

SELECTIVE EXTRACTION OF PAHS FROM ORGANIC MIXTURES BY MEANS OF MULTI-STEP SUPERCRITICAL FLUID EXTRACTION

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Introduction

Current analytical techniques for toxic organic compounds such as dioxins or PAHs, consist of a lot of procedures. The major procedure involves i) sampling, ii) extraction, iii) cleanup, and iv) GC/MS quantification. Since environmental samples frequently contain unwanted compounds for the analysis at higher concentrations, the cleanup step becomes an important role in the sample preparation. This problem is originated in the extraction technique which employs Soxhlet method using organic solvent, because organic solvent generally has no compound-selectivity.

Supercritical fluids have been extensively studied as alternatives for organic solvents. Among supercritical fluids, CO₂ is widely used because of its low critical pressure and temperature, and inertness. The prominent advantage of SFE is the high extraction speed. As an earlier example, Alexandrou et al¹ reported that only 2 hrs of SFE can yield over 95 % recovery (taking a 20 hrs Soxhlet extraction = 100 %) of PCDDs and PCDFs from fly ash particles. As they reported, the extraction of PCDDs and PCDFs frequently requires high pressure (~40 MPa) and the aid of a modifier. However, the shortening of extraction time is not particularly effective for realizing speedy and simple analysis, because the cleanup of unwanted compounds is still required.

Another characteristic of SFE is variability of its solubility by changing the temperature and pressure. Generally, the solubility is maximized with the maximum density of CO₂ at a given temperature. At a constant pressure, the solubility is increased with the temperature despite the decrease in the CO₂ density². Although the pressure and temperature effect on the recovery has not been generalized enough, such a variability of solvent property is attractive for the investigation of simple method of compound-selective extraction from organic mixtures.

This study aims to investigate primitive property of SFE in the extraction of alkanes, chlorinated aromatics and PAHs, and to devise a multi-step extraction methodology with different fluid pressure and temperature for performing a compound-selective extraction.

Methods and Materials*Reagents and Samples*

Carbon dioxide with a purity >99.5 % (Suzuki Shokan Co. Ltd., Tokyo, Japan) was used. Model compounds in the investigation of extraction properties were *n*-alkanes, chlorinated aromatic compounds, PAHs, and dibenzofuran. Activated neutral alumina with a mean diameter range 63~200 μm (Merck KGaA, Darmstadt, Germany) was used as a model adsorbent. Model samples were

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prepared by spiking the compounds to the particles. First, a dichloromethane solution containing a model compound at 1 mg/g was prepared in a beaker. Then 1 g alumina particles was fed into the solution, and dried up for 5 hrs in room air. The nominal spiking level corresponds to 1 ppm. Another model sample used in the two-step extraction was fly ash collected at an electrostatic precipitator in a coal thermal power plant. Prior to spike the model compounds, the fly ash was treated with a 1N HCl solution for 1 hr to remove surface alkaline salts. Spiking procedure was the same as mentioned above. Sample in the last experiment was suspended particulate matter (SPM) collected by a roadside in Tokyo. The sampling device was a low volume air sampler and a quartz glass filter was used as the sampling filter. No pretreatment prior to SFE was done.

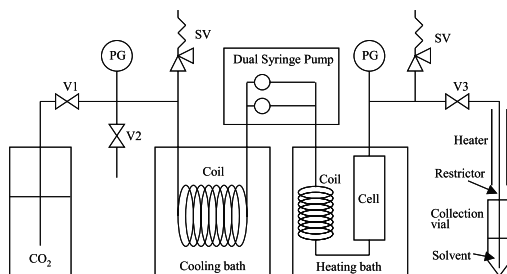


Figure 1. Supercritical CO₂ extractor for multistep extraction. (V1,2,3: stop valves, PG: pressure gauge, SV: safety valve)

Supercritical CO₂ Extraction

All the experiments were performed with an SFE apparatus made by the authors. A schematic illustration of the apparatus is shown in Fig.1. Carbon dioxide is liquefied in a cooling bath maintained at -15°C , and then pressurized with a dual syringe pump (CCPD, Tosoh Corp., Japan) at a flow rate of 8 mL/min. The CO₂ fluid is then heated in an oven (GC-8A, Shimadzu, Japan), and is reached at a supercritical state. The oven temperature can be set up to 399°C . The maximum extraction pressure is 35 MPa. An extraction cell with an internal volume 8 mL was made from a 1/2" stainless tube. The cell pressure is maintained with a fused-silica capillary restrictor (GL-science, Japan) with 30 mm i.d. and 65 cm length. The restrictor is heated at 100°C using a resistive heater. Extracts in the exit gas are collected with dichloromethane in a glass vial by directly inserting the end of the capillary.

GC/MS Analysis

For analysis of extracts in case of spiked samples, a GC/MS (HP6890 gas chromatograph coupled with HP5973A quadrupole mass selective detector) was used. A capillary column used in the GC/MS analyzes was a length of 30 m, inner diameter of 0.249 mm, and a DB-5 liquid phase (0.25 mm thickness). The temperature program in the analyses was: 50°C rising $10^{\circ}\text{C}/\text{min}$ to 300°C and held for 5 min. In the last experiment on SPM particles, a HRGC/HRMS apparatus (VG Autospec Ultima) was used. A capillary column DB-5 was employed in the GC, and its temperature program was: 60°C held for 1 min then raised to 180°C at $20^{\circ}\text{C}/\text{min}$ rate, finally up to 280°C at $10^{\circ}\text{C}/\text{min}$ and held for 10 min.

Results and Discussion

Primitive properties of extraction

In the first experiment, primitive property of SFE was investigated by using spiked samples. Figure 2 shows the percent recoveries of spiked compounds at three different pressures. The measured

recovery curves were classified into two types. One is the moderate dependence on the pressure, which was found in 1,2,4,5-tetrachlorobenzene and *n*-octadecane. The other is strong enhancement at higher pressures in the cases of PAHs. Since in this experiment the temperature was kept at 100 °C, only the solubility through the fluid density could be changed with the pressure. Therefore, the former tendency can be understood by little effect of solubility on the recovery within the pressure range. In other words, compounds with higher vapor pressures can be extracted with lower pressure and temperature. In the next, the pressure dependence was measured at 50 °C and compared with those at 100 °C. The result is shown in Fig.3. The recovery of tetrachlorobenzene showed again a moderate dependence on the pressure at 50 °C, whereas dichloroanthracene showed strong enhancement at higher pressure and temperature. This result confirms that the above consideration that the solubility is not a limiting factor on the recovery in the cases of tetrachlorobenzene and octadecane.

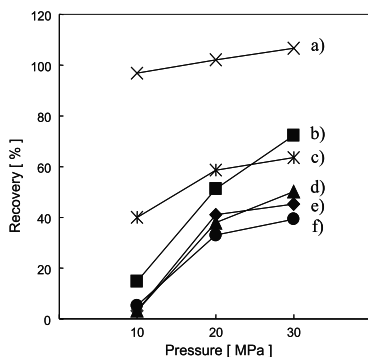


Figure 2 Recoveries at three extraction pressures (100°C). a) 1,2,4,5-tetrachlorobenzene, b) 9,10-dichloroanthracene, c) *n*-octadecane, d) pyrene, e) anthracene, f) chrysene

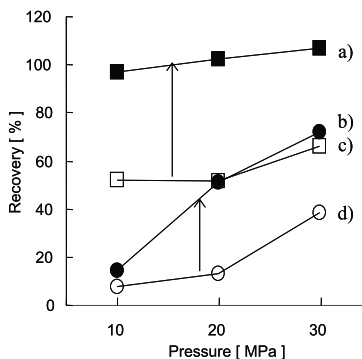


Figure 3. Recoveries at different temperatures. 1,2,4,5-tetrachlorobenzene at 100°C (a) and 50°C (b), 9,10-dichloroanthracene at 100°C (c) and 50°C (d).

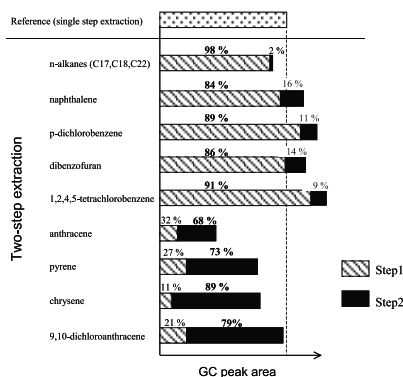


Figure 4. Relative recoveries (GC peak area) of compounds spiked onto fly ash particles. The length of each bar shows the recovery relative to single step extraction. (C17: *n*-heptadecane, C18: *n*-octadecane, C22: *n*-docosane)

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Two-step extraction of PAHs from flyash

Based on the knowledge about the compound-preference at different CO₂ pressure and temperature, selective extraction of PAHs from organic mixtures was examined. The model compounds were spiked onto thermal power plant fly ash. In the step 1, SFE at 60 °C-8 MPa was performed for 180 min. Then the condition was changed to 100 °C-30 MPa for 30 min (step2). Figure 4 shows the normalized GC-peak area intensity of each compound. In the step1, compounds with higher vapor pressures (*n*-alkanes to tetrachlorobenzene) were preferentially extracted at 84 to 98 % of the sum of step1 and 2. On the other hand, greater than 68 % of PAHs (anthracene to dichloroanthracene) were extracted in the step2. This result means that PAHs were selectively recovered in the second fraction, and there is little need for cleanup of *n*-alkanes and other low molecular weight aromatics.

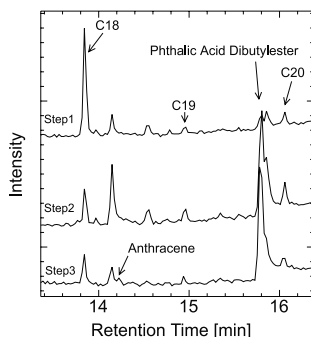


Figure 5. Total ion chromatograms of extracts from SPM in three step SFEs

Application to suspended particulate matters

Multi-step methodology was applied to real SPM particles collected by a roadside in Tokyo. Three conditions were applied in the extraction; Step1: 60 °C-10 MPa, Step2: 80 °C-20 MPa and Step3: 120 °C-30 MPa. Each step consisted of static extraction for 10 min and dynamic extraction for 30 min. Figure 5 shows a part of total ion chromatogram at each step. *n*-alkanes (C18, C19, and C20) were extracted in the all steps. Particularly C18 was extracted mainly in the step1 and was decreased in the following steps. Contrary to alkanes, anthracene was extracted only in step2 (not visible in the TIC) and more in step3. Phthalic acid dibutyl ester showed a halfway property between alkanes and anthracene. This result indicates that material preference in SFE at different conditions was observed also in the real sample. And a cleanup effect has been integrated in the extraction process of PAHs only by changing SFE conditions sequentially.

Acknowledgments

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References

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