



New perspective on the determination of flame retardants in sewage sludge by using ultrahigh pressure liquid chromatography–tandem mass spectrometry with different ion sources

G. Mascolo^{a,*}, V. Locaputo^a, G. Mininni^b

^a Istituto di Ricerca Sulle Acque, Consiglio Nazionale delle Ricerche, Via F. De Blasio 5, 70123 Bari, Italy

^b Istituto di Ricerca Sulle Acque, Consiglio Nazionale delle Ricerche, via Salaria km 29, 3, P.O. Box, 10-00016 Monterotondo (Rome), Italy

ARTICLE INFO

Article history:

Received 17 February 2010

Received in revised form 19 April 2010

Accepted 3 May 2010

Available online 7 May 2010

Keywords:

Atmospheric pressure photoionization

Ultrahigh pressure liquid chromatography–tandem mass spectrometry

Hexabromocyclododecanes

Polybrominated diphenyl ethers

Tetrabromobisphenol A bis

2,3-dibromopropylether

Tetrabromobisphenol A

Tetrachlorobisphenol A

ABSTRACT

Analysis of 11 polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A bis 2,3-dibromopropylether (TBBPA-bis), tetrachlorobisphenol A (TCBPA), tetrabromobisphenol A (TBBPA) and hexabromocyclododecanes (HBCDs) was optimized by ultrahigh pressure liquid chromatography/tandem mass spectrometry (UPLC–MS/MS) operating in negative ion (NI) mode. Electrospray ionization (ESI), atmospheric pressure photoionization (APPI) and atmospheric pressure chemical ionization (APCI) sources were tested and for PBDEs APCI gave higher sensitivity than APPI while for TBBPA-bis APCI and APPI showed similar performance. ESI was the best option for TCBPA, TBBPA and HBCDs. Detection limits were between 20 and 59 fg for the compounds analyzed by ESI, 0.10 and 0.72 pg for PBDEs and 6 pg for TBBPA-bis. The matrix effect of sewage sludge extract was also tested showing negligible ion suppression for APCI and an increase of the background level of all investigated pollutants leading to a worsening of the limits of quantification by a factor between 1.2 and 3.3. The UPLC–APCI/MS/MS method for PBDEs, after pressurized liquid extraction (PLE), was validated by comparison with the concentration values from the NIST 1944 standard reference material. The advantages of the methods include low detection limits, PBDE congeners specificity using selected multiple reaction monitoring (MRM) transitions, and the absence of thermal degradation of higher PBDE congeners, especially BDE-209. The methods were applied for the determination of the above reported flame retardants in sewage sludge in order to get more information about the degradation on PBDEs (in particular BDE-209) during municipal wastewater treatments.

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1. Introduction

Brominated flame retardants (BFRs) are nowadays well known to be ubiquitous in the environment due to their widespread use in many industrial products as a consequence of fire prevention policies requiring the presence of such compounds in plastics, manufacture of printed electronic circuit boards, clothing, drapery, furniture foams, automotive interiors and many other consumer products. Their usage is justified by the effective electron-scavenging action of bromine leading to chain scission and flame poisoning [1]. More than 175 different types of flame retardants exist but BFRs are the largest market group because of their low cost and high efficiency for protection against flammability. Among BFRs three classes represent the highest production volumes, namely those based on tetrabromobisphenol A (TBBPA), hexabromocyclododecanes (HBCDs) and polybrominated diphenyl

ethers (PBDEs). BFRs based on bisphenol A (BPA) are mainly used as reactive flame retardants but, despite this should theoretically avoid any release into the environment, they have been found in many environmental matrices [2]. More than 200,000 metric tons of BFRs are produced each year [3] and as a consequence of diffuse discharges to the environment they have been detected in many area indicating persistence and bioaccumulation [4–10]. This lead to both concern about their usage [11] and to BFRs inclusion in the European chemicals policy of REACH in order to protect the human health and the environment from the risks posed by these compounds [12]. In addition, concern about BFRs is exacerbated from toxicity test studies showing several effects. For TBBPA action as a thyroid hormone, estrogen agonist [13] and immunotoxic effect [14] was evidenced. For HBCDs there are indications they disrupt the thyroid hormone system [15] and induce cancer through a non-mutagenic mechanism in humans [16]. PBDEs showed similar results to those derived from exposure to polychlorinated biphenyls [17] and many other effects including potentially significant changes in thyroid homeostasis [18–20], endocrine-related effects [21,22]

* Corresponding author. Tel.: +39 080 5820519; fax: +39 080 5313365.

E-mail address: giuseppe.mascolo@ba.irsra.cnr.it (G. Mascolo).

and moderate dioxin-like activities to human estrogen receptors [23,24].

As far as the environmental fate of BFRs is concerned, a suitable monitoring strategy of sewage sludge must be taken into consideration since it is generally accepted that most of these pollutants tend to concentrate in sludge because of their non-polar character and resistance to biodegradation during municipal wastewater treatment processes [25,26]. If sewage sludge is disposed of to incineration the combustion temperature has to carefully set as it has been reported that PBDEs are transformed into polybromodibenzodioxins and polybromodibenzofuranes when they are incinerated at temperatures up to 900 °C [27].

As for PBDEs, a fewer number of congeners than the theoretical possible (209) is practically found in environmental samples varying in both number and position of bromination. This reflects the number of congeners of commercial PBDEs formulation. In fact, PBDEs were typically produced commercially as three main formulation, namely penta-BDE, octa-BDE and deca-BDE each of which being a suite of congeners [28]. Due to environmental and human health concern, the latter two formulations were banned in the European Union and voluntarily taken off the market in the USA [29,30]. However, as these restrictions do not eliminate PBDEs release from products currently in-service or new products manufactured with recycled PBDE-containing material, it is expected to find several congeners in environmental samples and, in particular, the BDE-209. The high number of congeners normally found in environmental samples also makes the analytical determination of PBDEs quite challenging. Several GC–MS methods have been proposed based on EI or electron capture negative ionization (ECNI). However, limitations still exist for both the chromatographic separation and MS detection [31]. In fact, GC analysis of congeners with more than eight bromines has proven to be difficult for thermal degradation problems. This drawback is particularly severe for BDE-209 when it is exposed for long periods to high temperatures in both injector and column. A possible solution is the employment of short columns but, in turn, this is detrimental for the separation of the other congeners if a suitable selective detection is not used. As for MS detection, EI is more selective than ECNI because molecular fragments, mainly $[M-Br_2]^+$, are monitored while with ECNI non-specific bromide ions (m/z 79 and 81) are monitored. It follows that for quantification of PBDEs the employment of isotopically labeled surrogate standards is possible only with EI detection. The only exception is represented by BDE-209 for which an abundant $[C_6Br_5O]^-$ ion relative to bromide is produced making possible the use of isotopic dilution method [32]. In contrast, sensitivity with EI detection is about 20 times lower than ECNI [33] and a large drop in sensitivity is observed for congeners with more than six bromine atoms [31]. It follows that GC–ECNI/MS is the analytical technique currently employed when trace levels of PBDEs have to be determined.

LC–MS can be suitable for the detection of PBDEs because also the highly brominated congeners can be determined and the proper selectivity is provided by the MS–MS detection mode. In addition, the employment of LC–MS can have the benefit of detecting metabolites of PBDEs, namely hydroxylated PBDEs and glucuronic acid or glutathione conjugates that are usually encountered as xenobiotic metabolites. These compounds, in fact, cannot be determined by GC–MS due to their high polarity. However, although these potentialities, few papers have been reported about the analysis of PBDEs by LC–MS [34–37]. This may be related to several factors including (i) the necessity to use atmospheric pressure photo ionization (APPI) source that is not yet widespread with LC–MS systems being ESI and APCI only suitable for HBCDs and BPAs, (ii) the detection limits not comparable to those of GC–ECNI/MS and (iii) the limited resolving power of LC with respect to GC.

The present work reports about the LC–MS/MS determination of PBDEs with both a sensitivity as high as that of GC–ECNI/MS and a high chromatographic resolving power employing ultrahigh pressure liquid chromatography (UPLC). The main objective was to provide a powerful analytical method able to overcome the above reported drawbacks especially for the high brominated congeners that are those more likely to be found in environmental samples. APPI and APCI were tested showing similar signal intensities but APCI was finally employed due to its lower background level.

The method, including a pressurized liquid extraction (PLE), was validated using NIST standard reference material New York/New Jersey Waterway Sediment 1944 whose PDBE concentrations are available [38] and applied for the determination of BFRs in sewage sludge in order to get more information about the degradation on PBDEs (in particular BDE-209) during municipal wastewater treatments. The method also included the determination of tetra-bromobisphenol A bis 2,3-dibromopropylether (TBBPA-bis) for which, to the best of our knowledge, only one analytical method employing LC–DAD/MS has been reported [39]. In addition, other flame retardants, namely HBCD, TBBPA and tetrachlorobisphenol A (TCBPA) were searched in the sludge samples in order to get information about the relative abundance of the different classes of pollutants.

2. Experimental

2.1. Chemicals

LC–MS grade methanol (Sigma–Aldrich) was used as organic modifier in LC analyses. Water used for LC (18.2 M Ω cm, organic carbon content $\leq 4 \mu\text{g L}^{-1}$) was obtained from a Milli-Q Gradient A-10 system (Millipore). Toluene used for APPI was HPLC grade (Sigma–Aldrich). Toluene and methylene chloride used for extracting BFRs from environmental samples were pesticide grade (Sigma–Aldrich). Hydromatrix diatomaceous earth (Varian), aluminium oxide 90 active neutral (Merck) and copper powder (Sigma–Aldrich) were used as PLE dispersant matrix, in-cell cleanup agent and sulfur-removal, respectively. Individual PBDE standards, prepared at $50 \mu\text{g L}^{-1}$ in isoctane, of BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-203, BDE-205 and BDE-209 were purchased from AccuStandard. HBCDD, TCBPA and TBBPA powders were purchased from Sigma–Aldrich while TBBPA-bis was from TCI Europe.

2.2. Sewage sludge collection and PLE

Seven municipal treatment plants were sampled taking both secondary and digested sludge 2 times a day for 5 consecutive days to achieve a representative sample. Each final sample was carefully homogenized and an aliquot was freeze-dried. Two PLE methods, for PBDEs and for HBCDs and BPAs, respectively, including an in situ cleanup by inclusion of sorbents in the extraction cell, were optimized on the basis of a analytical procedure for sediments [40]. Briefly, a 66 mL extraction cell (Dionex) was loaded by inserting two cellulose filters into the cell outlet, followed by 20 g of alumina. For PBDEs 5 g of freeze-dried sludge, was ground with neutral alumina and copper (1:3:3). The resulting mixture was transferred into the cell on top of alumina and the dead volume was filled with diatomaceous earth. The extraction cell was filled with toluene until the pressure reached 1500 psi, and then heated to 100 °C (1 psi = 6894.76 Pa). After 5 min heating time three static extractions of 10 min at constant pressure and temperature were performed. At the end of the last static period, fresh solvent (80% of the extraction cell) was introduced to flush the lines and cell, and the extract was collected in a vial. The volume of the resulting extract was about 150 mL. The collected solvent volume

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