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Analytica Chimica Acta 342 (1997) 41–50

ANALYTICA CHIMICA ACTA

Effects of analyte–matrix interactions on supercritical fluid extraction efficiencies of polycyclic aromatic hydrocarbons

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Received 13 September 1996; received in revised form 24 October 1996; accepted 11 November 1996

Abstract

The effects of different variables for analyte–matrix interactions on supercritical fluid extraction (SFE) efficiencies of polycyclic aromatic hydrocarbons (PAHs) were investigated. The results indicated that the main factors for describing a matrix, e.g., the chemical properties of the matrix surface, surface area, and pore size, could significantly influence the analyte–matrix interactions. The polarizability of an analyte was demonstrated to be yet another significant factor for influencing analyte–matrix interactions. Either elevating the temperature or adding modifiers could also increase the SFE recoveries. The underlying mechanisms of these variables are discussed.

Keywords: Analyte–matrix interactions; Supercritical fluid extraction; PAHs

1. Introduction

Supercritical fluid extraction (SFE) is a highly promising alternative to conventional Soxhlet extraction of a solid sample in environmental analytical applications. Some researchers have thoroughly reviewed the advantages of SFE over conventional methods in preparing organic compounds from hazardous wastes, as well as having summarized current developments in SFE [1–5]. The primary advantage of a supercritical fluid over a general liquid solvent is that its properties, e.g., density, solvent power, and solute diffusivity, can be controlled by varying the applied pressure and temperature. These properties lead a supercritical fluid to greater selectivity, more rapid mass transfer, and a higher flow-rate than a liquid. Additionally, carbon dioxide, the most widely used SFE solvent, possesses the advantages of a low critical point, non-toxicity, and economical price. Therefore, SFE has become an effective technique in environmental sample pretreatment.

Many investigators suggested that SFE recovery could be enhanced by utilizing a more polar solvent, adding a modifier, or increasing the density of the supercritical fluid through an applied pressure and/or temperature [1,2]. All these methods generally were based on increasing the solubility of the analyte. However, some researchers showed that high solubility in the extraction fluid was not always a sufficient condition to yield high extraction efficiency. They further suggested that the sample matrix, the analyte type and kinetic factors could adversely affect SFE [6–8].

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PII S0003-2670(96)00564-8

The physical and chemical properties of an environmental matrix are very complex. Thus, experimentally interpreting the effects of an individual matrix characteristic in SFE is extremely difficult. Such a difficulty makes the interaction between the analyte and the matrix unclear in SFE as well as in most other extraction methods. Furthermore, the capability of removing an analyte from a matrix in SFE depends both on the analyte's solubility in the extraction supercritical fluid and on the analyte's desorption from the matrix. Therefore, it is impossible to decide the effects of the individual matrix characteristics only from the recoveries. In addition, only a small amount of solubility data are available in the literature, thereby making the analyte–matrix interactions in SFE more difficult to understand.

Many polycyclic aromatic hydrocarbons (PAHs) are considered toxic and some have been proven to be carcinogenic in animals. SFE has been employed to extract PAHs from environmental solid samples. Adsorption is used to sample PAHs distributed in water and the atmosphere. After sampling, SFE is a highly effective alternative to recover PAHs. However, the SFE recoveries of PAHs from various matrices significantly differ, possibly owing to the complicated interactions among the matrix, the PAHs and the supercritical fluid [1].

In the present study, we have attempted to investigate the effects of the individual matrix characteristics and analytes on SFE by studying the recoveries of PAHs from different model adsorbents. Since this study is a model study rather than an actual sample study, the effects were investigated on the bases of five PAHs. The effects of elevating the temperature and adding modifiers to recover PAHs were also examined. Two series of adsorbents, i.e., XAD resin (polystyrene divinylbenzene copolymer) and silica gel were selected to be matrices. The XAD resin is the most widely used adsorbent in pretreating PAHs in water and in the atmosphere. Silica gel is another kind of adsorbent which has different chemical properties from the XAD resin. Since the properties of these adsorbents are less complex than of actual matrices, the mechanisms controlling the analyte–matrix interactions can be perceived more precisely by this simplified matrix arrangement. Moreover, ratios of the recoveries were obtained by extracting analytes from various matrices under identical conditions. Such an operation was performed to discuss the effects of the individual matrix characteristics and analytes on SFE without solubility data for the analytes.

2. Experimental

2.1. Samples

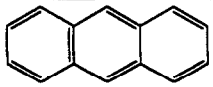
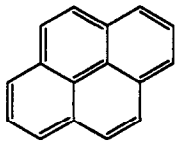
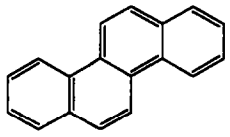
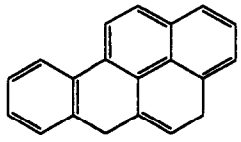
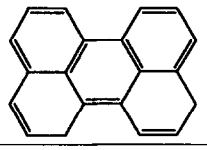
Five PAHs (anthracene, pyrene, chrysene, benzo[*a*]pyrene and perylene (Sigma, St. Louis, MO)) were chosen as the test compounds in this study. Table 1 lists the structures and the physical parameters of these compounds. The values of polarizability and the farthest distance between the two intramolecular hydrogen atoms were calculated with the standard parameterizations of the AM1 semi-empirical quantum-chemical method available in the MOPAC 5.0 program. The adsorbents used as matrices were categorized into two series: the XAD resin series (Amberlite XAD-2, XAD-4, and XAD-16 (Supelco, Bellefonte, PA)) and the silica gel series (silica gel 40 and silica gel 100 (Supelco)).

The "immersed" spiking method was adopted to evenly distributed analytes over the matrix [9]. A 20 g portion of purified adsorbent was placed in a 100 ml brown glass vial, and methylene chloride was added so that it completely covered the adsorbent. A 2 ml standard solution containing 500 $\mu g\ ml^{-1}$ PAHs in methylene chloride was spiked into the vial, then the mixture was sonicated for 1 h to ensure homogeneity [7]. Finally, the methylene chloride was evaporated at room temperature in a fume hood for more than 24 h. The dried adsorbent contained 50 $\mu g\ g^{-1}$ of each PAH.

2.2. Supercritical fluid extraction

SFE was performed by using SFE-grade carbon dioxide on an ISCO modular SFE series 1100 system (ISCO, Lincoln, NE). This system consisted of a syringe pump and a dual-chamber extraction system. Extractions were operated in constant-pressure mode and flow-rates were controlled by a stainless steel capillary restrictor. The 2.5 ml stainless steel sample cartridge was completely filled with PAHs-contaminated adsorbents and equilibrated in the extractor for more than 10 min prior to extraction. SFE was

Table 1
The structures and physical parameters of the PAHs used in this study

Compound	Structure	Molecular weight (g mol^{-1})	Distance [a,b] (Å)	Melting point (°C)	Boiling point (°C)	Polarizability [b] ($\times 10^{-23}$esu)
Anthracene		178	9.56	218	342	41.41
Pyrene		202	9.23	156	404	46.33
Chrysene		228	11.49	254	448	53.02
Benzo[*a*]pyrene		252	11.46	179	310	62.37
Perylene		252	9.62	277	350–400	60.14

[a] The greatest distance between two intramolecular hydrogen atoms.
[b] Distance and polarizability were calculated by a semi-empirical quantum-chemical method.

performed at a given temperature (70°C~140°C) and pressure (220 bar~450 bar) in the static mode for 5 min followed by the dynamic mode. The total volume of liquid CO_2 was 40 ml. The restrictor was heated to prevent it from plugging. The extracted analytes were collected in methylene chloride. Fluorene was applied as an internal standard. The collection solvent was maintained by small additions of pure methylene chloride throughout the extraction. The collection efficiency was confirmed by exhaustive extraction.

Methanol, methylene chloride, and toluene were used as modifiers in this study. Once a modifier was applied, part of the extraction procedure was changed. A modifier was added by pipeting 250 μl (10%, v/v) into the sample in the extraction cartridge as described in a previous report [10]. After adding a modifier, the cartridge was immediately sealed and placed into the heating extraction chamber. SFE was carried out at 90°C and 295 bar in the static extraction mode for 10 min without prewarming, followed by the dynamic mode. The collection steps were as mentioned above.

2.3. Gas chromatographic analysis

Individual PAH congeners were quantitated on a Hewlett-Packard (North Hollywood, CA) 5890 Series II gas chromatograph equipped with a flame ionization detector (FID) using nitrogen as the carrier gas and the detector's makeup gas. Autosampler injections were performed in the splitless mode with the split valve open 2 min after the sample (1 μl) was injected.

Separation was achieved by a 30 m×0.25 mm i.d. (0.25 μm film thickness) DB-5 fused-silica capillary column (J&W Scientific, Folsom, CA). The chromatographic oven temperature was held at 120°C for 3 min, followed by a temperature ramp at 15°C min^{-1} to 200°C, then to 300°C at 25°C min^{-1}. Finally, the oven temperature was maintained at 300°C for 8 min.

3. Results and discussion

Some variables are expected to play prominent roles in SFE according to their effects on the separation efficiency of the stationary phase in chromatography. These variables include the chemical properties of the matrix, viz., surface, surface area, pore size of the matrix, and the melting point, boiling point and molecular size of the analyte. Moreover, the PAH polarizability is a critical factor in studying PAH adsorption. Two series of adsorbents, the XAD resins and the silica gels, were conscripted in this study as matrices. Their physical parameters are shown in Table 2. Each of the three XAD resins has about 20% cross-linkage, thus their chemical properties are similar. The properties of the two series of adsorbents are less complex than real matrices. Therefore, the effects of an individual matrix property on SFE could be more easily discussed in this simplified matrix arrangement.

For a better understanding of the effects of an individual matrix or an analyte property, two assumptions were proposed. First, for a given analyte, the analyte–solvent interactions (their contributions to recoveries) are assumed to be nearly identical in the extraction from different matrices at the same temperature and pressure. Second, for the adsorbents in a series with similar chemical properties, the solvent–matrix interactions (their contributions to recoveries) are assumed to be alike during extraction at an identical temperature and pressure. On the bases of these two premises, the effects of analyte–solvent interactions can be cancelled by taking the ratio of the recoveries from two adsorbents under identical extraction conditions. The effects of solvent–matrix interactions can also be eliminated by taking the ratio of recoveries from two adsorbents belonging to the same series. Besides, differences in the recovery pairs resulting from the contrasted matrix property were examined for significance by *t*-tests [11]. If the difference is significant, the recovery ratio could be an index to estimate the extent of the difference. The higher the ratio implies the a greater difference from the contrasted matrix property.

Table 2
Physical parameters of the silica gel and XAD adsorbents used in this study

Absorbent	Particle size (mesh)	Mean surface area ($m^2 g^{-1}$)	Mean pore size (Å)
XAD-2	20~60	300	90
XAD-4	20~60	750	40
XAD-16	20~60	800	100
Silica gel 40	63~200	750	40
Silica gel 100	63~200	300	100

3.1. Effects of chemical properties of the matrix

Figs. 1 and 2 illustrate the recoveries of PAHs extracted from the XAD resin series and the silica gel series, respectively. Interestingly, there was an increasing recovery tendency from the XAD resin (Fig. 1) with increasing temperature for each PAH, whereas such a tendency was not obvious from the silica gel, as shown in Fig. 2. Overall, the recoveries of PAHs from the silica gels were higher than those from the XAD resins. This phenomenon is discussed in detail in the following sections.

The recovery differences between silica gel 40 and XAD-4 (same surface area) and between silica gel 100 and XAD-2 (similar surface area) under identical extraction and temperature conditions were significant (*t*-tests, α=0.05). The recoveries from the XAD resin were always lower than those from the silica gel. The results imply that the matrix surface's chemical properties are a prominent factor for recovery of a specific compound by SFE. Since the XAD resins are styrene–divinylbenzene copolymers, the conjugated π electrons on the benzene rings provide the XAD resins with high polarizability. Such a provision allows the dispersion interactions between the XAD resins and PAHs to prevail over the dipole/induced-dipole interactions between the silica gels and PAHs [12]. Also, the recovery differences resulting from different chemical properties of the matrix were more significant for the PAHs with a greater molecular weight.

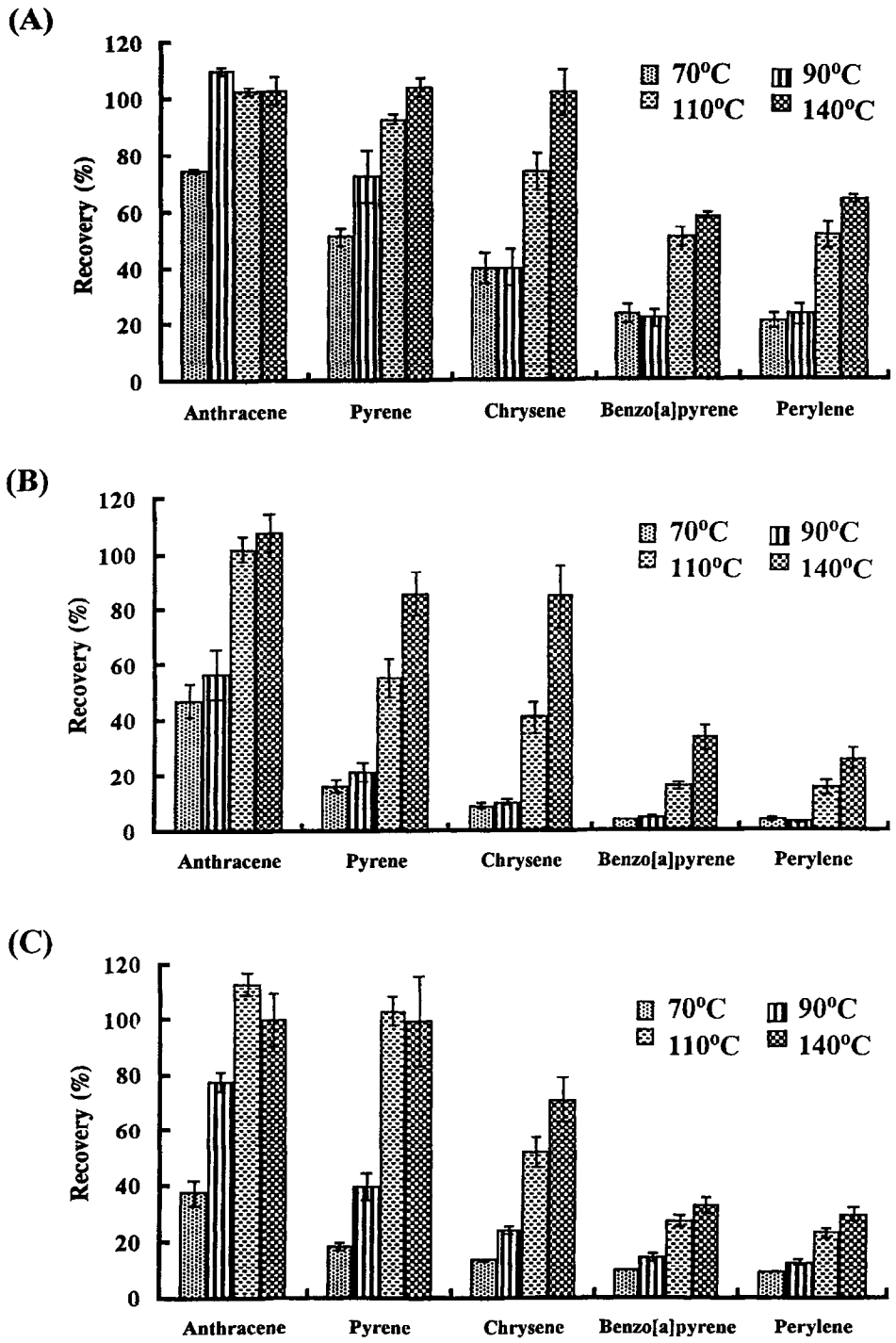


Fig. 1. Mean recoveries of five PAHs from (A) XAD-2, (B) XAD-4, and (C) XAD-16 with constant CO_2 density (d=0.7 g ml^{-1}). Error bars represent one standard deviation (n=3).

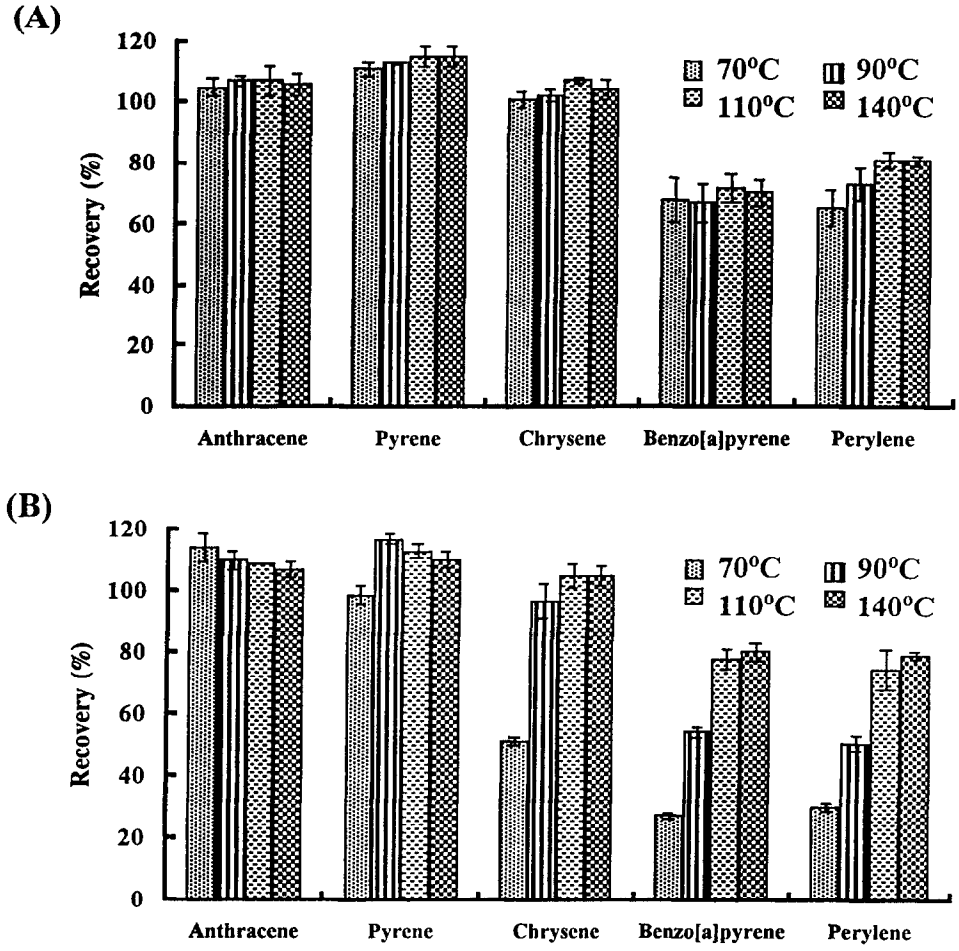


Fig. 2. Mean recoveries of five PAHs from (A) silica gel 100, and (B) silica gel 40 with constant CO_2 density (d=0.7 g ml^{-1}). Error bars represent one standard deviation (n=3).

3.2. *Effects of surface area and pore size of the matrix*

Tables 3 and 4 list the recovery ratios of silica gel 100 over silica gel 40 and XAD-2 over XAD-4, respectively. Since silica gel 40 has a larger surface area and a smaller pore size than silica gel 100, the recoveries from silica gel 100 were significantly higher than those from silica gel 40 (shown in Table 3). Results obtained from the comparison of XAD-2 with XAD-4 (Table 4) were similar. Our experimental results thus indicated that a larger surface area and/or a smaller pore size of a matrix could reduce the SFE recovery. Additionally, Clifford et al. suggested that two processes could influence the efficiencies of SFE [13]. One was a reversible release process, such as desorption and readsorption; the other was transportation through the matrix by normal diffusion or otherwise. The main factors that effectively control the rate of these processes are believed to be surface area, pore size, and the diffusion coefficient of solute in the solid [14]. Such an explanation based on the SFE model correlates with our results.

Recovery ratios of XAD-2 over XAD-16 are shown in Table 5. Since the pore sizes of XAD-2

Table 3
The ratios of the recoveries from silica gel 100 to the recoveries from silica gel 40

d (g ml^{-1})	T (°C)	Anthracene	Pyrene	Chrysene	Benzo[a]pyrene	Perylene
0.8	70	0.904	1.01	0.982	1.41[a]	1.36[a]
0.7	70	0.921	1.12[a]	1.95[a]	2.46[a]	2.15[a]
0.8	90	1.00	1.01	1.12[a]	1.18	1.32[a]
0.7	90	0.973	0.966	1.05	1.23[a]	1.43[a]
0.6	90	0.972	1.37[a]	2.04[a]		
0.7	110	0.982	1.02	1.02	0.924	1.08
0.6	110	1.00	1.07[a]	1.40[a]	1.82[a]	1.91[a]
0.5	110	1.21[a]	1.91[a]	2.03[a]		
0.7	140	0.991	1.05	0.991	0.876	1.02
0.6	140	0.972	1.00	1.05	0.964	1.15
0.5	140	1.02	1.11	1.50[a]	1.48[a]	1.52[a]

[a] The difference between two recoveries from the different absorbents was testified by a t-test to be significant at the 0.05 (5%) level.

Table 4
The Ratios of the Recoveries from XAD-2 to the Recoveries from XAD-4

d (g ml^{-1})	T (°C)	Anthracene	Pyrene	Chrysene	Benzo[a]pyrene	Perylene
0.9	70	1.21[a]	2.11[a]	2.60[a]	3.54[a]	4.52[a]
0.8	70	1.46[a]	2.10[a]	2.88[a]	3.95[a]	3.95[a]
0.7	70	1.57[a]	3.10[a]	4.42[a]	5.77[a]	5.47[a]
0.8	90	1.58[a]	3.43[a]	3.75[a]	5.09[a]	5.79[a]
0.7	90	1.76[a]	3.37[a]	3.92[a]	4.36[a]	7.69[a]
0.6	90	2.44[a]	3.18[a]	5.42[a]	5.23[a]	5.41[a]
0.7	110	1.01	1.67[a]	1.81[a]	3.16[a]	3.32[a]
0.6	110	1.32[a]	2.68[a]	3.07[a]	4.77[a]	5.47[a]
0.5	110	1.39	3.19[a]	6.70[a]	8.80[a]	7.77[a]
0.7	140	0.954	1.22[a]	1.20	1.73[a]	2.47[a]
0.6	140	1.24[a]	2.05[a]	3.17[a]	2.81[a]	3.93[a]
0.5	140	1.07	2.22[a]	2.80[a]	2.64[a]	2.73[a]

[a]The difference between two recoveries from the different absorbents was testified by a t-test to be significant at the 0.05 (5%) level.

Table 5
The Ratios of the Recoveries from XAD-2 to the Recoveries from XAD-16

d (g ml^{-1})	T (°C)	Anthracene	Pyrene	Chrysene	Benzo[a]pyrene	Perylene
0.9	70	1.25[a]	1.41[a]	1.78[a]	2.18[a]	2.41[a]
0.8	70	1.22	1.19	1.47[a]	1.76[a]	1.55[a]
0.7	70	2.00[a]	2.70[a]	2.91[a]	2.38[a]	2.23[a]
0.8	90	1.41[a]	2.46[a]	2.39[a]	2.69[a]	3.25[a]
0.7	90	1.28[a]	1.82[a]	1.66[a]	1.49[a]	1.82[a]
0.6	90	1.63[a]	1.57	1.99[a]	1.57[a]	1.43[a]
0.7	110	0.912	0.903	1.43[a]	1.84[a]	2.20[a]
0.6	110	0.956	1.32[a]	1.52[a]	1.86[a]	2.02[a]
0.5	110	0.873	1.59[a]	2.92[a]	2.63[a]	2.28[a]
0.7	140	1.03	1.05	1.43[a]	1.78[a]	2.16[a]
0.6	140	1.03	1.24[a]	2.31[a]	1.61[a]	1.98[a]
0.5	140	1.05	1.57[a]	1.94[a]	1.10	1.06

[a]The difference between two recoveries from the different absorbents was testified by a t-test to be significant at the 0.05 (5%) level.

and XAD-16 are similar, the recoveries of PAHs from XAD-2 were substantially higher than those from XAD-16 because of a smaller surface area of XAD-2. These data further demonstrated that surface area was an important variable for the analyte–matrix interactions in SFE. This finding coincides with the statement made by King et al. [15]. They claimed the adsorbent surface area to be the most significant factor contributing to the retention of sorbates on the porous polymeric sorbents in supercritical fluid CO_2. In addition, the recovery differences related to surface area were more marked for heavier PAHs as their recovery ratios were higher, as shown in Table 5.

3.3. Effects of analytes

While the solubility of pyrene was higher than that of anthracene at 70°C [16], the recoveries of pyrene from the XAD resin were always lower than those of anthracene in this study. A similar phenomenon could be observed by comparing chrysene with benzo[*a*]-pyrene. More specifically, a trend arose in which benzo[*a*]pyrene's solubility was higher than that of chrysene, but benzo[*a*]pyrene's recoveries were lower than those of chrysene. Such results are compatible with earlier findings that some compounds have a high bulk solubility in supercritical CO_2, but are difficult to extract at trace levels [7,8]. Additionally, no significant correlations were found in the present study between the SFE recoveries and the melting points and/or boiling points of the analytes, whereas significant correlations were reported for the SFE of polychlorinated biphenyls (PCBs) [8]. Thus, in the present study, the tendency of decreasing recoveries of PAHs with increasing molecular weight could not be accounted for by the solubility effect (the analyte–solvent interactions) or the properties of analyte itself (melting point and/or boiling point).

The above results suggest that other analyte–matrix interactions play important roles for the tendency of decreasing recoveries of PAHs with increasing molecular weight. Such a tendency seems to be understandable on the basis that the dispersion interaction between the XAD resin and PAHs is enhances by higher polarizability of PAHs which increase with increasing molecular weight (Table 1). Consequently, the heavier PAHs such as perylene, could be more strongly adsorbed on the XAD resin, thereby causing the recovery differences between various adsorbents to be more significant.

3.4. Effects of temperature

Temperature is an essential experimental variable for SFE as it affects three extraction steps: desorption, diffusion and dissolution. While the CO_2 density may decrease with raised temperature at constant pressure, the solubility of many organic compounds can dramatically increase because of an increase in the solute's vapor pressure. Unfortunately, very little solubility data are available in the literature to assess the effects of elevated temperature [17]. Consequently, isolating the effects of temperature on analyte–matrix interactions is extremely difficult.

Fig. 3 depicts the relationship between the temperature and the recovery ratios of silica gel 100 compared to XAD-2 at a constant fluid density. The differences of recoveries decreased with an increase in the extraction temperature. As described earlier, the recovery discrepancies between silica gel 100 and XAD-2 were primarily attributed to the effects of the chemical properties of the matrix. Such discrepancies could be compensated for by increasing the extraction temperature because the recoveries from XAD-2 were more markedly enhanced than from silica gel 100 when the temperature was increased, as illustrated in Fig. 1(a) and Fig. 2(a). Such a phenomenon indicates that increasing the temperature is likely to provide the analyte molecules with more energy to overcome the energy barrier of the dispersion forces. Therefore, an

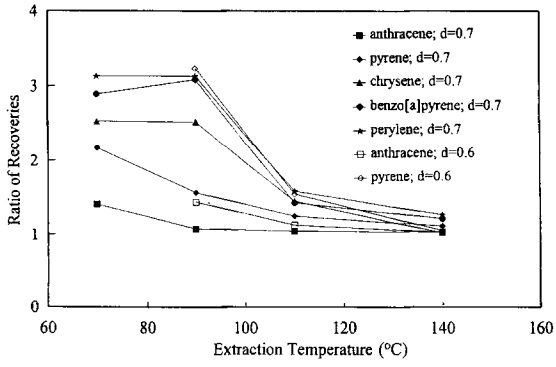


Fig. 3. Influence of the extraction temperature on the ratios of the recoveries from silica gel 100 to XAD-2 at CO_2 d=0.6 and 0.7 g ml^{-1}.

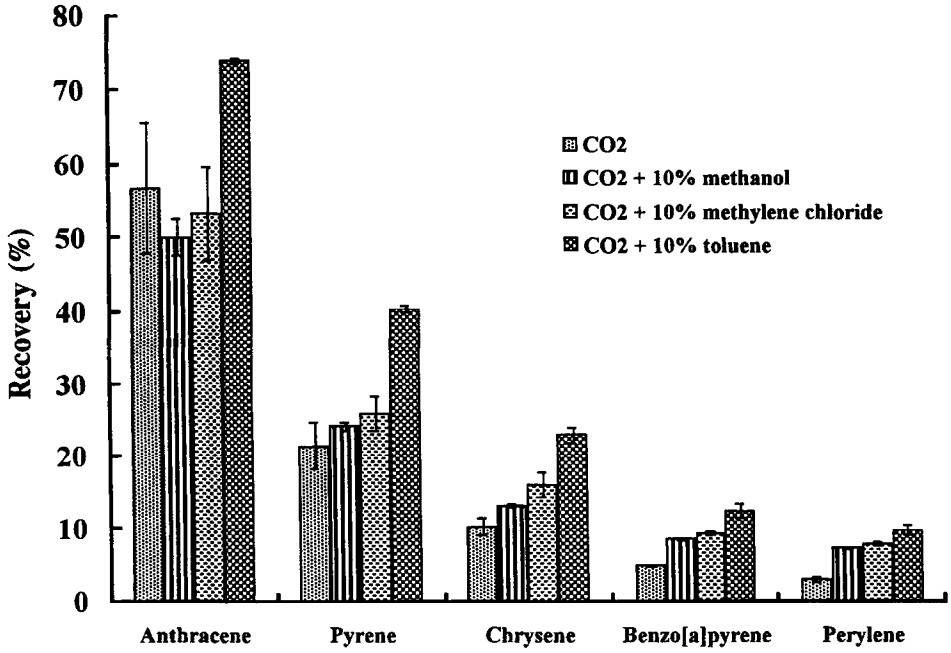


Fig. 4. Effect of adding a modifier on the mean recoveries of PAHs from XAD-4 at 90°C with constant CO_2 density (d=0.7 g ml^{-1}). Error bars represent one standard deviation (n=3).

increasing temperature not only increases the analytes' solubilities as proposed by several researchers [18,19], but it also provides more energy to enhance PAHs' recovery.

3.5. *Effects of modifiers*

Methanol, methylene chloride, and toluene were the modifiers used in this study. The selection of modifiers was based on their polarizabilities, even though two of them had already been studied in respect of their acidic or aromatic properties [10]. A modifier's polarizability affects its capability of competing against the analytes to access the active sites of the matrix, i.e., the locations of conjugated π-electrons, because the dispersion forces dominate the analyte–matrix interactions in the SFE of the PAHs from the XAD resins. The analytes, once in the desorptive state, have less likelihood of readsorbing on the matrix because of the presence of the modifiers. Thus, it was expected that the enhancement of recovery should be more significant if the modifier can more aptly compete with the analytes to occupy the active sites of the matrix.

Fig. 4 confirms the above inference, in which PAH recoveries from XAD-4 using methanol, methylene chloride, and toluene as modifiers are demonstrated. The polarizabilities of methanol, methylene chloride, and toluene are 3.29, 7.93, and 12.3 ($\times 10^{-24}$ cm^3), respectively [20]. When methanol and methylene chloride were used, the enhancement of anthracene and pyrene recovery was not noticeable; however, recoveries of chrysene, benzo[a]pyrene, and perylene were somewhat improved. Nevertheless, the recoveries of the PAHs were all successfully enhanced when toluene was used as a modifier.

Although the analytes' solubilities in pure CO_2 were sufficient, the recoveries from XAD-4 where toluene was used as a modifier remained lower than those from silica gel 100 extracted with pure CO_2 under identical conditions. Therefore, increasing the solubilities of analytes by use of a modifier should not be the primary reason for enhancing recovery. Consequently, competing against the analytes to cover the active sites of the matrix is likely to be the most important function of modifiers in this case.

4. Conclusions

The present study has demonstrated that the concrete factors for describing a matrix, e.g., the chemical properties of the matrix surface, surface area and pore size, can significantly affect SFE recovery. More specifically, the dispersion interactions between the XAD resins and PAHs prevailed over the dipole–induced dipole interactions between the silica gels and PAHs. The recoveries of PAHs were relatively higher if they were extracted from a matrix with a smaller surface area and a larger pore size. In view of analyte–matrix interactions, from a given matrix, the polarizabilities of PAHs would also contribute to the trend of decreasing recoveries of PAHs with increasing molecular weight. Additionally, the effects of increased temperature on analyte–matrix interactions were demonstrated to provide analytes with more energy to override the energy barrier of desorption. On the other hand, the effects of adding modifiers on analyte–matrix interactions were observed by a different mechanism in which modifiers would compete with the analytes to cover the active sites of the matrix. Overall, our results not only reconfirm the previous findings but also provide more detailed information on analyte–matrix interactions. Consequently, the present study serves as a complement of previous studies.

In conclusion, experimental conditions for SFE are more easily manipulated than conventional liquid solvent extraction and thermal desorption. The approaches employed in the present study not only can be used to increase the SFE recovery but also can give SFE an extended potential, thereby making it an extremely useful technique for studying analyte–matrix interactions. To more thoroughly understand the analyte–matrix interactions, SFE could be directed toward areas such as the properties of active sites on the matrix surface and the adsorptive capacity of the matrix on the analyte.

Acknowledgements

The authors thank Dr. Steven B. Hawthorne for helpful suggestions. Calculating the sizes of PAHs by Y.-T. Lin is appreciated. This study was supported by Grand NSC 85-2113-M-009-007 from the National Science Council of the Republic of China, Taiwan.

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