

Development of Molecularly Imprinted Sol-Gel SPME Devices for the Determination of Polybrominated Diphenyl Ethers

Maggie Ka-Yi LI¹, Ka-Ho LAM¹, Hongxia YU^{2*}, Michael Hon-Wah LAM^{1*}

¹ Centre for Coastal Pollution & Conservation, Department of Biology & Chemistry, City University of Hong Kong, Hong Kong SAR, China

² State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, China

Introduction. Polybrominated diphenyl ethers (PBDEs) are undoubtedly the most important group of organohalogenated compounds that captures the attention of environmental scientists in recent years. PBDEs are widely used flame retardant additives in polymers and textiles and are present in nearly all of our daily appliances. There are growing evidences that these brominated flame retardants are entering the global ecosystem at a significant rate (de Boer *et al.*, 2000; Ikonomou *et al.*, 2002; Norstrom *et al.*, 2002; Kierkegaard *et al.*, 2004). In order to assess their risk to the environment and public health, their levels in the various environmental compartments have to be closely monitored. This relies on the development of reliable, rapid and sensitive analytical techniques for polybrominated organic compounds. Solid-phase microextraction (SPME) is one of the advanced sampling and sample preparation techniques that are useful in the determination of trace organics in environmental samples (Polo *et al.*, 2004; Salgado-Petinal *et al.* 2006). There are already numerous reports on the use of SPME for PBDE determination in water and solid samples. However, there are still problems to be solved before the technique can be applied to more demanding sample matrices, such as blood plasma. We have examined the applicability of most commercially available SPME coatings in the direct sampling of PBDEs in aqueous media and found them to show rather poor analyte affinity and repeatability, especially towards heavier PBDE congeners. There is a call for the development of new and more robust SPME coatings that possess selective affinity for PBDE congeners. In this context, we explored the feasibility of using molecularly imprinted sol-gel silica films as SPME coatings. A series of ORMOSIL films of various compositions were fabricated and examined for stability under the SPME sampling and GC desorption conditions. The sol-gel silica coating from phenyltrimethoxysilane and tetraethoxysilane (TEOS) is found to be the most suitable candidate. Molecular imprinting of BDE209, the heaviest PBDE congener, into the sol-gel SPME coating can be easily accomplished by dissolving the congener into the sol prior to gelation. The resulting sol-gel SPME coating is found to possess much higher stability and affinity towards PBDE congeners. In this work, we present the detail fabrication procedures for the molecularly imprinted SPME coating and the evaluation of its performance in the determination of BDE209 and other lighter PBDE congeners in various environmental sample matrices.

Materials and Methods. The protective PDMS coating on a 1-cm segment of fused-silica optical fibre was removed by burning with a butane torch. The exposed fused-silica surface was treated with a mixture of aqueous NH₃ / H₂O₂ / H₂O (1:1:5 v/v/v) for 1 hr, rinsed with Milli-Q water, followed by another treatment with a mixture of HCl / H₂O₂ / H₂O (1:1:5 v/v/v) for 30 min. The resultant fused-silica surface was rinsed with Milli-Q and air-dried.

The ORMOSIL sol containing BDE209 templates was prepared from 269 μl of phenyltrimethoxysilane, 107.5 μl of tetraethoxysilane, 112 μl of absolute ethanol, 138 μl of Milli-Q water, 2 μl of trifluoroacetic acid and 20 mg of BDE209 in 80 μl of DMSO. The mixture was vigorously mixed and sonicated for 1 min. and warmed to 70 $^{\circ}\text{C}$ in a water bath for 45 min. before another 1 μl of trifluoroacetic acid was added. The fused-silica optical fibre was dipped into the resultant jelly-like sol for 5 min. followed by air-drying for 7 days. The air-dried ORMOSIL coating on the fused-silica optical fibre was then cured by heating to 120 $^{\circ}\text{C}$ for 2 hr. then 200 $^{\circ}\text{C}$ for 4 hr in a furnace. After cooling to room temperature, the fibre was immersed into a stirring DMSO solution for 12 hr followed by inserting into the GC injector port at 270 $^{\circ}\text{C}$ for 3 hr. No GC peak of BDE209 was observed throughout the baking period. All SPME sampling studies were carried out at room temperature. BDE compound sampled by the SPME device were analysed by an Agilent 6890 GC with a 10 m DB-5MS column and an μECD .

Results and Discussion. Sensitivity of SPME determinations depends on the affinity of the targeted analytes for the SPME stationary phase. Such an analyte-affinity can be expressed by the partitioning coefficient, K_{SPME} , of the analyte between the sample media and the SPME stationary phase:

$$K_{SPME} = \frac{n_S / V_{SPME}}{n_V / V_V}$$

where n_S and n_V are amount of analyte distributed in the SPME stationary phase and the sample media respectively; V_{SPME} and V_V are volume of the SPME stationary phase and the sample media respectively.

In the determination of non-polar organic contaminants, such as PAHs, in water using a non-polar SPME stationary phase, such as PDMS, K_{SPME} can be as high as 10^6 . Very high pre-concentration of analytes can be achieved, resulting in outstandingly low detection limits and relatively small interference. On the other hand, although there are literature reports about the headspace determination of selected PBDEs by SPME with commercially available stationary phases, it remains unclear whether those stationary phases are suitable for measuring the broad spectrum of PBDE compounds. Physical strength of commercially available SPME devices is usually insufficient to withstand frequent and repetitive uses. There are also studies demonstrating that the polyacrylate (PA) stationary phase, which is taken to be the most appropriate SPME stationary phase for PBDE determination, has preference towards the partitioning of small to medium size BDE compounds (tetra- and pentabromodiphenyl ethers) (Polo *et al.*, 2004; Salgado-Petinal *et al.* 2006). Its affinity for heavier BDE compounds is significantly smaller. We used the heaviest BDE congener, BDE209 (decabromodiphenyl ether), to check the extraction efficiency of two commonly adopted commercially available SPME stationary phases, PDMS and PA, for heavy BDE compounds in water. Table 1 show that the partitioning coefficients of BDE209 for the two stationary phases are rather poor.

Table 1 Partitioning coefficients of BDE209 for selected SPME stationary phases

SPME stationary phase	Partitioning coefficient, K_{SPME} *	
	No NaCl added	15% NaCl added
PDMS	2×10^{-2}	17×10^{-2}
PA	7×10^{-2}	21×10^{-2}

Although BDE209 is not as frequently monitored as other smaller BDE compounds in the literature, we pick this BDE compound as our model analyte because: (a) it is one of the mostly used flame retardant additives; (b) preliminary monitoring data show that its level in the coastal aquatic environment is high (Liu *et al.*, 2005; Thomas *et al.*, 2005; Law *et al.*, 2006), and (c) it is known to degrade into other BDE congeners of fewer number of bromine substituents (McDonald, 2002).

In view of the apparent deficiencies of commercially available SPME stationary phases for PBDEs, we developed an organically modified silicate (ORMOSIL) based SPME stationary phase containing special molecularly imprinted receptor sites for PBDE compounds. Molecular imprinting is a template-directed polymerization process that enables the fabrication of rigid and inert polymeric materials with analyte-specific receptor sites without tedious molecular design and synthesis (Bartsch & Maeda, 1998; Komiyama *et al.*, 2003). In fact, there are already few literature examples on the use of molecularly imprinted polymers (MIPs) as SPME stationary phases (Mullett *et al.*, 2001; Fan, *et al.*, 2005). Most of the SPME devices involved were in-tube SPME instead of conventional fibre-type SPME devices. For PBDE determinations, a fibre-type MIP-SPME is more appropriate as it can directly transfer the sampled analytes into the GC injector port. The ORMOSIL matrix of the MIP-SPME coating is sufficiently thermally stable for GC applications (Zheng *et al.*, 2001). This stationary phase coating is formed on a fused-silica optical fibre and the resultant SPME fibres resemble conventional, commercially available SPME devices.

In this work, we chose BDE209 as the molecular template for the fabrication of the MIP-SPME stationary phase. Besides the justifications given above, we proposed that with the imprinting of binding cavities for the largest BDE compound in the ORMOSIL-MIP-SPME stationary phase should also show considerable affinity for other, smaller, BDE compounds. In this way, an ORMOSIL-MIP-SPME stationary phase specialized for the sampling of PBDEs can be obtained. All the optimizations and evaluations of the ORMOSIL-SPME stationary phase were performed in aqueous media.

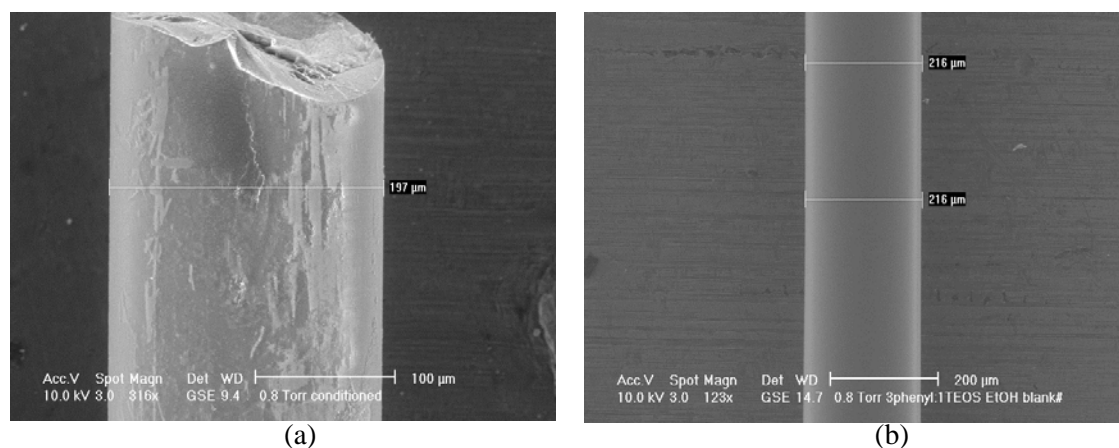


Fig. 1 SEM images of the SPME devices with the ORMOSIL coating: (a) fused-silica optical fibre after surface treatment; (b) an even layer (ca. 9.5 µm thick) of ORMOSIL coating on the fused-silica optical fibre substrate after curing at 120 °C (2 hr) and 200 °C (4 hr) and conditioning at 280 °C for 1 hr.

Using the largest, and probably the most difficult to analysed, BDE209 compound as the molecular template, we are able to fabricate an ORMOSIL-MIP-SPME stationary phase that shows much greater affinity for the heavy BDE compound (ca. 38,000-folds) than commercially available SPME stationary

phases. The ORMOSIL SPME coating also possesses much better physical strength and thermal stability than commercial SPME products. We hope that such an ORMOSIL-MIP-SPME approach can contribute to the more sensitive determination of PBDEs in more complex sample matrices, such as human blood plasma and other biological fluids.

Results will be presented/discussed at the workshop.

Acknowledgement. This work was supported by a NSFC/RGC grant (N_CityU110/05).

Reference.

Bartsch, R. A., Maeda, M. Eds. (1998). American Chemical Society, Washington D. C.

de Boer, J., de Boer, K., Boon, J. P. (2000). In J. Paasivirta ed., *The Handbook of Environmental Chemistry*, Vol. 3, Springer-Verlag, Berlin, Heidelberg, pp. 61 – 95.

Fan, Y., Zhang, M., Feng, Y. –Q. (2005). *J. Chromatogr. A*, 1099, 84 – 91.

Ikonomou, M. G., Rayne, S., Addison, R. F. (2002). *Environ. Sci. Technol.*, 36, 1886 – 1892.

Kierkegaard, A., Bignert, A., Sellström, U., Olsson, M., Asplund, L., Jansson, B., de Wit, C. A. (2004). *Environ. Pollut.*, 130, 187 – 198.

Komiyama, M., Takeuchi, T., Mukawa, T., Asanuma, H. Eds. (2003). Wiley-VCH, Weinheim.

Law, R. J., Allchin, C. R., de Boer, J., Covaci, A., Herzke, D., Lepom, P., Morris, S., Tronczynski, J., de Wit, C. A. (2006). *Chemosphere*, 64, 187 – 208.

Liu, Y., Zheng, G. J., Yu, H., Martin, M., Richardson, B. J., Lam, M. H. W., Lam, P. K. S. (2005). *Mar. Pollut. Bull.*, 50, 1173 – 1184.

McDonald, T. A. (2002). *Chemosphere*, 46, 745 – 755.

Mullett, W. M., Martin, P., Pawliszyn, J. (2001). *Anal. Chem.*, 73, 2383 – 2389.

Norstrom, R., Simon, M., Moisey, J., Wakeford, B., Chip Weseloh, D. V. (2002). *Environ. Sci. Technol.*, 36, 4783 – 4789.

Polo, M., Gómez-Noya, G., Quintana, J. B., Llompart, M., García-Jares, C., Cela, R. (2004). *Anal. Chem.*, 76, 1054 – 1062.

Salgado-Petinal, C., Garcia-Chao, M., Llompart, M., Garcia-Jares, C., Cela, R. (2006). *Anal. Bioanal. Chem.*, 385, 637 – 644.

Zheng, Z., Qiu, W., Huang, Z. (2001). *Anal. Chem.*, 73, 2429 – 2436.