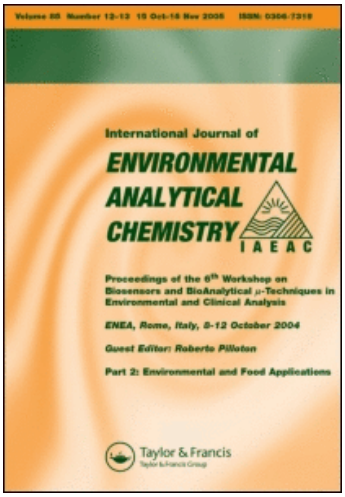

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SOLID PHASE MICROEXTRACTION (SPME) OF THE HERBICIDE ATRAZINE IN AQUEOUS SOIL SUSPENSIONS

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A new method for the direct SPME of atrazine in soil slurries (20 g soil/L) followed by cleaning of the fibre has been developed enabling sequential extraction of at least 15 soil samples with good reproducibility. No relevant interferences were observed using an EC detector at the lowest atrazine concentration examined ($<10^{-7}$ mol/L). Good resolution was obtained and the method was linear over the range of concentrations studied ($<10^{-7}$-10^{-4} mol/L). Data from the SPME-GC method correlate very well with the data from microfiltration-HPLC measurements, suggesting that by both methods the freely dissolved atrazine alone is being measured. Thus a new simple, clean, solventless extraction technique, easily compatible with capillary GC, has been added to the arsenal of methods available for the analysis of less volatile compounds from soils and water bodies with a high content of particulate and humic materials.

Keywords: Atrazine; analysis; soil; solid phase microextraction; SPME; gas chromatography; freely dissolved

INTRODUCTION

Atrazine is a herbicide that has been used in large quantities all over the world, particularly in corn crops. Atrazine is a moderately hydrophobic organic contaminant with moderate to high persistence in the environment. It is known to form a range of intermediates (most of them non-phytotoxic or less phytotoxic than the parent compound) and associations with soil system components. Because of its relatively long life and capacity to leach through the soil to the

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water table[1], atrazine is considered to be a pesticide of concern and its concentration in natural waters is closely regulated[2, 3]. More recently, atrazine has appeared on the list of chemicals with a widespread distribution in the environment which have been reported to have long term reproductive and endocrine-disrupting effects[4].

Many analytical procedures have been developed for atrazine in natural waters, soils, and soil slurries. From the analyst's point of view, the problem with classical, solvent-using methods is that the extraction step is the most time consuming and the most expensive, involving the use of large quantities of organic solvents[5-9]. The reported values for the concentrations of the pesticide residues in soils are highly dependent on the analytical method used for analysis, particularly on the extraction procedure. Notions such as "total residues", "dissolved pesticide", "reversibly bound pesticide", "irreversibly bound residues" are currently largely operationally defined terms. Accurate description of transport and biological phenomena of pesticides in soils, which is of paramount importance for environmental risk assessment and remediation, depends on such analytical data. Analytical methods using a direct water phase extraction step appear to be the most useful approach to the study of pesticide speciation in soils, because data are easier to correlate with the bioavailability and the mobility of pesticide residues in natural environments[10].

A new method for atrazine analysis by direct water-phase extraction from soil slurries using a solid phase microextraction (SPME) device is presented. The technique uses a fused silica optical fibre coated with polydimethylsiloxane to extract the organic analyte from an aqueous phase[11-14]. The SPME extraction is non-exhaustive, based on a process of equilibrium partitioning. In view of previous successes in the use of SPME in conjunction with a GC-ECD analytical procedure for pesticide analysis of water samples in our laboratory[15], the technique was examined for the direct extraction of atrazine residues from soil slurries. The method is based on the direct partitioning of the analyte (atrazine) between the water phase of the soil slurry and the organic coating of the fibre. Other equilibria occur in parallel in the soil suspension between the atrazine free in solution, the atrazine sorbed to the soil organic matter (SOM), and the atrazine sorbed to the dissolved organic matter (DOM) sometimes termed the water soluble soil organic matter (WSSOM). SPME had been previously used as an extraction method for a variety of analytes, including atrazine, from different aqueous phases but has been generally believed to be impossible to use in such a "dirty" environment as a soil slurry. Analysis of soil samples has been reported, but such methods use either the "head-space" technique[14, 17], based on the sampling of the air phase above the soil sample, or a preliminary solution separation by centrifugation[18].

Headspace SPME involves mass transfer processes between three phases: the sample matrix, the sample headspace and the coating material, according to the affinity of the analyte for each of the phases. The difference between the chemical potentials of the analyte in the three phases is the driving force of the headspace extraction procedure. There are two partitioning processes involved: between the matrix and the headspace and between the headspace and the coating. For aqueous samples, the headspace/water partition coefficient (K_{hs}) is limited by the air-water partition coefficient (Henry's law constant) value of the contaminant and the water content of the sample matrix (soil)[14, 17]. For moderately hydrophobic organic contaminants with a limited volatility such as atrazine, the analyte will partition in small proportion into the head-space of the sample, leading to a poor sensitivity of the head-space SPME based analytical methods.

Bengtsson and Berglof[18] have proposed a method using a separation of the soil solution by centrifugation prior to the SPME procedure. From a practical point of view this method is more difficult to perform, requires more expensive instrumentation and does not take full advantage of the possibilities of SPME to simplify analytical work. From a theoretical point of view, the centrifugation step interferes with equilibrium processes in soil solution, introducing experimental artifacts into an already complicated system. Depending on centrifugation conditions a different proportion of the dissolved organic matter fraction (DOM), the so called "unsettling phase" or "third phase" will be added to the soil organic matter fraction (SOM) or remain in the supernatant.

The new method does not use any organic solvent and has no preliminary separation steps (filtration, centrifugation, or chromatographic clean-up). It is thus less likely to perturb the already complicated soil-water system and appears to be the simplest approach to study equilibrium processes in soil-water systems.

Only if the measured species is well defined can the results of the analytical procedure be used for predicting the fate of the contaminant, its mobility, and its toxicological and ecotoxicological relevance. In an attempt to define the atrazine fraction measured by the new SPME method and to evaluate the performance of the new method, a comparison between the concentration of atrazine in soil slurries acquired by SPME-GC with the concentration of atrazine in the same slurries, measured by an established technique, microfiltration-HPLC[19] was conducted.

EXPERIMENTAL

Atrazine Standard Solution

Atrazine Pestanal® standard 98% (Riedel de Haen AG, Seelze, Germany) was used to prepare stock solutions. Atrazine was dissolved in distilled water (HPLC-grade

TABLE I Properties of the soils.

Soil Property	%Organic matter	%Sand	%Silt	%Clay	pH	CEC (mequiv/100g)
Miniota soil	2.0	80	11	7	6.21	9.3
Fifi Road soil	3.7	81	3	3	4.52	21.5

water, Accusolv from Anachemia, Rouses Point, NY, USA) with stirring and occasional heating (50°C-60°C) for 48 h. Atrazine concentrations in the standard stock solutions used throughout the experiments were 4.8×10^{-4}, 1.08×10^{-4} and 0.78×10^{-4} mol/L.

Soil Characteristics

A Manitoba (Canada) soil (Miniota sand) and a tropical soil (Fifi Road soil, collected from the Caribbean island nation of Dominica) were used for sorption experiments. Soil properties are listed in Table I.

Soil Slurry Samples

Soil samples (0.5 g, previously sieved) were weighed into specially constructed 30 mL round bottom vials equipped with septum screw caps, and to each of the vials, 25 mL distilled water (HPLC-grade water, Accusolv from Anachemia, Rouses Point NY, USA) and atrazine standard solution (respectively 2, 3, 5, 10, and 15 mL, in HPLC grade water) were added. The soil slurry was stirred for two weeks before the measurements were made and kept stirred, at constant temperature (20°C) during the course of the experiment. Soil concentration for all soil slurry samples used was 20 g/L.

SPME-GC Analysis

SPME extraction was performed using a Supelco No. 5-7300 manual 100 μm polydimethylsiloxane (PDMS) solid-phase microextraction fibre and fibre holder assembly (Supelco No. 5-7330) from Sigma-Aldrich Canada Ltd., Mississauga, ON, Canada. The extraction was performed by piercing the septum of the 25 mL vials containing the soil slurry samples with the septum-piercing needle and extending the fibre directly into the magnetically stirred soil solution. The SPME assembly was clamped in place above and resting on the vial cap. After 30 min, the fibre was retracted into the septum-piercing needle and the needle was withdrawn from the septum.

The syringe needle was used to pierce the septum of the GC injection port and the fibre was extended into the splitless injector. Desorption conditions: 10 min, 220°C (max. recommended), purge off.

A Hewlett-Packard 5890 GC system equipped with an EC detector (Hewlett-Packard Canada Ltd., Mississauga, ON, Canada) and operating in the splitless mode was used to perform the gaschromatographic analyses. A 30 m J&W Scientific DB-5, 0.32 mm i.d., 1.0 mm column, (Chromatographic Specialties Inc., Brockville, ON, Canada) was used. Chromatographic conditions: injector temperature, 220°C; column, 100°C (10 min), 10°C/min to 250°C (5 min); flow-rates: helium carrier, 1.0 mL/min; argon-methane (5%) make-up gas, 60 mL/min. The purge was off for the 10 min desorption time and on for the rest of the run.

Soil slurry samples were spiked with atrazine in quantities corresponding to total slurry concentrations ranging between 0.67 mg/L and 103.4 mg/L and were analyzed using the above procedure. A calibration curve (atrazine in HPLC-grade water) was constructed for each fibre.

Cleaning of the Fibre

An Ultrasonic Cleaner model No. BP-1 (Electromation Components Corp., Farmingdale, NY, USA) was used to clean the fibre in between extractions. Ultrasonic cleaning of the fibre was performed combined with a gentle mechanical cleaning of the fibre with a camel hair brush. After each injection the fibre was immersed for 15 min in an ultrasonic bath filled with HPLC grade water, then gently brushed and immersed for another 10 min in the ultrasonic bath. The cleaned fibre was then desorbed in the injection port of the GC for 10 min.

The base assisted cleaning of the fibre was performed by immersing the fibre for 25 min in the cleaning solution, using the ultrasonic cleaning bath. Cleaning solutions used were 0.01 M NaOH solution and 5% sodium pyrophosphate solution. After each cleaning the fibre was desorbed in the injection port of the gas chromatograph for 10 min at 220°C.

Monitoring of the Fibre

The physical appearance of the fibre surface was monitored by direct observation under an optical microscope (40× and 75× magnification) and by scanning electron microscopy (SEM) (150×, 800× and 2000× magnification). Observation under an optical microscope was nondestructive: the fibre was extended using the fibreholder and positioned in the optical field. For observation using the

scanning electron microscope, the fibre was cut from the supporting metallic rod, glued to a special sample holder using an electron conducting carbon paint and coated with a thin gold layer (<100 Å). A scanning secondary electron microscope (SEM) Cambridge Instruments (model 120) at 150×, 800× and 2000× magnification was used to monitor the aspect of the fibre coating surface during the experiment.

Microfiltration-HPLC Analysis

Immediately after an SPME injection, a small aliquot (~ 100 μL) of the soil suspension was filtered and injected into the HPLC system. Filtration was performed manually, using disposable tuberculin, Luer tip, syringes (Becton Dickinson & Comp., Franklin Lakes, NJ, USA) and Cameo 3N syringe filters, Nylon, 3 mm, 0.45 μm (MSI, Westboro, MA, USA).

Analyses were performed on a HPLC system consisting of a Waters 6000A pump (Waters Canada Ltd., Mississauga, ON, Canada), an Rph BioSil-ODS 10 column from BioRad and a Waters 440 UV fixed wavelength detector (λ = 254 nm). Water-methanol (35:65), prepared from HPLC-grade water and HPLC grade methanol-Acusolv (Anachemia, Rouses Point N Y, USA), at flow rate of 1 mL/min, under a pressure of 1200 psi (8.3×10^6 Pa).

The analyses were considered to be essentially simultaneous. The atrazine concentrations determined by HPLC analysis were calculated using a multiple point calibration curve based on the measurement of aqueous standard solutions.

RESULTS AND DISCUSSION

The 100 μm PDMS fibre was chosen for this study based on satisfactory extraction capacity, good selectivity for atrazine compared with coextractants from the soil matrix, very good stablity, low bleed, and good reproducibility of the extraction capacity among fibres. The sensitivity of the method was sufficient for the study performed.

The extraction time was set at 30 min. A long equilibration time for atrazine on the 100 μm PDMS fibre under static conditions was reported in the literature[20]. Using extraction at equilibrium was considered to be impractical for analytical purposes, but, considering the shape of the equilibration curve, an extraction time was chosen which allowed for good reproducibility if extraction times were maintained consistent.

Vigorous magnetic stirring was used. Stirring is very important in all SPME extractions, because the partition between the matrix and the fibre coating is

diffusion limited. According to mathematical models which describe the diffusion of the analyte through the matrix and through the water[12], if diffusion through water could be neglected, for most analytes equilibrium with the fiber coating would be achieved in a comparatively short time[21] because the fibre coating is very thin. The determining factor in the extraction time is the diffusion through the aqueous matrix; thus, vigorous agitation methods (sonication, magnetic stirring) can substantially shorten extraction times. In the case of soil slurries, vigorous stirring is doubly important because of the necessity to maintain an equilibrated homogenous soil-water system.

Desorption time was set at 10 min. "Memory" effects were observed during experiments when shorter desorption times were used. Other authors[20] have reported similar desorption times for atrazine. During the desorption of the analyte in the injection port, the purge was off to prevent the loss of the analyte. Complete desorption was achieved, as shown by clean blank runs between the analytical runs. The coextractants from soil do not interfere with atrazine quantitation (see chromatogram in Figure 1).

A linear relationship between the amount of analyte sorbed by the fibre coating and the initial concentration of the analyte in soil slurry samples was found in the range of concentrations used in this study. The reproducibility of the analytical results for pure water extraction was checked for several atrazine concentrations and showed to be >95% in accordance with earlier results[22-24].

During the extraction of the analyte, the coating of the fibre was subjected to mechanical impact from soil particles in the stirred soil slurry. Following observation of the fibre surface under an optical microscope, exfoliation of the fibre surface was ruled out; rather, deposition of small amounts of soil particles on the fibre surface was observed. Soil particles deposited on the surface of the fibre coating after each use led to the loss of about 10-20% of its performance for subsequent analyses. The physical appearance of the fibre was monitored by direct observation under an optical microscope (40× magnification) and documented by pictures of the clean fibre as well as the fibre used in soil slurry extractions. To the authors' knowledge, this was the first time that the fibre coating surface had been studied in such detail, using microscopy techniques. It was observed that the variations in the extraction capacity of the fibre coating were due to variations in the coverage of the surface of the coating caused by soil particle deposition. No loss of the organic coating could be seen and the soil particles appeared to be loosely bound to the surface of the coating. These observations were valuable, because they showed that the decline in the extraction capacity of the fibre the was not due to an irreversible destruction of the coating material. It appeared therefore possible to clean the surface of the

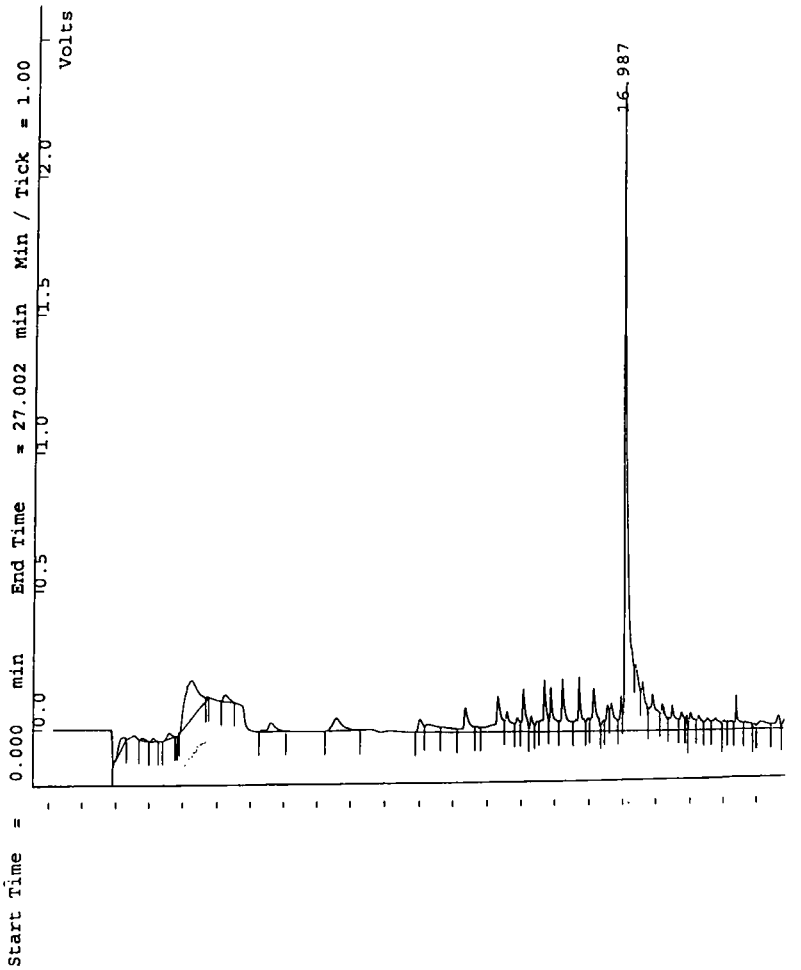


FIGURE 1 Chromatogram of atrazine in soil slurry (1.05 μg/g).

coating between extraction procedures and to maintain constant the extraction efficiency of the fibre.

An optical microscope was used to monitor the fibre surface throughout the experiment. The observations under an optical microscope were valuable because they gave a "real" image of the fibre (no pre-treatment of the fibre surface is required for optical observation; the fibre retains its "glass-like" appearance) and especially because observations under an optical microscope do not require the destruction of the fibre. However, it was difficult to obtain a well

focused picture because of the shallow depth of field of the optical microscope.

Through the use of scanning electron microscopy (SEM) (150×, 800× and 2000× magnification) the changes in the appearance of the surface of the coating during extraction were easy to follow and the technique allowed for a more detailed observation. Unfortunately, owing to the necessity to gold-coat the object under observation, the method was destructive for the fibre. SEM photos of the fibres were taken at relatively low magnification (150×) to give a more comprehensive image of the fibre and make the whole process of "coating" by the soil particles easier to see. Photos at higher magnification (800× and 2000×) were taken to enable the study of the changes of the coating surface during the process in more detail. No significant further information was produced at higher magnification.

Photos of the new fibre (Figure 2. a, b) showed a cylindrical fibre coating, with a smooth outer surface. The tip of the fibre was rough, (photo not included) resulting from an imperfect cutting in the manufacturing process.

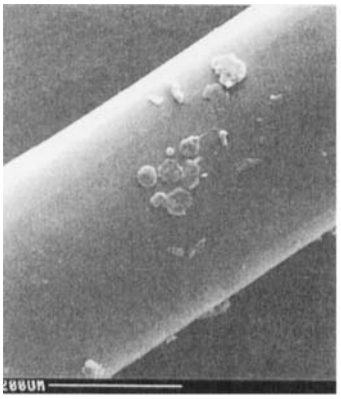
A fibre used for only one extraction from a soil slurry showed a different picture: the appearence of the coating surface itself was not changed, but a good part of the surface was covered with soil particles adhering on the coating surface (Figure 2 c). At higher magnification, the soil particles seemed to adhere to the surface by some kind of fibrilar structures derived from their own surface material (photo not included), which suggested that if this material were of organic nature and if an appropriate chemical agent could be found to dissolve this material, the soil particles could be expected to loosen from the fibre coating surface and allow it to be cleaned.

Further observation of fibres used in 15 successive extractions from soil slurry (Figure 2.d) showed that particles were continually being deposited on the surface. The surface coverage increased, smaller particles were deposited between and over the initially seen large particles during subsequent extractions and forming an apparently compact secondary "coating". More detailed observation revealed that the structure of the "coating" was segranular, consisting of successive deposits of soil particles (Figure 3.a). The appearence of the soil particle "coating" was similar for both soils, suggesting that the deposition process was also similar and that a similar cleaning process might be applicable.

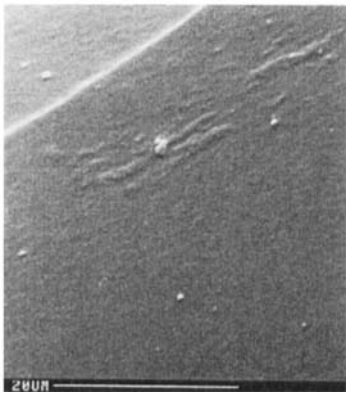
In conclusion, the variations in the extraction capacity of the fibre coating appear to have been due to variations of the surface of the coating caused by soil particle deposition. No loss of the organic coating was observed and the soil particles present appeared to be loosely bound to the surface. A more and more

complete coating of soil particles was deposited on the fibre surface as the number of extractions increased.

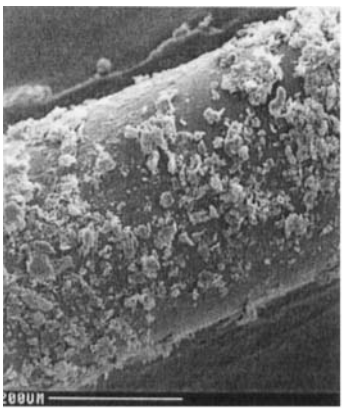
Ultrasonic cleaning in HPLC grade water for 25 min combined with a gentle mechanical cleaning of the fibre with a small camel hair brush was initially successfully used. After each extraction-desorption cycle, the fibre was cleaned,



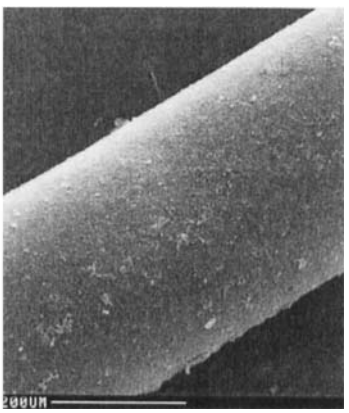
a). SEM photo: Clean fibre (150X).



b). SEM photo: Clean fibre (2000X).

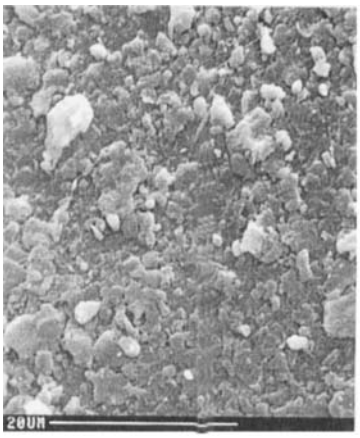


c). SEM Photo: Fibre after one soil slurry extraction (150 X).



d). SEM Photo: Fibre after 15 soil slurry extractions (150X).

FIGURE 2 a) SEM Photo: clean fibre-150× magnification b) SEM Photo: clean fibre-2000× magnification c) SEM Photo: fibre after 1 soil slurry extraction (Miniota soil)-150× magnification d) SEM Photo: fibre after 15 soil slurry extractions (Miniota soil)-150× magnification.



a). SEM Photo: Fibre after 15 soil slurry extractions (2000X).

b). SEM Photo: $Na_2P_2O_7$ treatement effect (2000X).

FIGURE 3 a) SEM Photo: fibre after 15 soil slurry extractions (Miniota soil)-2000× magnification b) SEM Photo: $Na_2P_2O_7$ treatment effect-2000× magnification.

then desorbed in the GC injector port for 10 min at 220°C. Using this procedure it was possible to maintain almost constant the performance of the fibre for at least 15 injections when sampling from soil slurries containing a 20 g/L concentration of suspended soil. In the absence of the cleaning procedure the performance of the fibre continuously declined (Figure 4).

The chemical cleaning agents were selected for their expected properties of dissolving and dispersing humic compounds. Sodium hydroxide solution, as well as sodium pyrophosphate solution have been used in the isolation of humic substances.

The use of sodium hydroxide solution (0.01 M) as a cleaning agent in an ultrasonic bath was not successful, continually increasing the apparent extraction ability of the fibre. A possible explanation for this effect might be a surface hydrolysis process of the siloxane coating under highly alkaline conditions, changing the polarity of the coating and increasing its affinity for atrazine. At the same time, the sodium hydroxide solution did not seem to have a very important dispersing effect on the soil particle "coating", as shown by SEM observations. The much lower dispersing effect of sodium hydroxide solution on humic compounds compared with sodium pyrophosphate solution may be due to a much lower ionic strength of the sodium hydroxide solution used in this experiment (0.01 M NaOH compared to a 0.23 M sodium pyrophosphate solution). A higher sodium hydroxide solution concentration was not considered for experiments

because it was expected to be even more aggressive to the siloxane surface of the fibre coating.

Ultrasonic cleaning in a saturated $Na_2P_2O_7$ solution for 25 min proved to be very efficient in dispersing the soil particles from the surface of the coating, as shown by the SEM observations (Figure 3.b), and by analytical results (Figure 4)). The cleaned fibre was then desorbed in the GC injection port for 10 min. The temperature and the time used to desorb the cleaned fibre was the same as the desorption temperature and time used in the analytical procedure (220°C) in order to remove any contamination which might occur during the cleaning process. The SEM photos show the dramatic effect of this cleaning procedure on the secondary soil particles "coating". The fibre shown in the SEM photographs had been used for 15 extractions from soil slurry. The cleaning procedure was performed after each slurry extraction-desorption. After 15 samplings, most of

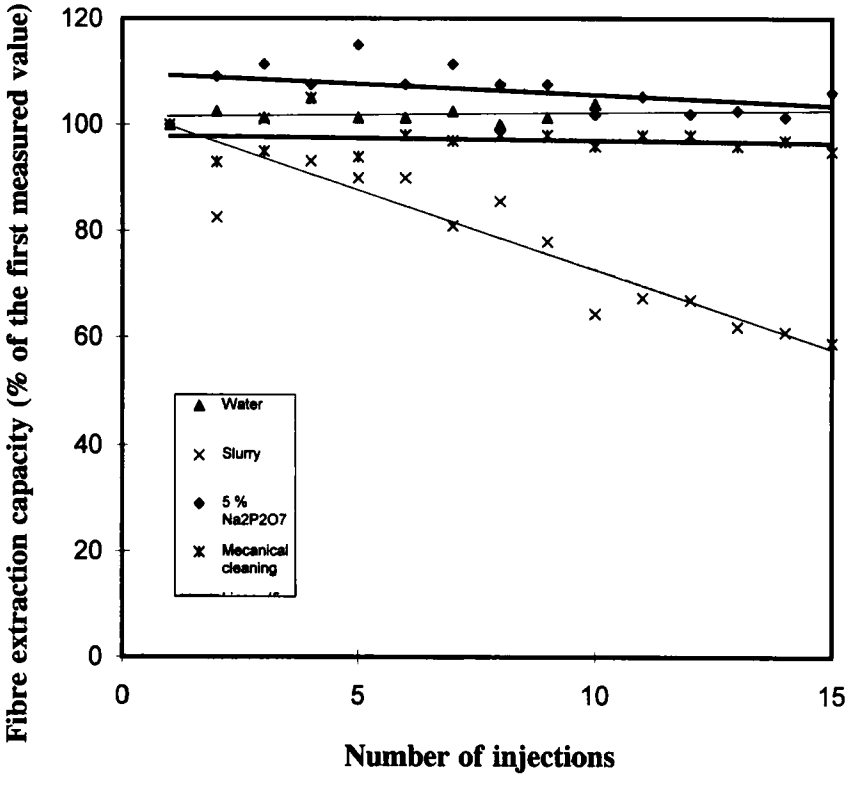


FIGURE 4 Fibre stability.

the surface was free of soil particles. The first cleaning seemed to slightly increase the extraction capacity of the fibre, a one-time effect. The extraction capacity of the fibre remained unchanged during the experiment. The effect of the initial cleaning procedure might be due to removal of dust particles from the fibre or of other particles accumulated on the surface of the fibre during manufacturing and storage. An initial preconditioning by an ultrasonic treatment in the sodium pyrophosphate solution, before the use of the fibre for extraction is therefore recommended. The ultrasonic cleaning using a sodium pyrophosphate solution enabled maintenance of constant performance of the fibre for at least 15 samplings from soil slurries. It was more effective than the ultrasonic-mechanical cleaning.

The design of an effective cleaning procedure completes the development of a reliable direct analysis method for atrazine in soil slurry and encourages the development of analysis methods from other "dirty" matrixes, traditionally considered inaccessible by such an apparently delicate technique as SPME. Appropriate cleaning procedures would have to be designed according to the properties of the matrix.

No fibre bleed was observed during SPME of atrazine from pure water. When sampling from pure water solutions, the life of the fibre was virtually unlimited. The most likely end to its use was from mechanical accident. When sampling from real water samples (run-off water, natural surface water) with low organic matter content and low solid particle content the fibre life is limited to 25-30 extractions[25] when no cleaning procedure is used. For the direct sampling of soil slurries, if the cleaning procedure was used in between the analytical runs, the fibre could be used with good results for at least 15 samplings. Compared with traditional solvent extraction methods and other solid phase extraction (SPE) methods, the SPME porcedure is cost effective.

Does SPME Affect the Soil-Water System?

A theoretical problem related to the use of the SPME method in the study of pesticide sorption-desorption processes on soils is related to the degree to which the sorption of the analyte to the fibre coating affects the soil solution equilibrium. An estimation of this influence can be made assuming the extraction process to be an equilibrium process and the partition coefficient of atrazine between water and the organic coating of the fibre to approximate the octanol-water partition coefficient. Using the equation which defines the number of moles of analyte extracted by the fibre in an SPME procedure [26], $n = K\ V\ c_o$, if

TABLE II The calculated decrease in concentation of atrazine in solution (mol/L) after one SPME procedure assuming $K_{SPME} = K_{ow}$ for atrazine

	SOLUTION 1	SOLUTION 2	SOLUTION 3
Before SPME	1.0×10^{-7}	4.8×10^{-6}	1.0×10^{-4}
After One SPME	0.986×10^{-7}	4.732×10^{-6}	0.986×10^{-4}

$K = K_{ow}$ atrazine = 562[1]
V = the volume of the coating = 6.34×10^{-7} L, for the 100 μm fibre
$c_o = 4.8 \times 10^{-6}$ mol/L

the calculated concentration after one sampling, c_o', would be 4.732×10^{-6} mol/L.

The results of similar calculations for three initial concentrations are shown in Table II. The calculations reflect a decrease in concentration which is analytically indistinguishable by this method.

In view of these theoretical estimations the sorption of the analyte by the fibre coating was not expected to observably deplete the atrazine in soil solution even after several extractions from the most diluted soil slurry. Repeated sampling with the SPME device was not expected to have any significant impact on the equilibrium between the dissolved atrazine and the atrazine sorbed on soil components.

During the experiments, no decrease in concentration was measured even after sampling the same standard water solution 10 times in the range of concentrations 10^{-4}-10^{-6} mol/L. These experimental results, and associated theoretical considerations support the idea that, due to the limited hydrophobicity of atrazine, SPME does not deplete observably the soil solution in the range of concentrations considered and, consequently, does not disturb the equilibrium of the atrazine-water-soil system. For highly hydrophobic analytes (PCBs; PAH) repeated samplings have been found to deplete the solution (W. H. J. Vaes, personal comunication). The use of a more extraction-efficient coating in the case of atrazine might improve the sensitivity of the analytical method, but might also disturb the equilibrium of pesticide-water-soil system under study if the soil-sorption equilibrium were rapid.

Comparison Between the New SPME-GC Method and the Microfiltration-HPLC Method [19] for Dissolved Atrazine in Soil-Water Systems

The necessity to compare the new SPME analysis method with an already established method arises from both a theoretical and a practical point of view. One of the most important aspects in developing a new method of analysis for such systems is related to defining which pesticide fraction is measured by that

specific method. The "off-line" microfiltration in the microfiltration-HPLC method separates the dissolved atrazine and atrazine bound to DOM from the atrazine bound to soil particles; the HPLC step separates the dissolved atrazine from the atrazine bound to DOM by reverse-phase chromatography. The net result is that the method measures only the truly dissolved atrazine in solution [19]. The moderately hydrophobic atrazine is retained by the C_{18} column and is then chromatographed and detected on the HPLC system; whereas, the polar complexes formed by atrazine with fulvic acids are not retained by the chromatographic column and are not detected. The detector detects and quantifies only the atrazine retained by the stationary phase (the "truly dissolved atrazine").

The SPME-GC method is also expected to measure only the dissolved atrazine because it does not significantly influence the equilibrium between dissolved and sorbed atrazine in the soil slurry. From a practical point of view, the comparison with an already established method enables evaluation of the performance of the new SPME-GC analytical procedure.

Atrazine concentrations determined by the SPME-GC-ECD method were correlated with atrazine concentrations of the same soil slurry samples determined by the "off-line" microfiltration-HPLC method. The calibration curves for HPLC measurements in the range of concentrations measured were found to be linear. The correlations have been made for both soils investigated (the Miniota sand and the Fifi Road soil). For the Miniota soil three series of experiments were conducted in an attempt to obtain more detailed sorption The data obtained by the SPME-GC method correlate very well with the data from the microfiltration-HPLC measurements for both soils under investigation (Figure 5). The atrazine species measured by SPME-GC and microfiltration-HPLC appears therefore to be the same: the truly dissolved atrazine in the soil solution. This result is important because it provides a theoretical basis for the use of data provided by the SPME-GC analysis method in the ecological risk assessments for atrazine residues in soils.

CONCLUSIONS

The new SPME method, previously demonstrated to be useful for extracting a wide range of analytes from relatively clean aqueous solutions, has now been successfully used for the direct extraction of atrazine residues from soil slurries. This adds a simple, clean, solventless extraction technique, easily compatible with capillary GC, to the arsenal of methods available for the analysis of less volatile compounds from soils and water bodies with a high content of humic and other particulate and dissolved materials.

A remarkable observation is that no relevant interference of coextracted soil components was observed, even at the lowest atrazine concentration (0.67 ppm) for any of the soils under study (using an EC detector). Good resolution of the peaks was obtained for all samples. Experiments reported in this paper did not approach the LOD of the method. The method was, however, linear over the range of concentrations studied.

The new method for atrazine residues analysis in soil slurries, based on direct SPME sampling and capillary GC analysis has important advantages related to the simplicity of the extraction method, the short analysis time and the zero solvent consumption and, consequently, the low cost per analysis. Because it is based on a direct extraction of the water phase in the soil slurries, using the SPME device this new method appears to be the simplest approach to study equilibrium processes in soil-water systems. The new method does not use any organic solvent and has no separation steps (filtration, centrifugation, chromatographic clean-up) and it is therefore less likely to perturb the already complicated

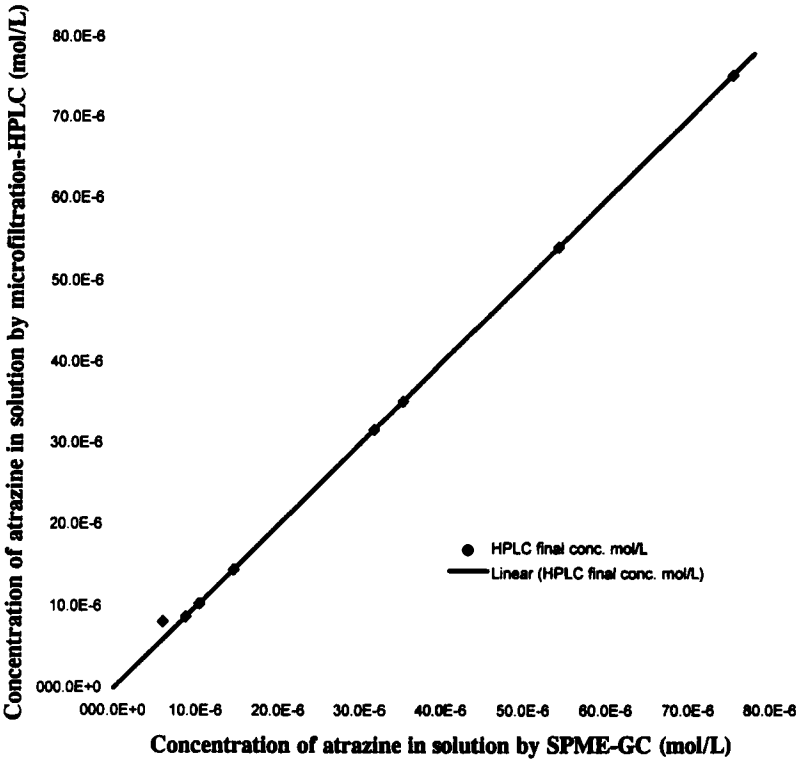


FIGURE 5 Comparison between SPME-GC and microfiltration-HPLC measurements.

pesticide-soil-water system. The results of the new SPME-GC method correlate very well with the results of the "off-line" microfiltration-HPLC method, suggesting that the new method measures the "truly" dissolved atrazine, which makes the method very valuable for ecotoxicological risk assessment studies.

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