

Short communication

Dynamic extraction in rotating coiled columns, a new approach to direct recovery of polycyclic aromatic hydrocarbons from soils

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Abstract

A new approach to the direct recovery of polycyclic aromatic hydrocarbons (PAHs) from environmental solid samples has been proposed. It has been shown that rotating coiled columns (RCCs) earlier used mainly in countercurrent chromatography can be successfully applied to the fast continuous-flow extraction of PAHs from soils. A particulate solid sample was retained in the rotating column as the stationary phase under the action of centrifugal forces while a mixture of organic solvents (acetone–cyclohexane, 1:1, v/v) was continuously pumped through. The separation procedure requires less than half an hour, complete automation being possible. No clean-up step is needed before the subsequent HPLC- analysis of extracts. Besides, the dynamic multistage extraction performed in the rotating column at room temperature and normal pressure may have nearly the same efficiency as accelerated batch solvent extraction repeated three times at 150 °C and 14 MPa. Contents of PAHs in extracts obtained by using both methods are in good agreement with the certified data on the PAHs concentrations in the soil samples. The use of appropriate “mild” solvents for the dynamic extraction in rotating columns may be very perspective for the simulation of naturally occurring processes and determination of environmentally-relevant forms of PAHs and other pollutants in environmental solids. A particular emphasis could be placed on time-resolved (kinetic) studies of the mobilization of toxicants in soil systems.

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1. Introduction

Organic contaminants, e.g. polycyclic aromatic hydrocarbons (PAHs), are widespread in the environment as a result of human activities. The fast and correct determination of these pollutants in soils, sediments and sewage sludge is a vital necessity for the environmental management. The extraction of analytes from solid samples remains the critical step in the analysis of contaminants. To evaluate an appropriate extraction method, the following important features should be taken into consideration: selectivity towards the components of interest, recoveries of analytes, volume of organic solvents needed, toxicity of solvents, extraction time, and number of clean-up steps required after extraction. Besides, extraction methods should be matrix-independent [1].

A series of extraction methods have been proposed for the recovery of PAHs. However, simple liquid–liquid extraction followed by adsorption chromatography is very laborious and requires several separation and clean-up steps [2]. Soxhlet extraction is always solvent and time consuming [3,4]. In most cases it yields crude extracts that need complex clean-up procedures. Automated Soxhlet extraction with ethyl acetate as solvent allows one to minimize the sample pre-treatment and reduce to some extent the clean-up steps [5]. Supercritical fluid extraction (SFE) employing carbon dioxide is less time consuming and in some cases allows one to separate PAHs from environmental solids with a satisfactory product yield [6,7]. This technique has gained acceptance and was applied in many laboratories [4,8–10]. In recent years other schemes for extracting PAHs have been also developed: subcritical water extraction [11,12], microwave-assisted extraction [13–15], pressurized liquid extraction (PLE; Dionex trade name: ASE for accelerated solvent extraction) [4,16,17], acid-induced cloud point

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extraction [1], hollow fiber membrane solvent microextraction [18], and solid phase microextraction [19]. All the enumerated methods have advantages and disadvantages. It should be noted that in most cases more or less laborious clean-up procedures are required before the instrumental determinations of PAHs in extracts.

In the present paper the potential of using rotating coiled columns (RCCs) for the direct recovery of PAHs from soils is discussed. So far, RCCs have been successfully applied in counter-current chromatography (CCC). The technique is based on the retention of one phase (stationary) of a two-phase liquid system in a RCC under the action of centrifugal forces while the other liquid phase (mobile) is being continuously pumped through [20]. Solutes are subjected to a partition process between two phases and eluted in order of their partition coefficients. A few devices providing retention of the stationary phase in the field of mass forces in the absence of a solid support have been suggested. Among the various possible designs, the planetary centrifuge retains the liquid stationary phase effectively and enables the fastest and most efficient separation to be achieved. A column (or a column unit) of a certain configuration rotates around its axis and simultaneously revolves around the central axis of the device with the aid of a planetary gear.

Recently it has been shown that RCCs can be used for the separation of both solutes and particles not only in liquid–liquid systems but in liquid–liquid–solid and liquid–solid systems as well [21–24]. A procedure has been developed for the fractionation of trace metals in soils. The sample of soil was retained in a rotating column as the stationary phase whereas aqueous solutions of complexing reagents, mineral acids and salts were used as mobile phase [23]. Some preliminary studies have demonstrated the possibility of the direct recovery of some polyaromatic hydrocarbons from a sewage sludge medium without any sample pre-treatment [24]. It has been revealed that heterogeneous samples can be successfully retained in the column. The liquid sewage sludge sample (being in fact a concentrated suspension) was the stationary phase in the column whereas organic solvents (heptane, dichloromethane) or their mixtures were used as mobile phase. It can be assumed that RCCs can be also attractive for the extraction of organic contaminants from environmental solids. In the present study the recovery of PAHs from a series of reference soil samples will be considered. The results obtained by use of RCCs and PLE (significantly advances in the last few years [25,26]) will be compared.

2. Experimental

2.1. Apparatus

The dynamic extraction of PAHs was performed on a planetary centrifuge with a vertical one-layer coiled column drum fabricated in the Institute of Spectrochemistry

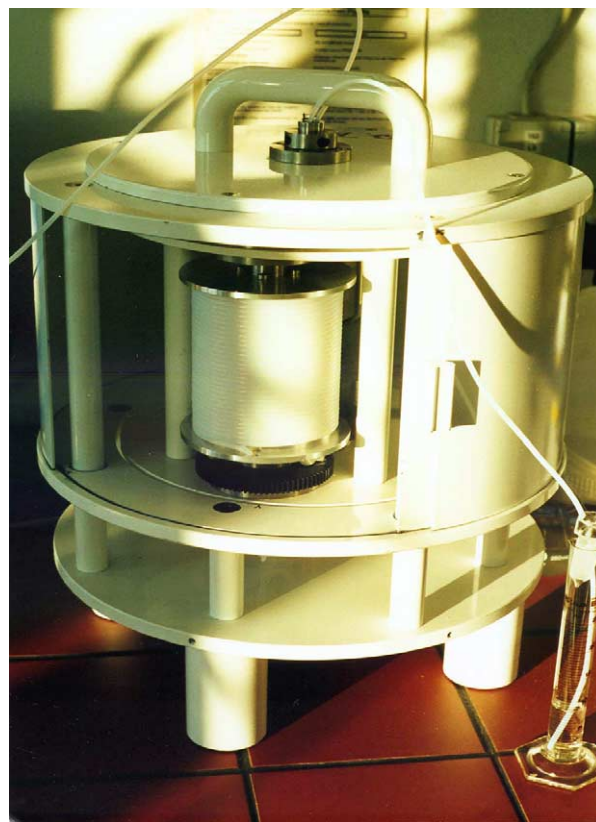


Fig. 1. Planetary centrifuge with a vertical column drum.

and Applied Spectroscopy (Dortmund, Germany). This prototype is presented in Fig. 1. The planetary centrifuge has a revolution radius $R = 140$ mm and a rotation radius $r = 50$ mm. The β value ($\beta = r/R$) is 0.36. Two axis of the instrument are parallel. The column was made of a PTFE tube with an inner diameter of 1.5 mm and the total inner capacity of the column was 20 ml (consequently, the tube length was about 10 m). The rotation and revolution speeds (ω) were 600 rpm. The mobile phase pumping rate (F) was 1 ml/min.

2.2. Samples and reagents

Acetonitrile (HPLC, Ultra Gradient Grade) and water were purchased from Baker. The PAH calibration mixture (10 μg of each compound per ml in acetonitrile) was delivered by Supelco. Concentrate solutions were prepared in acetonitrile. The PAH contaminated soils (A-990119, B-990140, and C-990128) were prepared for a round robin test by r-concept, Friedland, Germany. The certified values of the PAH concentrations including the confidence intervals are given in Table 1.

2.3. Dynamic extraction in RCCs

Before commencing the extraction procedure, the spiral column in the stationary mode was filled with the mobile

Table 1

Comparison of the data obtained by using a RCC, a simple extraction method (SE) and PLE (recovery of PAHs, mg/kg)

PAHs	A-990119				B-990140				C-990128			
	RCC	SE	PLE	C.V.*	RCC	SE	PLE	C.V.*	RCC	SE	PLE	C.V.*
Naphthalene	0.025	0.002	0.057	(0.064)	0.160	0.003	0.282	(0.126)	0.094	–	0.320	(0.203)
Acenaphthene	0.070	0.006	0.116	0.126 ± 0.088	0.116	0.010	0.146	0.169 ± 0.164	0.701	0.140	1.77	1.71 ± 1.39
Fluorene	0.073	0.021	0.297	0.251 ± 0.156	0.086	0.060	0.279	0.253 ± 0.228	0.355	0.22	1.40	1.51 ± 1.32
Phenanthrene	2.16	0.930	2.70	2.36 ± 1.17	3.85	1.65	3.63	3.04 ± 2.02	7.38	4.63	10.7	8.22 ± 5.06
Anthracene	0.192	0.182	0.474	0.400 ± 0.254	0.417	0.310	0.603	0.528 ± 0.390	0.671	0.520	2.00	1.59 ± 0.95
Fluoranthene	2.43	2.54	3.70	3.04 ± 1.83	6.54	5.24	7.22	5.89 ± 4.16	11.1	9.44	13.1	10.1 ± 5.78
Pyrene	1.66	1.47	2.46	2.06 ± 1.19	5.72	3.91	5.84	4.80 ± 3.52	8.56	6.19	10.5	8.01 ± 5.44
Benzo[a]anthracene	0.824	0.853	1.32	1.19 ± 0.53	2.05	1.66	2.48	2.29 ± 1.66	2.75	2.31	3.27	2.89 ± 1.53
Chrysene	1.10	1.32	1.18	1.09 ± 0.64	3.54	3.07	3.00	2.62 ± 2.01	4.33	3.84	4.39	3.39 ± 2.38
Benzo[b]fluoranthene	0.750	0.741	0.851	0.814 ± 0.490	2.79	2.13	2.52	2.52 ± 1.93	3.31	2.64	3.14	2.86 ± 1.61
Benzo[k]fluoranthene	0.375	0.436	0.516	0.501 ± 0.31	1.26	1.08	1.34	1.25 ± 1.01	1.73	1.34	1.62	1.33 ± 0.65
Benzo[a]pyrene	0.624	0.657	0.877	0.663 ± 0.398	2.71	2.05	2.80	2.35 ± 1.51	2.76	2.35	3.22	2.60 ± 1.24
Dibenz[a,h]anthracene	0.071	0.089	0.133	(0.268)	0.207	0.200	0.413	0.711 ± 1.30	0.326	0.230	0.43	0.64 ± 0.98
Benzo[ghi]perylene	0.686	0.685	0.673	0.419 ± 0.442	2.84	2.12	2.15	1.46 ± 1.51	2.33	2.45	2.48	1.51 ± 1.50
Indeno[1,2,3-cd]pyrene	0.719	0.752	0.683	0.488 ± 0.386	2.77	2.09	2.60	1.59 ± 1.17	2.73	2.37	2.80	1.54 ± 1.31
Σ15 PAHs	11.8	10.7	16.1	13.7 ± 4.5	35.1	25.5	35.3	29.6 ± 18.7	49.3	38.6	61.1	48.6 ± 15.8

* Certified values, $\alpha = 0.05$.

phase (acetone–cyclohexane, 1:1, v/v), after which the solid sample (about 0.5 g) was introduced into the column as a suspension in 10–12 ml of the same solvent mixture with the flow rate 10 ml/min, a peristaltic pump equipped with Tygon tubes stable in organic solvents being used. Then, while the column was rotated, the mobile phase (eluent) was continuously fed to the column inlet with the flow rate 1 ml/min. The solid sample was retained inside the rotating column as the stationary phase under the action of centrifugal force field throughout the experiment. The recovery of solutes in the effluent was controlled by UV spectrometry at 254 nm. Two fractions of the effluent (about 10 ml each) containing organic solutes were collected for the subsequent HPLC analysis. After the extraction procedure has been finished, the rotation was stopped and a residue of the solid sample was removed from the column. To clean up the column for the next run, 50 ml of water–ethanol (3:1, v/v) were pumped through it with the flow rate 10 ml/min.

2.4. Simple extraction procedure

A sample (0.5 g) was shaken in a test tube with 20 ml of acetone–cyclohexane (1:1, v/v) mixture during 20 min. The extract was filtrated, heated to dryness, and dissolved in 1 ml of acetonitrile.

2.5. PLE

The extractions were performed using a Dionex ASE 200 accelerated solvent extractor with 11 ml stainless-steel extraction cells. Solvent was acetone–cyclohexane (1:1; v/v). A system pressure of 14 MPa, an extraction time of 5 min (three times) and an oven temperature of 150 °C were chosen. The flush volume amounted up to 60% of the extraction

cell volume. The extracts were unified and subjected to a solvent exchange (acetonitrile) and homogenized by sonification. A further clean-up was not necessary.

2.6. Liquid chromatography–fluorimetry

For PAH analysis an HP 1050 system with a programmable fluorescence detector was used. The PAHs were separated on a LichroCART 250-3, Lithosphere PAH (5 μ m) column at a temperature of 20 °C. The conditions were as follows: acetonitrile (ACN) and water were used as mobile phase at a flow rate of 0.5 ml/min. The composition gradient started with ACN–water (1:1, v/v). Then, the ACN content was increased up to 60% (0–3 min) and afterwards up to 100% (3–14 min). This level was held constant for 23 min until the end of the run. The following excitation and emission wavelengths were programmed for detection: naphthalene (220/325 nm), acenaphthene, fluorene (237/315 nm), phenanthrene (244/360 nm), anthracene (252/372 nm), fluoranthene (237/376 nm), pyrene (237/385 nm), benzo[a]anthracene, chrysene (277/376 nm), benzo[b]fluoranthene (258/442 nm), benzo[k]fluoranthene, benzo[a]pyrene (255/420 nm), dibenz[a,h]anthracene, benzo[ghi]perylene (300/415 nm), and indeno[1,2,3-cd]pyrene (250/495 nm).

3. Results and discussion

3.1. Dynamic extraction of PAHs using rotating columns

Two fractions of the effluent (10 ml each) were collected for each soil sample in order to study the dynamics of the PAH recovery. All fractions are completely transparent and

contain no soil particles. Taken into consideration that the flow rate was 1 ml/min, the total contact time between the solid sample (stationary phase) and continuously renewed extractants (eluent) was about 20 min. Preparing the suspension and its introduction into the column usually takes less than 2 min. Hence, the time for the batch “pre-extraction” of PAHs at these stages is not of great importance. Total contents of 15 PAHs in the separated fractions (more precisely, recoveries of PAHs in mg per kg of the sample) are the following: 8.42 and 3.37, 30.1 and 5.02, 47.7 and 1.56 for samples A-990119, B-990140, C-990128, respectively. As

is seen, in all cases the greater contents of PAHs (71–97%) are recovered in the first fraction. Thus, a multistage extraction process occurring in RCC may be sufficiently effective to separate PAH from a solid sample within 10–15 min without any increase in pressure or temperature. However, this assumption should be proved by the data obtained by independent methods.

It should be also noted that not only the cyclohexane–acetone mixture, but other solvents or their mixtures can be applied as the mobile phase in the rotating column. Investigating the dynamics of PAHs extraction in different solvent

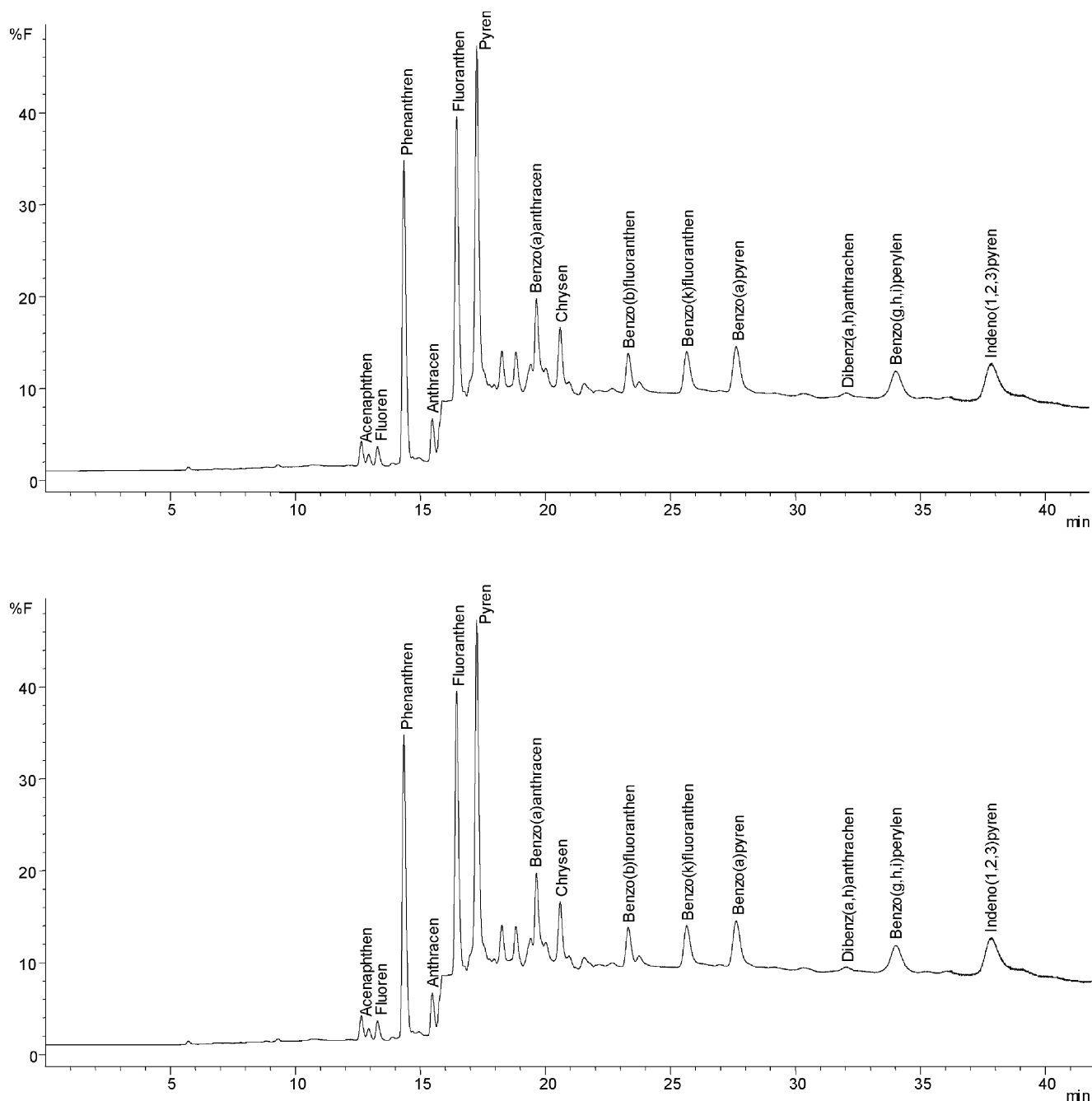


Fig. 2. HPLC chromatograms of extracts obtained from the soil sample C-990128 using RCC (above) and PLE (below).

systems may provide additional information on the mobility of PAHs in the soil matrix.

3.2. Comparison of simple shaking, PLE, and dynamic extraction in rotating columns

Contents of PAHs in extracts separated by using RCCs, simple extraction, and PLE are correlated in Table 1. For the extraction in RCC the sum of two fractions separated from each samples is given. For comparison, certified values are also presented. As is seen, for sample B-990140 the PLE and dynamic extraction in the rotating column result in the close recoveries of PAHs, whereas for samples A-990119 and C-990128 recoveries of PAHs are somewhat higher if PLE is used. Nevertheless, results obtained by both methods are in good agreement with the certified values. The data on simple extraction also fall within the wide confidence intervals of the certified values. However, in this case the recoveries of PAHs are rather low, especially for samples B-990140 and C-990128.

Hence, the efficiency of dynamic continuous-flow extraction in RCCs at room temperature and normal pressure is comparable to the efficiency of pressurized triple batch extraction at elevated temperature (150 °C, 14 MPa), the contact time between sample and liquid phase being practically the same (20 min and 3 min × 5 min, correspondingly). This may be explained in the following way. Since the powdered sample retained in the column is distributed along the all tube [27], the eluent being in contact with the solid phase is constantly renewed. First of all, a better efficiency of extraction can be observed due to this phenomenon. Besides, the solid sample pressed to the tube wall moves slightly forward and back along the tube because it is agitated to some extent under the action of the asymmetrical centrifugal force field and mobile phase (eluent) flow. This also may contribute to the extraction efficiency.

HPLC chromatograms of extracts obtained from sample C-990140 using a RCC and PLE are shown in Fig. 2. (In the case of RCC the chromatogram of the first fraction containing 97% of extractable PAHs is given). As it is seen from the figure, both chromatograms look quite similar though some peaks differ a little bit in height. It should be noted that the extract obtained in the RCC was used for the subsequent HPLC analysis (after the solvent exchange procedure) without any filtration, homogenization, or clean-up step. Nevertheless, the absence of these steps has no impact on the HPLC analysis.

4. Conclusions

Both procedures, continuous-flow extraction in a RCC and pressurized batch solvent extraction, can be successfully applied to the fast and efficient recovery of PAHs from soils. Procedures require almost the same time and similar volumes of organic solvents. No filtration, homogenization, or clean-up steps are needed for the extracts obtained in a RCC.

Dynamic extraction in a RCC should be further tested on the recovery of different organic contaminants not only from soils but also from sediments and sewage sludge.

Besides, it is of great importance not only to estimate the total concentrations of pollutants, but also to recover their environmentally-relevant forms. The use of appropriate “mild” solvents for the dynamic extraction in a RCC may be very attractive for the simulation of naturally occurring processes.

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