

Isolation of Polycyclic Aromatic Hydrocarbons (PAHs) From Water by C-18 and Clean-Up by XAD-2 Resin

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Determinou-se a eficiência de extração e recuperação da fase C-18 para amostras de água destilada dopadas com 16 hidrocarbonetos policíclicos aromáticos (PAHs). Procedeu-se ao "clean-up" para os 16 PAHs que foi baseado na adsorção cromatográfica na resina XAD-2, seguido de eluição seletiva com metanol, n-pentano e acetato de etila. Deste modo separou-se a fração que contém PAHs que foi analisada por cromatografia gasosa capilar. Obteve-se boa recuperação (81,1-96,2%) para os PAHs de alto peso molecular, usando-se 0.3 g de fase C-18. O procedimento de "clean-up" na resina XAD-2 com a posterior eluição seletiva provou ser adequado para a separação dos interferentes polares.

The recovery efficiency of a C-18 phase is determined using distilled water samples containing organic pollutants and a clean-up procedure is developed for 16 polycyclic aromatic hydrocarbons (PAHs). It is based on adsorption chromatography on XAD-2 resin and stepwise elution with metanol, n-pentane and ethyl acetate. The PAH fraction in water is isolated by this method and determined by capillary gas chromatography. The efficiency of group isolation is demonstrated with a mixture of 16 PAHs, hydrocarbons (C₁₅-C₂₀), 2,6-dimethylphenol, 1-octanol, 2-octanone and 2,6-dimethylaniline. Good recoveries were obtained for higher molecular weight PAHs (81.1 - 96,2%) by using 0.3 g of the C-18 phase. Clean-up by a XAD-2 resin provided clean PAHs with total elimination of polar and non-polar organic contaminants.

Key Words: aromatic hydrocarbons; PAH; XAD-2 resin.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a class of organic compounds named "unambiguous priority pollutants" by the US Environmental Protection Agency (EPA)¹. This class of compounds has been shown to contain several potent carcinogens².

Identification and quantification studies of this class of compounds in water matrices are necessary for solving several environmental problems arising from their biologic activity. The difficulty is to find an adequate support that could be used to pre-concentrate and isolate such compounds in order to minimize matrix interferences.

In fact, bonded phase silica is widely used to pre-concentrate organic compounds in natural waters³⁻⁹. A large variety of these supports chemically bonded to silica allow the choice of the more efficient sorbent in the particular application of interest¹⁰⁻¹². An accurate determination of PAHs requires an efficient separation from polar and non-polar compounds that exist in large concentrations in natural waters. Thus, some methods like gel silica chromatography,

sephadex LH-20¹³ and thin layer chromatography¹⁴ have been used. XAD-2 resin, due the large quantity of aromatics, can strongly adsorb PAHs¹⁵.

In this work we investigated the performance of C-18 phase (octadecylsilane) to concentrate 16 PAHs and XAD-2 resin (DVB-styrene copolymer) to separate them from other polar and non-polar organic pollutants in water.

Materials and Methods

Reagents and standards

A stock solution was prepared from PAHs, n-alkanes and polar organic compounds. This stock solution was prepared from a naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene (Supelco Bellfonte, PA, USA) mixture with nominal concentrations of 2000 ppm in benzene/methyl chloride (1:1 v/v) and from another stock solution of n-alkanes (C₁₅, C₁₆, C₁₇, C₁₈ and C₂₀), 2,6 dimethylphenol, 1-octanol, 2-oc-

tanone and 2,6 dimethylaniline (Supelco, Bellefonte, PA, USA) at the 500 ppm level in methyl chloride. Further dilutions were made with methanol (Merck) using a Hamilton Syringe (100 μ l) with final concentrations of 5 ppm each.

Solvents were glass-distilled through a column 150 cm long. Water was purified in Milli-Q Purifier System (Millipore). XAD-2 (Rohm and Hass Company) of particle size 20-50 mesh and C-18 phase (Sigma Chemical Company) of particle size 40-63 μ m were purified by sequential soxhlet extractions with methanol for 8h, acetonitrile for 8h and ethyl acetate for 8h.

Sample preparation

A micro-column 5.0 cm long and 0.5 cm I.D. was filled with C-18 phase in different weights. It was then conditioned with 1 ml of methanol followed by 5 ml of distilled water. 1 ml of the stock solution (PAHs, n-alkanes and polar organic compounds) at concentrations of 5 ppm was diluted to 1000 ml of water (5 ppb each compound) and perylene was used as internal standard. This solution was passed through the micro-column and its flow rate was adjusted to 30 ml/min by a peristaltic pump (HP 89052 A). After the adsorption the column was dried with nitrogen gas at 40 °C. The adsorbed material was eluted with 2 ml of ethyl acetate allowing an equilibrium period of 60 s between the solvent and the C-18 phase. A glass column of 0.5 cm I.D. was filled with 1.25 g of XAD-2 resin to a height of 9 cm. A solvent reservoir was placed on top of the column. The eluted material from the C-18 was transferred quantitatively to the top of resin bed. The column was then eluted successively with 5 ml portions of methanol (polar fraction), 5 ml of n-pentane (non-polar fraction) followed by 10 ml of ethyl acetate (PAH fraction). Solvent flow rate was adjusted to 3 ml/min. Finally, a further volume of 10 ml of ethyl acetate was passed through the column, followed by 15 ml of ethanol. The column was then ready for the next sample.

The fractions were evaporated to 0.5 ml and analysed by high resolution gas chromatography (HRGC).

Gas Chromatography

Extracts were analysed on a HP 5890 gas chromatograph, equipped with a flame ionization detector and a HP Ultra-1 column (25 m x 0,32 mm I.D., WCOT), with 0.17 μ m thick film. The oven temperature was programmed from 100 to 280° C at 5° C/minute during each chromatographic run.

Results and Discussion

Good recoveries of most of the sixteen PAHs in water were obtained by using C-18 and perylene as internal standard (Table 1).

Except for naphthalene and acenaphthylene, good recoveries were obtained for the higher molecular weight PAHs (81.1 - 96.2%). The decrease recovery of lower molecular weight PAHs like naphthalene and acenaphthylene, 52.6% and 72.0%, respectively, was attributed to losses during the drying step.

The use of a peristaltic pump brings some advantages such as the increasing of the reproducibility of the extraction method due its constant flow and an unlimited volume of sample can be eluted. However the small size of the particles of C-18 phase causes a great compaction of them and over 0.3 g of C-18 the peristaltic pump losses its capacity to elute the sample.

Isolation of PAHs

Desorption of organic compounds from XAD-2 resin is strongly influenced by the type of solvent. Table 2 lists the volumes of different solvents required for complete elution of non-polar compounds (n-alkanes, C₁₅-C₁₈ and C₂₀), polar compounds (2,6-dimethylphenol, 2,6-dimethylaniline, 1-octanol and 2-octanone) and PAHs at 5 μ g level of each compound.

Table 1. Recoveries of Polycyclic Aromatic Hydrocarbons by using different weights of C-18 phase.

peak	compound	Recovery (%)*		
		0.12g	0.25g	0.3g
5	naphthalene	50.5	51.2	52.6
6	acenaphthylene	67.4	69.6	72.0
7	acenaphthene	69.3	70.6	87.2
9	fluorene	67.7	75.1	81.1
12	phenanthrene	64.4	88.5	85.3
13	anthracene	48.6	79.9	86.0
15	fluoranthene	54.5	87.4	88.9
17	pyrene	53.9	88.2	84.6
18	benzo[a]anthracene	17.7	76.5	91.0
19	crysene	16.8	77.8	95.0
20	benzo[b]fluoranthene	18.0	82.4	96.1
21	benzo[k]fluoranthene	14.1	77.5	95.8
22	benzo[a]pyrene	16.0	75.9	91.1
23	dibenzo[a,h]anthracene	15.8	78.8	96.2
24	benzo[ghi]perylene	15.4	73.3	91.0
25	indeno[1,2,3-cd]pyrene	16.0	77.6	92.3

* each experiment was made in triplicate.

These values were obtained by collecting 5 ml portions from the column eluate and analysing by gas chromatography.

Table 2. Required volumes (ml) for the complete desorption of classes of compounds from XAD-2.

solvent	non-polar	polar	PAHs
methanol	50	10	50
toluene	5	5	5
n-pentane	5	10	50*
ethyl acetate	5	5	5

* except for naphthalene, acenaphthylene and acenaphthene.

Methanol is a strong eluent for polar compounds and a weak one for n-alkanes and PAHs. For the elution of non-polar and PAHs a large volume of methanol is necessary; n-pentane is a strong eluent for n-alkanes, but it shows inadequate results for lower molecular weight PAHs, such as naphthalene, acenaphthylene and acenaphthene; n-pentane shows good elution for these compounds. The same occurs with three ring PAHs, such as phenanthrene and anthracene, but with less intensity.

Toluene and ethyl acetate are strong eluents and do not get any group separation on XAD-2 if they are used separately. Due to these difficulties, a clean-up with three different solvents was developed by using 5.0 ml of methanol to eliminate polar compounds, 5.0 ml of n-pentane to eliminate non-polar compounds and 10.0 ml of ethyl acetate to eliminate PAHs.

Recovery efficiencies were tested by using reference mixtures with 5 µg each of the sixteen PAHs and the other nine organic pollutants, by using external standardization. They are listed in Table 3. The chromatograms (Figures 1-4) were obtained by injection of 2.0 µl aliquots on the gas chromatograph.

Table 3. Recoveries of polar, non-polar compounds and PAHs after clean-up on XAD-2.

Compound	Recovery (%)*		
	fraction 1	fraction 2	fraction 3
2-octanone	86.6	13.5	-
1-octanol	87.1	13.1	-
2,6-dimethylphenol	94.7	5.3	-
2,6-dimethylaniline	84.6	14.4	-
C ₁₅	-	100	-
C ₁₆	-	100	-
C ₁₇	-	100	-
C ₁₈	-	100	-
C ₂₀	-	100	-
naphthalene	-	74.0	26.0
acenaphthylene	-	41.0	59.0
acenaphthene	-	20.0	80.0
fluorene	-	-	100
phenanthrene	-	10.0	90.0
anthracene	-	11.0	89.0
fluoranthene	-	-	100
pyrene	-	-	100
benzo[a]anthracene	-	-	100
crysene	-	-	100
benzo[b]fluoranthene	-	-	100
benzo[k]fluoranthene	-	-	100
benzo[a]pyrene	-	-	100
dibenzo[a,h]anthracene	-	-	100
benzo[ghi]perylene	-	-	100
indeno[1,2,3-cd]pyrene	-	-	100

* each experiment was made in triplicate.

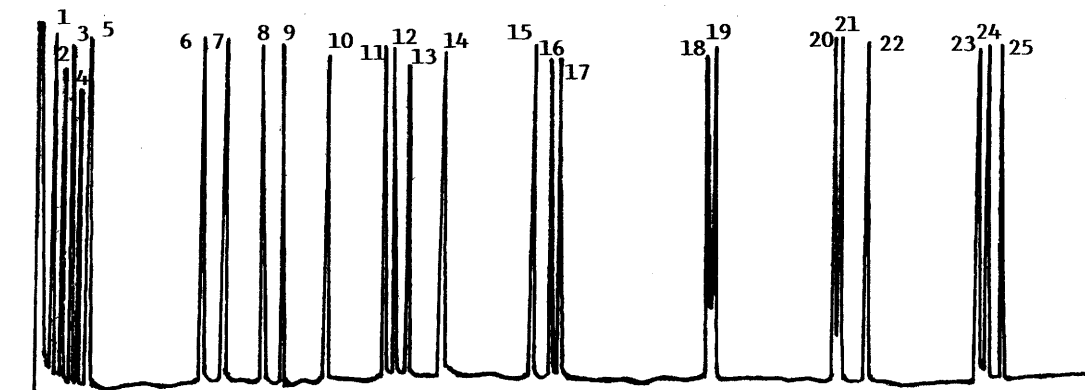


Figure 1. Gas chromatogram of all compounds studied.

1. 2-octane, 2. 1-octanol, 3. 2,6-dimethylphenol, 4. 2,6-dimethylaniline, 5. naphthalene, 6. acenaphthylene, 7. acenaphthene, 8. C₁₅, 9. fluorene, 10. C₁₆, 11. C₁₇, 12. phenanthrene, 13. anthracene, 14. C₁₈, 15. fluoranthene, 16. C₂₀, 17. pyrene, 18. benzo[a]anthracene, 19. crysene, 20. benzo[b]fluoranthene, 21. benzo[k]fluoranthene, 22. benzo[a]pyrene, 23. dibenzo[a,h]anthracene, 24. benzo[ghi]perylene, 25. indeno[1,2,3-cd]pyrene.

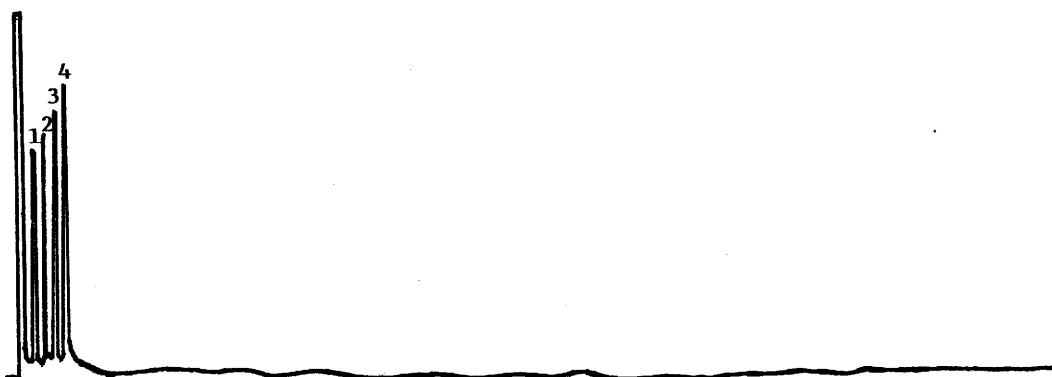


Figure 2. Gas chromatogram of polar fraction. 1. 2-octane, 2. 1-octanol, 3. 3,6-dimethylphenol, 4. 2,6-dimethylaniline.

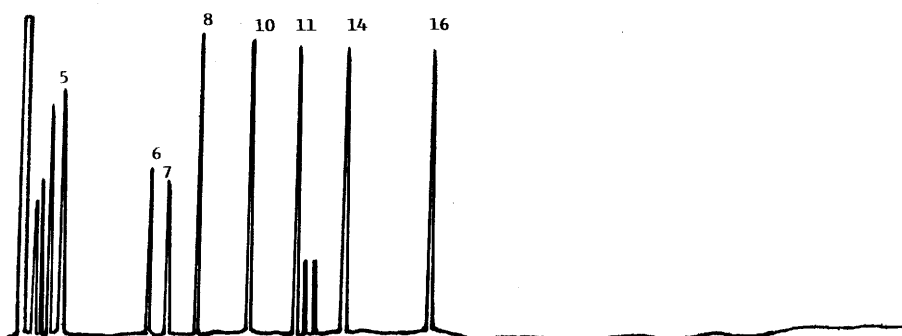


Figure 3. Gas chromatogram of the non-polar fraction. 5. naphthalene, 6. acenaphthylene, 7. acenaphthene, 8. C₁₅, 10. C₁₆, 11. C₁₇, 14. C₁₈, 16. C₂₀

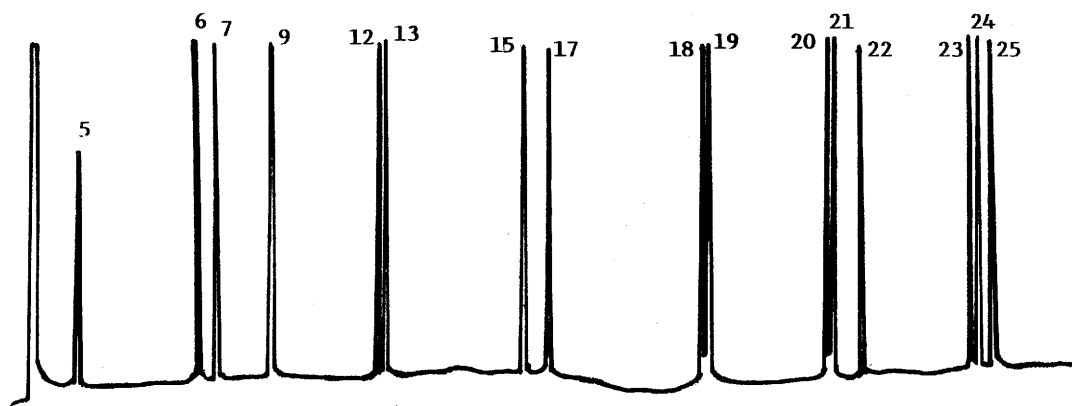


Figure 4. Gas chromatogram of the PAH fraction.

5. naphthalene, 6. acenaphthylene, 7. acenaphthene, 9. fluorene, 12. phenanthrene, 13. anthracene, 15. fluoranthene, 17. pyrene, 18. benzo[a]anthracene, 19. crysene, 20. benzo[b]fluoranthene, 21. benzo[k]fluoranthene, 22. benzo[a]pyrene, 23. dibenzo[a,h]anthracene, 24. benzo[ghi]perylene, 25. indeno [1,2,3-cd]pyrene.

Figure 2 shows the elimination of polar compounds after elution with methanol. The total elimination of non-polar compounds after elution of n-pentane and partial elimination of PAHs of two and three rings is shown in Figure 3. Clean-up by XAD-2 provided clean PAHs with total elimination of polar and non-polar organic contaminants (Figure 4).

Conclusions

The extraction of PAHs using C-18 phase showed good recoveries and further advantages compared with conventional solvent extraction methods. It was observed that the extraction step simultaneously involves the sample concentration, decreasing the preparation time and minimizing the background interferences due to the adsorption and selective

elution the sample. The extraction limit for PAHs was determined by the amount of the sample in the micro-column, since another solute present in large concentrations do not saturate the phase capacity.

The XAD-2 resin proved to be a good adsorbent for the separation of PAHs from polar and other non-polar organic contaminants from water matrices.

These factors improve the precision and accuracy of the analysis.

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