

# APPLICATION POTENTIAL OF MICROEXTRACTION IN PACKED SYRINGE COUPLED WITH GAS CHROMATOGRAPHY TIME-OF-FLIGHT MASS SPECTROMETRY IN ANALYSIS OF BROMINATED FLAME RETARDANTS IN WASTE WATER

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## Introduction

In last years, miniaturized analytical techniques had gained attention due to its many special features over classical approaches. Among many advantages, usage of little or no solvent, increasing of sensitivity of analysis and user-friendly system, should be pointed out. Microextraction in packed syringe (MEPS) is a new technique for miniaturized solid-phase extraction that can be connected online to gas chromatography (GC) or liquid chromatography (LC) without other sample pre-treatment.<sup>1-4</sup> In MEPS, approximately 1mg of the solid packing material (usually silica based C2, C8, C18) is inserted into a syringe (100–250  $\mu\text{L}$ ) as a plug. The sample (10–250  $\mu\text{L}$ ) is withdrawn through the syringe by an autosampler. When the sample has passed through the solid support, the analytes are adsorbed to the solid phase packed in a barrel insert and needle (BIN). The solid phase is washed afterwards by water to remove any interfering material, and the elution of analytes is performed directly into the instrument's injector by organic solvent (in case of GC), or the LC mobile phase. The large injected volume, typically from 10 to 50  $\mu\text{L}$ , may imply the use of programmed temperature vaporiser (PTV) and large volume injection (LVI). Moreover, large variety of special packed materials in BIN, such restricted access material (RAM) or molecular imprinted polymers (MIPs), can be used.<sup>5</sup>

In this work we aimed to evaluate new MEPS sample preparation approach in analysis of polybrominated flame retardants (BFRs). The best microextraction settings has been optimized in order to obtain fast and reliable analytical methods for routine control of water samples. Appraisal of mentioned technique with respect to the cost and time demands was also done.

## Materials and Methods

Standard solutions containing polybrominated dibenzo diethers (PBDE) congeners (concentration 50  $\mu\text{g mL}^{-1}$  in nonane) are 2,4,4'-triBDE (BDE-28); 3,4,4'-BDE (BDE-37); 2,2',4,4'-tetraBDE (BDE-47); 2,2',4,5'- tetraBDE (BDE-49); 2,3',4,4'- tetraBDE (BDE-66); 2,2',3,4,4'-pentaBDE (BDE-85); 2,2',4,4',5-pentaBDE (BDE-99); 2,2',4,4',6-pentaBDE (BDE-100); 2,2',4,4',5,5'- hexaBDE (BDE-153); 2,2,4',4,5',6'-hexaBDE (BDE-154) and 2,2',3,4,4',5',6-heptaBDE (BDE-183). All were obtained from Cambridge Isotope Laboratories ( $\geq 98\%$  pure; CIL, Andover, MA, USA). Stock standard solutions were prepared in isooctane and were stored in a refrigerator (5°C). From the stock solution a dilution was made in isooctane to obtain 500 and 100  $\mu\text{g L}^{-1}$  mixed standards. The calibration was prepared using spikes into the blank water at the concentration range from 0.1 to 100  $\mu\text{g L}^{-1}$  (0.1, 1, 10, 50, 100  $\mu\text{g L}^{-1}$ ). Prior addition of the water (1 mL), appropriate volume of mixed isooctan standard was gently dried by nitrogen stream.

Real life samples were obtained from a local water treatment facility (Prague, CZ) and filtered through polytetrafluoroethylene filters (PTFE, 5  $\mu\text{m}$ ; National Scientific, USA) prior performing MEPS. The schematic view of sample preparation used within presented work is shown in Figure 1. MEPS was performed using 1mg of solid-phase material (silica-C18) inserted into a 250  $\mu\text{L}$  gas-tight syringe. The packed syringe was conditioned first with methanol and then with water (50  $\mu\text{L}$ ) before being used for the first time. The water sample was drawn through the syringe 50 times (50  $\mu\text{L}$  each) by the autosampler. The analytes were then eluted with 15  $\mu\text{L}$  of isooctane directly into the GC injector. MEPS was cleaned using isooctane and methanol (10 times 75  $\mu\text{L}$  each), to avoid any carry-over. The schematic view of the whole MEPS process is shown in Figure 1.

A Pegasus 4D instrument (Leco, St Joseph, MI, USA) consisting of an Agilent 6890N gas chromatograph equipped with a PTV Inlet (Agilent Technologies, Palo Alto, CA, USA) and a Leco Pegasus III high-speed time-of-flight mass spectrometer (TOF MS) was used for the experiments. A 15 m × 0.25 mm i.d., 0.1 µm film thickness, DB-XLB column (Agilent Technologies) was used for separation of sample components. The oven temperature was held at 80 °C with 2 min then programmed at 50° min<sup>-1</sup> to 320 °C which was held for 6 min. The carrier gas (helium) flow was held at 1.5 mL min<sup>-1</sup> (7.2 minutes) and ramped (50 mL min<sup>-1</sup>) to 3 mL min<sup>-1</sup>. The PTV conditions were: multi baffled deactivated PTV liner (Agilent Technologies, 2 mm i.d., 150 µL volume), injection volume 15 µL, vent flow 50 mL min<sup>-1</sup>, vent time 1 min and vent pressure 50 p.s.i. The injector temperature was set at 50 °C and after the vent period the temperature was raised by 400 °C min<sup>-1</sup> to 300 °C. The interface temperature was 280 °C. The MS acquisition rate was 11 Hz, the mass range 35–850 amu, the ion-source temperature 300 °C, and the detector potential -1875 V. A typical chromatogram of spiked water sample analyzed by MEPS-GC TOF MS is shown in Figure 2.

## Results and Discussion

The performance characteristics of MEPS-GC TOF MS method applied for analysis of water are summarized in Table 1. The recovery was measured as the response of a spiked water sample expressed as analytes peak area compared to that of pure standard solution (100 µg L<sup>-1</sup>). To increase the sensitivity of the method, the sample was pumped up and down through the syringe 50 times by the autosampler with a speed of 35 µL s<sup>-1</sup>. The extraction time was approximately 4 min and the recoveries for all BFRs were above 70%. The limits of detection (LOD), defined as the lowest detectable concentration (S/N≥3), was ranging from 0.5 to 9.5 ng L<sup>-1</sup>. The limits of quantification (LOQ) were estimated as a lowest calibration level (LCL). This value corresponded to the lowest standard (100 ng L<sup>-1</sup>) prepared for validation purposes. At this particular concentration measured signal-to-noise ratio was ranging from 30 (BDE-183) to 600 (BDE-28), which indicated, that LOQs could be further decreased. This fact proved, that coupling MEPS with PTV-GC TOF MS would express good potential for quantification of BFRs at their native concentration range (10<sup>0</sup> - 10<sup>1</sup> ng L<sup>-1</sup>) in releases of a waste water treatment plant effluent or sewage water.<sup>6,7</sup> The ability of the presented technique to determine BFRs in real life samples was tested by analyzing water obtained from local sewerage plant. It should be noted that the trace level target analysis as well as analysis of unknown sample components could be facilitated when working with TOF mass spectrometers due to their excellent confirmation power.<sup>8</sup> As an example, the identification of BDE-28 is documented in Figure 3. The full mass spectrum obtained as a result of electron ionization (70 eV) was obtained after automatic spectral deconvolution.

Presented results showed new possible concepts in rapid water analysis by employing MEPS. This approach minimizes sample handling and reduces time/cost of measurement. In addition to qualitative information regarding brominated compounds provided by TOF MS, quantification at tens ng L<sup>-1</sup> could be potentially performed. Further tests will be facilitated in order to widen spectrum of environmental contaminants (other poly-halogenated compounds, pesticides) analyzed by MEPS-GC(× GC) TOF MS.

## Acknowledgements

This study was undertaken within the project MSM 6046137305 supported by the Ministry of Education, Youth and Sports of the Czech Republic. The authors wish to thank to SGE Analytical Science for a loan of the MEPS system for testing purpose

## References

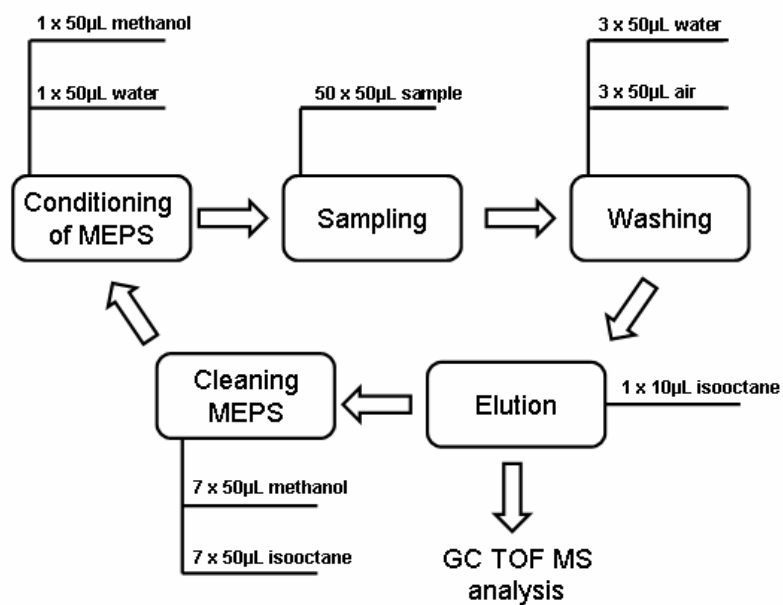
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**Table I. Selected method performance characteristics of BFRs analyzed using MEPS-GC TOF MS.**

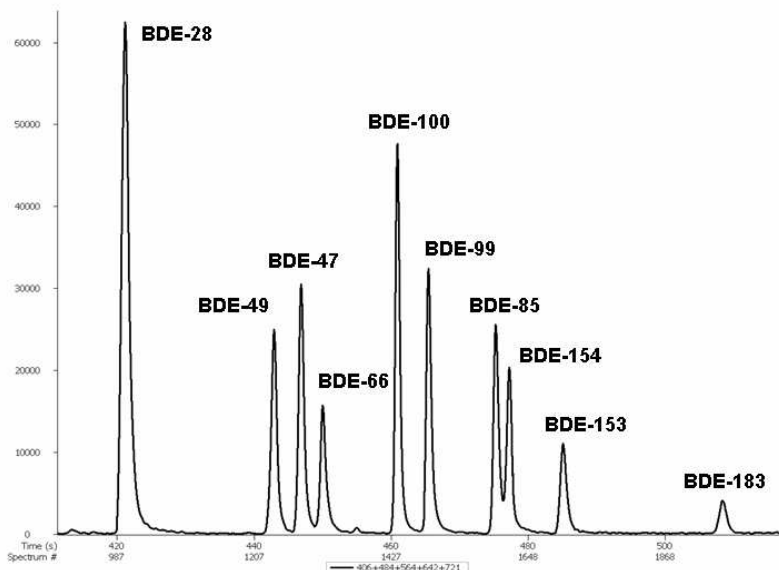
| Compound | Regression coefficient (R <sup>2</sup> ) | LOD (ng L <sup>-1</sup> ) | LOQ (ng L <sup>-1</sup> ) <sup>1</sup> | RSD (n=3, 100 µg L <sup>-1</sup> , %) | Recovery (n=3, 100 µg L <sup>-1</sup> , %) |
|----------|------------------------------------------|---------------------------|----------------------------------------|---------------------------------------|--------------------------------------------|
| BDE-28   | 0.9987                                   | 0.5                       | 100                                    | 2                                     | 108                                        |
| BDE-47   | 0.9954                                   | 2                         |                                        | 4                                     | 84                                         |
| BDE-49   | 0.9891                                   | 2.5                       |                                        | 5                                     | 89                                         |
| BDE-66   | 0.9930                                   | 3.5                       |                                        | 3                                     | 91                                         |
| BDE-85   | 0.9912                                   | 1.5                       |                                        | 4                                     | 74                                         |
| BDE-99   | 0.9854                                   | 2.5                       |                                        | 5                                     | 84                                         |
| BDE-100  | 0.9900                                   | 3                         |                                        | 5                                     | 86                                         |
| BDE-153  | 0.9827                                   | 4                         |                                        | 4                                     | 72                                         |
| BDE-154  | 0.9819                                   | 4.5                       |                                        | 7                                     | 74                                         |
| BDE-183  | 0.9802                                   | 9.5                       |                                        | 12                                    | 82                                         |

<sup>1</sup>Expressed as a lowest calibration level.

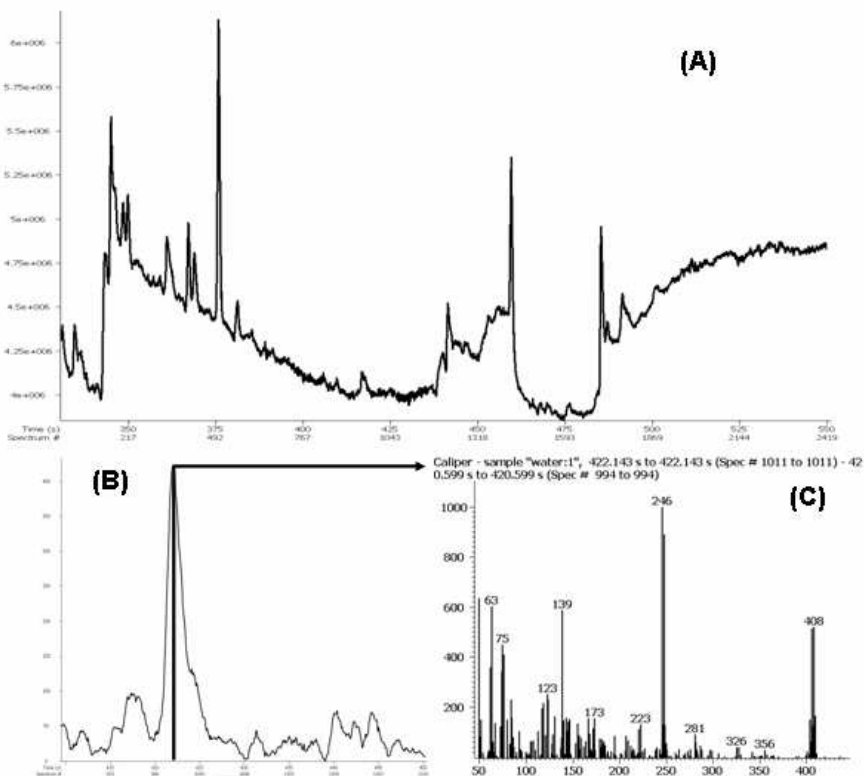
**Figure 1: Schematic view of the MEPS sample preparation process in analysis of sewage water.**



**Figure 2: MEPS-GC TOF MS analysis of sewage water spiked with BFR at level 1  $\mu\text{g L}^{-1}$  - chromatogram with selective BFR masses is displayed.**



**Figure 3: MEPS-GC TOF MS analysis of sewage water sample.**



**(A) TIC chromatogram of sewage water.**

**(B) Zoomed part of chromatogram – masses 406+408 are displayed.**

**(C) Measured mass spectrum of natively present BDE-28**