Multivariate Optimization of a Stir Bar Sorptive Extraction-Capillary Gas Chromatography-Mass Spectrometry Method for the Determination of Polybrominated Diphenyl Ethers in Environmental Samples and Printed Board Circuits

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Polybrominated diphenyl ethers (PBDEs) are a group of chemical additives extensively used as flame retardants to reduce the risk of ignition in manufacturing commercial products including plastics, textiles, electrical and electronic equipments (e.g. computers, televisions, etc.), furniture and small motor appliances. Due the extensively use of PBDEs, there has been a growing concern regarding the occurrence of these emerging contaminants in the environment, contributing to human and wildlife exposure [1]. As a consequence of a detailed risk assessment, the European Union has banned the use of penta and octaBDE particularly in new electrical and electronic equipment by July 2006 and several analytical methodologies has been proposed to monitor trace levels of those compounds particularly in environmental matrices.

In the present contribution, SBSE followed by capillary gas chromatography coupled to mass spectrometry (GC-MS) was applied for the first time to the analysis of traces of eleven PBDEs (BDE-47, BDE-100, BDE-99, BDE-85, BDE-154, BDE-153, BDE-183, BDE-197, BDE-196, BDE-207 and BDE-206) in environmental and electronic equipment matrices. In this approach, liquid desorption (LD) was implemented instead of thermal desorption to prevent thermal degradation of the high molecular weight PBDEs congeners [4]. A multivariate optimization strategy was also performed to simultaneously evaluate the most important parameters affecting SBSE-LD efficiency. Randomize complete design established a standard equilibrium time of 240

min, 40% (v/v) of methanol content on a 30 mL aqueous sample stirred at 1250 rpm and room temperature (25°C) followed by ultrasonic back-extraction with acetonitrile during 15 min, as optimal conditions for the determination of PBDEs from different sources. The optimized method using a low sample volume reveals good linearity ($R^2 > 0.997$) within 0.003 and 14.0 µg/L, for all PBDEs studied with the exception for the two higher hydrophobic, BDE-207 and BDE-206. Remarkable accuracy (65.6 - 116.9%) and precision (RSD < 12.1%) were obtained and detection levels ranging from 0.3 to 203.0 ng/L were founded, under optimized conditions. The methodology was applied to real samples including wastewater and sediment matrices and printed circuit boards, using the standard addition approach. In the sediment matrices, BDE-47, BDE-99 and BDE-100 were detected within 0.2 and 0.7 ng/g. In the composition of printed circuit boards, BDE-207, BDE-183 and BDE-206 appear as the major congeners at concentrations ranging from 297.0 to 675.0 ng/g [5].

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References

[1] F. Rahman; K.H. Langford; M.D. Scrimshaw; J.N. Lester, *Sci. Total Environ.* 2001, 275, 1-17.

[2] Directive 2003/11/EC amending Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether), European Council, Brussels, Belgium, 2003.

[3] Decision No 2455/2001/EC establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC, European Council, Brussels, Belgium, 2001.

[4] GC Sample Preparation by mouse-click, Gerstel worldwide solutions nº5, 2005.