

The amount of each analyte extracted by a 95 μm poly(acrylate) coated fibre was determined at equilibrium and used to calculate the K values from Eq. 1. The results are presented in Table 1 together with literature values for the analytes' solubility in water. It is immediately clear that there is a correlation between solubility in water



(a)



(b)

Fig. 1. Chromatograms of 50-minute extractions of 100 ng/ml herbicide standards. (a) Mass spectral detection, total ion plot; (b) nitrogen–phosphorous detection. Peak identification: 1 = EPTC; 2 = Butylate; 3 = Vernolate; 4 = Pebulate; 5 = Molinate; 6 = Propachlor; 7 = Cycloate; 8 = Trifluralin; 9 = Benfluralin; 10 = Simazine; 11 = Atrazine; 12 = Propazine; 13 = Profluralin; 14 = Terbacil; 15 = Metribuzin; 16 = Bromacil; 17 = Metolachlor; 18 = Isopropalin; 19 = Pendimethalin; 20 = Oxadiazon; 21 = Oxyfluorofen; 22 = Hexazinone.

and K values, the more soluble an analyte the lower the K. Therefore, by decreasing the solubility of a given analyte in water, the amount extracted can be increased. There are several ways that this could be achieved, including addition of salt to the matrix, variation of the matrix pH, or formation of derivatives. Consequently, both the effect of ionic strength and pH were determined. The effect of varying the ionic strength was tested by comparing three concentrations of NaCl. The addition of salt at each concentration generally caused an increase in the amount extracted, with the exception of the nitroanilines, oxadiazon and oxyfluorofen. The investigation of pH effect was undertaken with the aim of finding a pH at which the extraction of these compounds was enhanced and at which the extraction of the other classes was not significantly decreased. Varying the pH from 4 to 11 had no significant effect on the extraction of any of the analytes, however, at pH 2 the extraction of the nitroanilines and oxyfluorofen was enhanced. The success of salt and pH 2 individually warranted extraction of the analyte mixture under conditions of salt and pH 2, to optimise extraction of all analytes. The results are shown in Fig. 2 and indicate that although the combination is effective for the extraction of most triazines, substituted uracils and thiocarbamates, it is not as effective as salt alone. Furthermore, the combination is detrimental to the extraction of nitroanilines, oxyfluorofen and oxadiazon which are best extracted under neutral or pH 2 conditions. Not surprisingly, different classes of analytes have different conditions under which optimum extraction occurs, however even under neutral conditions, the limits of detection (Table 3) are sufficiently low with the GC–MS to enable determination of all the analytes at low to sub ng/l levels.

The precision of the method was investigated for a set of seven replicates using both the MS and NPD detectors (Table 2). Differences in the precision achieved with the two detector systems are primarily due to the difficulty in accurately integrating small, broad peaks on the NPD. The majority of analytes were extracted with precision ranging from 2–20%. Since the US EPA only requires that methods which are to be accepted as standard methods have R.S.D. values below 30%, the precision of the new method

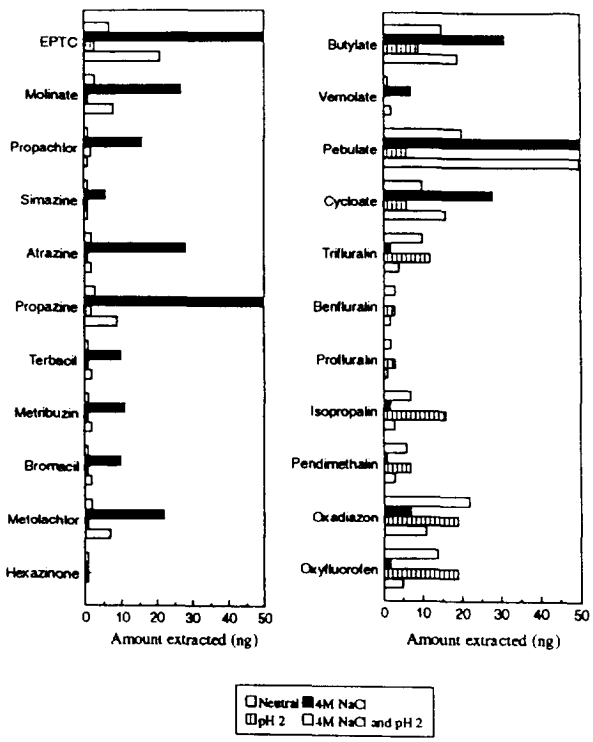


Fig. 2. The effect of salt, pH 2 and combined salt and pH 2. Triplicate standards (100 ng/ml) extracted for 50 min.

Table 2
Precision data obtained from 50-minute extractions of selected herbicides

Herbicide	Amount extracted[a] (ng)	% R.S.D. (NPD)	% R.S.D. (MS)
EPTC	1.9	9	10
Butylate	4.1	13	13
Vernolate	1.5	12	13
Pebulate	12	12	13
Molinate	1.7	7	12
Propachlor	1.2	9	5
Cycloate	4.4	12	14
Trifluralin	5	13	16
Benfluralin	1.6	13	11
Simazine	0.42	9	2
Atrazine	1.1	14	9
Propazine	0.7	12	14
Profluralin	1.5	7	7
Terbacil	0.54	10	13
Metribuzin	0.52	9	13
Bromacil	0.58	22	10
Metolachlor	0.6	10	15
Isopropalin	2.8	20	21
Pendimethalin	2.5	14	17
Oxadiazon	4	18	22
Oxyfluorofen	7	14	14
Hexazinone	0.34	22	4

[a] Average of seven replicates, containing 10 ng/ml of each analyte.

can be considered good. It is expected that precision will be improved with the use of an autosampler.

The linearity of the method has been investigated over the range 0.1–1000 ng/ml, with the GC–MS, GC–NPD and GC–FID. Of the 22 analytes analysed, 21 had correlation coefficients greater than 0.99 when linear regression analysis is performed, both when the y intercept is fixed at 0, or when it is allowed to vary.

The calculated limits of detection are presented in Table 3. The values were calculated from 100 ng/ml, 1 ng/ml and 0.01 ng/ml extractions for the FID, NPD and MS, respectively and refer to the concentration of a sample from which a sufficient quantity will be extracted by the fiber to be detected. The limits of detection are generally improved by three orders of magnitude with the MS when compared with the FID. The predominant difference in the limits of detection using the FID and NPD actually stems from the very low noise levels found in the NPD chromatograms rather than from a significant improvement in area counts for analytes. The limits of detection for US EPA methods 507 and 508 are shown for comparison, they are estimated detection limits [3] of the respective methods, obtained with GC–NPD and GC–ECD. All the relevant herbicides analysed by SPME–GC–MS had limits of detection well below those required by the EPA. Most of the analytes are also sufficiently extracted to provide NPD limits of detection which would be satisfactory for the EPA.

After the method development stage was complete, real samples were analysed with the GC–MS. Both contaminated soil and commercial wine samples were analysed. The soil samples were suspended in water and analysed as a

Table 3
Limits of detection for 50-minute extraction of selected herbicides

Herbicide	FID[a] (ng/l)	NPD[b] (ng/l)	MS[c] (ng/l)	EPA 507/508[3] (ng/l)
EPTC	2000	50	0.8	200
Butylate	1000	20	0.1	100
Vernolate	1000	20	0.5	100
Pebulate	1000	20	1	100
Molinate	2000	60	0.3	100
Propachlor	6000	800	15	500
Cycloate	800	20	0.05	200
Trifluralin	400	30	0.02	20
Benfluralin	300	30	0.4	NA[d]
Simazine	1000	70	1	100
Atrazine	7000	40	3	100
Propazine	10 000	50	0.3	100
Profluralin	200	30	0.1	NA
Terbacil	15 000	200	1	4500
Metribuzin	14 000	200	3	100
Bromacil	19 000	400	0.1	2500
Metolachlor	1000	200	0.01	700
Isopropalin	300	10	0.1	NA
Pendimethalin	200	20	0.1	NA
Oxadiazon	300	30	0.01	NA
Oxyfluorofen	200	300	6	NA
Hexazinone	2000	6000	1	800

[a] Determined from 100 μg/l solutions.
[b] Determined from 10 μg/l solutions.
[c] Determined from 10 ng/l solutions.
[d] NA = Not Applicable, i.e. not analysed by EPA 507 or 508.

purely qualitative experiment by the new procedure. Fig. 3 shows a portion of the GC–MS chromatogram obtained from extraction of a sample taken from a lawn to which a common herbicide had been applied. The total ion plot and two selected ion plots (292 and 335) are shown. The retention time and mass spectrum of the peak at 22:26 min are both indicative of the presence of Benfluralin (M_r 335, base peak, 292) in the soil sample. Several wine samples were analysed by the standard addition procedure after initial screening with the method indicated the presence of some herbicides. An example is the identification of nine of the twenty-two herbicides in a white wine from the Rhone valley, France. The herbicides found, together with their concentration in the sample, are given in Table 4. Concentrations ranged from 0.4 to 3.1 ng/ml. However, since the samples were spiked at 10 and 20 ng/ml, the accuracy of the calculated results for some analytes is limited. It is however indicative of the ability of the method to successfully analyse real samples.

4. Conclusions

This paper has demonstrated SPME to be a precise, reproducible technique for the analysis of nitrogen-containing herbicides from clean water. The new method is linear over several orders of magnitude, with either FID, NPD or MS detection. The detection limits required by EPA methods 507 and 508 are easily achieved with the use of the ion-trap MS in the total ion current mode. The use of salt enables substantial

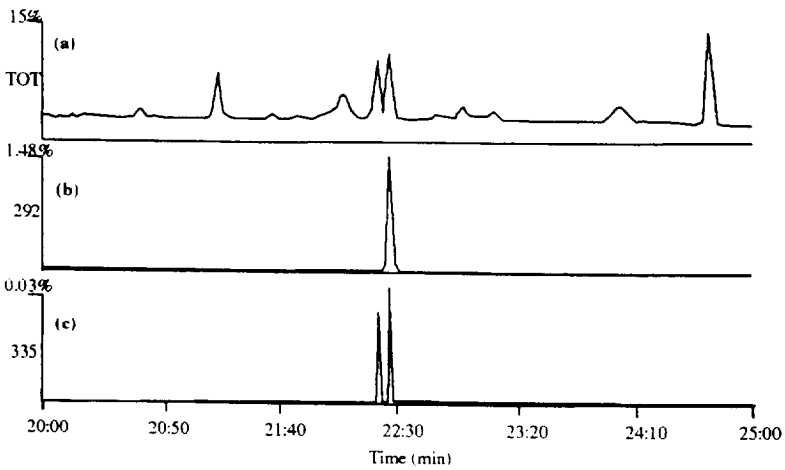


Fig. 3. GC–MS of pesticide residues extracted from soil by SPME. (a) Total ion plot, (b) selected ion plot, base peak = 292, (c) selected ion plot, M^{+} = 335.

increases in the amount extracted of most analytes and can be used to improve the limit of detection if sub-ppt levels need to be detected with the NPD or FID.

Analysis of herbicide standards from more complex matrixes, such as those found in wine, have also been successfully performed. The standard addition procedure, combined with MS detection, enabled identification and quantitation of herbicides already present in the samples.

Table 4
Herbicides found in a wine sample

Herbicide	Concentration (ng/ml)[a]
Butylate	0.7
Pebulate	3.7
Trifluralin	2.2
Benfluralin	2.0
Profluralin	3.1
Isopropalin	0.8
Pendimethalin	0.9
Oxadiazon	0.4
Oxyfluorofen	1.0

[a] Triplicate samples quantified by standard addition at three concentrations.

The application of the method to the analysis of solid samples was exemplified by the identification of herbicides in contaminated soil.

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