

**Extract of the Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Municipal Incinerator Fly Ash with Supercritical Carbon Dioxide**

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**Introduction [1]**

Extract of the dioxins in the environmental samples, such as fly ash, was achieved traditionally by using liquid extractions. Fly ash is leached with an organic solvent, such as toluene, in a Soxhlet apparatus. Method 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 to the long extraction times and generally high toxicity of the organic solvent. 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 Carbon dioxide was used to polycyclic aromatics, halogenated hydrocarbons and halogenated aromatic hydrocarbon, PCDDs and PCDFs from a municipal incinerator fly ash matrix. At this study, We primarily investigated of property of fly ash and verified of the traditional analysis method for dioxins. Generally, dioxins contained fly ash were distributed heterogeneity. This imperfectly distribution of dioxins in the fly ash prevented for evaluating of the amount of extracts. So, we were investigated on the concentration of dioxins in fly ash, composition of inorganic and organic matter, particle size distribution, porosity of fly ash particle, gravity of the particle and surface area of the particle. At the next, We researched on the effects of the pressure and extraction time for supercritical fluid extraction of dioxins from fly ash.

**Material and Methods [2], [3]**

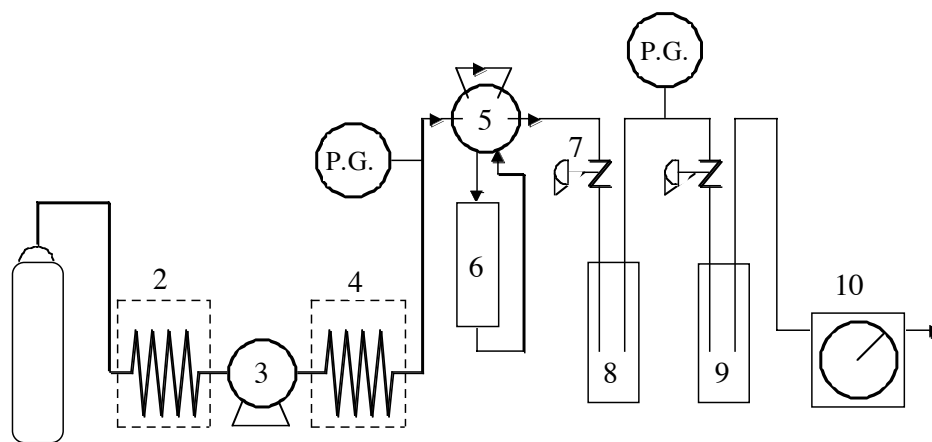
Carbon dioxide used as a solvent for extraction supplied from high pressure cylinder. Carbon dioxide from cylinder was quenched with coolant to keep liquid condition. Liquefied carbon dioxide was into a liquid pump. The extractor was used a stainless-steel column (20mm250mmL) for liquid chromatography and consisted of a liquid plunger pump (NP-CX-100, NIHON SEIMITU KAGAKU CO.,LTD, Japan). Discharged liquefied carbon dioxide by the pump was into the mixer that was in the thermostatic water bath. The phase of carbon dioxide changed liquid phase to supercritical phase in the mixer. The extractor was also in the thermostatic water bath to maintain the fluid temperature that was about 300K over. Supercritical carbon dioxide was through

the extractor, where the dioxins in fly ash were dissolved into it. The back-pressure regulator was set after extractor to control the pressure in the extractor. After through the extractor, carbon dioxide that was changed supercritical phase to gas phase by the back-pressure regulator and extracted dioxins were in the first and second separator those were refrigerated solvent trap containing toluene. A schematic diagram of supercritical carbon dioxide extraction apparatus is shown in Fig.1.

Municipal incinerator fly ash as experimental sample was homogenized by sieving it to < 150 $\mu$ m.

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 500L by a gentle stream of a 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.



1. CO<sub>2</sub> cylinder   2. Cooling bath   3. High pressure pump   4. Thermostat bath  
 5. 6-port valve   6. Extraction column   7. Back-pressure regulator   8. First separator  
 9. Second separator   10. Wet gas meter   P.G. Pressure gage

Before each set of analysis, the instrument was turned with the compound perfluorotributylamine (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 compound as syringe spike was injected before a new set of 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

Extracts were obtained at five pressures and extraction time each. Efficiency of extract was proceeding with pressure in the extractor was increased. Supercritical carbon dioxide extraction was performed at 10,15,20,25 and 30MPa at 330K in the extractor. In the case of addition organic solvent used as entrainer, yields of extracted dioxins were increased considerably. This phenomenon is rely on the solubility of dioxins to the supercritical carbon dioxide. Therefore, efficiency of the extract was improved with the pressure in an extractor was increased. Hepta- and octa-chlorinated dibenzodioxin and dubenzofuran were easy to extract.

Yields of extract was increased with increasing of extraction time. Supercritical carbon dioxide extraction was performed for 1,2,4,8 and 16h at 30MPa, 330K in the extractor.

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