Optimization of Parameters for the Analysis of the Deca-brominated Diphenylether using PTV and split/splitless Injectors and the consecutive Setup of a Dual Column Analysis Method

Dirk Krumwiede[1], Helmut Muenster[1], Jens Griep-Raming[1]

[1]Thermo Electron corporation, Bremen

Introduction

Brominated diphenyl ethers (BDEs) are widely used as flame retardants in electronics industry. However, for the following reasons the mass spectrometric analysis of BDEs by high resolution magnetic sector mass spectrometry is more complicated than e.g. analysis of polychlorinated dioxins and furans: i) a high mass range from m/z 248 (mono-BDE) to m/z 960 (deca-BDE) is required, therefore demanding a reference compound that provides sufficient intensity on high m/z ions, ii) large electric jumps are necessary for window defining measurements, which demands for a stable and rugged electric mass calibration, and iii) the Deca-BDE being thermally labile, requiring optimized chromatographic methods. The first and second complication can be overcome by the correct selection of instrument parameters and by proper selection of the reference compound. Probably the most severe complication is that the deca-BDE is thermally labile, and decomposes during GC analysis. Optimized chromatographic parameters are needed in order to achieve good sensitivity for deca BDE. However, such chromatographic parameters usually sacrifice separation efficiency for the other congeners.

In the following it will be shown how different chromatographic parameters influence the analytical sensitivity for the thermolabile deca BDE. Furthermore a method setup is presented, which combines optimum sensitivity for the deca BDE and at the same time good separation efficiency for mono to hepta BDE.

Materials and Methods

All analyses were carried out on a Finnigan MAT 95 XP magnetic sector mass spectrometer (Thermo Electron Corp.) coupled to a Finnigan Trace GC Ultra gas chromatograph (Thermo Electron), equipped with a split/splitless and a PTV injector. Samples were injected using a GC PAL autosampler (CTC Analytics, Zwingen, CH). 1ul of each sample was injected. J&W DB-5ms GC columns (Agilent Technologies,) with the following dimensions were installed inside the GC as single columns: i) 30m, 0.25mm ID, 0.1um film thickness and ii) 15m, 0.25mm ID, 0.1um film thickness, attached to a PTV or split/slitless injector .

For a dual column setup the above mentioned 30 m DB5 column together with a 6 m, 0.2 mm, 0.1um film (Optima5; Macherey Nagel) were attached to the transfer line of the mass spectrometer by a custom-designed Y-shape adaptor. Both columns were directly introduced into the ion source of the mass spectrometer (MS). The ion source of the MS had been modified to allow for insertion of two GC columns. Calibration solutions for the BDEs were obtained from Wellington Laboratories, Ontario, Canada.

Results and Discussion

A number of chromatographic parameters and their effects on the analytical response for the deca BDE have been investigated in this study.

The mass traces in figure 1 and figure 2 show hexa BDE together with the deca BDE, thus the relativ intensity of the deca can be easily verified. It could be shown that the oven temperature at the elution time of the compound is the decisive factor for the analysis sensitivity of the deca congenere. In figure 1 the elution temperature for deca BDE is 319 ºC in the upper trace and 330 ºC for the trace below. In Figure 2 the deca congenere eluted at 322 ºC from the 15 m column and at 330 ºC from the 30 m column respectively. By increasing the column flow the elution temperature on a 15 m column could be further decreased to 314 ºC.

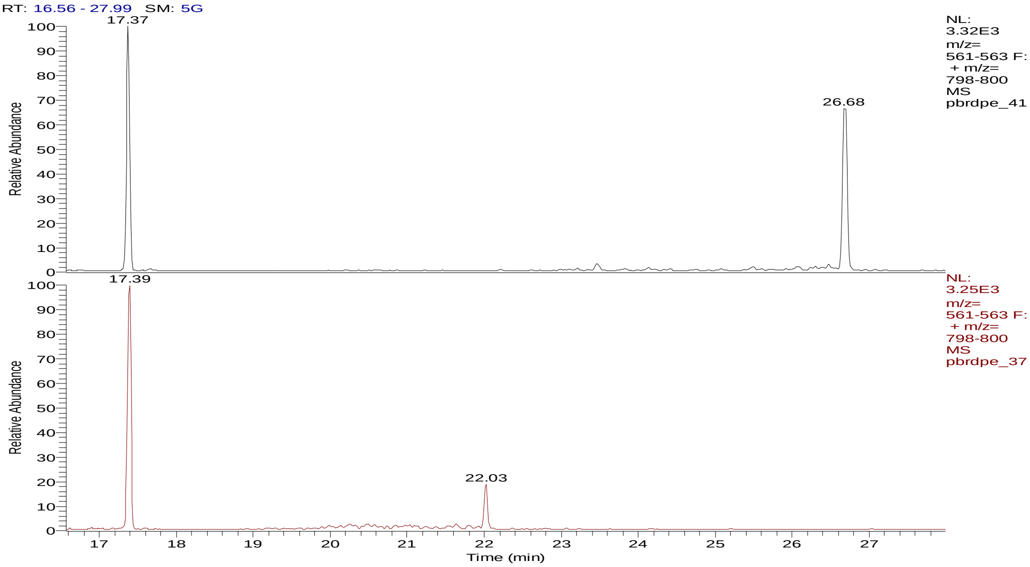

Figure 1: Mass chromatograms for decabromodiphenyl ether with different GC oven programs. (DB5ms 15*0.25(0.1)) a.) upper trace: 120°C(2min)-15°C/min/205°C-6°C/min/330°C b) lower trace: 120°C(2min)-15°C/min/205°C-6°C/min/268°C- 40°C/min/330

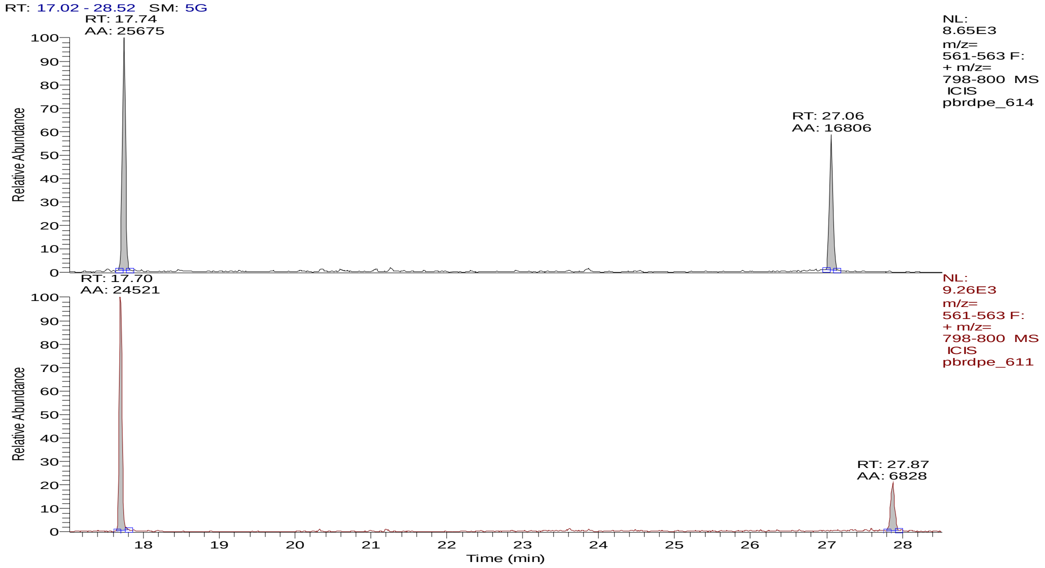

Figure 2: Mass chromatograms for decabromodiphenyl ether for different column lengths. (DB5ms 0.25(0.1)) a.) upper trace: 15 m column; 120°C(2min)-15°C/min/205°C-6°C/min/330°C b) lower trace: 30 m column; 120°C(2min)-20°C/min/230°C-6°C/min/330°C

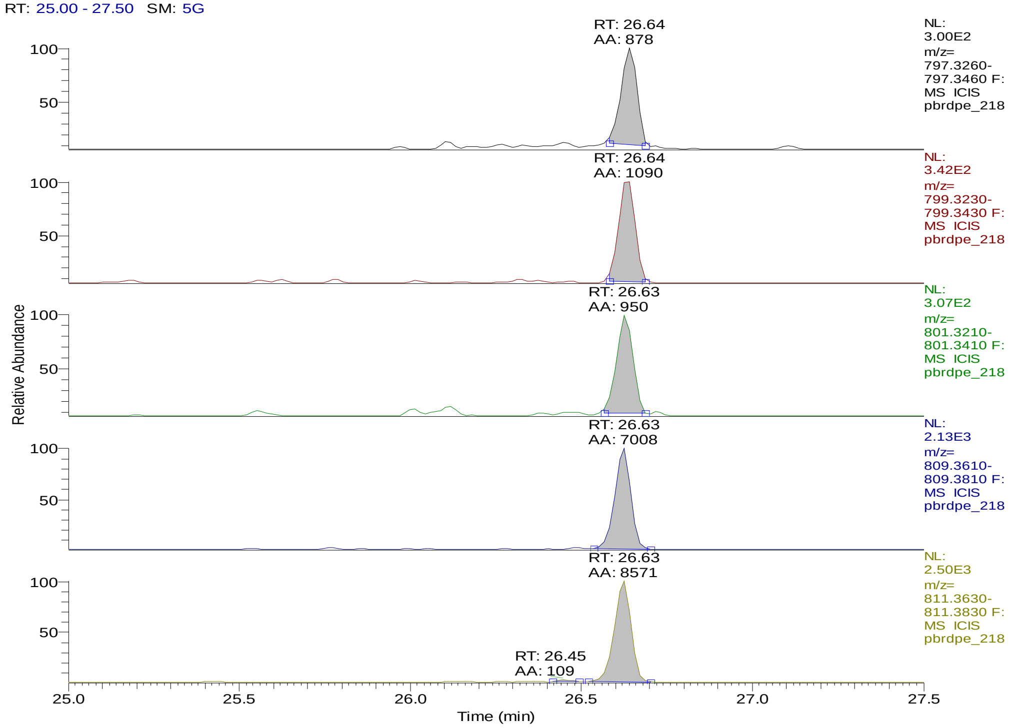

Figure 3: Mass chromatogram for decabromodiphenyl ether on a 15m DB5ms column (15*0.25(0.1)).
A CS1 PBrDPE standard was diluted 1:10 giving a concentration of 1000 fg for the native deca BDPE (10 pg internal standard). 3 mass traces shown for the native deca congenere (1 quantification mass, 2 ratio masses) and 2 mass traces (below) given for the ^{13}C labeled internal standard compound (1 ratio mass, 1 quantification mass).

As a rule of thumb it can be stated that the lower the elution temperature for the deca BDE the better the sensitivity. This is also the main factor for a shorter column giving better analysis results. Comparing split/splitless and PTV injectors for BDE analysis it can be concluded that the PTV using an apropriate temperature program provides better sensitivity and stability for the deca BDE whereas for the remaining BDE congeneres the response is comparable on both injectors.
Figure 3 shows chromatograms for an injection of 1 pg native deca BDE (10 pg labeled deca BDE). For a 15 m column connected to a PTV injector this was the optimum that could be achieved. For a 30 m column it is already difficult to obtain good results for amounts as high as 50 pg of deca BDE.

Two column setup

As a conclusion from the results presented above, a dual column setup was employed. Two GC columns were introduced into the mass spectrometer by means of a custom-designed Y-piece adaptor. This setup is more economic than a dual GC system and offers the special advantage of injecting out of the same vial on two different columns in sequential runs.
This way the advantages of both, a short and a long column, can be combined on one analytical system resulting in good sensitivity for the deca BDE and good separation efficiency for all remaining BDE congeners

Conclusion

It has been shown that the optimization of chromatographic parameters is crucial for good sensitivity when analysing deca BDE. The elution temperature of the deca congenere from the column proved to be the decisive factor for a succesfull analysis at lower concentrations.
An optimized method for the analysis of brominated diphenyl ethers using a dual column GC/MS interface on a Finnigan MAT 95 XP mass spectrometer has been presented using a regular length column for the analysis of tri to hepta BDE, and a very short column for the analysis of deca BDE.

Acknowledgement

The authors thank Wellington Laboratories for providing the BDE calibration solutions.