

## ASSESSMENT OF AMBIENT ENVIRONMENTAL LEVELS OF DECABROMODIPHENYL ETHER (BDE-209) WITH HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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### Introduction

Polybrominated diphenyl ethers (PBDE) were introduced in 1960s, and has been used extensively as a fire retardant. Among the 209 different congeners, pentabromodiphenyl ether (penta-BDE), octabromodiphenyl ether (octa-BDE) and decabromodiphenyl ether (deca-BDE) were most widely produced and used. These chemicals were most widely used in plastic components of electric and electronic equipments. As its usage continued to grow, however, evidence of widespread environmental contamination also began to grow. PBDEs have been found in sludges of industrial wastewater, as well as in river sludge and other ambient environment.<sup>1-2</sup> More studies have also shown the presence of PBDEs in human tissues,<sup>3-8</sup> although the health hazards of PBDEs on humans have not been explicitly confirmed.

Typically, analyses of PBDEs have relied on gas chromatography and mass spectroscopy (GC/MS), and advancement of high-resolution GC/MS (HRGC/HRMS) have increased the sensitivity and specificity of the instrumental methods. Nonetheless, the vaporization process within GC is prohibitive in nature for the analysis of compounds with high boiling point. This is especially problematic when analyzing for decabromodiphenyl ether (BDE-209), which has a melting point of ~300°C and breaks down before a boiling point could be reached. In contrast, high-performance liquid chromatograph (HPLC) separates compounds with liquid mobile phase, hence avoiding the limit for substances with high boiling point, and provides an option for qualitative and quantitative analysis of BDE-209.

In this article, we present analytical method for BDE-209 with HPLC. Instrumental settings and analytical conditions are presented in the article, and potential application in environmental assessment is briefly discussed.

### Materials and Methods

In this study, an HPLC equipped with UV detectors and a diode array detector was used for instrumental analyses (Agilent Model 1100, Agilent Technologies, Taiwan). The analytical conditions were modified after Riess and van Eldik<sup>9</sup> and was tested with BDE-209 purchased from Sigma-Aldrich (Germany). In addition, an external standard (50 mg/L BDE-209 in isooctane) was purchased from AccuStandard (New Haven, CT, USA). The instrumental settings are shown in Table 1.

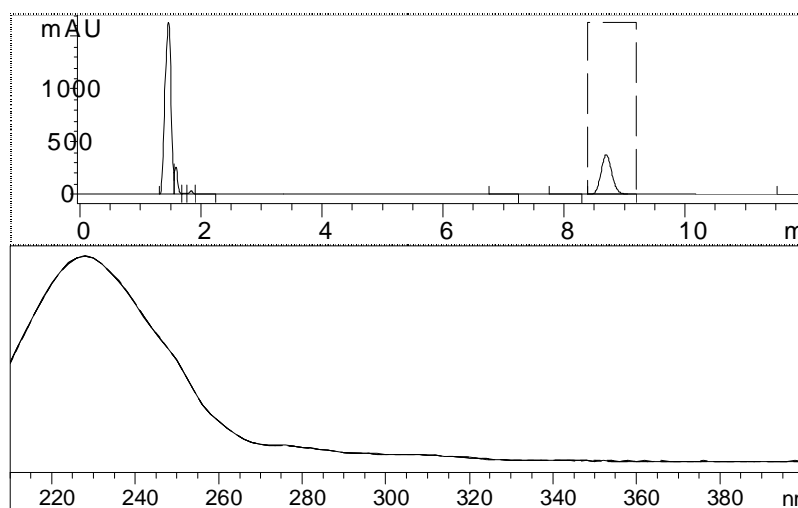
**Table 1. Instrumental parameters for BDE-209 analysis**

Column	Eclipse XDB-C18 (4.6 ×150 mm, 3.5 μm)
Solvent	(1) Toluene and Isooctane (1:9) (2) Acetone
Mobile phase	(1) 97% methanol and 3% Buffer water (pH = 7) with 0.1509 g/100 ml KH <sub>2</sub> PO <sub>4</sub> and 0.2477 g/100 ml Na <sub>2</sub> HPO <sub>4</sub> (2) 100% methanol
Sample injection volume	10 μl
Mobile phase flow rate	1 ml/min

Calibration standards were prepared with mixture of toluene and isooctane (1:9) and acetone. Selected quality assurance quality control indicators were also evaluated, including limit of quantification (LOQ), limit of detection (LOD), method detection limit (MDL), reproducibility (RSD) and accuracy.

### Results and Discussion

With acetone as the solvent and the UV detector set at 230 nm, a single peak could be identified for BDE-209 at approximately 8.7 minutes after injection with 10  $\mu\text{l}$  of BDE-209 standard. The detention time was longer when the toluene-isooctane solution was used to dissolve BDE-209. Calibration standards prepared at 5 - 100  $\mu\text{g/ml}$  and both methods yielded good linear response with  $r^2 > 0.99$ . Repeated analyses with the same calibration standard (5  $\mu\text{g/ml}$ ) yielded measurement precision of 0.1%, limit of detection (LOD) at 3.10  $\mu\text{g/ml}$ , limit of quantification (LOQ) at 3.21  $\mu\text{g/ml}$ , and the method detection limit was 0.06  $\mu\text{g/ml}$ . Measurement with the external standard solution (50  $\mu\text{g/ml}$ ) yielded an accuracy of 97.8%. The analytical capacity was somewhat improved from data reported by Riess and van Eldik.<sup>9</sup>



**Figure 1. Top: UV chromatogram with BDE-209 dissolved in acetone at 10  $\mu\text{g/ml}$ . Bottom: UV-spectra of BDE-209 at various wavelengths, showing best response at 230 nm.**

Studies of PBDE contamination have been reported in soil, sediment, sludge as well as biota. The reported data from human serum and adipose tissue with elevated PBDE suggested that the compounds have somehow entered the human body. In 2006, the International Electrotechnical Commission (IEC) has put in effect new standard for PBDE. Under this new rule, the content of PBDE (except for decaBDE) may not exceed the 1000 ppm limit in the electric and electronic products. Besides the European standards, countries such as Japan, United States and Canada have also proposed their own rules. Because of the new regulatory standards, utility (and thus environmental releases) of PBDEs are expected to decrease. Nonetheless, because of the chemical stability, PBDE levels may continue to persist in the ambient environment. Routine monitoring of the pollutants may be essential to identify potential environmental problems.

As the IEC rule took effect, more efficient analytical method is called for to quickly and accurately identify PBDE (as well as other brominated fire retardants) levels in plastic products, and the use of HPLC/UV has been presented by Schlummer *et al.*<sup>10</sup> and Pöhlein *et al.*<sup>11</sup> Both studies presented method that allows quick analysis of relatively high levels of fire retardants (including decaBDE) in plastic materials. The limits of detection for various PBDE ranged up to 1500  $\mu\text{g/g}$  plastic, which was deemed sufficient for determining compliance of the new IEC limit for PBDE (which is set at less than 1000 ppm m/m). As ambient PBDE (decaBDE) levels are not at as high levels as in the plastics, the above methods may not be appropriate for environmental samples.

Many studies have been reported in the literature for PBDEs in the ambient environment, biota and human tissue.<sup>12,13</sup> Nonetheless, relatively few data were reported for BDE-209 despite its high usage. It was suggested that under certain conditions, BDE-209 may degrade into other congeners, but this is yet to be verified in the ambient environment, and the possibility that instrumental limitation might have caused failure to detect ambient BDE-209 can not be completely ruled out.

Table 2 compares various environmental measurement data for decaBDE. The concentration ranges differed substantially among study areas as well as with environmental media measured. Because of its high melting point and low water solubility, decaBDE is expected to accumulate in soil, sludge and sediment. Nonetheless, as it is used widely in various plastic materials, substantial airborne emissions could result from the waste recycling facility with limited or no emission controls. As shown in Table 2, relatively small amount of sample would be needed for quantification of decaBDE in these sampling media. The estimated amounts of sample needed for analyses are, however, based on assumptions with a high sample recovery rate, which is yet to be determined.

**Table 2. Comparisons of ambient decaBDE levels from selected literatures, and estimated sample amount needed for HPLC analysis**

Reference	Study area and sample source	Reported decaBDE levels	Sample needed*
Watanabe <i>et al.</i> <sup>14</sup>	Osaka, Japan: river sediment	25 - 11600 ng/g	0.5 - 100 g
Allchin <i>et al.</i> <sup>15</sup>	UK, river sediment	1700 ng/g dry weight	2 g
	Netherlands: sediment	200 ng/g dry weight	10 g
Sellström <i>et al.</i> <sup>16</sup>	Stockholm: sewage sludge	140 - 350 ng/g dry weight	5 - 20 g
Bergman <i>et al.</i> <sup>17</sup>	Recycling plant: air (dust)	36 ng/m <sup>3</sup>	55 m <sup>3</sup>
Hoh and Hites <sup>18</sup>	Chicago, USA: ambient air	6 - 30 ng/m <sup>3</sup>	60 - 300 m <sup>3</sup>
Sharp and Lunder <sup>19</sup>	United States: household dust	400 - 7150 ng/g (avg. 2394 ng/g)	1 - 3 g

\* Minimum sample needed for analysis with method presented in this study; assuming >90% sample recovery from solvent extraction with 100 ml solvent, and quantification at ~ 20 µg/ml.

Because of budgetary constraint, we have not been able to collect samples from the ambient environment (e.g., soil, sediment, dust). Nonetheless, by comparing with ambient measurement data from the literature (see Table 2), it was determined that analysis for decaBDE with the HPLC/UV/DAD method may be done with reasonable amount of sample. Currently, laboratory testing is under way for sample extraction procedure as well as evaluation of sample recovery rate, and the environmental sampling campaign is expected to take place in the summer of 2007.

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