HALF THE COLUMN, SAME CHROMATOGRAM: TRIMMING THE GC COLUMN FOR MAINTENANCE WHILE MAINTAINING CRITICAL RESOLUTION BETWEEN BDE 49 AND BDE 71

Misselwitz M*, Cochran J, Thomas J

Restek Corporation, 110 Benner Circle, PA, USA

Introduction

Polybrominated diphenyl ethers (PBDEs) have been found to be persistent and bioaccumulative in the environment. The technical mixtures containing penta and octa congeners were voluntarily withdrawn in the United States in 2005 and the last remaining PBDE mixture, decaBDE, should be completely phased out by the end of 2013. While these mixtures have been phased out of production and use, the concentrations in the environment have not been declining and are currently still widely monitored.

The analysis of PBDEs is challenging due to structural isomers that need to be chromatographically separated and thermally label compounds of interest that may breakdown during gas chromatography. PBDEs included in EPA Method 1614 are well resolved on a 15 m x 0.25 mm x 0.10 µm Rtx-1614 GC column, a 5% diphenyl, 95% dimethyl polysiloxane type phase that was specifically designed to meet method resolution requirements [1]. Using a short, thin film column also allows the elution of decabromodiphenyl ether (BDE 209) without on-column thermal degradation.

Monitoring efforts of the levels of PBDEs include a wide array of biota and environmental matrices. Non-volatile material may still persist even in cleaned-up final extracts, requiring GC column and inlet maintenance to be performed. Using a 15 m x 0.25 mm x 0.10 µm column, how many loops of the GC column can one clip for maintenance before the Method 1614 resolution requirements of BDE 49 and BDE 71 can no longer be met? The resolution between BDE 49 and 71 must be less than 40% valley height to meet method criteria.

Materials and methods

A 15m, 0.25mm, 0.10µm Rtx-1614 column was used for the column trimming experiments. A 1 µL splitless injection of a native PBDE/BFR mix from Wellington Laboratories (BFR-PAR) into a split/splitless inlet set to 340°C with a Sky Cyclo Double Taper Inlet Liner was performed for all analyses. The instrument was an Agilent 7890/5975 GC-MS with electron ionization operated in selected ion monitoring (SIM) mode.

The initial GC oven conditions were optimized by using the thermodynamic modeling software Pro ezGC Methods Development Software from Restek Corporation. The modeled separation provided an analysis which maximizes resolution of target PBDEs with a maximum analysis time of 25 min. This GC oven temperature program started at 75°C (hold 1 min), then ramped at 18°C/min to 210°C, then ramped at 8°C/min to 310°C (hold 4 min). The column length was determined experimentally by measuring the holdup time of an unretained air peak.

As each loop was cut off from the inlet side of the column, a holdup time was calculated to find the exact column length. This new column length was then used to translate the original GC oven program to a new GC oven program that would elute BDEs at approximately the same temperatures as the original program.

Results and discussion

The initial column length was calculated to be 16 m and the GC oven program used produced baseline resolution of BDE 49 and BDE 71 and a 25 min analysis time. Trimming one loop off of the front of the column is often required routine maintenance when analyzing complex samples that have nonvolatile material deposited at the head of the column. Even when starting with a shorter column (15 m) it is still possible to trim multiple loops off of the column and maintain critical resolution (Figure 1).

By translating the method, the column flow remains the same but the oven programming rates are faster to accommodate the higher linear velocity through the column. Analysis time and peak widths are reduced when trimming the column and translating the method, therefore it is important to adjust the data acquisition rate to properly define the peak for quantitation. The Agilent 7890/5975 GC-MSD that we used for this work was a 208V instrument with a fast ramping oven. The two ramp program allowed faster programing for the shorter columns.

While column length did not yet prohibit the ability to meet BDE 49 and 71 resolution requirements for EPA Method 1614, instrument limitations dictated the need to install another column. As the column length was decreased, the head pressure was also decreasing. At 7.9 m the inlet pressure was 0.8 psi. With another loop trimmed off of the column to ~ 7.2 m length and with a vacuum-outlet detector (MS), the inlet pressure would be negative. By not properly translating the method, and keeping the inlet pressure the same, the column flow would be very fast (+3 mL/min) which would decrease resolution and detectability. This flow may also exceed the pumping capacity of many mass spectrometers.

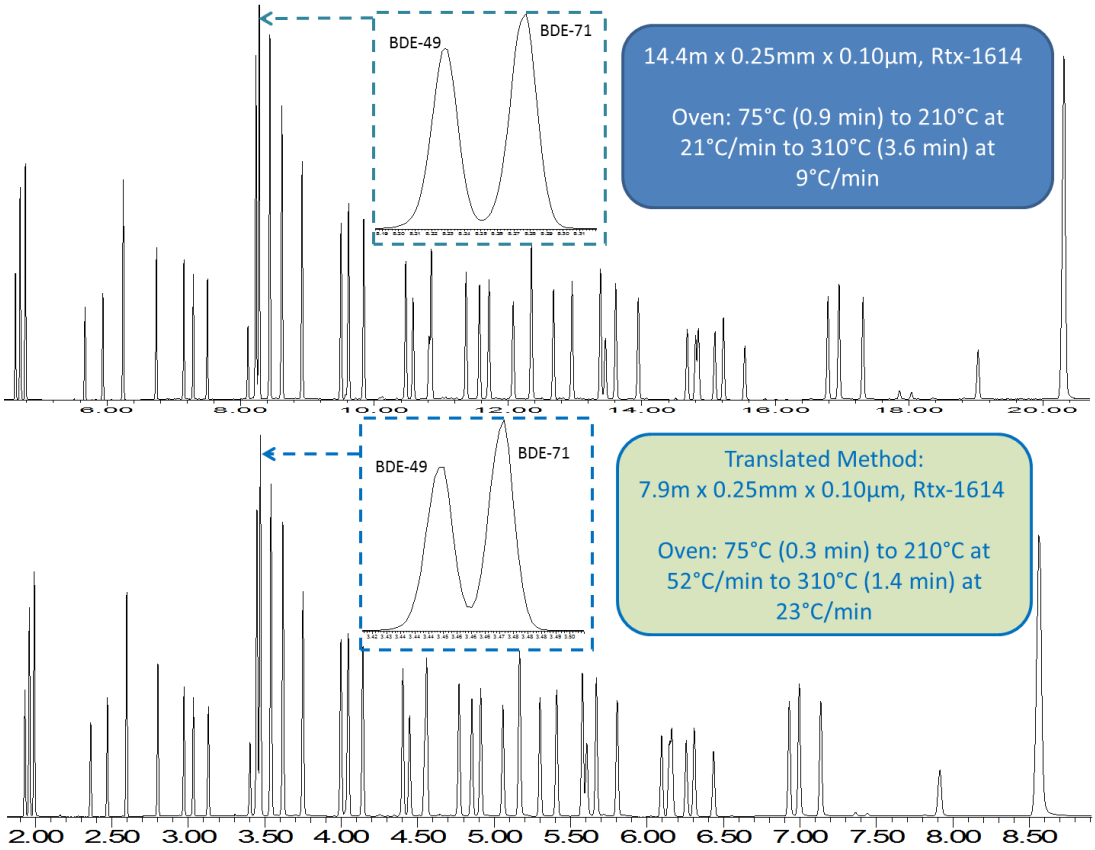

Figure 1: Elution profile of 14.4m column and 7.9m column with translated method, essentially identical, except for retention time.

Conclusions

Trimming the GC column for routine maintenance can extend the lifetime of the analytical column. By translating the method for the new column length, resolution of target analytes can be maintained. The 15 m x 0.25 mm x 0.10 µm Rtx-1614 column still exceeds the Method 1614 resolution requirement for BDE 49 and 71

for up to 12 loops trimmed from the column. Instrumentation may be the limiting factor when deciding how much you can trim off the column.

References

1. EPA Method 1614. *"Brominated Diphenyl Ethers in Water, Soil, Sediment and Tissue by HRGC"* (2007)