



ENVIRONMENTAL

## Reliable Quantification of Brominated Flame Retardants by GC/MS

### Using a New Rtx<sup>®</sup>-1614 Column for PBDE Analysis

By Jason Thomas, Environmental Innovations Chemist, and Jack Cochran, Director of New Business and Technology

- Higher sensitivity and inertness for BDE-209 than the method-specified column, for more accurate, reproducible results.
- Meets all method requirements for resolution, tailing factors, and retention.
- Optimized short column conditions give improved BDE-209 response and 3 times faster run times.

Polybrominated diphenyl ethers (PBDEs) are ubiquitous in humans and in the environment. Rapid and accurate PBDE methods are increasingly in demand as adverse effects have been associated with PBDE exposure. EPA Draft Method 1614 presents a considerable challenge to the analytical column due to the large number of PBDE compounds and stringent activity guidelines. One target compound, decabromodiphenyl ether (BDE-209), is of particular concern as it is frequently encountered and is the primary component in the only remaining commercial PBDE mixture. Column inertness is critical for BDE-209 analysis, as the breakdown mechanism is predominately column-related.

#### Maximize BDE-209 response with an Rtx<sup>®</sup>-1614 column in new short column dimensions.

EPA Draft Method 1614 stipulates a 5% phenyl methyl column in a 30m x 0.25mm x 0.10 $\mu$ m format, with a 15m shorter column option. Here we compare the performance of a method-specified (DB-5HT) column to the new Rtx<sup>®</sup>-1614 column, a 5% phenyl methyl column with a unique deactivation for maximum inertness to BDE-209 (Table I). Although this method requires analysis on a high-resolution mass spectrometer, the columns were evaluated first on an Agilent 6890 GC with  $\mu$ -ECD to assess inertness and

general chromatographic performance. Columns were then analyzed on an Agilent 7890/5975 GC/MS to verify separation requirements under vacuum outlet conditions.

The Rtx<sup>®</sup>-1614 column meets the method requirements for the resolution of critical pairs, tailing factors, and retention. The data in Figure 1 demonstrate the separation of a large list of PBDEs on the Rtx<sup>®</sup>-1614 column; note the baseline resolution of congeners 49 and 71, which are required to have a 40% valley height of the smallest peak. The Rtx<sup>®</sup>-1614 column also performed exceptionally well for inertness to BDE-209. (Table I) Compared to the performance of the DB-5HT column, shown in Figure 2, the Rtx<sup>®</sup>-1614 column shows a greater response for BDE-209 and less peak fronting, indicating less on-column breakdown.

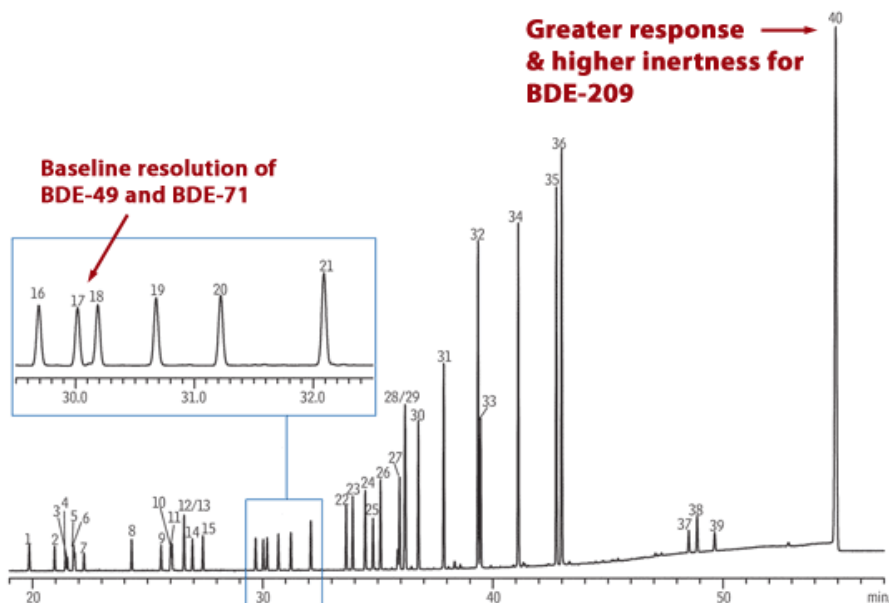
Although the method originally stipulated that BDE-209 must elute at least 48 minutes from injection, eliminating the possibility of much method optimization, a new revision provides a short column option which can greatly improve analysis time and BDE-209 response. Since BDE-209 breaks down primarily in the column, reducing column residence time by using a shorter 15m column, in combination with higher flows and quicker ramp rates, dramatically improves performance (Figure 3). Even applying optimized parameters to a 30m column results in greatly enhanced analyses, relative to the original method-stipulated operating conditions. To further optimize this method, BDE-209 degradation was reduced by using a maximum oven temperature of less than 300°C and setting the injection temperature at 340°C, to ensure complete

vaporization, resulting in a consistent and high response.

In conclusion, the Rtx®-1614 is an excellent column choice for analyzing EPA Draft Method 1614, as well as any routine screening analysis of PBDEs, due to its selectivity, sensitivity, and inertness, specifically with respect to BDE-209.

**Figure 1: Separate PBDEs accurately and reliably on an Rtx®-1614 column.**

- |            |            |             |             |
|------------|------------|-------------|-------------|
| 1. BDE-10  | 11. BDE-25 | 21. BDE-77  | 31. BDE-153 |
| 2. BDE-7   | 12. BDE-28 | 22. BDE-100 | 32. BDE-138 |
| 3. BDE-8   | 13. BDE-33 | 23. BDE-119 | 33. BDE-166 |
| 4. BDE-11  | 14. BDE-35 | 24. BDE-99  | 34. BDE-183 |
| 5. BDE-12  | 15. BDE-37 | 25. BDE-116 | 35. BDE-181 |
| 6. BDE-13  | 16. BDE-75 | 26. BDE-118 | 36. BDE-190 |
| 7. BDE-15  | 17. BDE-49 | 27. BDE-85  | 37. BDE-208 |
| 8. BDE-30  | 18. BDE-71 | 28. BDE-155 | 38. BDE-207 |
| 9. BDE-32  | 19. BDE-47 | 29. BDE-126 | 39. BDE-206 |
| 10. BDE-17 | 20. BDE-66 | 30. BDE-154 | 40. BDE-209 |

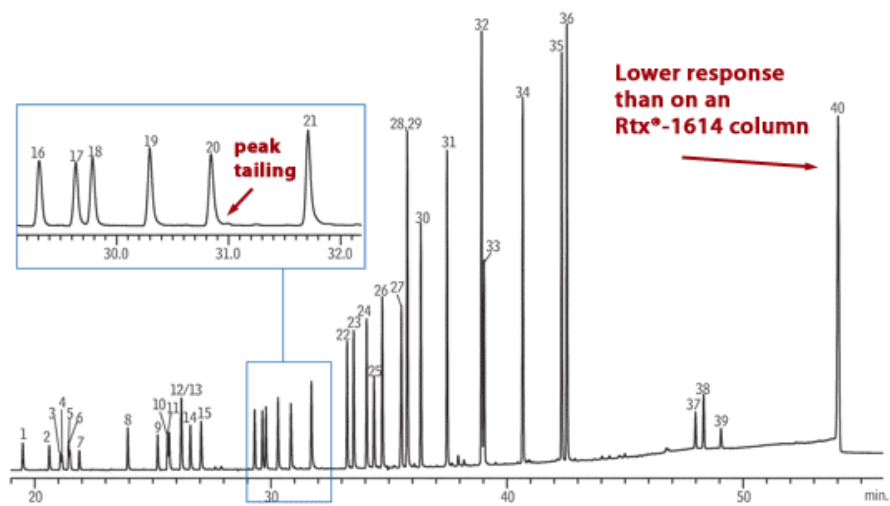


Column: Rtx®-1614, 30m, 0.25mm ID, 0.10µm (cat.# 10295)  
 Sample: 100-300ppb PBDE PAR Solution (Cat.# EO-5113, Cambridge Isotope Laboratories Inc.), 500ppb decabromodiphenyl ether (cat.# BDE-209, Wellington Laboratories)  
 Inj.: 1µL splitless (hold 1 min.), 4mm cyclo double gooseneck liner (cat.# 20896)  
 Inj. temp.: 300°C  
 Carrier gas: helium, constant flow  
 Linear velocity: 20cm/sec. @ 100°C  
 Oven temp: 100°C (hold 3min.) to 320°C @ 5°C/min. (hold 15 min.)  
 Detector temp.: µ-ECD @ 340°C

GC\_EV01019

**Figure 2: More BDE-209 peak fronting on the method-specified column indicates greater on-column breakdown.**

- |            |            |             |             |
|------------|------------|-------------|-------------|
| 1. BDE-10  | 11. BDE-25 | 21. BDE-77  | 31. BDE-153 |
| 2. BDE-7   | 12. BDE-28 | 22. BDE-100 | 32. BDE-138 |
| 3. BDE-8   | 13. BDE-33 | 23. BDE-119 | 33. BDE-166 |
| 4. BDE-11  | 14. BDE-35 | 24. BDE-99  | 34. BDE-183 |
| 5. BDE-12  | 15. BDE-37 | 25. BDE-116 | 35. BDE-181 |
| 6. BDE-13  | 16. BDE-75 | 26. BDE-118 | 36. BDE-190 |
| 7. BDE-15  | 17. BDE-49 | 27. BDE-85  | 37. BDE-208 |
| 8. BDE-30  | 18. BDE-71 | 28. BDE-155 | 38. BDE-207 |
| 9. BDE-32  | 19. BDE-47 | 29. BDE-126 | 39. BDE-206 |
| 10. BDE-17 | 20. BDE-66 | 30. BDE-154 | 40. BDE-209 |

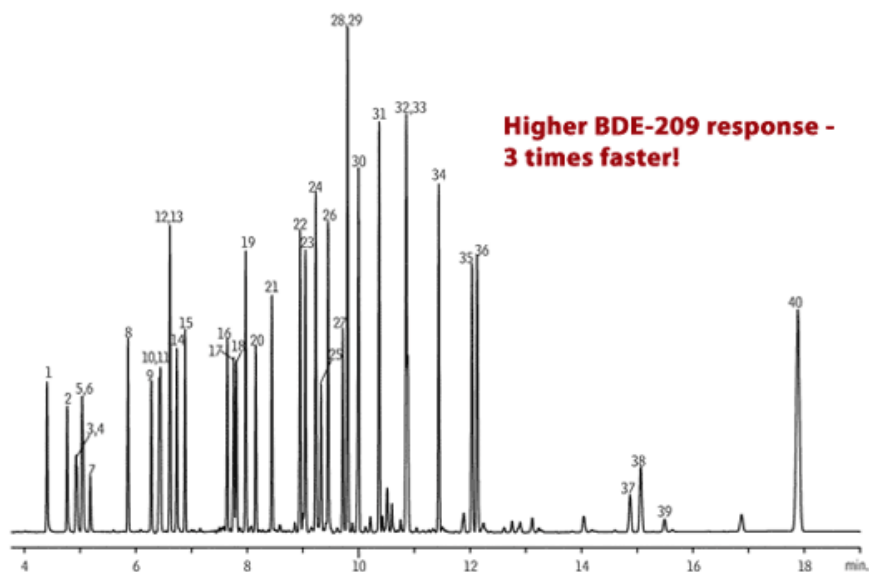


Column: competitor column, 30m, 0.25mm ID, 0.10µm  
 Sample: 100-300ppb PBDE PAR Solution (Cat.# EO-5113, Cambridge Isotope Laboratories Inc.), 500ppb decabromodiphenyl ether (cat.# BDE-209, Wellington Laboratories)  
 Inj.: 1µL splitless (hold 1 min.), 4mm cyclo double gooseneck liner (cat.# 20896)  
 Inj. temp.: 300°C  
 Carrier gas: helium, constant flow  
 Linear velocity: 20cm/sec. @ 100°C  
 Oven temp: 100°C (hold 3min.) to 320°C @ 5°C/min. (hold 15 min.)  
 Detector temp.: µ-ECD @ 340°C

GC\_EV01020

Figure 3: Analysis times and BDE-209 response can be significantly improved with optimized run conditions using the short column option.

|            |            |             |             |
|------------|------------|-------------|-------------|
| 1. BDE-10  | 11. BDE-25 | 21. BDE-77  | 31. BDE-153 |
| 2. BDE-7   | 12. BDE-28 | 22. BDE-100 | 32. BDE-138 |
| 3. BDE-8   | 13. BDE-33 | 23. BDE-119 | 33. BDE-166 |
| 4. BDE-11  | 14. BDE-35 | 24. BDE-99  | 34. BDE-183 |
| 5. BDE-12  | 15. BDE-37 | 25. BDE-116 | 35. BDE-181 |
| 6. BDE-13  | 16. BDE-75 | 26. BDE-118 | 36. BDE-190 |
| 7. BDE-15  | 17. BDE-49 | 27. BDE-85  | 37. BDE-208 |
| 8. BDE-30  | 18. BDE-71 | 28. BDE-155 | 38. BDE-207 |
| 9. BDE-32  | 19. BDE-47 | 29. BDE-126 | 39. BDE-206 |
| 10. BDE-17 | 20. BDE-66 | 30. BDE-154 | 40. BDE-209 |



Column: Rtx®-1614, 15m, 0.25mm ID, 0.10µm (cat.# 10296)  
 Sample: 100-300ppb PBDE PAR Solution (cat.# EO-5113, Cambridge Isotope Laboratories Inc.), 500ppb decabromodiphenyl ether (cat.# BDE-209, Wellington Laboratories)  
 Inj.: 1µL splitless (hold 1 min.), 4mm cyclo double gooseneck liner (cat.# 20896)  
 Inj. temp.: 340°C

Carrier gas: helium, constant flow  
Linear velocity: 60cm/sec. @ 120°C  
Oven temp: 120°C (hold 1 min.) to 275°C @ 15°C/min. to 300°C @ 5°C/min.  
(hold 5 min.)  
Detector temp.:  $\mu$ -ECD @ 345°C

GC\_EV01025

**Table 1: Maximize BDE-209 response with an Rtx®-1614 column.**

| Column         | BDE-209 Average RRF* |
|----------------|----------------------|
| Rtx-1614 (15m) | 0.681                |
| Rtx-1614 (30m) | 0.636                |
| DB-5HT (30m)   | 0.502                |

\* Relative response factors based on internal standard hexabromopiphenyl (n=5). Analyses run under optimized conditions.