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Screening of Polycyclic Aromatic Hydrocarbons in Soil by On-Line Fiber-Optic-Interfaced Supercritical Fluid Extraction Spectrofluorometry

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An interface for spectrofluorometric measurements in the supercritical (SC) CO_2 emerging from the extraction cell of a supercritical fluid extractor prior to depressurization was developed. The windowless flow cell designed for this purpose is furnished with an inlet and outlet for the SC-CO_2 stream; it can withstand pressures up to at least 350 bar and is connected to the light source and detector by means of two fiber-optic cables. The combined system allows the real-time on-line fluorometric monitoring of the supercritical fluid extraction (SFE) process and provides qualitative and semiquantitative information from supercritical extracts of real and spiked samples. The determination of five polycyclic aromatic hydrocarbons (PAHs) in spiked soil by SFE with on-line fluorescence detection provided relative standard deviations less than 5%, as well as benzo[*k*]fluoranthene recoveries from several spiked soils between 93 and 107%, with an RSD less than 10%. Also, crysene−benzo[*a*]anthracene binary mixtures in spiked soil were resolved with recoveries of 89−103% and an RSD of about 10%. The use of the proposed equipment for screening real soil samples for PAHs using on-line SFE spectrofluorometry is demonstrated.

Responsive tools are being increasingly demanded by regulatory laboratories under heavy workloads, particularly for solid samples, the processing of which involves labor-intensive, time-consuming preliminary operations. The development of screening systems providing a rapid yes/no answer for solid samples is highly desirable, as the answer dictates whether or not a given sample is to be subjected to the whole analytical prosses; a prompt answer can save time and reagents. In this context, supercritical fluid extraction (SFE) has emerged as a promising alternative to liquid extraction methods, and fiber-optic-assisted measurements of the effluent from the extraction chamber have proved highly useful.

Supercritical fluid extraction is a rapid preparation technique for use before chromatographic analysis of solid samples, where it simplifies and facilitates automation of the preliminary operations of the analytical process.[1−3] The ability to adjust the solvent power of the supercritical fluid (usually CO_2) simply by changing the pressure and temperature makes SFE extremely selective and suitable for class-selective extractions. In addition, the preconcentration achieved in using a supercritical extractant, which is gaseous under ambient conditions, results in increased sensitivity and allows the use of smaller samples. Finally, SFE is a clean method for extracting analytes from solid matrices because it avoids the use of large amounts of liquid organic solvents and the production of polluting wastes.

Fluorescence and ultraviolet/visible spectroscopy detectors furnished with high-pressure flow cells can be used for continuous monitoring of supercritical fluid extracts; however, "windowless" fiber-optic-based interfaces are superior in terms of ease of cleaning and of replacement if fouled or damaged. Dunham et al.[4] used a modified HPLC flow cell as an on-line supercritical fluid extraction detector, but they confined measurements to pressures below 150 atm because the cell shattered above 250 atm and some leakage was observed above 150 atm. The cylindrical geometry of the cell was also unfavorable. A more robust flow cell[5] was constructed by a straightforward alteration of a stainless steel cross, using thick sapphire windows seated in two of the cross connectors, placed at an angle of 90° or 180° for sampling scattered or transmitted light, respectively. This view cell was used to investigate phase changes in multicomponent mixtures of CO_2 or chlorodifluoromethane with methanol, triethylamine, and water. Other types of sapphire window view cells have been used to determine phase behavior,[6] water solubility,[7] and the extent of swelling of modifier-saturated plant and clay matrices.[8] Fiber-optic-based interfaces were previously used[9−12] to facilitate spectroscopic measurements in supercritical solvents. Also, an SFE-FT-IR interface based on chalcogenide fiber optics and a stainless steel union cross was used for the determination of total petroleum hydrocarbons in soils using on-line static SFE-FT-IR.[13]

This paper reports a new interface design that was used to perform fluorometric measurements in dynamic SFE processes for the first time. The normally arranged optical fibers used in place of a bifurcated fiber-optic probe[11] avoid the need for epoxy

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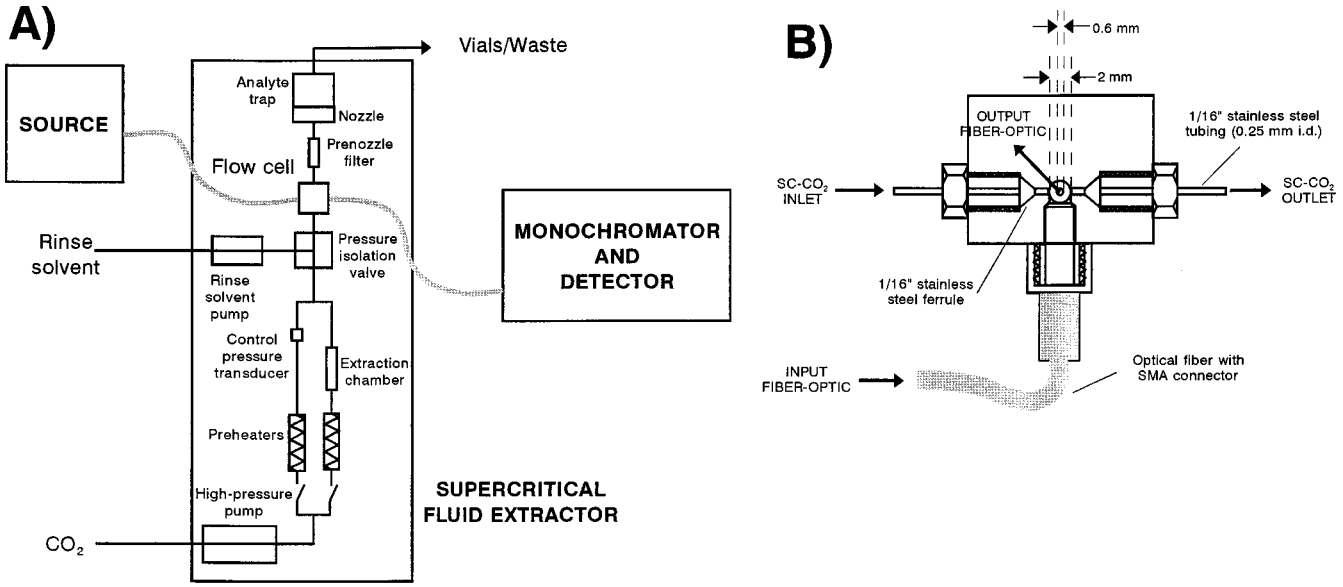

Figure 1. (A) Supercritical fluid extractor coupled on-line to a fiber-optic-based spectrophotometer for the screening of PAHs in soils. (B) Schematic diagram of the fluorometric flow-cell used as interface. For details, see text.

resin to fix the fibers and the thin plug of dental amalgam required to shield the epoxy from the supercritical solvent; as a result, the flow cell can operate at high temperatures. The fiber-optic-coupled system was used to screen a family of priority fluorescent pollutants, viz. polycyclic aromatic hydrocarbons (PAHs), in soils. Detection was performed prior to depressurization, in contrast with an on-line SFE sensor-coupled system previously reported for sulfoquinoxaline screening.[14]

EXPERIMENTAL SECTION

Apparatus. A Hewlett Packard HP7680A supercritical fluid extractor furnished with a 7 mL extraction vessel and an analyte trap packed with stainless steel balls was used. A fiber-optic scanning spectrophotometer (Guided Wave, Model 260), equipped with a 1200 line/mm grating and an auxiliary ultraviolet deuterium lamp (Model DTL200) and connected to a personal computer, was set up for use as a spectrofluorometer. The supercritical fluid extractor was connected to the spectrophotometer via a fiber-optic-based interface consisting of a laboratory-made windowless stainless steel flow cell, fiber-optic cables, $^1/_{16}$ in. o.d. stainless steel tubing (0.25 mm i.d.), and $^1/_{16}$ in. stainless steel ferrules and screws. As shown in Figure 1A, the fluorometric flow cell (2 mm light path length, ~10 μL inner volume) was inserted between the prenozzle filter and the pressure isolation valve. Measurements were made prior to depressurization, and the flow cell was rinsed after each extraction. Commercially available 2 m UV/visible fiber-optic cables with a black nylon outer jacket and hexagonal-nut SMA connectors (Oriel Corp., Stratford, CT) were used to connect the optical devices with the flow cell. The refractive indexes of the core and cladding were 1.452 and 1.438, respectively, at 850 nm. The core, cladding, and jacket diameters were 600 μm, 750 μm, and 1.7 mm, respectively. The fluorometric flow cell, a drilled stainless steel block, is depicted in Figure 1B. The SC-CO_2 inlet and outlet were aligned with the same axis. Fittings for fiber connectors were arranged normal to each other and to the previous axis. The unit is robust and can withstand pressures up to at least 350 bar.

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Table 1. Particle Size Analysis of the Spiked Soil Samples

sample	% clay	% sand	% silt	textural class
soil I	43.7	12.1	44.2	silty clay
soil II	29.3	41.0	29.7	clay loam
soil III	29.0	27.4	43.6	clay loam
soil IV	17.9	49.4	32.7	loam
soil V	35.8	27.1	37.1	clay loam

Reagents and Samples. The polycyclic aromatic hydrocarbons (PAHs) fluoranthene (Flu), benzo[*j*]fluoranthene (BjF), triphenylene (Tri), chrysene (Cry), benzo[e]pyrene (BeP), indeno[1,2,3-*cd*]pyrene (IndP), and indeno[1,2,3-*cd*]fluoranthene (IndF) were obtained from BCR (Belgium); benzo[*k*]fluoranthene (BkF) from Interchim (Holland); benzo[*a*]pyrene (BaP) and benzo[*a*]anthracene (BaA) from Fluka; and benzo[*ghi*]perylene (BghiP) from Aldrich. They were used to prepare standard solutions in HPLC-grade acetonitrile from Romil Chemicals. The concentrations of the stock standard solutions ranged from 200 to 280 μg/mL, depending on the particular PAH (except for Pyr, which was used at 1000 μg/mL).

Diatomaceous earth (Sigma) was used as the solid support, and SFE/SFC-grade carbon dioxide (Air Products) and industrial CO_2 were used as extraction fluid and coolant, respectively.

Soil samples, with oxidizable organic matter contents ranging from 0.92 to 2.05% and pH values between 7.93 and 8.51, were provided by the Laboratorio Agroalimentario de Córdoba (Spain). The soils were sieved, ground, and air-dried. Plant blades, visible organic materials, and large particles (stones) were previously removed. The proportions of clay, sand, and silt in each of the soils studied, as well as their textural class, are shown in Table 1. The spiking procedure was as follows: first, 5 g of soil was weighed on aluminium foil. Then, a microvolume (25−600 μL) of stock solution of the analyte was slowly added to the soil dropwise while spreading the analyte throughout the sample. Finally, the soil sample was allowed to stand for 30−60 min in order to evaporate acetonitrile.

Jet milled soils R and J (particle size < 63 μm), obtained from the IRMM (EU. Steenweg of Retie, 2440 Geel, Belgium) were

Table 2. Composition of the Real Soil Samples

analyte	soil R (mg/kg)[a]	soil R (mg/kg) ± SD[b]	soil J (mg/kg)[a]
Pyr	80	62 ± 1	20
BaA	50	56 ± 2	10
BbF	30	46 ± 4	5
BkF	20	20 ± 1	5
BaP	30	22 ± 1	5
IndP	40	23 ± 2	3
BnT	5		1
BeP	30		3
Flu		123 ± 2	
Tri		25 ± 1	
Cry		52 ± 1	
total cyanide	500		80
phenol	0.5		2
o-cresol	0.5		2
m- + *p*-cresol	0.5		2

[a] Estimated values provided with the samples. [b] Determined by HPLC after SFE with CO_2 + methanol.[15] BnT denotes benzo-[*b*]naphtho[2,1-*d*]thiophene.

used as samples. Soil R contained between 20 and 130 μg of each target analyte per gram. The PAH concentrations obtained for soil R by off-line HPLC analysis after SFE with methanol-modified CO_2 in the extraction cell[15] are listed in Table 2, which also shows the estimated concentrations for soils R and J provided with the samples. Soil powders R and J, candidate BCR reference materials for the determination of PAHs and phenols, were collected from an industrial area of Germany.

SFE Procedure. CO_2 was aspirated from a cylinder furnished with a dip-tube at a constant flow rate of 2 mL/min (liquid) by using a double-piston pump and passed through the extraction vessel. The sample (1−5 g) was placed in a 7 mL stainless steel extraction cell that was accommodated in the extraction chamber and allowed to equilibrate at the preset temperature before extraction. Once the target pressure (281 bar) and temperature (40 °C) had been attained, the CO_2 bypassed the extraction cell, and the sample was extracted in the static mode for 0.5 min, after which the CO_2 was passed through the sample and the dynamic extraction period (15 min) started. A variable restrictor that virtually suppressed plugging allowed the flow rate and extraction pressure to be controlled separately during extraction. It also provided a constant flow rate, which was mandatory in order to ensure reproducible results during on-line monitoring. After CO_2 depressurization, the analytes were deposited in a stainless steel bead trap at 35 °C. In a subsequent step, an acetonitrile stream was pumped at 0.5 mL/min through the flow cell, nozzle, and trap by means of a syringe pump, and the analyte solution was collected in a 2 mL vial. The nozzle temperature during the extraction and rinsing steps was 45 °C and 35 °C, respectively.

On-Line Fluorometric Monitoring of the SC Extract. The fiber-optic input and output were arranged normal to each other, and the percent transmittance was used as the analytical signal in order to perform spectrofluorometric measurements. Transmittance measurements were made at a fixed wavelength (pointer monitoring) or over a preset range (scanner monitoring). Data were acquired during dynamic extraction only. The reference value (100% transmittance) was established by driving the source light directly to the detector (the two were connected via a 1 m × 400 μm core diameter fiber). Using an excitation grating monochromator (Model 77250, Oriel Corp.) resulted in markedly decreased signals because some radiation intensity was lost in monochromation. No excitation monochromator was used in order to increase sensitivity, so only emission spectra could be recorded. In this way, the system allowed the excitation of a wider range of PAHs at different excitation wavelengths.

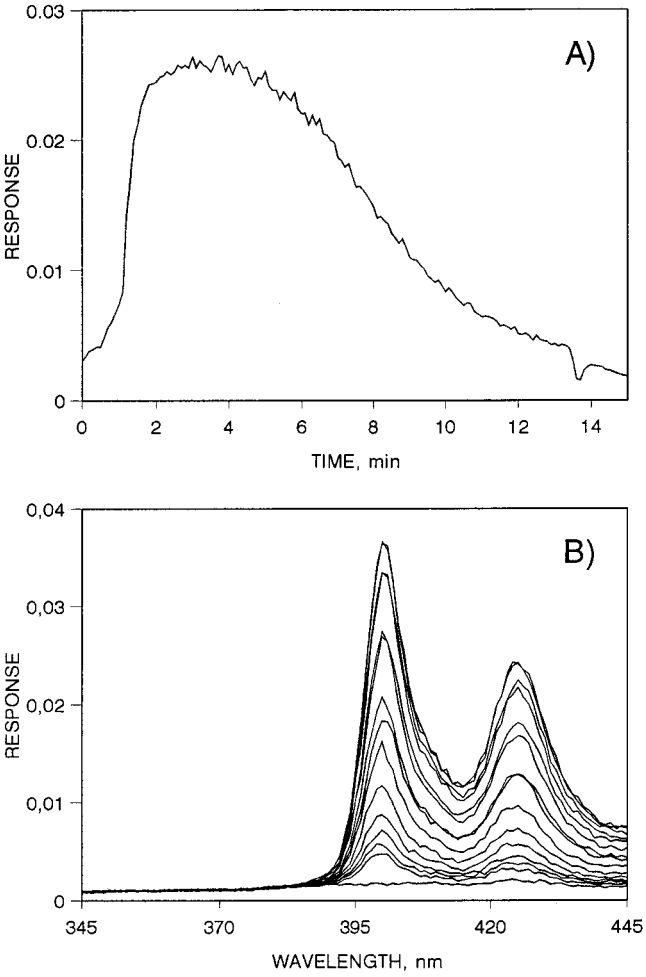

Figure 2. Transmittance recording at 394 nm (A) and successive emission spectra (B) obtained during the extraction of a soil sample spiked with 20 μg of benzo[*k*]fluoranthene using SC-CO_2. Time between scans was 1 min.

When monitoring was done in the pointer mode, transmittance data at a fixed wavelength were acquired at 0.1 min intervals. In the scanner data acquisition mode, transmittance data were acquired from 345 to 445 nm, with a wavelength step of 1 nm. Five readings were made at each wavelength. The readings were averaged; the highest and lowest values were discarded, and the average of the remainder was stored. Data acquisition and storage of each scan took 0.517 min, so the throughput was ~2 scans/min. Figure 2 shows typical recordings obtained in both monitoring modes.

BASIC programs were developed for data processing. Fluorescence values at a fixed wavelength were obtained as a function of the extraction time (SFE kinetic curve) from successive scans acquired during the extraction process. The area under the curve was calculated by using Simpson's rule-based software.

RESULTS AND DISCUSSION

PAH Spectra in Supercritical Fluid Media. Successive scans of the extraction chamber effluent were carried out during

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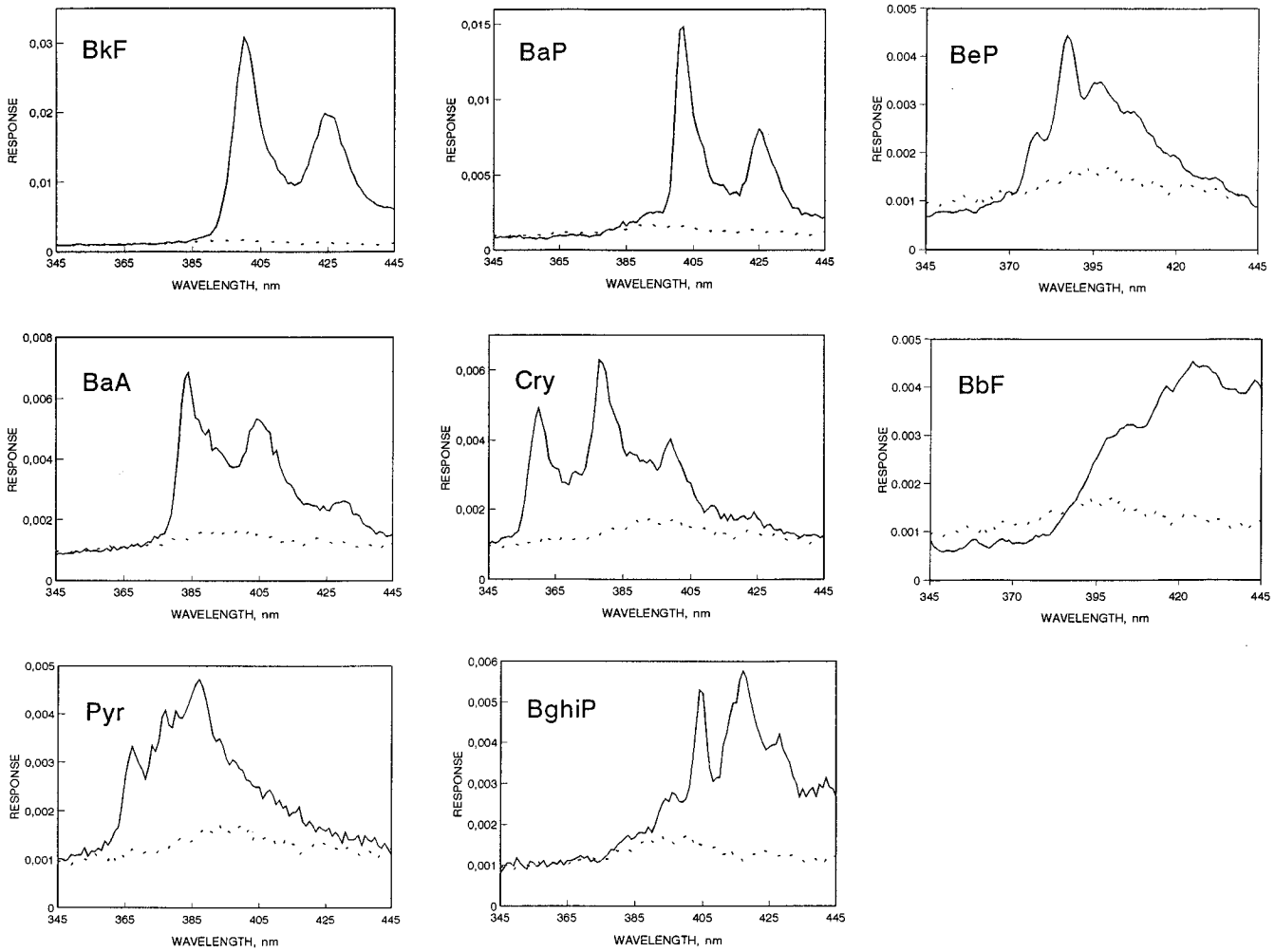

Figure 3. Spectra for polycyclic aromatic hydrocarbons in supercritical CO_2 at 281 bar at 40 °C. The percent transmittance was recorded at the elution apex of each PAH. Abbreviations are defined in the text.

the extraction of PAH-spiked diatomaceous earth with SC-CO_2 (281 bar, 40 °C) at a flow rate of 2 mL/min (liquid). Variable volumes from 100 to 500 μL of each PAH solution in acetonitrile were added to 0.5 g of diatomaceous earth. The emission spectra obtained for eight of the PAHs are shown in Figure 3. The dotted line corresponds to the scatter of the excitation light. The fluorescence of some of the polycyclic aromatic hydrocarbons studied (viz. Tri, BjF, and IndF) was too low; on the other hand, Flu and IndP exhibited fluorescence at emission wavelengths above 400 nm. As can be seen in Figure 3, the emission spectra showed several maxima (except for BbF, which exhibited a broad spectrum band): at 400 and 425 nm for BkF; 402 and 425 nm for BaP; 383 and 405 nm for BaA; 361, 380, and 400 nm for Cry; 372 and 391 nm for Pyr; 404 and 417 nm for BghiP; and 378, 387, and 397 nm for BeP.

Determination of individual PAHs. Individual calibration graphs were run by using 5 g of soil spiked with different amounts of each polycyclic aromatic hydrocarbon. Calibration samples were prepared from soil II as described under Reagents and Samples in the Experimental Section. Extractions were carried out under the conditions given in the SFE Procedure section and monitored in the scanner mode. The area under the extraction curve at the maximum emission wavelength was plotted against the amount of analyte added to the soil. The areas under the extraction curve at each wavelength for SFE of the empty extraction vessel and nonspiked soil II were also determined in order to evaluate the scatter and soil blank contributions. For instance, triplicate extractions gave rise to mean areas at 400 nm of 0.0223 and 0.0228, and relative standard deviations of 3.26% and 1.84% for the empty vessel and soil blank, respectively; these values suggest the absence of matrix contributions to the analytical signal. The emission wavelength used, the linear range studied (in micrograms spiked), the intercept and slope of the linear graph, the regression coefficient, and the precision (expressed as the relative standard deviation, % RSD) for each of the six polycyclic aromatic hydrocarbons studied are listed in Table 3.

Figure 4A shows typical SFE kinetic curves obtained from triplicate scanner recordings for BkF-spiked soils. Although the shapes of some extraction curves differed, the area under each was reproducible and proportional to the amount of analyte added. Therefore, the extraction rate did not affect the precision of the method, provided that SFE was complete. This was not the case with BghiP, as is apparent from Figure 4B, which shows the extraction curves for several PAHs. The regression coefficient and RSD for BghiP were not satisfactory because extraction of this high-molecular-weight PAH was slow (and hence incomplete at 15 min).[16]

The sensitivity, which was dictated by the specific fluorescence intensity and the extraction rate for each PAH (determining PAH concentration in SC-CO_2), was higher for BkF and BaP than for the other PAHs studied. These two analytes are among the most carcinogenic PAHs[17] and exhibit very similar spectra. Even

Table 3. Figures of Merit of the Proposed Method for the Determination of Individual PAHs in Soil

analyte	λ_{em} (nm)	linear range studied (μg)	intercept (s_b)	slope (s_a)	r	RSD (%)[a]
BkF	400	5−50	0.043 (0.007)	1.01×10^{-2} (0.03×10^{-2})	0.9989	4.4
BaP	402	10−110	0.002 (0.006)	2.38×10^{-3} (0.09×10^{-3})	0.9975	3.0
Cry	380	20−105	0.0210 (0.0005)	5.0×10^{-4} (0.1×10^{-4})	0.9994	4.0
Pyr	391	100−400	0.032 (0.003)	1.58×10^{-4} (0.08×10^{-4})	0.9962	4.1
BaA	383	25−125	0.027 (0.001)	6.0×10^{-4} (0.1×10^{-4})	0.9988	3.2
BghiP	417	40−120	0.017 (0.003)	4.4×10^{-4} (0.4×10^{-4})	0.9907	20.8

[a] $n = 3$; 23.2 μg of BkF, 44.4 μg of BaP, 41.0 μg of Cry, 100 μg of Pyr, 48.2 μg of BaA, and 80.0 μg of BghiP in 5 g of soil.

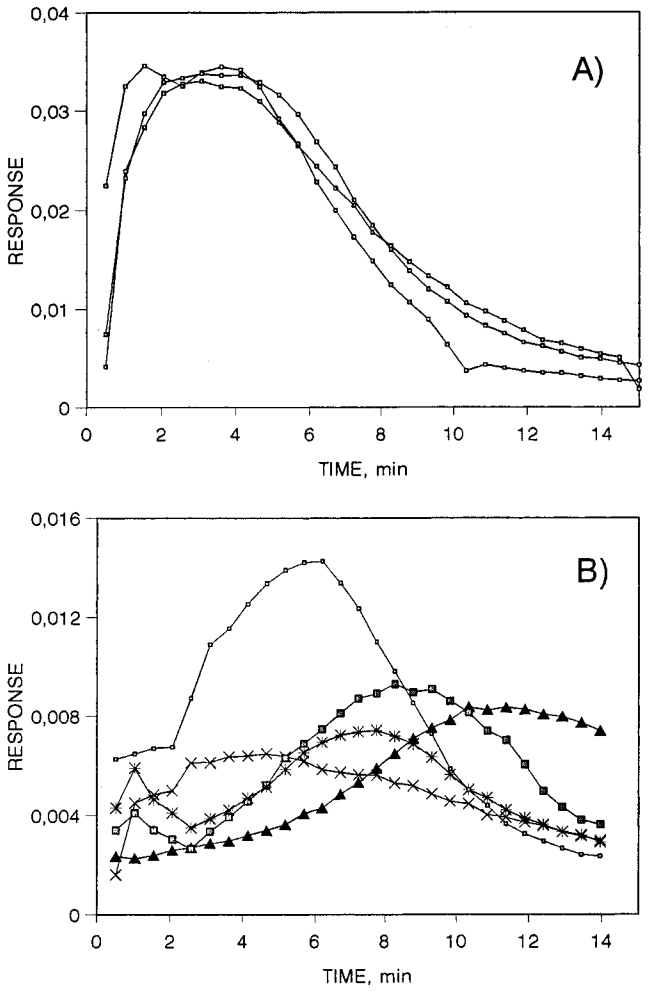

Figure 4. SFE kinetic curves obtained from scanner recordings. (A) Triplicate for BkF (23.2 μg spiked to 5 g of soil). (B) Other PAHs: 44.4 μg of BaP (□), 102 μg of Cry (*), 400 μg of Pyr (■), 72 μg of BaA (×), and 100 μg of BghiP (▲) spiked to 5 g of soil. Monitoring wavelengths are given in Table 4.

though the sensitivity for BkF and BaP is quite high, their spectral similarities call for extremely high signal/noise ratios in order to distinguish these two PAHs.

Influence of the Soil Matrix. The reproducibility of BkF extraction from five spiked soils was determined in triplicate for each soil sample. An amount of 23.2 μg of BkF was spiked to 5 g of soil. The percent recovery (calculated from the area under the extraction curve at 400 nm by using the equation for BkF in Table 3) and the standard deviation for each soil (in parentheses) were 96 (5), 97 (6), 93 (4), 107 (7), and 93 (5) for soils I, II, III, IV, and V, respectively.

An analysis of variance (ANOVA) was used to assess the influence of the matrix soil on recovery. The F value obtained as the ratio of the between-sample to the within-sample mean squares was 3.075. Therefore, sample means were not significantly different, since the calculated F value was smaller than the critical F value ($F_{4,10} = 3.478$, $P = 0.05$).

Table 4. Calibration Graphs and Precision for BaA and Cry at the Wavelength Used To Resolve Binary Mixtures

analyte	wavelength (nm)	slope (s_a)	intercept (s_b)	r	RSD (%)[a]
BaA	361	0	0.0159 (0.0001)		0.94
	405	5.2×10^{-4} (0.2×10^{-4})	0.022 (0.001)	0.9969	8.86
Cry	361	3.89×10^{-4} (0.09×10^{-4})	0.0163 (0.0005)	0.9992	4.24
	405	1.8×10^{-4} (0.1×10^{-4})	0.0205 (0.0003)	0.9976	4.76

[a] $n = 3$.

Resolution of Binary Mixtures. Two major assets of scanner monitoring are the abilities to use several wavelengths (almost simultaneously) and to determine individual analytes with differential spectra in mixture. The latter advantage was demonstrated with Cry and BaA, the emission spectra for which were sufficiently different for this purpose. The wavelengths used, 361 and 405 nm, were selected in order to boost differences between the analytes. BaA is not fluorescent at 361 nm, where Cry exhibits a maximum. The other wavelength used, 405 nm, where Cry is only slightly fluorescent, corresponds to the second maximum in the BaA spectrum. The scanner recordings previously obtained in order to characterize the individual determination methods were used for calibration. Calibration graphs were constructed from the areas under the extraction curves at the new wavelengths used. The slope, intercept, regression coefficient, and RSD for each analyte at each wavelength are listed in Table 4. The scatter values at 361 and 405 nm were 0.0159 (RSD = 1.09%) and 0.0204 (RSD = 2.46%), respectively. The intercepts of the calibration curves for Cry and BaA coincided with the scatter values at each wavelength. On the assumption of additivity of the analytical signals, the following equations were used to calculate the Cry and BaA contents in soil:

$$\mu\text{g of Cry} = \frac{A_1 - 0.016}{3.894 \times 10^{-4}} \quad (1)$$

$$\mu\text{g of BaA} = \frac{A_2 - (1.829 \times 10^{-4})m - 0.022}{5.178 \times 10^{-4}} \quad (2)$$

where A_1 and A_2 are the areas under the kinetic extraction curves

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Table 5. Resolution of Cry/BaA Binary Mixtures

Cry/BaA ratio in soil sample	amount spiked (μg)		amount found ± SD[a] (μg)		% recovery ± SD[a]	
	Cry	BaA	Cry	BaA	Cry	BaA
1:1	41.0	48.2	39 ± 7	48 ± 9	96 ± 16	89 ± 3
1:2	41.0	96.4	39 ± 4	93 ± 7	95 ± 10	97 ± 7
1:3	41.0	144.6	37 ± 4	138 ± 10	90 ± 9	95 ± 7
2:1	82.0	48.2	85 ± 9	50 ± 3	103 ± 11	103 ± 5
3:1	123.0	48.2	117 ± 12	49 ± 5	96 ± 9	102 ± 11

[a] $n = 3$.

at 361 and 405 nm, respectively, and m is the amount of Cry (in μg) calculated from eq 1.

The performance of the proposed method was evaluated by using it to resolve Cry/BaA binary mixtures in spiked soils. Variable ratios of Cry and BaA in soil from 1:3 to 3:1 were assayed. Table 5 lists the amounts of PAH added and found and the percent recoveries achieved. The last ranged from 89 to 103%, and the RSD was about 10% (3−16%).

Screening of Real Samples. The ability to detect PAHs in solid samples by using the proposed fiber-optic-interfaced system was tested by proccessing two real soils (soil powders R and J). Duplicate extractions for each soil (sample size 1 g) as described under SFE Procedure were monitored in the scanner mode. The emission spectra obtained for soils R and J and a nonpolluted soil, after 7 min of SFE, are shown in Figure 5A. The emission spectra for various PAHs are shown in Figure 5B for comparison. The maxima at 361, 383, and 400 nm suggest the presence of Cry, BaA, and BkF/BaP, respectively. Therefore, the system provides a fingerprint for the PAH mixture contained in the sample. There are usually too many PAHs in real samples to be determined individually by chemometric procedures. In addition, SFE is less efficient with real samples than with spiked ones, so use of a polar CO_2 cosolvent[18] or a higher extraction temperature[19] is mandatory in order to achieve quantitative extraction. In any case, the coupled SFE spectrofluorometer system is useful for screening purposes, as it allows qualitative and semiquantitative information to be directely obtained from the sample. For instance, the areas under the extraction curve at 400 nm were 0.204 ± 0.034 (SD) and 0.081 ± 0.002 (SD) in duplicate extractions of soils R and J. BkF and BaP were the two PAHs with the highest contributions to the fluorescence signal at 400 nm (particularly BkF, to which the method is more sensitive). The areas obtained from the calibration curve for BkF correspond to ~16 and 4 μg of BkF for soil R and J, respectively. These results are quite acceptable, taking into account that the extraction of real samples with pure SC-CO_2 at 40 °C is not quantitative.

CONCLUSIONS

The proposed fiber-optic interface is effective for on-line SFE monitoring. Qualitative and quantitative information from supercritical extracts can be obtained by using the coupled devices prior to depressurization and analyte collection. In addition to enabling on-line monitoring, the system provides a final liquid extract for subsequent chromatographic determination, if required. The proposed method for PAH screening in soils provides a fingerprint for the PAH mixture for positive samples, thus avoiding the need to chromatograph every negative extract in routine determinations. Binary mixtures of coextracted compounds were resolved by monitoring the supercritical extract at two different wavelengths. However, the system can be used to resolve more complex mixtures by chemometric computation of spectral data.

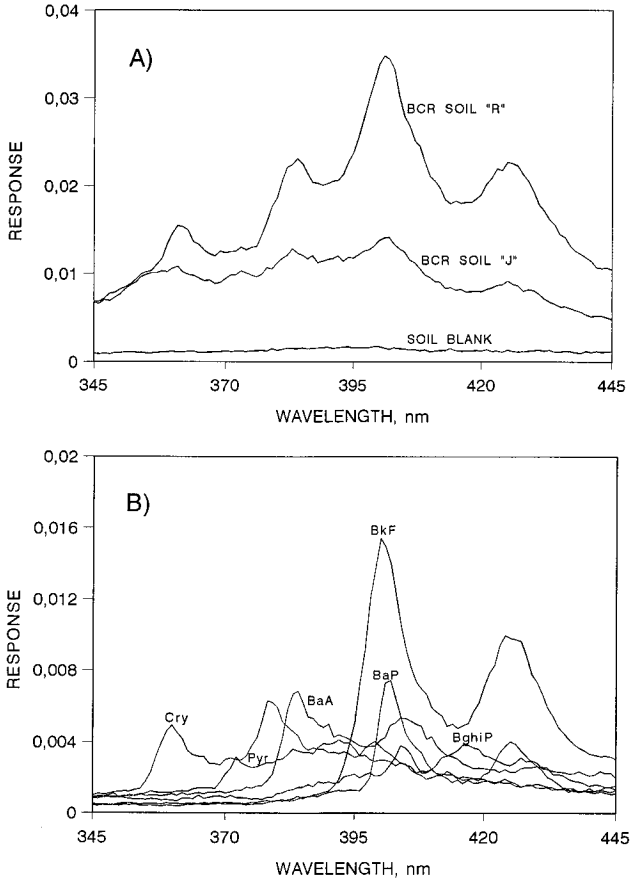

Figure 5. Screening of real samples (A) and PAH spectra for comparison and identification (B). Abbreviations are defined in the text.

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