

Innovative fast SPE for the extraction of PCDD/Fs and dl-PCBs in aqueous samples – preliminary assessment

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Introduction

U.S. EPA Methods 1613b¹ and 1668b² are the basis for the determination of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls (PCBs) in water samples. They are both “performance-based” methods, as every modification is allowed, provided that all performances and criteria are met. As for the extraction of aqueous samples, for both methods the sample can be extracted using solid-phase extraction (SPE) or liquid/liquid extraction (LLE). There are many good experimental reasons for using SPE in preference to liquid-liquid extraction (LLE) for extracting large volume environmental samples. For example, exposure to and consumption of large volumes of organic solvents is avoided; operator dedication to manually shaken separatory funnels, which are expensive to purchase, tedious to clean, and subject to breakage, is eliminated; increased production through multiple simultaneous extractions is realized; and the formation of emulsions is reduced.

As for SPE, the most common adsorbent used is octadecyl (C₁₈) bonded silica. In this paper, the use of activated carbon fiber will be described.

Activated carbons are widely used for purification in many fields and are common in pelletized, granular, powdered, or molded form. Recent development of activated carbons in fiber form is increasing applications of activated carbons in various areas due to its unique characteristics. Activated carbon fibers (ACFs) have unique characteristics compared with granular or powder activated carbons. Since ACFs are considered to have rather defined pore structures and surface characteristics, fundamental studies on adsorption have been tried from various aspects³.

Materials and methods

Parallel monthly rainwater samples were collected, in order to have a real sample and evaluate the matrix effect. The bulk deposition (wet deposition and dry particles) sampling was performed with two glass funnels (30 cm in diameter), which were installed 120 cm above the ground in an open place. In an open place samples were collected through funnels into 10-liter glass (Pyrex) bottles. The bottles were covered with a shelter to avoid photodegradation and heating of the sun.

A commercial ACF with a certified SSA > 2000 m²/g and a thickness of 1.5 mm, was used. The BET surface area analysis yielded a real SSA of ~2500 m²/g and a microporosity with a pore diameter of ~60 nm. As for the analysis, a solution of ¹³C₁₂-labeled cleanup spikes (1613LCS and WP-LCS, for PCDD/Fs and dl-PCBs, respectively; Wellington Laboratories, Canada) in acetone were added to the water sample. The water was passed in a 6ml-glass cartridge containing 1g of ACF between two quartz wool plugs. ACF and quartz wool plugs were Soxhlet extracted with toluene. The extract was then subjected to cleanup procedure. The cleanup consisted of a multilayer silica column (extract eluted with hexane) and an alumina microcolumn to separate PCDD/Fs from dl-PCBs. The eluates were concentrated and added with ¹³C₁₂-labelled syringe spike (WP-ISS and EPA1613-ISS for PCBs and PCDD/Fs, respectively). The instrumental analysis was performed by a triple quadrupole gas chromatograph/mass spectrometer (Trace 1310 GC/TSQ 8000 Evo, Thermo); the chromatographic separation was performed by a DB-XLB column (60m x 0.25mm, 0.25 μm I.D., Agilent J&W).

Results and discussion

Laboratory test

The extraction efficiency of the SPE system and the liquid/liquid extraction (LLE) system were compared, analyzing two deionized water samples, spiked with ¹³C₁₂-labelled standards. After adding internal standards, 2L sample was extracted three times in a funnel with dichloromethane, and the extracts collected together, before the clean-up phase. A same volume of water was extracted using SPE and Soxhlet. Each extract was then

subjected to clean up procedure and GC/MS analysis. Both methods showed similar recoveries, within the limits of EPA methods.

Following the results obtained in the laboratory and on a reduced volume of water, the SPE method was applied to a real sampled, consisting of 1 month bulk deposition.

Bulk deposition analysis

The collected sample of 1 month was of about 13 L of rain water. Two sampling systems were placed, in order to repeat parallel sampling and analysis. Due to the large volume of water collected, two SPE in series were connected, and extracted separately, in order to preliminary evaluate the breakthrough. Figure 1 shows a schematic representation of the extraction system. Sample breakthrough is a function of the strength of the interaction between the analyte and sorbent, the sample volume and the mass of sorbent. The two SPE were then subjected to cleanup procedure and GC/MS analysis, as described in the previous section.

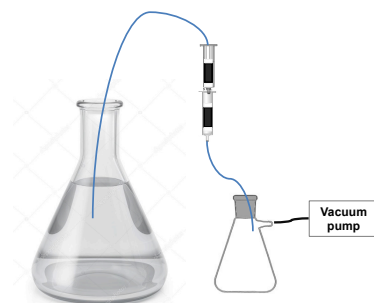


Figure 1 – Schematic representation of the extraction system

Method performance of the ACF sampler was assessed comparing percentage recoveries of the labeled compounds spiked in the water sample with the corresponding recovery tables in EPA 1613b and 1668b methods. Recoveries are within the limits of EPA methods (25-150%) for each congener (fig. 2); recoveries on the second SPE were below 5%, so it can be assumed that this method is suitable for water samples.

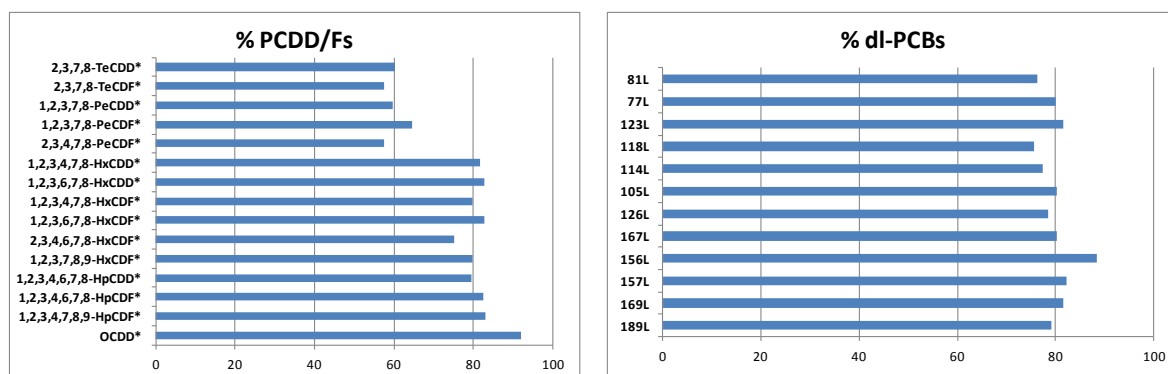


Figure 2 – Percentage recoveries of ¹³C₁₂-labeled compounds

Conclusions

In this study an easy and cheap method to extract large volume of water is presented. One critical feature of an extraction method is to fulfill limit of quantification; it can be achieved concentrating the sample, extracting large amount of sample without loss of analyte in the breakthrough volume. The preliminary analysis show that 1g ACF is suitable for the extraction of PCDD/Fs and dl-PCB from rain water.

Further study will evaluate breakthrough curves, considering sample volume, potential concentration of pollutants and total organic matter.

References:

1. US EPA 1613b (1994) *Tetra Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution High Resolution Gas Chromatography/High resolution Mass Spectrometry (HRGC/HRMS)*, EPA 921-B-94-005, 1994, re-issued March, 2012
2. US EPA 1668b (2008) Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids and Tissue by HRGC/HRMS
3. Sakoda A, Kawazoe K, and Suzuki M. (1987); *Water Research* 21:717.