Acid-induced cloud point extraction and preconcentration of polycyclic aromatic hydrocarbons from environmental solid samples

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Abstract

The effectiveness of the acid-induced phase separation of anionic surfactants (acid-induced cloud point extraction, ACPE) to extract polycyclic aromatic hydrocarbons (PAHs) from different environmental samples (soils, sediments and sludges), prior to chromatographic analysis, was evaluated. Variables affecting the ACPE efficiency were optimised using a natural matrix (a harbour sediment, CRM 535). Temperature, surfactant concentration and stirring were of primary importance to maximise recovery, whereas temperature and surfactant/hydrochloric acid concentration influenced the volume of the surfactant-rich phase and therefore the preconcentration factor achieved. The optimal conditions (2% sodium dodecanesulphonate (SDoS), 4.2 M HCl, 60 °C, 1 h) were applied to the extraction of PAHs from various matrices and the ACPE recoveries compared to certified results from Soxhlet extractions. Recoveries obtained for four to five aromatic ring PAHs ranged from 71 to 98%. Uncertainties obtained using ACPE were similar to or lower than those provided for the certified values. The volume of the extracts ranged from 1 to 2 ml. The method did not require additional clean-up or preconcentration steps. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Acid-induced cloud point extraction; Preconcentration; Extraction methods; Soil; Sediments; Polynuclear aromatic hydrocarbons

1. Introduction

The analysis of organic contaminants in environmental solid samples such as soils, sediments and sewage sludge is a necessity for environmental management. Fast and accurate determinations are required in order to assess the effectiveness of environmental policy, to check compliance with environmental quality criteria and to make appropriate decisions regarding site clean-up and remediation. A critical step in organic contaminant analysis continues to be the extraction of analytes from the solid matrix. Generally, this step is the limiting factor in the number of samples that can be processed and the origin of most of the quantification errors.

Traditional extraction methods including Soxhlet and sonication are both time and solvent consuming. They often yield dirty extracts that require extensive clean-up steps in order to achieve accurate determinations. Therefore new approaches such as supercritical fluid extraction (SFE) [1,2], microwave-assisted extraction (MAE) [3–5], pressurised liquid extraction (PLE) [6,7] and subcritical water extrac-

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tion [8–10] have been developed in the last few years in order to replace them. Important chemical characteristics to take into account in developing a new extraction method are recoveries of analytes, amount of organic solvent, time of extraction, selectivity towards the target analytes, no toxicity of the extractant and number of post-extraction clean-up steps required. On the other hand, because of the variety of environmental samples, extraction methods should not be matrix-dependent.

According to the results obtained by different authors [1–11] all new extraction approaches reduce considerably extraction times and organic solvent requirements compared to Soxhlet extraction. Also, acceptable recoveries are often achieved for most organic pollutants. However, it now appears that PLE has significantly advanced in the last few years, whereas SFE and MAE have not reached the status of widely applicable technologies [12].

This paper discusses the potential of the acid-induced cloud point extraction (ACPE) of anionic surfactants [13] for the extraction and preconcentration of organic contaminants from environmental solid samples as a step prior to liquid chromatography. Aqueous solutions of nonionic surfactants are well-known for their propensity to undergo clouding and liquid–liquid separation at elevated temperatures [14]. Certain zwitterionic surfactants [15] as well as some ionic surfactants in the presence of high concentrations of added electrolyte [13,16] also exhibit such phase separation. The two isotropic phases obtained are, respectively, a surfactant-rich phase of very low volume and an aqueous phase containing a surfactant concentration close to the critical micellar concentration (CMC). Analytes solubilised in the micelles will separate and become concentrated in the surfactant-rich phase.

To date, cloud point extraction (CPE) applications have focused on the design of efficient liquid–liquid extraction methods for the separation, preconcentration or purification of different inorganic and organic compounds from aqueous samples [14,17]. Applications of CPE to the extraction of analytes from solid samples prior to LC separation are scarce ([17,18] and references cited therein) in spite of the fact that the results obtained have proved that CPE can be advantageously used for this purpose. In order to assess the real advantages/limitations of CPE for

solid–liquid extractions, thorough studies about the factors influencing these extractions should be carried out.

The investigation presented here attempted to elucidate some of the factors affecting solid–liquid extractions by the cloud point methodology. For this purpose, the extraction of several polycyclic aromatic hydrocarbons (PAHs) from different environmental samples (soil, sediment and sewage sludge) using the acid-induced phase separation of the anionic surfactant sodium dodecanesulphonate (SDoS) [13] was studied. Some applications of CPE for extraction of PAHs from aqueous [18–22] and solid [20,23] samples, prior to LC separation have been described. The application of ACPE to the extraction of PAHs from aqueous samples has also been proved [24].

Several intrinsic advantages are associated with the use of ACPE for solid–liquid extractions, namely, easily biodegradable surfactant solutions are used as extractants, low volume extracts are obtained, wet samples can be analysed and no special extraction equipment is required.

2. Experimental

2.1. Apparatus

The liquid chromatographic system used (Spectra System SCM1000, ThermoQuest, San Jose, CA, USA) consisted of a P4000 quaternary pump, a FL3000 fluorescence detector and a UV6000LP diode-array detector. In all experiments, a Rheodyne 7125NS injection valve, with a 20-μl sample loop was used (ThermoQuest, San Jose, CA, USA). The inner surface of the valve was coated with Teflon in order to prevent the possible corrosion caused by the acidity of the sample. The stationary-phase column was a 30-cm Nova-Pack C_{18} column, with 3.9 mm I.D., from Waters (Milford, MA). For separation of the surfactant-rich phase, a Selecta Angular 6 centrifuge was employed.

2.2. Chemicals

All reagents were of analytical reagent-grade and were used as supplied. Sodium dodecanesulphonate

(SDoS) was obtained from Fluka. Hydrochloric acid and HPLC-grade acetonitrile were obtained from Panreac. PAH compounds were supplied by Aldrich [pyrene (Pyr), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*b*]naphtho[2,1-*d*]tiophene (BbN)], Fluka [benz[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), indene[1,2,3,-*cd*]pyrene (IP)] and Sigma [benzo[*e*]pyrene (BeP)]. A standard mixture solution of the PAHs, at 1 mg/l each, was prepared in acetonitrile. Ultra-high-quality water was obtained from a Milli-Q water purification system (Millipore, Madrid, Spain).

2.3. Samples

Certified reference materials were obtained from the Community Bureau of Reference of the European Commission (BCR, Brussels, Belgium) and included a harbour sediment (CRM No. 535), an industrial soil (CRM No. 524) and a sewage sludge (CRM No. 088). Certified concentrations of PAHs in these samples are shown in Table 1.

2.4. Cloud point extraction (ACPE) procedure

Fig. 1 summarises the sequential steps followed by ACPE for the extraction of PAHs from environmental materials. The sample (0.1 g of the sediment or sewage sludge and 0.05 g of the industrial soil) was mixed with 10 ml of 0.1 *M* HCl and stirred at 700 rpm for 10 min. The acid solution containing alkaline and alkaline-earth metals was separated by centrifugation and discarded. Then, 20 ml of 2% SDoS in 4.2 *M* HCl was added to the solid sample

and the mixture stirred at 700 rpm and 60 °C for 1 h. Afterwards, it was centrifuged at 5000 rpm for 10 min. Three phases were observed in the centrifuge tube: the non dissolved solid matrix at the bottom, a little volume of surfactant-rich phase containing the PAHs at the top and an aqueous phase between both, containing the surfactant at a concentration near the critical micellar concentration. In order to make easier the separation of the surfactant-rich phase, the temperature was lowered to 0 °C, then this phase turned gelatinous, dense enough to be separated from the liquid phase using a simple tool (e.g. a spatula). Under room temperature, the gelatinous phase rendered liquid (between 1.4 and 1.6 ml) and it was diluted to 2 ml with acetonitrile in a standard flask. Before injecting an aliquot in the chromatographic system, the sample was filtered through a 0.45-μm nylon membrane filter.

2.5. Liquid chromatography/fluorimetry

Acetonitrile and water were used as eluent solvents at a flow-rate of 1.5 ml/min. The gradient elution program was: 0–20 min (isocratic conditions with acetonitrile/water 60:40); 20–30 min (linear gradient from 60 to 80% of acetonitrile); 30–35 min (isocratic conditions with acetonitrile/water 80:20). Detection was performed with fluorescence wavelength programming in order to obtain better sensitivity. The excitation/emission wavelengths were set as follow: 240/374 nm at 0 min, 286/388 nm at 15 min, 260/358 nm at 20 min, 300/430 nm at 24 min, and 296/496 nm at 30 min.

Table 1
Mean concentrations (mg/kg)±uncertainty and average recoveries of PAHs[a] from several solid samples obtained by the ACPE approach

PAH	Industrial solid		Harbour sediment		Sewage sludge	
	CRM	Found	CRM	Found	CRM	Found
Pyr	173±11	168±14.1	2.52±0.18	2.48±0.07	2.16±0.09	2.12±0.07
BaA	22.5±1.8	21.3±1.6	1.54±0.10	1.33±0.07	0.93±0.09	0.91±0.03
BbN	3.8±0.6	3.3±0.2	–	–	0.42±0.05	–
BbF	13.5±1.6	12.5±1.5	2.29±0.15	1.86±0.10	1.17±0.08	1.08±0.07
BeP	10.6±0.13	8.6±0.4	1.86±0.13	1.45±0.08	1.02±0.07	1.00±0.03
BkF	6.2±0.15	5.3±0.4	1.09±0.15	0.87±0.07	0.57±0.05	0.49±0.02
BaP	8.6±0.10	6.9±0.5	1.16±0.10	0.87±0.04	0.91±0.10	0.75±0.03
IP	5.1±0.14	4.2±0.3	1.56±0.14	1.12±0.09	0.81±0.06	0.64±0.03

[a] Based on 11 replicates of the solid samples.
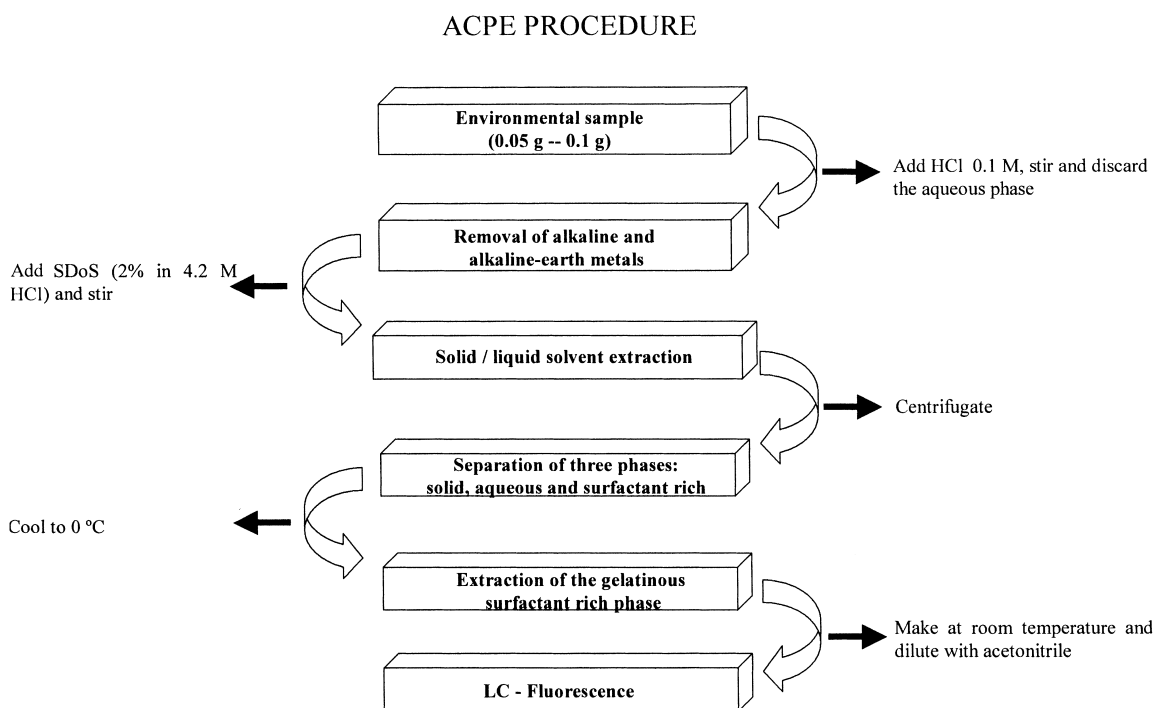
ACPE PROCEDURE

Fig. 1. Schematic diagram of the cloud point extraction procedure.

3. Results and discussion

3.1. Analytical separation of PAHs

Eight low volatile PAHs ranging from four to five aromatic rings, which are strongly adsorbed on solid environmental samples, were considered for chromatographic separation. The selection of PAHs was based on the composition of the reference materials used (Table 1). Fluorescence detection was used in all experiments.

Different gradient programs using acetonitrile–water as mobile phase were tried in order to achieve the best resolution for the eight PAHs in the minimal time. It was found that isocratic conditions were unable to obtain resolution at an acceptable analysis time. Separation of BbF and BeP was good with the use of a linear gradient between 20 and 30 min (60–80% of acetonitrile). The surfactant SDoS used for the cloud point extraction was not retained and it gave a peak that did not interfere with analytes. As a result, the surfactant-rich phase had no effect on the chromatographic separation achieved for the PAHs

tested and calibrations obtained in the absence and presence of the surfactant-rich phase were identical. This is a clear advantage on the use of nonionic surfactants that coelute with analytes since they modify the analyte response and calibrations require the cloud point extraction of standards [25]. No change in the C_{18} column efficiency was observed after repeated injections of the surfactant acid solution.

Linearity was obtained in the concentration range 20–120 μg/l for BbN and BbF and 5–120 μg/l for the rest of the PAHs studied. The detection limits, calculated as threefold the noise, ranged between 0.1 and 5 μg/l.

3.2. Parameters influencing PAH extraction by ACPE

Parameters considered to potentially affect the extraction efficiency of PAHs were temperature, surfactant amount, HCl concentration and time of extraction. Their influence was assessed from the recovery achieved for the individual PAHs. Three

replicates were made to obtain a mean value. Each variable was investigated keeping constant the others. A certified reference material (a harbour sediment, CRM 535) was used in the experiments. The certification of PAHs for these materials was fundamentally based on the Soxhlet-extraction standard technique and therefore it was considered very convenient to investigate the feasibility of using ACPE as an alternative extraction method. On the other hand, the importance of using materials with native contaminants in extraction method development instead of those artificially fortified has been extensively discussed [26,27].

Preliminary experiments in which SDoS solutions were directly applied to 0.1 g of the sediment showed that the surfactant precipitated to a great extent in the course of the extraction and therefore poor PAH recoveries were obtained. The same behaviour was observed for the extraction of the soil and sewage sludge reference materials. The amount of precipitate obtained was dependent on the amount of sample extracted. It has previously been found [13] that alkaline metals salts (i.e. NaCl) insolubilize anionic surfactants under cloud point conditions when their concentrations surpass about 0.7 M. On the other hand, it has been described [28] that alkaline-earth metals yield very insoluble salts with anionic surfactants. We checked that SDoS (3.7×10^{-2} M in 1.2 M HCl) precipitates in the presence of calcium (1.5×10^{-3} M). Taking into account that calcium carbonate is a phase nearly always present in solid environmental samples (i.e. in the sediment reference material used in this investigation, the amount of calcium carbonate constituted about 9% of the dry matter) and that it dissolves in the acid medium used for extraction, we considered that alkaline-earth salts, and to a lesser extent alkaline salts, were the origin of the precipitate yielded in the course of the extraction. In order to remove this interference, the sediment sample (0.05–0.1 g) was mixed with hydrochloric acid solutions in a range of concentrations and times. After centrifugation, the aqueous phases were separated and analysed for PAHs by LC/fluorimetry. Then, the sample was extracted with 20 ml of 1% SDoS in 4.2 M HCl solution by stirring at 700 rpm for 1 h, at room temperature. From the results obtained, it could be concluded that stirring of the sample with 10 ml of 0.1 M HCl for 10 min was enough to remove the interference of alkaline and alkaline-earth metals in the ACPE method without losses of PAHs in the acid phase discarded. Environmental samples with a high percentage of calcium carbonate could require a greater concentration of hydrochloric acid in order to remove this phase, but if there is any interference for this reason it can be easily detected since the precipitate produced is different enough from the sample matrix.

A high partition of the analytes to the surfactant-rich phase from the water phase was obtained because of the increased solubility of PAHs in the micellar medium [29]. Analysis of the water phase gave undetectable concentrations of PAHs. In this way, PAHs were assumed to partition between the solid sample and the surfactant-rich phase.

3.2.1. Influence of temperature

The effect of this parameter on the efficiency of ACPE to extract PAHs from the sediment reference material was studied in the range 20–80 °C. Two facts were obvious from the results obtained; first, there was a trend of significantly lower recoveries for the higher molecular mass PAHs (e.g. BaP and IP), and second, there was a noticeable enhancement in PAH recoveries at the higher temperatures. This behaviour is commonly found in the extraction of analytes from environmental matrices, independently of the solid–liquid extraction technique used (e.g. Refs. [1,2,11]). PAHs strongly adsorb inside the porous matrix of environmental samples, the higher molecular mass PAHs being the most strongly adsorbed [30]. For PLE and subcritical water extractions, the lower recoveries for high-molecular-mass PAHs are also attributed to the decreased solubility of these compounds in both supercritical carbon dioxide and subcritical water [31,32]. Because the solubility in the micellar medium increases with the hydrophobicity of analytes, the lower recovery obtained for the higher molecular mass PAHs with ACPE can be attributed to their stronger adsorption on the environmental matrix. A temperature value of 60 °C was chosen as optimal for extraction of PAHs. A slight increase (4–5%) in the recovery was observed at 80 °C for all PAHs tested, however the precision of the measurements slightly decreased.

3.2.2. Influence of the surfactant concentration

The effect of SDoS concentration on PAH recoveries was examined in the range between 0.5 and 3% (w/v). Recovery of PAHs increased by about 30–40% when the percentage of SDoS ranged from 0.5 to 2%. No significant increments were observed for larger surfactant concentrations. The surfactant-rich phase volume increased with SDoS concentration. The phase volume ratio (volume of surfactant-rich phase/volume of aqueous solution, after the extraction step) was linearly dependent on the percentage of SDoS used as extractant, and ranged from 0.05 to 0.15 for SDoS percentages between 1 and 3%. Therefore, SDoS concentration influences the volume of the extracts obtained and as a result the detection limits that can be achieved. So, non excess of surfactant should be used in ACPE extractions, and 2% of surfactant was selected for this application as a compromise between recovery and preconcentration.

3.2.3. Influence of the HCl concentration

The separation of SDoS in two isotropic phases is achieved at hydrochloric acid concentrations in the range 2.5–5 M. On the other hand, a hydrochloric acid concentration of about 0.2 M is required in order to dissolve SDoS concentrations around 1–3% and therefore the influence of lower acid concentrations on the recovery of PAHs could not be examined. For extractions under no cloud point conditions (e.g. hydrochloric acid concentrations lower than 2.5 M), the volume of acid necessary to achieve a final concentration of about 4.2 M was added after extraction, in order to obtain phase separation before measurement. For ACPE conditions (e.g. hydrochloric acid concentration, between 2.5 and 5 M) no additional acid was added to the extract for measurement. Below are the main results derived from this study.

The recovery of PAHs was hardly affected by hydrochloric acid concentrations in the range examined (0.2–5 M). Excess of protons did not help in the desorption of PAHs. The more noticeable influence of this variable was related to its ability to modify the volume of the surfactant-rich phase and as a result the detection limits achieved. The phase volume ratio decreased exponentially up to about 4 M hydrochloric acid concentration and then it was

kept practically constant for higher concentrations. A 4.2 M hydrochloric acid concentration is recommended for extraction of PAHs from the sediment sample.

3.2.4. Influence of the extraction time

The kinetics of extraction of analytes from the aqueous phase to SDoS micelles is very rapid and as a result the partition equilibrium is achieved in about 2 min. In solid samples, the kinetics of partition between the solid and the micellar phase will be mainly governed by the kind and site of binding of analytes to the porous matrix. In order to investigate the influence of the time of extraction on the ability of SDoS to extract PAHs from the sediment sample, this variable was tested in the range between 5 min and 4 h. From the results obtained, it can be concluded that about 1 h was required to reach maximum recovery of PAHs from the sediment. After this time, only the recovery of the more hydrophobic PAHs (e.g. BaP and IP) slightly increased with time. So, 1 h is recommended for this extraction. Stirring of the solution during extraction was found essential to facilitate desorption of analytes from the matrix. Recoveries obtained from experiments carried out without stirring were considerably lower although they were performed at high temperatures (e.g. the recoveries of the PAHs at 100 °C without stirring were Pyr 37.8%; BaA 29.5%; BbF 25.3%; BeP 27.5%; BkF 29.8%; BaP 28.3% and IP 28.1%). The use of sonication was not found advantageous versus magnetic stirring in terms of recovery or extraction time.

3.3. Influence of the sample matrix

In order to determine the potential of the proposed ACPE technique to the extraction of PAHs, it was applied to matrices presenting different physicochemical characteristics. An industrial soil (CRM 524) and a sewage sludge (CRM 088), containing an overall concentration of PAHs above and similar to that of the sediment, respectively (Table 1), were selected. The experimental conditions used for ACPE extractions were those specified under Procedure (Experimental section). The results obtained are shown in Table 1. They are expressed as mean values±the uncertainty, calculated as $t \cdot s / \sqrt{n}$.

Eleven ACPE extractions were carried out for each matrix in order to detect homogeneity problems in the CRMs used since the sample intake for ACPE was lower than that used in the homogeneity assays of CRM certification (soils 0.25 g; sediment 0.5 g and sludge 1 g). Confirmation of the compounds was carried out through their UV spectra by using the diode array detector. Because of the lower sensitivity of the UV detection, confirmation of the chromatographic peak corresponding to BbN could not be obtained for the sludge sample, therefore, data on this PAH are not reported. Recoveries for most PAHs after 1 h of extraction ranged from about 71 to 98%.

The results were less dependent on the matrix than other methods such as SFE and ASE. The ANOVA test, applied to the results obtained from the different matrices and analytes, showed that there was no statistically significant difference between the means obtained for the PAHs determined in sludge and soil samples, except for BeP, at the 95% confidence level. More significant differences were found for the sediment and sludge since results for BaA, BeP, BaP and IP were different statistically, although these differences were no higher than about 5% in any case.

Uncertainties were of similar order that those specified for the certified reference materials indicating that no problems of homogeneity were derived from the amount of sample treated by ACPE. In fact, some laboratories participating in the certification process of these materials also used a lower sample amount than that used in the homogeneity assay of the certification procedure. Fig. 2 shows a typical chromatogram obtained for the harbour sediment sample used in this study. No clean-up or preconcentration steps were required to determine the PAHs in the environmental samples.

4. Conclusions

The experimental results of this study allow us to draw some conclusions about the analytical and practical characteristics of the ACPE technique for the extraction of analytes from complex solid samples. However, more thorough and extensive investigation is necessary in order to determine the real potential of ACPE for this application.

The study of various parameters that influenced the efficiency of ACPE showed that the temperature and surfactant concentration, in addition to stirring, were of primary importance to maximise the recoveries. On the other hand, as was expected, the volume of the extracts obtained and as a result the detection limits achieved, were dependent on variables such as temperature and surfactant/hydrochlo-
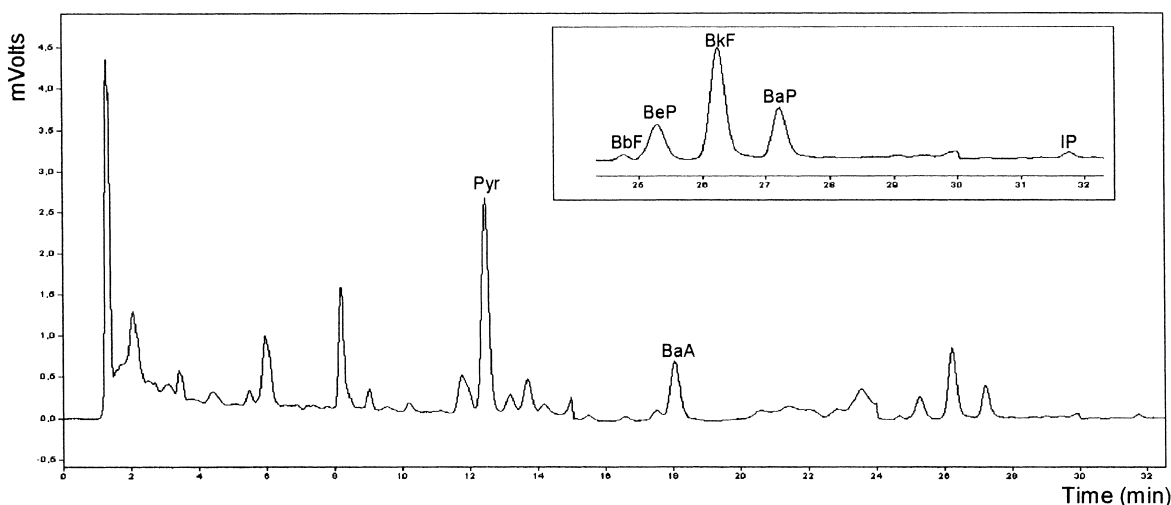

Fig. 2. Chromatogram obtained for the injection of a surfactant-rich phase of the harbour sediment sample. For conditions, see the Experimental section.

ric acid concentration. Typical volumes of the extracts were in the range 1–2 ml and therefore the extraction step also involved preconcentration.

The results obtained in this investigation and the advantages associated with the use of ACPE establish this technique as a serious alternative to the use of Soxhlet extraction prior to chromatography. Two aspects should be investigated thoroughly: first, if ACPE will be a technique for selected applications or if it could become a widely applicable technology, and, second, the way to automate it. Research in this area is being carried by our research group at the present time.

Acknowledgements

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