

COMPARATIVE EFFICIENCY OF PCDD/Fs WITH A VARIETY OF EXTRACTION METHODS

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Introduction

Chemical analysis of Persistent Organic Pollutants (POPs) has been relayed on exhaustive extraction using liquid extraction techniques. Among them, the Soxhlet method is conventionally used to liquid-solid extraction for the analysis of PCDD/Fs. Since the extraction normally requires large volumes of organic solvents in combination with long times, the alternative method for the reducing of the solvent waste and faster analyses, which improve the environment and cut costs for PCDD/Fs monitoring.

Supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE) are examples of such alternative extraction techniques. SFE has been proposed as a more selective substitute for the Soxhlet method for PCDDs¹. In SFE the use of carbon dioxide is desirable since no organic solvent is required. However, SFE of certain polyaromatic hydrocarbons (PAHs), pesticides, and PCDD/Fs requires solvents such as methanol^{2,3,4} in view of its extraction yields. In contrast, ASE is performed in minutes for fast and easy extraction with low solvent consumption.

In this study, three modern techniques to conduct at least one of these goals have been compared: (1) Supercritical Fluid Extraction (SFE), (2) Accelerated Solvent Extraction (ASE) and (3) Automated Soxhlet techniques.

Methods and Materials

Standards and reagents

All PCDD/Fs used as internal, recovery and calibration standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All solvents used were for organic trace analysis and were obtained from Kanto Kagaku (Tokyo, Japan). To purify, the silica gel (Merck-Schuchardt, Hohenbrunn, Germany) was prepared to allow Soxhlet extraction with acetone during 48h.

Extract instruments

A Jasco Model CO-1560 extractor equipped with an SCF-Get supercritical fluid pump, an automatically pressure controller (Model SCF-Bpg), and a multi-channel detector (Model MD-1510, Jasco, Japan) was used for SFE experiment. ASE was carried out with an ASE-200 extractor (DIONEX, USA). Automated Soxhlet was carried out with a model B-811 (BÜCHI, Switzerland).

Extraction experiments

Extraction experiments with spiking of native and 17 kinds of ¹³C-labelled analogues of 2,3,7,8-Cl-substituted congeners were performed with ultra pure silica gel before extraction, respectively.

HRGC-HRMS

Detection of PCDD/Fs were determined by of HRGC (6890 plus, Hewlett Packard, US) with a DB 5MS column (J&W Scientific, US) and an SP 2331 column (Supelco, INC., US), coupled to a HRMS

ANALYSIS II

(AutoSpec-Ultima, Micromass, UK) operation on a resolution of 10,000 using a positive electron ionization source and operating in the selected ion monitoring (SIM) mode. Verification of resolution in the working mass range was obtained by measuring perfluorokerosene (PFK) reference peaks. The current trap was 500 mA and the ionization energy was 30 eV. Ion source and injector temperatures were 260 °C. The samples were injected in the splitless mode.

Results and Discussion

Relative efficiency of different extraction procedures/techniques of PCDD/Fs from a solid sample was compared. Figure 1 shows the percentage recovery of PCDD/Fs of all tried extraction experiments. Soxhlet extraction with toluene for twenty-four hour is taken as reference, and it is considered as 100 % extraction. The percentage recovery of first SFE experiments (supercritical CO₂ flow-rate 4 mL/min., pressure 2900 p.s.i, oven temperature 70 °C) was found to be less than 5 % of HpCDD, OCDD, HpCDF, and OCDF. The percentage recovery of remainder varied from 19 to 28 %. This result indicates that the extraction of PCDD/Fs is not easy. To overcome this problem, the cosolvent can be added to the supercritical CO₂. Methanol, which is the most often used modifier, has been tested as cosolvent. Five percent was added to supercritical CO₂, the percentage recovery of HpCDD, OCDD, HpCDF, OCDF was increased from 20 to 25 % by auxiliary pump. The cosolvent (methanol) gives better results than supercritical CO₂ in SFE, but the difference of remainder was quite small. These results were probably attributed to analyte solubility and analyte-matrix binding. Unfortunately, adding methanol did not significantly improve the recovery.

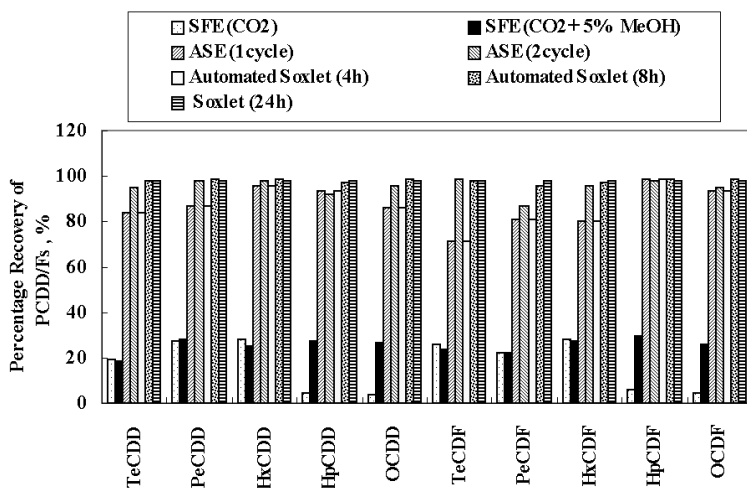


Figure 1. Percentage recovery of PCDD/Fs of different extraction methods and procedures

The percentage recovery of ASE extraction (pressure 2000 p.s.i, oven temperature 150 °C, toluene, 1-cycle extraction, 20 min.) was 71 % of TeCDF and above 80 % of remainder. An improvement of the extracting efficiency was observed when 2-cycle extraction with the same sample was used under the same condition. The percentage recovery of all congeners was above 90 %. Therefore, 2-cycle extraction method provides a more efficient extraction yields than that of 1-cycle extraction.

A comparison of the classical Soxhlet and the automated Soxhlet (hot Soxhlet mode) was made with two conditions. In combination with a raised time (8 hr.), extracting efficiencies could be improved by the use of several temperature processes: increased diffusion rates and solubility of PCDD/Fs. When the automated Soxhlet is compared to the classical Soxhlet extraction, it is confirmed by the pattern of the isomers is no significant difference. The percentage recovery of all congeners was above 97 %.

The efficiency of PCDD/Fs based on a variety of extraction techniques was shown. It was demonstrated that, by careful consideration of the experimental parameters, ASE and automated Soxhlet techniques are capable of replacing method such as the classical Soxhlet extraction.

All extracting techniques were somewhat faster than the classical Soxhlet, but the classical Soxhlet method guarantees the extraction recovery of PCDD/Fs.

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