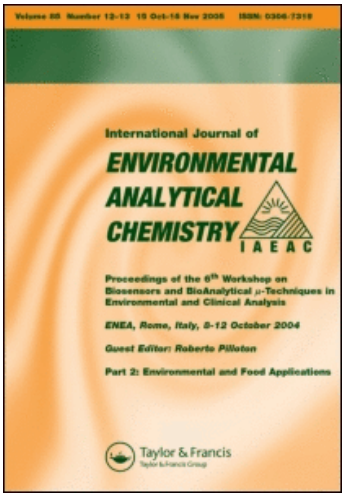

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Quantitative Determination of Trace Concentration of Organics in Water by Solvent Extraction and Fused Silica Capillary Gas Chromatography: Aliphatic and Polynuclear Hydrocarbons

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Solvent extraction procedures with six different solvents on aqueous model systems of aliphatic (C_{12}–C_{22}) and polynuclear aromatic hydrocarbons (PAHs: Naphthalene, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene) were studied for the analysis in the trace concentration range (20–50 ng ml^{-1}) by fused silica capillary gas chromatography. Recovery efficiencies, reproducibilities and detection limits for each analyte and procedure are reported. The effect of the PAHs on the extracting rate of the aliphatic hydrocarbons at the trace concentration range is discussed.

KEY WORDS: Trace water pollutants, PAHs, aliphatic hydrocarbons, solvent extraction, capillary gas chromatography.

INTRODUCTION

Several polynuclear aromatic and aliphatic hydrocarbons enter natural waters and thereby public water supplies with the discharge of urban and domestic sewage, intentional or accidental oil spillages, industrial wastes and through rain and storm-water containing atmospheric and surface contaminants from automobile exhausts, forest fire, etc.

Although there is no epidemiological evidence to prove that PAHs and aliphatic hydrocarbons (with $n > 10$ carbon atoms) in drinking water are related to the incidence of cancer, danger of continuous exposure to carcinogenic, cocarcinogenic or tumour promotor hydrocarbons through drinking water should not be overlooked, even at low concentration.

The contribution of the PAHs to drinking water is small compared to other sources[1] and generally aquatic PAHs represent a minor source of PAHs in the human environment[2] but their importance is not possible to minimize according to the above exposed considerations.

The cocarcinogenecity or tumor promotor evidences of several compounds, which were chosen for the recovery studies, have been reported in the literature, namely dodecane,[3] octadecane,[4] eicosane,[4] fluoranthene,[5] pyrene,[5] etc.

Analysis of these hydrocarbons at trace range in water could be performed by several methods, which have been developed and reported in the literature. Two techniques are generally used: solvent extraction (with or without concentration of the extract)[6-8] and sorption onto an appropriate sorbent.[1,9,10] The first method is the most employed due to its higher overall sensitivity, time requirements and simplicity of the equipment employed.

This paper reports the results obtained in the isolation and analysis of several PAHs and aliphatic hydrocarbons on model systems in the trace range (20–50 ng ml^{-1}) using solvent extraction and fused silica capillary gas chromatography. Recoveries, reproducibility and sensitivity of the overall method were calculated for each analyte using different solvents (*n*-hexane, cyclohexane, *n*-pentane, chloroform, tetrachloromethane and dichloromethane), which lead to the determination of optimum experimental conditions when organic traces in water have to be analyzed.

EXPERIMENTAL

1. Reagents

Solvents: Dichloromethane, chloroform, tetrachloromethane, *n*-pentane, cyclohexane and acetone (analytical reagent Lachema, n.p. Brno, Czechoslovakia) *n*-hexane (analytical reagent, Reachim, USSR).

Analytes: Naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene (Chem. Service, inc., USA). Dodecane, tetradecane, hexadecane, octadecane, eicosane and docosane (Supelco, inc., USA).

2. Glassware

The glassware for each experiment was carefully cleaned with liquid detergent and rinsed with tap water, distilled water and rectified acetone successively. Afterward, it was dried with compressed air.

Procedure: Recovery studies were performed on model systems of the selected hydrocarbons in water. Model solution was prepared by diluting various amounts of the stock solution in acetone ($0.2\,mg\,L^{-1}$) with distilled water.

3. Isolation of the analytes from the model system

Without evaporation of the organic solvent: a glass vessel was devised for isolating the analytes from the matrix (see Figure 1). The inlet port heads (A) were made of thick-walled capillaries (1.5 mm i.d.) where a silicon-rubber (B) and PTFE septa (C) (2 and 0.1 mm thick, respectively) were clamped with a nut (D) and a screw (E). 20 ml of distilled water was brought into the vessel and it was tightly closed. 5 μl of the acetone solution was injected into the water, giving a concentration of $50\,ng\,ml^{-1}$ (ppb) of each analyte. 0.6 ml of solvent was injected into the system at once. All the injections were made with Hamilton syringes (Bonaduz, Switzerland). The vessel was manually shaken for 2 or 10 minutes at room temperature (25°C). After this time, the vessel was placed in a vertical position for 15 minutes and 1 μl of the organic phase was taken out through the corresponding inlet port head and injected into the GC

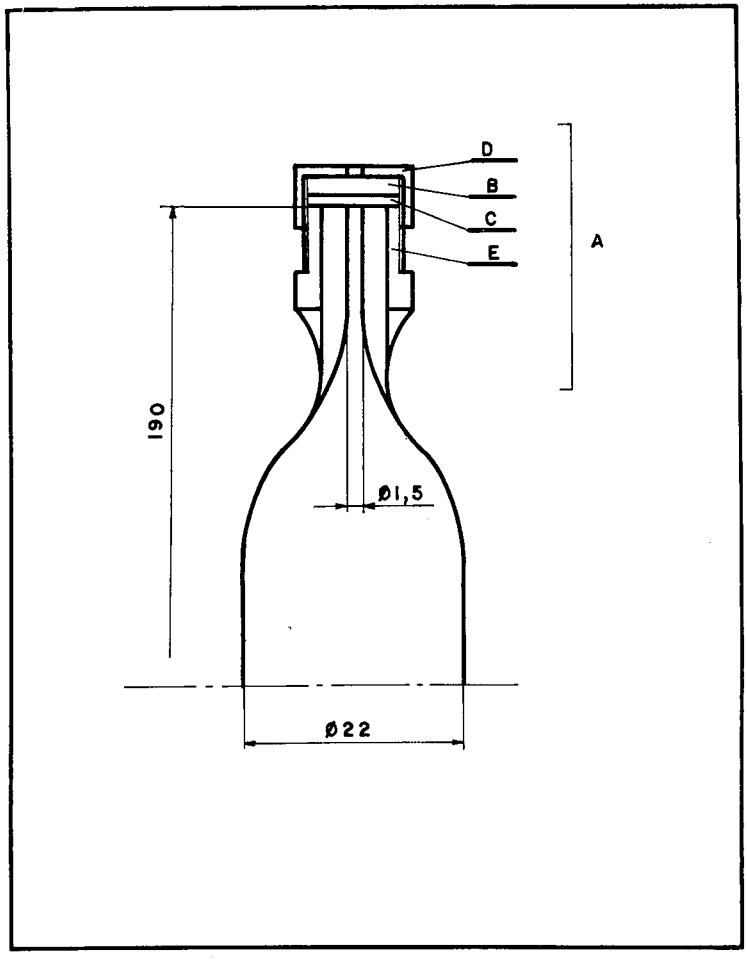

FIGURE 1 Glass vessel used for isolation of studied analytes from water matrix. A = inlet past head; B = silicone rubber septa; C = PTFE septa; D = nut; E = screw.

column. For solvents lighter than water it was necessary to raise the level of the water–solvent system up to the upper inlet port head, injecting slowly through the lower one a 50% solution of saccharose.

With evaporation of the organic solvent: A separating funnel (1 L) provided with ground-in stopper and stopcock was used for isolating the analytes with subsequent solvent evaporation. 1 L of distilled

water and 100 μl of the acetone solution were brought into the funnel giving a concentration of 20 ng ml^{-1} for each analyte. Only *n*-hexane and chloroform were employed in these experiments according to results obtained in part A. 30 ml of the solvent was added to the system and it was immediately shaken by hand for 10 minutes. After 15 minutes of repose the aqueous phase was separated and passed through a funnel containing 1–2 g of anhydrous sodium sulphate. 5 ml of solvent were used for rinsing the dryer medium and poured into the extract. The extract was concentrated in a modified Kuderna–Danish concentrator up to 0.5 ml putting it into a beaker with flowing water kept at 80–81°C (for *n*-hexane) or 72–73°C (for chloroform) with a thermostat.

In order to calculate the losses during the concentration step several experiments were carried out taking a volume (30 ml) of a model solution of analytes (20 μg each) in *n*-hexane and chloroform respectively and carefully evaporating it up to 0.5 ml at the same conditions as above described. The recoveries were individually calculated for each analyte and expressed in percents.

A blank was obtained for both *n*-hexane and chloroform from water free of analytes, including all sample processing steps of the analytical technique.

Recovery calculations

The recoveries were determined by direct comparison of the peak areas on the chromatogram of 1 μl of the extracts and those obtained from the analysis of 1 μl of a solution simulating a 100% recovery efficiency for each solvent (the solvent solubility in water was taken into account).

The method detection limit (MDL)

The calculation of the MDL was carried out according to B. Kolb *et al.*[11] taking a small peak on the chromatogram of the blank as the least abundant signal necessary to achieve identification at the fixed chromatographic conditions.

Gas chromatographic analysis

A Hewlett–Packard 5880A gas chromatograph with split-splitless

injector and a flame ionization detector (FID) was used for the analyses. Splitless injection technique was used. A fused silica capillary column (12 m × 0.2 mm i.d.) deactivated with Carbowax 20M and coated with methylsilicone phase was used. The column temperature was programmed from 35°C (0.6 min) to 150°C at 20°C min^{-1} and then to 220°C at 5°C min^{-1}. The final temperature was held for 10 minutes. The injector temperature was 300°C and the FID temperature was 300°C.

Gas flows were: carrier gas (nitrogen): 0.250 ml min^{-1}; air: 300 ml min^{-1}; hydrogen: 30 ml min^{-1}; auxiliary gas (nitrogen): 30 ml min^{-1}.

Typical chromatograms of analytes and appropriate blanks are shown in Figure 2.

RESULTS AND DISCUSSION

In order to avoid the introduction of uncertainties in the quantitative analysis of the samples, the devised glass vessel was arranged to ensure that contact between the sample and the septa was reduced to a minimum (see Figure 1). The use of separate septa for introducing the volume of the starting solution into the water and sampling the organic phase prevented the samples from becoming contaminated by possible traces of the analytes included in the septum.

The water-solvent ratio of 33:1, is appropriate to obtain high recoveries. All the extractions were made by manual shaking because the experiments made with a mechanical shaker did not give reproducible results. This finding is in agreement with the facts reported by K. Grob *et al.*[9]

The recoveries obtained using six different extractants at 10 minutes of extraction period are shown in Tables I and II. With a few exceptions the recoveries were greater than 70% and for the majority of the studied compounds they were around 80–100%. For both the aliphatics and the PAHs, *n*-pentane showed smaller recoveries as compared with other solvents.

The reproducibility of the recoveries was acceptable.

Table III shows that procedure A permits the determination of tenths of $\mu g\,L^{-1}$ of the studied compounds.

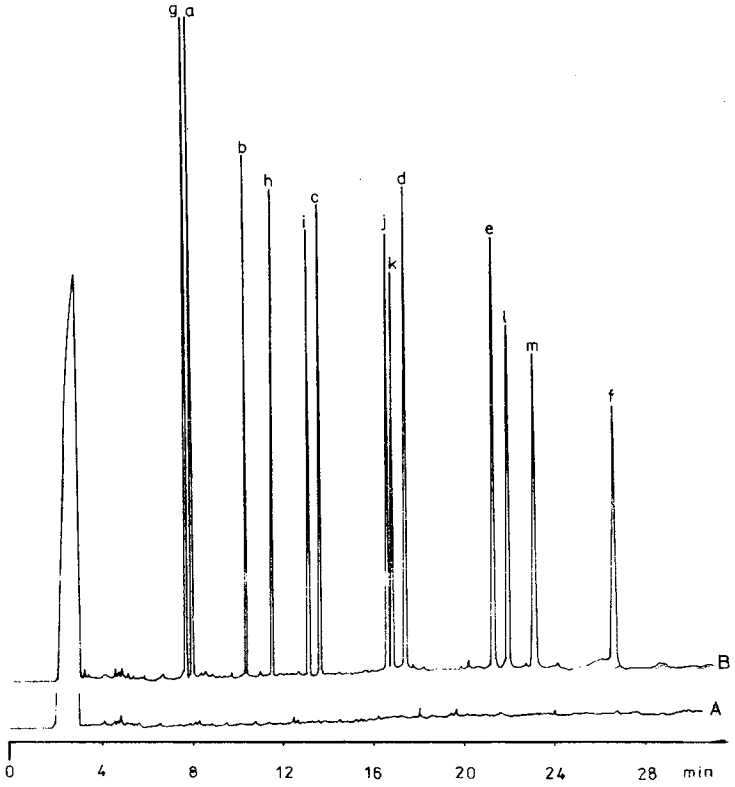

FIGURE 2 Gas chromatogram of chloroform extract.
A Blank (no analytes added).
B Concentration of analytes 50 $\mu g\,L^{-1}$ in water.
a = dodecane; b = tetradecane; c = hexadecane; d = octadecane; e = eicosane; f = docosane; g = naphthalene; h = acenaphthene; i = fluorene; j = phenanthrene; k = anthracene; l = fluoranthene; m = pyrene.

The above model extraction experiments showed that the reached sensitivity (MDL) is still insufficient for many applications in water pollution control, specially when it is necessary to check drinking water. Therefore, improvement of sensitivity is of great interest. For this purpose single step liquid–liquid extraction experiments with solvent evaporation were carried out taking the same analytes and employing chloroform and *n*-hexane as solvents (B). A modified Kuderna–Danish concentrator was used for extract concentration.

TABLE I

Recoveries (%) of the aliphatics isolated (together with the PAHs) by single step extraction with six different solvents at 10 minutes of extraction interval (no concentration step). Analyte concentration 50 $\mu g\,L^{-1}$ of each, each value is an average of six measurements.

Compound	Solvent					
	1	2	3	4	5	6
n-C_{12}	91 ±10	91 ±8	113 ±13	110 ±16	81 ±14	78 ±22
n-C_{14}	82 ±14	86 ±10	111 ±11	100 ±22	78 ±18	82 ±18
n-C_{16}	85 ±14	87 ±9	89 ±9	96 ±21	78 ±18	74 ±14
n-C_{18}	79 ±14	86 ±10	99 ±15	83 ±16	74 ±15	66 ±11
n-C_{20}	75 ±15	94 ±11	104 ±21	83 ±21	88 ±17	72 ±14
n-C_{22}	66 ±17	94 ±10	99 ±24	70 ±20	70 ±11	58 ±8

Solvents: 1 = chloroform; 2 = tetrachloromethane; 3 = dichloromethane; 4 = n-hexane; 5 = cyclohexane; 6 = n-pentane.

TABLE II

Recoveries (%) of the PAHs isolated (together with the aliphatics) by single step extraction with six different solvents at 10 minutes of extraction interval (no concentration step). Analyte concentration 50 $\mu g\,L^{-1}$ of each, each value is an average of six measurements.

Compound	Solvent					
	1	2	3	4	5	6
Naphthalene	102 ±13	113 ±4	120 ±34	110 ±6	102 ±8	91 ±17
Acenaphthene	99 ±8	100 ±12	107 ±18	109 ±13	104 ±10	90 ±13
Fluorene	97 ±6	112 ±13	105 ±25	99 ±14	98 ±6	77 ±9
Phenanthrene	95 ±12	98 ±22	98 ±34	99 ±20	87 ±7	70 ±22
Anthracene	62 ±15	—	91 ±32	88 ±14	82 ±9	—
Fluoranthene	77 ±19	93 ±20	78 ±26	75 ±15	94 ±26	61 ±22
Pyrene	83 ±20	89 ±11	75 ±26	74 ±18	78 ±24	67 ±13

Solvents: 1 = chloroform; 2 = tetrachloromethane; 3 = dichloromethane; 4 = n-hexane; 5 = cyclohexane; 6 = n-pentane.

TABLE III

Method detection limits (MDL), ($\mu g\,L^{-1}$) of selected compounds reached by single step extraction with six different solvents at 10 minutes of extraction interval, without concentration step. (Each value is an average of six measurements.)

Compound	Solvent					
	1	2	3	4	5	6
n-C_{12}	0.44	0.47	0.45	0.51	0.57	0.57
n-C_{14}	0.71	0.76	0.70	0.80	0.84	0.72
n-C_{16}	0.78	0.90	0.72	0.97	0.99	0.86
n-C_{18}	0.86	0.94	0.69	1.01	1.03	0.87
n-C_{20}	0.96	0.89	0.64	1.00	0.85	0.86
n-C_{22}	1.87	1.46	1.10	1.04	1.65	1.63
Naphthalene	0.48	0.46	0.54	0.57	0.46	0.50
Acenaphthene	0.96	0.95	0.85	1.09	0.89	0.97
Fluorene	1.08	1.07	0.98	1.17	1.03	1.19
Phenanthrene	1.00	1.02	0.90	1.14	0.87	1.29
Anthracene	1.58	—	1.16	1.50	1.03	—
Fluoranthene	2.15	2.07	2.07	1.05	1.12	2.45
Pyrene	3.13	2.58	2.31	1.29	1.53	2.81

Solvents: 1 = chloroform; 2 = tetrachloromethane; 3 = dichloromethane; 4 = *n*-hexane; 5 = cyclohexane; 6 = *n*-pentane.

It has been reported in the literature that the Kuderna–Danish concentrators are very suitable for volatile solvents such as diethyl ether and *n*-pentane[6] and exhibit some drawbacks when they are used for heavier solvents requiring a very long time (about 4–5 h) for the concentration of the extracts and therefore some analytes may decompose. The Kuderna–Danish concentrator used in this work consists of a round bottom flask connected by means of a watertight connector to a receiving vessel 70 mm long and 3.5 mm i.d. and gauged for 0.5 ml. The flask is coupled to a Vigreux column 180 mm long and 12 mm o.d. This arrangement permits to insert the flask up to its neck, thus facilitating the concentration step. The results obtained by the above mentioned procedure are shown in Table IV.

The recoveries and errors for both the aliphatics and the PAHs with *n*-hexane were similar and gave better results than chloroform. Moreover, the modified Kuderna–Danish concentrator which was used for concentrating the extracts reduced losses of compounds,

TABLE IV
Recoveries (%) of aliphatics and PAHs isolated by single step extraction with *n*-hexane and chloroform as solvents at 10 minutes of extraction interval (with concentration step). Analyte concentration 20 $\mu g\,L^{-1}$ of each, each value is an average of six measurements.

	Solvent	
Compound	*n*-hexane	chloroform
n-C_{12}	82±8	85±12
n-C_{14}	86±11	96±9
n-C_{16}	90±12	104±5
n-C_{18}	90±11	100±8
n-C_{20}	89±10	89±17
n-C_{22}	87±10	80±20
Naphthalene	83±7	86±12
Acenaphthene	87±10	100±7
Fluorene	87±11	103±4
Phenanthrene	88±11	102±10
Anthracene	85±11	106±10
Fluoranthene	83±13	99±22
Pyrene	80±13	100±22

which permits the conclusion that overall losses of analytes during the procedure were in general caused by the extraction step rather than by the concentration process.

On the other hand a short time of about 20 minutes was required for the above concentration step which allowed to minimize possible decomposition of the studied analytes. Table V lists the MDL for each analyte with this procedure.

The data show that concentrations of tenths of ng L^{-1} could be determined. However, this sensitivity could be improved by careful evaporation of the final volume of 0.5 ml down to less solvent volume.

In Figure 3 results obtained from the determination of alkanes in presence and absence of PAHs in the solution are shown. Extraction periods were 2 and 10 minutes. The presence of PAHs affected kinetics of extraction of alkanes. On the other hand data of recoveries shown in Figure 4 indicate that the presence of *n*-alkanes

TABLE V

Method detection limits (MDL), ($ng\,L^{-1}$) of selected compounds reached by single step extraction with chloroform and *n*-hexane respectively at 10 minutes of extraction interval, with concentration step. (Each value is an average of six measurements.)

	Solvents	
Compound	chloroform	*n*-hexane
n-C_{12}	10.5	11.9
n-C_{14}	10.9	10.2
n-C_{16}	15.2	13.5
n-C_{18}	18.6	19.7
n-C_{20}	21.7	21.8
n-C_{22}	16.8	14.0
Naphthalene	18.4	16.2
Acenaphthene	26.1	17.2
Fluorene	17.7	13.5
Phenanthrene	21.4	14.2
Anthracene	31.6	23.0
Fluoranthene	39.1	26.9
Pyrene	43.0	23.9

changed neither kinetics of extraction nor partition equilibrium of PAHs.

Similar behavior was found employing *n*-hexane and cyclohexane as extractants.

According to the two-resistance theory and resistance additivity principle of Whitman[12,13] one should expect a normal interface transfer of the analytes between the water and organic phase without any interfacial resistance. Ward and Brooks[14] studied the transfer of lower fatty acids across a toluene-water interface and found that the ratio of concentration at the interface in two liquids agreed with static equilibrium values. Gordon and Sherwood[15] found the same behavior for a large variety of organic acids and bases. The work of Drickamer,[16] on the other hand, shows in less direct fashion that interfacial resistance to mass transfer may exist under some circumstances. Liquid–liquid interfaces are ordinarily mobile, turbulence and motion in one liquid being easily transmitted across the

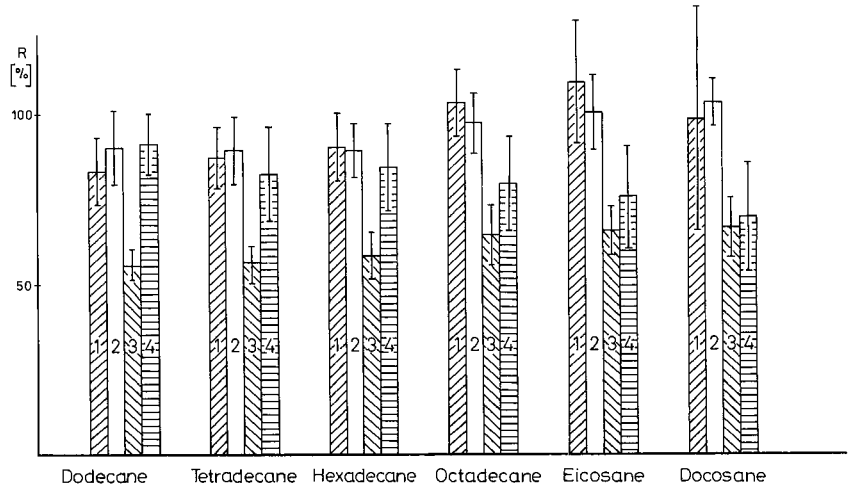

FIGURE 3 Recoveries of aliphatics isolated by single step extraction with chloroform at 2 and 10 minutes extraction interval. Concentration of analytes 50 $\mu g\,L^{-1}$ of each. 1 = aliphatics only, 2 min extraction; 2 = aliphatics only, 10 min extraction; 3 = aliphatics and PAHs, 2 min extraction; 4 = aliphatics and PAHs, 10 min extraction.

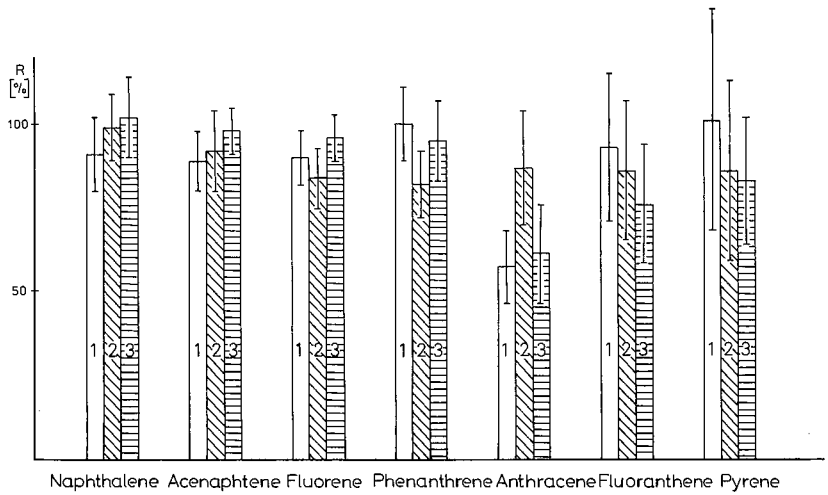

FIGURE 4 Recoveries of PAHs isolated by single step extraction with chloroform at 2 and 10 minute extraction interval. Concentration of analytes 50 $\mu g\,L^{-1}$ of each. 1 = PAHs only, 2 min extraction; 2 = PAHs and aliphatics, 2 min extraction; 3 = PAHs and aliphatics, 10 min extraction.

interface and therefore it affects the magnitude of the mass transfer coefficient in the other liquid. There are good evidences that certain trace substances adsorbed at the liquid–liquid interface may affect the normal surface motion, thus reducing the rate of interface transfer. Lewis[17,18] found that a rigid protein film adsorbed at the interface retarded transfer markedly. The described effects have been always caused by the presence of surface-active substances. However, the facts show that the PAHs, which are not surface active substances, affected the kinetics of extraction of the aliphatic hydrocarbon under the studied conditions.

According to the experiments carried out the single step liquid–liquid extraction with evaporation of the extract which is an easy and simple analytical technique, was found to be suitable to determine the aliphatic hydrocarbon together with the PAHs at rather low concentrations. However, the presence of the PAHs in the matrix can interfere with the normal interface transfer of the aliphatics, thus affecting their recoveries.

Therefore, the choice of the correct extraction interval and manner of shaking is essential.

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