RAPID ANALYSIS OF POLYBROMINATEDDIPHENYLETHERS USING SIMULTANEOUS DUAL COLUMN GAS CHROMATOGRAPHY – HIGH RESOLUTION MASS SPECTROMETRY

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Introduction

Polybrominated diphenyl ethers (PBDEs) are an example of flame retardant compounds. They are used in plastics, electronic circuitry and textiles to prevent combustion. PBDEs are lipophilic and have structures similar to those of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs). PBDEs are persistent and certain congeners have been shown to bioaccumulate[1]. Technical PBDEs are produced by brominating diphenyl ether under catalytic conditions resulting in a mixture of brominated diphenyl ethers with varying degrees of bromination. The three main commercial products are Pe-BDE (penta-), Oc-BDE (octa-) and De-BDE (deca-) formulations which is the most common PBDE formulation in use.

Similar to PCBs there are 209 congeners in the PBDE family with the same substitution pattern. However, unlike PCBS, the molecular weight distribution of PBDEs ranges between 240 and 970 amu, which is relativelt difficult to analyse using a single capillary column. Many analysts presently perform analysis of PBDEs using two analytical runs[2], one for mono- to hepta- BDE and the other for octa- to deca-BDE. The second analytical run is performed on a short capillary column to facilitate the rapid elution of the compound. The use of simultaneous dual column chromatography for the analysis of PCBs and PCDD/Fs has been demonstrated[3] saving time and cost. The use of narrower bore and thinner film thickness (microbore) columns has been investigated[4] and it has been shown that analysis times may be shortened considerably with little loss, if any, of chromatographic resolution. In fact, some combinations of bore and film thickness have been shown to actually improve the number of theoretical plates in a column whilst at the same time reducing analysis time by half. The application of both of these techniques to PBDE analysis is presented here

Method

Lake trout CRM was extracted according to Alaee et al[5]; in short 10 g of homogenized wet tissue were Soxhlet extracted with 250 mL of dichloromethane. Extracts were dried by passing them through sodium sulphate and concentrated to 2-5 mL with rotary evaporation. Lipids were removed by size-exclusion chromatography. The second 100 mL fraction eluted was solvent exchanged into hexane and concentrated to 2-5 mL with rotary evaporation. The extract was fractionated on silica gel as described below.

Lake Ontario surface sediment was collect in October 2001 from station 41 (43°42'58"N, 78°01'35"W) using a ponar sampling technique. The surface sediment samples were transferred to pre-

cleaned jars and were frozen in field and shipped frozen to the laboratory for analysis. Surface sediment samples were freeze-dried, and 10 g of sample was extracted 3 times with DCM at 100 °C and 2000psi. The extract volume was reduced using rotary evaporator, and nitrogen evaporator. The extract was subsequently fractionated using 8 g of 100 % activated 60-mesh silica gel. Two fractions were collected, first fraction was eluted with 65 mL of hexane, and the second fraction was eluted with 75mL of 1:1 DCM/Hexane.

All sample data were acquired using voltage SIR.

Single column GC-MS

A mixture of 42 PBDEs (including PBDEs 47, 66, 77, 100, 99 and 85) were analysed on the above GC-MS system utilising a J&W DB5-MS 60m x 0.25 mm ID, 0.25 ìm df column only (1 ìl injections) to obtain detection limits for these compounds. Standards ranging from 25 fg /ìl to 500 pg/ìl were prepared. The GC operating conditions were as follows:

Injector 280 °C, splitless, 1 min purge time. He carrier gas, 1.0 ml/min constant flow.

GC oven program:

Time	Rate (°C/min)	Temp (°C)
1.0	0.0	140
1.0	20.0	280
5.0	5.0	320

Dual column GC-MS

Analysis was performed using an Agilent 6890+ GC coupled directly to a Micromass AutoSpec Ultima-NT HRMS. A CTC GC-PAL autosampler was utilised to perform the sequential injections of 1ìl (0.18 mm column) or 0.2 ìl (0.1 mm column) of the same sample onto each of the columns. The columns were installed into the two split/splitless injectors of the GC. The two GC columns used were a J&W DB5-MS, 20 m x 0.1 mm ID, 0.1 ìm df (front injector) and a J&W DB5-MS 40 m x 0.18 mm ID, 0.18 ìm df (rear injector). The acquisitions were performed using MassLynx with CTC Cycle Composer software control of the autosampler performed from within MassLynx.

The autosampler was controlled in such a way that there was a delay of the injection onto one of the columns so that the elution of BDE-209 was after the elution of the nona-BDEs from the other analytical column.

Results and discussion

High resolution mass spectrometry has the advantages of being very selective in analysis and, when used in the voltage SIR mode, extremely high sensitivity. Figure 1 shows a voltage SIR chromatogram for 3 BDEs (47, 77 and 66) for only 25 fg injected. The signal to noise for the BDE 47 peak (Peak to Peak, ± 2 s.d., raw, unsmoothed data) using the single 60m column method was found to be 12.5 for 25 fg injected. By extrapolation, this would give an LoD, based on 3 times signal to noise, of approximately 6 fg injected. This LoD increased as the level of bromination increased. The dual column method was developed to give a similar LoD but with improved productivity.

HRMS also has a very wide dynamic range as illustrated in Figure 2 which shows a typical calibration curve for BDE 47 from 25 fg to 500 pg.

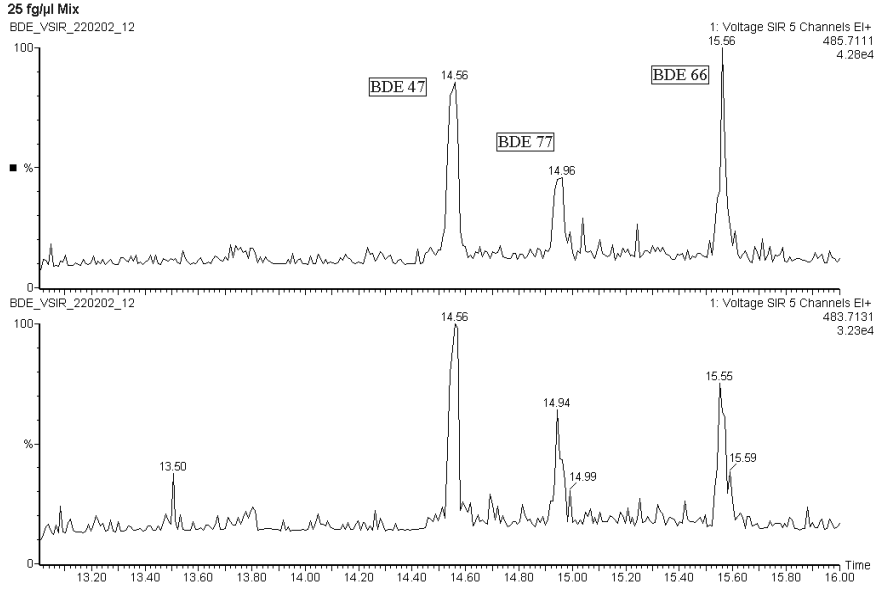

Figure 1. 25 fg injection of PBDEs 47, 77 and 66.

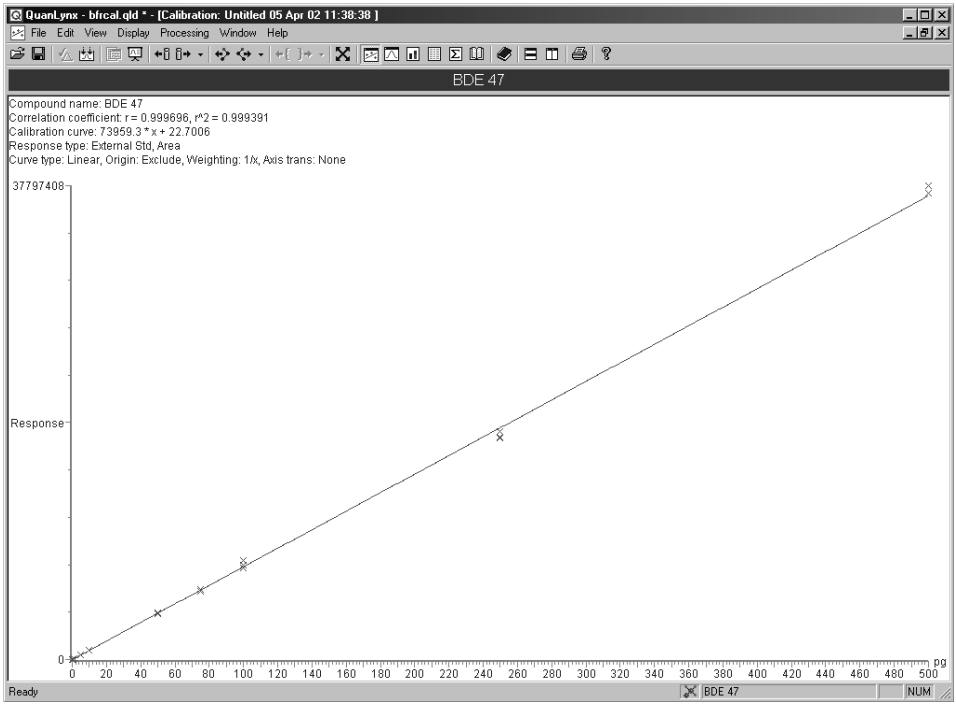

Figure 2. Calibration curve for BDE 47 from 25 fg to 500 pg.

ANALYSIS II

It is also possible, when using GC-MS techniques (as opposed to ECD for example) to use isotope labelled standards as internal standards which behave identically to the native analytes during extraction and clean-up. The use of these standards has been extensive in dioxin and PCB analysis, and it seems appropriate to extend the use of isotope dilution to the analysis of PBDEs.

Using a single 60m capillary column for analysis of PBDEs gives long analysis times. The use of microbore capillary columns drastically reduces these analysis times. By judicious selection of capillary columns and optimistation of GC conditions it is possible to use two such microbore columns simultaneously to achieve in one short analytical run an analysis that would previously have required two; one much longer run and a similar length second analysis.

The use of the two narrow bore/thin film columns here has not only demonstrated that analysis time may be reduced per column but also that by use of two columns and optimised chromatography that significant savings on time of analysis per sample may be realised.

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