

# Comparison of Two Extraction Methods for the Determination of Polycyclic Aromatic Hydrocarbons in Surface Soils Using Headspace SPME with GC–FID

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## Abstract

Two simple methods using headspace solid-phase microextraction (HS-SPME) coupled to a gas chromatograph with a flame ionization detector were compared for the determination of polycyclic aromatic hydrocarbons (PAH) in soils. These compounds were included in the US Environmental Protection Agency's *Priority Pollutants* list. Direct hot water HS-SPME extraction and sonication organic extraction followed by HS-SPME were optimized using experimental designs. The first method was chosen for PAH determination. The validation of the proposed method was carried out by analyzing PAHs in the certified soil reference material RTC-CRM 123. The accuracy obtained for the PAHs was shown to be inside the prediction interval with the certified material. The optimized method was applied to the analysis of several superficial soils from Gipuzkoa (Basque Country, North Spain).

## Introduction

Determination of polycyclic aromatic hydrocarbons (PAHs) in environmental samples has drawn increasing concern because of their toxic, carcinogenic, and mutagenic effects. These compounds have been commonly carried into the environment in solvents such as coal, tar, creosote, or in gas factories as combustion byproducts. Depending on the characteristics of the site, contamination of the surface soil may be followed by contamination due to migration of liquid hydrocarbons and dissolution into rain or groundwater. Also, the diffuse contamination of these compounds is generalized basically due to atmospheric transport; however, deposition and dispersion in the environment and residual levels have been found in urban, rural, and industrial areas. Because of their hazardous properties, the U.S. EPA has classified them as priority pollutants (1).

Extraction of pollutants from soils by conventional techniques has several disadvantages, such as high sample preparation costs, high risk of laboratory pollution, and high extraction times (2,3).

The development of effective extraction and enrichment techniques to selectively determine these organic compounds in environmental samples is of great interest. The extraction of

these soil or sediment compounds from a solid matrix can be achieved with conventional extraction techniques such as Soxhlet and sonication (3). In recent years, other extraction techniques have been studied to reduce the consumption of organic solvent, improve the precision of analyte recoveries, and reduce extraction time and sample preparation. The solid-phase microextraction (SPME) method has beneficial features when compared to other methods; however, its best aspect is that no solvent is necessary for extraction, and it can be carried out directly from the liquid phase (DI) or from the headspace (HS) over the liquid samples (4–6).

Two strategies of SPME, direct-extraction with headspace on soils and sonication-extraction with organic dissolvent followed by HS-SPME, have been applied. Direct extraction with headspace has been used to analyze volatile organic compounds such as pesticides and polychlorinated biphenyls (PCBs) in environmental samples (7–9). Sonication extraction with dissolvent has been applied for different solid environmental samples (10–12).

One of the main problems for the use of HS-SPME is the high number of variables involved in the process that can affect the extraction performance. In this sense, experimental design seems the most useful approach for establishing the optimum operating conditions in these procedures. Screening is the first stage in the determination of the significant factors affecting the analytical system, and the second stage is the application of the optimization of significant variables with a central composite design (13). Numerous studies have applied these statistical techniques for the optimization method in the determination of several contaminants (12,14–17) in soils that do not include PAH compounds.

Calibration of SPME is usually carried out by a standard addition method in solid samples. However, in complex matrix samples, such as soils, it is rather difficult to find the same kind of matrix, and the matrix effect normally appears. For this reason, spiked soil was used for the application of experimental design and optimization of the extraction variables of PAHs. From an analytical point of view, the development of new extraction methods that are capable of analyzing these organic compounds in environmental samples is essential. For validation of the extraction method, it was necessary to use reference material.

The aim of this research is to provide a feasible analytical

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methodology for PAH screening in soils. Two methods for the determination of PAHs using different extraction procedures were investigated; once they had been compared, the confirmation of the best response was tested by applying certified material. Afterwards, the chosen method was applied to real samples taken from different sampling points.

## Experimental

### Chemicals

Naphthalene (NAP) (99.0%), anthracene (ANT) (96.0%), acenaphthene (ACE) (95%), fluorene (FLU) (90%), and fluoranthene (FLT) (98.5%) were purchased from Fluka (Sigma-Aldrich Química, Suisse). Acenaphthylene (ACY) (75%), phenanthrene (PHE) (98%), pyrene (PYR) (98%), and chrysene (CHR) (98%) were purchased from Aldrich. Benzo(a)anthracene (BaA) (98%) was purchased from Supelco (Bellefonte, PA). SPME holders and fibers [100  $\mu\text{m}$  thickness poly(dimethylsiloxane) (PDMS)], 85- $\mu\text{m}$  polyacrylate (PA), sample vials (40 mL, amber glass), and PTFE-silicone septa were obtained from Supelco. The fibers were conditioned in the hot injector of the gas chromatograph (GC) according to instructions provided by the supplier. Standard solutions of PAHs (1000 mg/L) were prepared in acetone and stored at 4°C. Working standards were prepared just before use.

A certified reference material RTC-CRM123 that was available for optimization and validation of analytical procedures was purchased from LGC Promochem (Barcelona, Spain).

### Apparatus and conditions

A Hewlett Packard 6890 GC, with split-splitless injection port and an FID detector (Agilent Technologies, Wilmington, DE) was used for the experiments. The injector was configured in the splitless mode, with the split-splitless purge valve opened 3 min after injection. The injection port temperature was 250°C, and helium served as a carrier gas with a flow-rate of 2.0 mL/min. The capillary column used was an EQUITY-5 (30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu\text{m}$  of 5% diphenyl-95% dimethyl polysiloxane) from Supelco. The temperature program used was: 40°C for 1 min, increased to 220°C at a rate of 20°C/min and held for 1 min, and again increased at 40°C/min to 300°C, and then held for 9 min. The temperature of the detector was 300°C. A PC interfaced to the GC using Chemstation software (Agilent Technologies) was used for data acquisition and processing.

For the extraction, a reaction vessel with thermostatic jacket joined to a cooling thermostat LAUDA ecoline RE 104 with a digital programmable E 100 (GmbH & Co. KG, Lauda, Germany) was used. Inside this vessel, a 40-mL amber vial capped with a phenolic screw cap and PTFE-coated silicone septa was placed.

A Heidolph MR 3003 magnetic stirrer (GmbH & Co KG, Kelheim, Germany) was used. PTFE coated stir bars of 20 mm were put in the 40-mL vials just before the runs. A Fungilab (Barcelona, Spain) Fungisonic LU 5.7 ultrasonic cleaner bath, programmable for temperature (up to 90°C) and time (up to 15 min), was used to facilitate the extraction. A Centronic centrifuge from Selecta (Barcelona, Spain) was used to separate the

solid and liquid phases.

A LECO CHNS-932 (LECO Corporation, St. Joseph, MI) microanalyzer was used to determine of total organic compounds (TOC) in soils.

The experimental design matrix was performed and the results were evaluated using the STATISTICA software package (Statsoft, Tulsa, OK).

### Soil sampling and spiking procedures

Surface soil samples (0–10 cm) were collected at 10 different sampling points of the province of Gipuzkoa (Northern Spain). The sampling took place in 2005. Soil samples were taken in glass vials that were completely filled, covered with aluminum foil to avoid the contact with plastic materials, and then transported to the laboratory. Additionally, an extra 100 g was collected to analyze pH, TOC, and total carbon (TC). The dried samples were ground in a grinder, sieved (2 mm and 63  $\mu\text{m}$ ), and stored in dark glass vials in a refrigerator at 4°C until analysis.

The location of the sampling points was varied. Some points were located in an old demolished gas works of San Sebastian city (Amara 1 and 2), and in a creosoted wood store; they were close to residential zones (Oriamendi 1 and 2 and Zumaia). The other samples were near to highways or industrial areas.

In the developing of the two methods for the determination of PAHs, one uncontaminated soil was spiked with PAHs as follows. A 100 g sample of dry soil and 500 mL of acetone containing 2 mg/L of three PAHs were mixed in a 1000 mL round-bottomed flask. The acetone was evaporated with a rotary evaporator at 30–35°C (18), leaving the PAHs in the soil matrix. This contaminated soil was stored in glass vials and kept in the refrigerator at 4°C until it was used for the optimization of the extraction methods. When the procedure was selected for PAH determination in real soil samples, the number of PAHs was extended to ten analytes. The determination was done by applying standard addition.

### Soil characteristics

The values of pH, TOC, and TC of each soil sample were also determined. To measure the pH, 10 g of air-dried soil (passed through a 63  $\mu\text{m}$  mesh) was suspended in 25 mL deionized water, and after mixing for 10 min and a 30-min rest, the measurements were taken with a pH-meter. TOC and TC were analyzed with a microanalyzer LECO CHNS-932 and the organic total content was measured using HCl treatment in order to eliminate all the inorganic carbon (19).

In order to calculate the water content, a sub-sample was heated for 4 h at 150°C until the weight loss was constant. All concentrations of soils obtained are referring to dry weight.

The mean pH of soils was 8.02 (7.65–8.33), they can be considered as moderately alkaline while the mean content of total organic carbon in the soil samples was 6.8% (1.0–34.9%). Some of these values were considered to be a very high level for urban soil, probably due to human disturbance. Also, the C/N ratios of different soils were similar except in three samples, where a high ratio was observed due to high organic matter content and low nitrogen content, probably due to human activities (20). All these values are given in Table I.

## Results and Discussion

Two extraction procedures were optimized and compared for the determination of PAHs in soils. One extraction was tested using sonication with acetone–methanol dissolution added to the soil; the vial was centrifuged, and then a 0.2-mL aliquot was taken and added directly to water (final volume was fixed in 20 mL). After this, HS-SPME technique was applied. The fiber was desorbed in a GC–FID.

Hot water direct extraction (HWD) HS-SPME was applied with bi-distilled water on the soil. The mixture (water–soil) was stirred for 1 h, and then it was exposed to the fiber.

On the basis of the literature and the experience of the laboratory (21–25), different variables were selected to define the experimental field in each extraction method depending of the procedure.

### Sonication organic extraction HS-SPME

In order to select the best conditions, two experimental designs were carried out: firstly, a Plackett–Burman design was carried out to evaluate the influence of the main factors affecting the sonication and extraction process with organic dissolution and after determination by HS–SPME. For this study, a spiked soil sample with three target PAHs (naphthalene, anthracene, and fluoranthene) with 500 ng/g concentration was used. Eleven variables were selected to define the experimental field. The variables are shown in Table II. A diagram of apparatus disposition is shown in Figure 1A.

The data obtained was evaluated by ANOVA test to assess the significance of the model and the factors or variables.  $R^2$  values showed that the adjusted model accounted for 0.85 to 0.98 of the variability of the peak area. The qualitative variables were fixed in the better conditions for the extraction deduced from the Pareto charts; PA fiber, 63  $\mu\text{m}$  size, and acetic acid–methanol mixture with a relation of 1:4. The PDMS fiber showed good absorption efficiency for PAHs of low molecular weight, but globally for all PAHs analyzed, PA fiber was better. PA fiber has a more polar coating and has a better affinity to high-ring PAHs. The conditions of the sonication bath were fixed at 25°C and 60 min, and desorption time in the GC was 3 min. The significant variables considered in the optimization step were: volume of aliquot, weight of soil, SPME extraction time, and temperature.

Secondly, in order to optimize the significant variables, a complete central composite design (CCD) consisting of a factorial design  $2^4$  with eight star points located at  $\pm 1.483$  from the centre of the experimental domain was performed. The design was also completed with four experiments in the central point. Therefore, the design matrix had 28 runs randomly carried out trying to nullify the effect of extraneous or nuisance variables.

The optimized values obtained after CCD applications were an aliquot of 0.2 mL (a large aliquot could saturate the fiber), 2.0 g soil

weight, SPME extraction time of 120 min, and SPME extraction temperature of 70°C.

### HWD HS-SPME

Firstly, a  $2^{6-2}$  fractional factorial screening method was applied to evaluate the influence of the main factor. In this case, the chosen factors were identified as significant before the screening method was applied. Also, for this study, a spiked soil sample with three target PAHs was employed. The experimental parameters studied are shown in Table II. A diagram of apparatus disposition is shown in Figure 1B.

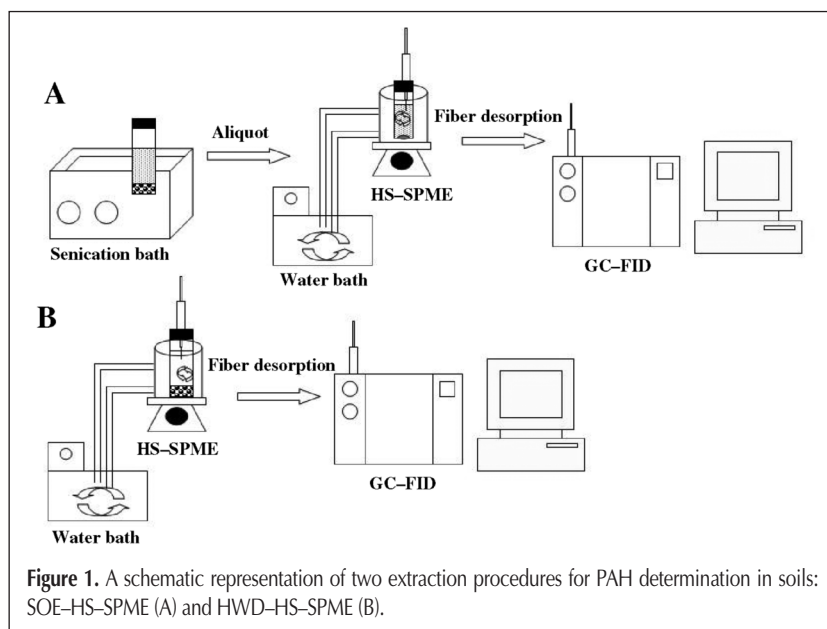
The most significant variables were salt concentration and extraction temperature. The results of the other variables were fixed: 0.5 g soil weight; headspace volume, 20 mL; extraction time, 60 min; and desorption time, 3 min.

Secondly, in order to find the optimal values for the two significant factors, a CCD consisting of a factorial design  $2^2$  with four star points located at  $\pm 1.483$  from the center of the experimental domain was applied. The design was also completed with others two runs in the central point. Therefore, a total of 10 experiments were randomly performed.

We observed that the best responses were obtained at 80°C and

**Table I. Characteristics of Soil Samples**

Soil	pH	TC (%)	TOC (%)	C/N ratio
Amara 1	7.65	3.2	1.0	23.0
Amara 2	8.33	43.3	34.9	43.3
Oriamendi 1	8.01	3.9	3.2	8.6
Oriamendi 2	8.21	13.4	7.8	39.3
Zumaia	7.99	5.2	2.5	23.9
Tolosa	8.17	9.6	3.7	43.5
Zarautz	7.80	14.6	9.7	6.6
Maltzaga	7.85	4.1	2.5	17.0
Arrasate	7.98	1.5	1.4	10.2
Bergara	8.31	1.2	1.1	9.5



with 30% sodium chloride concentration. Increasing temperature to 80°C enhanced the extraction of the less volatile compounds studied.

### Comparison of methods

The comparison between methods was done with the mean of three independent replicates of spiked soil using the three target PAHs. The obtained results were normalized considering peak area and weight soil because the amount of weight in sonication and direct extraction were different for 2 g (SOE-HS-SPME) and

0.5 g (HWD-HS-SPME), respectively

The selected method for PAH determination in soils was HWD-HS-SPME. The SOE-HS-SPME method obtained better results than HWD-HS-SPME. Better results have been obtained with the SOE-HS-SPME because the extraction time was 120 min. If we compared the results obtained with both procedures with the same time (60 min), the data obtained with the HWD-HS-SPME method were significantly superior to those obtained with the SOE-HS-SPME method. The aim of the work was to find a good screening method for PAH determination. Taking into account these reasons, the chosen method was HWD-HS-SPME. The method offers very good reproducibility, short time consumption, and, in addition, is solvent-free. All these characteristics turn this method into an easily applicable screening method.

Once the method was optimized, it was applied to other PAHs of three and four aromatics rings: naphthalene, anthracene, acenaphthylene, acenaphthene, fluorene, fluoranthene phenanthrene, pyrene, chrysene, and benzo(a)anthracene.

### Analytical characteristics and validation of the method with a certified reference material

The detection limit (LOD) for each analyte is expressed as the mass of the analyte, which gives a signal that is three times the standard deviation above the mean blank signal. The LODs obtained ranged between 0.97 ng/g for NAP and 42.50 ng/g for CHR.

The repeatability, expressed as relative standard deviation (RSD) value, was obtained from the results of six consecutive and independent samples made on the same day. The concentration of each of the analytes was 10 µg/g. The results obtained ranged between 7.2% and 9.3%. The reproducibility, expressed as RSD value, was obtained from the results of

six samples made on different days; also, with the concentration of 10 µg/g. The results varied between 2.4% and 9.8%

To confirm that the method is suitable for its intended use, a validation process was carried out by establishing the basic analytical requirement of the performance quantification of 10 PAHs in soil. The SPME method was validated by using reference soil RTC-CRM123. The accuracy obtained for the 10 PAHs showed an acceptable agreement with the certified results, because most of data were inside of prediction interval. The results are given in Table III.

### Soil sample application

The developed HWD-HS-SPME method was applied to the quantitative analysis of a several contaminated soil samples from Gipuzkoa (Northern Spain). The results are given in Table IV. Firstly, 20 mL bi-distilled water with 30% NaCl was added to a 0.5 g soil sample ( $\leq 63 \mu\text{m}$ ). The slurry was placed in a 40-mL

**Table II. Resume of the Variables Used in the Sonication Organic Extraction and Hot Water Direct Extraction Experimental Design**

SOE-HS-SPME				HWD-HS-SPME			
<i>Screening design</i>							
Placket-Burman design			$2^{6-2}$ fractional Factorial design				
Factors	Low level	High level	Factors	Low level	High level		
1 Weight of soil (g)	0.5	5.0	Weight of soil (g)	0.1	1.0		
2 Sieved size of soil	63 µm	2 mm	SPME ext. temp. (°C)	20	80		
3 Time in sonic. bath (min)	30	60	SPME ext. time (min)	20	60		
4 Temp. in sonic. bath (°C)	20	40	NaCl salt (%)	0	20		
5 Vol. of aliquot (mL)	0.5	2.5	Headspace volume (mL)	15	25		
6 Organic extr.*	A	B	Desorption time (min)	1	5		
7 Organic relation	1/4	4/1					
8 Fiber type	PA	PDMS					
9 SPME ext. temp. (°C)	20	80					
10 SPME ext. time (min)	20	100					
11 Desorption time (min)	1	5					
<i>Optimization design</i>							
$2^4$ Central composite			$2^2$ Central composite				
	Low	Medium	High	Low	Medium	High	
1 Weight of soil (g)	0.5	1.0	1.5	NaCl salt (%)	20	24	28
2 Vol. of aliquot (mL)	0.5	1.0	1.5	SPME ext. temp. (°C)	74	80	86
3 SPME ext. temp. (°C)	60	70	80				
4 SPME ext. time (min)	60	90	120				

\* A = Acetic acid-methanol; B = acetone-methanol.

**Table III. Validation of the HWD-HS-SPME Method with Reference Material RTC-CRM 123**

	Reference value (µg/kg)	SD	Prediction interval (µg/kg)	Found value	
				Mean (µg/kg)	SD
NAP	9.73	2.45	4.84–14.6	10.81	1.60
ACE	7.52	2.61	2.31–12.7	7.89	0.96
ACY	7.24	2.94	1.37–13.1	7.27	1.04
FLU	6.88	1.92	3.05–10.7	10.93	1.35
PHE	7.94	1.94	4.07–11.8	9.30	1.90
ANT	6.94	2.06	2.83–11.1	9.01	13.80
FLT	9.31	2.44	4.44–14.2	11.21	7.34
PYR	6.75	1.89	2.98–10.5	8.56	6.01
CHR	11.3	2.54	6.23–16.4	8.84	15.22
BaA	8.38	2.26	3.87–12.9	16.73	9.44

**Table IV. Concentration (mg/kg) of PAH Compounds Found in 10 Soil Samples by Standard Addition Calibration**

Sample	NAP	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	ΣPAH
1. Amara 1	0.040	0.138	0.040	0.130	1.754	0.640	3.366	2.387	0.922	2.971	12.36
2. Amara 2	3.584	4.800	0.644	7.133	21.640	15.884	20.600	20.790	20.019	21.162	136.25
3. Oriamendi 1	0.050	0.054	0.003	0.006	0.033	0.007	0.192	0.222	0.129	0.150	0.85
4. Oriamendi 2	0.110	0.890	–	1.010	4.960	1.850	4.990	7.110	2.710	6.380	30.01
5. Zumaia	–	0.461	0.020	–	0.251	0.011	0.385	0.329	0.840	0.315	2.61
6. Tolosa	0.028	0.025	0.003	0.003	0.016	–	0.213	0.096	0.023	0.281	0.69
7. Zarautz	0.085	0.177	0.031	0.093	0.033	0.037	0.076	0.077	0.160	0.261	1.03
8. Maltzaga	–	0.096	–	–	0.005	–	0.009	0.025	0.027	0.042	0.20
9. Arrasate	–	0.121	–	0.004	0.002	0.017	0.025	0.026	0.050	0.025	0.27
10. Bergara	0.015	0.110	0.004	0.015	0.003	0.001	0.004	0.003	0.007	0.107	0.27

vial. Magnetic stirring with 20-mm long Teflon-coated stir bars was used to agitate the solution at 800 rpm. PAH extraction was performed in HS mode, exposing 85 µm PA fiber over a stirred soil sample. The extraction was made for 60 min at 80°C. After sampling, the fiber was withdrawn into the needle of the holder, immediately placed in the GC injector, and analysis was carried out. After extraction, the fiber was thermally desorbed for 3 min into the glass liner of the GC injector port at 250°C. Furthermore, blanks were run periodically during the analysis to confirm the absence of contaminants.

In order to avoid the matrix effect, the standard addition method was used for quantitation of PAHs in soil samples. In the analyzed soil, the predominant PAHs were phenanthrene, fluoranthene, pyrene, and chrysene. These PAHs indicate that most of the samples are from a mixture of pyrolytic and petrogenic origin (26–28). In the sample taken from the wood store, the presence of pyrene and chrysene was found. This indicated that wood treated with creosote was a product, because the wood had been formerly used for railway sleepers and power poles, and is now used as decorating wood for public gardens. Taking into account the classification of soils contamination by Maliszewska-Kordybach (29), soil could be contaminated when the PAH concentrations is higher than 200 µg/kg. The maximum value found in all the sampling sites corresponded to the creosote wood store with 136.25 mg/kg (heavily contaminated). The rest of the sample values are higher than 200 µg/kg. Consequently, all sampling points analyzed could be considered weakly contaminated, contaminated, or heavily contaminated.

## Conclusion

Two extraction procedures have been compared, and the results showed that for rapid screening, HWD HS-SPME extraction is most feasible. The screening method, based on a 60 min headspace extraction of a 0.5 g soil samples with water at 80°C, has been developed. The main experimental parameters affecting the SPME step were optimized by applying an experimental design which allowed us to obtain maximum information with a minimum number of runs. The validation of the procedure with a reference material showed good results for the ten studied PAHs.

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## References

1. U.S. EPA Environmental Protection Agency: <http://www.epa.gov/iris/subst/index.html>.
2. V. Pino, J. Ayala, A. Afonso, and V. González. Determination of polycyclic aromatic hydrocarbons in marine sediments by high performance liquid chromatography after microwave-assisted extraction with micellar media. *J. Chromatogr. A* **869**: 515–22 (2000).
3. J.D. Berset, M. Ejem, R. Holzer, and P. Lisher. Comparison of different drying, extraction and detection techniques for the determination of priority polycyclic aromatic hydrocarbons in background contaminated soil samples. *Anal. Chim. Acta* **383**: 263–75 (1999).
4. J. Pawliszyn. *Solid Phase-Microextraction: Theory and Practice*. Wiley-VCH, New York, NY, 1997.
5. D. Cam, S. Gagni, L. Meldolesi, and G. Galletti. Determination of polycyclic aromatic hydrocarbons in sediments using solid-phase microextraction with gas chromatography-mass spectrometry. *J. Chromatogr. Sci.* **38**: 55–60 (2000).
6. S. Fuster, J. Beltran, F.J. López, and F. Hernandez. Application of solid phase microextraction for the determination of soil fumigants in water and soil samples. *J. Sep. Sci.* **28**: 98–103 (2005).
7. R.A. Doong, S.M. Chang, and Y.C. Sun. Solid-phase microextraction and headspace solid phase microextraction for the determination of high molecular-weight polycyclic aromatic hydrocarbons in water and soil samples. *J. Chromatogr. Sci.* **38**: 528–34 (2000).
8. R.A. Doong and P.L. Liao. Determination of organochlorine pesticides and their metabolites in soil samples using headspace solid-phase microextraction. *J. Chromatogr. A* **918**: 177–88 (2001).
9. O. Ezquerro, G. Ortiz, B. Pons, and M.T. Tena. Determination of benzene, toluene, ethylbenzene and xylenes in soils by multiple headspace solid-phase microextraction. *J. Chromatogr. A* **1035**: 17–22 (2004).
10. A. Bouaid, L. Ramos, M.J. González, P. Fernández, and C. Cámara. Solid-phase microextraction method for the determination of atrazine and four organophosphorus pesticides in soil samples by gas chromatography. *J. Chromatogr. A* **939**: 13–21 (2001).
11. L. Ke, K.S.H. Yu, Y.S. Wong, and N.F.Y. Tam. Spatial and vertical distribution of polycyclic aromatic hydrocarbons in mangrove sediments. *Sci. Total Environ.* **340**: 177–87 (2004).
12. B. Chen, X. Xuan, L. Zhu, J. Wang, Y. Gao, K. Yang, X. Shen, and B. Lou. Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. *Water Res.* **38**: 3558–64 (2004).

13. R.G. Breton. *Chemometrics. Data Analysis for the Laboratory and Chemical Plant*. John Wiley & Sons Ltd, Chichester, U.K. 2003, pp. 15–117.
14. M. Llompart K. Li, and M. Fingas. Headspace solid phase microextraction (HSSPME) for the determination of volatile and semivolatile pollutants in soils. *Talanta* **48**: 451–59 (1999).
15. M. Llompart, M. Lourido, P. Landin, C. García-Jares, and R. Cela. Optimization of a derivatization-solid-phase microextraction method for the analysis of thirty phenolic pollutants in water analysis. *J. Chromatogr. A* **963**: 137–48 (2002)
16. D. Cam, S. Gagni, N. Lombarda, and M.O. Punin. Solid-phase microextraction and gas chromatography-mass spectrometry for the determination of polycyclic aromatic hydrocarbons in environmental solid matrices. *J. Chromatogr. Sci.* **42**: 329–35 (2004).
17. M. Polo, M. Llompart, C. García-Jares, and R. Cela. Multivariate optimization of a solid-phase microextraction method for the analysis of phthalate esters in environmental waters. *J. Chromatogr. A* **1072**: 63–72 (2005).
18. A. Sawada, K. Kanal, and M. Fukushima. Preparation of artificially spiked soil with polycyclic aromatic hydrocarbons for soil pollution analysis. *Anal. Sci.* **20**: 239–41 (2004).
19. J.I. Hedges and J. Stern. Carbon and nitrogen determinations of carbonate-containing solids. *Limnol. Oceanogr.* **29**: 657–63 (1984).
20. X.C. Wang, S. Sun, H.Q. Ma, and Y. Liu. Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. *Marine Pollut. Bull.* **52**: 129–38 (2006).
21. J. Dron, R. Garcia, and E. Millán. Optimization of headspace solid-phase microextraction by means of an experimental design to determine methyl tert-butyl ether in water by gas chromatography–flame ionization detection. *J. Chromatogr. A* **963**: 259–64 (2002).
22. J. Salafranca, C. Domeño, C. Fernández, and C. Nerín. Experimental design applied to the determination of several contaminants in Duero River by solid-phase microextraction. *Anal. Chim. Acta* **477**: 257–67 (2003).
23. A.J. King, J.W. Readman, and J.L. Zhou. Determination of polycyclic aromatic hydrocarbons in water by solid-phase microextraction-gas chromatography-mass spectrometry. *Anal. Chim. Acta* **523**: 259–67 (2004).
24. I. Arambarri, M. Lasa, R. Garcia, and E. Millán. Determination of fuel dialkyl ethers and BTEX in water using headspace solid-phase microextraction and gas chromatography-flame ionization detection. *J. Chromatogr. A* **1033**: 193–203 (2004).
25. E. Cortazar, O. Zuloaga, J. Sanz, J.C. Raposo, N. Etxeberria, and L.A. Fernández. Multisimplex optimization of the solid-phase microextraction-gas chromatographic-mass spectrometric determination of polycyclic aromatic hydrocarbons, polychlorinated biphenyls and phthalates from water samples. *J. Chromatogr. A* **978**: 165–75 (2002).
26. H. Budzinski, I. Jones, J. Bellocq, C. Piérard, and P. Garrigues. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chem.* **58**: 85–97 (1997).
27. M.B. Yunker, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette, and S. Sylvestre. PAH in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* **33**: 489–515 (2002).
28. L.L. Ma, S.G. Chu, X.T. Wang, H.X. Cheng, X.F. Liu, and X.B. Xu. Polycyclic aromatic hydrocarbons in the surface soils from outskirts of Beijing, China. *Chemosphere* **58**: 1355–63 (2005).
29. B. Maliszewska-Kordybach. Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. *Applied Geochem.* **11**: 121–27 (1996).

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