

SOXTERM WITH CAPE COUPLED CARBON-ACID SILICA COLUMN AS A METHOD FOR FAST ANALYSES OF PCDD/Fs AND DIOXIN-LIKE PCBs IN ENVIRONMENTAL SAMPLES

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Abstract

We use a fast and relatively cost effective method, Soxtherm with CAPE coupled carbon-acid silica column, to improve the efficiency for the analyses of PCDD/Fs and dioxin-like PCBs in environmental samples. We choose three kinds of certified reference samples to evaluate the Soxtherm extraction system and the results are in good agreement with certified values. We have tested 101 real samples of different environmental matrices using this method from 2006 to 2007. The recovery range of the $^{13}\text{C}_{12}$ -PCDD/Fs is 50~93% and $^{13}\text{C}_{12}$ -PCBs isotopes is 57~72%. It meets the QA/QC criteria of US EPA Methods 1613B and 1668A. We have successfully applied this technique in samples such as soil, sediment and waste matrices and will extend it to applications in other matrices.

Introduction

The “Belgium Crisis” in 1999 is a milestone for the analysis of dioxin-like compounds. Traditional Soxhlet extraction and time-consuming cleanup procedures such as silica, alumina and carbon column were widely adopted before that event. However, in an urgent case such as “Belgium Crisis”, it is obvious that the conventional methods are not enough to deal with huge amount of samples in such short time. Recently, more and more contamination cases involving dioxin-like compounds have caused great general public concern and urged government to improve response action time. Therefore, a lot of research projects using new techniques such as Accelerated Solvent Extraction¹ (ASE) and Pressurized Liquid extraction (PLE)² have been conducted to improve the extraction efficiency. On the other hand, there are also research projects endeavored to shorten the time of cleanup procedure. Automatic systems, such as Automatic Cleanup Robot³ and Power-Prep System⁴ were involved in these tests. Though these facilities exhibit outstanding performances, the cost of these equipments is generally too expensive for most commercial labs to afford. Therefore, we would like to apply an alternative method, the Soxtherm with CAPE coupled carbon-acid silica column, which is fast and more cost-effective. This method can be useful for those labs urgently needing to improve their efficiency of the analyses of PCDD/Fs and dioxin-like PCBs in environmental samples with limited budget.

Materials and Methods

Soxtherm extraction

The extraction apparatus adopted in this study are Soxtherm SOX414 and SOX416 manufactured by Gerhardt in Germany. Soxtherm extraction is a kind of “fast Soxhlet” system. The extraction setting of each step in the Soxtherm system is listed in Table 1. Extraction procedure for the Soxtherm system is cited as 5 stages in the followings as illustrated in Figure 1⁵. With this technique, the extraction time can be reduced to about 3 hours.

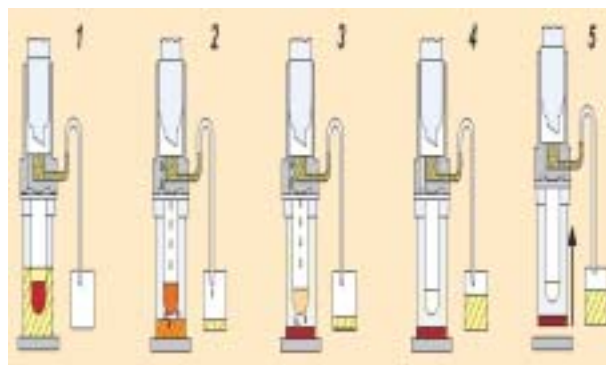


Fig. 1: The extraction procedures of Soxtherm

Table 1: The extraction settings of Soxtherm

Item	Setting
Solvent/Volume	Toluene/135 mL
T-classification	300
Extraction	270
Reduction Interval	6.0 min
Reduction Pulse	3 sec
Hot Extraction	1 h 0 min
Evaporation A	4 × Interval
Rinsing Time	1 h 30 min
Evaporation B	0.0 × Interval
Evaporation C	0 min
Program Length	2 h 54 min

Stage1-Samples are weighed into thimbles and extracted with boiling solvent.

Stage2-Reduce the solvent level to just below the thimble bottom. Evaporated solvent is collected in a recovering tank.

Stage3-More extractable material from the sample is extracted out from the thimble through refluxing.

Stage4-Most solvent is distilled and collected in the recovering tank.

Stage5-The extraction beakers are raised automatically from the heating plates. Part of the residual solvent can be removed at this stage.

CAPE coupled carbon-acid silica column

The coupled carbon-acid silica column is taken from the Dioxin/Furan Immunoassay Kit manufactured by the CAPE Technologies. It is originally used for a biological screening method for the USEPA Method 4025⁶. We developed this method in our lab as a backup method for the screening method DR-CALUX[®] that we established in 2004. Surprisingly, we found this coupled column can be applied in the chemical confirmation method too. In order to get better recovery of isotope standards and meet the QA/QC criteria of US EPA Methods 1613B and 1668A, the original cleanup procedures^{6, 7} were modified to the procedure as cited in the followings: Pre-clean the extract from Soxtherm extraction by acid-silica column if needed. (Add copper to remove sulfur for sediment samples.) CAPE coupled carbon-acid silica column is set up as the picture in Figure 2. Use stopper/stopcock assembly and syringe to pressurize the column and maintain a drop-wise flow rate of 0.5-1.0mL per minute when eluted by solvent. Add 8mL n-hexane, 2mL n-hexane /time x 4 times, to transfer sample extract to column. Add 15mL n-hexane to elute column. Add 15mL n-hexane to elute column again and start to collect all solvent passed through column for dioxin-like PCBs fraction. Remove and transfer carbon mini-column to a clean empty column. Add 6mL of 1:1 toluene: n-hexane to elute column and collect all solvent passed through column for dioxin-like PCBs fraction. Reverse the direction of carbon mini-column. Add 20mL of toluene to elute column and collect all solvent passed through column for PCDD/Fs fraction.



Fig. 2: CAPE coupled carbon-acid silica column

HRGC/HRMS

The analysis of samples was performed on a HRGC (HP 6890)/ HRMS (JEOL JMS-700) using DB-5MS column.

Validation of Soxtherm extraction

We focused on the fast analyses of PCDD/Fs. Three kinds of certified reference samples, including EDF-2513 of soil matrix (Cambridge Isotope Laboratories), DX-1 of sediment matrix (National Water Research Institute, Canada) and 2004FA of fly ash matrix (2004 International Calibration Study, Sweden), were used to evaluate Soxtherm extraction system. The resulting data are summarized in the section of results and discussion.

Real Sample Testing

We have tested 101 samples of different environmental matrices using Soxtherm with CAPE coupled carbon-acid silica column since 2006 till now. These samples include 33 soil samples, 45 waste samples (solid waste and fly ash) and 23 sediment samples. We analyzed PCDD/Fs for soil and waste samples and analyzed both PCDD/Fs and dioxin-like PCBs in others. Experimental results are shown in next paragraph.

Results and Discussion

As we can see in Table 1, the extraction time of the Soxtherm system is less than 3 hours. The samples can be extracted in parallel while ASE extracts samples in sequence. For batch extraction of 8-10 samples, Soxtherm is

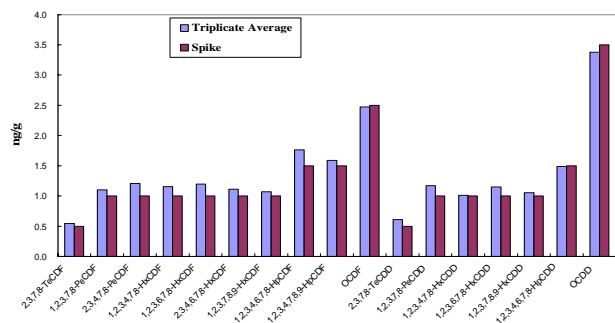


Fig. 3: The validation result of EDF-2513(soil)

about as fast as ASE. However, the facility cost is much lower than ASE. Also, ASE uses the same tubing system for continuous extraction of different samples continuously with small volume of solvent washing of the tubing system. For samples of large range of concentrations, especially for those environmental matrices samples, you have to watch carefully about the cross-contamination problem. Such problem does not exist in Soxtherm system. The validation results using the Soxtherm system for the certified reference samples are shown in the Figure 3 through Figure 5. It is demonstrated that the results of three matrices are in good agreement with the certified values.

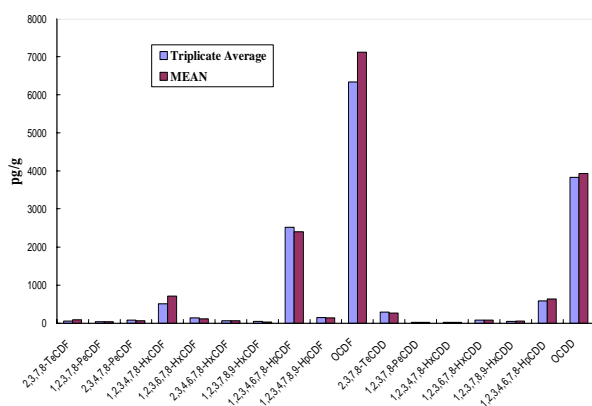


Fig. 4: The validation result of DX-1(sediment)

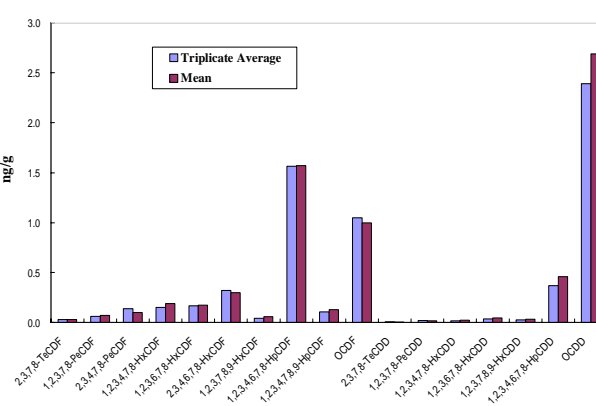
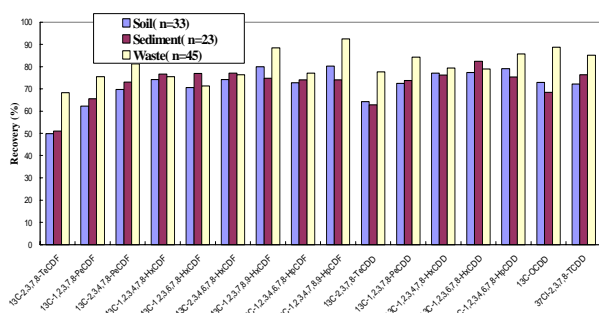
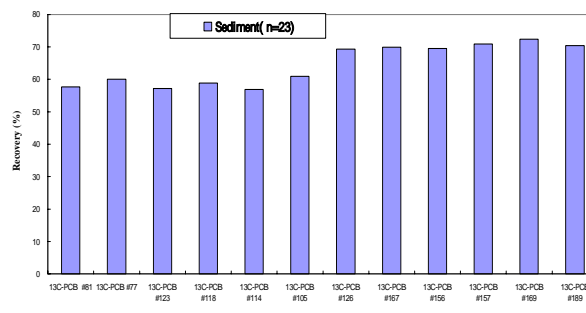


Fig. 5: The validation result of 2004FA(fly ash)

For real sample testing, the recovery of the $^{13}\text{C}_{12}$ -PCDD/Fs and PCBs isotopes are shown in Figure 6 and Figure 7. In Figure 6, it is shown that waste (68~93%) matrix samples have better recovery than soil (50~80%) and sediment (51~82%) matrices in $^{13}\text{C}_{12}$ -PCDD/Fs isotopes. It might be caused by the higher concentration of waste samples. As told by CAPE Technologies, the materials used mini-carbon column is very similar to AX-21 and will tend to trap PCDD/Fs and PCBs congeners. As we use only very little solvent to elute the column, the samples of higher concentration of PCDD/Fs and PCBs are easier to be eluted out and has better recovery accordingly. The recovery of $^{13}\text{C}_{12}$ -PCBs isotopes of sediment matrix samples is 57~72% as shown in Figure 7.

Fig. 6: $^{13}\text{C}_{12}$ -PCDD/Fs recovery of real samplesFig. 7: $^{13}\text{C}_{12}$ -PCBs recovery of real samples

These results are not as good as those using the Power-Prep System⁴, but are good enough to meet the QA/QC criteria of US EPA Methods 1613B and 1668A. CAPE coupled carbon-acid silica column is much less costly as the column of Power-Prep System. The cleanup procedure is simple, user-friendly and need much less amount of

solvent. The total operation time of 8-10 samples is about 3 hours. As each coupled carbon-acid silica column can be operated independently, it allows several analysts to operate the clean-up procedure in the same time. This will enhance the productivity substantially in the analysis of PCDD/Fs and PCBs.

In this study we have successfully worked on samples of soil, sediment and waste matrices. It can be extended to other environmental matrices without much difficulty. The key bottleneck step will be in the Soxtherm system. We have already analyzed more than 600 samples covering various environmental matrices using CAPE coupled carbon-acid silica column. We have enough data to support that CAPE coupled carbon-acid silica column can be used to other matrices, such as stack gas, ambient air, water, biological tissue, plant, and so on. However, more extraction space is needed to accommodate these matrices samples. In addition, it would be desirable for the Soxtherm system to have options for extraction beakers, so Soxtherm can be used to other application. We have designed by ourselves a specific glass filter as shown in Figure 8 that will substitute the thimble and allow stack gas, ambient air and water samples to be extracted by the Soxtherm system. Hopefully, we might get significant progress in the near future.



Fig. 8: Custom-made glass filter for the Soxtherm system

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