Analytica Chimica Acta 892 (2015) 140–147

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

“One-shot” analysis of polybrominated diphenyl ethers and their hydroxylated and methoxylated analogs in human breast milk and serum using gas chromatography-tandem mass spectrometry

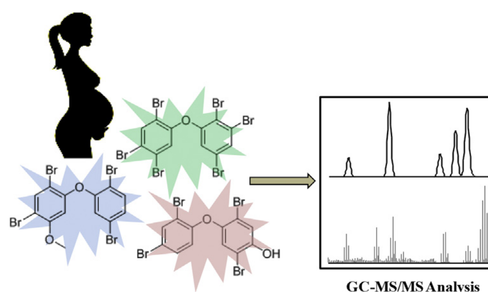
Deena M. Butryn [a], Michael S. Gross [a], Lai-Har Chi [b, c], Arnold Schecter [d], James R. Olson [b, c], Diana S. Aga [a, *]

[a] Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA
[b] Department of Pharmacology and Toxicology, University at Buffalo, The State University of New York, Buffalo, NY 14214, USA
[c] Department of Epidemiology and Environmental Health, University at Buffalo, The State University of New York, Buffalo, NY 14214, USA
[d] Department of Pharmacology and Toxicology, University of Louisville College of Medicine, Louisville, KY 40202, USA

HIGHLIGHTS

- A sample preparation method was developed for the “one-shot” simultaneous analysis of PBDEs, OH-BDEs, and MeO-BDEs.
- Method positively correlated with previously published literature on PBDE concentrations in the same paired samples.
- Findings provide insight on the different partitioning behavior of PBDEs, OH-BDEs, and MeO-BDEs in humans.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 June 2015
Received in revised form
21 July 2015
Accepted 8 August 2015
Available online 25 August 2015

Keywords:
Polybrominated diphenyl ethers
Hydroxylated polybrominated diphenyl ethers
Methoxylated polybrominated diphenyl ethers
Breast milk
Serum
Brominated flame retardants

ABSTRACT

The presence of polybrominated diphenyl ethers (PBDEs) and their hydroxylated (OH-BDE) and methoxylated (MeO-BDE) analogs in humans is an area of high interest to scientists and the public due to their neurotoxic and endocrine disrupting effects. Consequently, there is a rise in the investigation of the occurrence of these three classes of compounds together in environmental matrices and in humans in order to understand their bioaccumulation patterns. Analysis of PBDEs, OH-BDEs, and MeO-BDEs using liquid chromatography-mass spectrometry (LC-MS) can be accomplished simultaneously, but detection limits for PBDEs and MeO-BDEs in LC-MS is insufficient for trace level quantification. Therefore, fractionation steps of the phenolic (OH-BDEs) and neutral (PBDEs and MeO-BDEs) compounds during sample preparation are typically performed so that different analytical techniques can be used to achieve the needed sensitivities. However, this approach involves multiple injections, ultimately increasing analysis time. In this study, an analytical method was developed for a “one-shot” analysis of 12 PBDEs, 12 OH-BDEs, and 13 MeO-BDEs using gas chromatography with tandem mass spectrometry (GC-MS/MS). This overall method includes simultaneous extraction of all analytes via pressurized liquid extraction followed by lipid removal steps to reduce matrix interferences. The OH-BDEs were derivatized using N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide (TBDMS-MTFA), producing OH-TBDMS derivatives that can be analyzed together with PBDEs and MeO-BDEs by GC-MS/MS in “one shot” within a 25-min run time. The overall recoveries were generally higher than 65%, and the limits of detection ranged from 2 to 14 pg in both breast milk and serum matrices. The applicability of the method was successfully validated

* Corresponding author.
E-mail address: dianaaga@buffalo.edu (D.S. Aga).

http://dx.doi.org/10.1016/j.aca.2015.08.026
0003-2670/© 2015 Elsevier B.V. All rights reserved.

on four paired human breast milk and serum samples. The mean concentrations of total PBDEs, OH-BDEs, and MeO-BDEs in breast milk were 59, 2.2, and 0.57 ng g^{-1} lipid, respectively. In serum, the mean total concentrations were 79, 38, and 0.96 ng g^{-1} lipid, respectively, exhibiting different distribution profiles from the levels detected in breast milk. This "one-shot" GC-MS/MS method will prove useful and cost-effective in large-scale studies needed to further understand the partitioning behavior, and ultimately the adverse health effects, of these important classes of brominated flame retardants in humans.
© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are additive flame retardants that are mixed with, or coated onto consumer products to prolong flame dispersion. Because these compounds are not chemically bound to the polymer, they are leached into the surroundings more readily [1]. Consequently, PBDEs are ubiquitous in the environment and have been found to bioaccumulate in humans [2]. Furthermore, the hydroxylated (OH-BDE) and methoxylated (MeO-BDE) analogs of PBDEs have become a concern to environmental chemists and toxicologists because of their retention in higher trophic level organisms such as in fish, birds, seals, polar bears, sharks, and humans [3–8]. The OH-BDEs and MeO-BDEs are not commercially produced; they are biotransformation products of anthropogenic PBDEs and are also known to be naturally occurring in the environment [9]. These three classes of brominated diphenyl ethers (BDEs) have also been linked to the development of neurological disorders, and are considered endocrine disrupting chemicals with effects related to developmental delays, disruptions of neurotransmitter release, and cytotoxicity [10–12]. Due to their lipophilic nature, BDEs have been detected in human blood (maternal and fetal), breast milk, and umbilical cord tissue; their levels vary depending on age, diet, occupation, and geographical location [13–17]. Therefore, understanding BDE accumulation patterns can ultimately provide information on their sources and metabolism patterns in humans.

Established methods for analyzing PBDEs in human samples often include extraction with a non-polar solvent, sample clean-up, and separation by gas chromatography (GC) or liquid chromatography (LC) followed by mass spectrometric detection [1]. However, inclusion of OH-BDEs and MeO-BDEs necessitates that the sample treatment and instrumental analysis be modified in order to account for these classes of compounds. While simultaneous determination of PBDEs, OH-BDEs, and MeO-BDEs is theoretically possible using liquid chromatography-tandem mass spectrometry (LC-MS/MS), limits of detection (LOD) for PBDEs and MeO-BDEs are significantly higher than OH-BDEs due to their poor ionization efficiencies [8]. Therefore, to achieve the necessary detection limits, PBDEs, OH-BDEs, and MeO-BDEs have been analyzed separately through fractionation using an acidified silica column and then analyzing the OH-BDEs by LC-MS/MS, and the PBDEs and MeO-BDEs by GC-MS [18]. Another common technique used to separate the neutral (PBDEs and MeO-BDEs) and phenolic (OH-BDEs) analytes involves partitioning with potassium hydroxide [13,14,17,19–22]. However, an added concern of this method is that small amounts of PBDEs can be detected in the phenolic fractions resulting from incomplete separation, which may lead to erroneous results [22]. Gel-permeation chromatography can be used to isolate target analytes from interfering lipids as well as fractionate compounds based on polarity and size; however this approach is laborious and not environmentally friendly because of the high organic solvent requirement [6,23].

BDEs have been analyzed by GC with an electron capture detector (ECD) because of its inherently high sensitivity for halogenated compounds [24]. However, GC-ECD is less selective than GC-MS because the former relies solely on retention times, hence co-eluting compounds cannot be distinguished from each other in GC-ECD. Therefore, GC with electron capture negative ionization mass spectrometry (ECNI-MS), high resolution mass spectrometry (HRMS), and triple quadrupole mass spectrometry (QqQ-MS) have gained popularity because of their enhanced selectivity. While ECNI-MS is very sensitive, it generally monitors for the signal of the bromine isotopes m/z 79 and 81. Consequently, structural isomers of BDEs are difficult to differentiate, and isotopically-labeled standards (^{13}C-BDEs) are not as useful for quantification. On the other hand, the use of electron ionization (EI) coupled to HRMS or QqQ-MS can take advantage of isotopically-labeled compounds for accurate quantification based on isotope dilution. The latter technique also has the additional advantage of identifying co-eluting BDEs based on the characteristic mass spectral fragmentation obtained from the collision cell [25].

The objective of this study is to develop an efficient extraction, clean-up, and detection method for the simultaneous analysis of 12 PBDEs, 12 OH-BDEs, and 13 MeO-BDEs using gas chromatography with tandem mass spectrometry (GC-MS/MS). Derivatization via silylation with N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide (TBDMS-MTFA) was chosen based on the high analytical responses and distinct fragmentation patterns observed in the derivatized OH-BDEs (OH-TBDMS-BDEs) [26]. A programmable temperature vaporizer (PTV) injector was optimized to avoid thermal degradation and analyte discrimination of BDEs due to their range of vapor pressures, molecular weights, and degree of bromination [27]. The GC-MS/MS was operated under selected reaction monitoring (SRM) mode to achieve high selectivity and signal-to-noise ratios. Four paired breast milk and serum samples were used for method validation to demonstrate the applicability of the method in analyzing human samples for trace levels of PBDEs, OH-BDEs, and MeO-BDEs. The novelty of this "one-shot" GC-MS/MS method lies in its ability to simultaneously quantify the three classes of BDEs, with high specificity and sensitivity, without the need for tedious fractionation steps. The method can prove useful in epidemiological studies requiring large number of samples for analysis, such as in determining the partitioning behavior of the three classes of BDEs in complex biological samples.

2. Materials and methods

2.1. Chemicals and reagents

Chromatographic silica gel (60 Å, 40–63 um) was purchased from Sorbent Technologies (Norcross, GA). The derivatization agent, MTBSTFA, was obtained from Sigma Aldrich (St. Louis, MO) and analytical standards including all individual PBDEs, OH-BDEs, and MeO-BDEs were purchased from Accustandard (New Haven, CT). A surrogate mix containing nine stable isotope-labeled ^{13}C-PBDEs (^{13}C- PBDE-3, -7, -15, -28, -47, -99, -153, -154, -183) and the internal standard solution of ^{13}C-PBDE-77 were obtained from

Download English Version:

https://daneshyari.com/en/article/1163431

Download Persian Version:

https://daneshyari.com/article/1163431

Daneshyari.com