Analyzing PBDEs in House Dust Samples with the Thermo Scientific TSQ Quantum XLS Ultra GC-MS/MS in EI-SRM Mode

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Key Words

Polybrominated diphenyl ethers (PBDE), house dust samples, selected reaction monitoring, timed-SRM, SIM, negative chemical ionization

Introduction

Polybrominated diphenyl ethers (PBDEs) were introduced in the 1960s as flame retardants and are currently used in a wide variety of household apparatuses, consumer electronics, furniture and more. Environmental levels of PBDEs have been continuously increasing due to their special persistence. Certain congeners have been banned completely and are currently in the list of the Stockholm convention's persistent organic pollutants.[1,2] Sources of human intake are typically via ingestion (nutritional) and the inhalation of indoor and house dust.

Due to growing concerns over the health risks from constant exposure to this class of compounds and the accumulation effects in the food chain, suitable analytical methods are required to quantify flame retardant compounds at low levels in a variety of matrices.

Current analyses are performed using either electron impact (EI) or negative chemical ionization (NCI) GC/MS as a detection technique. In this application note, the EI-selected reaction monitoring (SRM) method is highlighted, and a short comparison is made with a NCI technique. A broad range of PBDE samples and congeners were analyzed, ranging from tri- up to deca-BDEs.

Experimental Conditions

Sample Preparation

The sample preparation method is summarized in Figure 1. House dust samples (0.5 g) were extracted using pressurized liquid extraction with the Thermo Scientific Dionex ASE 350 Accelerated Solvent Extractor (Figure 2). In-cell extraction and clean up was achieved by placing a cellulose filter at the exit of a 22 mL cell and placing 2.5 g of silica above the filter to remove polar compounds that would have been co-extracted. The extraction took place using dichloromethane at 100 °C and 6.80 MPa in three static cycles. Approximately 30 mL was collected and subsequently evaporated to 150 µL under nitrogen[4]. No further clean-up of the extracts was performed.

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┌─────────────────────┐
│     0.5 g dust      │
└─────────────────────┘
           │
           ▼
┌─────────────────────────────────────┐
│ Dionex ASE™ 350: 100 °C at 6.80 MPa │
│   Solvent: Dichloromethane          │
│   Clean up in cell: 2.5 g silica    │
└─────────────────────────────────────┘
           │         ┌──────────────────┐
           │         │  Collect 3 times │
           │         └──────────────────┘
           ▼
┌─────────────────────────────────────┐
│     Evaporate under nitrogen        │
│       End volume: 150 µL            │
└─────────────────────────────────────┘
           │
           ▼
┌─────────────────────┐
│   GC/MS Analysis    │
└─────────────────────┘
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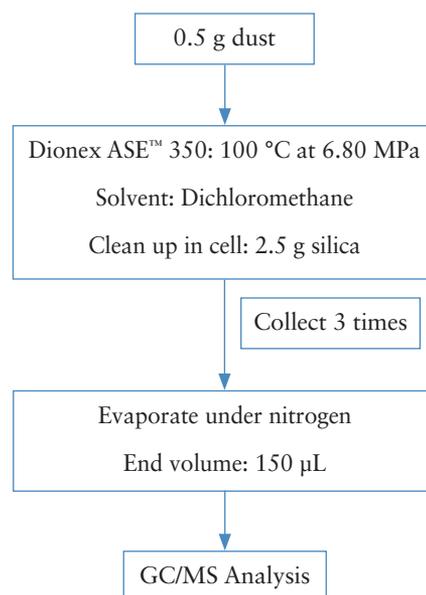
Figure 1. Sample preparation flowchart

Figure 2. ASE 350 Accelerated Solvent Extractor

Method Setup

The Thermo Scientific TSQ Quantum XLS Ultra GC-MS/MS system, run in both EI and NCI modes, was used for analysis. The experimental conditions are described in Table 1, and the EI-SRM and NCI-selected ion monitoring (SIM) parameters are provided in Table 2.

Switching the ionization mode from EI to NCI on the TSQ Quantum XLS Ultra™ GC-MS/MS is done by simply exchanging the appropriate ion volume type. There is no need to vent the mass spectrometer when changing ion volumes, which makes the switch from EI to NCI easy and straightforward. This also ensures the most accurate and sensitive performance achievable, which combination sources lack.

Table 1. Selected instrument conditions for the TSQ Quantum XLS Ultra GC-MS/MS system

Thermo Scientific Gas Chromatograph

Injection Volume:	2 µL injection
Liner:	Siltec baffled liner, p/n 453T2120
Carrier Gas:	He, constant flow, 1.5 mL/min
Column Type:	Thermo Scientific TraceGOLD TG-5HT column (5% phenyl film) of 15 m length, 0.25 mm inner diameter and 0.10 µm film thickness. p/n 26095-0350
Oven Temperature:	Initial 120 ˚C, Hold 1 min, Ramp 20.0 ˚C min - 320 ˚C, Ramp 5.0 ˚C min, Hold 5.0 min.
Transfer Line:	330 ˚C

PTV Injection Program

Injector Temperature:	80 ˚C, Splitless Injection 2 min
PTV Inject:	80 ˚C, 0.1 min, 10 ˚C/sec to transfer step
PTV Transfer:	300 ˚C, 6 min, 14.5 ˚C/sec to clean step
PTV Clean:	340 ˚C, 20 min, clean flow 25 mL/min

TSQ Quantum XLS Ultra Mass Spectrometer in EI Mode

Source Temperature:	260 ˚C, CEI volume
Ionization:	EI, 70 eV
Emission Current:	50 µA
Resolution:	0.7 Da Q1, Q3
Collision Gas:	Argon, 1.3 mTorr

TSQ Quantum XLS Ultra Mass Spectrometer in NCI Mode

Source Temp.:	260 ˚C, CI volume
Ionization:	EI, 70 eV
Emission Current:	50 µA
Resolution:	0.15 Da Q1
CI gas:	Argon, 2 mL/min

Table 2. MS selective ions in EI-SRM and NCI-SIM

Compound	EI-SRM	NCI-SIM
BDE28	405.80 → 245.89	78.9, 80.9
BDE47	485.71 → 325.84	78.9, 80.9
BDE99	563.65 → 403.81	78.9, 80.9
BDE100	563.65 → 403.81	78.9, 80.9
BDE154	643.53 → 483.73	78.9, 80.9
BDE153	643.53 → 483.73	78.9, 80.9
BDE183	721.44 → 561.76	78.9, 80.9
BDE209	799.35 → 639.53	408.7, 78.9, 80.9

Results and Discussion

Chromatography

The decabromodiphenyl ether (BDE 209) is notably difficult to analyze due to its thermally labile nature. The breakdown can be minimized by reducing the residence time in heated zones using a PTV injector, increasing the flow by using a short column with a small film thickness, and using moderate oven temperature ramping. The longer this compound resides in the analytical column and elutes at elevated temperatures, the smaller the compound's response will be.[3] It is important to note that typically commercial standards are sold with increased BDE209 concentrations compared to other congeners.

In this case, a short 15 m column with a thin film thickness of 0.1 µm was chosen for optimal elution of BDE209.

The PTV injector plays a key role in ensuring a complete sample transfer of compounds (no loss) and as an inert injector. The cleaning phase added to the injection program helps keep the liner and analytical column free from high boiling sample matrix contaminants, thus ensuring optimum chromatographic separation injection after injection.

In Figure 3, it is clearly demonstrated that when using the GC parameters as described, there is good correlation between the lower BDE and BDE 209, which has a ten-fold higher concentration in this standard than the other BDE congeners.
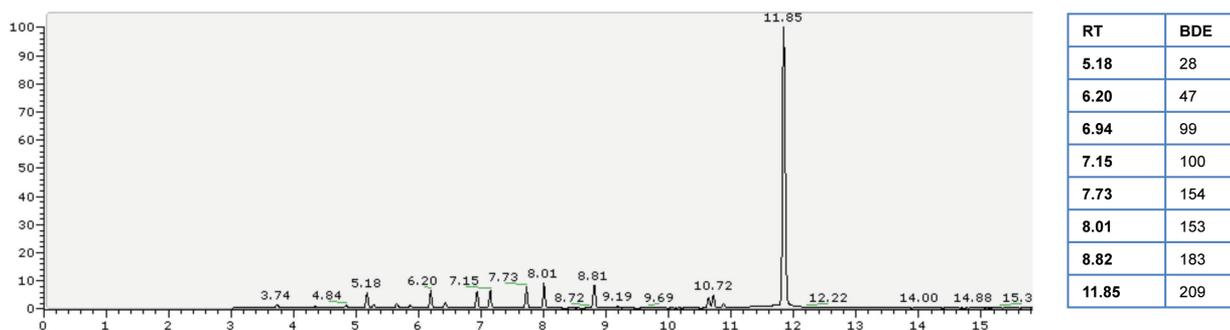
RT	BDE
5.18	28
6.20	47
6.94	99
7.15	100
7.73	154
8.01	153
8.82	183
11.85	209

Figure 3: Chromatogram of PBDE standard at 100 ppb with BDE209 at 1000 ppb in NCI mode

Analytical Performance

The analytical performance is defined by several parameters including the calibration curves and the repeatability at low concentration levels. For this application, the instrument detection limit was determined using 10 repeat injections of neat solutions of standard at the 1 ppb level. The calculated standard deviation was multiplied by three according to the Eurachem Guide[5].

For calculation of the samples, a calibration curve was set up using external calibration. Ideally, internal standards would be used for extraction and recovery controls, but they were not available during these experiments. All results, therefore, were based on external standard calibration and were not corrected for fluctuations as with the use of an internal standard.

Detection limits

Detection limits were calculated in spiked neat solutions by multiplying the standard deviation of ten repeat injections times three (Table 3). Overall, the method detection limits in neat solutions are lower when using negative chemical ionization than SRM.

Table 3. Detection limits

	EI-SRM	EI-SRM	EI-SRM
Compound	3*stdev at 1 µg/L	DL (µg/L) (n=10)	DL in sample (µg/kg)
BDE28	0.1296	<0.2	<0.06
BDE47	0.1293	<0.2	<0.06
BDE99	0.3051	<0.5	<0.15
BDE100	0.2721	<0.5	<0.15
BDE154	0.4227	<0.5	<0.15
BDE153	0.3228	<0.5	<0.15
BDE183	0.7308	<1	<0.3
BDE209*	11.85	<15	<4.5

* BDE 209 has a ten-fold higher concentration in the standard, see Figure 3.

Repeatability and ion ratio repeatability in matrix

Several house dust samples were spiked at various levels and repeat injections were performed. Table 4 shows the repeatability of several PBDE congeners at different concentration levels. The ion ratio deviation was determined by comparing the quantifier ion with the qualifier ion.

Multiple injections of samples allowed for determination of area repeatability and ion ratio repeatability. The repeatability values are good, even at low levels, and the ion ratio deviation is very low. The ion ratio was calculated on the EI-SRM measurements. The negative chemical ionization experiments detected the two isotopes of bromine, i.e. m/z 79 and 81.

Table 4. Area and ion ratio repeatability

Compound	Concentration in dust	RSD n=5	RSD ion ratio n=5
BDE47	3 ppb	2.99%	4.14%
BDE99	1 ppb	1.61%	3.46%
BDE100	8 ppb	2.33%	2.82%
BDE154	1.5 ppb	5.50%	10.62%
BDE153	1.5 ppb	5.50%	10.62%
BDE209	150 ppb	3.24%	5.62%

Calibration curves

Calibration curves of BDE in EI-SRM mode are shown in Figure 4.

BDE peaks around the detection limits in house dust samples

Figure 5 displays quantifier and qualifier ion peaks. The concentration of BDE209 is often higher in commercially available solutions due to low response when analyzing with GC. Using an inert liner in the PTV and a short thin film column overcomes the lower response for BDE209. In the chromatogram we clearly see a higher response for this compound.
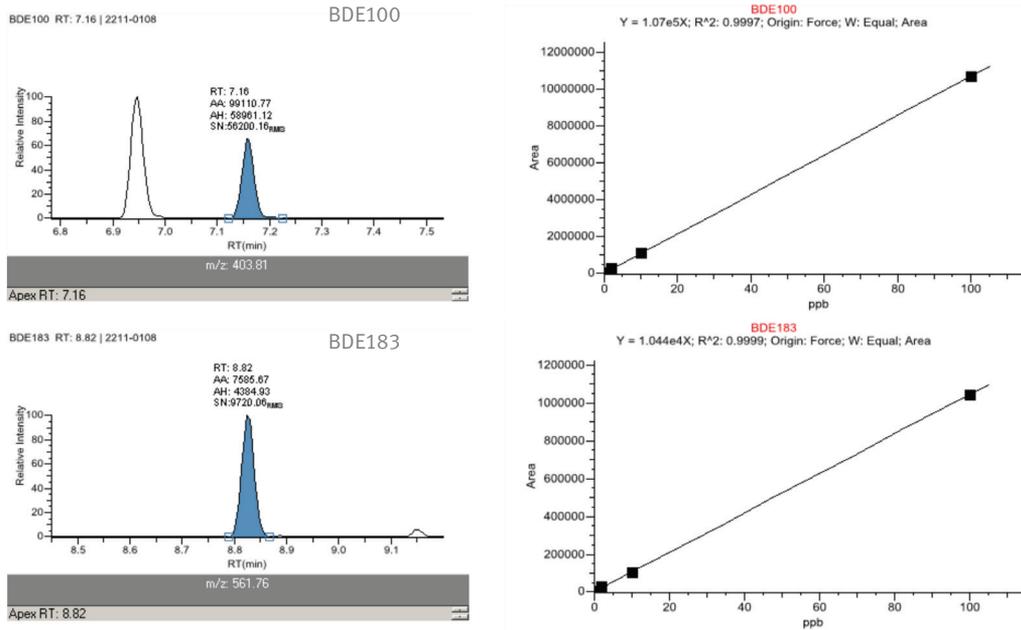
Figure 4. Calibration curves of BDE in EI-SRM mode, showing the quantifier peak at 1 µg/L; zoomed in on the lower regions of the calibration curve.

Quantifier Ion		Qualifier Ion	
	BDE28@0.05 ppb 405.80 → 245.89		BDE28@0.05 ppb 407.80 → 247.89
	BDE47@0.03 ppb 485.71 → 325.84		BDE47@0.03 ppb 487.71 → 327.84
	BDE99 & 100 @ 0.3 ppb 563.65 → 403.81		BDE99 & 100 @ 0.3 ppb 565.65 → 405.81
	BDE154 & 153 @0.3 ppb 643.53 → 483.73		BDE154 & 153 @0.3 ppb 641.53 → 481.73
	BDE183 @0.3 ppb 721.44 → 561.76		BDE183 @0.3 ppb 723.44 → 563.76
	BDE209 @20 ppb 799.35 → 639.53		BDE209 @20 ppb 801.35 → 641.53

Figure 5. BDE peaks around the detection limits

Selectivity in EI-SRM and NCI

The method evaluation started with the initial validations of repeatability, establishing the limits of detection in neat solutions, and checking the calibration linearity. After these experiments were performed, the method was evaluated in the matrix, which revealed the strengths and weaknesses of the chosen detection.

Figures 6 and 7 are comparisons showing the EI-SRM using the TSQ Quantum XLS Ultra GC-MS/MS and the negative chemical ionization measurements using a single quadrupole GC-MS system in two samples. The measurements in EI-SRM mode for house dust show clearly defined peaks for the target analytes, whereas the measurements in NCI mode have many more interferences for the target compounds.
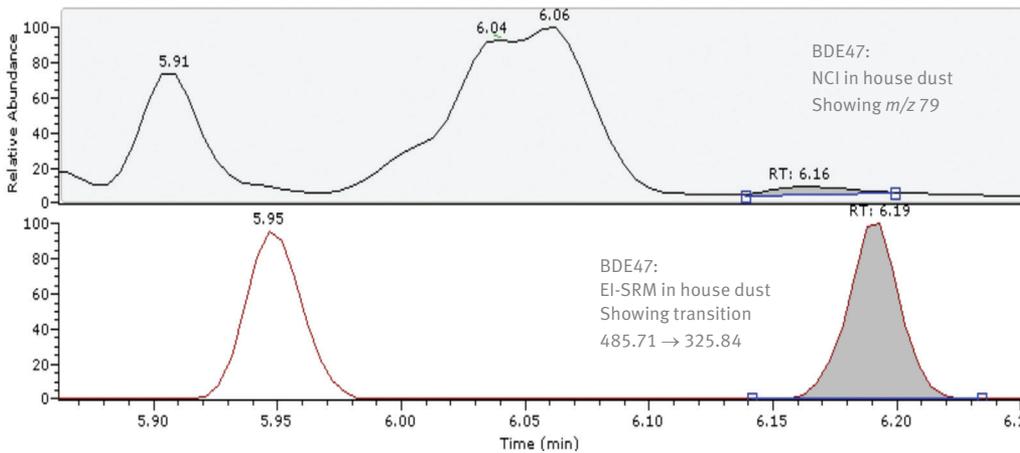
Figure 6. House dust sample in NCI (above) and EI-SRM (below) showing BDE47 at a level of 0.07 ppb
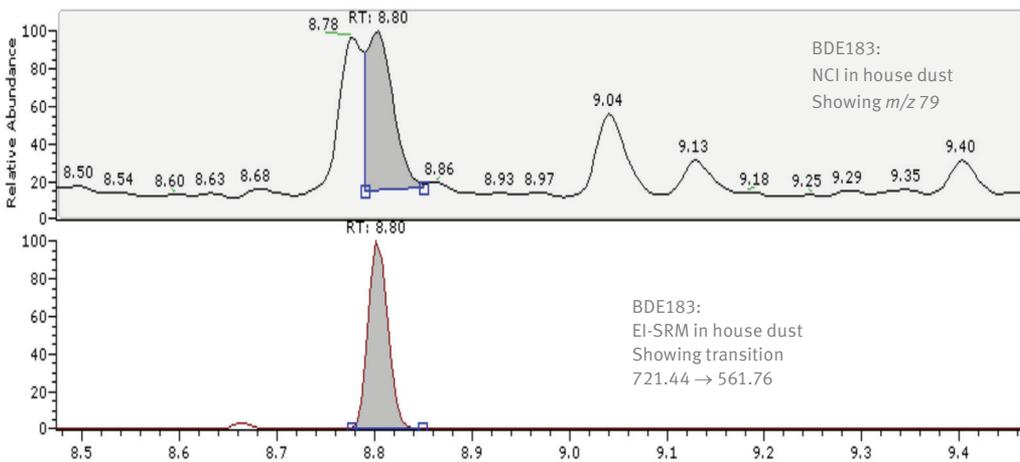

Figure 7. House dust sample in NCI (above) and EI-SRM (below) showing BDE183 at a level of 0.17 ppb

Conclusions

Using the Dionex ASE 350 solvent extractor in combination with an in-cell clean-up offers a quick and easy methodology for extracting BDE in solid/semi-solid matrices.

PBDE flame retardants are a class of compounds that degrade easily in the injector, and the PTV proves to be both highly inert and rugged for these analytes.

For PBDEs in EI-SRM mode, the measurements undertaken took advantage of the high selectivity achieved through the 0.15 Da resolution setting of Q1. It offered the best detection sensitivity in matrix. In the case of polybrominated compounds, negative chemical ionization provided unbeatable sensitivities, but with lower selectivity as seen with the most prominent ions *m/z* 79 and 81, (except decabromodiphenylether). It is, therefore, essential to compare in matrix, as well as in neat solutions.

For PBDEs, the lowest detection limits may be obtained using negative chemical ionization. When analyzing heavy matrix laden samples such as house dust, the excellent selectivity achieved with the Ultra XLS triple quad at 0.15 Da provided pronounced peaks that were easier and more reproducible to integrate. This led to decreased processing time and higher productivity, resulting in faster data evaluation by the analyst. The combination of 0.15 Da resolution combined with choosing a more selective mass in EI, gives better sensitivities in matrix than a non-selective mass of 79 and/or 81 used in NCI.

Because of the enhanced selectivity that is obtained using EI-SRM with a GC-MS/MS capable of 0.1 Da resolution, it is the better choice when analyzing BDEs in difficult matrices.

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