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Determination of polybrominated diphenyl ethers and novel brominated flame retardants in human serum by gas chromatography-atmospheric pressure chemical ionization-tandem mass spectrometry

Yuwei Wang[a], Yanmin Sun[a], Tian Chen[a], Zhixiong Shi[a,*], Xianqing Zhou[a], Zhiwei Sun[a], Lei Zhang[b], Jingguang Li[b,*]

[a] School of Public Health and Beijing Key Laboratory of Environmental Toxicology, Capital Medical University, Beijing 100069, China
[b] The Key Laboratory of Food Safety Risk Assessment, Ministry of Health, and China National Center for Food Safety Risk Assessment, Beijing 100021, China

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ABSTRACT

The accurate detection of brominated flame retardants (BFRs) in humans is an area of high scientific interest and regulatory need due to their potential toxicity. The instrumental analysis of BFRs was commonly performed on gas chromatography-mass spectrometry (GC-MS) operating in electron ionization (EI) or negative chemical ionization (NCI) modes. However, soft ionization techniques, such as atmospheric pressure chemical ionization (APCI), may be more suitable for the analysis of BFRs because the BFRs show high fragmentation in EI and low selectivity in NCI. Additionally, accurate quantifications of BFRs in complex matrices is challenging due to their low concentrations and therefore, a highly sensitive technique is desperately needed. In this study, a new methodology based on gas chromatography-atmospheric pressure chemical ionization-tandem mass spectrometry (GC-APCI-MS/MS) analysis was developed for the determination of thirteen BFRs (eight usually monitored polybrominated diphenyl ethers (PBDEs) congeners and five additional novel BFRs) in human serum. The primary task was to evaluate the potential of the GC-APCI-MS/MS technique for the trace analysis of BFRs in human serum. The results of the spiked recovery test using fetal bovine serum showed that mean recoveries of the analytes ranged from 83.4% to 118% with reduced swing differential signaling (RSDs) of ≤21.1%. The methodological limits of detection (mLOD) of the analytes ranged from 0.04 to 30 pg/mL, and these values were at least one order of magnitude lower than those estimated by the authors in a previous study using GC-NCI-MS or GC-EI-MS/MS, indicating that GC-APCI-MS/MS is more sensitive. Specially, compared to GC-NCI-MS and GC-EI-MS/MS, when GC-APCI-MS/MS was used for the detection of highly brominated BFRs, such as BDE-209 and decabromodiphenyl ethane (DBDPE), a notable improvement in sensitivity and reliability was obtained using a deactivated capillary column connected to the analytical column as the transfer line and maintaining a high temperature to improve the chromatographic behaviors. The developed methodology was successfully used for the analysis of BFRs in human serum collected from residents living in a BFR production area and Beijing.

1. Introduction

Brominated flame retardants (BFRs) are widely used in a variety of products including electronic equipment, textiles, foams and building materials for fire prevention. Polybrominated diphenyl ethers (PBDEs) are a class of the most important BFRs that have been produced and used since 1970s. PBDEs are additive BFRs and can therefore leach or volatilize from products and enter the environment [1,2]. There are three types of commercial PBDE products: Penta-BDE (mainly composed of BDE-47 and BDE-99 and with some tri- to hepta-BDEs), Octa-BDE (mainly composed of hexa- to deca-BDEs), and Deca-BDEs (92–97% BDE-209, plus tiny amounts of nona- and octa-BDEs) [3]. Penta-BDE and Octa-BDE were added to the list of persistent organic pollutants (POPs) under the Stockholm Convention in 2009 and were therefore globally phased out [4]. Deca-BDE was also listed as a POP in 2017. However, the production and application of Deca-BDE continues in China to date. With the regulation of PBDEs, the production and application of a series of novel BFRs (NBFRs), including decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB) and pentabromotoluene (PBT), have risen sharply [5,6]. Decabromodiphenyl ethane (DBDPE) has been produced only since 2005 in

* Corresponding authors.
E-mail addresses: szx0127@ccmu.edu.cn (Z. Shi), lijg@cfsa.net.cn (J. Li).

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China and is regarded as a deca-BDE replacement. Its production increases 80% per year [5], and it has become the most popular NBFR in China [6]. BTBPE is an octa-BDE replacement, and the worldwide production/usage of BTBPE was estimated to be 16,710 tons in 2001 [7]. Pentabromotoluene (PBT), pentabromoethylbenzene (PBEB) and hexabromobenzene (HBB) belong to polybromobenzenes that have one phenyl ring with several bromine atom substituents. These three NBFRs are all used as additive FRs. PBT is normally added to unsaturated polyesters, and PBEB is mainly used in thermoset polyester resins. HBB is primarily added to paper and wood and is mainly used in Japan and China. Although PBT, PBEB and HBB are presently produced and used at lower volumes, they have higher vapor pressures than do PBDEs and DBDPE. Therefore, they are more likely to evaporate into the surrounding environment [5,8]. Since these several NBFRs are all currently used in China, they are included in the present study.

BFRs are ubiquitous in various matrices in China [2,6], which indicates that development of an accurate and sensitive analytical technique for BFR detection is not only of scientific interest but is also a regulatory need. Nevertheless, accurate quantification of BFRs in complex matrices (serum, breast milk, etc.) is quite difficult due to their low concentrations [5,9]. For sample treatment, interfering substances (lipids, proteins, etc.) present in complex matrices require extensive clean-up procedures. In some studies, multistage liquid-liquid extraction and subsequent sophisticated purification step were used [10,11]. In our previous studies, a QuEChERS (quick, easy, cheap, effective, rugged and safe) approach was introduced for BFRs analysis and proved to be a simple, fast and efficient sample treatment technique [12,13]. For instrumental analysis, the most frequently used detection techniques of NBFRs and PBDEs were developed on GC-NCI-MS or GC-EI-MS/MS [11,14]. However, EI-MS/MS has proven to be unsuitable for the analysis of highly brominated BFRs because of its low sensitivity [13]. NCI-MS is more sensitive for bromine than is EI. Nevertheless, tandem mass spectrometry shows much better selectivity, which is especially important when analyzing complex matrices. Atmospheric pressure chemical ionization (APCI) is an alternative soft ionization technique which was designed to compensate for the sensitivity limitation of the EI source. In APGC, minimal fragmentation of the molecular ion can be obtained and therefore results in higher signal intensity compared to EI ionization [15]. More importantly, a combination of APCI and tandem mass spectrometry shows higher selectivity than NCI-MS. Gas chromatography-atmospheric pressure chemical ionization-tandem mass spectrometry (GC-APCI-MS/MS, sometimes written as APGC-MS/MS) has been successfully used to detect POPs, such as dioxins, furans, pesticides and polyaromatic hydrocarbons, in various matrices [16–18]. In the present study, a QuEChERS approach coupled to GC-APCI-MS/MS was developed and optimized for the simultaneous pretreatment and detection of eight PBDE congeners and five currently used NBFRs in human serum. Additionally, this study is part of our research project entitled, “The association between BFR exposure and female cancer”, and the developed methodology was then applied to the analysis of two groups of female serum samples.

2. Materials and methods

2.1. Chemicals and reagents

HPLC-grade organic solvent (n-hexane, acetone, etc.) was purchased from Dikma (Lake Forest, CA, USA) or Merck (Darmstadt, Germany). Formic acid (96%) was purchased from Dikma. Anhydrous magnesium sulfate ($MgSO_4$) and sodium chloride (NaCl) were purchased from Beijing Chemical Factory (Beijing, China). Primary secondary amine (PSA) and octadecyl-modified silica (C18) were obtained from Agilent Technologies (Palo Alto, CA, USA). The individual PBDE standards, BDE 28, 47, 99, 100, 153, 154, 183, and 209, and the individual NBFRs standards, 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), PBT and DBDPE, were all provided by AccuStandard Inc. (New Haven, CT, USA). The ^{13}C-labeled internal standards, including $^{13}C_{12}$-BDE-28, 47, 99, 153, 154, 183, and 209, and $^{13}C_6$-BTBPE and $^{13}C_{14}$-DBDPE, were all provided by Wellington Laboratories (Guelph, Ontario, Canada).

The standard reference material (organic contaminants in fortified human serum) SRM 1958 was purchased from the National Institute of Standards and Technology (Gaithersburg, MD, USA). Fetal bovine serum was purchased from Tianhang Biotechnology (Hangzhou, China) for method development and validation. Two groups of human serum samples were collected. One group is from nonoccupational volunteers (30 female donors) who lived in Weifang City, Shandong Province of China. Weifang city is the largest BFR production base in China at present. For comparison, another 30 female donors were recruited from Beijing, the capital of China. Serum sample was collected when the donors participated in routine physical examinations at a local hospital. After fasting for at least 12 h, approximately 10 mL of blood was collected with a BD Vacutainer serum tube (Franklin Lakes, NJ, US) by medical professionals and then processed within 2 h to isolate serum by centrifugation at 3000 rpm for 15 min. The serum was then kept at −80 °C until analysis. This study was launched with the authorization of the Ethics Committee of Capital Medical University, and all participants were clearly informed of the objective and gave their informed consent before sample collection.

2.2. Sample treatment

Internal standards, including 5 ng each of $^{13}C_{12}$-BDE-209 and $^{13}C_{14}$-DBDPE, and 0.5 ng each of $^{13}C_{12}$-BDE-28, 47, 99, 154, 153, 183 and $^{13}C_6$-BTBPE, were introduced into a 5 mL polypropylene (PP) tube. For the matrix spiking test, fetal bovine serum was used as the matrix and was fortified with an appropriate volume of standard solution. Solvent of the standard solution (n-hexane) was completely dried under nitrogen. Subsequently, 0.5 mL each of serum and water were added and mixed by vortexing. After that, 2 mL of acetone/hexane (1:1, *v/v*), 400 mg of anhydrous $MgSO_4$ and 100 mg of NaCl were loaded, and the PP tube was shaken vigorously for 1 min, followed by centrifugation at 4000 rpm for 5 min. The upper layer was transferred into a new PP tube containing 50 mg of $MgSO_4$ and 100 mg of C18 and then immediately shaken vigorously for 1 min for the removal of lipid and other interfering substances. The tube was then centrifuged at 10,000 rpm (4 °C) for 5 min. The upper layer was then transferred, concentrated to dryness, and reconstituted in 100 μL of n-hexane for GC-APCI-MS/MS analysis.

2.3. GC-APCI-MS/MS analysis

Instrumental analysis was performed on a triple-quadrupole mass spectrometer equipped with an APCI source (Xevo TQ-S, Waters Corporation, Milford, MA, USA) and coupled to a gas chromatograph (7890B, Agilent Technologies, Santa Clara, CA, USA). A DB-5MS capillary column (15 m × 0.25 mm, 0.10 μm film thickness, J&W Scientific, Folsom, CA, USA) was used for the chromatographic separation with helium as a carrier gas (3 mL/min). An Agilent UM tubing methyl deactivated capillary column (approximately 0.4 m, 0.25 mm id, Agilent Technologies, Santa Clara, CA), which was installed in the transfer line between the GC and the ion source, was connected to the end of the DB-5MS column by a straight two-way valve, and the transfer line temperature was maintained at 390 °C. The oven temperature of the GC was set as: initial 100 °C hold for 1 min, 30 °C/min to 310 °C and held at 310 °C for 10 min. The GC injector was performed in pulsed spitless mode and the pulsed pressure was maintained at 50 psi for 1 min. The injection volume was 1 μL with the injector temperature was 280 °C.

On the Xevo TQS MS, the ion source was carried out in APCI + mode and run under dry conditions to promote charge transfer ionization. Nitrogen was used as an auxiliary gas and cone gas and maintained at

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