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DETERMINATION OF POLYBROMINATED DIPHENYL ETHERS AND POLYBROMINATED DIBENZO-*P*-DIOXINS/DIBENZOFURANS IN FLUE GAS ANALYSIS

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Introduction

Flame-retardants are used to reduce the likelihood of fire in many commercial materials. Polybrominated diphenyl ethers (PBDEs) are a class of additive, halogenated flame-retardants that are used in a wide range of products including paints, plastics, textiles, and electrical components such as computers, televisions, electrical appliances, furniture, building materials, carpets, and automobiles [1,2]. They are both persistent and lipophilic. Environmental pollutant caused by organic brominated compounds have been reported and their effect on the environment and human health have been a cause of concern. This increasing trend is alarming and has resulted in a voluntary ban on their use and production in the European Union, with government restrictions expected in the near furture. In addition, there is the problem of Polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs) formation as by-products in the process of manufacturing brominated flame retardants and during the combustion of products containing brominated flame retardants [3,4] Because of similarities in chemical structure and in the pattern of responses, PBDD/Fs are believed to share a common mechanism of action with PCDDs/PCDFs and other related halogenated aromatic hydrocarbons. It is important to initiate investigations on environmental concentrations or the exposure to humans through environmental contamination by PBDEs and related contaminants such as PBDD/Fs. Owing to lack of reference standards, it is difficult to identify each PBDD/Fs. Furthermore, the presence of PBDEs may interfere quantitative analysis of PBDFs . A few studies [5,6] reported that PBDEs can be separated from PBDD/Fs using florisil column and active carbon column. The primary objectives of this study were to completely separately PBDD/Fs from PBDEs, and to identify and quantify PBDEs and PBDD/Fs congeners in flue gas analysis using HRGC/ HRMS.

Methods and Materials

Target Compounds and Column Clean-up

Reference Standards Native and Mass-Labelled PBDE congeners including BDE-MXA, BDE-MXB, BDE-100, MBDE-MXA, MBDE-MXB and MBDE-139 were obtained from WELLINGTON LABORTTORIES INC. (Ontario, Canada). Native and Mass-Labelled PBDD/Fs congeners including EDF-2046, EDF-2530 and EF-1452 were obtained from CAMBRIDGE ISOTOPE LABORTTORIES, INC.

(USA). The PBDD/Fs and PBDEs calibration standards were prepared within our laboratory using congeners mentioned above.

Acid Silica Column Forty percent H_2SO_4 on silica was prepared by adding 80g of concentrated H_2SO_4 in small portions of 120g of freshly prepared silica in a 500 mL Erlenmeyer flask. An acid-silica column was prepared by adding 8g of 40% H_2SO_4 on silica to the column. Prewash column with 20 mL hexane .

Silver nitrate-on-silica column A total of 10g silica gel were combined and used. Silver nitrate-on-silica column was prepared by adding 1g of silica, 2g of 10% $AgNO_3$ on silica, 1g of silica, 6g of 40% H_2SO_4 acid silica and 2g of Na_2SO_4 to top off the column. Prewash column with 20mL hexane. After conditioning acid silica column and silver nitrate-on-silica column, reference standards were loaded on top of the column. These compounds were eluted with 100mL hexane and collect each 10mL hexane separately.

Active Carbon column Active carbon column was prepared by adding 1g silica, 0.6g 8% AX-21 carbon in celite and 1g silica, glass wool plugs were inserted on both ends of column. Prewash column with methanol, toluene, dichloromethane/benzene(1/1,v/v) and hexane. Reference standards were loaded on top of the column. These compounds were eluted with 100mL hexane, 50mL dichloromethane/benzene (1/1,v/v) and then reversed carbon column and eluted with 50mL toluene. Collect eluate by volume of 10 mL of each.

Analysis of PBDEs and PBDD/Fs Analysis of PBDEs and PBDD/Fs were performed on a JMS-700 HRGC/HRMS, equipped with an HP 6890 gas chromatograph and HP 7683 autosampler. The GC injection port was configured for 1ì L splitless injection, held at a temperature of 320℃, and operated in constant flow (1.0 mL/min) mode. GC chromatograph separation prior to MS was achieved using DB-5MS (30m×0.25mm×0.25 m) capillary column. For PBDEs analysis, the initial oven temperature was 120℃, held 2 min, raised to 320℃ at 10℃/min and held 5 min. For PBDD/Fs analysis, the initial oven temperature was 150℃, held 2 min, raised to 320℃ at 10℃/min and held 13 min. Ionization was performed by electron ionization (EI) at an electron voltage of 38eV. Source temperature was 250℃ and the resolving power of the analyzer was 10,000(10% valley). The instrument operated under selected ion recording (SIR) conditions. PBDEs and PBDD/Fs congeners were identified with ion ratios with correct tolerance range (±20%) and by comparing retention times of calibration standards (±5 secs) or 13C-labelled standards(±3secs).

Results and Discussion

Optimization GC injection port temperature Hot or vaporizing inlet temperature required 50 or more degrees above the boiling point of the solvent and major components during injection so that solvent and sample components evaporate quickly as they migrate through inlet to column entrance. PBDEs and PBDD/Fs have higher molecular weights than PCDD/Fs, and their physical-chemical properties include high melting points, low vapor pressures, and low water solubility. Fig. 1 shows the relationship between response area of PBDEs , PBDD/Fs and five different GC injection port temperatures. We may find that the higher the inlet temperature setting, the more response areas of PBDEs and PBDD/Fs. For higher-bromine-substituted compounds, the sensitivities decreased rapidiy from inlet trmperature 320℃ to 240℃, especially for PBDD/Fs. Improper choice of inlet temperature will reduce system performance and quality of data.

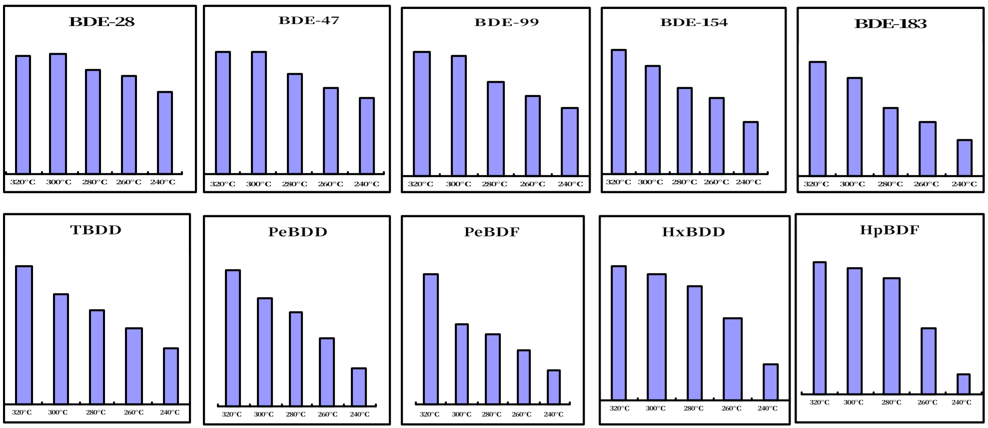

Fig. 1 Relation between response area (y axis) and inlet temperature setting (x axis)

Recoveries of PBDEs and PBDD/Fs from the acid silica column and silver nitrate-on-silica column For acid silica column, no separation of PBDEs and PBDD/Fs was observed in 100mL hexane elution. It took 30mL and 40mL of hexane to elute all PBDEs and PBDD/Fs, which recoveries ranged 100%~106% and 77%~114% respectively. A significant loss of selective PBDEs and PBDD/Fs congeners were observed for the use of 2g of 10% silver nitrate-impregnated silica gel column. It has been postulated that the aromatic ring donates electrons to the silver cation, Ag^+, in a solution and form a complex ($AgAr^+$, where Ar is an abbreviation of an aromatic ring). Due to weak electronegativity of bromine, the aromatic ring keeps electrons well. In the present work, the interaction between the π-electrons of aromatic ring and the Ag^+ site on the silica is probability responsible for the retention of PBDEs and PBDD/Fs. Therefore, this procedure for sulfur removal was replaced with a copper granule column after acid silica cleanup.

Recoveries of PBDEs and PBDD/Fs from the active carbon column Base on the column clean-up method for separation of PCBs and PCDD/Fs, we expected that PBDEs would separate well from PBDD/Fs on the active carbon column because of differences of planarity. Hexane was added to the column to remove the matrices that may interfere in the identification of PBDEs. Almost no PBDEs and PBDD/Fs were detected from 50mL hexane, except that only trace amount of BDE-100 (<6%) was found. 80%~97% of PBDEs were eluted within 30mL of dichloromethane/benzene (1/1,v/v). (Fig. 2) In the reverse elution by 30mL toluene, 70%~114% of PBDD/Fs were found. The surface area of AX-21 activated carbon is about $2800\,m^2/g$, which has strong affinity with plane structure of PBDD/Fs. Most of PBDD/Fs will be absorbed on top of AX-21 carbon column. It will take less amount of toluene elution only if we reverse AX-21 carbon column.

Concentrations in flue gas analysis One Municipal Solid Waste incinerator (five flue gas samples) and one electric arch furnace (three flue gas samples) were Soxhlet-extracted and cleaned-up by acid silica column and AX-21 active carbon column. Seven congeners of PBDEs can be detected for all the flue gas analysis. The mean concentration of total PBDEs (sum of BDE-28,-47,-100,-99,-154,-153 and–183) in MSW incinerator (99±31 ng/m^3, n=5) was higher in comparison to the electric arch furnace (68±25 ng/m^3 ,n=3). Analysis of the individual PBDEs congeners showed that

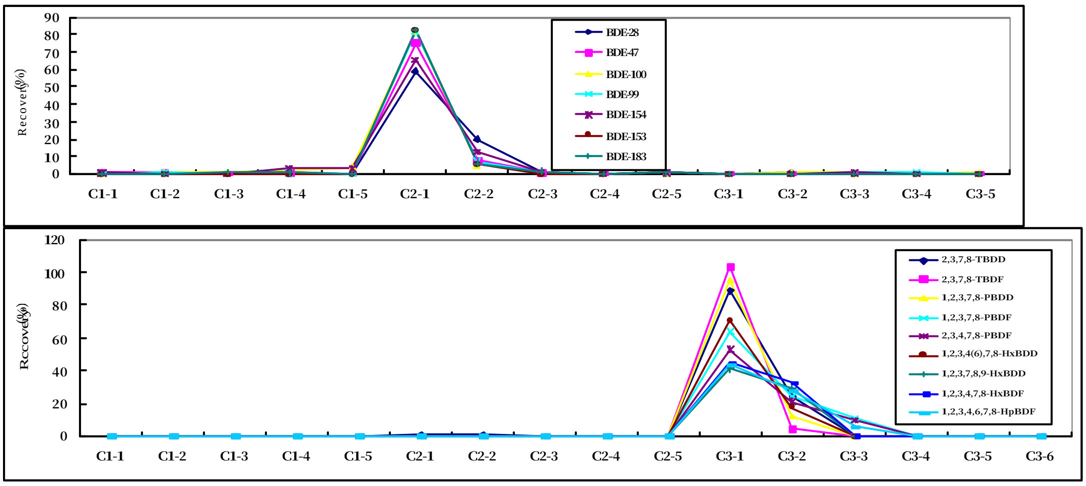

Fig. 2 Elution of PBDEs and PBDD/Fs on active-carbon column. C1-1~C1-5 (hexane fraction), C2-1~ C2-5(DCM/Benzene fraction,1/1), C3-1~C3-6(toluene fraction)

the three most predominant PBDEs congeners, BDE-47, BDE-99, and BDE-28. Both plants share the same distribution patterns. The concentration of PBDD/Fs in MSW incinerator ranges from 0.275 ng/m^3 to 4.01 ng/m^3, which were significantly higher in comparison to the electric arch furnace 0.079 ng/m^3 to 0.485 ng/m^3. Most of the congeners are below detection limits with the exception of 2,3,7,8-TBDD, 2,3,7,8-TBDF, and 1,2,3,4,7,8-HpBDF.

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