

Analysis of EPA Method 527 using New Capillary Column Polymer Technology

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Abstract

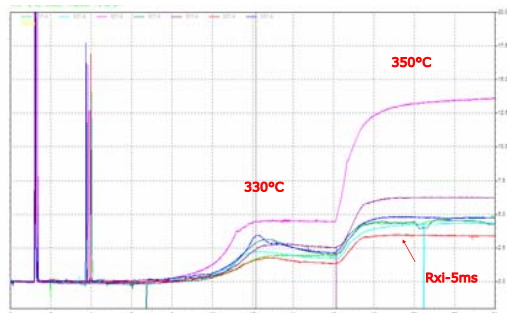
Because of their known or suspected toxicity, analysis of persistent organic pollutants in the environment has become ever more prevalent as the regulation of these hazardous materials becomes increasingly more stringent. As a result, target compound lists are evolving to become very complex and extensive in magnitude. In addition, the level of quantitation of these compounds continues to push toward lower and lower concentrations.

In order to keep up with these higher demands of analytical capability, capillary column performance must also improve to keep pace with the environmental communities' expectations. The column used in this analysis was designed to achieve this new level of chromatographic performance by vast improvements in two areas of column characteristics. The first of these is the much lower level of bleed exhibited by this column. Secondly, the higher degree of column inertness allows much improved low level quantitation for active compounds.

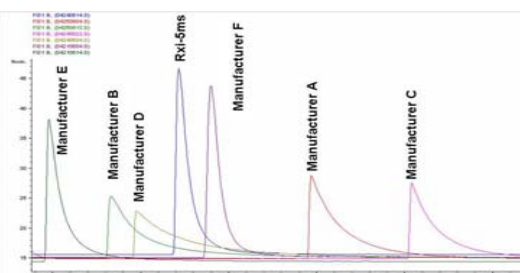
This poster will focus on the application of this technology to a new environmental compound list contained in EPA Method 527. This is one of the newest drinking water methods from the EPA and is part of the second Unregulated Contaminant Monitoring Rule (UCMR2) program and addresses a variety of target compound classes, including organophosphorus pesticides, pyrethroids, and brominated flame retardants. The low detection limits stipulated by this method require the type of performance provided by this column technology, as well as, an analytical instrument with an extended scanning range and excellent sensitivity such as that provided by the instrument utilized to obtain the EPA Method 527 data for this poster.

Column Requirements

In order to effectively analyze for the difficult components contained in EPA Method 527, two prerequisites must be met by the column of choice. One is that it must exhibit minimal bleed at elevated temperatures. This is due to the late elution and lower response of the heavier molecular weight compounds which would experience interference in quantification from elevated bleed, as well as, lowered sensitivity when using GC/MS. Secondly, because of the high activity and thermally labile nature of some of these compounds, they have a strong tendency to break down not only in the injector, but also on-column, necessitating a very inert column. The Rxi-5ms meets both of these criteria as illustrated below and was therefore used for this analysis.



Comparison of various bleed profiles from 30m x 0.25mm x 0.25µm columns obtained at a 135°C starting temperature and at 330°C & 350°C. Rxi-5ms is shown in red. Reference peak is 1ng Tridecane using a FID.



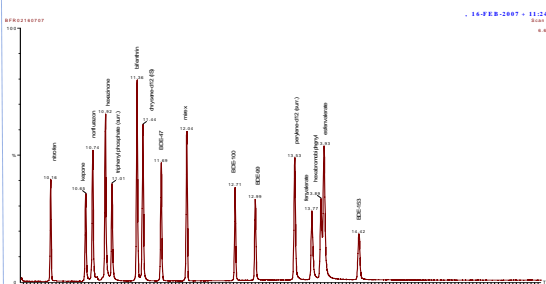
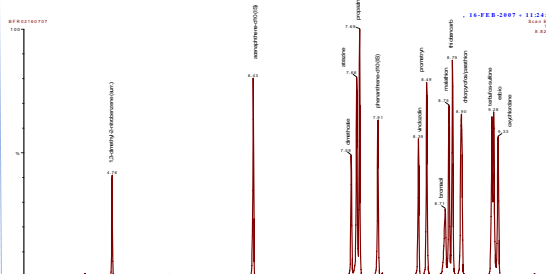
Overlay of different chromatograms illustrating the response and peak symmetries of a 2 ng. Injection of pyridine. Notice that although some of the other manufacturers have approximately equal response area, they exhibit significant peak tailing.

Analysis of EPA Method 527

Of the several types of compound classes included in this method, the PBDEs have been of particular interest and concern in recent years. The preponderance of PBDEs makes their occurrence in the environment very likely and has led to their inclusion into EPA Method 527. In addition to the low thermal stability of the compounds and high volatility, these compounds typically have high molecular weights and so when analyzing by GC/MS, requires an instrument with a broad scanning range, such as the PE Clarus system, below, with its scan range of up to 1200 amu and was used for analysis of EPA Method 527 which is illustrated in the following chromatograms.



EPA Method 527 @ 10 ppm



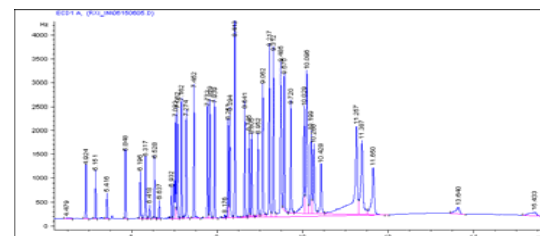
Run conditions:

Oven program: 60°C (hold 1 min.) to 210°C @25°C/min. to 320°C (hold 4 min.) @15°C/min.
Injector: 1.0µL split; 40:1, 2 mm Uniliner; 250°C
Carrier gas: Helium, constant flow, 2 ml/min.
MS conditions: Interface temperature 250°C, Source temperature 170°C
Scan time: 0.2 sec 50-650 amu

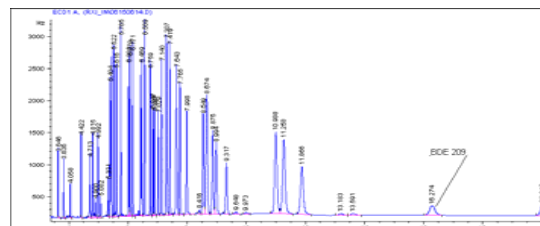
In addition to the current compound list, this method lends itself well to the analysis of additional PBDEs. BDE-209 was originally included in the list, but was removed during method development due to concerns of its high molecular weight requiring temperatures exceeding the capabilities provided by the column used in the method. It has been found, however, that relatively low oven and injector temperatures are actually prerequisites in the analysis of BDE-209, as well as, the other higher brominated PBDEs. These findings are illustrated in the following section.

Additional PBDEs with Method 527

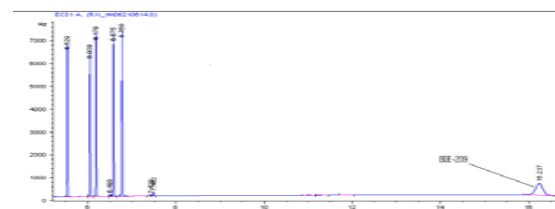
Regardless of column choice, there are several method parameters which need to be optimized in order to obtain reliable and reproducible results, when using EPA Method 527 to analyze for additional PBDEs. Of special interest and concern is BDE-209, the primary component in the "deca" commercial mixture, the most prevalent PBDE mixture in use. Because of its tendency to break down on-column, the residence time of DBDE needs to be minimized, therefore, using a high volumetric flow is highly important. Secondly, due to its thermally labile nature, the oven temperature needs to be kept below 300°C to ensure good chromatography for BDE-209, something which is often overlooked. The following two c-grams illustrate the importance of minimizing the maximum oven temperature in this analysis.



Proper temperature programming is critical to prevent on-column breakdown of the higher brominated species as is illustrated in these two chromatograms. The above chromatogram shows a comprehensive set of BFRs, (the "Wellington mix") run to a temperature of 320°C. The chromatogram below shows the same mix run to a maximum temperature of 295°C.



Injector activity is also a concern, as contact with metal injector components needs to be minimized, which is effectively dealt with by using a Siltek Uniliner. Additionally, glass or fused silica wool is often used in the inlet liner to improve response of low volatility compounds, but in the case of BDE-209, it has a detrimental effect on response due to the added activity of the wool.



With these method parameters optimized, good chromatography can be obtained for even BDE-209, as shown in the above chromatogram of the EPA Method 527 BFRs with BDE-209 included.

Conclusion

When quantitatively and reproducibly analyzing EPA Method 527, a properly optimized set of method parameters is a prerequisite. Also needed, is a capillary column with very low bleed, high inertness for a broad range of compounds, and proper selectivity. As illustrated by the data presented here, the Rxi-5ms provides these characteristics, and using the proper analytical conditions, is a suitable choice for use in the analysis of EPA Method 527, along with additional PBDE analysis, which is becoming increasingly more common in environmental laboratories today.