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ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS IN ENVIRONMENTAL WATERS BY HIGH-PRESSURE LIQUID CHROMATOGRAPHY

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SUMMARY

A quantitative procedure for the analysis of fifteen polynuclear aromatic hydrocarbons (PAHs) in environmental water samples is presented. The analytical technique utilizes a cyclohexane extraction of the PAHs, a cleanup and fractionation with alumina, high-pressure liquid chromatography, and ultraviolet (UV) detection. The analysis is capable of quantitating these PAHs in raw, finished, and distributed waters at concentrations of 1–3 ng/l.

The PAHs were detected by three UV detectors in series operating at fixed wavelengths. Compounds were initially identified by retention times, and concentrations were determined by comparing the peak heights of samples to those of PAH standards. Extraction efficiencies were then used to correct these results. Further confirmation of identity was afforded by fluorescence emission and excitation spectra.

A detailed study of recoveries and stabilities of PAHs at low nanogram-per-liter concentrations in water was conducted. The study revealed complete losses in chlorinated water, and selective losses in waters with no measurable chlorine residual. A sodium sulfate pellet spiked with perylene and benzo[*ghi*]perylene is proposed to monitor sample integrity during shipment.

INTRODUCTION

Organics in drinking waters and their sources of supply have been under scrutiny for several years[1]. Emphasis has been on the identification and quantification of compounds with potential adverse health effects on humans. Prominent among this group are polynuclear aromatic hydrocarbons (PAHs). These compounds, several of which are known or suspected carcinogens[2], occur naturally in the environment through biosynthetic and pyrolytic processes[3,4]. Human activity can also play a significant role in the release of PAHs into the environment. For example, automobile exhaust, industrial and domestic effluent, and urban runoff have been shown to contain significant concentrations of a wide molecular weight range of PAHs[3,5,6].

Concentrations of individual PAHs in drinking water sources and supplies

have been found to range between less-than-one to several hundred ng/l[7–10]. The techniques used to measure PAHs in environmental samples have been thin-layer chromatography (TLC), gas chromatography (GC), and GC–mass spectrometry (MS). However, each suffers certain inadequacies with respect to concentration, separation, detection or identification of the PAHs. Separation of isomeric PAHs has hindered packed column GC analysis with both conventional and MS detectors[11,12]. While TLC, utilizing a two-stage development process, has proven successful in the resolution of some PAH isomers (benzo[*b*]fluoranthene and benzo[*k*]fluoranthene), it has been generally limited to the analysis of the World Health Organization's six PAHs[13] (of which only three are considered carcinogenic). The restriction of small sample loads has hindered GC analysis with high efficiency glass capillary columns[8].

Recently, the use of high-pressure liquid chromatography (HPLC) has been applied to the analysis of PAHs[14–16]. Reversed-phase C_{18} columns have been used for separation of PAHs, although other chemically modified supports such as Nucleosil 5 NO_2 have also been recommended[17]. The detection systems predominately used have been UV absorption, and the more selective and sensitive fluorescence detectors[18]. However, many of the analytical schemes developed have dealt with only a limited number of PAHs in environmental samples, and few have been directed towards the analysis of water for low nanogram-per-liter concentrations.

Several PAHs have been effectively extracted from relatively small volumes of environmental waters and measured at 1–3 ng/l concentrations using HPLC–UV analysis preceded by a clean-up step[19]. This technique has been extended to fifteen PAHs using selective UV monitoring and fluorescence emission–excitation spectra for identification. The stability and recovery of some of these PAHs in water samples have been studied, and a procedure for monitoring sample integrity during shipment is suggested.

EXPERIMENTAL*

Reagents

All solvents used were "distilled in glass" (Burdick and Jackson Labs., Muskegon, Mich., U.S.A.). These included acetonitrile (UV grade), methylene chloride, pentane, and cyclohexane (UV grade). The inorganic reagents included alumina, Brockman activity I, 80–200 mesh; sodium sulfate, granular certified A.C.S., and sodium sulfite, granular certified A.C.S. (Fisher Scientific, Fair Lawn, N. J., U.S.A.).

PAHs used as received from the suppliers were: chrysene (Ch), fluoranthene (Fl), perylene (Per), benzo[*ghi*]perylene [B(*ghi*)P], phenanthrene (Ph), 1-methylphenanthrene (1-MPh), indeno[1,2,3-*cd*]pyrene (IP), and benzo[*e*]pyrene [B(*e*)P] (Aldrich, Milwaukee, Wisc., U.S.A.); 2-methylphenanthrene (2-MPh) and 1-methylpyrene (1-MP) (K & K Labs., Plainview, N. Y., U.S.A.); benzo[*a*]anthracene [B(*a*)A] dibenzo[*ah*]anthracene [DiB(*ah*)A], and benzo[*a*]pyrene [B(*a*)P] (Eastman Kodak, Rochester, N. Y., U.S.A.); pyrene (Pyr) (Tridom, Hauppauge, N. Y., U.S.A.; benzo-[*b*]fluoranthene [B(*b*)F] and benzo[*k*]fluoranthene [B(*k*)F] (Dr. James Meeker, U.S. Environmental Protection Agency, Research Triangle Park, N. C., U.S.A.); and anthracene (An) (RFR, Hope, R.I., U.S.A.).

* Mention of products, manufacturers and suppliers does not imply an endorsement by the U.S. Environmental Protection Agency.

Glassware

The glassware requirements were a Kuderna-Danish apparatus with Snyder column and 10-ml concentrator tube; a glass column (120 × 20 mm) with fritted glass disc and 300-ml reservoir; 50-ml and 100-ml volumetric flasks; micro-Snyder columns; 2000-ml separatory funnels; and 1- or 1/2-gallon flint glass containers. All glassware used was detergent washed, rinsed, and dried. Prior to use, all glassware was rinsed three times with cyclohexane or pentane.

Instrumentation

The chromatography was conducted using a Waters Assoc. (Bedford, Mass., U.S.A.) high-pressure liquid chromatograph Model 204 with dual Model 6000A solvent delivery pumps, a Model U6K universal injector, and a Waters μBondapak C_{18} column. Detection was accomplished via a Model 440 Waters absorbance detector, a Schoeffel SF-770 variable-wavelength absorbance detector (Schoeffel, Westwood, N. J., U.S.A.), and an Aminco-Bowman SPF-8820 spectrophotofluorometer fitted with a 35-μl flow cell (American Instrument, Silver Spring, Md., U.S.A.).

Preparation of standards and samples

The standard solutions of PAHs were prepared by dissolving 10 mg in a small amount of chloroform, methylene chloride, or acetone. Each was transferred to a volumetric flask and diluted with acetonitrile to afford solutions containing PAHs at concentrations of 0.5 or 0.2 mg/ml. These stock solutions and subsequent working standards were stored at room temperature in the dark[20].

A 1.5-l volume of sample was collected in a 1/2-gallon bottle which contained 50 mg of sodium sulfite. This amount was sufficient to reduce any free or combined residual chlorine which might have been present in typical drinking waters. When field samples are collected they should be shipped with ice and extracted immediately upon receipt. For selected samples, sample integrity in transport can be monitored by adding a sodium sulfate pellet (500 mg) which is spiked with Per and B(*ghi*)P.

Procedure

Prior to analysis, the pH and chlorine residual were measured as a preliminary check of sample integrity. The samples were then brought to room temperature in a warm water bath in preparation for the analysis illustrated in Fig. 1.

The sample was transferred to a 2000-ml separatory funnel. The sample container was rinsed with 50 ml of cyclohexane which was added to the separatory funnel. The funnel was shaken for 2 min and the phases allowed to separate for approximately 10 min. The aqueous phase was drained into a clean container and saved. The organic phase was poured through a drying column containing 35 g of anhydrous sodium sulfate and connected to a Kunderna-Danish appratus (KD). Both the drying column and the KD were previously washed with cyclohexane. The aqueous layer was returned to the separatory funnel and the cyclohexane extraction step repeated two more times with fresh solvent. The drying column was rinsed twice with approximately 10 ml of cyclohexane which was added to the extract.

The KD containing the combined cyclohexane extract was fitted with a Snyder column. This apparatus was placed on a hot water bath (90–100°), wrapped with a paper towel and aluminium foil, and heated until the volume of solvent was

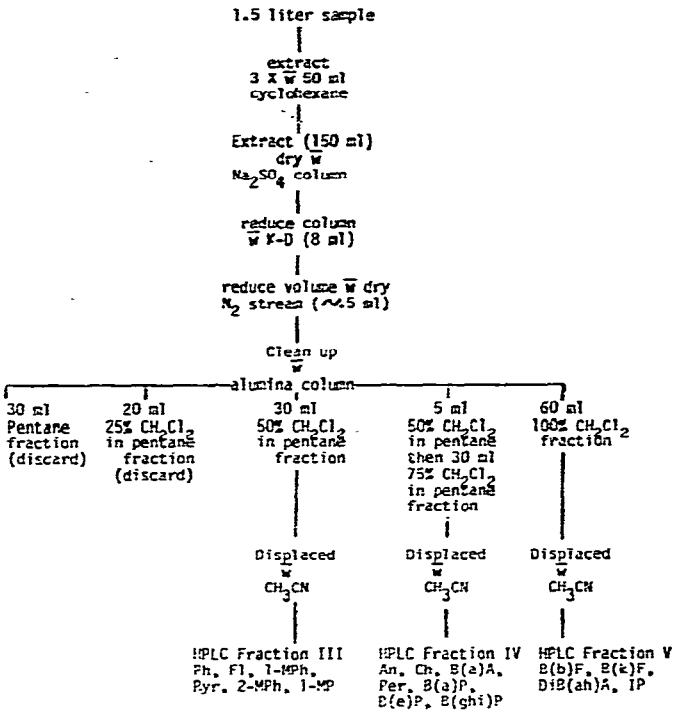

Fig. 1. Analytical scheme for PAHs.

reduced to 8 ml. The apparatus was removed from the bath and wiped dry before being allowed to cool. The concentrator tube was then removed and the outer portion of the male joint rinsed with cyclohexane (less than 1 ml). The tube was placed in a warm water bath and the volume of the extract further reduced to 0.5 ml with a gentle stream of dry nitrogen. This concentrate was added to an alumina column with two 0.5-ml rinses of pentane.

The column had been prepared by dry-packing 16 ml of alumina (3%, w/w, water) into a 1.1-cm diameter column, and wetting it with 15 ml of pentane. As the level of the pentane reached the top of the alumina, a sodium sulfate layer was added (3/4 in.). A 20-ml portion of methylene chloride was used to wash the column, and it was reconditioned by rinsing with 20 ml of pentane. The concentrate was then sequentially eluted with: I, 30 ml pentane; II, 20 ml methylene chloride–pentane (25:75); III, 25 ml methylene chloride–pentane (50:50); IV, 5 ml methylene chloride–pentane (50:50) then 30 ml methylene chloride–pentane (75:25); and V, 60 ml 100% methylene chloride. These five fractions were collected in beakers.

Fractions I and II were discarded, and the remaining fractions were transferred to separate 10-ml concentrator tubes with pentane rinses. The concentrator tubes were fitted with micro-Snyder columns, placed in a warm water bath, and the volume of the solution was reduced to about 1 ml. Since 10-ml concentrator tubes were used, volume reduction of the fractions was done in increments.

The concentrator tubes were taken from the bath, the micro-Snyder columns were removed, and the joints were rinsed with pentane. The tubes were again placed

in the bath and the extracts concentrated with a nitrogen stream to near dryness (less than 0.05 ml). Approximately 0.7 ml of acetonitrile was added to each tube, with rinsing of the tube walls, and the volume was reduced under the nitrogen stream, affording 0.10-ml concentrates in acetonitrile for HPLC analysis.

Using HPLC, the three fractions were analyzed separately by injecting half (50 μl) of the acetonitrile concentrate. This volume could represent from less-than-one to twenty nanograms of each PAH injected on column. The acetonitrile–water (70:30) mobile phase was maintained at a flow-rate of 1 ml/min. The column temperature was controlled at $30 \pm 0.5°$ with a constant temperature bath. The eluent from the column was monitored at 254, 280, and 340 nm for fraction III; 254, 280, and 267 nm for fraction IV; and 254, 280, and 308 nm for fraction V. The remainder of the three fractions was re-analyzed individually and stop-flow fluorescence spectra were obtained for the appropriate peaks. Identification of PAHs was achieved through comparison of retention times and fluorescence spectra of samples to those of standards. The standards and the fractions obtained from solvent blanks were analyzed separately from the samples.

Quantitation was accomplished by comparing sample peak heights (corrected for contributions from the solvent blanks) to those of the standards. This required that the injection volumes of the standard and sample be identical. The resulting concentrations were then corrected for extraction efficiencies.

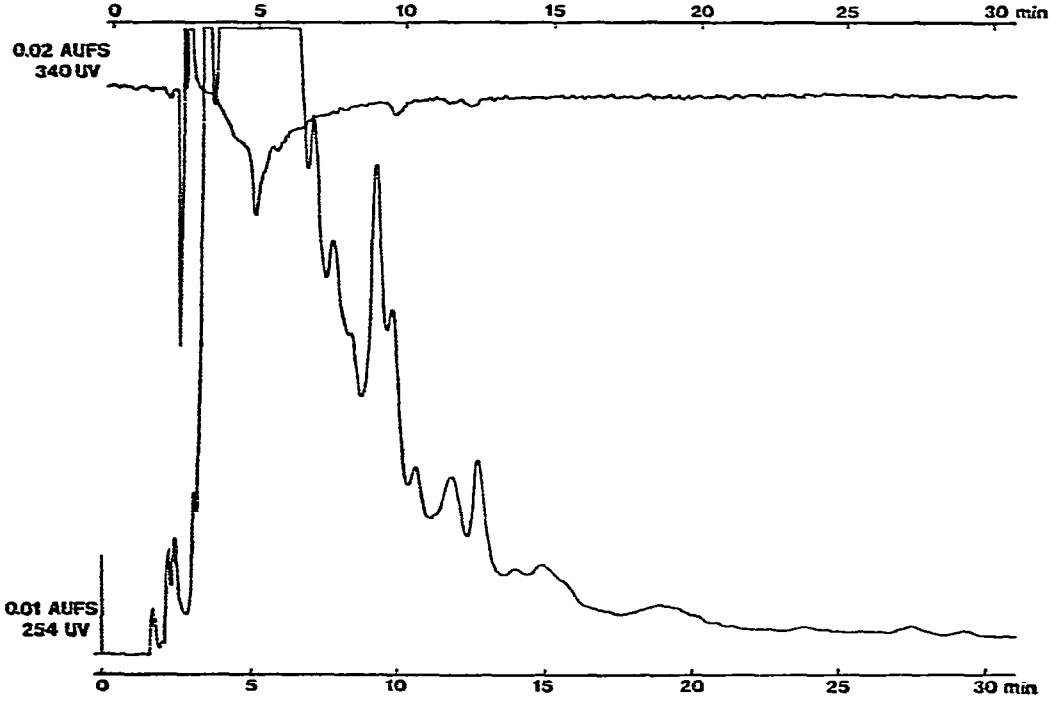

Fig. 2. 1.5 l of tap water concentrated to 0.2 ml without alumina cleanup.

RESULTS AND DISCUSSION

Chromatography and detection

A comparison of the HPLC chromatogram of an extract of tap water (Fig. 2) with that of an extract of spiked tap water eluted through alumina (Fig. 3) shows the effectiveness of the cleanup in removing UV-absorbing interferences. The dashed lines in Fig. 3 represent a solvent blank which was taken through the complete analytical procedure. The alumina also fractionated seventeen PAHs into three fractions. The two early-eluting fractions, which were discarded, may contain hydrocarbons, benzene, naphthalene, alkyl-substituted benzenes and naphthalenes, and other low-molecular-weight compounds.

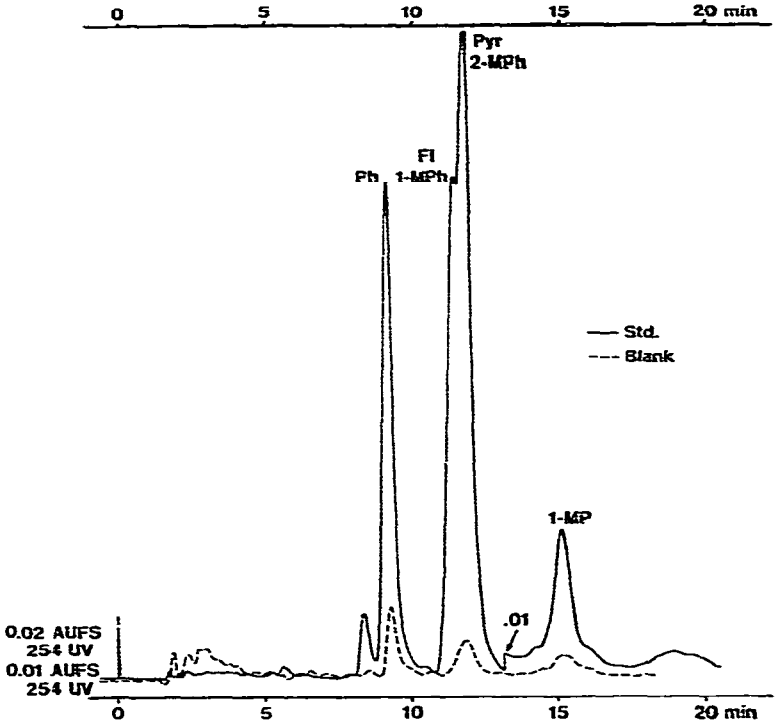

Fig. 3. Extract, with alumina cleanup, of spiked water (*ca.* 20 ng/l), and a solvent blank.

The HPLC chromatograms of the three retained fractions from the standard PAHs taken through the analytical procedure are presented in Figs. 4–6. The chromatography was performed isocratically and the column temperature was controlled. This permitted specific PAHs to be initially identified from their retention times (which varied less than 2% over a 9-month period), and eliminated the need for column re-equilibration. Although some co-eluting PAHs (*e.g.*, An, Ph) had been placed into different fractions, it was clear that no single UV wavelength was capable of resolving all of the PAHs within a fraction. However, instead of further manipulating the chromatography, the sensitivity and resolution of the analysis were optimized by selecting the available UV wavelengths so as to minimize the response of

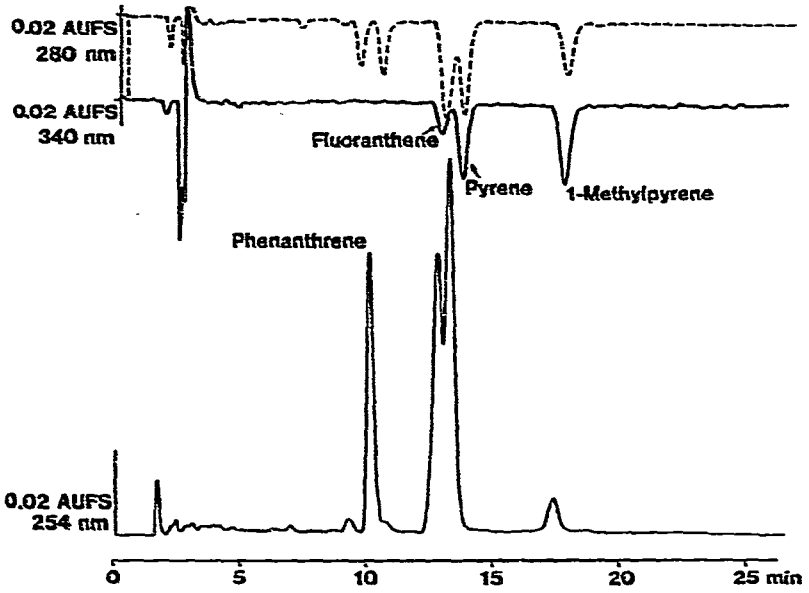

Fig. 4. HPLC analysis of fraction III from alumina column (*ca.* 10 ng of standards).

the interferences near a relative absorption maximum of the PAH of interest (Table I). Concentrations of the PAHs were determined from their UV responses. The sensitivity of the UV detectors, defined as a signal-to-noise ratio of 2, ranged from 0.25 to 1 ng/l.

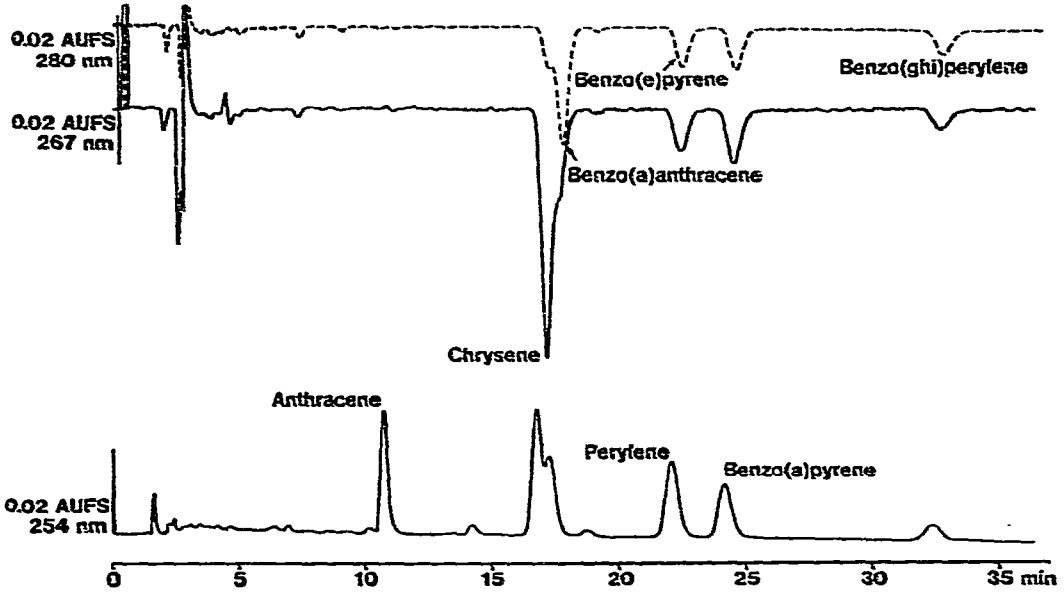

Fig. 5. HPLC analysis of fraction IV from alumina column (*ca.* 10 ng of standards).

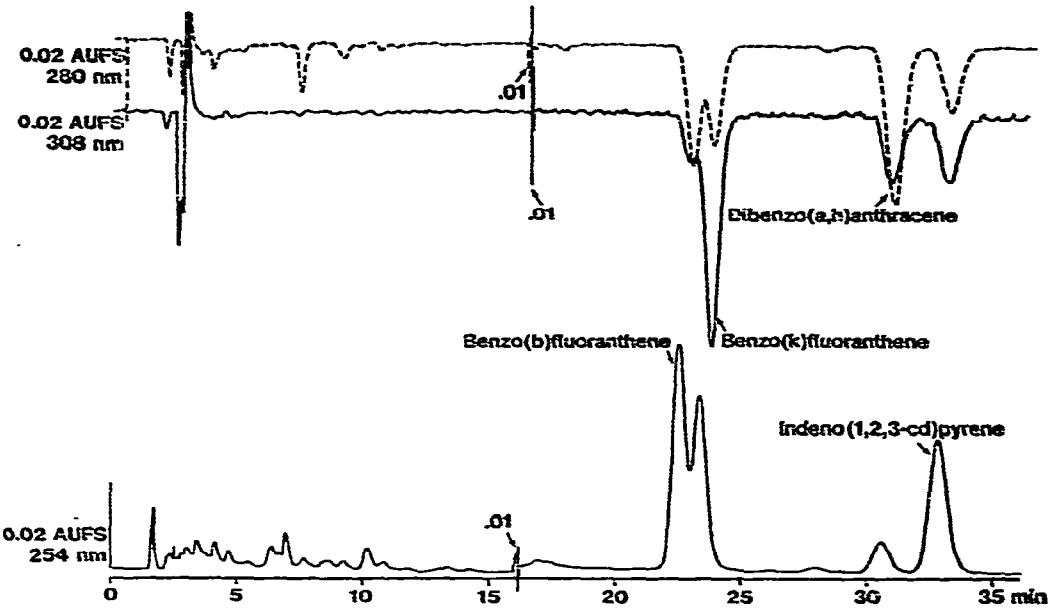

Fig. 6. HPLC analysis of fraction V from alumina column (*ca.* 10 ng of standards).

All but two (1-MPh and 2-MPh) of the seventeen PAHs could be sufficiently resolved from co-eluting PAHs and other interfering compounds by using the variable wavelength and the two fixed wavelength (254 and 280 nm) detectors. For example, 1-MPh, Fl and Pyr either co-eluted or were incompletely resolved, and all had a significant response at 254 nm (Fig. 3). In addition, despite the alumina cleanup, some interferences with a 254 nm response co-eluted with these PAHs and with 1-MP. Analysis by GC–MS has shown that di-*n*-octyl adipate and phthalate esters

TABLE I

WAVELENGTHS SELECTED TO QUANTITATE 15 PAHs

Compound	*Abbreviation*	*Wavelength (nm)*
Phenanthrene	Ph	254
Fluoranthene	Fl	340
Pyrene	Pyr	340
1-Methylpyrene	1-MP	340
Anthracene	An	254
Chrysene	Ch	267
Benzo(*a*)anthracene	B(*a*)A	280
Perylene	Per	254
Benzo(*e*)pyrene	B(*e*)P	280
Benzo(*a*)pyrene	B(*a*)P	254
Benzo(*ghi*)perylene	B(*ghi*)P	280
Benzo(*b*)fluoranthene	B(*b*)F	254
Benzo(*k*)fluoranthene	B(*k*)F	308
Dibenzo(*a,h*)anthracene	DiB(*ah*)A	280
Indeno(1,2,3-*cd*)pyrene	IP	254

were in this group of interferences[21]. However, since neither the interferences nor 1-MPh or 2-MPh had a significant response at 340 nm, the concentrations of Fl, Pyr and 1-MP could be measured (Fig. 4). Since no selective wavelength could be found for 1-MPh and 2-MPh, they were not quantified in this work.

This technique of selective wavelength monitoring was expanded from the suppression of impurities in fraction III to lowering the detection limits for PAHs in the other two fractions. An example of this application is Ch and B(*a*)A which were only partially resolved in fraction IV (Fig. 5). Since the response of Ch was twice that of B(*a*)A at 267 nm and one-fifth that of B(*a*)A at 280 nm, it was possible to determine the concentrations of both of these compounds. Even when there was no resolution of two compounds, as in the case of B(*e*)P and Per, it was possible to quantitate B(*e*)P separately at 280 nm, and subtract its contribution to the 254 nm response. The capability of multiple-wavelength monitoring has also proved useful for totally-resolved PAHs, by allowing quantitation at an optimum wavelength. For example, DiB(*ah*)A was quantitated from the 280 nm response since it was five times greater than the 254 nm response. In this way, an optimum wavelength was determined for which fifteen PAHs could be quantitated at concentrations of 1–3 ng/l (Table I).

Fluorescence, as a detection system, has the advantages of greater sensitivity and less susceptibility to interferences, since fewer compounds are fluorescent than are UV absorbant[22]. Given the capability to scan both emission and excitation wavelengths, fluorescence provided more unique spectra for PAHs than MS, and greatly augmented the preliminary identifications of PAHs via retention time.

Definitive fluorescence spectra of all the PAH standards (except IP) in Table I were obtained by trapping the compounds in the flow cell and scanning the excitation and emission spectra. The sensitivity of the spectrofluorometer generally afforded

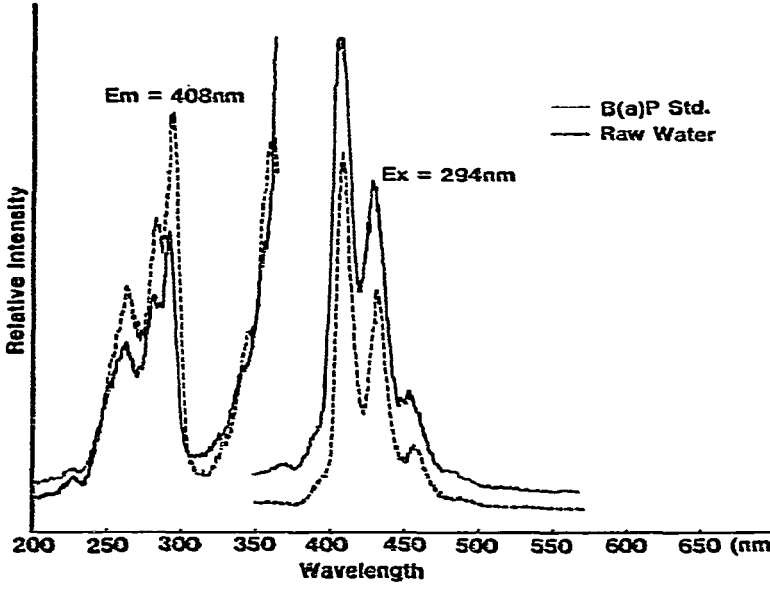

Fig. 7. Comparison of B(*a*)P standard with fluorescence spectrum of untreated water sample.

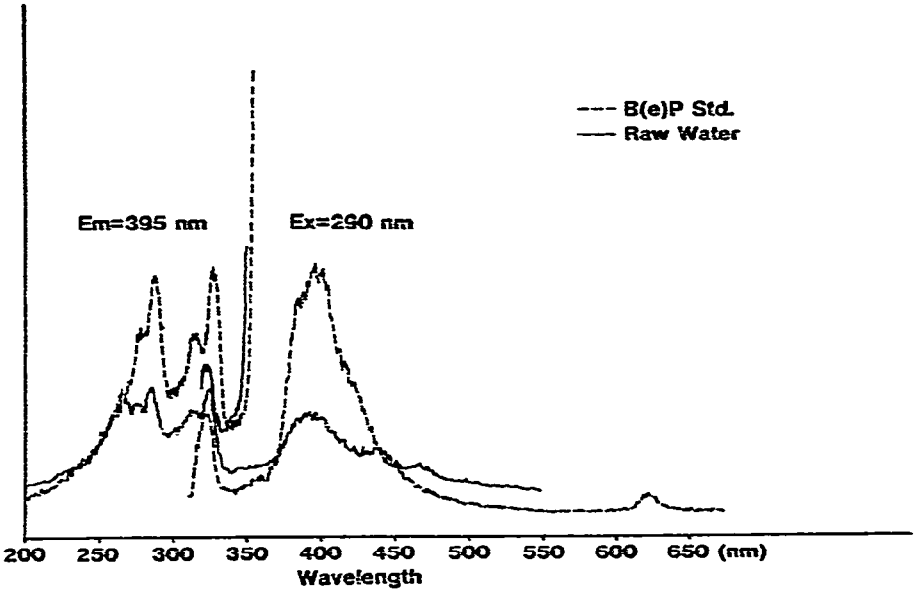

Fig. 8. Comparison of B(*e*)P standard with fluorescence spectrum of untreated water sample.

identification of most of the PAHs quantified in the environmental water samples. A spectrum of 6 ng of B(*a*)P detected in a raw water sample superimposed on that of 7 ng of a B(*a*)P standard (Fig. 7) shows the type of confirmation of identity afforded by this detection technique. Even in the presence of co-eluting fluorescent compounds, as in the case of B(*e*)P (Fig. 8) and Per (Fig. 9), the spectral features were individually

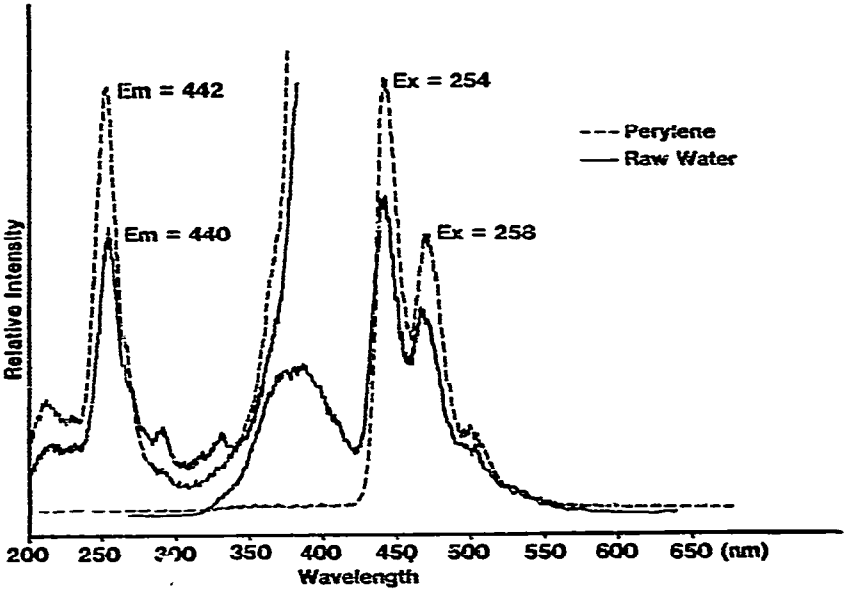

Fig. 9. Comparison of Per standard with fluorescence spectrum of untreated water sample.

recorded by manipulating the emission and excitation wavelengths (the B(*e*)P spectrum also appears to indicate the presence of a third compound). IP provided a very amorphous fluorescence spectrum which may be a characteristic of IP or due to a consistently present fluorescent interference[22].

Since the same UV wavelengths were recorded for each compound within a fraction, various peak-height ratios of these responses could be computed. It has been noted that these ratios can sometimes be used to identify compounds in samples[16,19] and they were calculated at 280 and 254 nm for the four PAHs which had responses apparently free of interferences at these wavelengths (Table II). However, except for Ph, there was a significant variation between the ratios for samples and those for standards which indicated that interferences were still present in the samples. Thus, the UV ratios were primarily used to determine the purity of the chromatographed compounds. If either these ratios or the fluorescence spectra indicated the presence of significant interferences, only an upper bound on the concentrations of the PAHs could be determined.

TABLE II

COMPARISON OF UV RATIOS* MEASURED FOR PAHs IN STANDARDS AND SAMPLES
n = number of analyses performed.

Compound	*Ratio*			
	n	*Standard*	n	*Samples*
Ph	12	0.17 ± 0.02	20	0.18 ± 0.01
B(*a*)P	18	0.73 ± 0.01	5	0.81 ± 0.03
B(*ghi*)P	18	1.42 ± 0.08	5	1.52 ± 0.22
IP	13	0.47 ± 0.02	3	0.40 ± 0.03

* Ratio of 280/254 nm Peak heights.

Recoveries and compound stability

An earlier study[19] using this procedure had shown the recoveries of six PAHs from distilled water to range from 61 to 91% and to average 78 ± 8% (Table III). Subsequent measurements of the recoveries of eleven PAHs from seven raw or finished (*i.e.*, environmental) water samples were made over a nine-month period. They ranged from 53 to 116% and averaged 86 ± 12% (Table III). These latter recoveries were determined by spiking previously extracted water samples with acetonitrile stock solutions of the PAHs at a concentration of 20 ng/l each. Since the sample was then taken through the entire analytical procedure, these recovery data represent more than just extraction efficiencies. They are a measure of the procedure efficiency which includes extraction efficiency, loss through cleanup, loss during blowdown, and error in dilution of samples and standards. The average recovery for each PAH in the environmental waters can be used as a correction factor.

In a third study, similar concentrations of six PAHs (Pyr, Fl, 1-MP, Per, B(*a*)P, and B(*ghi*)P) were spiked into four samples of un-extracted tap water and the recoveries were determined by analyzing the extracts directly (*i.e.*, without alumina cleanup). Corresponding, unspiked tap water samples were also extracted and analyzed directly to determine the background concentration of the PAHs. After correcting

TABLE III

PERCENT RECOVERY FROM VARIOUS TYPES OF WATERS

Compounds	*Distilled water**	*Environmental waters***,****							
		A	*B*	*C*	*D*	*E*	*F*	*G*	*Mean*
Phenanthrene	78 ± 1	83	96	87	98	—	—	—	91 ± 7
1-Methylpyrene	—	—	—	98	85	92	93	72	88 ± 10
Chrysene	—	86	86	87	84	86	93	86	87 ± 3
Benzo(a)anthracene	—	81	65	89	84	92	85	76	82 ± 9
Perylene	79 ± 7	92	75	105	95	94	82	75	88 ± 11
Benzo[*a*]pyrene	80 ± 4	89	54	110	105	79	67	73	82 ± 20
Benzo[*ghi*]perylene	89 ± 3	90	83	116	111	79	62	82	89 ± 19
Benzo[*b*]fluoranthene	76 ± 6	89	87	91	96	92	89	91	91 ± 3
Benzo[*k*]fluoranthene	—	80	84	91	91	93	76	95	87 ± 7
Dibenzo[*a,h*]anthracene	—	93	90	92	92	79	53	84	83 ± 14
Indeno[1,2,3-*cd*]pyrene	68 ± 7	94	89	86	95	80	55	89	84 ± 14

* The mean recovery of 3 samples spiked at 10 ng/l.
** Spiked at 20 ng/l.
*** A,B,D,G: treated waters; C,E: untreated waters; F: partially treated water.

for this background, the recoveries were calculated and ranged from 78 to 99%, averaging 88%. The average recovery (for all of the PAHs) from these three series of experiments was about 85%.

While the recovery efficiencies allowed quantification of PAH concentrations at the time of extraction, the relevancy of those values to the actual concentration at the time of sampling may be less certain. A preliminary experiment showed a complete loss of seven PAHs when spiked (about 27 ng/l each) into Cincinnati tap water and stored at 5° for 18 days. The identical water with no chlorine residual (excess sodium sulfite added) showed only a small loss for five of the PAHs and a somewhat larger loss for B(*a*)P and Per. A similar, more careful, 8-day study of the same tap water source looked at only the four PAHs which did not occur naturally. The results showed total and partial losses of the PAHs in the presence and absence of a chlorine residual, respectively. Again, B(*a*)P and Per showed greater losses than the other PAHs (Table IV). All of these analyses were done without alumina cleanup and the significance of the losses was interpreted in light of an expected 85% recovery.

TABLE IV

PERCENT RECOVERY OF PAHs FROM TAP WATER*

*Compound***	*Non-reduced**** *(8-day)*	*Sulfite reduced*†	
		2-day	*8-day*
1-MP	0	79	66
Per	0	68	41
B(*a*)P	0	36	18
B(*ghi*)P	0	92	63

* Samples stored in dark at 5° (pH 7.5).
** Spiked at about 27 ng/l each.
*** Chlorine residual was about 1.5 mg/l.
† Chlorine residual was <0.1 mg/l.

TABLE V

STABILITY* OF PAHs IN TAP WATER (SULFITE REDUCED)

*Compound***	*Days of storage***			
	0	*2*	*5*	*8*
Fl	87	73	88	83
Pyr	93	79	87	86
1-MP	102	93	83	87
Per	89	59	50	47
B(*a*)P	89	42	27	24
B(*ghi*)P	102	84	88	88

* As measured by percent recoveries.
** Stored in the dark at 5°.
*** Spiked at about 20 ng/l.

To examine this apparently greater loss of B(*a*)P and Per, sodium sulfite (25 mg/l) was added to twelve bottles of Cincinnati tap water. Eight of these samples were also spiked with about 20 ng/l each of six PAHs, and all were stored for varying amounts of time at 5°. The unspiked water samples were extracted and analyzed in duplicate on the initial and fifth days to determine and subtract the background PAH concentrations. The spiked samples were also analyzed in duplicate after 0, 2, 5, and 8 days. The results showed a gradual but noticeably greater loss of B(*a*)P and Per *versus* that of the other PAHs (Table V). From a log plot of the concentration (as peak height) of four of the PAHs *versus* time (Fig. 10), it was clear that the B(*a*)P and Per concentrations decreased at unequal rates.

The alumina cleanup was eliminated in the stability studies for several reasons. First, the PAHs selected, which represented a range of molecular weights, could be separated by HPLC alone and did not need fractionation. Second, the tap water used in the study contained only modest amounts of impurities at the retention times

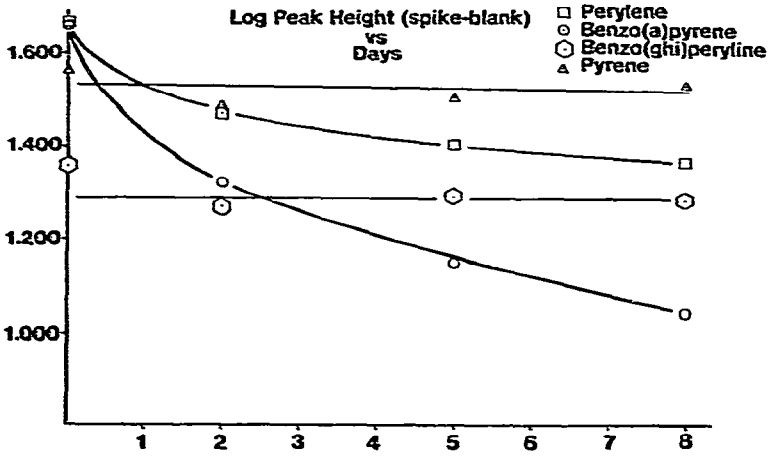

Fig. 10. Losses of selected PAHs at *ca.* 20 ng/l.

of the selected compounds which could be masked via selective UV monitoring. Third, this simplification speeded the analysis. Finally, and most importantly, by not being placed in different fractions, each PAH in a sample was treated equally with regard to potential loss during handling and in adjusting the final volume of the sample concentrate.

Others have used radio-labelled B(*a*)P[24,25] or deuterated PAHs[26] as internal standards. However, the former is not appropriate for shipping and the latter are not appropriate for UV and fluorescence detectors. Since field samples may not be extracted for some time after sampling, a suitable means of monitoring the loss of PAHs with time was devised. A pellet of sodium sulfate was spiked with 40 ng each of Per and B(*ghi*)P and placed in the finished water sample bottle. When the water was added, the pellet and the PAHs dissolved, and the loss, in transport, of the PAHs could be monitored by determining the difference between the measured and the expected recoveries of the pellet-spiked PAHs. PAHs dried on the surface of the pellets and stored in the dark at room temperature had been found to be quite stable (no loss after 3 days, a 20% loss after 30 days); thus, no significant loss would begin until the water was added.

A final time-storage experiment was conducted by analyzing in duplicate on different days, identical samples of tap water to which sulfite and a pellet spiked with six PAHs had been added (Table VI). The results indicated the utility of the spiked pellet as a method control, although the loss of the unstable PAHs was less than determined earlier. However, the range of initial recoveries observed with (Table III) and without alumina cleanup (Tables IV–VI) were comparable; thus, the observed decrease in recoveries of B(*a*)P and Per with time is probably due to a mechanism unrelated to the analytical procedure used.

TABLE VI

TIME STORAGE STUDY* OF SPIKED PELLET IN TAP WATER

*Compound***	*Days of storage***	
	0	*2*
Fl	69	73
Pyr	78	78
1-MP	92	89
Per	81	74
B(*a*)P	72	63
B(*ghi*)P	94	89

* As determined by percent recoveries.
** Stored in dark at 5°.
*** Spiked at about 20 ng/l.

CONCLUSION

The methodology presented in this paper can effectively quantitate fifteen PAHs in raw or finished waters at 1–3 ng/l concentrations, and is presently being used to analyze environmental samples[10]. At these concentrations, the technique requires a liquid–liquid extraction of the sample. The required sample size is only 1.5 l

thereby eliminating the need for large volumes and facilitating transport from the sampling site to the laboratory. A cleanup column reduces interferences and improves the chromatography by placing some co-eluting PAHs into different fractions. Remaining interferences can usually be suppressed using selective UV wavelength detection. Identification based on retention times and ratio of response alone does not appear to be adequate. However, fluorescence emission and excitation spectra can provide confident identification in most cases.

With this procedure, the recoveries averaged 85% and appeared to be largely independent of the PAH or water matrix studies. Since many drinking waters have a significant chlorine residual which can react with PAHs, a reducing agent should be added at the time of sampling. A stability study of six of the PAHs in tap waters with no chlorine residual, stored at 5°, indicated that B(*a*)P and Per may decompose over a period of several days but that the mechanism and extent of this loss are not well defined. However, this indicates that it should not be assumed that the concentrations of PAHs in environmental water samples remain constant between the time of sampling and extraction. Monitoring the integrity of selected samples during transport can be accomplished by the addition of a sodium sulfate pellet spiked with perylene and benzo(*ghi*)perylene.

Recent advances in instrumentation may make capillary GC–MS analysis of sub-nanogram quantities of organic compounds in the cleanup fractions feasible. This could aid in identifying: interferences, products of the reactions of PAHs with a chlorine residual, and products of the apparent decomposition of B(*a*)P and Per.

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