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Development and application of an efficient GC-HRMS method for the determination of PBDD/Fs in flue gas and fly ash samples

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ABSTRACT

Polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) are emerging trace persistent organic pollutants (POPs) whose toxicity is comparable to or even greater than that of their chlorinated analogs, polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs). However, the analysis of PBDD/Fs is particularly challenging due to the potential interference of polybrominated diphenyl ethers (PBDEs) and their pyrolytic property. In order to enhance the analysis efficiency, a time and solvent saving purification method, which was capable of effectively eliminating the interference from PBDEs, was developed for the analysis of PBDD/Fs. To improve the sensitivity of the analytical method, instrumental conditions such as inlet temperature, initial carrier gas flow rate, ion source temperature, and electron impact energy were optimized. Under the optimal conditions, the instrumental detection limit of PBDD/Fs ranged from 0.02 to 0.4 pg/μL. The recoveries of PBDD/Fs in spiked samples ranged from 79.7 % to 118 % (mean: 101 %), with an RSD value range of 2.6 %–10 % (mean: 6.0 %). The developed method was successfully applied for analyzing PBDD/Fs in four flue gas samples and two fly ash samples. The concentrations of $\sum_{14}$PBDD/Fs were 2.92–7.57 ng/Nm^3 and 0.042–8.78 ng/kg, respectively, in the flue gas and fly ash samples. Overall, this method greatly improved the efficiency and sensitivity for the analysis of PBDD/Fs, and it is expected to become an effective tool for the precise monitoring of PBDD/Fs.

1. Introduction

Polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) are a group of compounds that share similar chemical structure and toxicity to polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), and have recently gained significant attention. They have been found in plastic consumer products [1], chicken eggs [2–4], etc., and are suggested to be listed under the Stockholm Convention recently [5]. It has been reported that 2,3,7,8-PBDD/Fs are more toxic than 2,3,7,8-PCDD/Fs, and have longer half-life in the human body [6–8]. PBDD/Fs are unintentionally produced during the production and thermal processing of brominated flame retardants (BFRs) [9–14]. In certain cases, such as the thermal treatment of discarded printed circuit boards (PCBs), extremely high concentrations of PBDD/Fs could be detected [15]. These compounds are pervasive in environmental matrices, and have been detected in soil [16,17], sediment [18], atmosphere [19,20], dust and organisms [21,22]. Moreover, their presence has been established in foodstuffs [23,24] and human tissues [25–28]. They also occurred as contaminants in consumer products made of plastics from electronic waste [1,29,30].

As emerging persistent organic pollutants (POPs) [31], no standard method is available for the determination of PBDD/Fs. A two- or three-step chromatography column strategy is commonly used, with extracts typically first added onto a silica column (such as an acid silica or multilayer silica column), followed by one or two additional columns selected between an alumina column, Florisil column, or activated carbon column [14,21]. Wang et al. [32] used a sulfuric acid cleaning process followed by an acid silica gel column, an alumina column, and finally an activated carbon column. The above multi-step purification methods are time consuming with high consumption of solvent. Therefore, a simple and effective cleanup method is urgently desired for the analysis of PBDD/Fs.

Due to the similarity in mass numbers between $[PB_{n+2}DE\text{-}Br_2]^+$ and $[PBnDF]^+$, PBDEs can interfere the accurate qualitative and quantitative analysis of PBDD/Fs, even using high-resolution mass spectrometry

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[21,33]. To address this issue, the activated carbon [34] or Florisil column [35,36] is deployed for separating PBDEs from PBDD/Fs. Wyrzykowska et al. [33] also developed methods for separating target PBDFs from PBDEs on a 60 m DB-5 capillary column. However, the number of PBDE congeners involved in the study might not be large enough to cover all the cases, and another 15 m capillary column was required to analyze the higher brominated PBDD/Fs [33]. Therefore, removing PBDEs from the samples during the purification process is important for the accurate analysis of PBDD/Fs. If the interferences of PBDEs could be completely removed by the purification process, there is no need to consider the separation of PBDEs during the instrumental analysis.

Moreover, the instrumental analysis of PBDD/Fs faces considerable challenges due to their low concentration levels and thermal instability. Gas chromatography combined with high resolution mass spectrometry (GC-HRMS) is the preferred technique for the analysis of PBDD/Fs due to its high selectivity and sensitivity [14,22,28,37]. In order to obtain better analysis results, some strategies have been developed, such as setting optimal injector temperature, using short capillary columns with thin liquid film, and applying PTV injection [21,37,38]. However, thermal degradation of PBDD/Fs remains a big problem during the instrumental analysis, resulting in weak signal response and high instrumental detection limit (IDL), especially for highly brominated congeners [21,39]. Consequently, more extensive and in-depth research is necessary to improve the instrumental conditions of GC-HRMS for the analysis of PBDD/Fs.

In this study, we aimed to develop a simple and efficient purification method which could completely separate PBDEs from PBDD/Fs. Furthermore, in order to enhance the sensitivity of analytical method, instrumental conditions of GC-HRMS such as inlet temperature, initial carrier gas flow rate, ion source temperature, and electron impact are optimized. Finally, flue gas and fly ash samples from solid waste incineration plants were used to verify the established method.

2. Experimental section

2.1. Chemicals and materials

HPLC grade dichloromethane (DCM), acetone, hexane and toluene were purchased from Honeywell B&J (Morristown, USA). Silica gel (100–200 mesh), basic alumina (100–200 mesh) and Florisil (60–100 mesh) were obtained from Merck (Darmstadt, Germany). Analytical grade anhydrous sodium sulfate, sulfuric acid and sodium hydroxide were obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). Prior to use, all fillers require pretreatment. Anhydrous sodium sulfate was baked at 550 ℃ for 6 h and stored in a desiccator. Meanwhile, silica gel, alkaline alumina, and Florisil were activated by baking at 550 ℃ for 12 h and then stored in desiccators. To prepare 40 % acidic silica gel, 80 g of concentrated sulfuric acid was slowly added to 120 g of activated silica gel in a conical flask with a cover. The mixture was homogenized and then stored in desiccators. For the 33 % basic silica gel, 67 g of activated silica gel was mixed with 33 g of 1 M NaOH solution using a similar process. After activation and preparation, all materials were cooled to room temperature and subsequently stored in desiccators.

PBDD/Fs standards were purchased from Cambridge Isotope Laboratories (Andover, USA), including EDF-5407 (Bromodioxin/Furan Calibration Standard Solutions (CS1-CS5)), EDF-5408 (Bromodioxin/Furan Cleanup Spike), EDF-5409-A (Bromodioxin/Furan Syringe Spike), EDF-5410 (Bromodioxin/Furan Sampling Spike), and EDF-5517 (Bromodioxin/Furan Native PAR Solution). PBDE cleanup standards (including $^{13}C_{12}$-BDE 3, 15, 28, 47, 100, 99, 126, 154, 153, 169, 183, 197, 205, 207, 209) and injection standards (including $^{13}C_{12}$-BDE 79, 139, 180, 206) were purchased from Wellington Laboratories (Guelph, Canada).

2.2. Sample collection and extraction

The stack flue gases and fly ashes were sampled from a municipal solid waste incinerators (MSWIs). The stack flue gases collected isokinetically according to U.S. EPA Modified Method 23. Sorbent (XAD-2) cartridges were spiked with 10 ml 80 pg/mL sampling standard (EDF-5410) before sampling. The volumes of flue gas samples were normalized to the dry condition of 760 mmHg and 273 K, and denoted as Nm^3. For ash samples, 2 g was used for the analyses.

Before extraction, all samples were spiked with 10 ml 40 pg/ml $^{13}C_{12}$-labeled PBDD/Fs cleanup standards (EDF-5408) and extracted for 16 h with 250 ml toluene. The extractions were then concentrated using rotary evaporation to 1 mL for the next step.

2.3. Sample clean-up

To purify the samples, a composite multi-layer column was utilized. The column (300 mm × 25 mm i.d.) was packed in the following order: glass wool (0.5 cm), anhydrous sodium sulfate (1 cm), Florisil (1 g), alkaline alumina (3 g), 33 % basic silica gel (4 g), neutral silica gel (3 g), 40 % sulfuric acid silica (40 g), and anhydrous sodium sulfate (1 cm). Prior to use, the column was conditioned with 100 mL of hexane.

To establish an effective elution method that could complete separate PBDEs from PBDD/Fs, an elution scheme is designed as follows. First, the standard samples of $^{13}C_{12}$-labeled PBDEs and PBDD/Fs were prepared. The amounts of these standards are list in Table S1. Second, these samples were subsequently eluted using the method described below. After loading the standard samples, it was eluted sequentially with 120 mL of hexane (fraction 1), 20 mL of DCM: hexane (95:5, v/v) (fraction 2), 5 mL of DCM: hexane (95:5, v/v) (fraction 3), 80 mL of DCM (fraction 4), and 20 mL of DCM (fraction 5). Each fraction was then concentrated to approximately 20 μL under a gentle stream of nitrogen before changing the solvent to nonane in a mini-vial. Finally, injection standards were spiked before instrumental analysis.

2.4. Instrumental analysis

Instrumental analyses were performed using an GC (Agilent 7890A, USA) coupled with an HRMS (Waters Autospec Premier, USA), controlled by the MassLynx data system. The instrumental analysis methods of PBDD/Fs and PBDEs are as follows.

PBDD/Fs. Injections of 2 μL were made in splitless mode, using a DB-5MS capillary column (20 m × 0.25 mm i.d., 0.1 mm film thickness). The initial oven temperature was set at 130 ℃ (held for 2 min) and then increased to 230 ℃ at a rate of 30 ℃/min, followed by a gradual increase to 320 ℃ (held for 2 min) at a rate of 10 ℃/min. Helium was used as the carrier gas. The trap current and acceleration voltage were set at 650 mA and 7900 V, respectively, while the transfer line temperature was maintained at 280 ℃. A selected ion monitoring (SIM) mode with a resolving power of 10,000 (5 % valley definition) was employed, with monitoring ions shown in Table S2. Since neither nor isotope-labelled standards of 1,2,3,7,8,9-HxBDF, 1,2,3,6,7,8-HxBDF, 2,3,4,6,7,8-HxBDF and 1,2,3,4,7,8,9-HpBDF were commercially available, 13 kinds of 2,3,7,8-PBDD/Fs and 2,4,6,8-TBDF were analyzed in this study.

To determine the influence of instrument conditions on PBDD/Fs analysis results, a series of parameters were tested under different conditions including: (1) inlet temperature at 270 ℃, 280 ℃, 290 ℃, 300 ℃, 310 ℃, and 320 ℃; (2) initial flow rates at 1.0 mL/min, 2.0 mL/min, 4.0 mL/min, and 6.0 mL/min for 1 min, and then reduced to 1.0 mL/min at a rate of 15 mL/min; (3) electron impact energy levels of 34 eV, 36 eV, and 38 eV using EI mode; (4) ion source temperature at 260 ℃, 270 ℃, 280 ℃, 290 ℃, 300 ℃, 310 ℃, and 320 ℃.

PBDEs. Injections of 1 μL were made in splitless mode using a DB-5MS capillary column (20 m × 0.25 mm i.d., 0.1 mm film thickness). The injector temperature was set at 270 ℃, and the initial oven temperature was 90 ℃ (held for 2 min), which increased to 180 ℃ at a rate

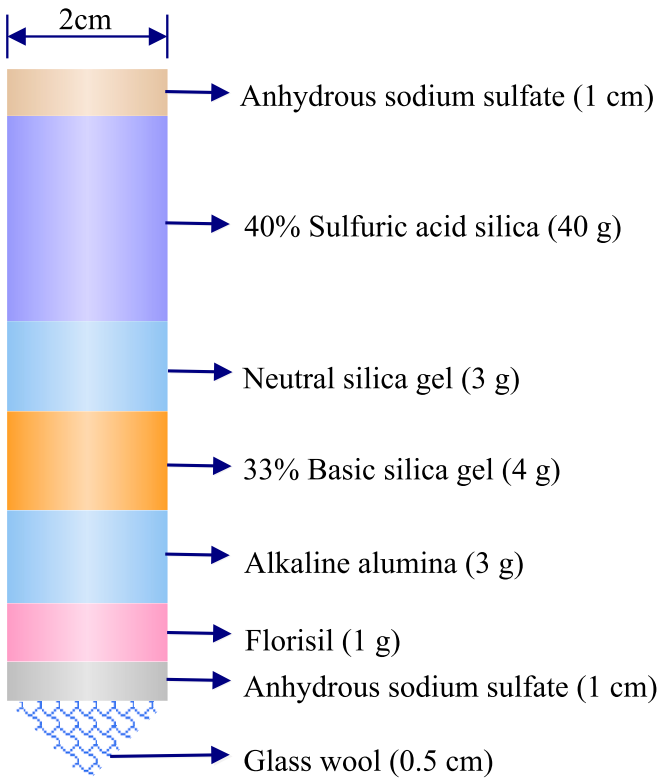

Fig. 1. Packing materials of the composite column.

of 15 ℃/min before increasing again to 240 ℃ at a rate of 5 ℃/min. The temperature was held for 2 min, after which it was raised to 310 ℃ (held for 1.7 min) at a rate of 3 ℃/min. Helium was used as the carrier gas with a flow rate of 1.0 mL/min. EI mode was employed with an electron impact energy level of 35 eV, while the trap current and acceleration voltage were set at 650 mA and 7900 V, respectively. The transfer line was maintained at a temperature of 280 ℃ and the MS ion source temperature was set at 290 ℃. The analysis was conducted using SIM mode with a resolving power of 8,000 (5 % valley definition), and monitoring ions of PBDEs are shown in Table S3.

2.5. Quality control/quality assurance

All samples, including blanks, were spiked with internal standards EDF-5408 before extraction and spiked with EDF-5409-A before analysis. One operational blank sample was included in each batch of ten samples. PBDD/Fs were not detected in the operational blanks, or detected in very low levels for some isomers, but were much lower than those of actual samples. Isotope ratio and retention time match was used to confirm the identity of the analytes. For two ions of a molecular ion cluster, the isotope ratio must be within ± 15 %. The retention time of the native compound had to be within ± 2 s compared with internal standard. Peak responses for each of the two selected molecular cluster ions were at least 3 times the noise level (S/N > 3). The medium concentration (CS3) standard was used for calibration verification, and the relative standard deviation for all native and labeled PBDD/Fs is within ± 20 %. To determine the instrument detection limit (IDL) of each PBDD/F congener, the CS1 solution was diluted to half of its original concentration (denoted as CS (1/2)) and analyzed seven times. The IDL value of PBDD/F congener was assigned to be 3.143 times of the standard deviation of CS (1/2).

3. Results and discussion

3.1. Establishment of the purification method

In this study, we developed a purification method for the analysis of PBDD/Fs. To remove potential interferences to PBDD/Fs, a composite column packed with acidic silica gel, alkaline silica gel, alumina and

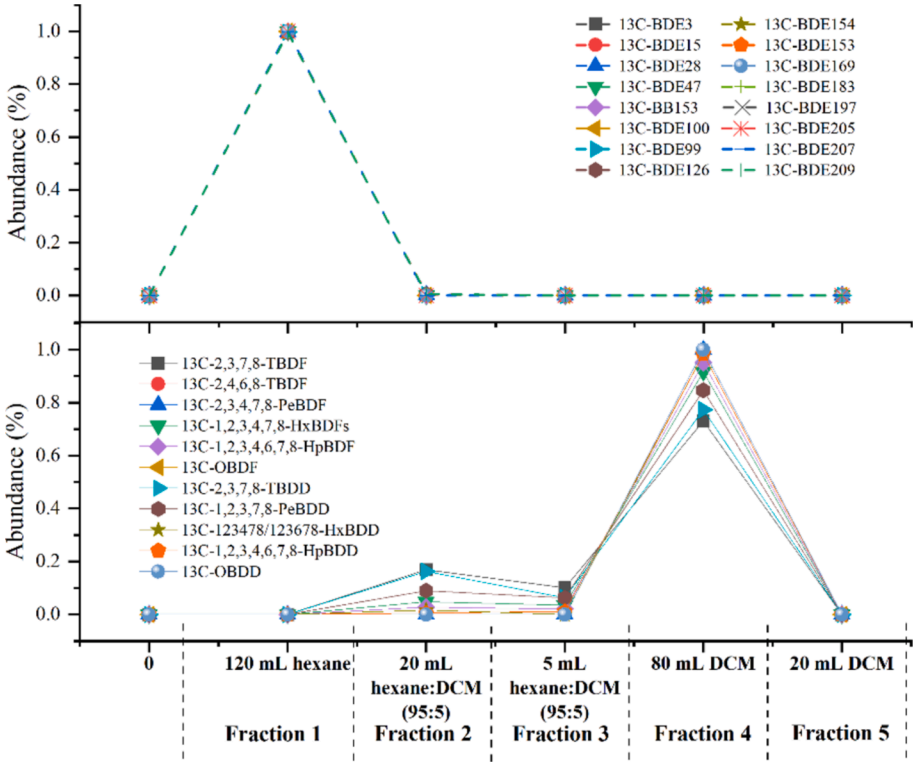

Fig. 2. The elution profiles of PBDEs and PBDD/Fs through the composite column.

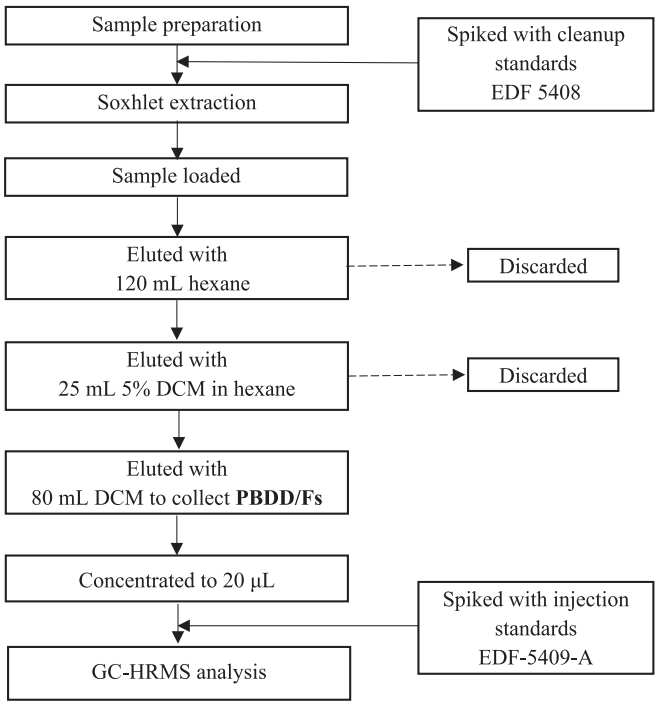

Fig. 3. Purification process of PBDD/Fs (DCM = dichloromethane).

Florisil was designed to purify the environmental samples according to our group's previous research on the analysis of PCDD/Fs (Fig. 1) [40]. Acidic silica gel and alkaline silica gel can remove most organic matter, phenols, alkaline substances, colorants, polycyclic aromatic hydrocarbons, and strongly polar substances. Alumina can remove weakly polar substances and organic halides, while Florisil is responsible for separating PBDEs from PBDD/Fs [36]. PBDEs have similar ion fragment mass numbers to PBDD/Fs, therefore, it is of great importance to remove the interferences of PBDEs. As demonstrated in Fig. 2, PBDEs were completely eluted with 120 mL of hexane (fraction 1), whereas no PBDD/Fs was eluted. 0 %~10 % PBDD/Fs were detected in the subsequent elution using 20 mL of hexane: DCM (95:5, v/v) mixture (fraction 2). Similarly, a small amount of PBDD/Fs were also detected in fraction 3 (5 mL hexane: DCM mixture, 95:5, v/v). PBDD/Fs eluted in fractions 2 and 3 mainly consisted of low brominated dioxins and few highly brominated dioxins. The remaining PBDD/Fs, approximately 73 % to 100 %, were effectively eluted with 80 mL of DCM (fraction 4), and no PBDD/Fs were identified in the final 20 mL of DCM (fraction 5). To ensure complete separation of PBDEs from PBDD/Fs and remove other weak polarity interferences, fractions 2 and 3 were also discarded despite it would result in a slight reduction in recovery rates of PBDD/Fs. The final elution method was demonstrated in Fig. 3, i.e., the column was eluted with 120 mL of hexane (discarded), 25 mL of hexane: DCM (95:5, v/v) mixture (discarded) and 80 mL of DCM (containing PBDD/Fs) in sequence.

As shown in Table S4, purification methods for the analysis of PBDD/Fs have also been established in previous studies, with two or three columns been used. For example, Wang et al. [32] used a sulfuric acid cleaning process followed by an acid silica gel column, an alumina column, and finally separating PBDEs from PBDD/Fs using an activated carbon column. Similarly, Wang et al. [41] established an analysis method that purified extraction through an acid silica and neutral alumina column before separating PBDEs from PBDD/Fs using a Florisil column. Different from the previously reported purification methods, only one composite column was used in the method established in the present work. Therefore, this method not only cuts the purification process time to half or one-third of the previous methods, but also saved 100–300 mL solvent compared to most previous methods using three columns for purification (Table S4).

3.2. Optimization of GC-HRMS conditions

3.2.1. Inlet temperature

A suitable inlet temperature is essential for effective analysis of PBDD/Fs. PBDD/Fs are chemicals with high molecular weight, lower inlet temperatures are not conducive to their sufficient vaporization, while higher temperatures will lead to too much degradation. Various inlet temperatures ranging from 250 ℃ to 300 ℃ have been used for the analysis of PBDD/Fs in previous studies. In the present work, to find the optimal inlet temperature for the analysis of PBDD/Fs, the inlet temperature was set at 270 ℃, 280 ℃, 290 ℃, 300 ℃, 310 ℃, and 320 ℃, respectively. As shown in Fig. 4A, the peak area of tetra- to hepta-PBDD/Fs increased with the increase of inlet temperature, reached its maximum at the 290 ℃, and then decreased with the increase of inlet temperature. Nevertheless, different from the tetra- to hepta-PBDD/Fs, the optimal inlet temperature for OBDD and OBDF was 300 ℃. The peak area of each congener obtained at the optimal inlet temperature was 1.6 ~ 3.9 times of that at the most inappropriate temperature in this study. Since the peak area of OBDD/F at 300 ℃ is only slightly larger than that at 290 ℃ (Fig. 4), 290 ℃ is recommended as the optimal inlet temperature for PBDD/Fs analysis. Our findings differ from Wyrzykowska et al. [33], who reported an optimal inlet temperature of 300 ℃ for PBDD/Fs analysis.

3.2.2. Initial flow rate

In order to investigate the impact of the initial flow rate, the initial flow rate was set as 1.0 mL/min, 2.0 mL/min, 4.0 mL/min and 6.0 mL/min, respectively, kept for 1 min, and then reduced to 1 mL/min. As shown in Fig. 4B, the higher the initial flow rate, the larger the peak area of PBDD/F congeners. When the initial flow rate was set as 6.0 mL/min, the peak area of PBDD/F congeners was 2.0 to 2.4 times that of flow rate 1.0 mL/min. The results showed that increasing the initial flow rate is an effective method to increase the detection limit of PBDD/F congeners. This may be due to that the higher initial flow rate can lead to higher inlet pressure, therefore mitigating the degradation of PBDD/Fs. However, excessive flow rate can harm the column, and thus, an initial flow rate of 6 mL/min is recommended in this study. Carrier gas flow rate programming was also reported for PBDD/Fs analysis in Xu et al. [42], where the flow rate of carrier gas was initially set at 4.0 mL/min, kept for 1 min, and then reduced to 1.0 mL/min.

3.2.3. Ion source temperature

Optimization of ion source temperature is also of great importance for effective analysis of PBDD/Fs using HRMS. The optimization of ion source temperature for PBDD/Fs has not been reported yet. As shown in Fig. 4C, the peak area of each congener increased significantly when the ion source temperature increased from 260 ℃ to 270 ℃, and then increased slowly with the increase of ion temperature, reaching a maximum value at 300 ℃. After that, the peak area of each congener decreased to 88 %~99 % and 48 %~75 % of the maximum value when the temperature reached 310 ℃ and 320 ℃, respectively. The results indicated that temperatures that were too low (260 ℃) or too high (320 ℃) were not conducive to the analysis of PBDD/Fs. The reason may be that lower source temperatures are not beneficial for sufficient ionization of PBDD/Fs, while higher temperatures will lead to excessive degradation of the chemicals. Based on the results of this experiment, the optimal ion source temperature is considered to be 300 ℃, which is higher than the values reported in many previous studies [11,22,28,38,43].

3.2.4. Electron impact energy

Electron impact energy is a key parameter of mass spectra and affects the ionization effect of target compounds. A value that is too low would result in incomplete ionization, while one that is too high would break

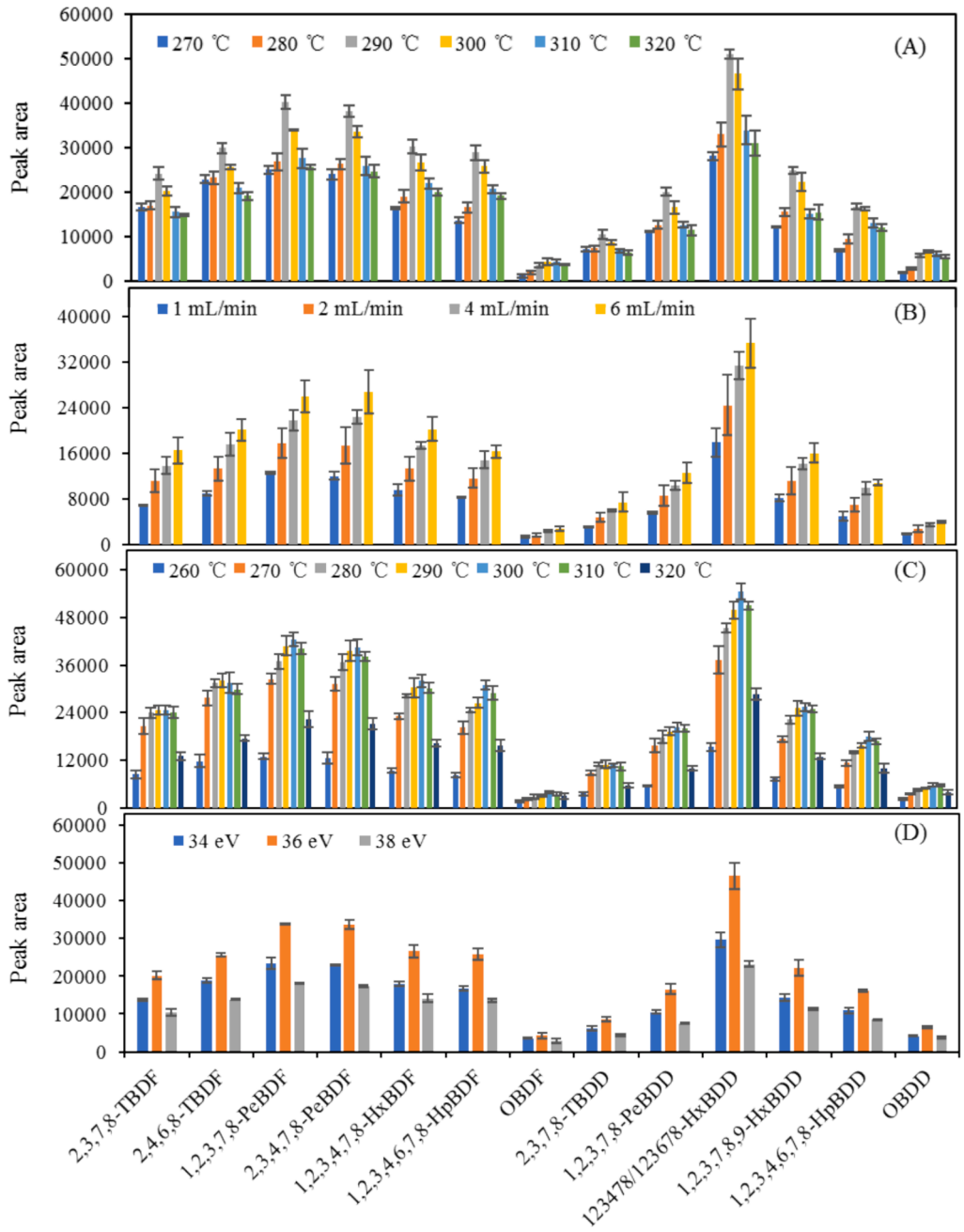

Fig. 4. Effects of inlet temperature (A), initial flow rate of carrier gas (B), source temperature (C), and electron impact energy (D) on the analysis of PBDD/Fs.

the target into smaller pieces resulting in lower monitored ion abundance. Therefore, optimizing the electron impact energy can obtain better monitoring ion abundance and enhance the response signal. As shown in Fig. 4D, the peak area of each PBDD/F congener increased when the electron impact energy increased from 34 eV to 36 eV, but decreased when the electron impact energy increased from 36 eV to 38 eV. Thus, an electron impact energy of 36 eV was recommended as the optimal ionization energy.

The above experiments showed that optimizing HRGC-HRMS conditions had a positive effect on improving the detection sensitivity of PBDD/Fs. In summary, the optimal values of the inlet temperature, initial flow rate, ion source temperature and electron impact energy were recommended to be 290 ℃, 6.0 mL/min, 300 ℃ and 36 eV, respectively. If these conditions are not chosen properly, the detected peak area may be more than ten times different from the optimal peak area.

3.3. *Validation of the instrumental analysis method*

The average RRF*i* (relative response factor of analyte *i*) of the calibration curve ranged from 0.09 to 1.95, with RSD (relative standard deviation) values ranging from 0.93 % to 18.7 %. Although there is no defined reference range for the RSD of PBDD/Fs, it is worth noting that the measured values of this method fall within the range of 20 % required by EPA 1613 for PCDD/Fs. Since PBDD/Fs and PCDD/Fs are similar compounds, the RSD values for PBDD/Fs are considered to be acceptable and satisfied. The IDL value of PBDD/F congener ranged from 0.02 to 0.4 pg/μL (Table S5). Additionally, the signal-to-noise ratio of PBDD/F congeners ranged from 3.2 to 62 (Figure S1). These results highlight that high sensitivity can be obtained using the optimized instrumental conditions, which is much better than those reported in previous studies (Table S4). For example, Wyrzykowska et al. [33] developed a method for the analysis of PBDD/Fs in flue gas samples with

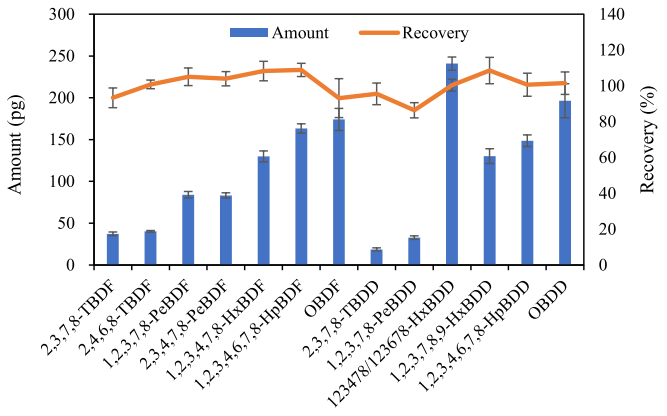

Fig. 5. Precision and accuracy of the established analytical method for PBDD/Fs.

detection limits of 0.12–1.2 pg/μL. Xu et al. [42] established a method for the determination of PBDD/Fs in soil samples with detection limits of 0.065–1.2 pg/μL.

The precision and accuracy of the established instrumental analysis method for PBDD/Fs were evaluated by analyzing six duplicate standard samples, each of which was spiked with a certain amount of native and labelled PBDD/Fs. As shown in Fig. 5, the recovery rates of native standards ranged from 79.7 % to 118 %, with an average of 101 %. The RSD was between 2.4 % to 10 %, with a mean value of 6.0 %. Additionally, the recovery rates of cleanup standards ranged from 60.7 % to 113 %, with an average of 90.1 %. These findings demonstrate that the established instrumental analysis method performs well in terms of precision and accuracy.

3.4. Analysis of environmental samples

3.4.1. Application of the method

The established analytical method was applied to analyze PBDD/Fs in four flue gas samples and two fly ash samples from a MSWI. The recoveries of the cleanup standards in these samples ranged from 34.9 % to 109 %. The results are well within the range of recoveries (25–200 %) suggested for $^{13}C_{12}$-labeled PCDD/Fs internal standards in the U.S. EPA Method 1613. The recoveries of the sampling standards in the flue gas samples ranged from 85.6 % to 99.5 %. Notably, some congeners in the flue gas and fly ash samples are at pg or fg levels, particularly in the samples with low concentrations of $\sum_{14}$PBDD/Fs (Fig. 6), demonstrating the importance of the high sensitivity obtained by the analytical method established in the present work. Fig. 7 shows the chromatograms of 2,3,7,8-TBDF (2.5 pg, S/N = 13), 2,4,6,8-TBDF (4.8 pg, S/N = 43), and their ^{13}C-labeled internal standards in a flue gas sample. The results suggest that the established analytical method is suitable for analyzing PBDD/Fs in flue gas and fly ash samples. Since flue gas and fly

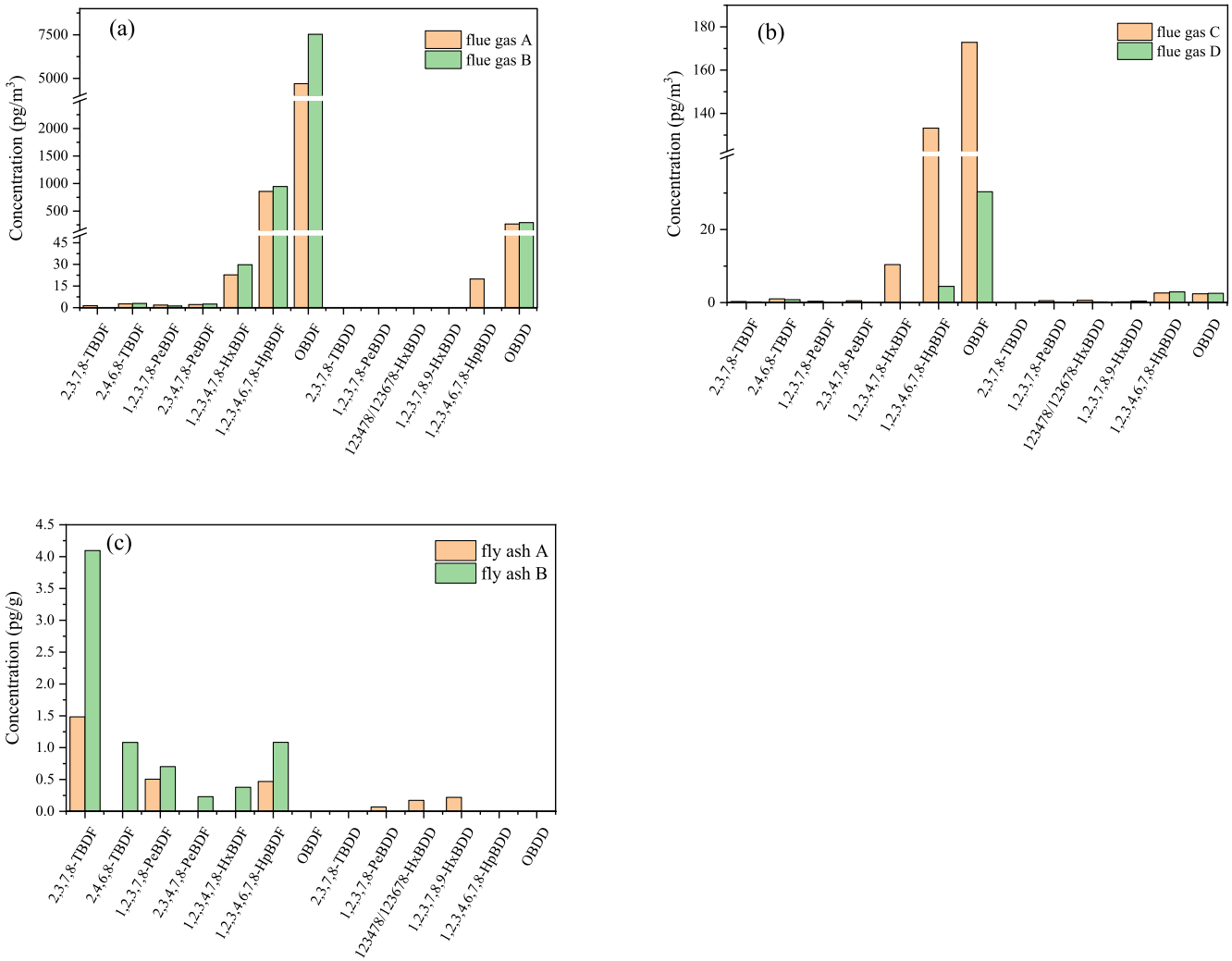

Fig. 6. Concentrations of PBDD/F congeners in the stack flue gas samples (a and b) and fly ash samples (c) from a MSWI.

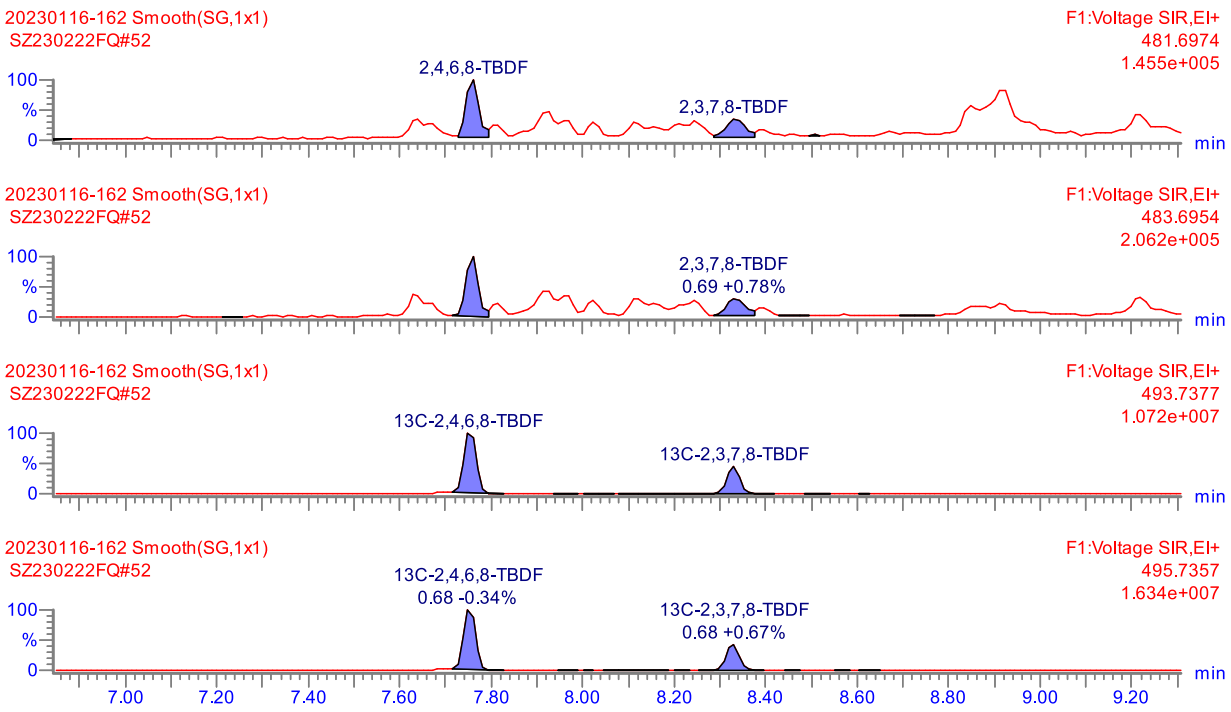

Fig. 7. Chromatograms of 2,3,7,8-TBDF, 2,4,6,8-TBDF and their ^{13}C-labelled internal standards in a flue gas sample from a MSWI.

ash samples are complex matrix, the method has the potential to analyze PBDD/Fs in other simpler environmental samples, such as ambient air and soil.

3.4.2. *Pollution characteristics of the PBDD/Fs in flue gas samples*

The international toxic equivalency factors (I-TEFs) (Table S6) of PCDD/Fs were used as tentative TEFs for PBDD/Fs to evaluate their toxicity [16,44]. It should be noted, since the concentrations of 1,2,3,7,8,9-HxBDF, 1,2,3,6,7,8-HxBDF, 2,3,4,6,7,8-HxBDF and 1,2,3,4,7,8,9-HpBDF were not analyzed in the present work, the I-TEQ value of PBDD/Fs in the flue gas and fly ash samples might be underestimated. The mass concentrations of $\sum_{14}$PBDD/Fs in the flue gas samples ranged from 0.042 to 8.78 ng/Nm^3, while the I-TEQ concentrations of $\sum_{14}$PBDD/Fs ranged from 0.0002 to 0.0216 ng /Nm^3 (Table S7). Among them, flue gas samples A and B were collected from the inlet of the air pollution control devices in the MSWI, while flue gas samples C and D were stack flue gas samples. The results in Table S7 suggested that the concentrations of PBDD/Fs in flue gas decreased significantly after purification. In detail, the average mass concentration and I-TEQ concentration of $\sum_{14}$PBDD/Fs decreased from 7.33 to 0.183 ng/Nm^3 and from 7.33 to 0.183 ng/Nm^3, respectively, with a removal rate of 97.5 % and 91.1 %, respectively. Specifically, as shown in Fig. 6, the concentrations of PBDD/F congeners range from 0 ng/Nm^3 to 7.53 ng/Nm^3. Among them, OBDF was identified as the most abundant congener, contributing 53 % to 86 % to $\sum_{14}$PBDD/Fs, followed by 1,2,3,4,6,7,8-HpBDF, with the abundance ranging from 11 % to 41 %. The congener profiles of PBDD/Fs in the flue gas samples of this study are similar to the results reported by Wang et al. [44] and Song et al. [43], where highly brominated PBDFs such as OBDF and 1,2,3,4,6,7,8-HpBDF were also the dominant congeners. Highly brominated PBDF/Fs were also the major congeners in the flue gas samples from industrial waste incineration, hazardous waste incineration and metallurgy [43,45–47].

The concentrations of PBDD/Fs in the stack gas samples from various sources are listed in Table S8. Compared with the results from other MSWIs, the concentration range of PBDD/Fs in stack gas in this study is similar to that reported by Song et al. [43], but higher than the values reported by other reports [34,44,45,48]. However, the TEQ values of $\sum_{14}$PBDD/Fs in the stack flue gas of this study are lower compared to the values reported for other MSWIs (Table S8), which may be due to that highly brominated PBDF congeners with lower TEFs are the dominant congeners in the present work. When compared to the stack flue gas samples from other sources, it was found that the mass concentrations of PBDD/Fs in the present work (a MSWI) were higher than those reported for industrial waste incinerators (0.0045–0.15 ng/Nm^3), crematory (0.04–0.075 ng/Nm^3), cement kiln (1.83–6.45 pg/Nm^3) and coal-fired power plant (21.3 ± 15.5 pg/Nm^3), but lower than those reported for metallurgical plants (0.470–7.53 ng/Nm^3) and hazardous waste incinerator (0.944–4.13 ng/Nm^3) (Table S8).

3.4.3. *Pollution characteristics of PBDD/Fs in fly ash samples*

The concentrations of $\sum_{14}$PBDD/Fs in the fly ash samples range from 2.92 ng/kg to 7.57 ng/kg, with the concentration of PBDD/F congener ranging from 0 ng/kg to 4.05 ng/kg. Unlike flue gas samples, lowly brominated 2,3,7,8-TBDF was the major congener detected in the fly ash samples (abundance: 51 % – 54 %), followed by 2,4,6,8-TBDF and 1,2,3,7,8-PeBDF, with the abundance ranging from 9 % to 14 %. The result differs from that reported by Wang et al. [44], where highly brominated PBDF congeners were the most abundant congeners in the fly ash samples. Compared to other studies on MSWIs (Table S8), the average mass and I-TEQ concentrations of PBDD/Fs in fly ash samples of this study were much lower than the values reported for fly and bottom ash samples from Sweden (22–140 ng/kg and 0.3–6.0 ng TEQ/kg) [49] and Taiwan (6.59–39.1 ng/kg, 0.0932–2.02 ng TEQ/kg) [44]. The mass concentrations (26 to 370 ng/kg) and TEQ values (0.5 to 3.9 ng TEQ/kg) of PBDD/Fs in biofuel fly ash samples in Sweden were also higher than this study [49]. Furthermore, higher average mass and I-TEQ concentrations of PBDD/Fs were also found for the bottom ash samples from MSWIs in Sweden (69–30000 ng/kg, 1.1–140 ng TEQ/kg) [49] and Taiwan (430–2600 ng/kg, 8.1 to 52 ng TEQ/kg) [44], as well as for the TEQ values in mixed fly and bottom ash samples from Phuket (2.8–3.3 ng WHO-TEQ/kg) [50]. Notably, the concentration of fly ash samples in the smelting industry is extremely high, with concentrations ranging from 100 to 23,000 ng/kg in mainland China and Taiwan, with TEQ concentrations ranging from 2 to 290 ng TEQ/kg [51,52], which may be related to their raw materials and smelting conditions.

4. Conclusions

In the present work, we developed an efficient analytical method to analyze PBDD/Fs in flue gas and fly ash samples using GC-HRMS. The following achievements were made: (1) A novel purification method using only one composite column was successfully developed to remove potential interferences from PBDD/Fs in environmental samples. This purification method not only simplified the clean-up process, but also reduced reagent consumption, improving the analysis efficiency. (2) After optimization of the instrument al conditions of GC-HRMS, higher sensitivity compared to other studies was obtained, with IDL ranging from 0.02 pg/μL to 0.4 pg/μL. In addition, the instrumental condition optimization method in this study provided a valuable optimization idea for the analysis of PBDD/Fs and other compounds with similar physicochemical properties as well. (3) The method has been successfully applied to analyze PBDD/Fs flue gas and fly ash samples, and it may also be useful for the analysis of PBDD/Fs in other environmental samples. Overall, by improving the purification method and instrumental conditions, a sensitive and reliable method for the determination of PBDD/Fs has been developed to better understand the sources, distribution, and environmental risk of these trace emerging POPs.

CRediT authorship contribution statement

Xian Qing: Writing – review & editing, Writing – original draft, Project administration, Investigation. **Danping Xie:** Formal analysis, Conceptualization. **Jinqiong Huang:** Data curation. **Guixian Feng:** Validation. **Changfeng Zhou:** Validation. **Haiting Liao:** Validation. **Jianping Fu:** Validation. **Manwen Zhang:** Formal analysis. **Sukun Zhang:** Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2024.112050.

Data availability

Data will be made available on request.

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