

## Supercritical Fluid Extraction of Chlorobenzene Compounds from Solid Samples

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### 1. Introduction

The extraction of organic pollutants from a variety of samples plays an important role as the first step in environmental analysis. This process is achieved traditionally by using liquid extractions. Methods based on solvent extraction, however, are often time-consuming and are very expensive. Additionally, the organic liquids are usually toxic to humans.

Supercritical fluid extraction (SFE), which process exploits the properties of the fluid at temperatures and pressures near the critical point, attracts much attention recently. SFE has many potential advantages compared with solvent extraction methods, including reduced extraction times and amounts of extraction solvents. It also gives more efficient extractions, increased selectivity and the possibility of coupling with other chromatographic techniques<sup>1)</sup>.

The interesting properties of SFE can contribute significantly to the application of analytical performance and the application studies have been done on environmental solids such as soil<sup>2)</sup>, sediment<sup>3)</sup>, fly ash<sup>4)</sup>, and adsorbent for sampling<sup>5)</sup>. However, the extraction characteristics are not entirely made clear and the optimal condition for the extraction on each analyte is selected empirically.

In this paper, several extraction characteristics are investigated using model solid sample spiked with chlorobenzene compounds. Further, the application to fly ash samples are shown.

### 2. Experimental Section

#### 2.1 Materials

# ANA

The model solid sample that is almost dry consists of diatomaceous earth, cellulose filter paper and granular activated carbon. An aliquot of ca. 2 g of the sample was taken into an extraction vessel having an internal volume of 10 ml and was spiked with a 25  $\mu$ l mixed solution (1000 mg/l) of the chlorobenzene compounds shown in Table 1. Consequently, the concentration of each compound in solid is approximately 12.5  $\mu$ g/g.

Table 1 Chlorobenzene compounds used

Number	Compound	Molecular weight	Melting point (°C)	Boiling point (°C)
1	1,2-Dichlorobenzene	147	-17	180
2	1,3-Dichlorobenzene	147	-24.8	173
3	1,4-Dichlorobenzene	147	53	174
4	1,2,3-Trichlorobenzene	181	52.6	218
5	1,2,4-Trichlorobenzene	181	17	214
6	1,3,5-Trichlorobenzene	181	63.4	208
7	1,2,3,4-Tetrachlorobenzene	216	47.5	254
8	1,2,3,5-Tetrachlorobenzene	216	54.5	246
9	1,2,4,5-Tetrachlorobenzene	216	140	243
10	Pentachlorobenzene	250	85.5	277
11	Hexachlorobenzene	285	231	321

## 2.2 Supercritical Fluid Extraction

The SFEs were performed on the ISCO instrument composed of two Model 260D syringe pumps and an SFX2-10 extraction unit as shown in Fig.1. Carbon dioxide ( $\text{CO}_2$ ) of 99.99% purity was used as the supercritical fluid because of its nonflammable and nontoxic properties, low cost and minimized waste problems. SFE flow rates were controlled at 0.8 - 1.0 ml/min (measured as liquid fluid at the pump) using 50  $\mu$ m-i.d. fused silica tubing for outlet restrictors under the condition of 30 min dynamic extraction. All extracts were collected by inserting the outlet end of the restrictor into a vial containing ca. 5 ml of hexane or methanol.

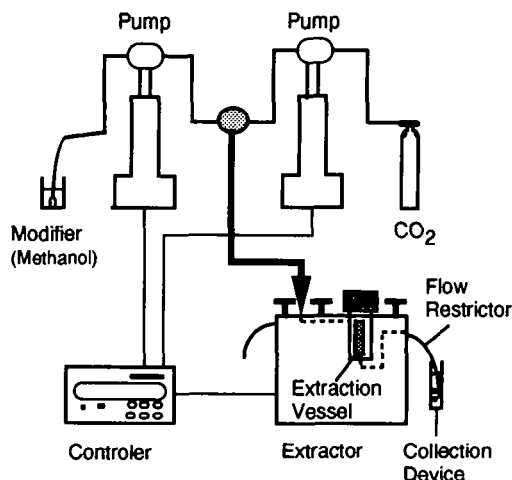


Fig.1 Schematic of SFE system

## 2.3 Analysis

The collected solution was diluted until 25 ml, then, an aliquot of the solution was analyzed using an HP 5890 gas chromatograph equipped with an

electron-capture detector and a 30 m x 0.53 mm i.d. fused silica capillary column (HP-5, HP, 0.88  $\mu$ m film). Recovery was determined from the ratio of the amount in the collected solution to that spiked.

### 3. Results and Discussion

#### 3.1 Effect of Pressure

It is found that the density of supercritical fluid significantly affects the dissolving power for organics. The density of supercritical fluid is recognized to depend on the pressure under constant temperature, and, accordingly, the ability of dissolution is expected to be controlled by changing pressure. Fig.2 shows the effect of pressure to the recovery of 1,2,3,4-tetrachlorobenzene. This figure demonstrates that the recovery varies according to pressure and that only poor recovery is attained near the critical point, 7.6 MPa. Another point noticed is that the increasing pressure is not proportional to the recovery increase. This phenomenon suggests that the density value which increases the ability of dissolution and extraction exists on SFE.

#### 3.2 Effect of Modifier

Fig.2 also shows that the recoveries were not sufficiently quantitative. A reason for this is that supercritical CO<sub>2</sub> corresponds to non-polar solvent, while chlorobenzene compounds have moderate dipole moments. As seen in Fig.3, methanol modifier added to CO<sub>2</sub> (5 vol %) satisfactorily improved recoveries at each pressure. The improvement of recovery has been accomplished except at 41 MPa. Nearly 100 % recovery was obtained at the pressures of 21 and 34 MPa.

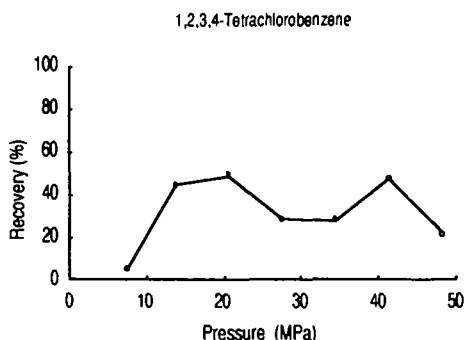


Fig.2 Effect of pressure on recovery (Temperature: 50°C)

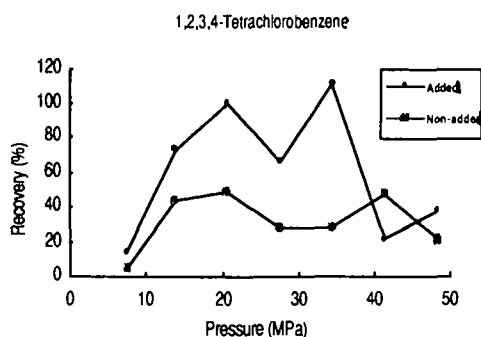


Fig.3 Effect of the addition of modifier on recovery (Temperature: 50°C)

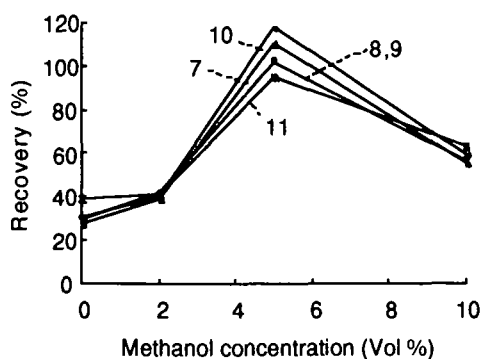


Fig.4 Effect of methanol concentration on recovery (Pres.: 34 MPa, Temp.: 50°C, Numbers correspond to compounds in Table 1.)

The effect of methanol modifier to recovery changed in accordance with the added amount of methanol as shown in Fig.4 and resulted in the most quantitative recovery at 5 vol %. It is assumed that there is an optimum modifier concentration for the dipole moment of an analyte molecule.

### 3.3 Recoveries of Chlorobenzenes

Fig.5 demonstrates the recoveries of the chlorobenzene compounds used. Quantitative recoveries were obtained for 1,2,3-tri-, tetra-, penta- and hexa-chlorobenzenes, whereas dichloro- and trichloro-benzenes except 1,2,3-isomer showed poor recoveries. The reason for this phenomenon is not clear and will be further investigated.

### 3.4 Effect of temperature

As shown in Fig.6, temperature does not much affect recovery under the condition of nearly constant fluid density (0.8 g/ml).

### 3.5 Determination of chlorobenzene compounds in fly ash sample

The preliminary study on the determination of chlorobenzene compounds in real-world samples with SFE was performed and the data were compared to those obtained by soxhlet extraction. However, we should take notice that the recovery characteristics obtained on spiked sample are not always applied to real-world sample, because extraction is limited not by the solubility of the analyte in supercritical fluid but rather the desorption process of the compound from the active site of matrix<sup>4</sup>). The results will be demonstrated in presentation.

## 4. References

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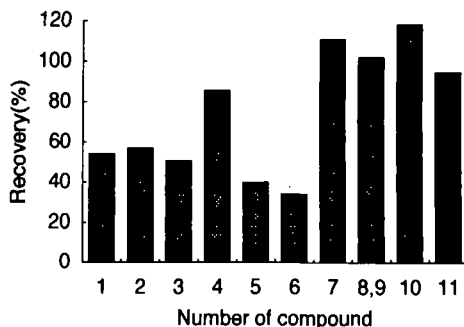


Fig.5 Recoveries of chlorobenzenes (Pres.: 34MPa, Temp.: 50 °C, Numbers correspond to compounds in Table1.)

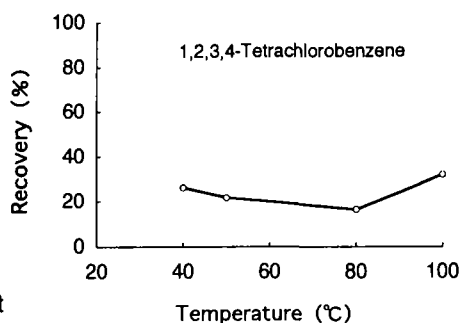


Fig.6 Effect of temperature on recovery (Fluid : CO<sub>2</sub> only)