

Breaking Down? Improve BDE-209 Response

Using a New Rtx[®]-1614 Column for PBDE Analysis

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- 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 3 times faster.

Polychlorinated biphenyls (PCBs) and polychlorinated dibenz-p-dioxins (PCDDs) are ubiquitous in humans and in the environment. Rapid and accurate PCB methods are increasingly in demand as adverse effects have been associated with PCB exposure. EPA Draft Method 1614 presents a considerable challenge to the analytical column due to the large number of PCB 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 PCB mixture. Column inertness is critical for BDE-209 analysis, as the breakdown mechanism is predominately column-related.

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

Table I Maximize BDE-209 response with an Rtx[®]-1614 column, in 15 or 30m lengths!

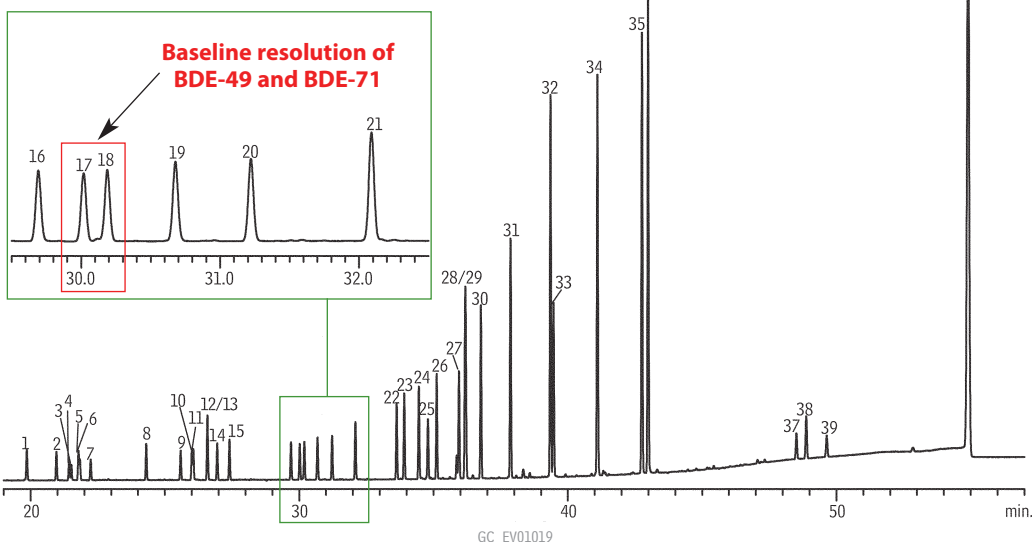
Column	BDE-209 Average RRF*
Rtx [®] -1614 (15m)	0.681
Rtx [®] -1614 (30m)	0.636
DB-5HT (30m)	0.502

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

The Rtx[®]-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 PCBs on the Rtx[®]-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[®]-1614 column also performed exceptionally well for inertness to BDE-209 (Table 1). Compared to the performance of the DB-5HT, shown in Figure 2, the Rtx[®]-1614 column

Figure 1 Separate PCBs accurately and reliably on an Rtx[®]-1614 column.

Column: Rtx[®]-1614, 30m, 0.25mm ID, 0.10µm (cat.# 10295)
 Sample: 100-300ppb PCB 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 3 min.) to 320°C @ 5°C/min. (hold 15 min.)
 Detector temp.: µ-ECD @ 340°C



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

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. 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 (Figure 3).

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.

Rtx®-1614 Columns (fused silica)

(5% phenyl methyl)

ID	df (µm)	temp. limits	length	cat. #
0.25mm	0.10	-60 to 330/360°C	15-Meter	10296
0.25mm	0.10	-60 to 330/360°C	30-Meter	10295

Splitless Liners for Agilent

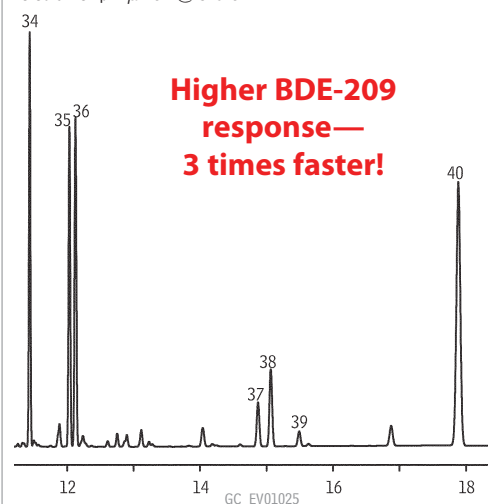
ID* x OD & Length	qty.	cat.#
Cyclo Double Gooseneck (4mm)		
4.0mm x 6.5mm x 78.5mm	5-pk.	20896

*Nominal ID at syringe needle expulsion point.



Figure 3 Improve BDE-209 response and analysis times with optimized conditions using the short column option.

Column: Rtx®-1614, 15m, 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.: 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.: µ-ECD @ 345°C

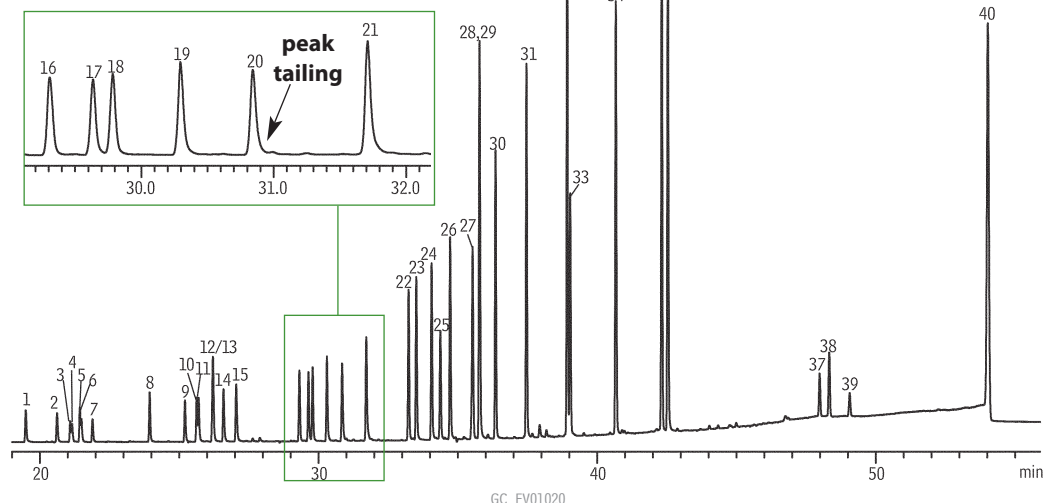


**Higher BDE-209 response—
3 times faster!**

See Figure 1 for peak list.

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

Column: DB-5HT, 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 3 min.) to 320°C @ 5°C/min. (hold 15 min.)
 Detector temp.: µ-ECD @ 340°C



**Lower response
than on Rtx®-1614**

See Figure 1 for peak list.