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Solid-Phase Extraction of Polycyclic Aromatic Hydrocarbons (PAHs) with a Chemically Modified Polymer-Supported Tetrakis(ρ-carboxyphenyl) Porphyrin(H_2TCPP)

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화학적으로 변형된 고분자지지체인 Tetrakis(ρ-carboxyphenyl) Porhyrin(H_2TCPP)의 다환 방향족 탄화수소화합물에 대한 고체상 추출방법에 관한 연구

백 대 진

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A chemically modified sorbent was evaluated as a preconcentration substrate in solid-phase extraction of polycyclic aromatic hydrocarbons(PAHs). Tetrakis(ρ-carboxyphenyl) Porphyrin(H_2TCPP) was chemically bonded to porous polymeric XAD resins by ketone linkage. Breakthrough volumes, recovery values were determined.

화학적으로 결합된 흡착제를 여러 고리 방향족 탄화수소 화합물(Polycyclic Aromatic Hydorcarbons. PAHs)의 고체상 추출법(Solid Phase Extraction, SPE)의 흡착제로 이용할 수 있는지 평가하기 위해 합성하였다. Tetrakis (ρ-carboxyphenl)porphyrin (H_2TCPP)를 ketone linkage로 다공성 고분자 XAD 수지에 화학적으로 결합시켰다. 분표계수, 돌파부피와 회수율의 결정은 최적화된 조건에서 수행하였다. 여러 고리 방향족 탄화수소화합물의 고체상추출법에서 화학적으로 변형된 고분자 흡착 물질을 흡착제로 이용할 수 있는지 알아보기 위해서 고성능 액체 크로마토그래피(high-performance liquid chromatogaphy, HPLC)를 사용하였다. 화학적으로 변형된 XAD2 + TCPP보다 XAD4 + TCPP가 PAHs의 회수율 및 돌파부피가 증가함을 알 수 있었다.

Key words: polycyclic aromatic hydrocarbons, solid-phase extraction, Polymer-Supported Tetrakis(ρ-carboxyphenyl) Porphyrin(H_2TCPP), π-π interaction

1. INTRODUCTION

Environmental organic pollutants such as pesticides, polycyclic aromatic hydrocarbons(PAHs), and chlorophenols are not biodegradeble because of their chemical stability. They are very toxic and accumulate in the human body even at low concentrations. Therefore, it is necessary to develop an analytical method that can detect pollutants at trace levels.

PAHs are widespread environmental contaminants resulting from emissions from a variety of soures including: industrial combustion and discharge of fossil fuels, residential heating (both fossil fuels and wood burning) and motor vehicle exhaust. Because of their mutagenic and carcinogenic properties, PAHs have been measured in a variety of environmental matrices including air, water, soil (sediment) and tissue samples. PAHs are usually present in environmental samples as extremely complex structures and alkylated isomers which vary greatly in relative concentrations of the individual components and in carcinogenic and/or mutagenic properties.[1] Because of low concentrations and the complex matrix of environmental organic pollutants, it is necessary to carry out preconcentaration and cleanup steps prior to separation and detection. Many techniques such as solid-phase extraction (SPE),[2,3] liquid-liquid extraction(LLE),[4] supercritical fluid extraction (SFE), accelerated solvent extraction (ASE),[5] microwave extraction, and solid-phase microextraction (SPME)[6] have been used. Solid-phase extraction has been developed in recent years and is now a widely used method because it has many advantages in comparison to liquid-liquid extarction. Many sorbents such as octadecyl-bonded silica (C_{18}),[7] polystyrene-divinylbenzene(PS-DVB) polymers,[8] activated carbons,[9] graphitized carbon black (GCB),[10] and ionexchange resin are used and combined to enhance the selectivity. For example, two or more sorbents and mixed in one column,[11] or two or more columns are coupled in tandem, including ion-exchange resin[12] and/or chemically modified sorbents.[13] Porphyrins are macrocyclic molecules in which four pyroles are bonded by sp^2-hybrid carbon and π electrons are delocalized over the molecule by conjugation. Metalloporphyrins can be synthesized by bonding between var- ious metal ions and porphyrin which can act as an anionic ligand. Kibbey and Meyerhoff[14] reported on the separation of polycyclic aromatic hydrocarbons using metalloporph.

In this study, the availability of polymer-bonded tetrakis(ρ-carboxyphenyl) Porphyrin(H_2TCPP) as a sorbent for solid-phase extraction of PAHs was evaluated. Chemically modified sorbents were synthesized by ketone linkage, then breakthrough volume, recovery, detection limits were determined.

2. MATERIALS AND METHODS

2.1. Chemicals and Reagents

Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz[a]anthracene, Benzo[k]fluorantene, Dibenz[a, h] anthracene were obtained from Aldrich (Milwaukee, WI). They were used as obtained without further purification. Stock solutions were prepared in acetonitrile and working solutions were prepared by diluting the stock solutions with acetonitile before use. Standard solutions for the determination of porphyrin content were prepared form manganese standard solutions from Aldrich (Milwaukee, WI).

2.2. Apparatus

A 50 mm × 2 mm-i.d. poly ether ether ketone(PEEK) column was used to retain the sorbents. Titanium frits (2 μm in pore size) were located above and below each sorbent bed. Sample elution was carried out with a Minipuls 3 peristaltic pump (Gilson, Villiers-le-bel), France). The high-performance liquid chrmatography (HPLC) ststem consisted of a Dynamax SD-200 pump (Rainin, Emeryville, CA), S-3350 Fluorescence detector (Soma, Tokyo, Japan), Autochro-WIN Data module (Younglin, Seoul, Korea), and Rheodyne Model 7125 injector having a 20-μl loop. Separation was carride out using a Hypersil Green PAH column (100×4.6 mm-i.d., 5 μm) from Alltech, and column temperature was maintained at 30°C. An isocratic mobile phase of acetonitrile (100%) was used at a flow rate of 1.0 ml/min. Fluorescence excitation and emission wavelengths were changed to achieve optimal sensitivity and /or selectivity for individual PAHs. The excitation and emission wavelengths currently used at NIST for the analysis of environmental samples are summarized in Table 1. For the breakthrough volume measurements, an PE 3300 atomic absorption spectrometer (Perkin Elmer, Norwalk, CT) having as light source a manganese hollow cathode lamp was used.

2.3. Synthesis Precedure

Amberlite XAD-2 and XAD-4 resins from Janssen Chimica (Geel, Belgium) were ground in a mortar and

Table 1. Fluorescence wavelength conditions for the determination of selected PAHs

Excitation wavelength (nm)	Emission wavelength (nm)	PAHs determined
260	340	Phenanthrene
260	400	Anthracene
285	450	Fluoranthene
333	390	Pyrene
285	385	Benz[a]anthracene
296	405	Benzo[k]fluoranthene, Dibenz[a,h]anthracene

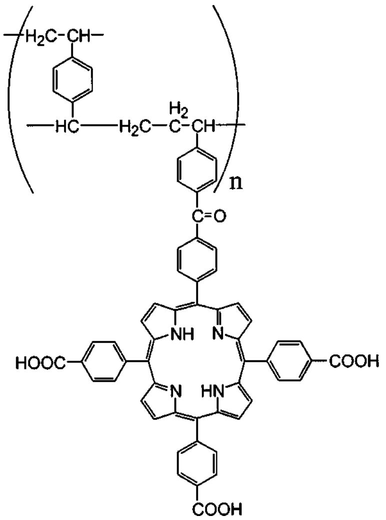

Fig. 1. Structure of chemically modified sorbent synthesized

sieved to 100-150 mesh. They were washed in a column with 1 M HCl/30% methanol, deionized water, acetone, and methanol successively, then purified in a Soxhlet extractor with methanol for 24 h. The purified resin was stored in methanol to maintain its high purity. H_2TCPP was synthesized according to the procedure described by Adler *et al.*[15] Chemically modified sorbents were prepared from XADs and then heated after adding a portion of XAD resin and 30 ml of 1, 1, 2, 2 tetrachloroethane. After cooling to room temperature, $AlCl_3$ was added, and the solution was kept at 10°C for 16 h. The slurry was filtered and washed with 1, 1, 2, 2 tetrachloroethane, methanol, basic aqueous solution. The resulting polymer-bonded porphyrin sorbents were stored in a vacuum desiccator. The structure of the sorbent synthesized is shown in Fig. 1.

3. RESULTS AND DISCUSSION

In this study, chemically modified sorbents synthesized by Friedel-Krafts reations of XAD resins and H_2TCPP were applied to solid-phase extraction of PAHs for the determination of trace-level environmental pollutants.

3.1. Characterization of Synthetic Resins

The amount of porphyrin bonded to XAD resin was determined as follows: after introduction of Mn metal into the porphyrin molecule, Mn was extracted with a small volume of concentrated acid and Mn content was determined by atomic absorption spectrometry. The correlation between the concentration of Mn in standard solution and absorbance was calculated by the least-squares method. As a result, it is calculated that about 0.5 mg of H_2TCPP for about 50 mg of XAD resin was bonded.

Table 2. Breakthrough Volumes for chemically modified sorbents

PAHs	XAD2+TCPP	XAD4+TCPP
Acenaphthylene[a]	1.59 mL	7.06 mL
Benzanthracene[b]	6.63 mL	8.77 mL
Benzo[a]pyrene[b]	7.19 mL	7.25 mL

[a]Concentration of sample in MeOH 0.1 ppm. [b]Concentration of sample in MeOH. 0.1 ppm. Flow rate: 1.0 ml/min

3.2. Breakthrough Volume

The measurement of breakthrough volume is important is solid-phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without loss of analytes during elution of the sample. After the sorbent was synthesized and characterized, it was tested for benzo [k]fluoranthene, which is a higher sensitivity at low concentration. To calculate the breakthrough volume, a breakthrough curve was plotted by eluting the sample into the sorbent column directly connected to the detector. The breakthrough volume values for benzo[k] fluoranthene calculated at 1% of the maximum absorbance value are listed in Table 2.

It can be predicted that chemically modified sorbents can reduce the loss of PAHs during the enrichment step in solid-phase extraction.

3.3. Recovery Test

A Comparative study of the different sorbents was performed by preconcentration 25 ml of a standard solution spiked at 100 ng/ml. 50°C of column temperature and 100% ACN 1 mL as eluting solvent were employed for recovery test.

The recoveries for two sorbents are shown in Table 3. This may result from the increase in π-π interaction between π electrons in porphyrin and those in PAHs owing to the introduction of porphyrin molecules. Fur-

Table 3. Recoveries and coefficient of Variation of PAHs obtained with different sorbents

	XAD-2[C=O]H_2TCPP		XAD-4[C=O]H_2TCPP	
	R (%)[a]	CV (%)[b]	R (%)	CV (%)
Phenanthrene	30.8	3.3	121.7	4.0
Anthracene	25.4	12.0	51.2	5.2
Fluoranthene	43.1	4.0	62.4	1.5
Pyrene	65.5	4.4	105.7	1.9
Benz[a]anthracene	67.1	3.1	114.8	2.0
Benzo[k]fluoranthene	82.2	2.3	119.6	0.3
Dibenza[a, h]anthracene	112.6	4.4	164.8	1.2

[a]Amount of compound spiked in ACN: 100 ng
[b]Coefficient of variation=standard deviation/mean ×100

thermore, the increase in surface area due to the porphyrin macromolecule may be an another factor.

4. CONCLUSION

The synthesized sorbent showed recoveries for the determination of PAHs. XAD4+TCPP showed better PAH recovery and breakthrouph volume compared with XAD2+TCPP. The increased π-π interaction due to the porphyrin molecule may be the major factor in the increase in breakthrough volumes and recoveries.

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