

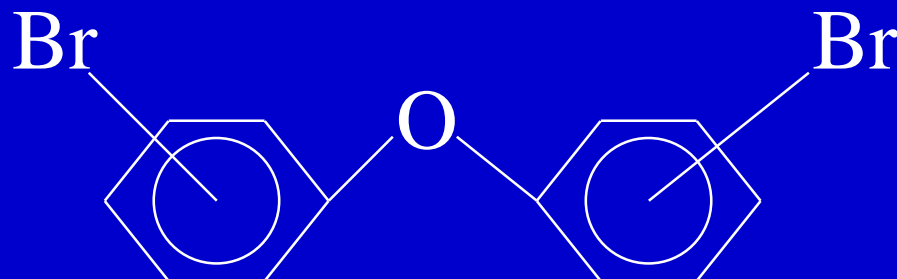
Gas Chromatographic Analysis of Polybrominated Diphenyl Ethers Using a Novel GC Column

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Brominated Flame Retardants:

- Products based on penta-, octa-, and decaBDE are commercially used as flame retardants
- Global production of DeBDE is approximately 40,000 tons/year
- Heavily used for furniture treatment and electronics in USA, Japan, and Europe
- May form PBDDs and PBDFs when combusted, and toxicity is estimated to be similar to PCDDs and PCDFs

Polybrominated Diphenylethers



Br 1-10

- Named similarly to PCB congeners (BDE 1-209)
J. High Resolut Chromatogr **15**:260
- Human exposure via the food chain is 0.2 – 0.7 mg/day
Organohalogen Compounds **35**:411
- Listed as Endocrine Disruptors
Environ Health Perspect **101**:378

Methods of Analysis

- Electron capture detection
 - Lower cost
 - More common to most labs
- High-resolution mass spectrometric detection
 - Additional specificity may improve sensitivity
 - Many dioxin labs are also interested in PBDEs
- Others not investigated
 - GC-NCI-MS
 - HPLC-MS

Prior Analyses

- GC-HRMS
 - Difficulty eluting nona's and decaBDE due to high molecular weight
 - Column bleed levels hurt sensitivity of higher bromination levels
 - Often done using two columns:
 - Longer column to separate lower bromination level congeners
 - Short column to analyze nona and decaBDEs

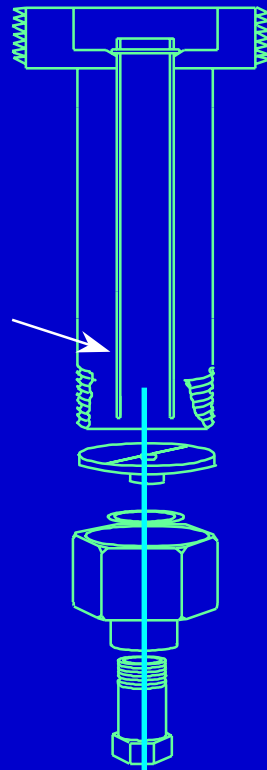
Prior Methods of Analysis

- Decision made if deca (and possible nona and octa) are desired
 - Higher molecular weight congeners are either analyzed separately, or not at all
 - Higher molecular weight congeners are allowed to “ghost” out on “standard” column (5% diphenyl)
- Loss of higher molecular weight congeners is also due to injection technique

Convert Split or Splitless Inlets to Direct Injection Mode

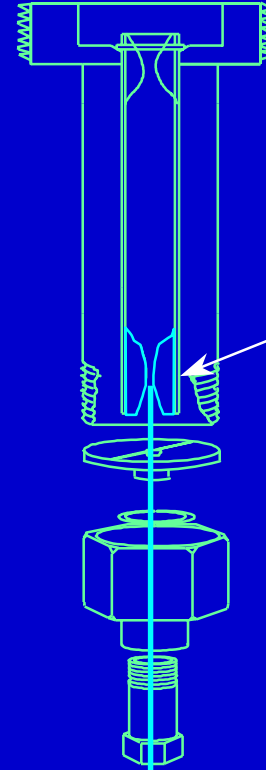
Always keep
split vent
purge off

Remove
the split
or
splitless
sleeve

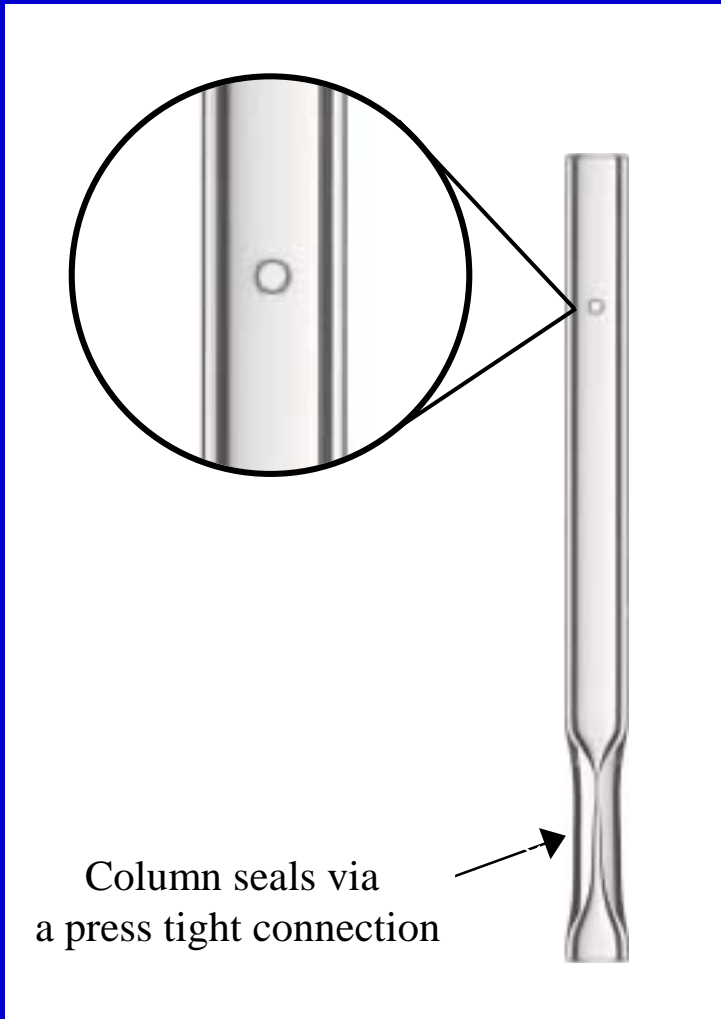


Install a Direct
Injection sleeve

Press-fit
connection



Uniliner w/ Hole



- Allows Direct injection and Splitless injection methods
- Minimizes injection port discrimination
- Reduces loss of active compounds for more accurate results

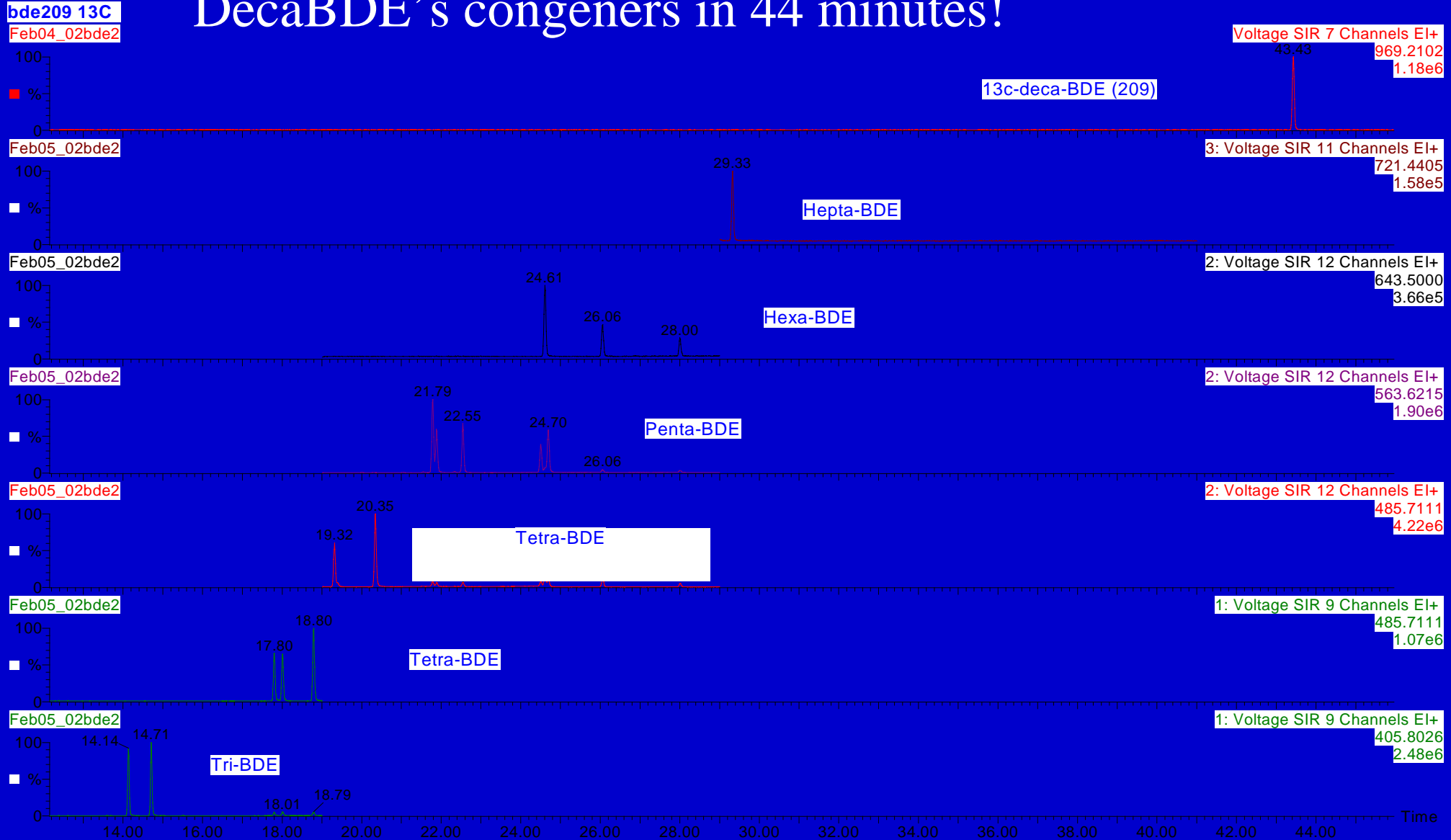
Rtx-500 Capillary GC Column

- Carborane-stabilized stationary phase
 - Maximum temperature of 380°C in “standard high-temperature” tubing
 - Maximum temperature of 440°C in passivated metal columns (Mxt-500)
- Extremely low bleed levels
 - Surpasses phenyl/methyl phases, and silphenylene stationary phases
- Common dimensions available

Wellington Laboratories BDE Mix-C

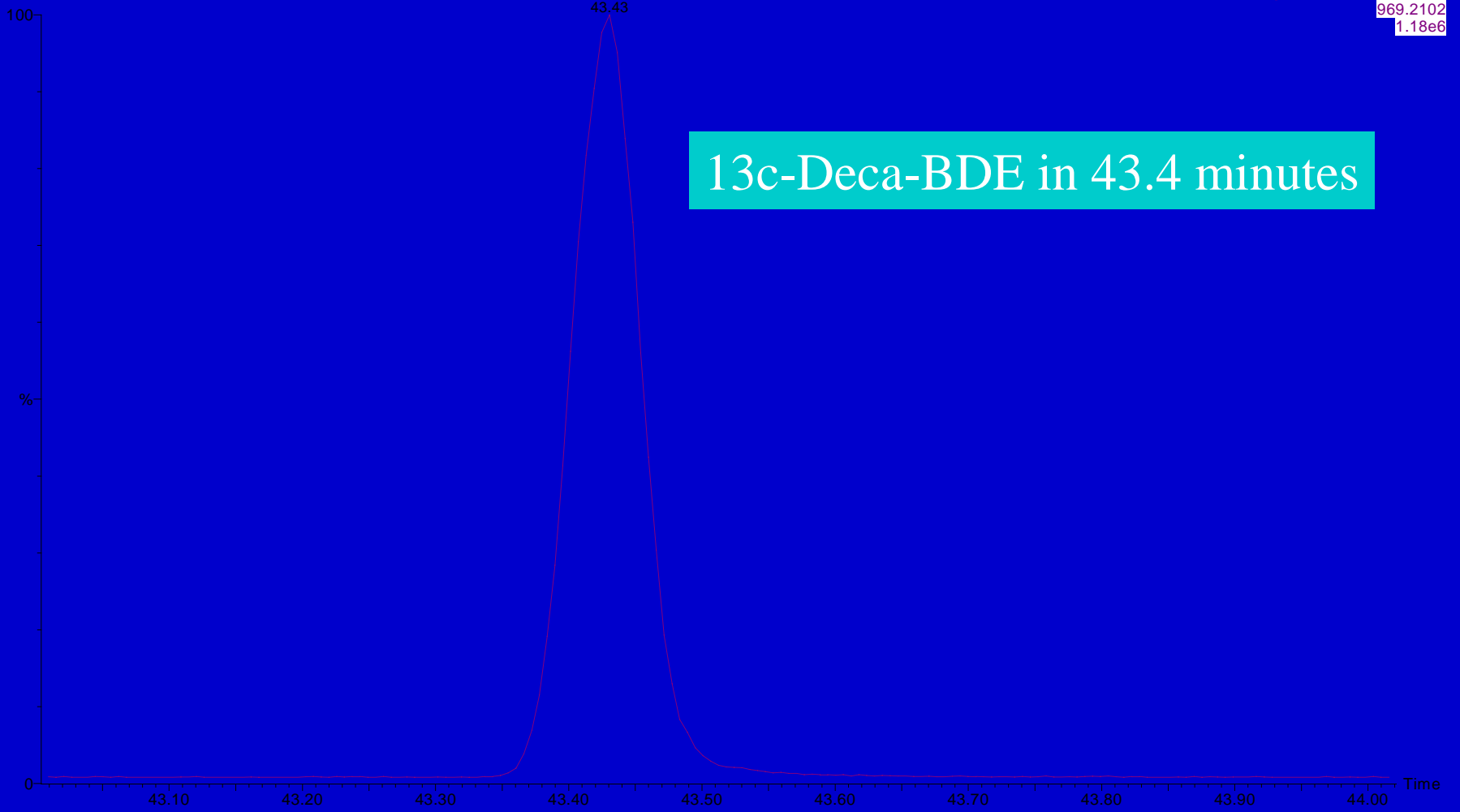
4-bromodiphenyl ether (3)	250	141,115
2,4-Dibromodiphenyl ether (7)	168	328,139
4,4'-dibromodiphenyl ether (15)	328	168,221
2,2',4-tribromodiphenyl ether (17)	248	408,406
2,4,4'-tribromodiphenyl ether (28)	406	248,246
2,2',4,5'-tetrabromodiphenyl ether (49)	326	486,328,324
2,3',4',6-tetrabromodiphenyl ether (71)	326	486,324,328
2,2',4,4'-tetrabromodiphenyl ether (47)	326	486,328,324
2,3',4,4'-tetrabromodiphenyl ether (66)	326	486,328,324
3,3',4,4'-tetrabromodiphenyl ether (77)	326	486,328,324
2,2',4,4',6-pentabromodiphenyl ether (100)	406	564,566
2,3',4,4',6-pentabromodiphenyl ether (119)	404	406,564
2,2',4,4',5-pentabromodiphenyl ether (99)	406	564,566
2,2',3,4,4'-pentabromodiphenyl ether (85)	406	564,566
3,3',4,4',5-pentabromodiphenyl ether (126)	566	564,568,406
2,2',4,4',5,6'-hexabromodiphenyl ether (154)	484	644,486
2,2',4,4',5,5'-hexabromodiphenyl ether (153)	644	484,486,482
2,2',3,4,4',5'-hexabromodiphenyl ether (138)	642	484
2,2',3,4,4',5',6-heptabromodiphenyl ether (183)	722	564
decabromodiphenyl ether (209)	956	

Baseline separation of Tri, Tetra, Penta, Hexa, Hepta, and DecaBDE's congeners in 44 minutes!



bde209 13C
Feb04_02bde2

Voltage SIR 7 Channels EI+
969.2102
1.18e6

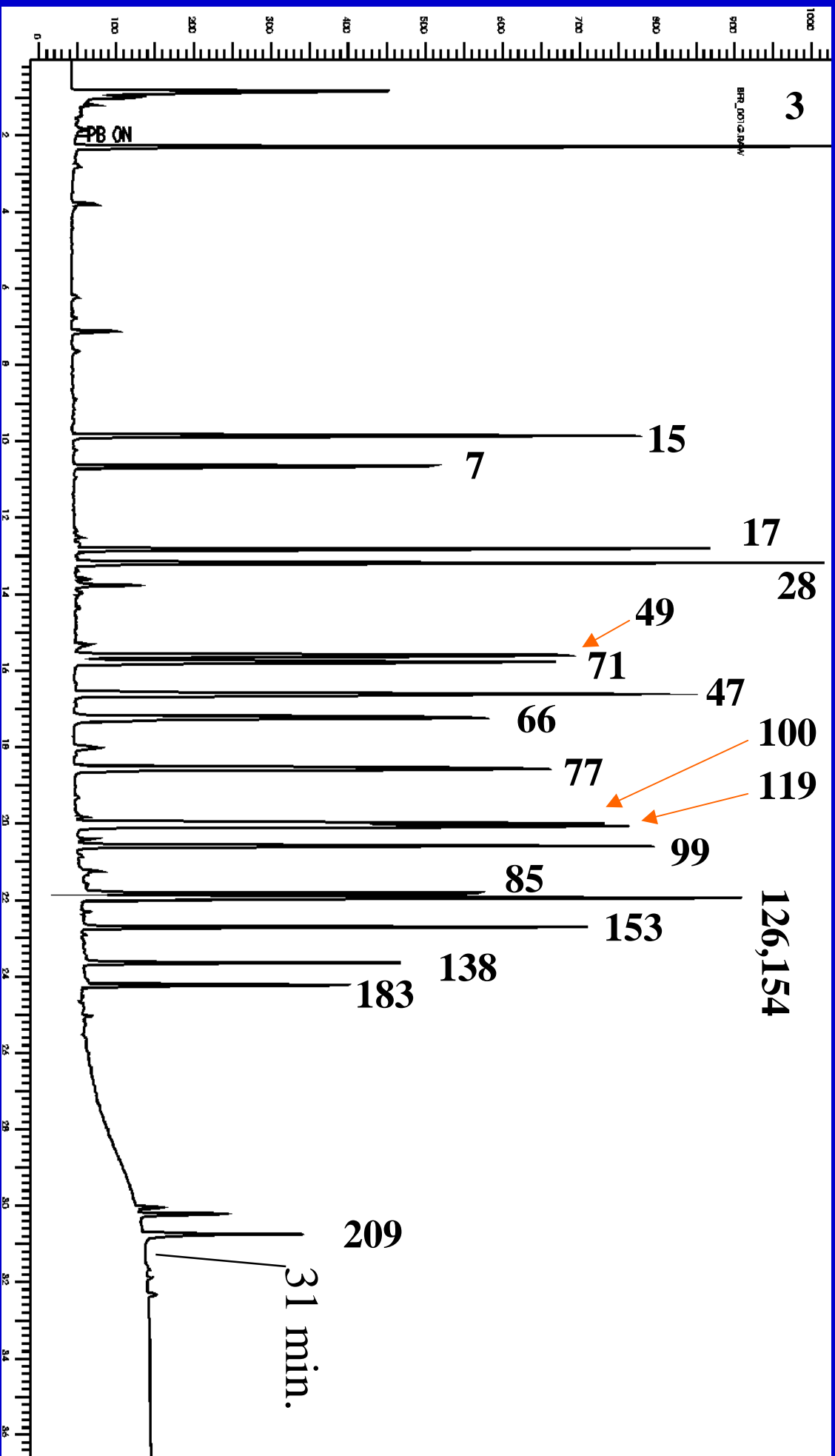


BROMINATED FLAME RETARDANT GC PROGRAM				
INSTRUMENT CONFIGURATION				
Micromass Autospec-UltimaNT (High Resolution Mass Spectro				
Source Temperature = 300°C				
GC CONDITIONS (HP 6890 +)				
Constant flow @ 1.5mL/min				
Injector Temp. 300°C				
Temp. Ramp Temp. Hold Time				
Start Temp. 100 1 min				
10 110 0.64				
80 180 0				
5 350 23				
TOTAL RUN TIME = 60.51				
**NB: DecaBDE (last elutor) elutes at ~43 min.				

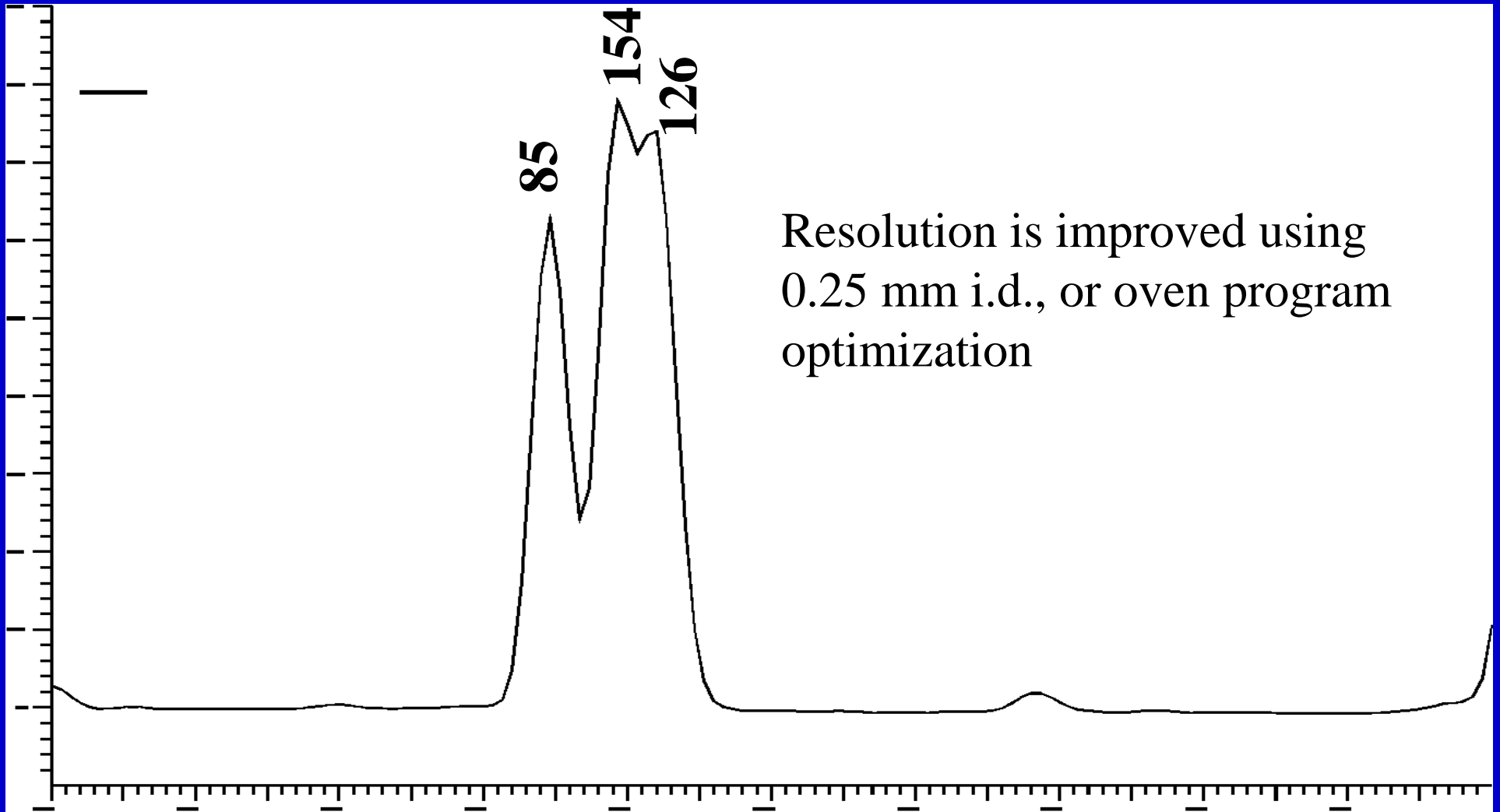
GC-ECD Analysis

- Electron capture detector is common to many laboratories
- Compounds have excellent response by ECD
- Higher flow rates may allow for more rapid separation using larger-diameter columns
- Instrumentation less expensive than HRMS
- Instrumentation is also field portable

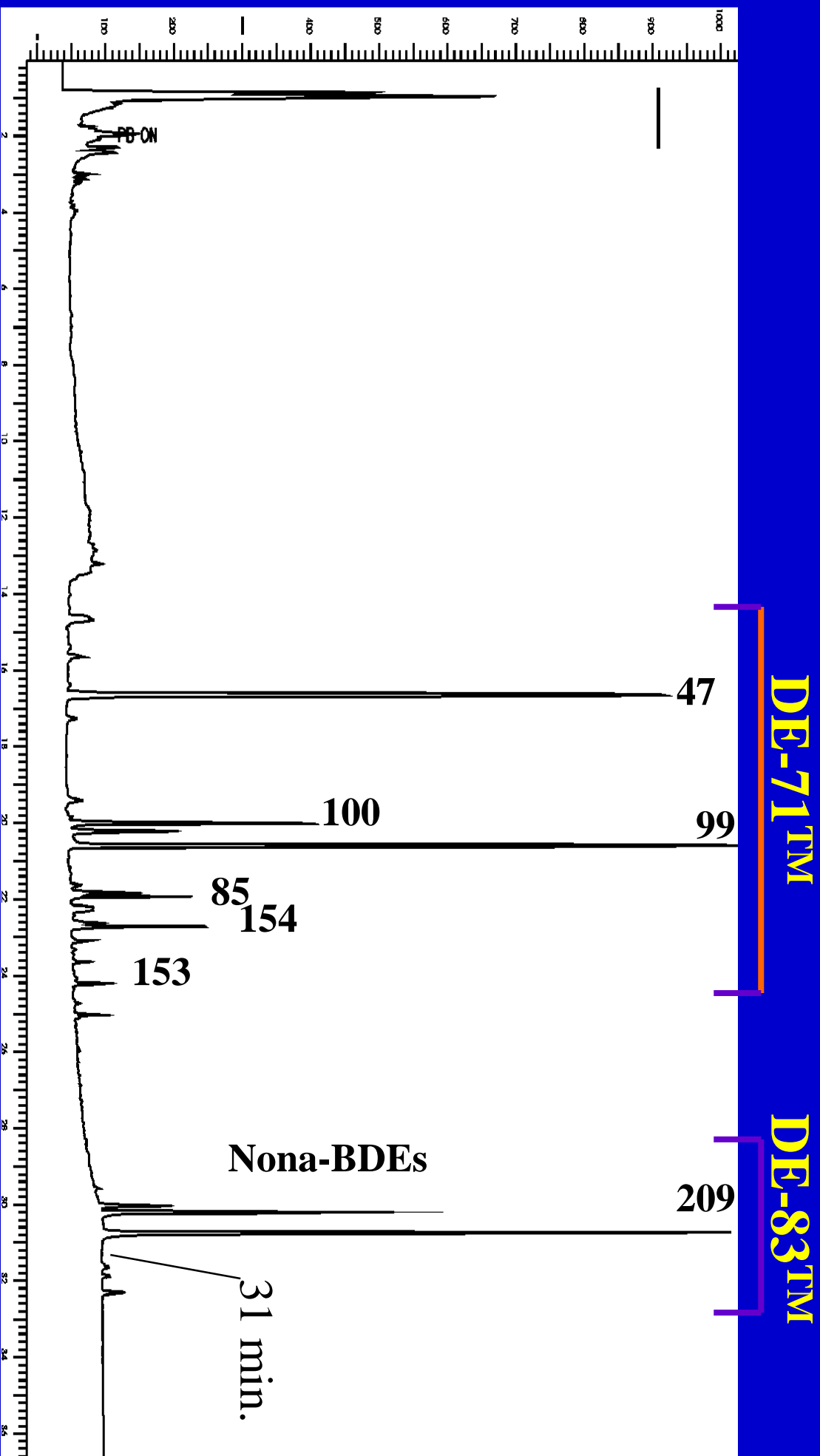
Wellington Laboratories BDE Mix-C



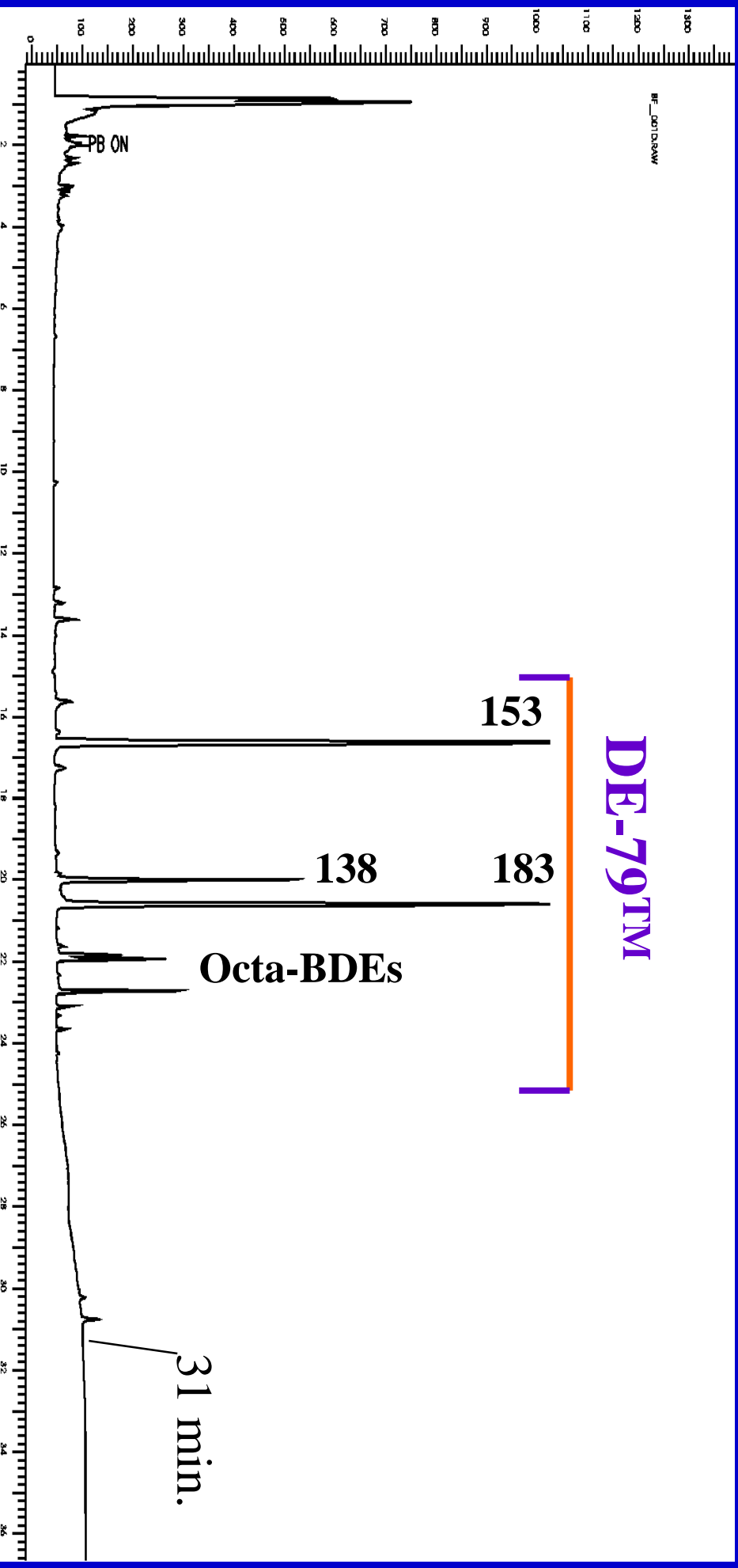
0.53 mm i.d. column partially resolves BDE 154 and 126 under these conditions



Commercially Available PBDE Mixes



Commercially Available PBDE Mixes



Conditions

Column: Rtx-500 30m x 0.53mm x 0.15 Ser# 233548
Flows: Hydrogen 7.69ml/min (66.7cm/sec) @ 100°C
Dead Time: MeCl₂ Headspace 0.76min @ 100°C
Oven: 100(1) 15/260(5) 15/380 (15) ~ 40 min runtime
Standards: Wellington Laboratory BDE-Mix C
1ul injection 30pg on column
Injection: Drilled Press-Tight Uniliner

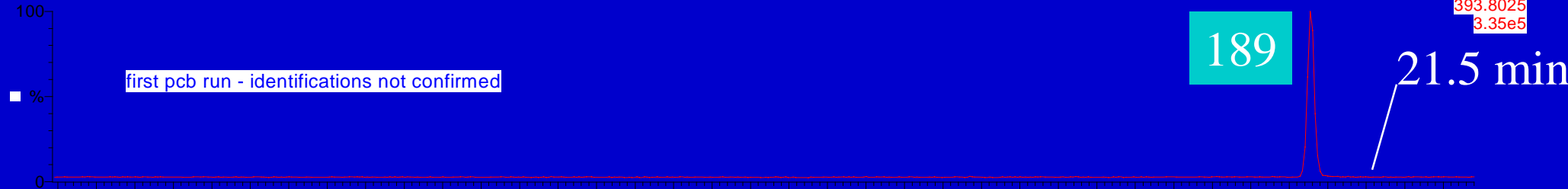
Other Uses of Rtx-500 Columns

- PCB Congener Analysis
 - Separation of World Health Organization 12 toxic congeners
 - Investigating use for larger lists of PCB Congeners
- PBB and PCBB Congeners
 - Similar separations to PCBs with higher temperature requirements
- PCDDs/PCDFs
 - Currently under investigation
- PBDDs/PBDFs
 - ?

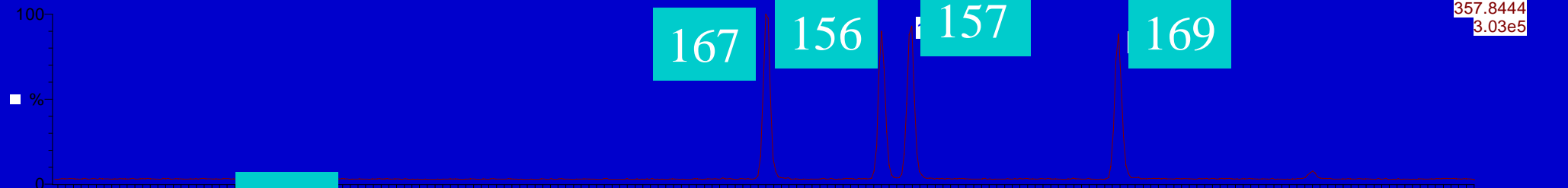
Toxic PCB Congeners

dlp-cs5 on htc

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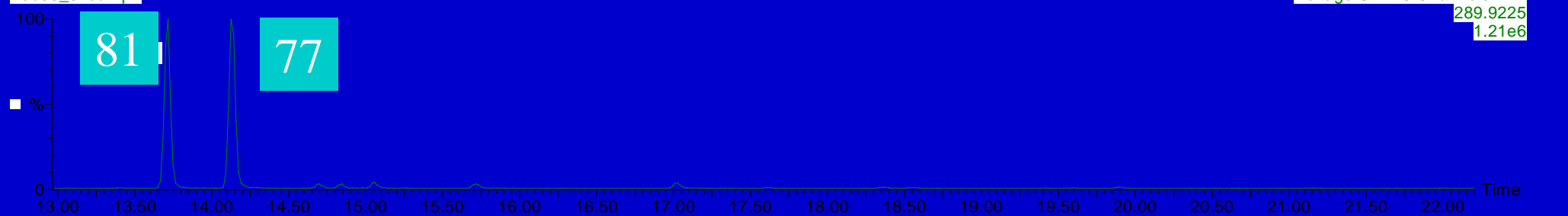
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Summary

- Rtx-500 Capillary GC Column
 - Consolidated PBDE analysis to a single column with excellent separation and reasonable run time
 - Extremely low-bleed polymer improves sensitivity of late-eluting compounds
 - Completely resolves all toxic PCB congeners
 - Very robust stationary phase which will not exhibit selectivity changes
 - Maximum thermal stability 380°C in fused silica, 440°C in passivated metal columns

Acknowledgements

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