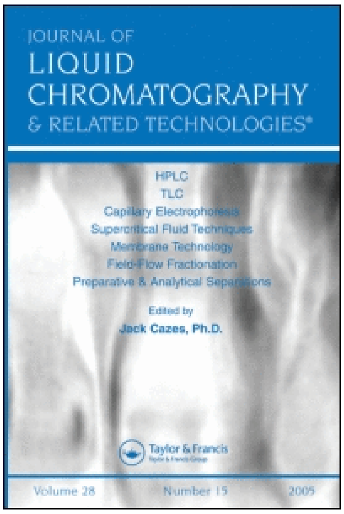

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# Supercritical $CO_2$ Extraction of PAHs from Contaminated Soil Treated by a Composting Method

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# Supercritical $CO_2$ Extraction of PAHs from Contaminated Soil Treated by a Composting Method

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**Abstract:** The method of supercritical $CO_2$ extraction was used to extract polycyclic aromatic hydrocarbons (phenanthrene, anthracene, pyrene) from contaminated soil treated by a composting method. The effect of various parameters, i.e., pressure, temperature, and modifier solvent on extraction efficiency was investigated through an orthogonal experiment to find the optimal conditions. Under the optimum conditions (30 MPa, 120°C, methanol as modifier), the recoveries for PAHs from the sample was measured by GC-MS and found to be greater than 90%.

**Keywords:** Polycyclic aromatic hydrocarbons (PAHs), Phenanthrene, Anthracene, Pyrene, Composting, Supercritical $CO_2$ extraction, GC-MS

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of well known carcinogenic compounds coming from incomplete combustion of organic compounds, or pyrolysis of organic material and the direct release of oil or its products. They have received much concern in recent years due to their toxic potential.[1,2] There are 16 PAH compounds that were listed as priority pollutants with the US Environmental Protection Agency (EPA).

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The soil system seems to be the important long term repository for PAHs and is considered to be a steady indicator of the environmental pollution state.[3,4] Accumulation of PAHs in soils may lead to further potential contamination of vegetables and food chains, and then cause direct or indirect exposure to humans.[5] Thermophilic composting is a low cost bioremediation technology for treating PAH contaminated soil development in recent years. It can effectively remove the PAHs from contaminated matrices.[6,7]

The conventional extraction method for PAHs from contaminated soil is Soxhlet extraction; but it is time and solvent consuming. Also, the organic solvents are often toxic. To find a low cost, minimal organic solvent volume, fast extraction way, supercritical fluid extraction (SFE) was used to extract PAHs from the contaminated soil. Supercritical fluid extraction of PAHs from solid environmental matrixes has received great attention in recent years.[8–11] SFE results in a dramatic decrease in extraction times and avoids the use of large quantities of organic solvents that are often toxic. Because supercritical fluid extraction has a greater selectivity, the operation of pretreatment and cleanup of the sample can be avoided. Carbon dioxide is often used for SFE because of its supercritical parameters ($T = 31^\circ\text{C}$ and $P = 73$ bar), its low toxicity, low price, and the capacity of solvating a large number of organic compounds.[12]

The aim of this experimental work is to find the optimum extracting conditions through an orthogonal test for PAHs from the contaminated soil treated by a composting method. The orthogonal method is often used in SFE experimental design, which is simple but very effective. It can determine the suitable parameters in a wide range with a minimum number of trials. Until now, reports on supercritical fluid extraction of PAHs with an orthogonal test to get suitable parameters haven't been seen. The SFE method was also compared with the typical Soxlet extraction method in this article.

## EXPERIMENTAL

### Reagents

PAHs at the concentration of $1000\,\text{mg/mL}$ were obtained from Supelco (Bellefonte, PA, USA). The supercritical grade carbon dioxide (99.99%) was supplied by Jinan gas factory of Shandong Province of China.

All other chemicals used were analytical grade reagents.

### Preparation of Sample

The sample of contaminated soil used is a mixture of sediments derived from clean areas of Shandong University, spiked with phenanthrene, anthracene, and pyrene, each at $50\,\text{mg} \cdot \text{kg}^{-1}$. Before composting, it was mixed with pig manure at 3:1, which was used to provide nutrition. The mixtures were composted for 30 days in a bench scale composting reactor. The dried and sterilized 50 g sample was supplied in a glass bottle. The PAHs were extracted by supercritical fluid extraction. As a comparison, Soxhlet extraction was also carried out. Gas chromatography coupled with a mass spectrometer (GC-MS) was used to determine the concentrations of PAHs.

## Apparatus

### SFE

All extractions were carried out using a supercritical fluid extraction system (Applied Separation, Inc., America). The scheme diagram of the system is shown in Figure 1. The modifier was added by a high performance liquid chromatography (HPLC) pump (WellChrom K-501, Germany) with 10% vol. modifier. Two 24 mL stainless steel extraction vessels were fitted with stainless steel needle valves, which can process two samples at the same time. Two micro metering valves are used as restrictor valves to control the flow rate of the supercritical $CO_2$ to the solvent collection. Extraction temperatures were monitored using a thermocouple, and were found to be accurate to within ±1 K. The precision of the pressure measurement was ±1 Pa.

### GC-MS

The determination of PAHs was performed on a SHMADZU GC-MS 2010 system equipped with a DB-5 fused silica capillary column (30 mm × 0.25 mm i.d., 0.25 μm).

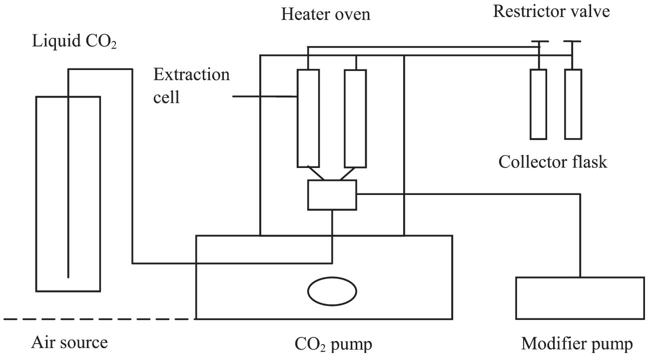

*Figure 1.* Scheme diagram of the SFE system.

## Optimization of SFE Conditions

A *Spe-ed* SFE system (Applied Separations, Inc., USA) is illustrated in Figure 1. Two 24 mL extraction cells were used to optimize extraction conditions. In order to determine a suitable experimental parameter in a wide range with a minimum number of trials, an orthogonal test design L9 $(3)^3$ was employed where pressure, temperature, and modifier solvent were considered to be three major factors for effective extraction. Combinations of the three different levels of each factor are listed in Table 1. In each test, a 15 g sample was placed into the extraction cell. After 20 min of static extraction, the sample was then subjected to dynamic extraction by flowing gaseous carbon dioxide at a rate of 2 L/min for 30 min. The extracts were trapped into a collection vessel containing about 10 mL of dichloromethane, and the sample was then analyzed by GC-MS. Due to the great selectivity of supercritical $CO_2$, sample cleanup can be avoided.

## Soxhlet Extraction

A spiked soil sample of 15 g was extracted with 100 mL dichloromethane for 8 h. The extract was concentrated to 10 mL by rotary evaporation, and then was cleaned by an alumina column using 15 mL dichloromethane. The extract was subsequently evaporated to 1 mL using a gentle stream of clean nitrogen and analyzed by GC-MS.

## GC-MS Analysis

The determination of PAHs was performed on a Shmadzu GC-MS 2010 system equipped with a DB-5 fused silica capillary column (30 mm × 0.25 mm i.d.,

***Table 1.*** L9 $(3)^3$ orthogonal test design

| Test no. | A (pressure, MPa) | B (temperature, °C) | C (modifier) |
|---|---|---|---|
| 1 | $A_1$ 20 | $B_1$ 80 | $C_1$ Methanol |
| 2 | $A_1$ 20 | $B_2$ 100 | $C_2$ Acetone |
| 3 | $A_1$ 20 | $B_3$ 120 | $C_3$ Dichloromethane |
| 4 | $A_2$ 25 | $B_1$ 80 | $C_2$ Acetone |
| 5 | $A_2$ 25 | $B_2$ 100 | $C_3$ Dichloromethane |
| 6 | $A_2$ 25 | $B_3$ 120 | $C_1$ Methanol |
| 7 | $A_3$ 30 | $B_1$ 80 | $C_3$ Dichloromethane |
| 8 | $A_3$ 30 | $B_2$ 100 | $C_1$ Methanol |
| 9 | $A_3$ 30 | $B_3$ 120 | $C_2$ Acetone |

0.25 μm). Oven temperature conditions were: 80°C for 1.0 min, then programmed heating to 220°C at a rate of $10°C \cdot min^{-1}$. Injector temperature was 250°C. The carrier gas, helium, was adjusted to a linear velocity of 1.1 mL/min. Ion source temperature was 250°C; the ionization energy was 70 eV and mass range of 20–500 amu. Samples were diluted to 0.1% (v/v) with dichloromethane before injection. Identification of the compounds was based on the comparison of their GC retention times and mass spectrum with individual standards. Also, mass spectra library was used as a reference.

## RESULTS AND DISCUSSION

### SFE

The PAHs obtained from each L9 $(3)^3$ test of the analytical SFE were quantitatively analyzed, and the results are shown in Table 2. Extraction efficiencies at different sets of pressure, temperature, and modifier were examined under the L9 $(3)^3$ test design. The results, shown in Table 2, indicate that there are great yield differences among each set of SFE conditions. The results in Table 2 are transformed to Table 3 after orthogonal analysis.

All of the three considered parameters have great impact on the extraction efficiency. Temperature was found to be the most important determinant of the yield. The yield of PAHs also significantly increased as the pressure increased. This may be due to the increase in pressure results in a higher density of the supercritical fluid, thereby, increasing the solvating power of the fluid and, hence, the extraction efficiency. The results indicate that methanol is much better than acetone and dichloromethane as modifier. This may be due to methanol having a high ability of building hydrogen

***Table 2.*** L9 $(3)^3$ test results

| | | | | Recovery (%) | | |
|---|---|---|---|---|---|---|
| Test no. | A | B | C | Phenanthrene | Anthracene | Pyrene |
| 1 | $A_1$ | $B_1$ | $C_1$ | 76.3 | 74.6 | 78.3 |
| 2 | $A_1$ | $B_2$ | $C_2$ | 78.6 | 75.3 | 81.6 |
| 3 | $A_1$ | $B_3$ | $C_3$ | 83.8 | 81.4 | 85.8 |
| 4 | $A_2$ | $B_1$ | $C_2$ | 75.6 | 72.5 | 77.6 |
| 5 | $A_2$ | $B_2$ | $C_3$ | 78.9 | 76.3 | 80.9 |
| 6 | $A_2$ | $B_3$ | $C_1$ | 94.3 | 92.7 | 96.4 |
| 7 | $A_3$ | $B_1$ | $C_3$ | 83.0 | 78.2 | 84.0 |
| 8 | $A_3$ | $B_2$ | $C_1$ | 89.0 | 87.5 | 89.7 |
| 9 | $A_3$ | $B_3$ | $C_2$ | 92.6 | 89.9 | 93.5 |

***Table 3.*** Analysis of $L_9\ (3)^3$ test results

| | Phenanthrene | | | Anthracene | | | Pyrene | | |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | A | B | C | A | B | C |
| $K_1$ | 238.7 | 234.9 | 259.6 | 231.3 | 225.3 | 254.8 | 245.7 | 239.9 | 264.4 |
| $K_2$ | 248.8 | 246.5 | 246.8 | 241.5 | 239.1 | 237.7 | 254.9 | 252.2 | 252.7 |
| $K_3$ | 264.6 | 270.7 | 245.7 | 255.6 | 264.0 | 235.9 | 267.2 | 275.7 | 250.7 |
| $k_1$ | 79.6 | 78.3 | 86.5 | 77.1 | 75.1 | 84.9 | 81.9 | 80.0 | 88.1 |
| $k_2$ | 82.9 | 82.2 | 82.3 | 80.5 | 79.7 | 79.2 | 85.0 | 84.1 | 84.2 |
| $k_3$ | 88.2 | 90.2 | 81.9 | 85.2 | 88.0 | 78.6 | 89.1 | 91.9 | 83.6 |
| $R$ | 8.6 | 11.9 | 4.6 | 8.1 | 12.9 | 6.3 | 7.2 | 11.9 | 4.5 |
| Optimal level | $A_3$ | $B_3$ | $C_1$ | $A_3$ | $B_3$ | $C_1$ | $A_3$ | $B_3$ | $C_1$ |

$K_i^A = \Sigma$ extraction recovery at $A_i$.
$k_i^A = K_i^A/3$.
$R_i^A = \max\{k_i^A\} - \min\{k_i^A\}$.

bonds, and it can break PAHs matrix interactions and substitute PAHs on the active site of the matrix.

Pressure of 30 MPa, temperature of 120°C, and 10% vol. methanol as modifier seem favorable for the extraction of all of the three kinds of PAHs. With the optimized extraction conditions, SFE was carried out once more. As a comparison, Soxhlet extraction was also performed.

## Soxhlet Extraction

Table 4 shows the recovery yields of the three kinds of PAHs on the modified sample by Soxhlet extraction and SFE under optimized extraction conditions. The result showed that under the optimized extraction conditions, a little higher extraction recovery of PAHs can be achieved by SFE compared to Soxhlet extraction.

***Table 4.*** Recoveries of PAHs from spiked soil samples

| | Soxhlet extraction | | SFE | |
|---|---|---|---|---|
| Analyte | Average recovery (%) (n = 3) | RSD (%) | Average recovery (%) (n = 3) | RSD (%) |
| Phenanthrene | 95.6 | 4.7 | 98.8 | 3.6 |
| Anthracene | 90.7 | 2.3 | 95.6 | 4.3 |
| Pyrene | 93.5 | 6.9 | 99.3 | 4.7 |

## CONCLUSION

In conclusion, it was found that under the optimum extraction conditions, similar result can be obtained by SFE compared to the traditional extraction method of Soxhlet extraction. Therefore, SFE could provide a low cost, minimal organic solvent volume, fast extraction way for extracting PAHs from contaminated soil treated by the composting method. Also, the data of the method are comparable with the requirements of environmental monitoring quality control, and the method is suitable for the determination of PAHs in contaminated soil.

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