A New Capillary Column for the Analysis of EPA Draft Method 1614

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Abstract

A new capillary column has been developed and evaluated for use with EPA Draft Method 1614, Brominated dipheyl ethers in water, soil, sediment, and tissue by HRGC/HRMS.¹ This column was evaluated first, on the basis of its adherence to method specified criteria given in section 6.9.1 of the method and secondly, upon its inertness to the thermally labile component, decabrominated diphenyl ether (BDE-209). This column was found to exceed the performance of the method recommended column. The method itself was evaluated and optimized, as well, with the intent of improving the response of BDE-209 and drastically reducing the analysis time with a single column.

Introduction

The widespread use of polybrominated diphenyl ethers in industry as an additive flame retardant has caused quite a bit of consternation among people in the health and environmental communities. Although many of these have already been banned and discontinued from production, the "penta" and "octa" commercial mixtures, "deca", which is a formulation consisting primarily of decabrominated diphenyl ether, is still produced in substantial quantities. The concerns arise due to the inadvertent release of these materials into the environment through various means and, due to their bioaccumulative nature, their eventual migration into humans. In fact, there has been an exponential increase in human PBDE concentrations observed since the 1970's and it appears that that concentration now doubles approximately very five years.²

With this discovery of the ubiquitous presence of polybrominated diphenyl ethers, in the environment, as well as, in humans, and the accumulation of data collected which suggest several potential adverse affects associated with exposure to these compounds³, there is a need for accurate and rapid analysis of these compounds. A crucial step in determining the success of this endeavor is the choice of capillary column. Like most environmental methods, the analysis for PBDE's places a high level of expectations on the capillary column. One such example is EPA Draft Method 1614. This method calls for the analysis of a voluminous number of compounds which need to be separated without losses to activity. One target compound of notable concern is decabromodiphenyl ether, which is one of the most frequently encountered, especially now, as it is the primary component in the only remaining commercial PBDE mixture being produced.

A study performed by Bjoerklund, et al.⁴ compared several different column phases and showed a vast disparity between the relative response factors for various PBDE's as the degree of bromination increased, with BDE-209 showing the greatest variability. In this study, we utilize a "5-type" phase as mandated by Draft Method 1614 and instead, focus on examining various deactivation types to determine the most effective for PBDE analysis and further optimized method parameters to show how the analysis could be improved.

Materials and Methods

Again, as the method specifies a 5% phenyl methyl type column, DB-5HT or equivalent, in 30m x 0.25mm x 0.10 μ m format, this evaluation was carried out using a "5-type" polymer of these dimensions. Several types of deactivation have been investigated in order to determine the most inert for BDE-209, whose breakdown mechanism is predominately on-column related, and was combined with a 5% phenylmethyl polymer, resulting in the creation of the Rtx-1614. Although this method requires analysis on a high-resolution mass spectrometer, the columns were evaluated using an Agilent 6890 GC with μ -ECD to determine inertness and general chromatographic performance, and on an Agilent 7890/5975 GC/MS to verify separation requirements under vacuum outlet conditions. Two evaluation standards were made for this study, one a simple mix consisting of the BFR's (Restek Corporation, USA) found in EPA Method 527⁵ with the addition of BDE-209 (Wellington Laboratories) and was used for comparison

of BDE-209 response verses lower brominated PBDE's under various conditions and to compare BDE-209 response difference between columns. A second, more comprehensive mix was used (Cambridge Isotope Laboratories) in order to evaluate other chromatographic performance characteristics.

Results and Discussion

It was determined that the Rtx-1614 meets the stipulations set forth in the method which address resolution of critical pairs, tailing factors, and retention. Figure 1 shows the separation of a large list of PBDE's as analyzed on this column. Notice the separation of congener 49/71 which is required to have an 80% valley depth of the smallest peak. Also, in figure 2 a chromatogram of the method specified column analyzed under the same conditions as figure 1 illustrates a difference in inertness between it and the Rtx-1614. Note the difference in the degree of fronting on the BDE-209 peak, which is indicative of on-column breakdown, as well as, the higher degree of tailing and lower selectivity between BDE-49 and BDE-71.

In an attempt to capitalize on the effectiveness of this column, the parameters in this method were optimized to show how effective a properly configured system can be in determining the performance of PBDE analysis and in particular, BDE-209. In a review by Stapleton⁶, various techniques and conditions were reported for analysis of PBDE's showing much new data and improvements in the understanding of the effects of method parameters on the chromatographic performance of PBDE's since the compilation of Draft Method 1614.

Although the method stipulates that BDE-209 must elute a least 48 minutes from injection, eliminating the possibility of much method optimization, the method can be greatly improved for analysis time, as well as, BDE-209 response for those analyzing PBDE's who are not operating under the constraints of this method . As was mentioned, BDE-209 breaks down primarily in the column, so residence time in column should be minimized, hence higher flow rates and quicker ramp rates, combined with a shorter, 15 meter column, dramatically improve BDE-209 performances. (figure 3) Also, to help prevent BDE-209 degradation, optimizing maximum oven temperature is critical, and it was found to be best to stay at or below 300°C to minimize thermal degradation. Notice the virtual elimination of the baseline rise from the nona congeners fronting up to the BDE-209 peak, which is indicative of on-column degradation, in this chromatogram relative to that obtained under method recommended conditions. Also, although it is not readily apparent from looking at the peak height, the area response of BDE-209 is considerably higher under these conditions. The reduction of the BDE-209 peak height seems to be a function of the longer isothermal time prior to the elution of BDE-209. A short, slow temperature ramp placed close to the elution time of BDE-209 should regain some of the peak height.

The injection temperature was optimized at 340°C using a Cyclo-double Gooseneck inlet liner (Restek Corporation), ensuring complete vaporization of the high molecular weight BDE-209 for consistent and high response. However, using a Uniliner direct injection liner (Restek Corporation) may reduce the need to operate at such high injector temperatures, helping to reduce injector induced breakdown of BDE-209. It was felt that the degree of nona response should be indicative of injector breakdown and could be correlated with changes in injector conditions, but this did not seem to be shown in this series of analyses. Even applying these parameters to a 30 meter column results in a greatly improved analysis relative to the method stipulated operating conditions. (figure 4)

In conclusion, the Rtx-1614 was found to be an excellent column choice for analyzing EPA Draft Method 1614, as well as any routine screening analysis of PBDE's due to its selectivity, inertness, (specifically with respect to BDE-209), and reproducibility.

References

1. United States Environmental Protection Agency. "Draft Method 1614 – Brominated diphenyl ethers in water, soil, sediment, and tissue by HRGC/HRMS", August 2003

2. Hites, R.A. Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, 38, 945-956.

3. Birnbaum, Linda S.; Staskal, Daniele F. Brominated Flame Retardants: Cause for Concern?. *Environ Health Perspect* **2004**, 112, 9-17.

4. Bjoerkland J, Tollbaek P, Hiarne C, Dyremark E, Oestman C. Influence of the injection technique and the column system on gas chromatographic determination of polybrominated diphenyl ethers. *J Chromatogr A*. **2004**, 1041, 201-210

5. United States Environmental Protection Agency. "Method 527 – Determination of Selected Pesticides and Flame Retardants in Drinking Water by Solid Phase Extractio and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)", April 2005

6. Stapleton, Heather M. Instrumental methods and challenges in quantifying polybrominated diphenyl ethers in environmental extracts: a review. *Anal Bioanal Chem.* **2006**, 386, 807-817.





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Figure 3. Rtx-1614 using optimized column and method parameters.



