

The Possibilities and Limitations of Capillary Extraction (CEx): The Case Study of Polycyclic Aromatic Hydrocarbons (PAHs) in Clean-Water Samples



Capillary extraction (CEx) is used to study the solventless in-tube extraction of naphthalene, acenaphthene, phenanthrene, fluoranthene, chrysene, benzo(a)pyrene and coronene in aqueous samples prepared by analyte spiking into clean waters or, as an alternative, by using the generator–column method of sample preparation. Analysis of laden extractors is conveniently performed by high-resolution gas chromatography (GC), with a flame-ionization detector (FID). Extraction set-ups and main extraction variables are investigated from a practical point of view. For 2- to 4-ring polycyclic aromatic hydrocarbons (PAHs), equilibrium times are within a few minutes, analytical sensitivity is in the parts-per-billion (ppb) range and reproducibility is better than 10% relative standard deviation (RSD) ($n = 6$). Coronene behaviour is unique and presumably determined by extreme hydrophobicity and thus very negligible aqueous solubility: in-tube extraction of coronene seems possible only if starting from oversaturated samples. This is remarkably easier if the sample matrix is tap water, rather than $18.2 \text{ M}\Omega \times \text{cm}$ water. Long, thinly-coated apolar extractors and uncoated but deactivated ones may be especially sensitive towards benzo(a)pyrene.

The analytical determination of PAHs is important because they represent a serious health risk for both human beings and ecosystems (1–6). Liquid–liquid extraction (usually followed by a concentration step) is the sample preparation approach classically used to analyse PAHs in aqueous samples (7,8). Nowadays, solventless extraction–preconcentration techniques are being studied to reduce solvent use. Among these, solid-phase micro-extraction (SPME) (9–11) and stir-bar sorptive extraction (SBSE) (12,13) have been successfully applied to aqueous sample analysis of PAHs (12,14–18). Both techniques exploit the high affinity of polydimethylsiloxanes (PDMS) towards hydrophobic sub-

stances.

Under pure absorptive conditions (partitioning), the amount m_{Sil} of an analyte taken from an aqueous phase into a polysiloxane gum phase, is given at equilibrium by

$$m_{\text{Sil}} = K_{\text{Sil}} V_{\text{Sil}} V_w C_o / (K_{\text{Sil}} V_{\text{Sil}} + V_w) \quad [1]$$

where K_{Sil} (the ‘distribution constant’ C_{Sil}/C_w) is the ratio between analyte concentration in the water-immiscible silicone phase and that in the aqueous phase at equilibrium; V_{Sil} and V_w are the volumes of PDMS and aqueous sample, respectively, C_o is the initial analyte concentration in water.

When headspaces and/or adsorptive losses are not negligible, the distribution

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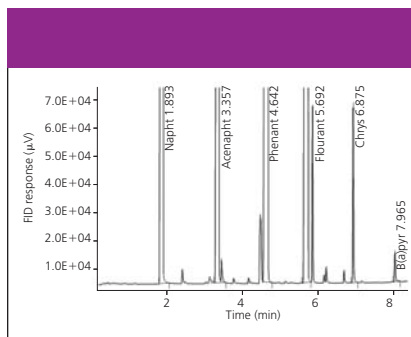


Figure 1: Overlay of two CEEx runs performed with a 260 cm \times 0.325 mm i.d. persilylated (DPTMDS) but uncoated capillary extractor. Sample: effluent coming from the generator columns tandem system; Sample volumes: 24 mL at 0.5 mL min⁻¹ in one case; 40 mL at 1 mL min⁻¹ in the second one. The approximate analyte concentrations estimated on the base of PAHs solubilities at 25 °C were: naphthalene (3×10^4 ppb), acenaphthene (4×10^3 ppb), phenanthrene (1×10^3 ppb), fluoranthene (2×10^2 ppb), chrysene (2 ppb), benzo(a)pyrene (4 ppb). Coronene went undetected. Note that both extractions reached equilibrium (as testified by the superimposable chromatograms) notwithstanding CEEx conditions differed substantially both concerning sample volume and sample flow-rate.

constant is given by

$$K_{sil} = (m_{sil} / V_{sil}) / (m_w^0 - m_{sil} - m_h - m_a) / V_w \quad [2]$$

in which m_w^0 is the initial analyte amount in water and m_h and m_a are the analyte amounts migrated into every available headspace and/or lost by adsorption, respectively.

Though a good correlation between octanol-water (K_{ow}) and PDMS-water distribution constants may generally be found for several organic compounds, such a correlation fails with very hydrophobic molecules such as highly chlorinated PCBs (19–26) or high-ring PAHs (Table I). In such instances the extractive behavior of PDMS gums may not be purely absorptive (i.e., “liquid-like”) and hence Equations 1 and 2, as such, cannot be applied.

Although capillary extraction (CEEx) (27) shares the same extraction principles with SPME and SBSE, these three techniques are clearly complementary to each other (27–32). For example, SPME and SBSE have slower extraction kinetics than CEEx (27,28,32). In addition, they are characterized by reduced accuracies with analytes whose volatility is either very high or very low (16,17) whereas CEEx is more accurate during the analyte GC

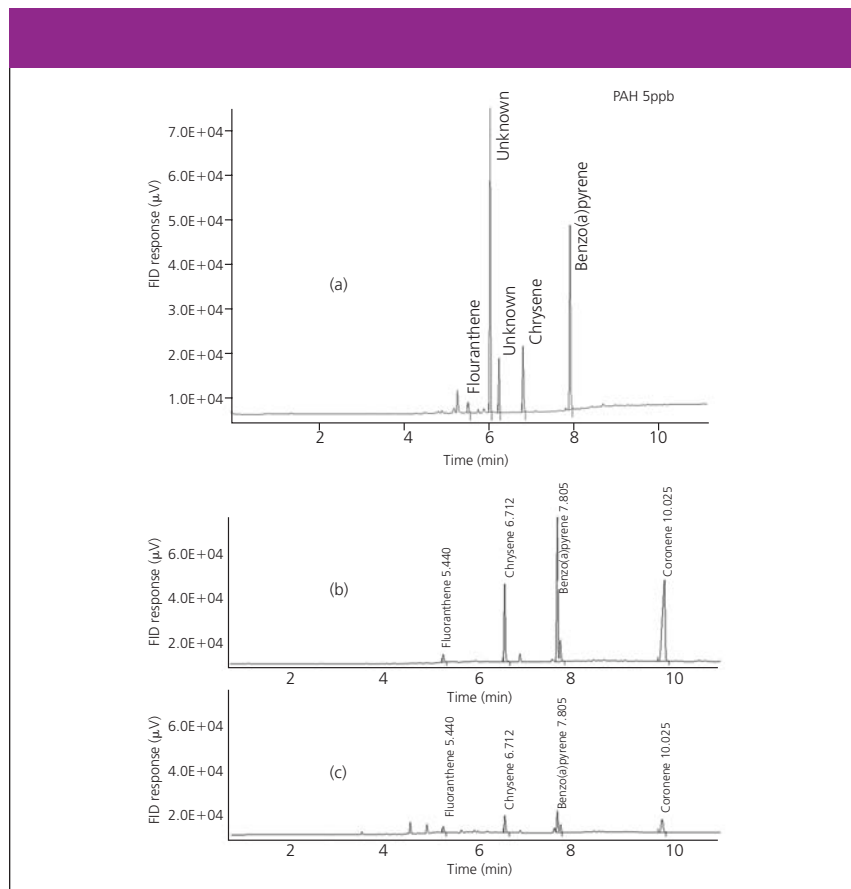


Figure 2: Extraction performance of an uncoated, deactivated capillary extractor 60 cm long \times 0.32 mm i.d., persilylated with HMDS/DPTMDS 1:1. (a) Sample: 21.5 mL of very pure water spiked with 5 ppb of PAHs (nominal coronene level). Extraction time: 5 min. Detection limits (3σ) of fluoranthene, chrysene and benzo(a)pyrene were 0.3 ppb, 0.08 ppb and 0.03 ppb, respectively. Coronene went undetected. (b) Sample: 10 ppb of PAHs in tap water. Extraction set-up: 23 mL of sample, recycled between DQP-1 pump and capillary extractor for 53 min at 3.8 mL min⁻¹. GC detection limits (3σ) were 0.12 ppb for chrysene, 0.04 ppb for benzo(a)pyrene and 0.09 ppb for coronene. Here coronene neatly overloaded the HRGC column. (c) 10 ppb of PAHs in tap water. Extraction set-up: Double syringe (Sec. 2.8) using just 2 mL of sample cycled 5 times (10 passages) through the extractor; Extraction time: less than 3 min.

injection step (27).

Without doubt, SBSE is the most sensitive technique because of a larger PDMS volume involved (25–200 μ L, in comparison with \sim 0.5–1 μ L used in SPME or 0.1–0.01 μ L employed in CEEx). However, this also implies substantial carryover risks. Interestingly, carryover is inherently null when using CEEx (because of sound modalities of analyte injection (27) used during analyte separation by GC) so the analytical possibilities of CEEx towards PAHs are worth studying.



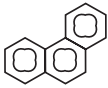
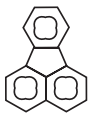
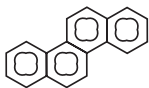
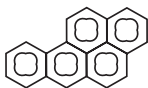

This article explores the performance of CEEx for the extraction–preconcentration and subsequent gas chromatographic analysis of seven PAHs covering a wide range of physicochemical properties (from naphthalene to coronene). PAH water

samples were prepared by fortifying simple matrices (some purified waters or otherwise tap water) thus allowing better confidence in the results of the work.

Experimental

Target analytes: Acenaphthene, phenanthrene, fluoranthene, chrysene, and benzo(a)pyrene were supplied by Supelco (PAH Kit 610-N, Supelco Inc., Bellefonte, Pennsylvania). Naphthalene was recrystallized (ethanol) from naphthalene for scintillation counting (Merck, Darmstadt, Germany). Coronene source was the BCR 388 standard reference material obtained from the Community Bureau of Reference, Brussels, Belgium. All PAHs were of + 99% purity, except chrysene,

Table I: Chemical structure solubility and some partition data of the selected PAHs.

		Water solubility ^a (mg/L)	Log K_{ow} ^a	Log K_{sil} (100 mm SPME fibre)	Log K_{sil} (7 mm SPME fibre)
Naphthalene		32	3.4	2.85 ^d 3.01 ^d 3.02 ^d	2.73 ^d
Acenaphthene		3.94	3.9	3.63 ^d	na
Phenanthrene		1.29	4.6	3.41 ^b 3.45 ^c 3.96 ^d	3.25 ^c 3.96 ^d 4.42 ^d
Fluoranthene		0.26	5.2	3.79 ^c 4.11 ^d 4.71 ^d	3.72 ^c 4.37 ^d
Chrysene		0.0020	5.9	3.97 ^d 5.69 ^d	4.72 ^d
B(a)pyrene		0.0038	6.5	3.47 4.14 ^c 5.39 ^d 4.86 ^d	4.66 ^c 4.27 ^d
Coronene		0.000114	na ^b	na	na

(a) Data from reference 44; 25 °C, (b) na 5 not available, (c) Reference 18, (d) Reference 20.

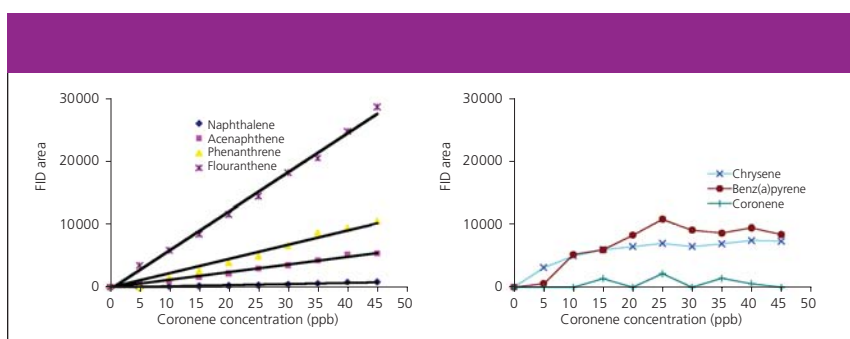


Figure 3: Linearity results of the PAH analysis by CEx-HRGC. Abscissa refers to nominal amounts of coronene, which spanned from 5 to 45 $\mu\text{g/L}$ (other PAHs were at the same molarity).

which was 93% pure.

PAH stock solutions: A few milligrams of each PAH were weighed (± 0.01 mg) separately in screw-cap glass vials that were reweighed after addition of a couple of millilitres of methanol, or isopropanol or tetrahydrofuran (THF); the vials were immediately capped and manually shaken

to solubilize the PAH crystals. The single-standard solutions were combined in a mixture that was aimed to contain 10^{-4} mol L^{-1} of every PAH, such as naphthalene (13 mg L^{-1}), acenaphthene (15 mg L^{-1}), phenanthrene (17 mg L^{-1}), fluoranthene (20 mg L^{-1}), chrysene (23 mg L^{-1}), benzo(a)pyrene (25 mg L^{-1}),

and coronene (30 mg L^{-1}). This mixture was aliquoted into several glass ampules that were sealed by fusion and stored in the laboratory refrigerator at 4 °C.

Aqueous PAH samples: Aqueous samples were prepared by two different approaches: (a) the classical “spiking” method and (b) the generator column one (39).

(a) Calculated amounts of the 10^{-4} mol L^{-1} PAH solution (see above) were added with a microsyringe into the intended volumes of matrix water kept under lively magnetic stirring. Sample containers, which were made of unsilanized glass, were rinsed in advance with plenty of the PAH solutions they were going to contain.

(b) Weighed amounts of solid PAHs [naphthalene (101.0 mg), acenaphthene (61.0 mg), phenanthrene (45.0 mg), fluoranthene (53.0 mg), chrysene (14.0 mg),

Table II: PAH peak heights resulting from each one of six serially connected capillary extractors of identical size.^a

Extractor no.	Naphthalene	Acenaphthene	Phenanthrene	Fluoranthene	Chrysene	B(a)pyrene
1	118	1050	1677	7530	8450	20235
2	105	965	1547	7426	8651	21218
3	73 (outlier)	918	1415	7519	8759	21422
4	114	1025	1712	7820	9396	24158
5	98	1073	1693	7855	9617	25099
6	106	1030	1681	7483	8885	25252
Average	102	1010	1621	7606	8960	22897
%RSD	7.0	5.7	7.2	2.4	5.1	9.6

a) 10 cm \times 0.2 i.d \times $d_f = 0.3 \mu\text{m}$ PS255. Extractors in the chain were connected with very short pieces of 0.32 mm i.d fused silica tube. Sample: 23 mL of 10 ppb PAHs in tap water; 20 min sample recycling, 3.8 mL min^{-1} , DQP-1 pump

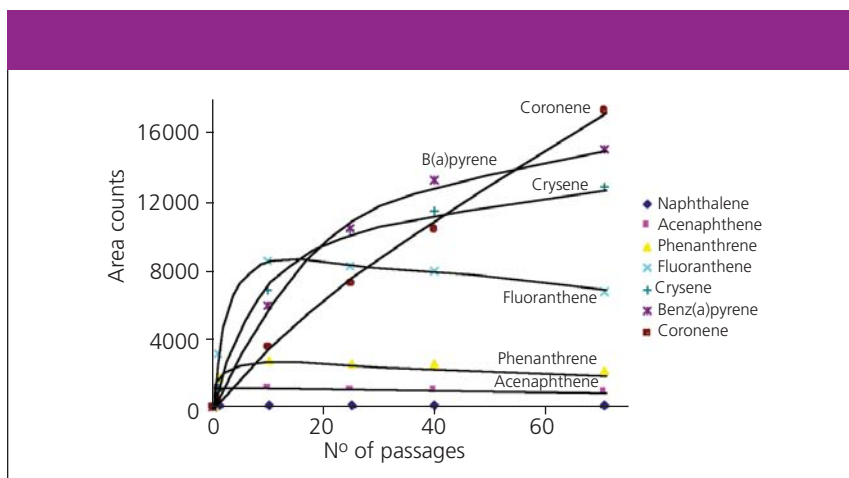


Figure 4: PAH-extracted amounts vs. number of sample crossings through a PS255-coated capillary extractor, which was 10 cm long \times 0.21 mm i.d. \times $d_f = 0.3 \mu\text{m}$. Sample: 2 mL of tap water spiked at 5 ppb. Extractant amount: 0.020 μL . Data points were acquired for 1, 10, 25, 40 and 71 passages of the sample through the extractor. Sample was renewed after each extraction; Contact times were, respectively, 0.2, 2.5, 5.2, 8.5 and 16 min.

benzo(a)pyrene (8.0 mg), coronene (1.30 mg)] were dissolved in a few millilitres of dichloromethane and the resulting solution was evaporated on to non-porous alumina powder (3.5 g, density 3.6 g mL^{-1} , 100–200 mesh). The resulting free-flowing powder was dry-packed into a Hibar stainless steel tube 30 cm \times 0.4 cm i.d., carrying 1/16in. end fittings and 2 μm stainless steel frits (Merck, Darmstadt, Germany). A second Hibar generator column, which was conceived to avoid an early naphthalene depletion, was made essentially in the same manner except that it contained substantially more naphthalene (570 mg).

A steady flow of a nearly-saturated aqueous solution of the seven target PAHs was prepared by pumping the water matrix at 0.5–1 mL min^{-1} (by a HPLC pump) through the tandem system made up with the two generator columns just described, connected in series. The tandem system provided plenty of freshly prepared PAH-saturated water, the com-

position of which was, within the variability of laboratory temperature ($\pm 2 \text{ }^\circ\text{C}$), constant for all practical purposes.

Water matrices: Three kinds of clean waters were used as matrices:

- “pure” water coming from an age-old MilliQ water purification system (Millipore SA, France)
- pure water with a resistivity of 18.2 $\text{M}\Omega \times \text{cm}$, provided by a recently bought MilliQ Gradient purification system (Millipore SpA, Milan, Italy)
- tap water from the laboratory faucet, having a specific conductivity of about 350 $\mu\text{S cm}^{-1}$ at 25 $^\circ\text{C}$.

Stir-bars: For sample mixing, several home-made glass-coated stir-bars of convenient small sizes (1–2 cm long, 1–3 mm as external diameter) were used. Glass-coated stirrers were preferred to polytetrafluoroethylene (PTFE) ones to reduce PAH losses and memory effects (15,22,33). Magnetic stirring was not needed to perform CEx experiments but only required in the preparation of the

aqueous samples by the PAH-spiking method.

Sample delivering methods: The intimate contact between (in-tube) moving aqueous samples and stationary extractant layers was obtained using three options:

- **Syringe squeeze method:** Sample was “squeezed” manually through a capillary extractor (or an extractor stack — see below) with a single syringe or by placing the extractor between two identical syringes operated alternatively (“double-syringe” set-up) (31). Syringes (SGE Scientific Pty, Melbourne, Australia) had glass bodies, PTFE-tip plungers, metal needles and volume capacities which spanned from 2 to 5 mL. In order to be connected easily with capillary extractors each syringe under use required its own fused silica transfer-line (27).
 - **Pump method:** Sample was delivered towards capillary extractor(s) either by means of a single head DQP1 piston pump (Dionex Corp., Sunnyvale, California), or using a double head APM-2 piston pump (also from Dionex). The flow path of these pumps included some PTFE tube, the removal of which was impracticable.
 - **Gas pressurization:** Capillary extractor(s) were fed with sample by using the hand-regulated pushing action of helium gas at 0.1–5 kg cm^{-2} . A Sovirel screw-cap glass vial of 30 mL capacity was the sample vessel; it was externally covered with adhesive tape to avoid the possibility of flying splinters should the glass rupture. Two leak-proof holes made in the vial cap allowed for gas pressurization and simultaneous sample delivering through a 50 cm piece of 0.32 mm i.d. raw fused silica tube.
- Salting-out recipe:** Increasing amounts (0.19–0.38–0.59–0.80–0.97 g) of reagent

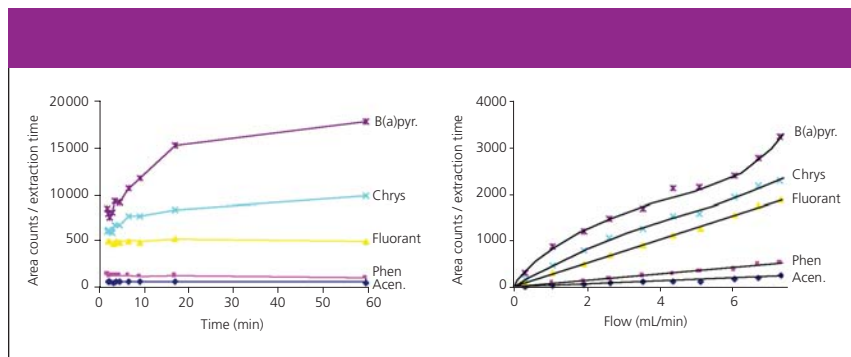


Figure 5: Influence of sample flow-rate on CEx of PAHs. An aqueous PAH sample at 5 ppb in pure water was delivered by gas pressure into a 10 cm \times 0.21 mm i.d. \times $d_f = 0.30 \mu\text{m}$ PS255 capillary extractor. Left graph: Absolute detector response vs. sampling time. Right graph: Extraction speed (total FID response divided by extraction time) vs. sampling flow-rate. Sample: PAHs solution at $5 \mu\text{g L}^{-1}$ in pure water. Capillary extractor: 10 cm long \times 0.21 mm i.d. \times $d_f = 0.3 \mu\text{m}$ PS255. Sample aliquots (19 mL) were delivered at a constant pressure until the selected sample amount had crossed the extractor. Contact time was varied from 60 to about 2.6 min (so that flow-rate was varied from 0.32 to 7.31 mL min^{-1}) by adjusting the gas pressure in the range 0.5 to 5.1 kg cm^{-2} .

grade sodium chloride (purity + 99.5%, Riedel-de Haën, Seelze, Germany) were weighed into 4 mL screw-cap vials. Matrix water (3.50 mL) was added to each vial that was presently sealed. Magnetic stirring assured rapid salt dissolution. By means of a micro-syringe, $1.2 \mu\text{L}$ of the $10^{-4} \text{ mol L}^{-1}$ PAH stock solution

was added to each vial below the surface of the stirred liquid. Extractions were then performed on 2 mL of these solutions ($10 \mu\text{g L}^{-1}$ coronene nominal concentration), using the double-syringe set-up described above.

Capillary extractors: Uncoated but deactivated extractors: Duran raw-glass

capillaries of various inner diameters (0.2–0.3 mm) and lengths between 5 and 30 m were leached with 20% HCl, rinsed with 0.5% HCl, dried under vacuum at $250 \text{ }^\circ\text{C}$ and then persilylated at $400 \text{ }^\circ\text{C}$ with hexamethyldisilazane (HMDS), diphenyltetramethyldisilazane (DPT-MDS) or their 1:1 v/v mixture.³⁴ Finally, uncoated but deactivated extractors were easily obtained by trimming off the coiled hanks of persilylated capillaries and by moulding extractor ends like press-fits (27,35,36).

- **Coated extractors:** Fabrication details of coated capillary extractors can be found elsewhere (27). Briefly, they were made by trimming off glass HRGC columns prepared by static coating (34) of polydimethylsiloxane gum PS255 (1% vinyl groups) or OV17 (50% phenyl) polyphenylmethylsiloxane stationary phases (Fluka, Italy) into Duran borosilicate glass capillaries. After polysiloxane immobilization by dicumylperoxide crosslinking and thermal conditioning at $330 \text{ }^\circ\text{C}$, plenty of new extractors of usual lengths (10–20 cm) could be

prepared simply by trimming short pieces from the newly prepared hanks and moulding the ends of these pieces like press-fits (27).

- **Snaked extractors:** Such extractors were prepared starting from some of the aforementioned coated extractors that were put under slow helium flow and subjected to a localized but quick glassblowing action (within the tiniest alcohol flame). About 40 bends were made that were 5–6 mm apart from each other. As soon as a brief conditioning at 330 °C under inert gas flow was performed the newly prepared snaked extractors were ready for use.

CEx modalities for the PAH linearity

check: 2 mL aliquots of aqueous PAHs solutions (in tap water) with nominal coronene concentrations from 5 to 45 $\mu\text{g L}^{-1}$ were extracted using a PS255 coated capillary extractor 10 cm \times 0.21 mm i.d. \times $d_f = 0.30 \mu\text{m}$ mounted according to the double syringe set-up. Each sample required 2 min to pass 10 times (i.e., 5 cycles) through the extractor. Regression lines were plotted using average data from duplicate extractions.

GC analysis: Analyte separations were performed by manually mounting each PAH-laden capillary extractor as a precolumn (28) into the oven of a PerkinElmer 8500 gas chromatograph provided with a PS255 glass capillary column that was 10 m long \times 0.21 mm i.d. \times $d_f = 0.30 \mu\text{m}$. FID temperature was 350 °C. No GC injector hardware was required (see below); this advantage is peculiar of the CEx technique independently of analyte volatility (27) The carrier gas was electrolytic hydrogen delivered at a constant pressure of 14 psig. Borwin software (Jasco SpA, Como, Italy) was employed both to acquire the detector signal (at a sampling rate of 10 Hz) and to review the chromatographic data.

Before GC elution, the laden capillary extractors were drained from the aqueous sample excess which was filling the capillary hold-up volume (it was sufficient to keep each extractor vertically while touching its lower end onto kimwipe paper, though longer extractors required a slow-sucking peristaltic pump). Finally, each laden extractor was mounted in the same way as a precolumn (28) and GC analysis performed by starting the following oven temperature programme: 80 °C for 0.4

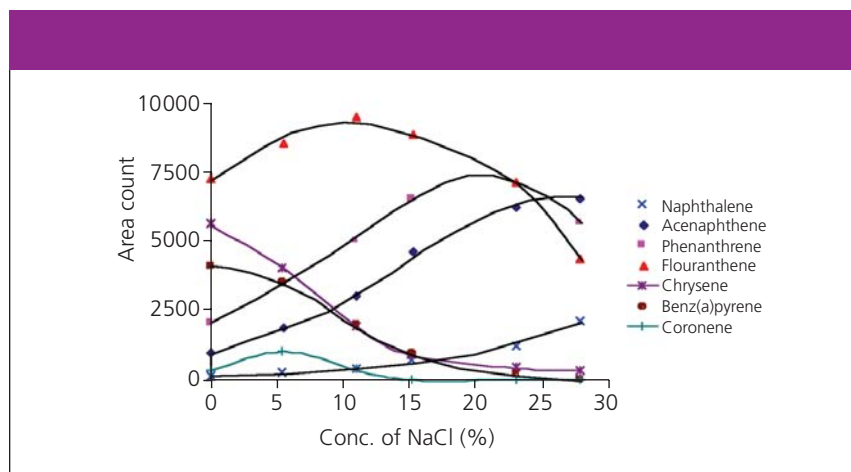


Figure 6: Effect of NaCl concentration (% w/v) on PAHs extraction by CEx. Experimental set-up: double-syringe, 10 passages of salted samples through a capillary extractor 10 cm long \times 0.21 mm i.d. \times $d_f = 0.3 \mu\text{m}$ PS255. Sample volume: 2 mL. Extraction time: ~2.5 min.

min; 30 °C min^{-1} up to 320 °C, final hold of 3 min. Total run time was 11.4 min.

Results and Discussion

Analysis of PAHs by “immersion SPME”-FID provides detection limits in the ppb-ppt range (9,21,37) with 10–20% RSD precision. Equilibration times of high-ring PAHs are, however, rather long (10,19,20,38) compared with the aqueous samples ageing rate (8,39). Possibility of leaks out of sample containers and adsorption onto their walls, interphase transfers, biodegradation, all suggest that sample preparations of aqueous samples are recommended to be completed in the shortest time. Even headspace-SPME (38,40) is not rapid enough for high-ring PAHs.

CEx may reduce both extraction equilibrium time and sample volume constraints in comparison with its sister techniques (42) by the use of very thin extractant films (0.01–1 μm). In this way, sample-to-extractant volume ratios of about 10^5 – 10^6 may be commonly employed (41).

The concept of PAH preconcentration from aqueous samples by using nothing more than a HRGC column was pioneered about 15 years ago by Kaiser and Rieder (43). They used the whole capillary GC column normally devoted to GC analyses both to extract and thereafter to separate the extracted substances by high resolution gas chromatography (HRGC) with FID detection. That procedure, though achieving parts-per-trillion sensi-

tivity, required uncommon skill and prolonged contact between the main GC column and the aqueous samples under examination. Conversely, in the CEx approach, GC analytical columns are not exposed to any liquid water contact, which only involves capillary extractors.

Extractor functioning and peculiarity of coronene behavior: PDMS extracts PAHs by non-specific interactions (namely dispersion and induction forces) that can be very easily broken (e.g., by rise of temperature) because of the low surface tension of PDMS (only $21.5 \cdot 10^{-3} \text{ J m}^{-2}$) (45).

Although thin-film apolar capillary extractors had a residual hydrogen-bonding activity toward basic solutes (28), which usually increased somewhat with use, no significant degradation of CEx–GC performance concerning PAHs was noticed during this study: the capillaries were reused with success independently from their size or film thickness, so capillary extractors’ reusability was appreciated throughout the study.

Similarly to SPME or SBSE, the static liquid layer adhering to the internal wall of capillary extractors opposes a diffusion resistance to analyte mass-transport (46–48) which is lower the higher the velocity (i.e., the flow-rate) of the moving liquid sample. At high flows, the resistance to diffusion into the silicone extractant (33,49,50) may be a main limiting factor of analyte transport.

In general, however, to raise the speed of extraction, PDMS film thickness should be as thin as possible. The thinnest

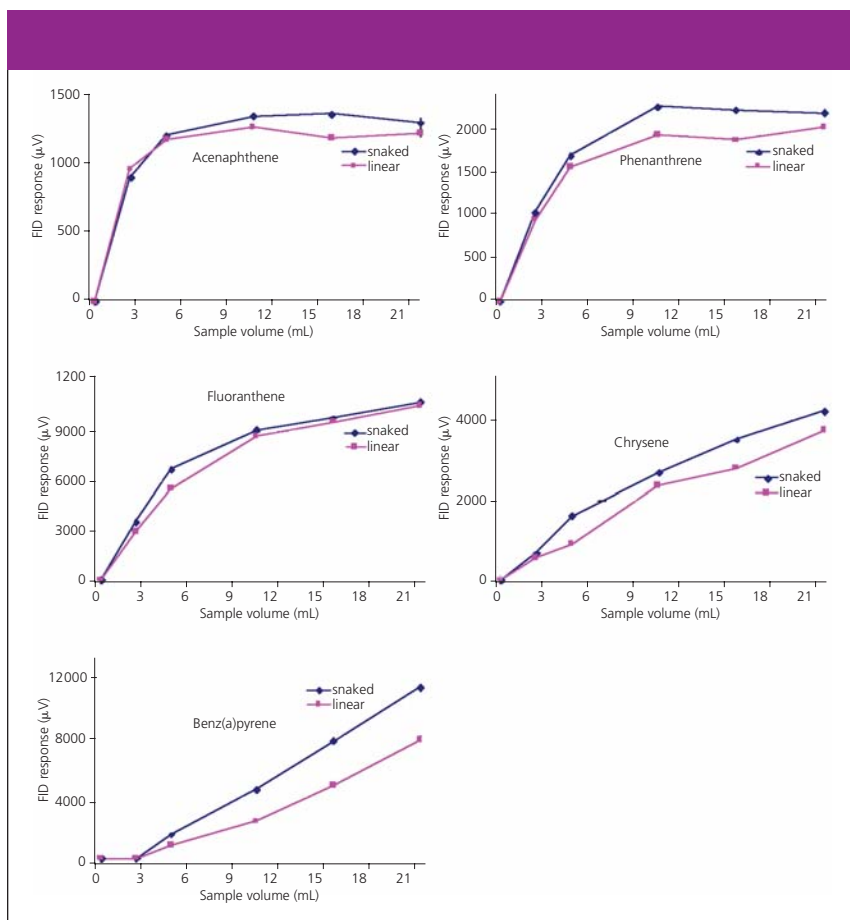


Figure 7: Effect of radial flow on CEx performance. Extraction-volume profiles obtained by using two 55 cm \times 0.21 mm i.d. \times $d_f = 0.048$ μm capillary extractors (a "linear" plus a snaked one) which were connected in series with the snaked extractor down-stream to the linear one. Sample: aqueous PAHs at 10 mg L⁻¹. Flow-rate: 7.5 mL min⁻¹ (APM-2 pump). Each point of the graphs was obtained by stopping the flow just after the wanted sample volume had been delivered, hence any data point represents a distinct CEx experiment.

conceivable apolar films are produced by persilanization (34) and indeed the extraction speed afforded by persilanized capillaries was very high. The example reported in Figure 1 refers to two CEx–GC analyses performed on different portions (24 and 40 mL) of a sample prepared with the PAH generator columns tandem system described above. Here, the excellent qualitative and quantitative agreement of the overlaid chromatograms testifies these extractions had reached full equilibrium. Chrysene and benzo(a)pyrene were sensitively detected (their concentrations in the sample were 2 ppb and 4 ppb, respectively) but coronene went undetected, as usual in samples prepared by the generator column method. Coronene behavior, however, was different when CEx was performed on samples prepared by spiking.

Figure 2 refers to one of these cases. Here a persilanized capillary was used to

extract a diluted PAH sample prepared either in very pure water (run 'a') or in tap water (runs 'b' and 'c'). As recurrently observed, the extraction of coronene was much easier when the matrix medium was tap water rather than the highest purity (MilliQ) water. Since coronene extraction was never obtained using those samples prepared with the generator column method (a situation which ruled out the possibility of finding suspended coronene crystals in resulting samples), the author believes that coronene bewildering behavior in spiked samples was caused by the adsorption of coronene microcrystals onto the internal walls of apolar capillary extractors. Certainly the subject would deserve further studies.

Among the different matrix waters evaluated, the one obtained from the age-old MilliQ system was spoiled with traces of organic solvents as well as phthalates and hence it was used only for comparison

purposes. Thus the matrices most often used were either tap water (which somehow made coronene extraction possible, as seen in Figure 2) or otherwise very pure deionized water (in which coronene extraction was in general extremely difficult).

CEx linearity trial: Paying attention to the behavior of the less soluble PAHs (see above) the CEx linearity experiments were done on water samples prepared by PAH spiking. A multipoint calibration was performed between 5 and 45 $\mu\text{g L}^{-1}$ using 2 mL sample aliquots, the double-syringe set-up and a PS255-coated capillary extractor 10 cm \times 0.21 mm i.d. \times $d_f = 0.3$ μm (thus containing 0.020 μL of the extractant). The overall contact time for every CEx experiment (5 cycle, i.e., 10 sample passages through the capillary) was 100 ± 5 s.

Calculated 3σ detection limits in units of $\mu\text{g L}^{-1}$ were naphthalene (8.5), acenaphthene (1.8), phenanthrene (1.1), fluoranthene (0.40), chrysene (2.1), and coronene (~ 40). Figure 3 summarizes the calibration results both for low-ring PAHs and high-ring PAHs (right diagram). The linear correlation coefficient (r^2) for naphthalene was 0.954 while it was 0.991, 0.970 and 0.995 for acenaphthene, phenanthrene and fluoranthene, respectively. Chrysene, benzo(a)pyrene and coronene nominal concentrations were clearly above their solubility limit. Note that despite a very short extraction time and troubles caused by oversaturation, analytical sensitivity (FID detection) was easily at low ppb levels.

PAH absorption profiles: The study of PAH extraction profiles was of obvious interest. A 5 ppb PAH sample in tap water was cycled for an increasing number of times between master and slave syringes (same extractor and set-up as used for the linearity trial). The CEx extraction profiles are reported in Figure 4. Fluoranthene and the lighter PAHs reached extraction equilibrium within 10 passages (i.e., in less than 2.5 min); the trends of extracted amounts passed through a maximum and then lowered down slightly (an effect caused by unwanted but unavoidable analytes' losses onto syringes, transfer-lines etc.). Even if a single sample passage was unable to extract coronene significantly, within 60 crossings it was the most extracted PAH. The (almost) lin-

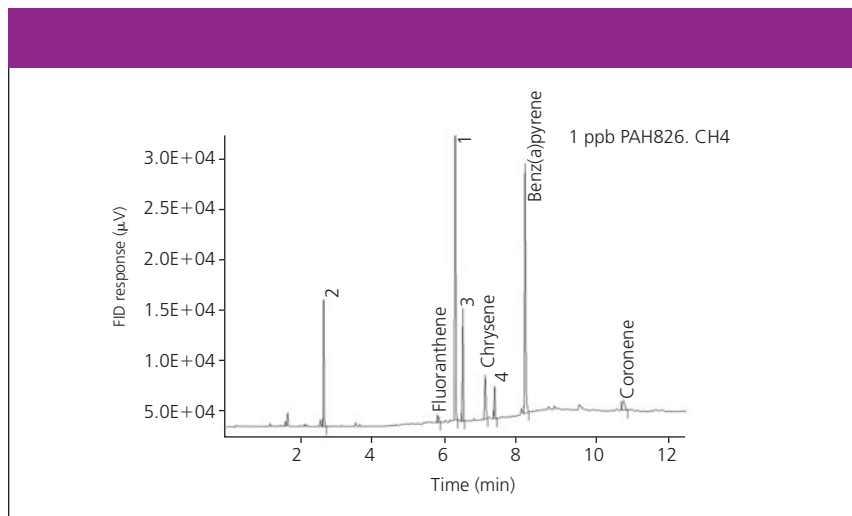


Figure 8: CEx results obtained using a PS255 extractor, 200 cm long \times 0.18 mm i.d. \times $d_f = 0.010 \mu\text{m}$. Sample: 20 mL of water spiked with PAH at 1 ppb. Set-up: pressurized vial (5 bar).

columns (33).

Flow-rate effects: Sample flow-rate has in CEx the same role that sample stirring has in SPME (40) so a meaningful impact of sample flow-rate on the extraction yields of PAHs was indeed expected. It was, however, noted that the effect of flow-rate was better understood by using the pressurized glass vial described above rather than by means of mechanical piston pumps; that is because sample integrity with time was better retained with the former approach. The left graph of Figure 5 shows the resulting extraction profiles of target analytes: fluoranthene and the lighter PAHs reached extraction equilibrium within 2.5 minutes, while both chrysene and benzo(a)pyrene required roughly 17 min to approach it substantially. As expected, the extraction speeds (right graph) increased almost linearly as the static liquid layer became thinner at higher sample flows. Both naphthalene and coronene were undetected: the former owing to a low K_{Si} , the latter because of its very negligible solubility in water (the probable presence of solid particles caused by oversaturation deviated

ear extraction profile of coronene suggests that (a) the sample was coronene-oversaturated and (b) the PDMS coating might have been crowded with coronene microcrystals physically adsorbed onto it.

Very similar qualitative profiles and even faster extraction kinetics were obtained by capillary extractors coated

with thinner films. In particular, a PS255 extractor carrying a 0.048 film was able to reach extraction equilibrium for naphthalene, acenaphthene and phenanthrene within a single passage (34 s). This extraction speed is remarkably high in comparison with SPME, SBSE or the extraction approach, which uses packed-PDMS

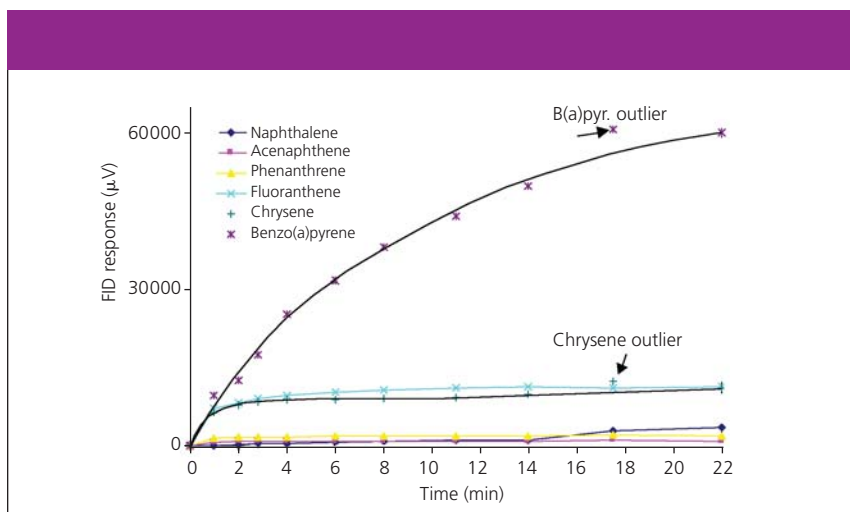


Figure 9: Extraction profile obtained using a capillary extractor containing only 12 nL of PS255. The extractor was 2 m long \times 0.18 mm i.d., $d_f = 0.01 \mu\text{m}$. Sample: aqueous PAHs at 10 mg L^{-1} in MilliQ Gradient water. Flow-rate: 4.13 mL min^{-1} (APM-2 pump).

the extractions away from simple partition principles).

OV-17 versus PS255 extractant: To test if a change in the aromatic character of the silicone coating would have had a promising effect on the CEx of PAHs, the performance of a $10 \text{ cm} \times 0.21 \text{ mm i.d.} \times d_f = 0.3 \mu\text{m}$ capillary extractor, containing $0.022 \mu\text{L}$ of PS255, was compared with that of a OV17 extractor ($13 \text{ cm} \times 0.24 \text{ mm i.d.} \times d_f = 0.15 \mu\text{m}$) containing $0.015 \mu\text{L}$ of stationary phase. The cited extractors were connected in series (see below) and then 23 mL of a 5 ppb PAH sample were passed through the stack at about 3 mL min^{-1} using the pressurized vial set-up. The results confirmed the usefulness of the “like dissolves like” principle. In comparison to the PAH amounts extracted with the PS255 extractor (assuming it as the 100% benchmark) and notwithstanding a lower extractant volume, the OV17 capillary extracted $(168 \pm 5)\%$ acenaphthene, $(175 \pm 2)\%$ phenanthrene, $(162 \pm 2)\%$ fluoranthene, $(107 \pm 26)\%$ chrysene, and $(111 \pm 7)\%$ benzo(a)pyrene (average \pm RSD of two replicates).

“In-series” assemblage of capillary extractors: Multiple extractions of PAHs could be performed simultaneously with the use of a chain of extractors, with advantages both in terms of time-saving and uniformity of temperature and hydrodynamics. One drawback of this “in-series” approach was, however, that at low flow-rates (less than 0.2 mL min^{-1}) the high-ring PAHs were preferentially

extracted by those extractors nearest to the sample inlet. On the base of breakthrough concepts (51) this discrimination effect should have been negligible at higher sample flow-rates.

Such a hypothesis was indeed found to be true. In particular, by connecting together six identical PS255 extractors of typical size, recycling through them a PAH sample at a relatively high flow-rate for a suitable time, then stopping the flow and analyzing the laden capillaries one at a time; the CEx variability within the extractor chain gave a results of less than 10% RSD for each analyte (Table II).

The array disposition was also advantageous to speed up the study of extraction-time profiles, since data points could be acquired while the main extraction trial was still proceeding. Following this idea, a chain of seven typical extractors ($10 \text{ cm} \times 0.21 \text{ mm i.d.} \times 0.3 \mu\text{m}$ PS255) was fed with a 1 ppb PAH-spiked tap water sample at 2.7 mL min^{-1} (DQP-1 pump). It resulted that fluoranthene and chrysene reached extraction equilibrium after 27 and 37 min, respectively; Benzo(a)pyrene approached equilibrium after 266 mL (99 min) whereas coronene was extracted at nearly constant speed (i.e., it was very far from equilibrium). (Expectedly, when extractors’ film thickness was reduced from 0.3 to $0.1 \mu\text{m}$, equilibrium time for fluoranthene and chrysene lowered to 5 and 20 min respectively).

The in-series approach provided an easy way to compare the performance of

differing capillary extractors. A chain of three extractors of the same size but different d_f , for example, was used to clarify the influence of film thickness on CEx of the PAHs. The experiment lasted enough time (0.5 h) to allow partition equilibrium to be reached throughout the chain. It was found, in fact, that for fluoranthene the extracted amounts were strictly proportional to the PDMS volumes; Enrichment of chrysene and benzo(a)pyrene in the thicker coatings, however, was less than expected. Coronene behavior, again, was uncommon: its extracted amount was almost the same independently from d_f , thus suggesting a mechanism based (mainly) on adsorption rather than partition. Moreover, if coronene had been partitioned into PDMS its capillary extraction would have been affected by solvent swelling (27) (i.e., by the increase of PDMS volume caused by the contact with plenty of a hydrophobic solvent) (52–54) but actually it was the only PAH which was unaffected.

Salting-out effects: It is known that PAH extraction from aqueous samples can be influenced by sample salting (55).

The performance of CEx vs. salt concentration was tested. Sensitivity for naphthalene and acenaphthene increased steadily by increasing NaCl concentration (Figure 6). Phenanthrene had a maximum near 20% of salt, that lowered to approximately 10% for fluoranthene, and disappeared for chrysene and benzo(a)pyrene. Coronene was the least influenced analyte, its extraction remaining a challenge independently from the concentration of NaCl.

Temperature influence: CEx extraction of chrysene, benzo(a)pyrene and coronene (chromatograms not shown) was more effective at $65 \text{ }^\circ\text{C}$ than at room temperature by 300–500%. On the contrary, naphthalene and fluoranthene decreased their extraction yield because of the lowering of K_{Sil} at increased temperatures. The intermediate-size PAHs were not remarkably affected by the rise of temperature; The increased mass transport at the higher temperature was evidently counterbalanced by the corresponding decrease of K_{Sil} (40)

Snaked extractors: It is known from HPLC theory that a radial flow (obtained for example by including coiled connecting tubes in the flow path) modifies the

common parabolic profile of mobile phase velocities so that convective mass-transport is enhanced and taller peaks can be obtained. It was hence interesting to test if CEx efficiency could be influenced by radial flows.

The shape of some typical (linear) extractors was thus modified to be serpentine-like (46) and the extractors used in a set of CEx experiments. These “snaked-extractors” were slightly more active than “linear” ones because of the thermal treatment required to make from 30 to 40 bends (PAHs, however, were nearly insensitive to this sort of activity). The mass exchange kinetics of snaked capillaries always resulted higher than those of unmodified extractors (Figure 7), confirming the usefulness of radial flows — enhanced turbulence and therefore thinner static liquid layer — in order to speed-up the capillary microextraction. Gain was remarkable for chrysene and benzo(a)pyrene and contact time was very brief (less than 3 min). Coronene, however, went undetected even with snaked extractors.

Sensitive detection of benzo(a)pyrene: In striking contrast to the difficulties of coronene detection, traces of benzo(a)pyrene were generally detected both sensitively and quickly by means of long, thinly-coated capillary extractors ($d_f \leq 0.1 \mu\text{m}$). One of such CEx-HRGC analyses, referring to a 1 ppb PAH sample, is shown in Figure 8. Despite the very brief contact time (2.5 min), the 3σ detection limit of benzo(a)pyrene gave a result of 10 ng L^{-1} , whereas coronene was only barely detected (probably as a result of a coronene-free concentration that was substantially lower than that of benzo(a)pyrene). The retention gap effect, which is indeed typical of thinly coated capillary extractors, gave excellent peak shape. Some extraction profiles are shown in Figure 9: the lower-ring PAHs had equilibration times of a few minutes, whereas benzo(a)pyrene was strongly enriched into the extractor. The extrapolated equilibration time was about 25–30 min. Benzo(a)pyrene uptake was so strong that it simultaneously affected the overall polarity of the stationary phase and hence, very clearly, the partition equilibrium of naphthalene (data not shown) (44).

Conclusion

The solventless determination of PAHs in clean waters by capillary extraction-HRGC–FID is characterized by the absence of carryover, notably high extraction speeds, operative simplicity and use of extractors which are both cheap and reusable. Sample salting, rise of sample temperature and use of snaked extractors are means to favorably influence the detection of PAHs. Chain (in-series) extractors are useful in determining CEx reproducibility and in the study of extraction profiles. CEx analytical reproducibility (RSD) is in the 6–10% range and sensitivity is at the parts-per-billion level. Thinly coated capillary extractors are effective for the determination of high-ring PAHs. Benzo(a)pyrene, in particular, can be detected down to 10 ppt.

Coronene extraction is, in general, very hard to perform, especially from spiked samples prepared in very pure waters rather than tap water. In this study, coronene has never been detected in those aqueous samples prepared by generator columns.

The puzzling coronene behavior may depend on:

- an extremely low aqueous solubility
- the almost certain presence of suspended coronene microparticles in those samples prepared by spiking
- the possibility of these particles to be uniquely latched by an adsorption mechanism onto the apolar coatings of capillary extractors.

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