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Original Research

Use of High-Pressure Carbon Dioxide Extraction with Modifiers for the Preliminary Isolation of Organic Pollutants

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Abstract

The effect of different solvents on extraction with liquid carbon dioxide was studied. Extracted polynuclear aromatic hydrocarbons (PAHs) were applied on Sephadex C-50 gel. The model PAHs were phenanthrene, pyrene and benzo(a)pyrene. It is stated that the percentage of PAH model extractions was diminished when water-immiscible solvents (cyclohexane, chloroform and benzene) and methanol were added to the system. The addition of acetone and dimethylformamide caused increases in extraction percentage. The optimum content of both these solvents was shown to be approximately 0.8% in relation to the volume of CO_2 used .Under these conditions, a single extraction in the presence of acetone made it possible to recover 67% of phenanthrene, 62% of pyrene and 86% of benzo(a)pyrene, whereas in the presence of dimethylformamide these numbers were 66%, 80% and 90%, respectively.

Keywords: high pressure, extraction, modifier, carbon dioxide

Introduction

One of the most important problems in PAH analysis in the human environment is quantitative isolation of the hydrocarbons from samples such as soils, sewage sludges, dusts, etc. because during isolation they can be subject of many reactions or even destruction. In such cases supercritical and high pressure extraction have been widely used recently because of numerous advantages such as the short time of the process, ease of solvent removal, low temperature, etc. [1]. Additionally, new solvents which wet solid samples may be used. These are mainly liquid carbon dioxide, nitrous oxide and chlorodifluoromethane [1, 2]. Under standard conditions they are gases and this makes it possible to easily isolate the extracted material without heating [1].

Liquid CO_2 is the most commonly used solvent due to its availability. Attempts to use liquid CO_2 in the extraction of PAHs from many environmental materials makes only partial hydrocarbon recovery possible. Then the use of substances modifying a solvent's properties are required [1]. The effect of the modifiers may be explained by their multiple influence: they may reduce surface tension of liquid CO_2 on solid organic and inorganic particles on which PAHs are deposited, they may damage the aqueous layer surrounding the particles, and they may increase PAH solubility in the mixture compare to pure liquid carbon dioxide.

Gere et al. [3] have defined the effect of methanol addition, obtaining an increase in extraction percentage in practically all cases, and especially for high molecular hydrocarbons such as benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene and indeno(1,2,3-c,d)pyrene (from 0% without modifier to 80-100% with methanol addition). Höfler et al. [4] in similar studies showed that the addition of 5-10% of methanol to CO_2 considerably improves extraction (approximately 10-20%) of naphthalene, biphenyl, phenanthrene, pyrene, dibenzo(a,h)anthracene and benzo(g,h)perylene isolated from soils and sewage sludge. Dankers et al. [5] showed that when using CO_2 as an extraction solvent the addition of dichloromethane enhances extraction percentages of the majority of 16 studied PAHs by 10-100%. In the case of ancenaphthylene and benzo(g,h)perylene the enhancement was from 0 to 100%. Lopez-Avila et al. [6] reported increased PAH recovery in a similar extraction system with CO_2. Hills and Hill [7] showed the advantageous effect of hexamethylsilane and trimethylchlorosilane on PAH extraction from urban dust at 300 atm pressure and 60°C.

These studies are aimed at improving high pressure extraction recovery of polynuclear aromatic hydrocarbons from solid environmental samples under moderate conditions (4.6 Mpa, 50°C), which limits the possibility of PAH

reaction and destruction. Organic material isolated in this way will be used for further separation and determination of particular hydrocarbons using chromatographic methods.

The purpose of this stage was to choose the best modifier under a lower range of pressure (50 atm.), which would permit enhanced extraction percentages of some PAHs.

Experimental

Sample Preparation

Sephadex C-50 silica gel (diameter 20-120 mm, 12.8% water content) was chosen as a model PAH carrier representing solid environmental samples. The standard hydrocarbons were phenanthrene Supelco (3 rings), pyrene Loba (4 rings), benzo(a)pyrene Aldrich-Chemie (5 rings).

On the basis of literature, the following solvents were typified as modifiers: cyclohexane, acetone, dimethylformamide, chloroform, methanol and benzene.

To 200g of Sephadex C-50 gel (dried for 2 hours at 130°C) 200 cm^3 of cyclohexane solution was added, in which concentrations of examined hydrocarbons were as follows:

phenanthrene	1.06 mg
pyrene	1.00 mg
benzo(a)pyrene	1.05 mg

After accurate mixing cyclohexane was evaporated.

Extraction

The sample of the gel (2g) with model PAHs was placed on an extraction thimble, which was then placed in a high-pressure Soxhlet extractor (J & W Scientific Inc., USA). The required amount of modifier (0.4 cm^3) was added to the extraction thimble, the extractor was closed and filled with CO_2, and the process was carried out for 2 hours. The other extraction conditions were:

CO_2 pressure inside the extractor	4.6 MPa
heater temperature	52°C
cooler temperature	0-4°C

The extraction percentages of examined PAHs without modifying solvents was estimated by carrying out extraction from examined samples twice. Each time, extracts were analyzed quantitatively assuming that in both extractions the extraction percentage was the same.

Extracts Analysis

Extracted polynuclear aromatic hydrocarbons were eluted with cyclohexane from a Soxhlet round-bottomed flask. The solutions were transferred into a measuring flask (25 cm^3), diluted with cyclohexane (to the mark) and then subjected to spectrophotometric analysis (ultraviolet range). Before determination, the solvents were removed from samples containing benzene, acetone and dimethylformamide as modifying additives, since they show absorption within the UV spectrum range. A UV-160A spectrophotometer (Shimadzu) was used to measure the concentration of extracted PAHs ("Multikomponent" programme). All results presented in tables are arithmetic means of 3 parallel measurements. Average standard deviations of each measurement were only slightly different and averaged from 1 to 3% (Table 2).

Results and Discussion

Quantitative recovery of polynuclear aromatic hydrocarbons placed on gel is not possible in a single extraction in chosen extraction conditions both with and without selected modifiers.

The amount of a given hydrocarbon permanently bounded with gel and unrecoverable in extraction was unknown and difficult to determine. That is why the real extraction percentage was only estimated. In order to do this two consecutive extractions were performed from the same sample and each time extracted masses were determined (extraction solvent volume was always the same). It can be proved that extraction percent p may be calculated from the formula:

$$p = 1 - \left(\frac{m_2}{m_1}\right) \cdot 100\% \qquad (1)$$

m_1 and m_2 refer to masses extracted in the first and second extractions, respectively.

This is a convenient way of determining real extraction percentages, for instead of concentrations (masses) proportional quantities can be used, e.g. absorbance. Then, instead of the m_2/m_1 ratio one can use the a_2/a_1 ratio, where a_1 and a_2 refer to extract absorbances in the first and second extractions. Adequate data determined to meet this aim are presented in Table 1.

The mass of substance extracted in the first extraction was assumed as 1 and m represents mass ratio m_2/m_1. Calculations performed on the basis of data presented in Table 1 show that extraction percent p of examined hydrocarbons according to formula (1) was as follows:

for phenenthrene	74%
for pyrene	88%
for benzo(a)pyrene	92%

In comparison to PAHs placed on gel the recovery percent was:

phenenthrene	65%
pyrene	80%
benzo(a)pyrene	85%

The addition of solvents affected extraction percentages of examined PAHs. In many cases recovery deteriorated and only in a few was improvement found. The results are collected in Table 2.

In comparison to extraction with pure CO_2, the best improvements in extraction of phenanthrene and benzo(a)pyrene were obtained after the addition of acetone and dimethylformamide. This is why both solvents were selected for further examinations. When checking them the extraction percentage changed, depending on the amount of solvent added. Results are presented in Figs. 1 and 2.

As can be found in Figs. 1 and 2, under experimental conditions the best results are obtained after introducing both 0.4 cm^3 of acetone and dimethylformamide (i.e. 0.8%

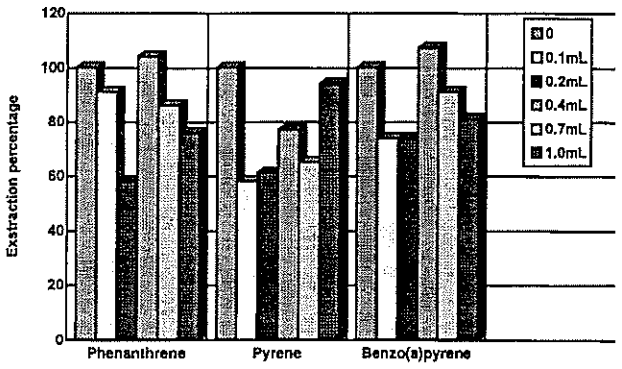


Fig. 1. Influence of acetone addition (cm^3) on extraction percentages of phenanthrene, pyrene and benzo(a)pyrene with CO_2 in high pressure conditions.

in relation to the volume of liquid CO_2 used). In a single extraction with the addition of acetone 67% of phenanthrene, 62% of pyrene and 86% of benzo(a)pyrene applied on gel are recovered. In extraction with dimethylformamide, the percentages are 66, 80 and 90, respectively.

Water (12.8%) present in gel could have influenced behaviour of the extraction system. Approximately 0.25 g of H_2O was introduced to extraction with a sample weighing 2 g. Water may form a thin layer surrounding gel grains with PAHs deposited, and make contact of these compounds with liquid CO_2 difficult. Water-immiscible solvents such as benzene or chloroform may form additional layers, making access of liquid CO_2 worse; despite the fact that they dissolve PAHs, they do not improve extraction. Water-miscible solvents DMF and acetone, (although they dissolve PAHs worse than, e.g., benzene), give positive results because they probably allow the acquous shell to rupture from gel grains and mix easily with liquid CO_2.

Conclusions

1. In studied conditions single supercritical extraction with liquid CO_2 without modifiers did not allow quantitative extraction of model PAHs placed on Sephadex C-50 gel.

2. Non-water-miscible solvents decrease the amount of extracted PAHs in comparison to the amount extracted with pure CO_2.

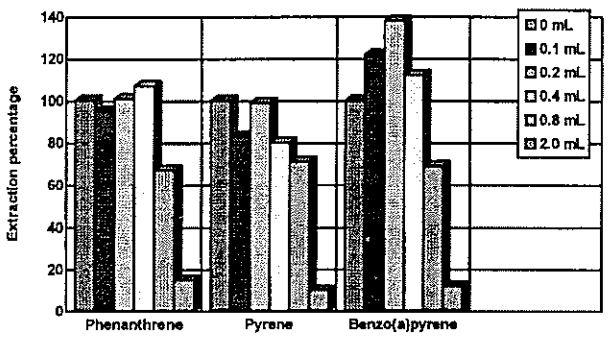


Fig. 2. Influence of DMF addition (cm^3) on extraction percentages of phenanthrene, pyrene and benzo(a)pyrene with CO_2 in high pressure conditions.

Table 1. Extraction percentages of chosen PAHs in the second extraction.

	Phenanthrene	Pyrene	Benzo(a)pyrene
First extraction (m_1)	1	1	1
Second extraction (m_2/m_1)	0.26	0.12	0.8

Table 2. Extraction percentages of chosen PAHs when using a mixture of carbon dioxide and tested solvent in relation to the one using pure CO_2.

	Extraction percentage after addition of:						
	Cyclo-hexane	Acetone	DMF	Chloro-form	Methanol	Benzene	Without any addition
Phenanthrene	85	104	101	79	82	64	100
Pyrene	49	77	99	49	32	45	100
B(a)P	75	107	138	89	78	30	100

B(a)P - benzo(a)pyrene
DMF - dimethylformamide

3. Some water-miscible solvents (acetone, DMF) may enhance extraction percentages.

4. Optimum addition of DMF and acetone for extraction in studied conditions is 0.4 cm^3.

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