

Extraction of Dioxins from Municipal Incinerator Fly Ash with Supercritical CO₂ in Comparison with Soxhlet Extraction

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Introduction

Extract of the dioxins in the environmental samples such as fly ash for the determination was achieved traditionally by using organic solvent extractions. Dioxins are leached from fly ash with an organic solvent such as toluene in a Soxhlet apparatus. Methods based on solvent extraction are often time-consuming, due to small diffusivities in the liquid organic solvents, and are very expensive because they require high-purity organic solvents and waste solution disposal fee. In addition, these solvents are generally high toxicity for the human. Therefore, sequential chromatographic techniques must often be used to separate complex mixtures after extraction procedure. This increases the time and cost of overall chromatographic analysis of environmental sample, especially solid sample. For instance, analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans often takes days or weeks to complete. So, extraction with an organic solvent in a Soxhlet apparatus is undesirable method for extraction of the dioxins from fly ash.

Supercritical fluid extraction with CO₂ was used to polycyclic aromatics, halogenated hydrocarbons and halogenated aromatic hydrocarbon, PCDDs and PCDFs from a municipal incinerator fly ash matrix¹. At this study, we researched on the effects of the pressure, extraction time, temperature and CO₂ flow rate to the supercritical CO₂ extraction of dioxins from fly ash.

Material and Methods

(Fly ash samples)

Fly ash samples were collected at the bottom of electric precipitator of municipal incinerator. To define of characteristic of fly ash samples, we measured of specific surface area, particle size, density (Bed, Solid) and concentration of dioxins of fly ash samples. These are shown in Table 1. Real concentrations of PCDD isomers of fly ash samples are shown in Fig.1.

Table 1 The property of Fly ash samples

		Before treated with HCL	After treated with HCL
Density	Bed	0.66g/cm ³	0.66g/cm ³
	Solid	2.29g/cm ³	2.51g/cm ³
Particle Size (50%)		21.18x10 ⁻⁶ m	22.50 x10 ⁻⁶ m
Specific Surface Area		8.36m ² /g	80.70m ² /g
Dioxins		3.00ng-TEQ/g	68.80ng-TEQ/g*

* Because of reducing volume of fly ash samples with acid washing (about 95%).

(Pre-treatment)

Fly ash samples were washed with 2N-HCL for 1~2hr to remove the alkalis covered with the fly ash. After washing with HCL, fly ash was separated from HCL by filtration with aspirator. Fly ash was dried overnight in an electric oven at 303K. After drying, fly ash samples were kept in a

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closeness vessel. The property of fly ash treated with HCl is also shown in Table 1. (Supercritical CO₂ extraction)

CO₂ used as a solvent for supercritical extraction supplied from high-pressure cylinder. CO₂ from cylinder was quenched with coolant to keep liquid condition. Liquefied CO₂ was into a liquid plunger pump (NP-CX-100, NIHON SEIMITU KAGAKU CO.,LTD, Japan). The extractor was used a stainless-steel column (20mmi.d.x250mm-L) for the liquid chromatography.

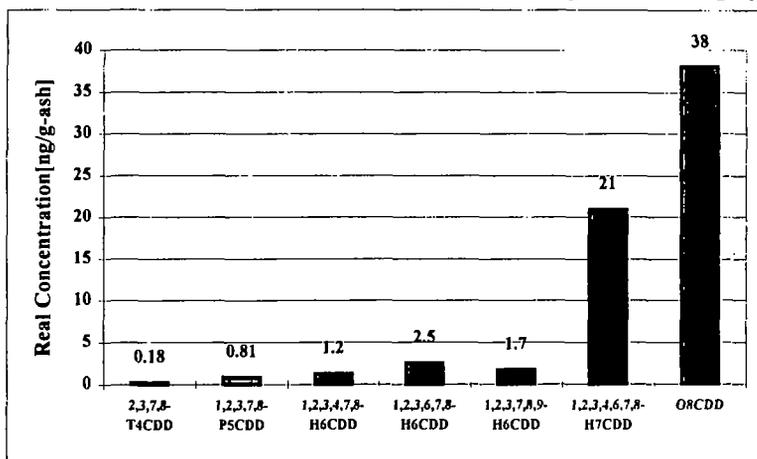


Fig.1 Real Concentrations of PCDD isomers

Discharged liquefied CO₂ by the pump was into the mixer that was in the thermostatic air bath. The phase of CO₂ changed liquid phase to supercritical phase in the mixer. The extractor was also in the thermostatic air bath to maintain the fluid temperature that was critical temperature of CO₂ (about 304K). Supercritical CO₂ was through the extractor, where the dioxins in fly ash were dissolved into it. The backpressure regulator was set after extractor to control the pressure in the extractor. After through the extractor, CO₂ that was changed supercritical phase to gas phase by the backpressure regulator and extracted dioxins were in the first and second separator those were refrigerated solvent trap containing toluene. A schematic diagram of supercritical CO₂ extraction apparatus is shown in Fig.2.

(Quantitation of dioxins^{1,2})

Municipal incinerator fly ash as experimental sample was homogenized by sieving it under 150x10⁻⁶m. The solutions were reduced in volume by rotary evaporation, transferred to a 25-mL pear flask for further concentration and then concentrated, in a vial, to 500x10⁻⁶L by a gentle stream of nitrogen. The samples were stored into a refrigerator to prevent evaporation.

Quantitation of the extracted polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) was achieved with a Hewlett-Packard HP-5890 GC/MSD system. An ionization voltage of 70-eV and ion source temperature of 573K were used.

Before each set of analysis, the instrument was turned with the compound per-fluoro-tributylamine (PFTBA). This compound was used since it is stable and produces fragments throughout the entire mass range. Three peaks of PFTBA were used since they are very close to the ion masses of the PCDDs and PCDFs. Since the mass of the PCDDs and PCDFs are known, selected ion monitoring (SIM) was used. To ensure correct identification and quantitation of PCDDs and PCDFs, a standard mixture of these compounds as syringe spike was injected before a new set of

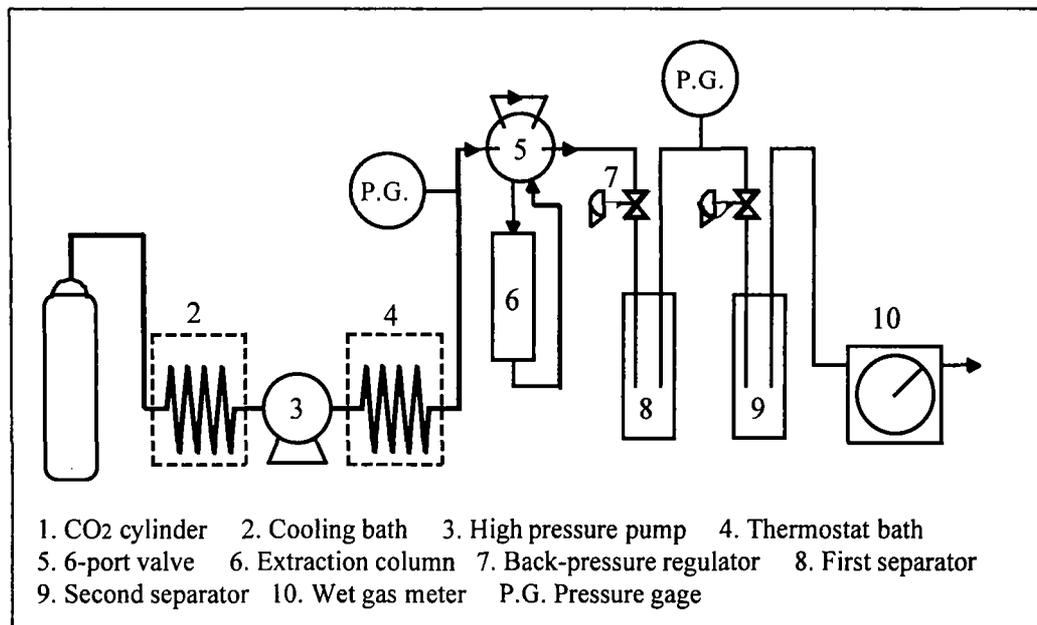


Fig. 2 Schematic diagram of supercritical CO₂ extraction apparatus

unknowns was analyzed. The capillary columns, SP2331 (SUPELCO division, SIGMA-ALDRICH JAPAN, inc.) and DB-17 (J&W Capillary Columns) were used for GC. SP2331 was used for analysis of tetra-chlorinated compound to hexa-chlorinated compound. On the other hand, DB-17 was used for analysis hepta-chlorinated compound and octa-chlorinated compound. The helium used as carrier gas flow rate was 2.0-mL/min.

Results and Discussion

Efficiency of extract was proceeding with pressure in the extractor was increased. Supercritical CO₂ extraction of fly ash treated with HCL was performed at 10, 20 and 30MPa at 323K in the extractor. This phenomenon is relying on the solubility of dioxins to the supercritical CO₂. Therefore, efficiency of the extract was improved with the pressure in an extractor was increased. Hepta- and octa-chlorinated dibenzodioxin and dibenzofurans were easy to extract. This result is shown in Fig.3.

Supercritical CO₂ extraction was performed for 1,2,4,8 and 16h at 30MPa, 323K in the extractor. Yields of extract were increased mildly with increasing of extraction time. But, it is little change between 8hr extraction and 16hr extraction.

The result of making a comparison between Supercritical CO₂ extraction and Soxhlet extraction with toluene is shown in Fig.4. Supercritical CO₂ extraction of fly ash treated with HCL was performed at pressure: 30MPa, extraction time: 1hr, temperature: 323K, CO₂ flow rate: 5ml/min-L.

Soxhlet extraction with toluene was performed at 1hr. As a result, Supercritical CO₂ extraction was better than Soxhlet extraction for extraction of dioxins. This result is shown in Fig.5.

Acknowledgements

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References

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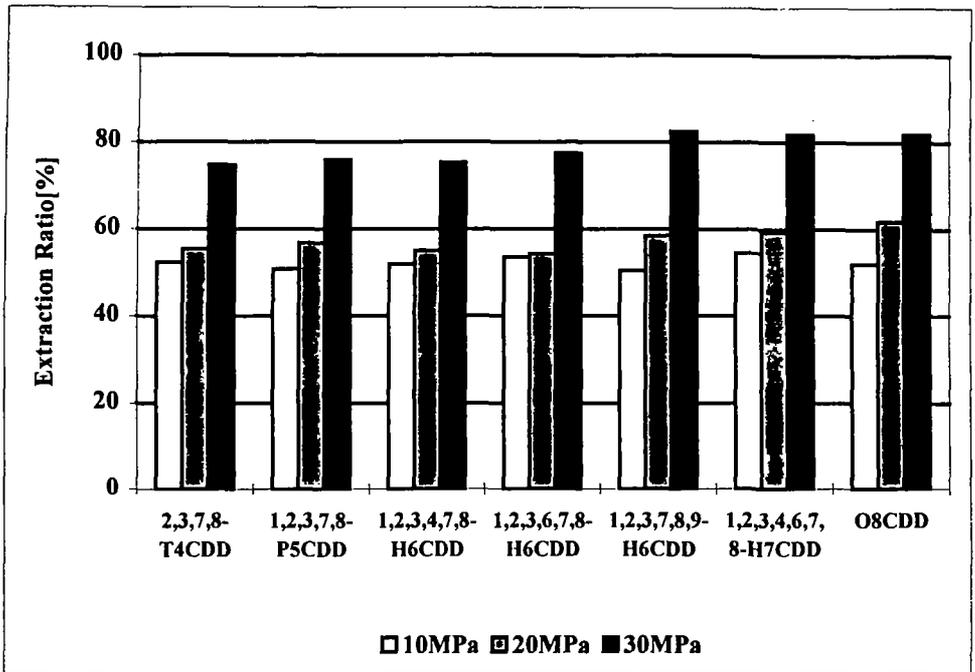


Fig.4 Effect of pressure to supercritical extraction of dioxins

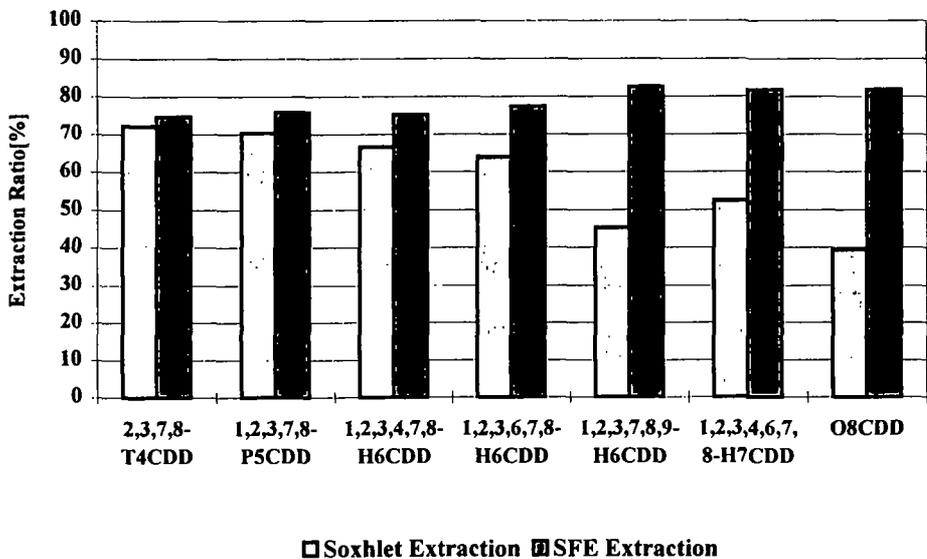


Fig.5 Comparison Supercritical extraction with Soxhlet extraction

