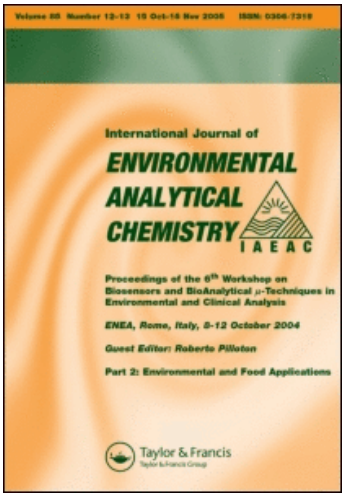


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# Application of Solid-Phase Microextraction for the Determination of Organonitrogen Pesticides in Aqueous Samples by Gas Chromatography with Nitrogen-Phosphorus Detector

Nicolas Le Calvez[a]; Laurent Bodineau[a]; Jean-Claude Fischer[a]
[a] Laboratory for Analytical and Marine Chemistry, UPRESA 8013, ELICO, University of Lille, Villeneuve D'Ascq Cedex, France

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# APPLICATION OF SOLID-PHASE MICROEXTRACTION FOR THE DETERMINATION OF ORGANONITROGEN PESTICIDES IN AQUEOUS SAMPLES BY GAS CHROMATOGRAPHY WITH NITROGEN-PHOSPHORUS DETECTOR

NICOLAS LE CALVEZ*, LAURENT BODINEAU
and JEAN-CLAUDE FISCHER

*Laboratory for Analytical and Marine Chemistry, UPRESA 8013, ELICO, University of Lille, Bât. C8, 59655 Villeneuve D'Ascq Cedex, France*



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A method based on solid-phase microextraction and gas chromatography nitrogen-phosphorus detector for the determination of common organonitrogen pesticides (ONPs) in aqueous samples was described. Three kinds of commercially available coated fused-silica fibres were compared: 100 μm PDMS, 85 μm PA, and 65 μm CW-DVB; 65 μm CW-DVB was the most sensitive fibre coating for the analytes' determination. The extraction time, the stirring, the content of salt, and the content of organic solvents were found to have a significant influence on extraction efficiency. The optimised conditions were 65 μm CW-DVB fibre, 40 min extraction time, with rapid stirring and concentration of NaCl was fixed at 0.25 g/mL. The linear range was 0.1–100 μg/L for most of the compounds. The limits of detection (LODs) ranged from 0.02 mg/L (for trifluralin, simazine, terbuthylazine, cyanazine, and pendimethalin) to 0.08 μg/L (for terbutryn) and RSD % of repeatability were for most of the compounds below 10%. Thus the maximum level set by the European Union for pesticides and drinking waters can be verified. The recovery of spiked water samples was compared and validated with the liquid–liquid extraction one. Environmental water samples were analysed and trifluraline was detected.

*Keywords:* SPME; Organonitrogen pesticides; GC-NPD; Water analysis

## INTRODUCTION

The presence of pesticides in the environment is a problem that has caused great social and scientific concern. The determination of pesticide traces in water has been optimised in recent years, especially since important developments of chromatography, immunoextraction, and detection techniques were introduced [1–6]. With the wide use of a range of phytosanitary products, more and more pollutants, especially organonitrogen

*Corresponding author. Fax: +33-0320-434-822. E-mail: Nicolas.Le-Calvez@univ-lillel.fr

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pesticides (majoritically with herbicide disposition) and their metabolisation products are found in river and estuarine waters [7,8], ground waters, soils [3,6] and food [9]. Triazines are often identified as the most commonly used herbicides [10]. The most common methods for isolation of these compounds from aqueous matrixes are the liquid–liquid extraction (LLE) [11] and the solid phase extraction (SPE) [12,13]. The analysis is usually performed by gas chromatography (GC) [1,2,14] or by high performance liquid chromatography (HPLC) [4,15]. However, these extraction methods are becoming increasingly unpopular. Indeed, the conventional LLE often needs large amount of toxic organic solvents and time-consuming procedures. The SPE is less time-consuming than the LLE and is used in environmental fields [16,17]. However, the SPE column needs a pre-treatment and still requires toxic organic solvents for the elution step.

Recently, the solid phase micro-extraction (SPME) has been introduced by Pawliszyn and co-workers [18–20]. The SPME is a solvent free technique which consists of absorbing analytes from aqueous solutions onto a fused silica fibre coated with various stationary phases. Partitioning of organic contaminants occurs between the sample and the polymeric absorbent:

$$n = \frac{K \cdot Vf \cdot Co \cdot Vs}{K \cdot Vf + Vs} \tag{1}$$

where $n$ is the mass of the analyte adsorbed by the coating, $Vf$ and $Vs$ are respectively the volumes of the coating and the sample, $K$ is the partition coefficient of the analyte between the coating and the sample matrix, and $Co$ is the initial concentration of the analyte in the sample. Analytes are subsequently thermally desorbed from the fibre in the GC injector. The SPME offers advantages as sampling rapidity, simplicity, and above all no use of toxic solvent. The SPME is an equilibrium method and not an exhaustive method such as the LLE or the SPE, whose primary aim is to obtain a quantitative extraction of the analytes in the extraction phase. As a consequence, with the latter methods selectivity is often sacrificed because many matrix components are co-extracted. Equilibrium methods such as the SPME are more selective since thy take full advantage of the differences in the partition process to separate target analytes from interference [21]. SPME methods have been developed for a variety of applications including the analysis of different groups of pesticides as organochlorine, organophosphorus and organonitrogen ones [22,23]. Methods have also been described for the analysis of pesticides in food plants, soils, biological samples and human body fluids [9,24–26]. Screening of antifouling pesticides was evenly reported [27]. Eisert and Levsen [28] determined organophosphorus pesticides, triazine and 2,6-dinitroaniline via gas chromatography with nitrogen-phosphorus detection (GC-NPD), but only two fibres were compared (85 μm PA and 100 μm PDMS).

The aim of this work was to confirm the ability of the SPME method for screening organonitrogen pesticides in environmental waters (mainly river and estuarine ones). To reach this objective, the influence of parameters as the time of extraction, the stirring, the type of coating, salt addition and the presence of organic solvent have been investigated and involved.

## EXPERIMENTAL

### Materials

The solid phase microextraction (SPME) fibre holder from Supelco (Bellefonte, USA) was used for our experiments. For comparative investigations three SPME fibres (purchased from Supelco) were tested: 100 μm film thickness polydimethylsiloxane (PDMS), 85 μm polyacrylate (PA) and 65 μm carbowax-divinylbenzene (CW-DVB). Fibres were conditioned according to the specifications of the manufacturer. Usually, this consisted in exposing the fibre to the hot gas chromatograph injector during times depending on the coating of the fibre: at 250°C during one hour for PDMS, at 300°C during two hours for polyacrylate fibre, and at 250°C for 30 min for the carbowax-divinylbenzene one. Extra caution must be used when handling the CW-DVB fibre because the coating can be inadvertently stripped off. The heating of the polyacrylate fibre will not hurt the performance of the fibre. All pescticide standards used in this study (ametryn, atrazine, cyanazine, pendimethalin, prometryn, propazine, simazine, terbuthylazine, terbutryn, trifluralin, metabolite desethylatrazine and internal standard 1-Bromo-2-nitrobenzene), mainly triazines and dinitroanilines (Fig. 1), were purchased from Restek (Evry, France) and Alltech (Templemars, France). They were most of purity > 97–99% and used as received. Methanol (chromanorm quality) was from Prolabo (Fontenary-sous-bois, France). Sodium chloride and potassium chloride of quality > 99.5% were purchased from Merck (Darmstadt, Germany). Extractions were performed in water (18.2 MΩ.cm) obtained from a milli-Q-water purification system (Millipore, St Quentin, France).



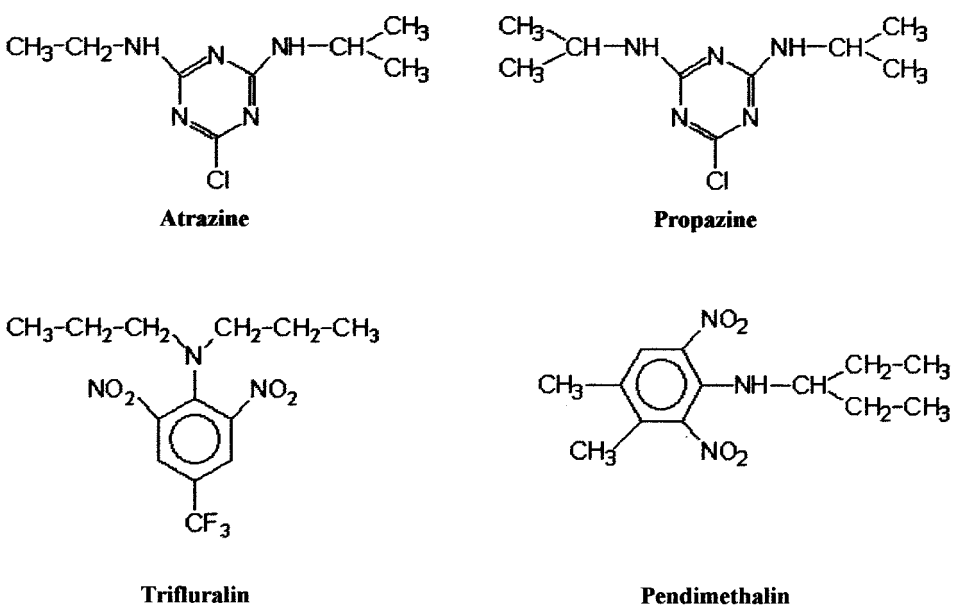


FIGURE 1 Chemical structures of some organonitrogen pesticides studied in our investigations.

### Gas Chromatography

Gas chromatography investigations were carried out with a Varian 3800 gas chromatograph equipped with a Nitrogen-Phosphorus Detector (NPD or TSD: Thermoionic Specific Detector). A 30 m × 0.25 mm id HP-1701 (0.25 µm of 14% cyanopropylphenyl-86% methyl polysiloxane) column and a 1079 universal injector (Varian) equipped with a SPME glass insert were used for all investigations. Helium was used as carrier gas to 0.8 mL/min flow thanks to an electronic flow controller (EFC). The column temperature programme was as follows: 100°C held 5 min, ramped to 200°C at 15°C/min, ramped to 250°C at 6°C/min with a final hold time of 2 min. Injector and detector temperatures were respectively 230 and 300°C. Injector and detector temperatures were respectively 230 and 300°C.

### Solid-phase Microextraction (SPME) Procedure

The theoretical partition process has been extensively studied since 1990 [18–20]. The principle of the technique consists in reaching an equilibrium partition of the target analyte between the stationary phase and the aqueous phase. This was carried out by introducing the fibre into the aqueous sample which was rapidly stirred by a little magnetic agitator (5 mm). The extractions were performed from 2 mL water samples in a glass vial. Actually, the SPME fibre holder is a modified chromatographic syringe which contains the retractable silica fibre (protected by a hollow needle). The SPME procedure can be separated in two steps. First, the fibre is exposed to the sample for a time. After piercing the septum of the sample vial, the coated fibre protected by the hollow needle is deployed into the vial. As soon as the extraction has reached the equilibrium, the fibre is retracted back into the hollow needle. Secondly, the fibre assembly is introduced directly into the GC injector. Then the thermal desorption of the compounds occurs. The desorption time has been fixed at 6 min since several tests showed that it was the minimum duration necessary to reach a complete desorption of the products. In this case, no memory effects were observed on the chromatograms obtained after analysis.



## RESULTS AND DISCUSSION

### Effects of Various Parameters

#### *Equilibrium Times*

Extraction time profiles for the fibres under study were investigated in order to establish a sufficient time for all compounds to reach equilibrium. In our investigations, extractions were improved by a magnetic stirring. Time profiles curves, which consist in reporting on a graph the peak area obtained when varying time from few minutes to an hour or more, are given in Fig. 2. As can be seen equilibrium was reached at different times according to the three polymeric coatings. The required time to attain this equilibrium also depends on the nature of the compounds. Using the CW-DVB fibre, the equilibrium is observed in less than 40 min, while with the PA fibre it is observed up to 60 min. At last, for the PDMS one, the equilibrium is less emphasized and observed near 30 min. Pendimethalin and trifluralin were little or none extracted by the last one.

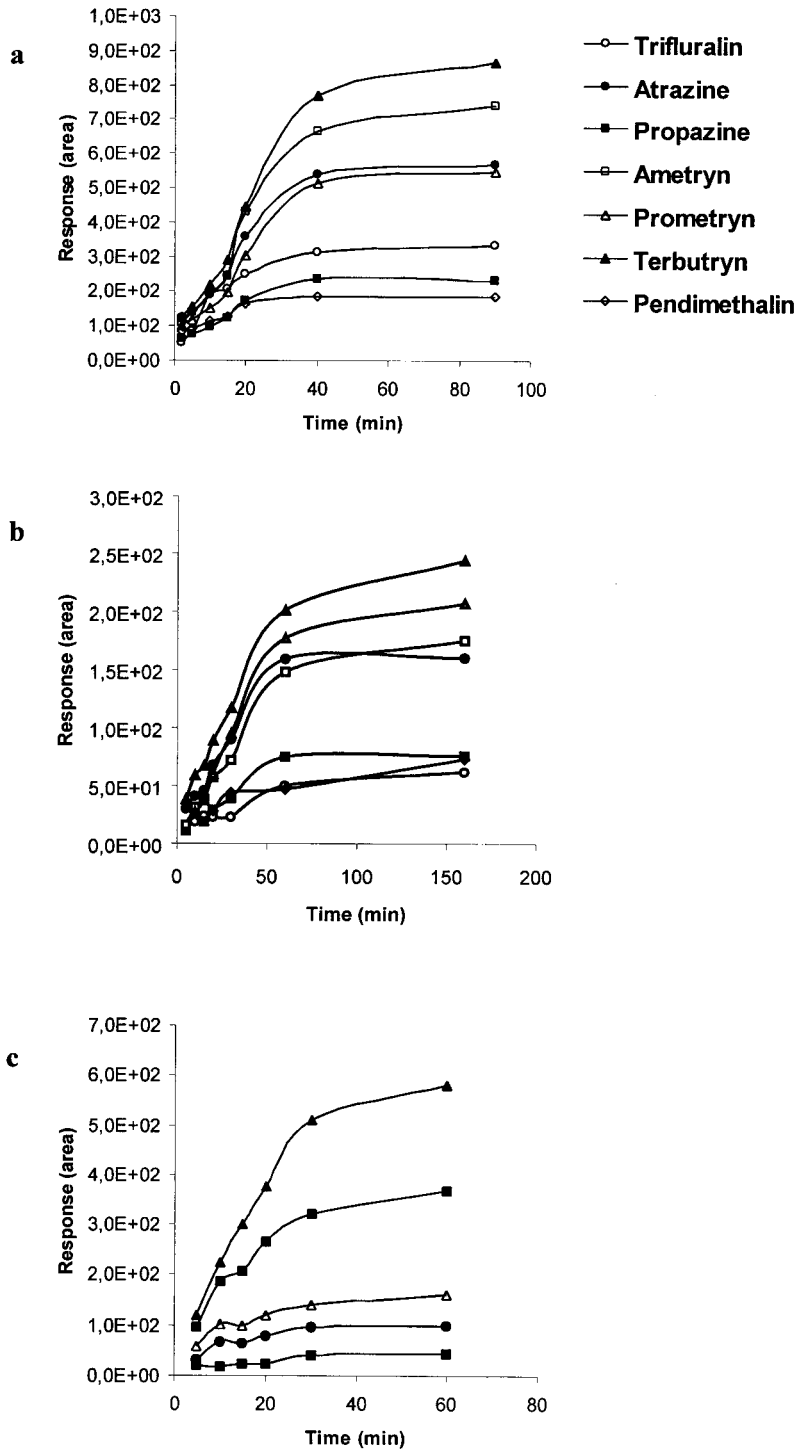


FIGURE 2 Extraction time profiles for organonitrogen pesticides extracted with the different coatings under study; (a) 65 μm CW-DVB, (b) 85 μm PA, (c) 100 μm PDMS.

And most of products are less extracted by the PDMS fibre (especially propazine, atrazine, prometryn). This observation can be related to the polarity of the molecules which is higher than the PDMS fibre one; which was the less polar fibre tested in this work. In general, the PDMS fibre is preferred for the extraction of non-polar pesticides, with a very low solubility in water, such as organochlorine pesticides and some of the non-polar organophosphorus insecticides, whereas the more polar coatings are shown to be more appropriate for the more polar nitrogen-containing pesticides [29]. The choice of the equilibrium time frequently consists in a reasonable compromise between a good peak response and an acceptable time (related to the GC-run time; [22]). In our case, an exposure time of 40 min kept not to penalise the time of the sample treatment.

### *Agitation Effect*

The necessary time to reach equilibrium is essentially linked to the mass transfer rate [14]. It is determined by the diffusion of analytes into the coating. Therefore, extraction was carried out in the conditions of a rapid stirring which improves the mass transfer. In Fig. 3 extraction time profiles for the three fibres are represented with and without agitation. Evidently, the extraction rates are higher in the case of the magnetic stirring which improves the transfer rate. However, it can be noticed that the improvement was different according to the compound. Indeed in our case, terbuthylazine appeared to be more sensitive than atrazine to the magnetic stirring. And this observation was true for all the investigated fibres.

### *Salt Addition*

The organonitrogen compounds studied in this work are qualified as water-soluble analytes. The modification of the ionic strength was to be considered for the extraction

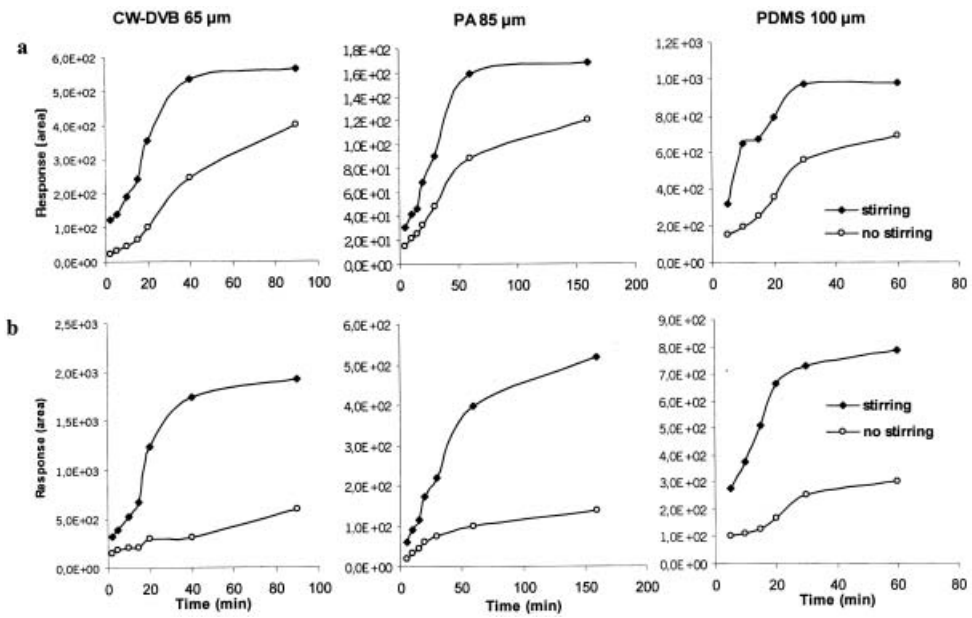


FIGURE 3 Effect of agitation onto extraction efficiency (peak response); (a) atrazine, (b) terbuthyazine.

of this kind of products [30]. On a theoretical point of view, the more soluble in water the analyte, the lower his affinity for the fibre is. The ionic strength of the aqueous matrix is increased by the salt addition, which decreases the solubility of the compounds. So the extraction by the fibre of the products is improved. It is apparent that the equilibration of the analyte between the aqueous and the polymeric phase essentially depends on the hydrophobicity. Finally, the more hydrophobic compounds are more readily absorbed by the polymeric phase [28]. The effect of varying the ionic strength was tested for the analytes with the three coatings by comparing the results obtained for unsalted and 0.3 g/mL NaCl solutions. The results are shown in Fig. 4. The responses at 0.3 g/mL NaCl (about 83% saturated solution) were higher for the majority of the analytes than with no salt addition. This improvement was verified for the three fibres. However, there were few exceptions to this general observation, desethylatrazine and terbutryn using the PDMS fibre. In recent works Valor *et al*. [23] have shown the specificity of triazines. The results indicated that the limits of detection could be easily improved by the salting out effect, which in the case of polar compounds permits an important increase of partition coefficient and thus the extracted amount. The tests about salt addition led us to select the CW-DVB fibre (sensitivity and rapidity of reaching equilibrium) for the extraction of the organonitrogen pesticides studied in this work.



The saturation rate of sodium chloride (0, 20, 39, 59, and 84% of saturated solution) was studied (Fig. 5). The extraction efficiency was influenced by salt addition in the way of improvement but up to 70% of saturated sodium chloride the extraction efficiency decreased drastically for ametryn and terbutryn. This observation for the *s*-triazines was also carried out by Eisert and Levsen (1995). In the case of terbuthylazine, the drop was observed up to 80% of saturated sodium chloride. The limits of the salt addition onto the extraction efficiency were evenly observed about the life-time of the fibres. Indeed, by using an optical microscope, Hernandez *et al*. [31] exposed the possible degradation of the fibre coating because of the presence of NaCl. This result forced them to diminish the concentration of NaCl; and under this condition, it was feasible to use a single fibre for the extraction of over 100 samples without significant degradation. In this article, the salt concentration was fixed to 0.25 g/mL (70% of saturated sodium chloride) which offered a good compromise of extraction efficiency for all studied compounds.

The nature of the salt was approached by comparing the extraction efficiency with the addition of sodium chloride (NaCl) or potassium chloride (KCl) (Fig. 6). The extraction capability was significantly higher using NaCl for trifluralin, atrazine, propazine and pendimethalin (comparison test of experimental means; student factor, confident threshold 95%). At the opposite, the use of KCl was more efficient for terbutryn, ametryn and cyanazine. Nevertheless, the global extraction efficiency was comparable for both salts. It can be seen that for the screening of a precise product, the choice of the salt could be important. In this work, the aim was to screen several compounds. So no difference were noticed about these two different salts apart from the possible presence of NaCl in natural samples (as marine influenced waters). So the use of NaCl was kept for further investigations.

### Influence of Organic Solvents

To study organic solvent effects, various amounts of methanol have been added to samples of organonitrogen pesticides as shown in Fig. 7. All pesticides demonstrated

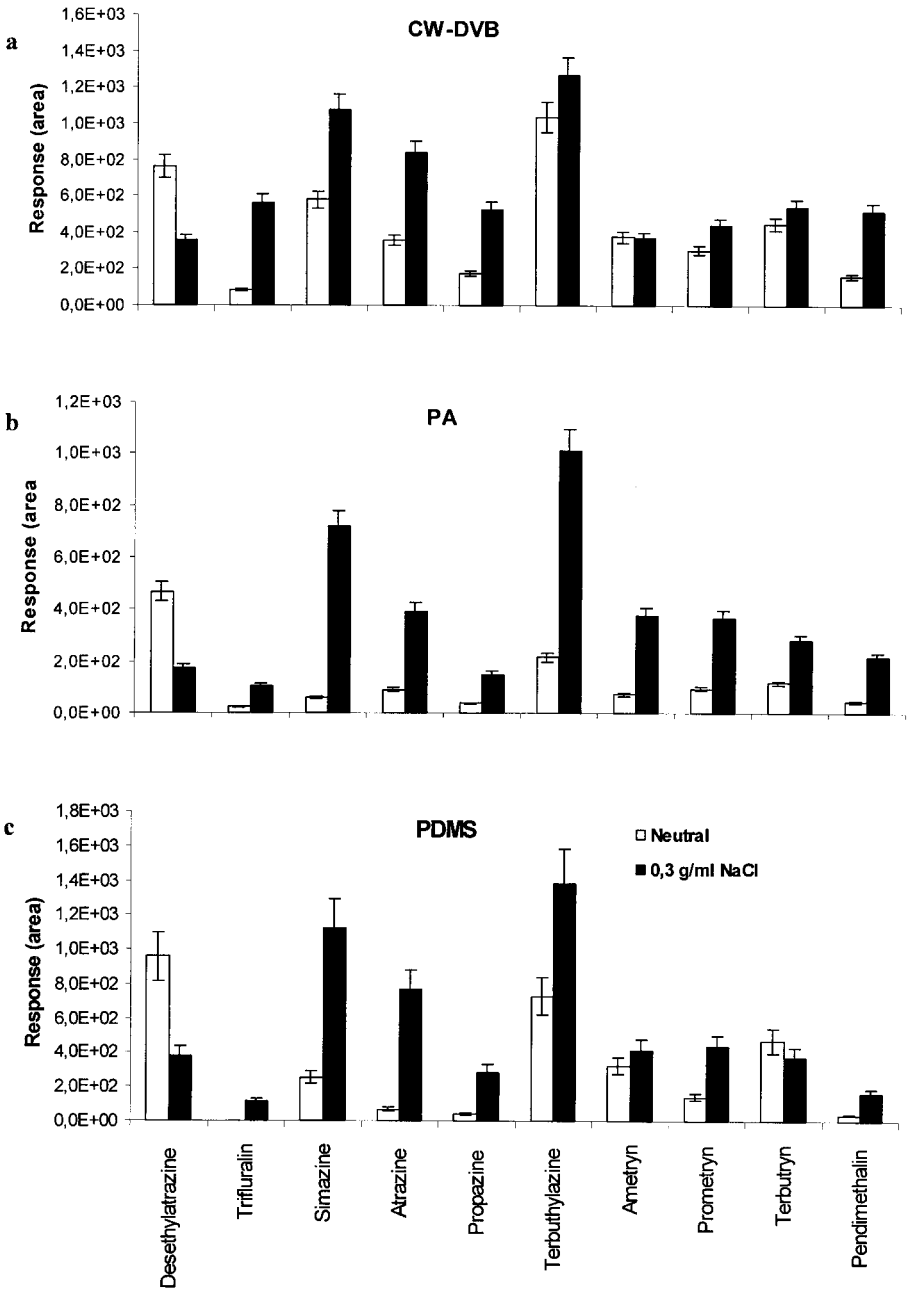


FIGURE 4 Effect of salt addition to the matrix for the extraction of organonitrogen pesticides with the three coatings: (a) 65 μm CW-DVB, (b) 85 μm PA, (c) 100 μm PDMS.

a decrease in the SPME absorptivity when methanol concentrations raised. An increase in the methanol content up to 20 vol.% reduced the peak response for ametryn, terbutryn, and cyanazine by a factor of about 2, for desethylatrazine and terbuthylazine by a factor about 3, for simazine and atrazine respectively by a factor about 4 and 6.

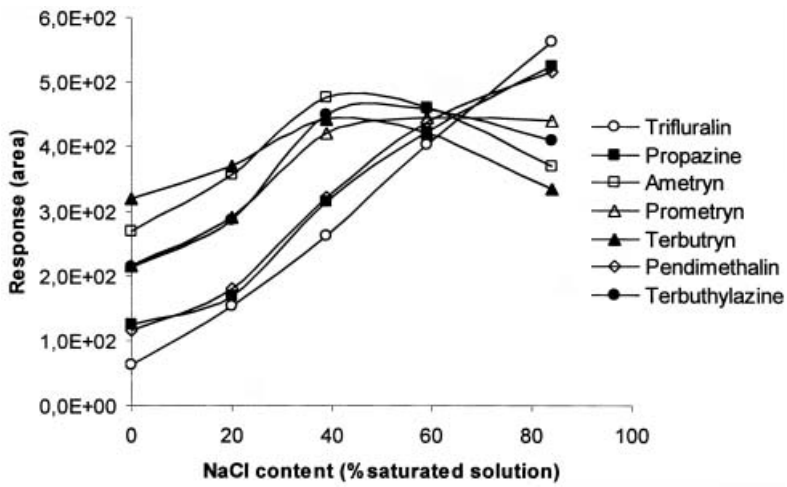


FIGURE 5 Effect of NaCl content (% of saturated solution) on SPME efficiency (peak response) for selected pesticides (peak response × 1/3 for terbuthylazine).



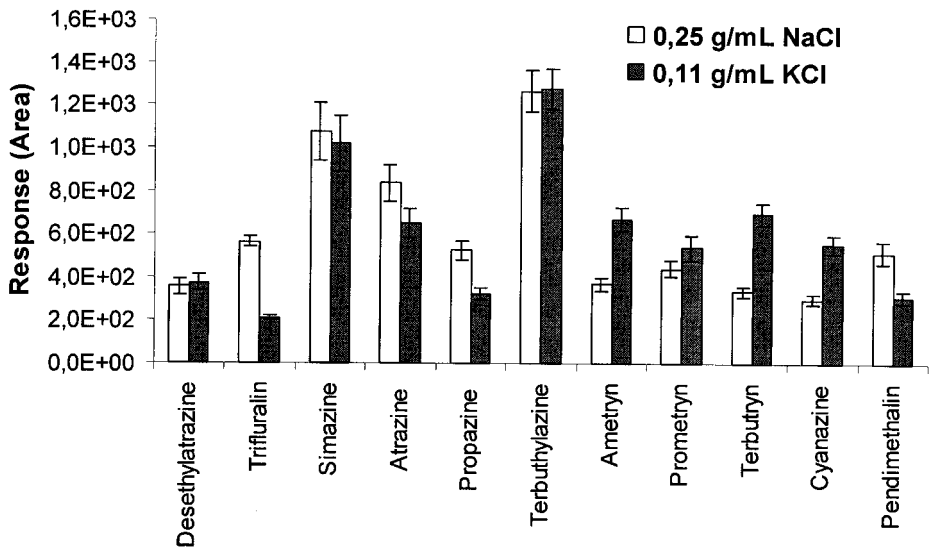


FIGURE 6 Dependence of extraction efficiency (peak response) on the salt nature (NaCl, KCl).

This factor even reached 8 for trifluralin, propazine and pendimethalin. Nevertheless, methanol can not be considered as a representative compound for all organics. But a few studies have shown the same effect with acetonitrile and acetone [31].

## Calibration-validation Method

The validation of analytical quantitative methods needs to carry out some experiments to obtain linearity, precision, and the limits of detection. Investigations were performed using the carbowax-divinylbenzene (65 μm thickness) fibre as follows: extraction time of

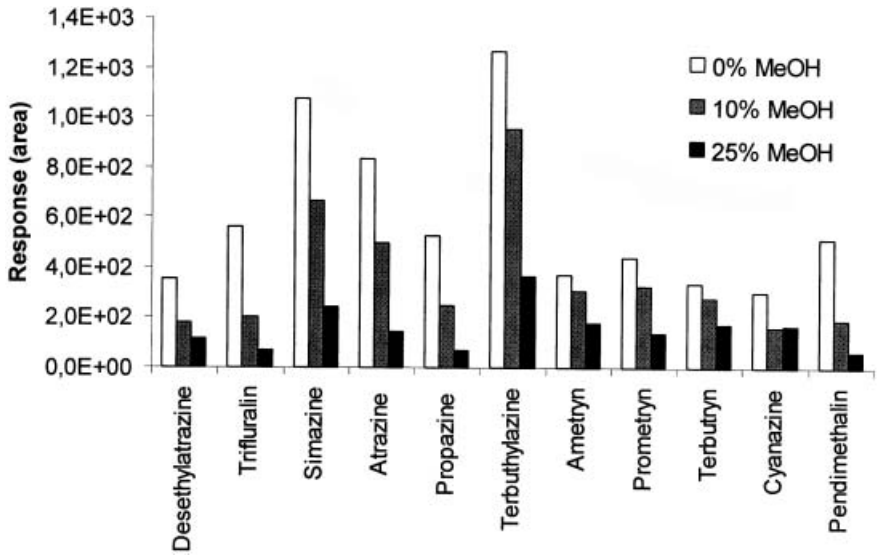


FIGURE 7 Effect of methanol content (vol. %) on SPME efficiency (peak response).



TABLE I Gas chromatographic determination of organonitrogen pesticides after solid phase microextraction, retention time, coefficients of correlation, limits of detection and precision ($n = 6$; 65 µm CW-DVB); SPE limits of detection [33]

| *Compound* | *Retention time (min)* | *Coefficient of correlation r* | *Limit of detection* (ng/mL) | *Precision* (%) | *SPE* (ng/mL) |
|---|---|---|---|---|---|
| Desethylatrazine | 12.714 | 0.9891 | 0.06 | 10.1 | 0.050 |
| Trifluralin | 13.555 | 0.9950 | 0.02 | 4.2 | – |
| Simazine | 13.981 | 0.9977 | 0.02 | 12.6 | 0.010 |
| Atrazine | 14.057 | 0.9986 | 0.03 | 10.1 | 0.010 |
| Propazine | 14.112 | 0.0084 | 0.04 | 8.6 | 0.025 |
| Terbuthylazine | 14.209 | 0.9966 | 0.02 | 7.6 | 0.010 |
| Ametryn | 15.335 | 0.9998 | 0.07 | 8.1 | 0.010 |
| Prometryn | 13.428 | 0.9977 | 0.07 | 8.8 | 0.010 |
| Terbutryn | 15.651 | 0.9997 | 0.08 | 7.0 | 0.010 |
| Cyanazine | 16.932 | 0.9999 | 0.02 | 7.4 | 0.050 |
| Pendimethalin | 18.402 | 0.9986 | 0.02 | 9.3 | 0.050 |

40 min, with rapid stirring and the concentration of NaCl was fixed at 0.25 g/mL. The linearity of the calibration curve has been studied for all pesticides at a concentration range of 0.1–100 ng/mL. The coefficients of correlation of the compounds are summarized in Table I. Except for desethylatrazine, the linearity is good to excellent ($r = 0.997$ for more compounds). The quantification of these products were carried out by the method of internal standardization (internal standard: 1-Bromo-2-nitrobenzene).

To evaluate the precision of the measurement, the repeatability of the method was determined by performing six times from an aqueous standard solution with the concentration of 10 ng/mL. For most organonitrogen pesticides the coefficient of variation was found to be below 10% using the CW-DVB fibre. An improvement of this precision is conceivable with the use of an automated system which is equally marketed (so injections would be performed by an autosampler).

Table I also shows the limits of detection (LOD). whose estimation was based on the lowest detectable peak that had signal/noise = 3. The LOD differed for the various pesticides; for most compounds LODs were below 0.07 μg/L. It should be noticed these low detection limits in touch with the small sample volume (2mL). For comparison, the limits of detection of these compounds by the solid phase extraction (SPE, [32]) were noticed in Table I. For both methods calculated LODs are in the same magnitude order but SPE LODs are lower than SPME ones. However, the permissible level of pesticide contamination (0.1 μg/L) set by the European drinking water regulation can be verified by this method [33].

Natural matrix (Authie river water, France) has been spiked with pesticides at level of 10 μg/L (Fig. 8). To validate the method, samples were extracted by the SPME and the liquid–liquid extraction (LLE). The LLE is the official method used by some US EPA (Environmental Protection Agency) standard methods (as method EPA 507: determination of nitrogen- and phosphorus-containing pesticides in water by gas chromatography with nitrogen-phosphorus detector; [34]). Table II summarizes the extraction rates of compounds and the precision of the two employed techniques. Standard



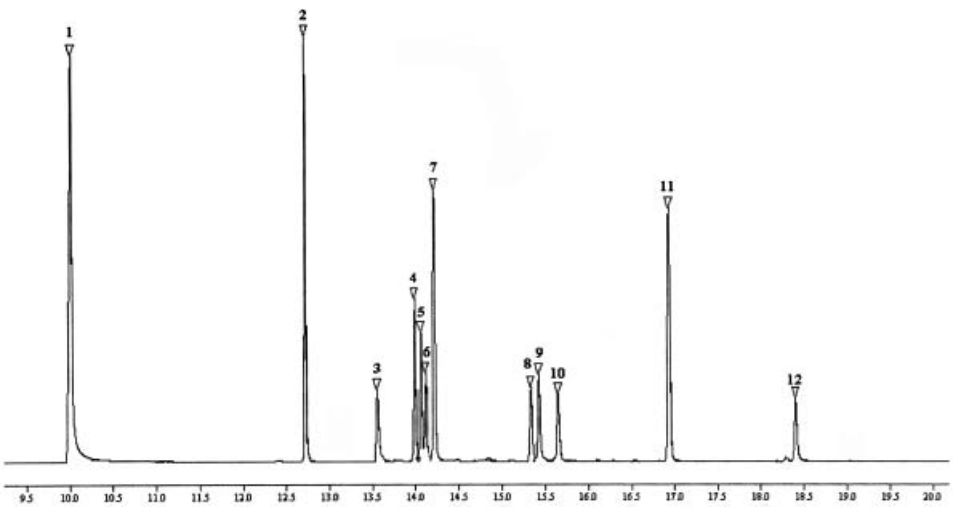


FIGURE 8 Gas chromatogram of a spiked water samples (10 μg/L); 1L 1-Bromo-2-nitrobenzène, 2: desethylatrazine, 3: trifluralin, 4: simazine, 5: atrazine, 6: propazine, 7: terbuthylazine, 8: ametryn, 9: prometryn, 10: terbutryn, 11: cyanazine, 12: pendimethalin.

TABLE II Extraction recoveries of pesticides by LLE ($n$ 3) and SPME ($n = 6$) for a spiked water sample (10 μg/L)

| *Compound* | *LLE* | *SPME* |
|---|---|---|
| Simazine | 90.4 ± 8.3 | 86.6 ± 13.3 |
| Atrazine | 99.5 ± 6.2 | 88.1 ± 12.4 |
| Propazine | 79.3 ± 5.2 | 75.3 ± 8.2 |
| Terbuthylazine | 97.8 ± 5.1 | 81.2 ± 11.8 |
| Ametryn | 81.2 ± 6.6 | 86.6 ± 12.4 |
| Prometryn | 71.6 ± 5.2 | 82.2 ± 11.3 |
| Terbutryn | 82.3 ± 5.3 | 86.7 ± 12.0 |

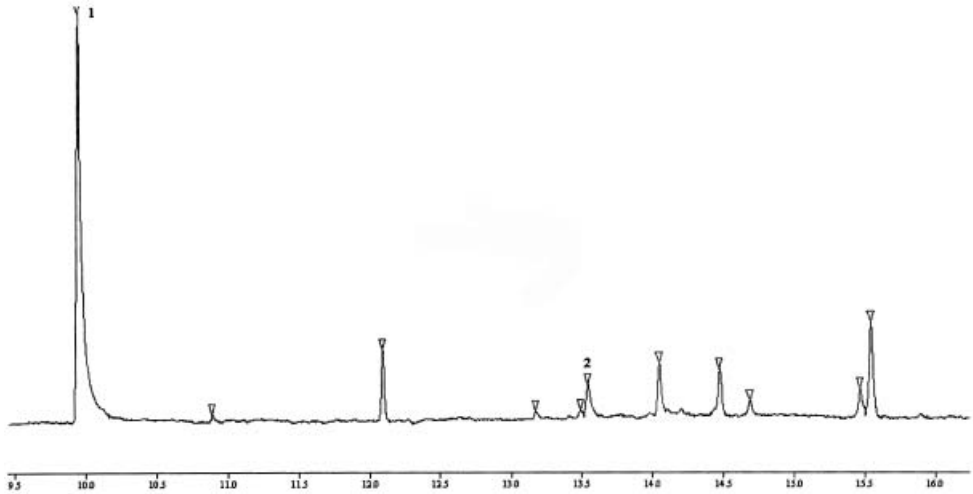


FIGURE 9 Gas chromatogram of a water sample (from the Authie Bay) by SPME (65 μm CW-DVB); 1: internal standard, 2L trifluralin.



deviations were higher using the SPME (9.2–13.3%) than via the LLE (4.1–8.2%), However, no significant difference was revealed by the comparison test of the experimental means for both methods (student factor, confident threshold of 95%). The recoveries of seven ONPs were between 75.3 and 88.1% using the SPME.

### Environmental Samples

The established SPME method was then successfully applied to analyse environmental water samples. Figure 9 shows a chromatogram of a water sample from the Authie bay. Solid phase micro-extractions were performed by CW-DVB (65 μm thickness) followed by gas chromatography analysis with a nitrogen/phosphorus detector. The gas chromatogram after the SPME as shown in the figure revealed the presence of trifluralin and several other non identified peaks. The identification of trifluralin was confirmed by GB-MS analysis (mass spectrometer detection). This compound was found in concentration of $52.5 \pm 9.4$ ng/L by the SPME and $46.1 \pm 3.3$ ng/L by the LLE. These results emphasized the applicability of the SPME method for the screening and the quantification of organonitrogen pesticides in natural waters.

## CONCLUSIONS

This article has established the SPME to be a method which can easily be qualified as rapid, simple and above all no consumer of toxic solvent for the environment and the laboratory technician's health. The results demonstrated the SPME-GC-NPD to be a precise, sensible and reproducible technique for the analysis of some organonitrogen pesticides (in this article triazines and dinitroanilines) in water samples using CW-DVB fibre. The SPME method was validated by comparison with the conventional liquid–liquid extraction method. Combined to a gas chromatograph with a nitrogen-phosphorus selective detector, low limits of detection (0.02–0.08 μg/L) can be achieved.

Then the maximum level of 0.1 μg/L set by the European Union for pesticides and drinking water can be verified, indicating the permissible use of SPME for routine analyses. Finally the extractions of natural samples show the capability of the SPME method to analyse environmental waters. Lifetime of carbowax-divinylbenzene fibre has to be studied in more detail in the future (above all for matrix and salt effects).

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