

BROMINATED FLAME RETARDANTS-POSTER

CLEAN-UP METHOD FOR PBDD, PBDF AND PBDE BY ACTIVE CARBON COLUMN – AND ITS APPLICATION TO SEDIMENTS

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INTRODUCTION

Polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs) are planar tricyclic aromatic compounds. PBDD/Fs have higher molecular weights than PCDD/Fs, high melting points, low vapour pressures, and low water solubilities (1). These compounds are often formed in the process of manufacturing brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs), tribromophenol, decabromobiphenyl (DBB) or tetrabromobisphenol A (TBBPA), and waste incinerators and the pyrolysis/combustion of BFR contained TV casing materials or circuit boards (2, 3). The Ministry of the Environment of Japan recently initiated investigations on environmental concentrations or the exposure to humans through environmental contamination by BFRs and related contaminants such as PBDD/Fs. However, there are very few experimental and environmental data on the physical and chemical properties of PBDD/Fs compared to reports on PCDD/Fs (1). Furthermore, the complete identification of each PBDD/F congener was impossible because of a lack of reference standards. The congener analysis of PBDD/F is often disturbed by the presence of PBDEs (4). Ebert et al. (4) reported that PBDD/Fs are completely separated from PBDEs using a florisol column. In the present study, we added an active carbon column, used in the PCDD/F analysis, to the final clean-up procedure for the further separation and clean up of sediments from industrialized area. The primary objectives of this study were to completely separate PBDD/F from PBDE, and to identify and quantify PBDE and PBDD/F congeners in sediments from an industrialized area of Japan.

MATERIALS AND METHODS

Target Compounds and Column Clean-up

Reference Standards ¹³C₁₂, ¹²C₁₂-PBDE congeners including ¹²C₁₂-4-monoBDE (BDE-4) and ¹²C₁₂-4,4'-diBDE (BDE-15) were obtained from WELLINGTON laboratories, (Ontario, Canada). ¹³C₁₂, ¹²C₁₂-PBDD/F congeners were purchased from Cambridge Isotope Laboratories, Inc. (USA).

Multi-layer Silica Gel Column A total of 16g silica gel were combined and used; 3g Silica gel 60, MERCK, Germany, 10g 44% sulfuric acid-impregnated silica gel, WAKO, Japan and 3g 2% Potassium hydroxide-impregnated silica gel, WAKO, Japan). Hexane was eluted to rinse the column, then a mixed reference standard in hexane was added to the column and it was eluted first with 100mL hexane and then with 100mL 10% CH₂CL₂/ hexane (v/v).

ORGANOHALOGEN COMPOUNDS

BROMINATED FLAME RETARDANTS-POSTER

Florisil Column According to the method of Ebert et al. (4), 5g florisil (60-100 mesh, KANTO CHEMICAL, Japan) containing 1% water was prepared. After conditioning of the column with hexane, reference standards were loaded onto the column. These compounds were eluted with 100mL hexane for PBDEs and then eluted with 100mL 60% CH₂CL₂/ hexane (v/v) for PBDD/Fs.

Active Carbon Column Based on the column clean-up methods for PCDD/Fs, 1g of active carbon impregnated with silica gel (WAKO, Japan) was prepared without any solvent conditioning. We expected that PBDEs would separate well from PBDD/Fs on the active carbon column because of differences of planarity, like separations of PCB and PCDD/F. Hexane was added to the column to remove the matrices that would interfere in the identification of PBDEs. The remaining reference standards on the carbon column were fractionated with 25%CH₂CL₂/hexane (v/v) for elution of PBDEs and toluene for PBDD/Fs.

Sediment Samples 10g of the dried marine sediments were extracted with toluene in a Soxhlet apparatus for > 16hrs. ¹³C-labelled internal spikes were added prior to extraction. Samples were cleaned-up and fractionated by the multi-silica gel column, florisil column and active carbon column according to the elution conditions determined in this study. A copper granule column was also added for sulfur removal prior to the florisil column. To calibrate a micro-syringe, 100 pg of ¹³C₁₂-labeled OCDD was added prior to HRGC/HRMS quantifications.

Analysis of PBDEs and PBDD/Fs

Analyses of PBDEs and PBDD/Fs were performed on an HRGC-HRMS (HP6890- JMS 700K, JEOL co., Japan) with selected ion monitoring (SIM) mode. HRMS was operated in electron impact mode at a resolution R>12,000 (10% valley). A gas chromatograph equipped with capillary columns DB5-HT (30m×0.25mm i.d., 0.1um, J&W SCIENTIFIC) for the mass spectrometric detector was used. An analytical blank was performed for 3 sediment samples from the Soxhlet extraction. PBDE and PBDD/F congeners were identified with ion ratios within the correct tolerance range (±20%) and by comparing retention times of standards (±0.125%). Ranges of detection limits (DLs) for sediments for PBDEs were from 0.8 pg/g for tri-BDEs to 10.3 pg/g for hexa-BDEs. DLs for PBDD/F congeners were 0.9 pg/g for TeBDDs to 2.6 pg/g for PeBDDs. After data acquisition, the selected ion chromatograms were integrated and calculated using a DioK data system (JEOL, Japan).

RESULTS AND DISCUSSION

Multi-layer Silica Gel Column In the preliminary test, a significant loss of selective PBDD/F congeners was observed for the use of 5g of 10% silver nitrate-impregnated silica gel in the multi-layer silica gel column. Therefore, this procedure for sulfur removal was replaced with a copper granule column after the multi-layer silica gel clean up. No separation of PBDD/F from PBDE was observed in 100mL hexane elution. The recoveries of PBDD/F and PBDE were >90%. PBDE and PBDD/F were not found in the further elution with 100mL 10% CH₂CL₂/ hexane (v/v).

BROMINATED FLAME RETARDANTS-POSTER

Florisil Column The separation and clean up method using a florisil column is based on Ebert et al. (1999). Using reference standards, PBDE was separated completely from PBDD/F on a florisil column containing 1% water by elution with 100mL hexane for PBDE and 100mL 60% CH₂Cl₂/hexane (v/v) for PBDD/F. The recovery rates were 60-80% for PBDD/F 80-95% for PBDE. However, small amounts of selective PBDE congeners were found in the PBDD/F fraction of the sediment sample treatment. Ebert et al. (1999) reported that fragment ions of PBDF cannot be distinguished from those of PBDE during GC/MS-determination. Though retentions time of the PBDE congeners were different to PBDF congeners when using the DB5-HT capillary column in the present study, a further separation procedure was needed.

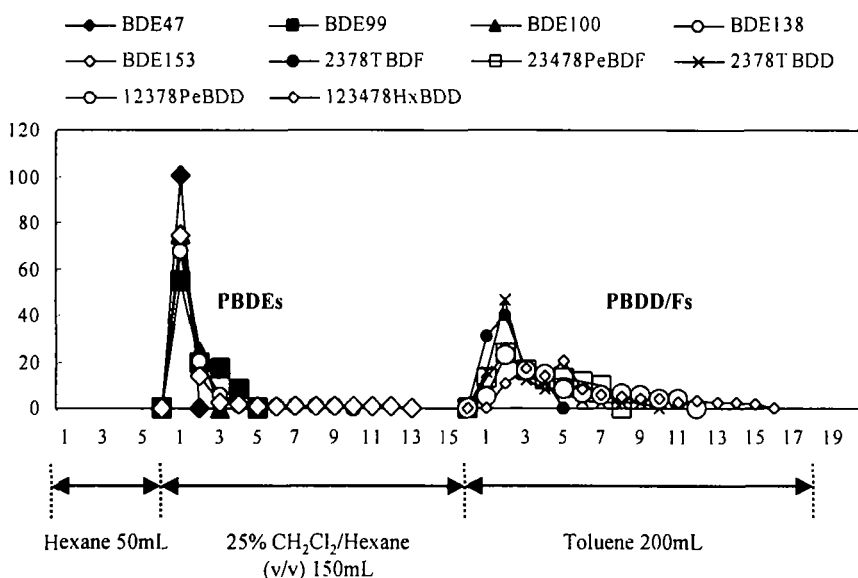


Fig. 1 Elution of PBDD/F and PBDE on active-carbon column

Active Carbon Column No PBDE or PBDD/F were detected from the pre-elution of 50mL hexane of the loaded sample to remove matrices. Above 90% of the total PBDEs were eluted within 20mL of 25% CH₂Cl₂/hexane (v/v) (Fig. 1). Remaining PBDE congeners were terminated at 150mL elution, and no PBDD/F congeners were found in the PBDE fraction. In the second elution by toluene, low brominated dibenzo-*p*-dioxins and dibenzofurans such as 2378-TeBDD and 2378-TeBDF eluted faster than highly brominated compounds from the active carbon column. No more PBDD/F was found in 170-200mL of toluene fractions. The recovery rates of PBDD/F and PBDE were 60-80%.

Concentrations in Sediments Dried sediments from three locations were Soxhlet-extracted and cleaned-up by the above columns including the copper granule column. Sediment A was quantifiable for PBDE and PBDD/F after florisil clean up, however, sediments B and C were significantly interfered with by unidentified matrices after the florisil column. To obtain improved

BROMINATED FLAME RETARDANTS-POSTER

chromatogram, sediments B and C were added to the active carbon column. Various PBDE congeners were found, for example BDE 47, dominant in the tetra-BDE, ranged from 10 – 312 pg/g dry wt in the sediments, and contributed 11.5-24 % to the total PBDEs. No PBDD/F congener was found in the PBDE fractions. A representative chromatogram of TeBDF is presented in Fig. 2. 2378-TeBDF was detected in three sediments and the concentration range was from 1.2 pg/g dry wt to 2.9 pg/g dry wt. However, a very small amount of BDE 47, which has a different retention time to 2378-TeBDF also remained in PBDD/F fractions. Though complete separation of PBDE from PBDD/F was performed on the florisil and carbon columns using reference standards, high concentrations of selective PBDE congeners remained on the florisil and active carbon columns and eluted with the PBDD/F congeners. Therefore, further separation and identification of these congeners is needed in HRGC/HRMS measurement using different retention times and a combination of m/z ion channels. In this study, we combined the ion setting of PBDD/F and PBDE according to Onodera et al. (5). For example, simultaneous measurement of PBDF and PBDE to identify the presence of TeBDE and PeBDE congeners in TeBDF and PeBDF mass channel was performed. In particular, TeBDF and PeBDF congeners were distinguished from PBDE congeners by measuring the [M⁺] ions including the [M+2] and [M+4] ions.

For further identification of each PBDD/F congeners in environmental samples, more verified reference standards are needed especially for non-2378 substituted congeners.

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BROMINATED FLAME RETARDANTS-POSTER

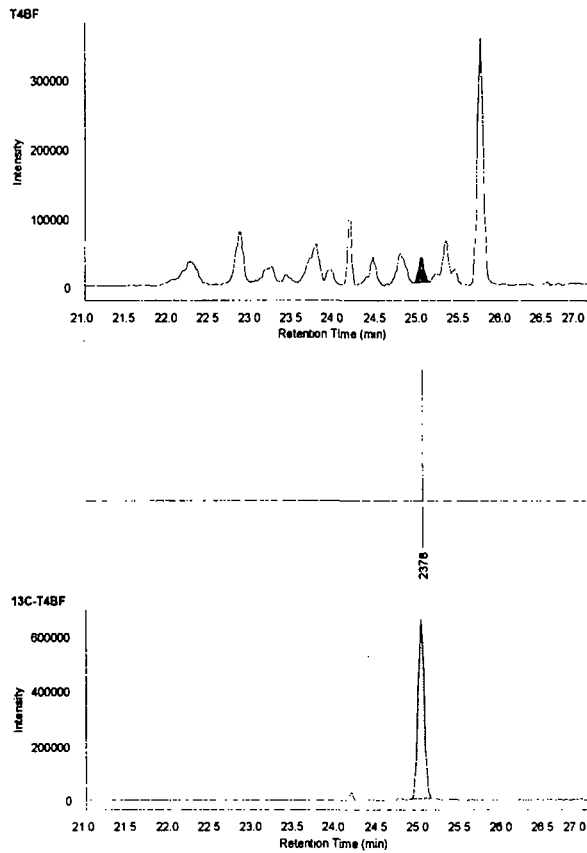


Figure 2. Chromatograms of TeBDF in sediments