Development and comparison of gas chromatography–mass spectrometry techniques for analysis of flame retardants

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A B S T R A C T

The restrictions on the use of legacy flame retardants (FRs) have increased the need of alternative FRs to comply with fire safety legislations. In this study, the feasibility of three different gas chromatography–mass spectrometry (GC–MS) techniques were investigated for the analysis of 102 legacy and alternative FRs including polybrominated diphenyl ethers (PBDEs, $n = 27$), halogenated FRs (HFRs, containing bromine and/or chlorine, $n = 46$), and organophosphorous FRs (OPFRs, $n = 29$). The tested techniques included GC-single MS with (i) electon impact (EI) ionization and (ii) negative chemical ionization (NCI), and (iii) GC-tandem MS (MS/MS) with EI ionization. Out of the tested FRs, 90 could be detected under the used conditions on at least one of the three instrument setups. Later experiments included a selection of these FRs. For the majority of tested PBDEs (5 out of 6) and HFRs (24 out of 26), EI-MS/MS provided the highest detectability (i.e. the lowest detection limits), while for most tested OPFRs (8 out of 13), EI-MS performed better. The influence of matrix components on the analysis of FRs ($n = 45$) was investigated by analyzing a fortified surface water sample with the technique with the lowest selectivity, EI-MS. Both peak enhancement and suppression were observed, and significant correlations between matrix effects and several physico-chemical properties (e.g., retention time and boiling point) were found for PBDEs. In a separate clean-up experiment using natural water spiked with legacy and alternative FRs ($n = 30$), alumina provided the highest mean recovery (90%) in comparison to acidified silica (67%) and Florisil (78%). This study provides new knowledge on analysis of FRs including a wide range of alternative FRs, and it will aid in the efforts of FR monitoring in the environment.

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1. Introduction

Flame retardants (FRs) are chemical substances designed to interrupt chemical reactions of combustion, thereby slowing down or quenching the fire. FRs are widely used in numerous everyday-life products such as textiles, furniture, carpeting, electronics and building insulation [1–3]. However, the added FRs may be released during usage, disposal and recycling. Many FRs are resistant to environmental degradation, and hence, FRs have been ubiquitously found in the abiotic and biotic environments [2,4]. Tetra- through hepta-polybrominated diphenyl ethers (PBDEs) are included in the Stockholm Convention, and the use of two out of three technical PBDE products (pentaBDE and octaBDE) is forbidden since 2009 in new materials in the European Union (EU) [5]. The third technical PBDE product (DecaBDE) is banned from use in electrical and

electronic appliances within the EU [6] and DecaBDE has been proposed to be listed in the Stockholm Convention [5]. The restrictions of these legacy FRs have increased the need of alternative FRs to be developed and used in order for product manufacturers to comply with current legislation of fire safety [7,8].

The alternative FRs can be divided into two major groups based on their structure: the halogenated FRs (HFRs), containing bromine or chlorine (or both), and the organophosphorous FRs (OPFRs), containing one or more phosphate groups. Some OPFRs (e.g., TCIPP, TDCIPP, and TTBNPP) also contain bromine/chlorine but are for simplicity classified as OPFRs throughout this study. The alternative FRs (e.g., BTBPE, PBT, HBB, and TBX) often have similar physico-chemical properties as the restricted ones [9], and some of them have been detected in the environment, e.g., BTBPE, HBB, DBE-DBCH, and PBT in Arctic biota [4,10]; TNBP, TCEP, and TCIPP in waste and surface water [11]; and HBB, PBT, and EH-TBB in sediment [12]. For other alternative FRs (e.g., DBS, CDP, and IDP), there are to our knowledge neither reported analytical methods nor information about their environmental occurrence. Until now, alternative FRs

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have mostly been analyzed with methods developed for analyzing legacy FRs, such as PBDEs. As a result, there is a need to develop new analytical methods for the alternative, non-legacy FRs in order to obtain accurate and reliable data about their presence in the environment [13].

A range of instrumental techniques have previously been applied for trace analysis of legacy and alternative FRs, e.g., [11,14–18]. The determination of FRs may, however, be severely biased. For example, sample matrix effects have been shown to result in decreased or enhanced analyte responses, or bad peak performance in analyses of PBDEs using gas chromatography (GC)-high resolution mass spectrometry (HRMS) with electron impact ionization (GC-(EI)HRMS) and GC–MS with negative chemical ionization (GC-(NCI)MS) [19,20]. To minimize the matrix effect, clean-up of sample extracts prior to instrumental analysis is often performed. A number of different sorbents have been used for clean-up of PBDEs and HFRs, e.g., Florisil [21,22], multilayer columns containing basic, neutral and acidified silica [16,23], and neutral silica in combination with alumina [24] (for details, see Table S1 in the Supporting information (SI)). For analysis of OPFRs in environmental samples, no clean-up step after the extraction is a common approach (e.g., [17,25–28]), although neutral silica, alone or in combination with gel permeation chromatography (GPC), [29–31] or Oasis HLB [32] have also successfully been used.

The aim of the current study was to develop and compare multicompound analytical methodologies for the analysis of in total 102 FRs, including 27 PBDEs, 46 HFRs, and 29 OPFRs. Multicompound methods have previously been described for analysis of HFRs and OPFRs in dust [33,34], for pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), PBDEs, and HFRs in fish [35], and for PBDEs, HFRs, and OPFRs in dust, sediment and sludge [33]. However, no comparison of instrumental techniques were conducted in these studies. The current study is comprehensive in that three classes of FRs, including legacy PBDEs, the novel OPFRs and HFRs were studied under the same experimental conditions using three different MS techniques. In addition, physico-chemical property parameters were provided for all compounds, the relation between matrix effects and compound properties were explored, and efficiency of clean-up methods were tested. There is a lack of studies on these issues, in particular for alternative FRs.

Specific objectives included (i) comparison of three MS techniques (GC-(EI)MS, GC-(NCI)MS, and GC-tandem MS with EI ionization (GC-(EI)MS/MS)) for the detection of FRs ($n = 102$), (ii) investigation of the influence of matrix on the instrumental analysis of a sub-set of FRs ($n = 45$), and (iii) testing the potential of three different adsorbents (Florisil, acidified silica, and alumina) for clean-up of freshwater samples containing FRs ($n = 30$).

2. Experimental

2.1. Selection of flame retardants

In the selection of target FRs, we aimed for including as many as possible of the organic FRs that were available as reference standards on the commercial market (from trusted sources). In total, 102 FRs were investigated based on their current or historical use as FRs, prioritization lists [13,36,37], and the availability of analytical reference standards. The GC–MS parameters were optimized for all detected FRs (Tables S6–S8 in the SI) using GC-(EI)MS, GC-(NCI)MS, and GC-(EI)MS/MS. A selection of these FRs were included in the comparison of detectability ($n = 45$), influence of matrix ($n = 45$, same FRs as in detectability experiment) and clean-up experiments ($n = 30$, all FRs also included in detectability and matrix experiments). This selection was primarily based on the

possibility of detecting the substances with all three techniques but also some other criteria (Table S9 in the SI), e.g., for the PBDEs it was considered adequate to include only a few representatives ($n = 6$) with different degree of bromination. Physico-chemical properties (molecular weight (MW), water solubility (S_W), octanol-water partition coefficient (K_{OW}), organic carbon-water partition coefficient (K_{OC}), octanol-air partition coefficient (K_{OA}), boiling point (Bp), vapour pressure (V_P), and Henry's law constant (H)) of the investigated FRs were estimated using EPI Suite 4.1 (US EPA) (for FRs included in the evaluation of matrix effects, see Tables 1–3; for all investigated FRs, see Tables S2–S4 in the SI). The investigated FRs cover a wide range of physico-chemical properties with, for example, log K_{OW} ranging from −0.66 (DMP) to 16.9 (4′-PeBPO-BDE208). The OPFRs have in general lower log K_{OW}-values (52% of the selected compounds have log $K_{OW} < 4$) compared to HFRs (6% have log $K_{OW} < 4$) and PBDEs (none has log $K_{OW} < 4$).

2.2. Chemicals and materials

Native FR standards were obtained from Wellington Laboratories (Guelph, ON, Canada), Sigma-Aldrich (St. Louis, MO, USA), Accu-standard (New Haven, CT, USA), BOC Sciences (Shirley, NY, USA), Chemos (Regenstauf, Germany), MolMall Sarl (Lonay, Switzerland), and Carbone Scientific (London, UK). Isotopically labelled standards ($^{13}C_{12}$-BDE139, $^{13}C_6$-HBB, and d$_{15}$-TPHP) were obtained from Wellington Laboratories. Information about supplier and purity for all FR standards is compiled in Table S5 in the SI.

Toluene, dichloromethane (DCM), hydrochloric acid (SupraSolv/Suprapur®) and alumina (active neutral 90) were purchased from Merck (Darmstadt, Germany). Glass wool, anhydrous sodium sulfate, silica gel and Florisil® were purchased from Sigma-Aldrich. Oasis HLB cartridges (35 mL, 6 g, 60 μm) were purchased from Waters (Milford, MA, USA). Sample containers (12 L) were made of stainless steel and purchased from Sharpsville container/NSF Component® (Sharpsville, PA, USA). Horizon DryDisk® separation membrane (Salem, NH, USA) was used to remove H$_2$O from the sample extract, and Biotage TurboVap II system (Uppsala, Sweden) and Organomation N-EVAP Nitrogen Evaporator (Berlin, MA, USA) were used to concentrate sample extracts. Millipore water was produced in house by filtration through MilliPak® 0.22 μm filter.

2.3. Development of GC–MS methods

Instrumental methods were developed using three types of instrumental setups: GC-(EI)MS/MS, GC-(EI)MS, and GC-(NCI)MS. The systems used were: (i) a GC (Agilent Technologies, Palo Alto, CA, USA) coupled to tandem MS (Agilent GC–MS 7890A Triple Quad 7010) using EI (high-efficiency source, G7008C), and a single MS (Agilent 7890 B Single Quad 5977A MSD) using (ii) EI (extractor ion source, G2591C) and (iii) NCI (with methane as reagent gas).

The FRs ($n = 102$, including isomers) were injected individually ($c = 2000$ ng mL^{-1}) on each MS-system operating in scan mode. Aliquotes of 2 μL were injected on a 15 m DB–5 ms column (J&W Scientific, Agilent Technologies) with an i.d. of 250 μm and a film thickness of 0.10 μm. A multimode inlet (MMI) injector was used with a programmed temperature ramp of 75 °C, hold for 0.45 min, rate 600 °C min^{-1} to 325 °C, and finally hold for 5 min. The inlet pressure was set at 6.6 psi and kept for 0.45 min with a solvent vent flow of 10 mL min^{-1}. After 2.95 min, the solvent vent flow was increased to 60 mL min^{-1}. The GC oven temperature program was as follows: 90 °C hold for 2.95 min, rate 20 °C min^{-1} to 325 °C, hold for 5 min. The same conditions, type of column and inlet were used on both the single and the tandem MS instruments. The ion source temperature (both in EI and NCI) was kept at 300 °C while the quadrupole temperatures were 150 °C. In total, 90 out of 102