Method development for the analysis of dioxins and dioxin-like PCBs in one single air sample

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Introduction

Dioxins (PCDD/Fs) and dioxin-like PCBs in environment have been of great concern due to their toxicity and potential health risks. The toxic compounds belong to persistent organic pollutions with long half-life, long-distance transport and intensive bioaccumulation in tissue cells.[1] Occurrence of dioxins and dioxin-like PCBs in the air has attracted growing public attention in Hong Kong and the dioxin-like PCBs have been highly recommended being included in environment monitoring and inventory programs.[2,3] However, currently in Hong Kong dioxins and dioxin-like PCBs are separately analyzed by using two individual procedures, which is time-consuming and costly.The separated analyses particularly hinder air monitoring and research because the air sample often cannot be divided into two portions and as a result, double samplings are often needed for the air analysis. Thus, a rapid, reliable, time- and resource-saving method for the simultaneous analysis of dioxins and dioxin-like PCBs in air samples is needed.

This paper describes method development based on individual standard analytical procedure for simultaneously analyzing seventeen 2,3,7,8-chlorine substituted PCDD/Fs and twelve WHO-specified dioxin-like PCBs in air samples. The performances of various chromatography columns on the separation of the PCBs from the PCDD/Fs and the further cleanup for PCBs are presented and discussed.

Materials and Methods

All solvents were absolve grade and were purchased from Tedia. Acidic alumina (150 mesh), celite 545, activated carbon (120-400 mesh) and florisil (60-100 mesh) were obtained from Sigma-Aldrich. Silica gel (0.063-0.200mm) was purchased from Merck. The absorbents except acidic silica gel (30%, w/w) were activated and stored at 170^{0}C in an oven. Bio-Beads SX-3 was purchased from Bio-Rad. Standard solutions of the PCDD/Fs and WHO-specified PCBs were purchased from Wellington Laboratories**.** Certified reference fly ash BCR615 was obtained from Institute for Reference Materials and Measurements.

The analytical procedure was presented in Fig. 1. Briefly, the air sample was spiked with ^{13}C-labeled surrogate standards prior to the 16-hour Soxhlet extraction with toluene. The extract was concentrated to dryness and the residue was dissolved in hexane. After the treatment with concentrated sulphuric acid, the extract was sequentially subjected to acidic silica gel, acidic alumina for cleanup. Next, dioxin-like PCBs were separated from dioxins. Then the fractions of the PCBs and dioxins were subjected to GPC and activated carbon chromatography column for further cleanup, respectively.Recovery standards of PCBs and PCDD/Fs were added prior to the GC injection.

The quantification of dioxins and dioxin-like PCBs was performed on an Agilent 6890 gas chromatography coupled with an AutospecUltima mass spectrometer operating with EI source in SIM mode. 2 ml of sample extract was injected with splitless mode into a DB-5MS fused silica capillary column (60 m * 250 mm i.d. * 0.25 mm film thickness) with helium as carrier gas. The details of the MS analysis and quality control are described in the EPA methods 23 and 1668A.

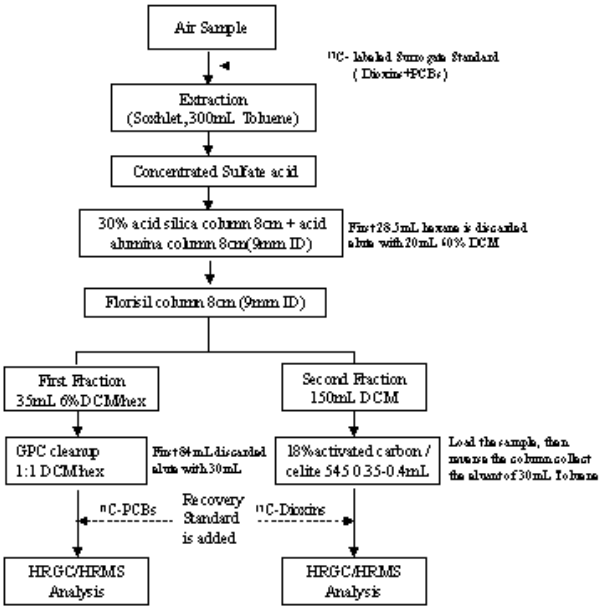

Figure 1. Procedure for analyzing dioxins and dioxin-like PCBs in a single air sample.

Results and Discussion

1. Method development

The key work of the method development for the analysis of dioxins and dioxin-like PCBs in one single sample was to separate the two groups of chemicals in the sample extract. The separation of dioxins and dioxin-like PCBs was studied by using different chromatography columns with various solvent mixtures. The obtained results showed that acidic alumina chromatography column could not be used to separate dioxins and dioxin-like PCBs because they were eluted out together. However, the separation could be achieved by using either florisil or activated carbon column (Fig. 2 and Fig. 3). As showing in Fig.2, PCBs could be eluted out of the florisil column in the first 20 mLeluent of 6% DCM in hexane, but no dioxins were eluted out until the eluting solvent was changed to 100% DCM, indicating a complete separation of dioxin-like PCBs from dioxins by using florisil column. Although the separation could also be achieved by changing the eluting solvent from the mixture of DCM, methanol and toluene to 100% toluene when using the activated carbon column (Fig. 3), florisil chromatography column was found simpler and more efficient on the separation of the two groups of chemicals. Moreover, the performance of activated carbon chromatography column was found inconsistent sometimes, which may be caused by the inconsistent absorbent packing.

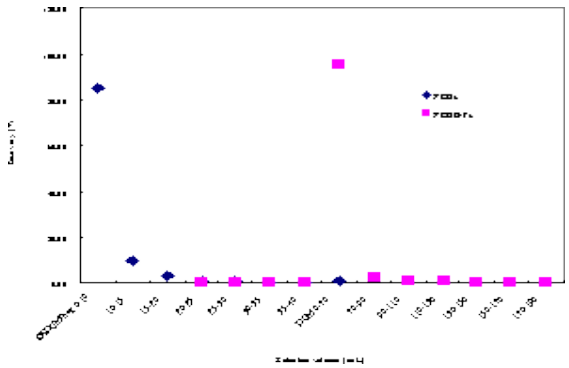

Figure 2. Elution curve of dioxins and dioxin-like PCBs on florisil column.

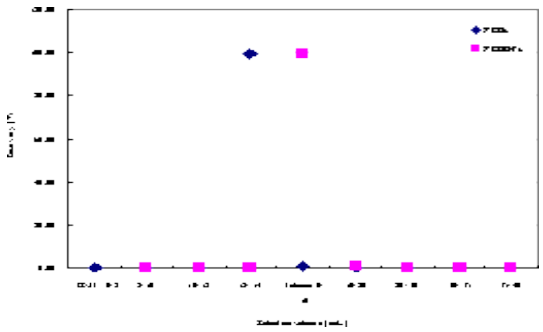

Figure 3. Elution curve of dioxins and dioxin-like PCBs on activated carbon column. DMT represents solvent mixture of DCM: Methanol: Toluene, 75:20:5 (V/V/V).

A gel permeation chromatography (GPC) column was used to remove high molecular weight interferences in the fraction of dioxin-like PCBs. The GPC was packed with pre-swollen and washed Bio-Beads SX-3 corresponding to 30g dry material by using 1:1 DCM:hexane as the solvent. After loading the sample extract containing dioxin-like PCBs, high molecular weight interferences were removed in the first 85 mL of 1:1 DCM:hexane, and the dioxin-like PCBs were then eluted with additional 30 mL of 1:1 DCM:hexane. It was found that GPC was efficient for removing the chemicals that interfered with the quantification of dioxin-like PCBs, which is consist with the literature reports.[4-6]

The method applicability was tested on air samples collected in Hong Kong. Eight stack air samples were analyzed by using the developed method. The levels of dioxins and dioxin-like PCBs in the air samples were found to range from 364.7 to 819.3pg TEQ /m^3 and 6.7 to 32.5 pg TEQ /m^3, respectively. The average recoveries (with relative standard deviation) of $^{13}C_{12}$-labelled dioxins and dioxin-like PCBs were in the range of 73-94% (13-18%) and 60-86% (8-23%), respectively.

2. Method validation

Because currently there is no CRM air standard available for the analysis of dioxins and dioxin-like PCBs, a fly ash CRM sample (BCR615) was analyzed to validate the developed single analysis method for the dioxins and dioxin-like PCBs. The results were satisfied (with Z-score<1 for all congeners except 2,3,4,6,7,8-HxCDF whose Z-score was 1.3). The recoveries of PCBs were 68-92%, which met the criteria specified in US-EPA method 1668A.

Method performance was also evaluated with quality control samples during the environmental air sample analyses. Method blank and spiked matrix samples were analyzed along with the air samples. The performances met the criteria specified in the US-EPA methods 23 and 1668A. The average recoveries (with relative standard deviation) of the $^{13}C_{12}$-labelled dioxin-like PCBs and dioxins obtained from 4 QC samples were in the range of 60-90% (6-22%) and 81-100% (5-9%), respectively. Moreover, the recoveries of the native PCBs and dioxins congeners spiked in matrix blank samples were in the range of 94-102% and 85-101%, respectively.

References

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