Determination of Polybrominated Diphenyl Ethers (PBDEs) and Hexabromocyclododecanes (HBCDs) in indoor dust and biological material using APPI-LC-MS/MS

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Overview

This note describes the application of LC-MS/MS with Atmospheric Pressure Photo Ionization (APPI) for the determination of PBDE target congeners and HBCD stereoisomers in indoor dust samples and biological material.

Instrumental detection limits (IDL) are included and range from 0.07 ppb to 0.24 ppb for selected PBDE congeners and from 0.12 to 0.32 ppb for HBCD stereoisomers.

Introduction

In recent years polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) have emerged as a subject of great concern because of their increasing levels in the human body, causing disturbance of the thyroid hormone homeostasis and chronic neurotoxicity (Alaee, 2003), and because of their ubiquity in the environment, especially indoors. Indoor dust and biological material have become a repository for PBDEs and HBCDs, resulting in developments of sampling strategies and analytical methodology for determination of these chemicals (Covaci, 2003). Traditionally, GC-MS has been employed for the analysis of PBDEs and HBCDs in environmental samples, but this technique causes thermal degradation of higher brominated PBDE congeners and interconversion of HBCDs. Hence, liquid chromatography coupled with tandem mass spectrometry (LCMS/ MS) has more recently been used for the determination of PBDEs and HBCDs (Lagalante, 2008; Vilaplana, 2008; Abdallah, 2009; Zhou, 2010).

Experimental

The SCIEX 4000 QTRAP® System was coupled with an Agilent 1200 series LC system for the determination of PBDE target congeners (BDE-47, 85, 99, 100, 138, 153, 154, 183, 190, 196, 206, 209) and α-, β-, γ-HBCD stereoisomers.

A Phenomenex Kinetex C18 (150x4.6mm) column was used for chromatographic separation using H2O (A) and methanol (B) mobile phases with a gradient from 90% B increasing at 4 min to 100% and holding for 9 min, with a 4 minute equilibration between runs. The mobile phase flow was set to 400 µL/min, and 10µL of standards and extracts were injected for analysis.

All experiments were performed on a SCIEX 4000 QTRAP® system with PhotoSpray® ion source operated in negative polarity. Nebulizer gas (GS1) and lamp gas (GS2) were supplied with nitrogen, resulting in a 3 fold increase in signal compared to the atmospheric air (Figure 1).

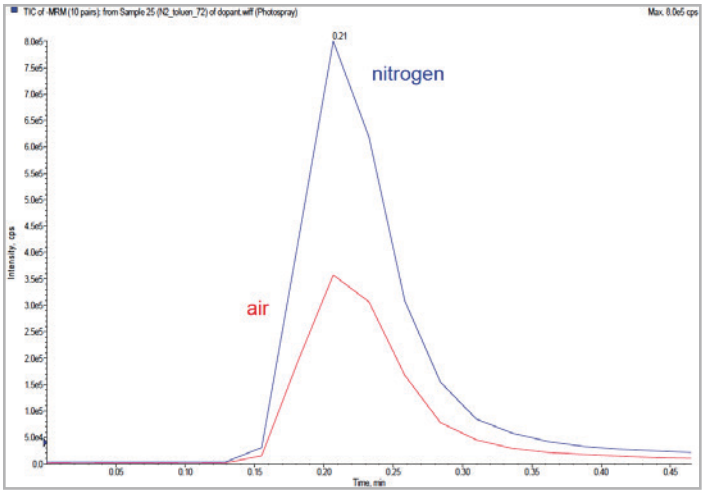

Figure 1. Sensitivity gain for PBDE congeners when using nitrogen as GS1 and GS2 in comparison to air.

Toluene was used as a dopant at a flow rate of 72 µL/min which was equal to 18% of the total mobile phase flow (Figure 2).

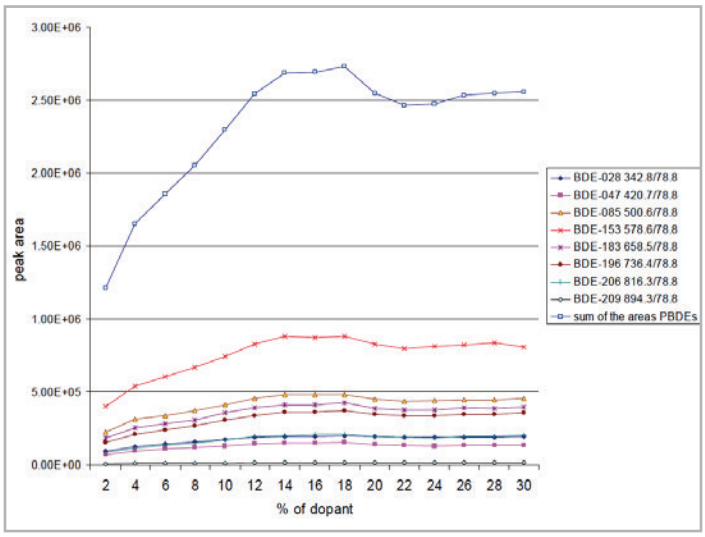

Figure 2. A comparison of peak area to the dopant flow rate (in % of total mobile phase flow).

All source parameters were optimized using automatic flow injection analysis using the Analyst® software and set for optimal intensity of MRM transitions for all analytes: CUR 12; CAD 12; TEMP 300°C; GS1 30 psi; GS2 30 psi; IS -700 V.

Analytes were monitored in Multiple Reaction Monitoring (MRM) using the *Scheduled* MRM™ algorithm with two transitions for each target compound. MRM conditions are listed in Tables 1 and 2.

HBCD	Q1	Q3	DP (V)	CE (V)
α-HBCD	640.6	78.8	-35	-40
		80.9	-35	-40
β-HBCD	640.6	78.8	-35	-40
		80.9	-35	-40
γ-HBCD	640.6	78.8	-35	-40
		80.9	-35	-40

Table 1. MRM transitions and optimized parameters for HBCDs.

PBDE	Q1	Q3	DP (V)	CE (V)
BDE-047	420.8	78.8	-36	-38
		80.9	-36	-38
BDE-085	500.7	78.8	-60	-90
		80.9	-60	-90
BDE-099	500.7	78.8	-60	-90
		80.9	-60	-90
BDE-100	500.7	78.8	-60	-90
		80.9	-60	-90
BDE-138	578.6	78.8	-50	-100
		80.9	-50	-100
BDE-153	578.6	78.8	-50	-100
		80.9	-50	-100
BDE-154	578.6	78.8	-50	-100
		80.9	-50	-100
BDE-183	658.5	78.8	-50	-110
		80.9	-50	-110
BDE-190	658.5	78.8	-50	-110
		80.9	-50	-110
BDE-196	736.4	78.8	-70	-90
		80.9	-70	-90
BDE-206	816.3	78.8	-60	-100
		80.9	-60	-100
BDE-209	894.3	78.8	-60	-100
		80.9	-60	-100

Table 2. MRM transitions and optimized parameters for PBDEs.

Results and Discussion

A standard chromatogram is shown in Figure 3. Two MRM transitions were monitored for each target analyte. The *Scheduled* MRM™ algorithm was used to maximize signal-tonoise and to collect enough data points across the LC peak for best accuracy and reproducibility.

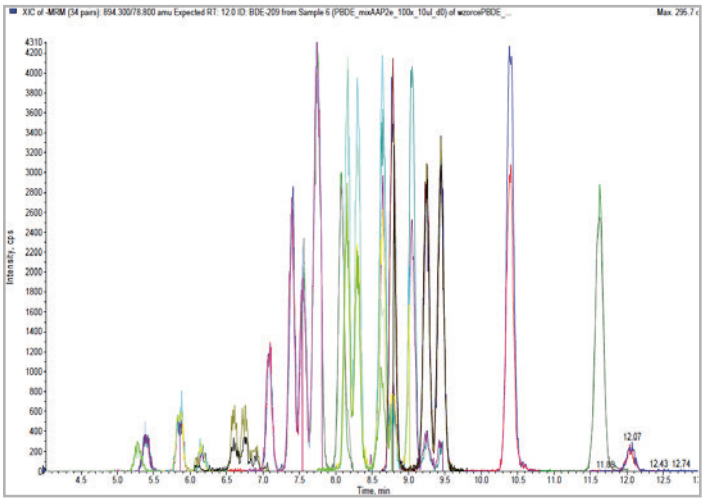

Figure 3. Chromatogram of a standard mix using the Scheduled MRM™ algorithm (the standard solution contained additional non-examined congeners).

Standards for calibration curves were prepared in a mixture of methanol/toluene (4/6) ratio in a concentration which depends on the PBDE congener. Example calibration curves for selected PBDE congeners are shown on the Figure 4. All studied PBDEs had excellent linearity with R values between 0.9994 and 0.999.

Based on these calibration lines instrument detection limits (IDL) and limits of quantitation (LOQ) were determined for individual congeners (Table 3).

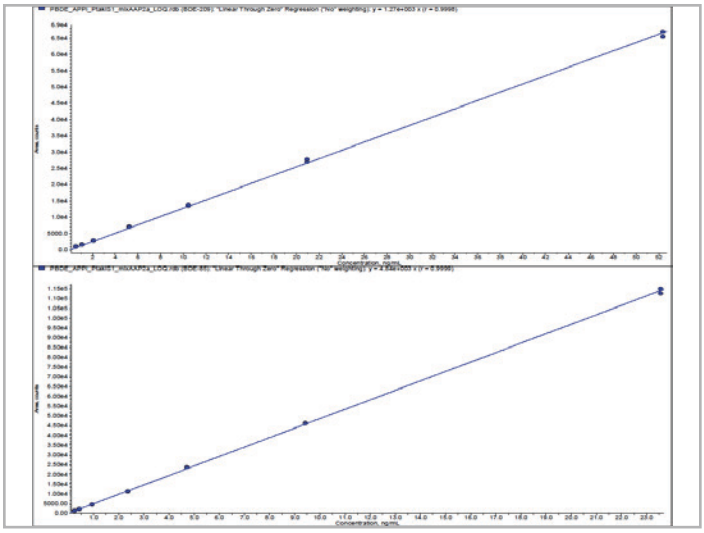

Figure 4. Calibration lines of selected PBDE congeners with an R value of greater than 0.999.

Compound	IDL (ppb)	LOQ (ppb)	Range (ppb)*	IDL (pg on column)
α-HBCD	0.12	0.58	0.58 - 5.24	1.22
β-HBCD	0.14	0.49	0.49 - 2.09	1.39
γ-HBCD	0.32	1.53	1.53 - 5.24	3.19
BDE-047	0.31	1.48	0.71 - 3.14	1.51
BDE-085	0.15	0.71	0.41 - 4.71	0.74
BDE-099	0.07	0.41	0.41 - 4.71	0.74
BDE-100	0.07	0.41	0.39 - 2.36	0.80
BDE-138	0.13	0.69	0.69 - 6.28	1.25
BDE-153	0.10	0.57	0.57 - 4.71	1.04
BDE-154	0.12	0.66	0.66 - 6.28	1.21
BDE-183	0.17	0.96	0.96 - 7.85	1.74
BDE-190	0.13	0.71	0.71 - 7.85	1.29
BDE-196	0.16	0.91	0.91 - 10.50	1.65
BDE-206	0.16	0.87	0.87 - 10.50	1.57
BDE-209	0.24	1.33	1.33 - 10.50	2.42
* Range used to determine the parameters IDL and LOQ				

Table 3. IDL, LOQ, and linear dynamic range for HBCDs stereoisomers and PBDE congeners.

The above described analytical method was used for the analysis of indoor dust samples and biological material which were extracted using toluene in a Soxhlet apparatus for 8 hours in a dark room. Extracts were concentrated using a rotary evaporator and purified by gel permeation chromatography (GPC) (Brezee 1525). The eluent, dissolved in methylene chloride, was evaporated to exchange the final sample solvent to methanol/ toluene (4/6).

Figure 5 and Table 4 show the results from an analysis of the dust reference material NIST SRM 2585 (µg/kg dry weight).

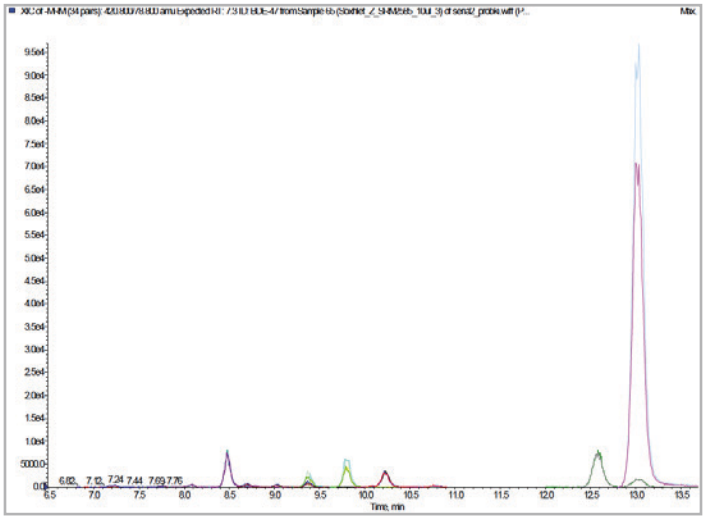

Figure 5. Chromatogram of the NIST dust reference material SRM 2585.

Summary

The developed LC-MS/MS method was used for the determination of PBDE congeners and HBCD stereoisomers in indoor dust and biological material after sample extraction. Obtained detection limits are acceptable and the influence of the matrix was not observed. The disadvantage of the described method is the lack of signal for one to two substituted PBDE congeners, however results for a NIST standard reference material showed acceptable results for 10 of 11 PBDE compounds, showing that this method is accurate and suitable for detection of PBDE congeners and HBCD stereoisomers in indoor dust and biological material.

PBDE	NIST certified concentration (µg/kg)	Found concentration (µg/kg)	Recovery
BDE-209	2510	2613	104.1
BDE-206	271	298	109.9
BDE-190	5.1	<LOQ	<LOQ
BDE-183	43.0	39.7	92.4
BDE-154	83.5	95.1	113.9
BDE-153	119	125	105.4
BDE-138	15.2	16.7	110.0
BDE-100	145	157	108.1
BDE-099	892	888	99.6
BDE-085	43.8	41.4	94.6
BDE-047	497	522	104.9

Table 4. Quantitative results of analyzing the reference material NIST SRM 2585.

Acknowledgements

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