

SIMPLE APPROACH BASED ON DISPERSIVE LIQUID-LIQUID MICROEXTRACTION TECHNIQUE FOR DETERMINATION OF POLIBROMINATED FLAME RETARDANTS IN WATER SAMPLES BY GC-MS/MS



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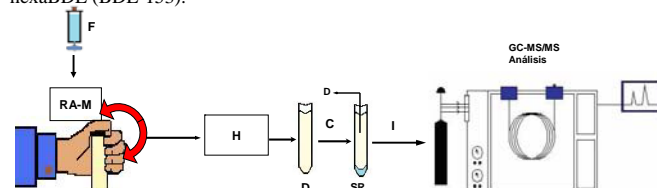
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INTRODUCTION

Polibrominated flame retardants (PBDEs) represent an important group of flame retardants additives, which are considered environmental persistent pollutants. PBDEs have a strong non-polar character, which makes them bioaccumulate in biota, reaching thus animals and humans via their food chain. Due to the low solubility of PBDEs in water, the concentration level of these analytes is generally low in this type of sample. Therefore, it is necessary to count on highly efficient and reliable pre-concentration techniques for their determination by GC. In this sense, new extraction techniques, especially in the microextraction category, have gained interest. In this work, it was developed and validated a dispersive liquid-liquid microextraction (DLLME) technique for extracting and preconcentrating PBDEs in water samples prior to their determination by GC-MS/MS.

MATERIAL AND METHODS

DLLME was applied for extraction and preconcentration of PBDEs. To this end, and based on PBDEs relative abundance in environmental samples, four target PBDEs were selected from the 209 possible congeners, which are the most studied in this type of samples: 2,2',4,4'-tetraBDE (BDE-47), 2,2',4,4,5-pentaBDE (BDE-100), 2,2',4,4,6-pentaBDE (BDE-100), and 2,2,4,4',5,5'-hexaBDE (BDE-153).



Schematic diagram of the extraction, preconcentration and analysis system. F: 100 mL of each sample is filtered through 0.22 μm pore size membrane filters. RA-M: Addition of 1 mL of acetone (disperser solvent) containing 20 μL of carbon tetrachloride (extraction solvent) to 5 mL of filtered sample containing 140 μL 6.15 mol L^{-1} NaCl and mixing. H: Thermostating at 35 $^{\circ}\text{C}$ for 5 min. C: Centrifugation. SR: supernatant removing. I: Injection of 1 μL of supernatant carbon tetrachloride phase into the GC-MS.

Table 1
GC-MS/MS parameters and physicochemical properties of target PBDEs

Analyte	RTT (min)	Target ion (m/z)	Confirmation ions (m/z)	b.p. ($^{\circ}\text{C}$)	Log Kow
BDE-47	0.80	485.7	483.7, 325.8	396	6.81
BDE-100	0.89	403.7	563.6, 405.7	434	7.24
BDE-99	0.92	403.7	563.6, 405.7	416	7.32
BDE-153	1.08	483.6	643.5, 485.6	453	7.90

RRT: relative retention times to PCB-209 (IS)

b.p.: boiling point

logKow: octanol/water partition coefficient

RESULTS

The proposed analytical methodology was applied for the analysis of PBDEs in environmental water samples. Several factors affecting DLLME were studied and optimized. Figures 1-3.

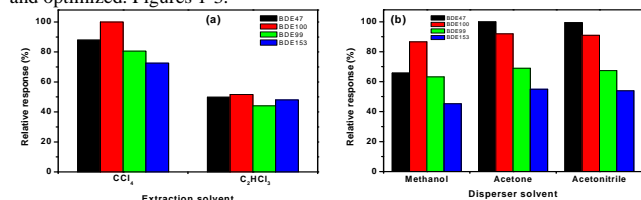


Figure 1: a) Extraction solvent effect on the relative response of target PBDEs.

b) Disperser solvent effect on the relative response of PBDEs.

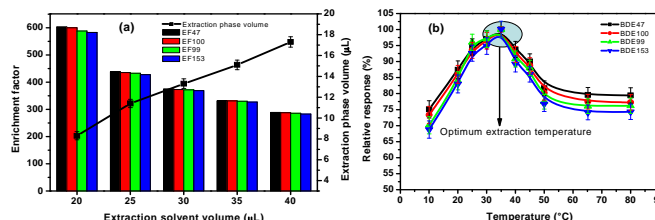


Figure 2: a) Relation between the CCl_4 added, extraction phase volume and the enrichment factor of analytes. **b)** Effect of extraction temperature on the relative response of PBDEs.

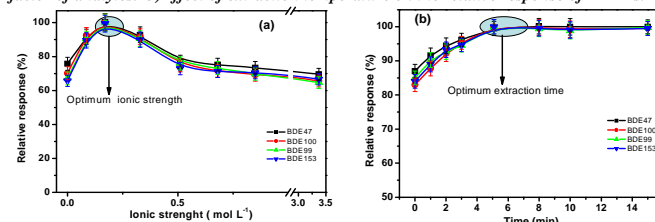


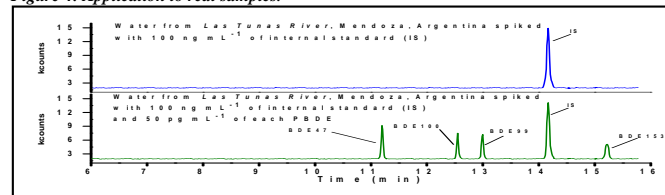
Figure 3: a) Effect of ionic strength on the relative response of PBDEs analyzed by DLLME-GC-MS/MS. **b)** Effect of extraction time on the relative response of PBDEs.

Table 2
Analytical performance of the proposed method^a

PBDEs	RSD (%)	Linear Range (pg mL^{-1})	r^2	LOD (pg mL^{-1})	EF ^b	R % ^c
BDE-47	9.4	2.0-1000	0.9993	0.2	603	96
BDE-100	10.7	2.0-1000	0.9995	0.4	600	103
BDE-99	12.1	2.0-1000	0.9991	0.3	588	97
BDE-153	12.9	2.0-1000	0.9998	0.2	583	104

^a95% confidence interval; n=5, ^bEnrichment factor, ^cRecovery in river water sample spiked with 20 pg mL^{-1} of each PBDE.

Figure 4: Application to real samples.



CONCLUSIONS

Remarkable analytical characteristics of the proposed methodology:

- Quantitative extraction of PBDEs with high enrichment factor.
- LODs in the order of low picogram per millilitre with an acceptable precision.
- LODs useful for real world applications.
- The absence of matrix effects allowed performing the quantification by using external standard calibration. This fact simplified the quantification routine improving the through put sample of the methodology.
- Other characteristics: low organic solvent consumption, which turns it into a low cost and environmental friendly technique.

ACKNOWLEDGEMENTS

