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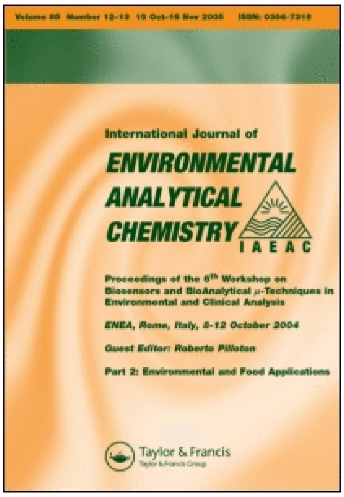

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Lombas-García, Eva , Gans, Oliver , Krska, Rudolf and Grasserbauer, Manfred(1998) 'Supercritical Fluid Extraction Versus Ultrasonic Extraction for the Analysis of Polycyclic Aromatic Hydrocarbons from Reference Sediments', International Journal of Environmental Analytical Chemistry, 72: 4, 289 — 300

To link to this Article: DOI: 10.1080/03067319808035900

URL: http://dx.doi.org/10.1080/03067319808035900

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Intern. J. Environ. Anal. Chem., Vol. 72(4), pp. 289-300
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SUPERCRITICAL FLUID EXTRACTION VERSUS ULTRASONIC EXTRACTION FOR THE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS FROM REFERENCE SEDIMENTS

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(Received 17 February 1998; In final form 2 July 1998)

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Supercritical Fluid Extraction (SFE) was investigated as a sample preparation and preconcentration method for the determination of Polycyclic Aromatic Hydrocarbons (PAHs) in sediment samples by HPLC. Two reference materials for PAHs were extracted under supercritical conditions. The data were compared with the certified values obtained by an interlaboratory investigation. A preliminary study was conducted in which the influences on recoveries of different variables were investigated. Additional to SFE a conventional ultrasonic extraction was carried out to compare and evaluate the method performance. The results from the preliminary method optimisation experiments indicate that, under the condition used, recovery was most affected by using polar modifiers. This study also showed that except for the higher condensed PAHs the extraction efficiencies of SFE are comparable with those obtained by ultrasonic extraction.

Keywords: Polycyclic aromatic hydrocarbons; sediments; supercritical fluid extraction; ultrasonic extraction

INTRODUCTION

One of the most important problems in environmental analysis is the separation of the analyte from an interfering and troublesome matrix. Analytes need to be measured at extremely low concentration levels over a wide polarity range. Hence the development of new techniques, which enables an efficient and quantitative separation between analyte and matrix, is required. Much progress has

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been made in the last decade in instrumental chromatographic techniques. However, extractions of organic compounds from solids are still performed by conventional methods (liquid-liquid, Soxhlet, ultrasonic extraction, etc). Traditional extraction techniques are time consuming for routine applications, require the use of large volumes of mostly toxic organic solvents and produce substantial amounts of waste. The attraction to supercritical fluid extraction (SFE) as an extraction technique is directly related to the unique properties of the supercritical fluids. Those fluids have a low viscosity, high diffusion coefficients and low flammability, all of which are clearly superior to the organic solvents normally used. The first use of SFE as an extraction technique was reported by Zosel[1]. Since then, there have been many reports on the use of SFE to extract organics from particulate matter, river sediment and plant tissue[2–5]. Carbon dioxide is the most common supercritical fluid to be used, since it is inexpensive and has a low critical temperature (31.3°C) and pressure (72.2 atm). However, CO_2 is a non polar solvent and this often precludes its use for the extraction of compounds of even moderate polarity. The addition of organic modifiers to the supercritical fluid has been shown to dramatically increase SFE applications and its efficiencies[6–8]. However, the use of SFE has expanded less rapidly than expected. One main reason for the slow breakthrough of SFE lies in the complexity of transferring a method optimised and validated for one single SFE system to another SFE system, because the few commercially available instruments differ too much in their technical specifications. All this makes it difficult to develop standardised SFE methods, which would in turn help to increase the general acceptance of SFE.

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds containing carbon and hydrogen only, and consisting of fused benzene rings. Their prevalent occurrence is due to the incomplete combustion of wood, petrol, oil and coal. Many studies relate the prevalence of PAHs in the environment, in urban air, in soils and in food[9–11]. PAHs are adsorbed, due to their low solubility and persistence, on the surface of small particles suspended in the water and are thus subject to possible sedimentation. In general only the finer fractions (<63 μm) will be transported by river currents. The most recent information concerning the amount of pollution in the sediment is contained in the sediment surface layers, that are in contact with the overlaying water (containing suspended particulate matter). Sediments and soils are difficult and complex matrices and an analytical method must be applied, which is not only highly sensitive but also highly selective. Due to the complexity of the analytical task a proficiency testing scheme for the determination of PAHs in sediments has been established in The Netherlands. The data supplied by several laboratories that have analysed those SETOC samples with different techniques are collected, statistically evaluated and the sediments are made available as "reference materials". The programme is run under the auspices of Wageningen Agriculture University (Department of Soil Science and Plant Nutrition, responsible for the organisation) and the Free University of Amsterdam (Institute for Environmental Studies, responsible for the scientific background). Such reference sediments are particularly useful for testing a new method since they represent a "real world" contamination whereas spiking experiments do not sufficiently simulate the strong matrix-analyte interaction. The so-called SETOC sediments (International Sediment Exchange for Tests on Organic Contaminants) were used in this work to evaluate the most important variables affecting the extraction efficiencies of SFE.

Several analytical techniques have been recommended for the final analysis of PAHs. These techniques are based on gas chromatography (GC), GC with mass spectroscopy (MS), or high performance liquid chromatography (HPLC). In the case of HPLC, Reversed Phase (RP) columns in conjunction with ultraviolet, fluorescence and photodiode array detectors are used for the analysis of PAHs[12–14]. The crucial step, however, is the extraction of the PAHs from the sediment. The extraction rates of PAHs, which are adequately soluble in supercritical fluids, are strongly dependent on the type of matrix. Therefore at the beginning of the study an optimisation of the trap packing, collection solvent and its flow-rate, modifiers and sample amount is carried out. In the present work the supercritical fluid extraction efficiencies are directly compared to those obtained using ultrasonic extraction with identical analysis methods.

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EXPERIMENTAL

Samples and standards

A PAH-standard mix (TCL Polynuclear Aromatic Hydrocarbons mix in acetonitrile:methanol, 90:10) was obtained from SUPELCO SIGMA-ALDRICH Handels GmbH (Austria)

In order to evaluate the accuracy and precision of the analytical procedures used, two SETOC samples, one river sediment (701) and one marine sediment (708), have been chosen. Both sediments contain the 16 PAHs listed in the US-EPA method 610 in concentrations from 18 to 646 μg/kg in SETOC-701 and from 170 to 2500 μg/kg in SETOC-708. Thirteen of those could be determined in this work: Naphthalene (Nap), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo[a]anthracene (Baa), Chrysene (Chr), Benzo[b]fluoranthene (Bbf), Benzo[k]fluoranthene (Bkf), Benzo[a]pyrene

(Bap), Dibenzo[a,h]anthracene (Dba), Benzo[ghi]perylene (Bgh) and Indeno[1,2,3 -cd]pyrene. Acenaphthylene is not fluorescent, therefore cannot be detected with HPLC-FLD. Acenaphthene and Fluorene peaks were not completely resolved with the short gradient programme. These sediment samples had been dried at 40 °C and milled to a fraction smaller than 250 μm. The samples were stored in the dark, in closed polyethylene containers under laboratory conditions. To ensure that all participants of SETOC receive representative samples, an automatic device for homogenisation and subsampling of large amounts of dry sediment material was used. For each compound, a median value and a median of absolute deviations (MAD) are calculated. The median is the middle observation of the sorted array of observations in the case of an odd sample size. Otherwise it is the mean of the two middle observations. Using the median instead of mean, extreme data are of less influence. The MAD is the median of the absolute values of the observations minus their median. A median and a MAD are used instead of a mean and a standard deviation because, in the latter case, deviating observations are concealed by an increased estimated standard deviation. All recoveries mentioned in this work are referred to the median values reported in the SETOC protocol. To avoid uncontrolled modifier effects of the water, the humidity was controlled before each extraction resulting that it was less than 2% for both sediments. Therefore, no kind of pre-treatment was necessary before the respectively extractions.

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Supercritical fluid extraction

All supercritical fluid extractions were performed using SFC-grade carbon dioxide (AGA-Gas; Austria) on a Hewlett-Packard 7680T SFE module equipped with an extraction chamber, a variable restrictor which regulates the system pressure, a solid trap, sample thimbles (V=7mL) and output vials.

A Hewlett-Packard 1050 LC pump was used for the delivery of the modifiers to be mixed with the supercritical fluid CO_2.

Ultrasonic extraction

5 g Na_2SO_4 were added to 10 g of sediment sample in a 50 mL Pyrex flask and were extracted with 20 mL tetrahydrofurane (p.r.a.) (THF) in an ultrasonic bath (Branson 2210) for 2 hours. However, due to the low water content of the SETOC sediments (<2%) the addition of Na_2SO_4 is not essentially necessary. A 10 mL aliquot was evaporated in a pointed flask nearly to dryness with a rotatory evaporator and was then transferred to a measuring flask. The pointed flask was

washed three times with acetonitrile and the measured flask was then filled up with acetonitrile to a total volume of 2 mL. The precipitate, which was formed during the transfer due to the different polarity of the solvent, was separated by centrifugation (12500 RPM for 10 min.). The clear extract was filled directly into a vial and prior to HPLC analysis 100 µL were diluted 1:10 with acetonitrile.

High performance liquid chromatography analysis

Extracts were analysed using a Hewlett Packard 1090 high performance liquid chromatograph. A C-18 analytical column [VYDAC 201TP52 (250 mm × 2.1 mm)] prepacked with 5 µm particle size was employed. This column is specially designed for the analysis of PAHs. In addition a RP C-18 guard column (20 mm × 2.1 mm) prepacked with 5 µm particle size was applied. The solvents were delivered by a dual pumping system allowing a gradient program. It was equipped with both a UV diode array detector (DAD) and a fluorescence detector (FLD). The DAD was used for the identification of the different peaks through their specific spectra and the FLD was utilised for the quantification. Quantification was done by comparison of the peak of the individual PAH against a calibration curve of peaks height obtained with standards (concentration range 0.2–10 µg/mL).

In order to get the highest sensitivity for the whole analysis, the FLD was programmed for the best excitation and emission wavelength of the individual PAHs. These optimal values were found by using the scan function incorporated in the instrument. The HPLC analysis was also performed by using a solvent gradient (Tables I and II).

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TABLE I Mobile phase gradient for the analysis of PAHs

Acetonitrile : Water	*minute*	*flow rate*
40 : 60	0	0.42 mL/min
60 : 40	3.5	0.42 mL/min
90:0	13.5	0.42 mL/min
100:0	21	0.42 mL/min
100 : 0	23.5	0.42 mL/min
40 : 60	26	0.42 ml/min
40 : 60	30	0.42 mL/min

TABLE II Wavelength program for the fluorescence detector

	FLD		
Time (*min*)	*Excitation* (*nm*)	*Emission* (*nm*)	*Compounds*
0.00	271	341	Nap
5.80	246	341	Phe
6.70	246	394	Ant
8.00	229	450	Flu
8.80	231	390	Pyr
10.50	246	390	Baa, Chr
13.80	246	415	Bbf, Bkf, Bap
18.00	294	403	Dba, Bgh
19.60	246	483	Ind

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RESULTS AND DISCUSSION

Optimisation of SFE

Since SFE of analytes from solid sorbents is controlled by a variety of factors including the affinity of the analytes for the sorbent, the tortuosity of the sorbent bed, the vapour pressure of the analytes and the solubility, the diffusion coefficient of the analytes in the supercritical fluid and a complex relationship between many experimental variables preliminary extractions were performed to study the influence of some of these variables.

In a first set of experiments pure CO_2 was used as supercritical fluid. During these experiments the reference sediment SETOC-701 was employed, always referring to the median value reported in the SETOC protocol as 100% recovery. To evaluate the influence of the trap system, two different trap packing materials, hypersil ODS and stainless steel, were tested. The experiments showed that owing to the better retention of the PAHs much better recoveries were achieved when employing the ODS trap. Once installed, the trap packing is the only parameter that cannot be changed during the execution of the complete method. Consequently all further experiments were carried out with an ODS trap.

Three different solvents, tetrahydrofuran (THF), acetonitrile (ACN) and petroleum ether (PE), were tested to elute the PAHs from the trap. The best results were obtained with THF, although the recoveries obtained with ACN were only slightly less. To avoid complications in the HPLC analysis which uses ACN as mobile phase, a mixture ACN/THF (1:1) was employed for the elution of the PAHs from the trap.

As a next step the influence of the rate the supercritical fluid flows through the extraction chamber was also studied. Higher flow-rates provide the sample with a larger quantity of fresh extraction fluid, while lower flow rates require less extraction fluid and often simplify collection of the extracted analytes. It seems intuitive that higher flow rates should yield faster extractions and higher recoveries since the sample is exposed to more extraction fluid during a set time period. However, the assumption of this theory is not correct for many samples, since recoveries are often more dependent on extraction time than on the volume of fluid used, in particular when the kinetics of the desorption of the solutes into the supercritical fluid limits the extraction rate. For our application a low flow-rate (1mL/min) was advantageous for the extraction of PAHs from sediments. Our experiments showed that decreasing the flow-rate from 2 to 1mL/min increases the recovery by a factor of 20%. It appears to be an inefficacy within the trapping step for higher flow-rates.

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The effect of the sample amount being extracted was also studied. However, it turned out that the use of different sample amounts (1–5g) did not alter the extraction efficiencies significantly. The only limitation was an overpressure of the modifier pump which occurred when sample amounts bigger than 3g were put into the extraction thimble. Hence, subsequent experiments were carried out with three grams of sediment, as it minimised the danger of overpressure in the system. Earlier studies in our laboratory had demonstrated that higher temperatures conduced to better extraction recoveries. Because of temperature limitations of existing commercial SFE instrumentation, our experiments were limited to T=120°C.

Preliminary experiments showed that pure CO_2 does not sufficiently extract the PAHs with recovery rates between only 16% for indeno(1,2,3 -cd)pyrene and 80% for naphthalene. Possible reasons for this observation might be an incomplete dissolution of the analytes in pure CO_2 or that CO_2 is too weak to compete for the PAHs, most probably strongly bound to relatively polar active sites in the sediment. Since supercritical CO_2 has a similar polarity as n-hexane, in which PAHs are well soluble, the second reason is more likely to explain the poor recoveries obtain with pure CO_2. Therefore, we tried to find a modifier that could disrupt the solute/active site interaction. The SFE apparatus used in this work enables the addition of the modifier to the CO_2 before the supercritical fluid enters the cryopump and the extraction chamber. Hence, instead of spiking directly onto the sample, the modifier was mixed with the extraction fluid at a constant rate. This provides a continuous and uniform supply of modified CO_2 through the entire dynamic extraction period. Two pure organic solvents, THF and methanol, were used as modifiers to study the effects of different quantities added to the CO_2. Especially for the four or more ring-PAHs methanol was the superior solvent to extract PAHs from the sediments. The recoveries were also improved when using 5% of modifier instead of 3%. But for the biggest PAHs (e.g. Bap, Dba, Bgh and Ind) the recoveries were still not satisfying at this stage (<40%). Finally, a method (see Table III), where a mixture methanol/water (1:4 v/v) was used as modifier, gave the best results (see Figure 1 results obtained with modifier). This method included three extraction steps. The purpose of the first step was to collect the more volatile PAHs. Consequently, the trap temperature was kept low to avoid any loss. By means of step two the involatile higher condensed PAHs, which are obviously strongly bound to the sediment particles, were extracted by adding the modifier mixture and increasing the density of the CO_2 via pressure enhancement. Finally the purpose of the third step was to sweep modifier from the instrument and raffinate before depressurisation and to reconstitute the involatile PAHs in the same vial containing the more volatile PAHs from step 1. As it is shown in figure 1 (with modifier) the extraction efficiency lay between 75 and 120% for nearly all the PAHs, just benzo(a)pyrene showed significantly lower recoveries around 45%.

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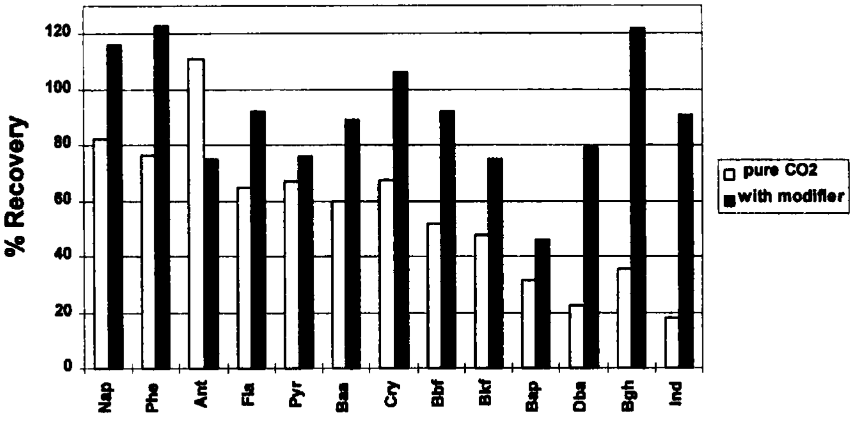

FIGURE 1 Recoveries of the PAHs obtained by SFE with and without modifier for SETOC-701

For comparison, the results obtained with pure CO_2 and with the modifier mixture are shown in Figure 1. As can be seen, the extraction efficiency has improved substantially with the use of modifier, especially for the four or more ring-PAHs. The mean of the recoveries with modifier was around 80%, while on the other hand mean recoveries lower than 60% were achieved when no modifier was used.

TABLE III Parameters of the SPE method

EXTRACTION STEP 1

FLUID DELIVERY	*EXTRACTION CHAMBER*	*ANALYTE TRAP*
density: 0.20g/mL	chamber temp.: 120°C	analytes: PAHs
pressure: 116bar	equilibration time: 2.00min	trap material: ODS
flow rate: 2.0mL/min	extraction time: 10.00min	nozzle temperature: 55°C
extraction fluid: CO_2	thimble volumes swept: 13.2	trap temperature: 5°C

FRACTION OUTPUT

Rinse substep	Solvent	Volume (mL)	Rate (mL/min)	Nozzle temp.	Trap temp	vial #
1	ACN/THF	0.8	1.0	45	60	1

EXTRACTION STEP 2

FLUID DELIVERY	*EXTRACTION CHAMBER*	*ANALYTE TRAP*
density: 0.63g/mL	chamber temperature: 120°C	analytes: PAHs
pressure: 335bar	equilibration time: 1.00min	trap material: ODS
flow rate: 4.0mL/min	extraction time: 30.00min	nozzle temperature: 45°C
extr.fluid:CO_2/MeOH/H_2O(95/1/4)	thimble volumes swept: 25.2	trap temperature: 80°C

FRACTION OUTPUT

Rinse substep	Solvent	Volume (mL)	Rate (mL/min)	Nozzle temp.	Trap temp	vial #

EXTRACTION STEP 3

FLUID DELIVERY	*EXTRACTION CHAMBER*	*ANALYTE TRAP*
density: 0.63g/mL	chamber temperature: 120°C	analytes: PAHs
pressure: 335bar	equilibration time: 5.00min	trap material: ODS
flow rate: 4.0mL/min	extraction time: 10.00min	nozzle temperature: 45°C
extraction fluid: CO_2	thimble volumes swept: 8.4	trap temperature: 60°C

FRACTION OUTPUT

Rinse substep	Solvent	Volume (mL)	Rate (mL/min)	Nozzle temp.	Trap temp	vial #
1	ACN/THF	0.8	1.0	45	80	1
2	ACN/THF	2.0	1.0	45	80	W

Finally, another sediment named SETOC-708 was investigated. Since the matrix of SETOC-708 is slightly different and in addition contains higher concentrations of PAHs, the results could differ from SETOC-701. However, employing the same three-step extraction procedure similar results were obtained (Figure 2).

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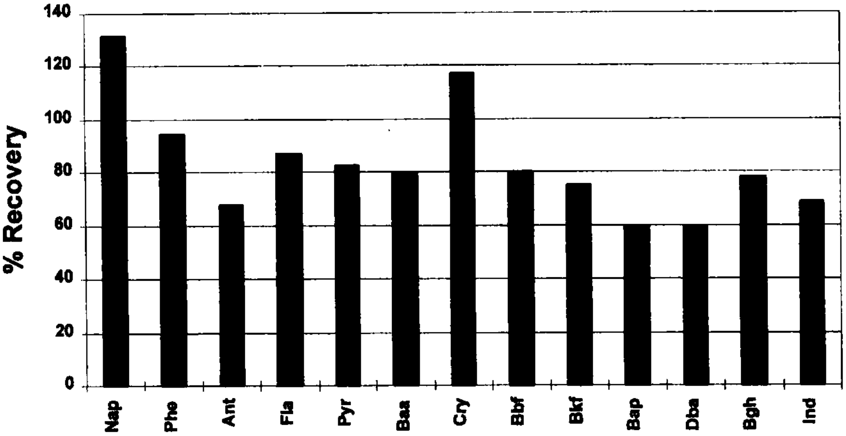

FIGURE 2 Recoveries of the PAHs obtained by SFE using modified CO_2 for SETOC-708

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Comparison of SFE versus USE

Results obtained by SFE are generally compared with a well established extraction technique in order to prove the performance of this rather new extraction method. Ultrasonic (US) extraction is such a technique, is often cited in the literature as an appropriate method for extracting PAHs from sediment samples and has been also tested in our laboratory obtaining recovery rates between 80 and 120 % compared to the medians of the SETOC values. Furthermore, standard addition experiments were carried out with 90 to 110 % recoveries for all the PAHs except Nap which was just above 80 % due to its high volatility. When the efficiencies of SFE and US extraction are compared (Figure 3) it can be noticed that the PAHs can be recovered from these real world sediment by SFE with US method-like recoveries. However, for four of the PAHs (Ant, Pyr, Bap, Dba), especially for Bap, recoveries are deteriorating (30–40% less). This stands in contrast to previously published results where PAHs are almost quantitatively recovered from soils with a comparable method[15]. It also has to be pointed out that the recovery for Bap obtained with US extraction was also not higher than 82%. Obviously, these problems are related to the strong analyte-matrix interactions in these sediments. Although the SFE apparatus required an almost daily service due to the small sediment particles (e.g. rinsing, cleaning filters and trap), the repeatability of the obtained results was in the range 2–13 %RSD for n=15.

Moreover, an US extraction was carried out after the SFE to get an idea of the remaining amount of analytes still bound in the sediments. The procedure for the

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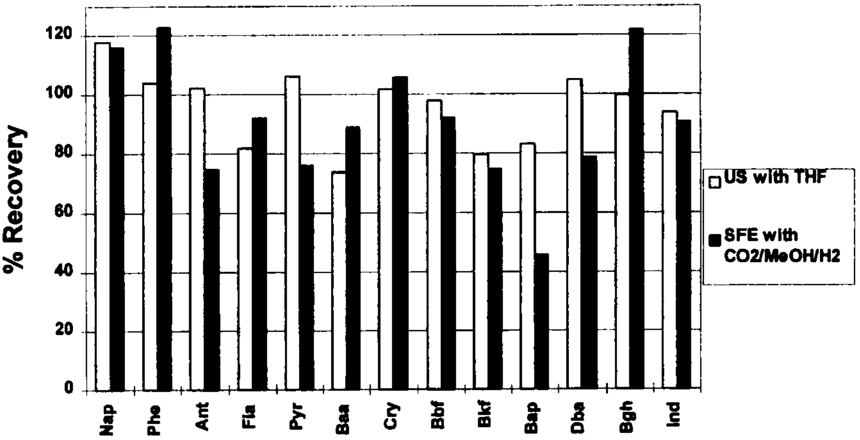

FIGURE 3 Comparison of the recoveries obtained for the PAHs with SFE and US mehtods for SETOC-701

US extraction was the following: 3 g of the SETOC sediment which had been first extracted by SFE were extracted with 5 mL THF in an ultrasonic bath for two hours. The mixture was centrifuged and from the clear extract an aliquot of 1 mL was transferred to a 10 mL measured flask and filled up with ACN. With SFE the higher condensed ring molecules showed lower recoveries and therefore further extraction of these compounds could be expected with US. The results corresponded quite well with this assumption (Figure 4).

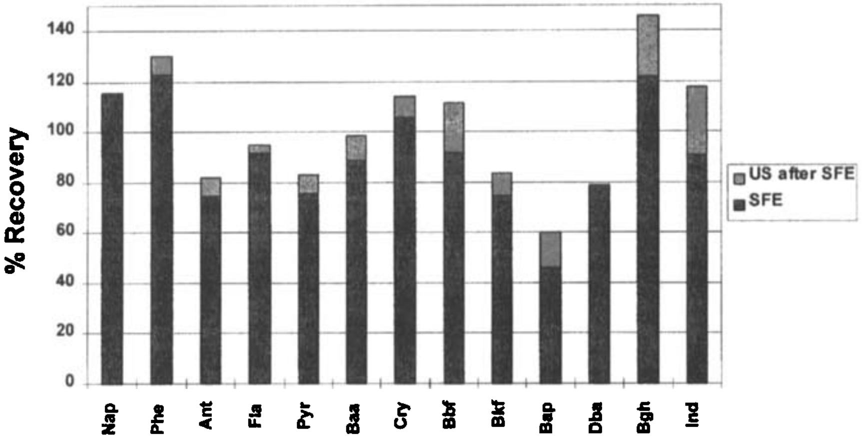

FIGURE 4 Mass balance: recoveries obtained for the PAHs when applying SFE and subsequent US extraction (SETOC-701)

CONCLUSIONS

Several parameters have been studied to analyse their effects on the extraction efficiency of SFE for reference sediments. The ODS trap packing gave the best results for all the PAHs. The other parameters like supercritical fluid flow-rate, rinse solvent identity and volume have just minor influence on the recoveries. When using pure methanol as modifier in concentration 3–5% the average extraction efficiencies could be improved from 60 to 70% when compared to pure CO_2. However, when a mixture of methanol/water was used as modifier the extraction yield could be further improved to an average of 80%.

The results obtained with the three-step SFE method were always inside the statistical limits (confidential interval (P=95%)) of the SETOC protocol.

However, when comparing the efficiency of SFE and US extraction, the simplicity of the methods and the service required, SFE, unlike to soil extractions, has not proven to be a satisfactory method for the extraction of PAHs from sediment samples so far. Further studies are needed to verify this conclusion and to establish whether the method used is also applicable to other kind of matrix.

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