



## Application Note GCMS-02

# The analysis of polybrominated diphenyl ether flame retardants by GC-MS/MS

### Abstract

A study was carried out using the Bruker EVOQ GC-TQ triple quadrupole gas chromatography mass spectrometer (GC-MS/MS) in multiple reaction monitoring mode (MRM) to analyse ocean sediment and sewage outfall extracts for polybrominated diphenyl ether (PBDE) flame retardants. The calibration range, method detection limits and precision were all determined on the EVOQ GC-TQ, which demonstrated excellent sensitivity and discrimination against matrix interferences in difficult extracts prepared with little or no clean-up.

### Introduction

PBDEs have been commonly used as flame retardants in a wide array of products, including plastics, building materials and textiles. Studies in Canada have found significant concentrations of PBDEs in foods such as salmon, butter, cheese and ground beef. High levels of PBDEs have also been found in indoor dust, sewage sludge and effluents from wastewater treatment plants, with increasing levels being detected in the blood of marine mammals including harbor seals.

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There is increasing concern as to the environmental and health effects caused by PBDEs. These compounds are very stable and will bio-accumulate in tissues and breast milk and have been shown to be related to increased infertility rates in humans, at levels that are normally found in US households. As a result stringent regulations have been placed on the manufacture, import or use of PBDEs by the US EPA.

A variety of methods for the analysis of PBDEs exist, including high-resolution gas chromatography mass spectrometry (HR-GCMS), gas chromatography with electron capture detector (GC-ECD) and GCMS. Although HR-GCMS is very specific, it is expensive and requires highly skilled technicians, which is disadvantageous for a laboratory performing routine analysis and quality control (QC). However both GC-ECD and GC-MS can be subject to interferences, particularly in samples that are prepared with little or no clean-up.

Tandem triple quadrupole GC-MS in multiple reaction monitoring mode is an ideal technique for the analysis of PBDEs, as it is easy to set up and can discriminate effectively against matrix with trace level detection. The Bruker EVOQ GC-TQ has several advanced developments that further improve sensitivity and instrument robustness, including the axial ion source and lens-free ion path. In this study the EVOQ GC-TQ was used to determine calibration range, method detection limits and precision, along with the analysis of ocean sediment and sewage outfall extracts.

## Experimental

A 15 M column was chosen to minimize thermal degradation of BDE-209 and yet maintain good separation of all PBDEs studied. The calibration and instrument detection limits were determined prior to the analysis of ocean sediment and sewage outfall. The calibration standards were prepared in dichloromethane with concentration range of 0.1 to 50 ppb. Instrument detection limits (IDLs) were performed by analysing seven replicates at 0.1 ppb, prepared in dichloromethane.

10 g of ocean sediment was extracted in 50:50 DCM: Acetone with an accelerated solvent extraction technique (ASE) at 2000 psi and 125°C. The extracts were dried with sodium sulphate and evaporated to 1 mL without any further clean-up. 1 L of sewage outfall was prepared by continuous liquid-liquid extraction (CLLE) with DCM, dried and concentrated to 1 mL. Both extracts were highly coloured, as seen in Figure 1.

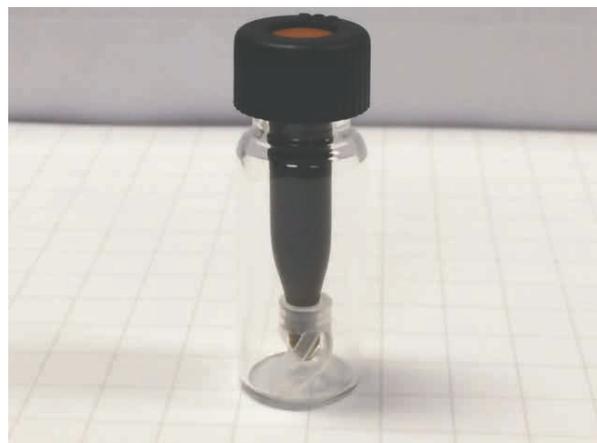


Figure 1: Ocean sediment (top) and sewage outfall (bottom).

The following instrument parameters were used:

Column: BR-5ms, 15 M x 0.25 mm id x 0.25  $\mu$ m; Carrier gas: Helium at 1.0 mL/min; Oven: 60°C (2 min), at 50°C/min to 150°C (1 min), at 10°C/min to 325°C (hold 8 min); Injection: 2  $\mu$ L pulsed splitless @ 280°C with 4.0 mm ID fritted liner; Ion source: EI @ 250°C; Transfer line @ 280°C

## Results and Discussion

The average relative standard deviation (%RSD) and  $r^2$  for the calibration of all compounds was 9.1% and 0.998 respectively. For the PBDEs, IDLs ranged from 0.01 to 0.54 ppb with mean of 0.1 ppb and average %RSD of 8.3%.

Matrix interference was not observed in the extracts, as can be seen in Figure 2, for the transitions studied. The MRM chromatograms for the ocean sediment and sewage outfall matrix spikes are virtually identical with no background peaks or elevated baselines.

However, recoveries for some PBDEs were highly biased either due to the presence of the compound in the unspiked sample and/or the result of matrix enhanced chromatographic response, which can be minimized by 'charging' the injector liner and column with the matrix prior to instrument calibration.

Decabromodiphenyl ether (BDE-209) sensitivity and precision can be further improved with the use of a thinner phase and even shorter column to reduce elution temperature, thus minimizing thermal degradation. However, care must be taken to ensure good separation of PBDE brominated isomer groups for accurate quantitation.

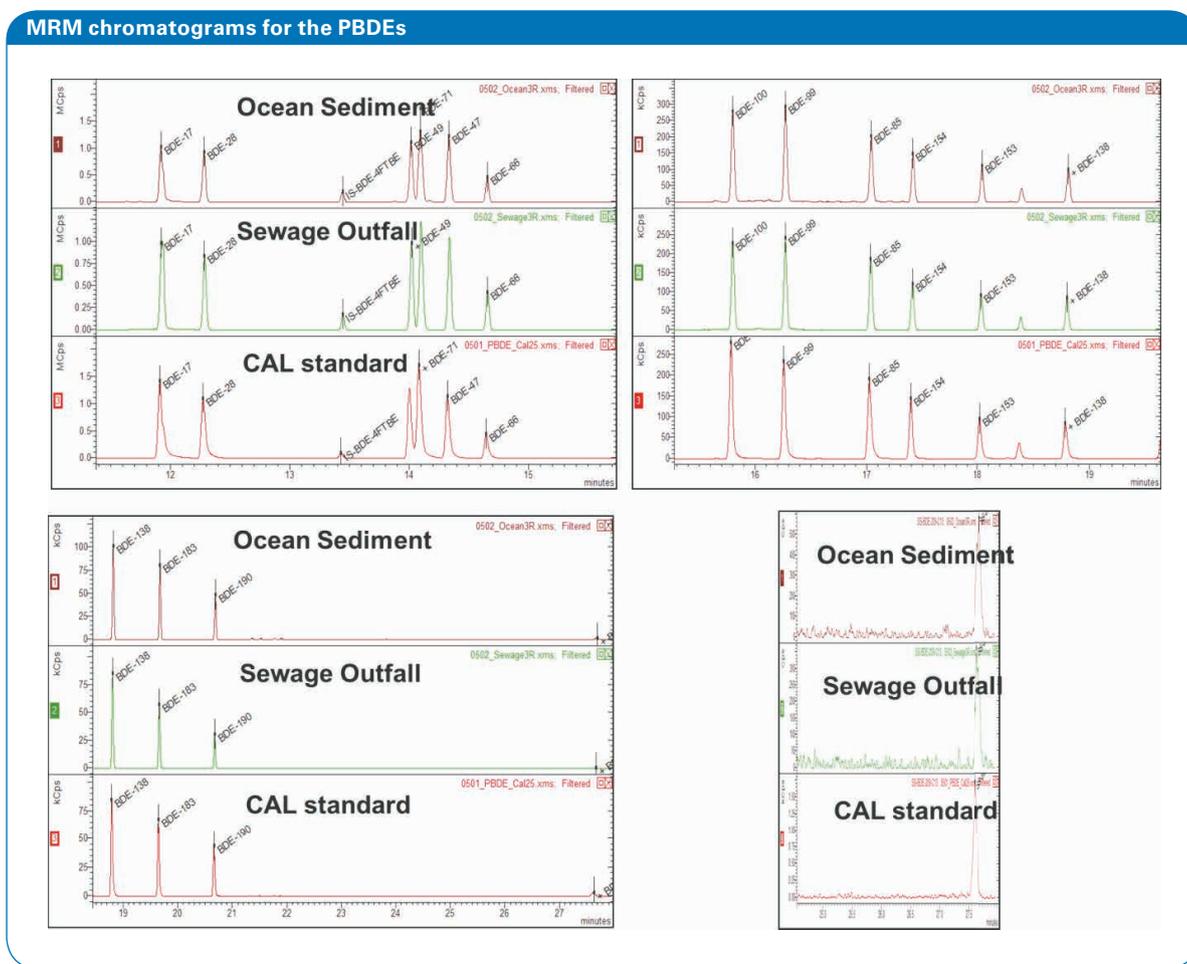


Figure 2: MRM chromatograms for the PBDEs in the two matrices studied (sewage and ocean sediment) compared to the calibration standard in pure solvent.

## Conclusion

The Bruker EVOQ GC-TQ triple quadrupole gas chromatography mass spectrometry system in MRM mode allowed for the analysis of PBDEs at very low concentrations, with easy instrument set-up.

Excellent sensitivity and discrimination were achieved against matrix interferences in difficult extracts prepared with little or no sample clean-up.

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