

Gas Chromatographic Analysis of Polybrominated Diphenyl Ethers Using a Novel GC Column and Direct Flash Injection

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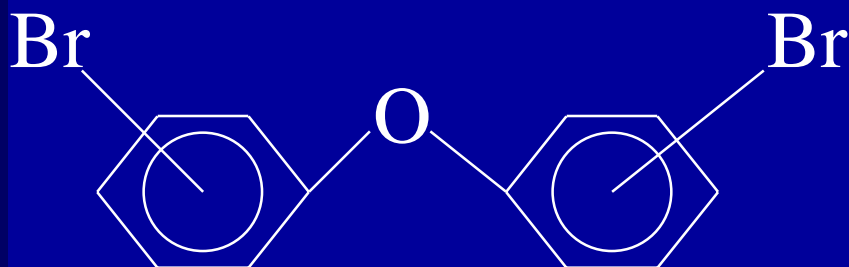
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Brominated Diphenylether Flame Retardants:

- 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

Common Amenable Methods of Analysis

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

Prior Reported Analyses

- GC-HRMS
 - Difficulty eluting nona's and decaBDE due to high molecular weight
 - On-column injection required to minimize molecular weight discrimination
 - May require more maintenance and cleaner sample extracts than hot flash techniques.
 - Column bleed levels hurt sensitivity of higher bromination level congeners
 - Often done using two columns:
 - Longer column to separate lower bromination level congeners
 - Short column to analyze nona and decaBDE's

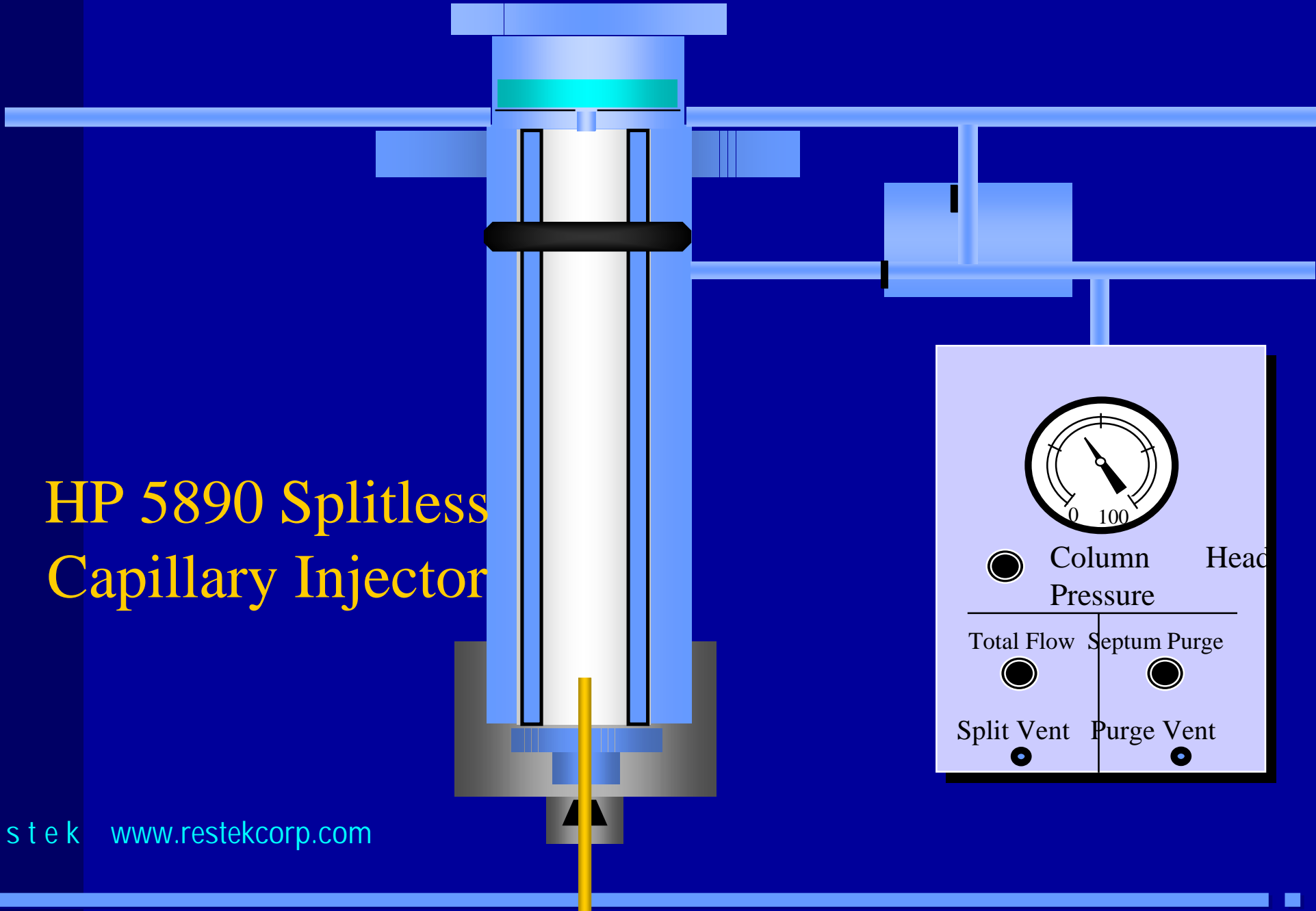
Prior Methods of Analysis

- Decision made if deca (and possibly 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)
 - If interested in BDE 209, longer run times are common
- Loss of higher molecular weight congeners is generally due to injection technique

Analytical Needs:

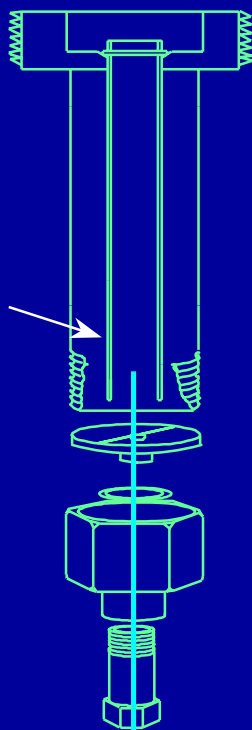
- Need injection technique which does not have discrimination issues like splitless
- Extracts may contain high levels of contamination, and not all labs will want to thoroughly clean the extracts
- High temperature stationary phase and column that has necessary selectivity, and low bleed levels

HP 5890 Splitless Capillary Injector



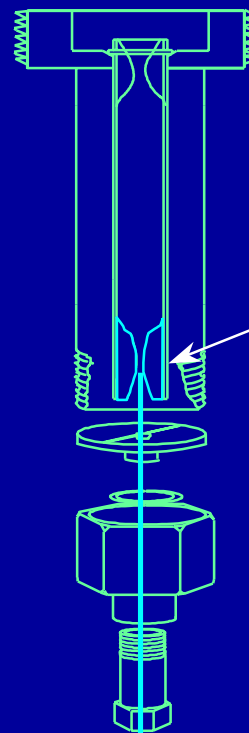
Convert Split or Splitless Inlets to Direct Injection Mode

Remove the split or splitless sleeve

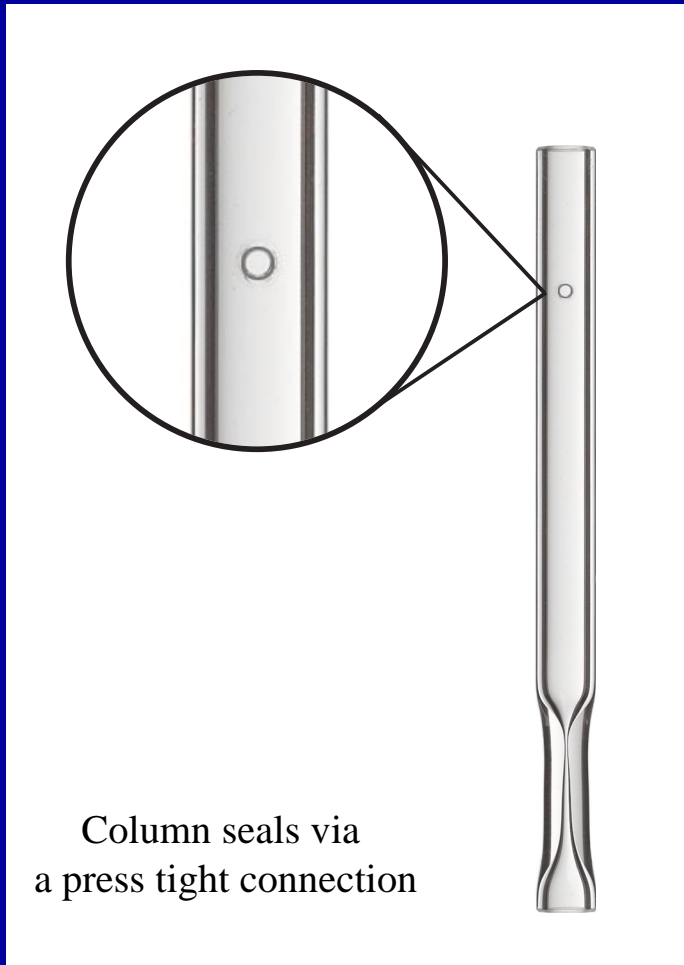


Install a Direct Injection sleeve

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

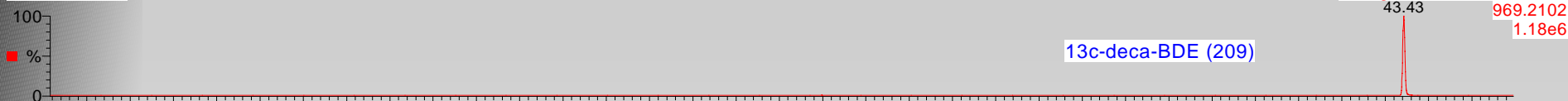
- Carborane-stabilized stationary phase
 - Maximum temperature of 380 C in “standard high-temperature” tubing
 - Maximum temperature of 440 C in passivated metal columns (Mxt-500)
- Extremely low bleed levels
 - Surpasses phenyl/methyl phases, and silphenylene stationary phases
- Common dimensions available

Wellington Laboratories BDE Mix-C

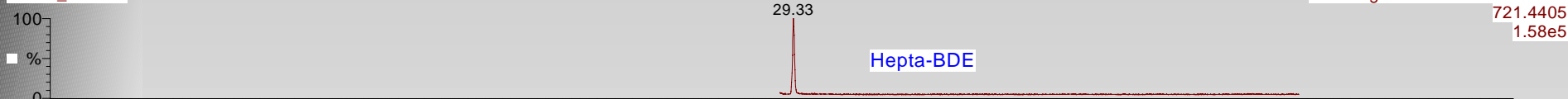
4-bromodiphenyl ether (3)	250	141,115
2,4-Dibromodiphenyl ether (7)	168	328,139
4,4'-dibromodiphenyl ether (15)	328	168,221
2,2',4-tribromodiphenyl ether (17)	248	408,406
2,4,4'-tribromodiphenyl ether (28)	406	248,246
2,2',4,5'-tetrabromodiphenyl ether (49)	326	486,328,324
2,3',4',6-tetrabromodiphenyl 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!

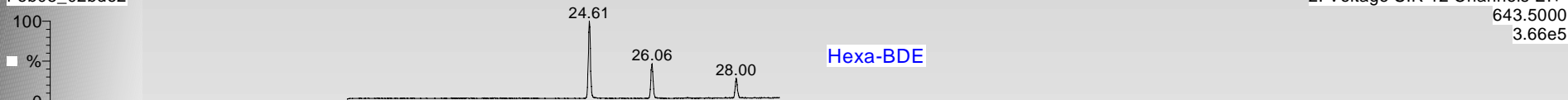
bde209 13C
Feb04_02bde2



Feb05_02bde2



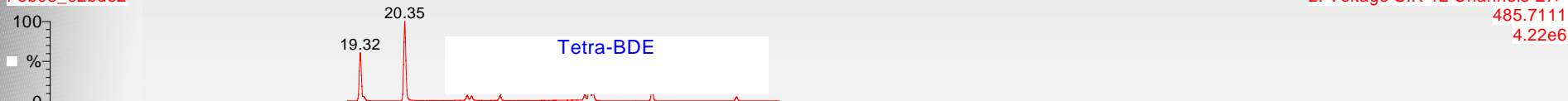
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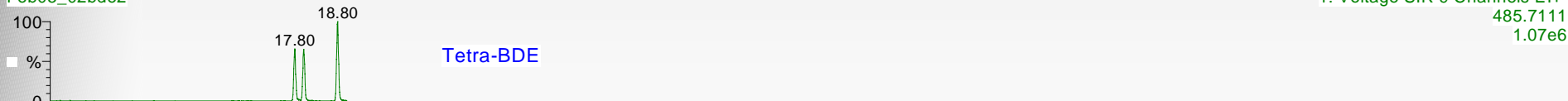
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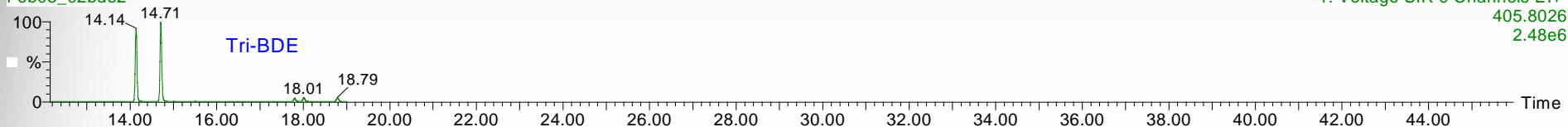
Feb05_02bde2



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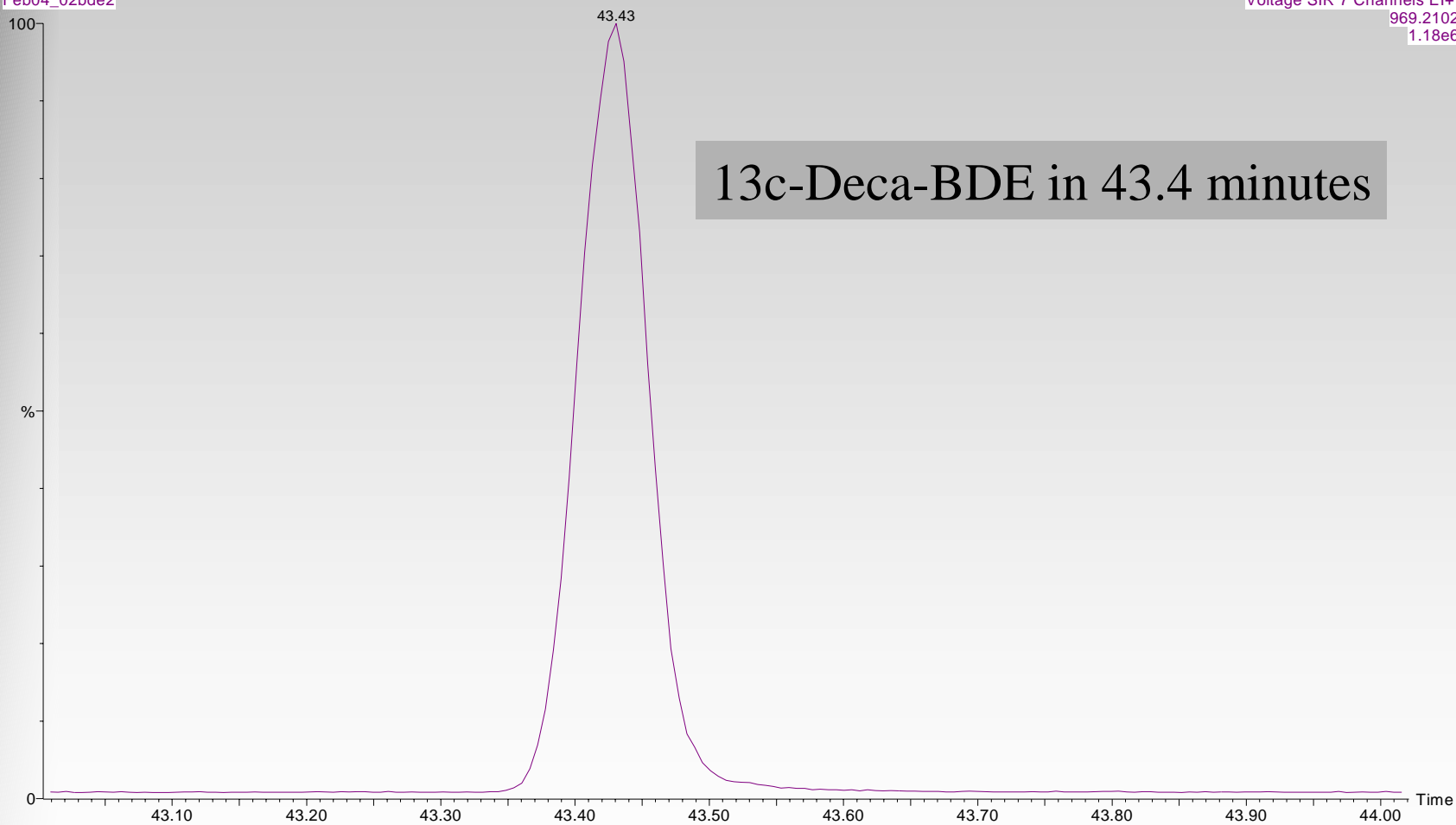


Feb05_02bde2



bde209 13C
Feb04_02bde2

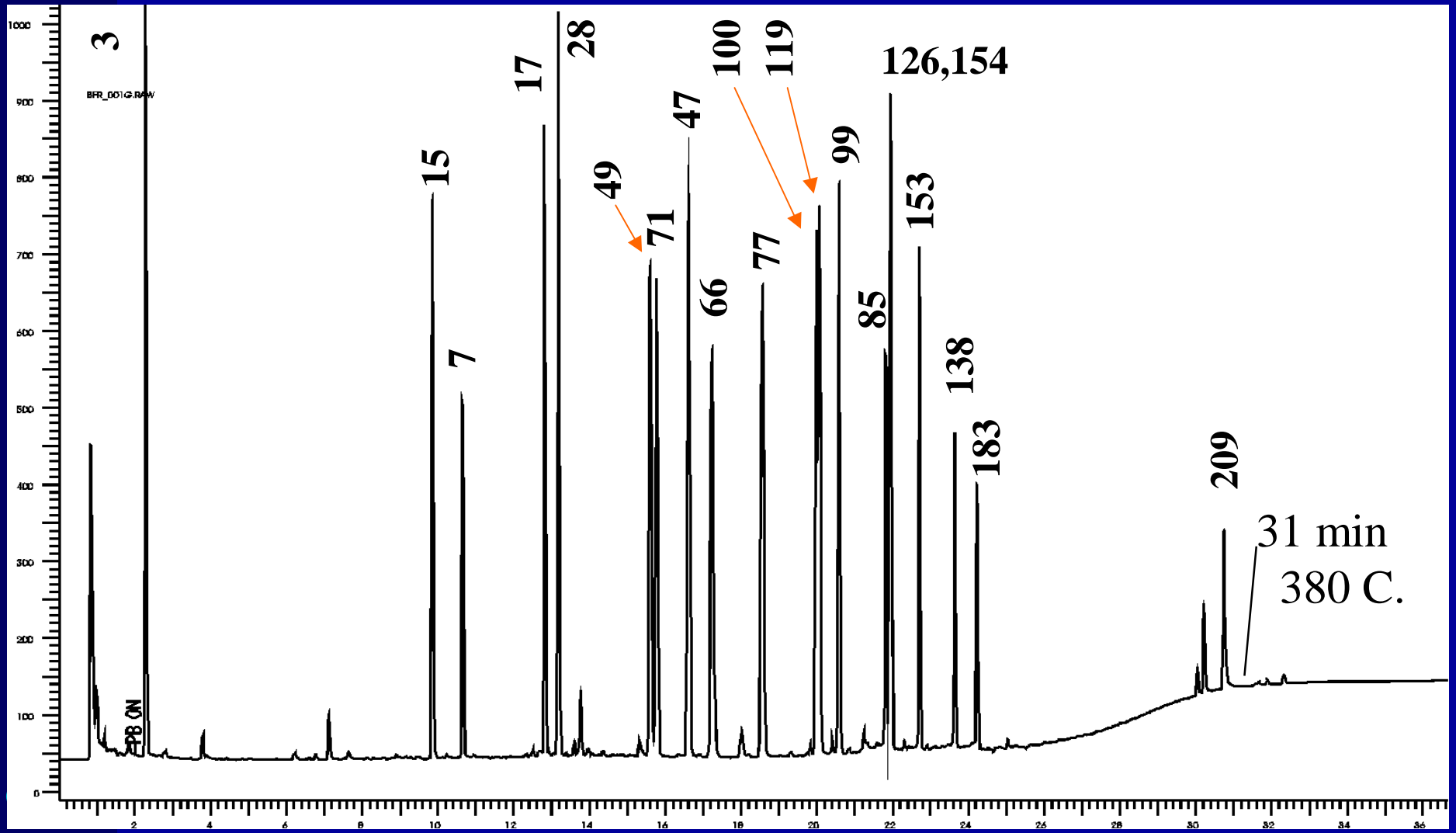
Voltage SIR 7 Channels EI+
969.2102
1.18e6



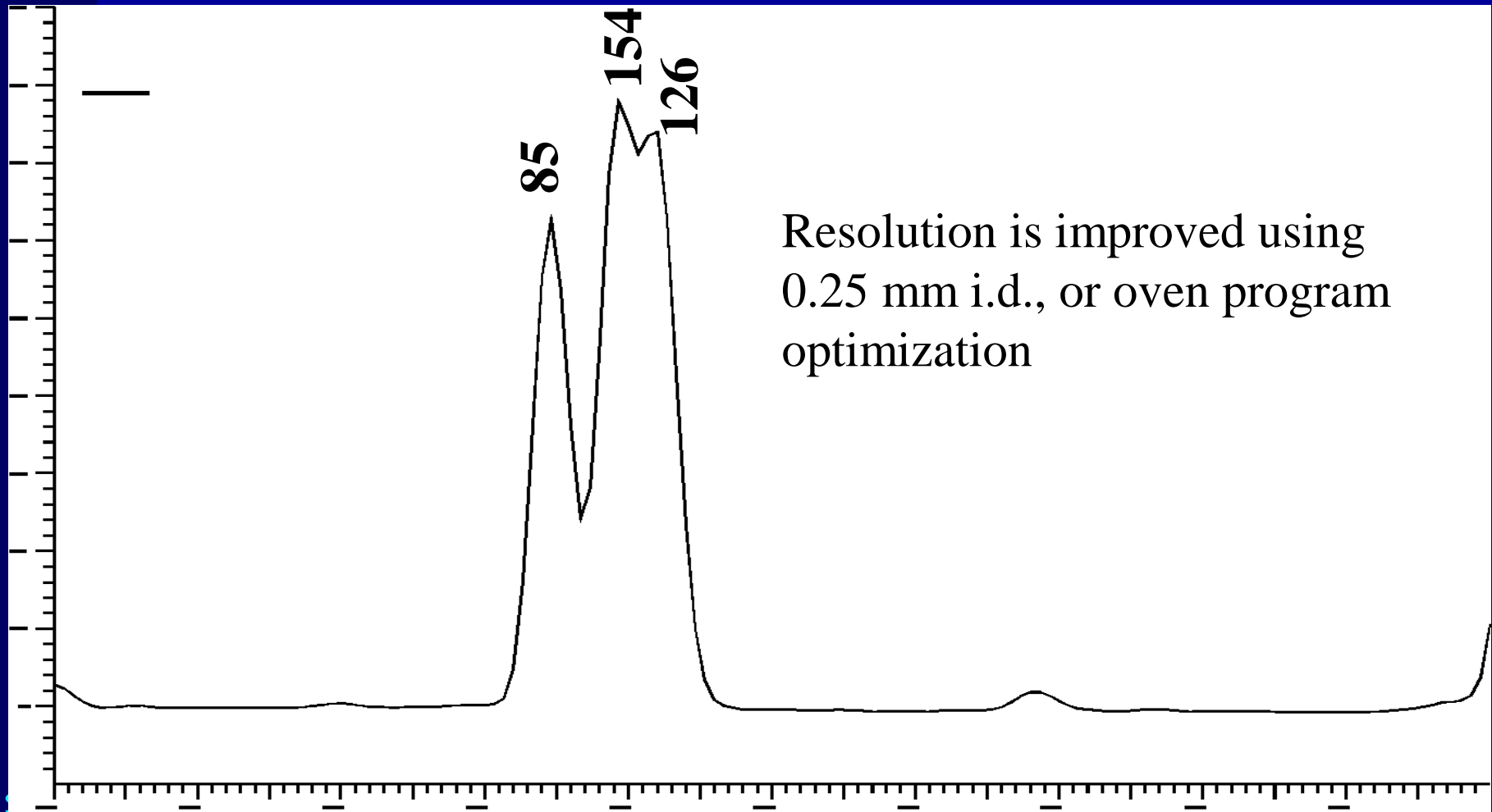
GC-ECD Analysis

- 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

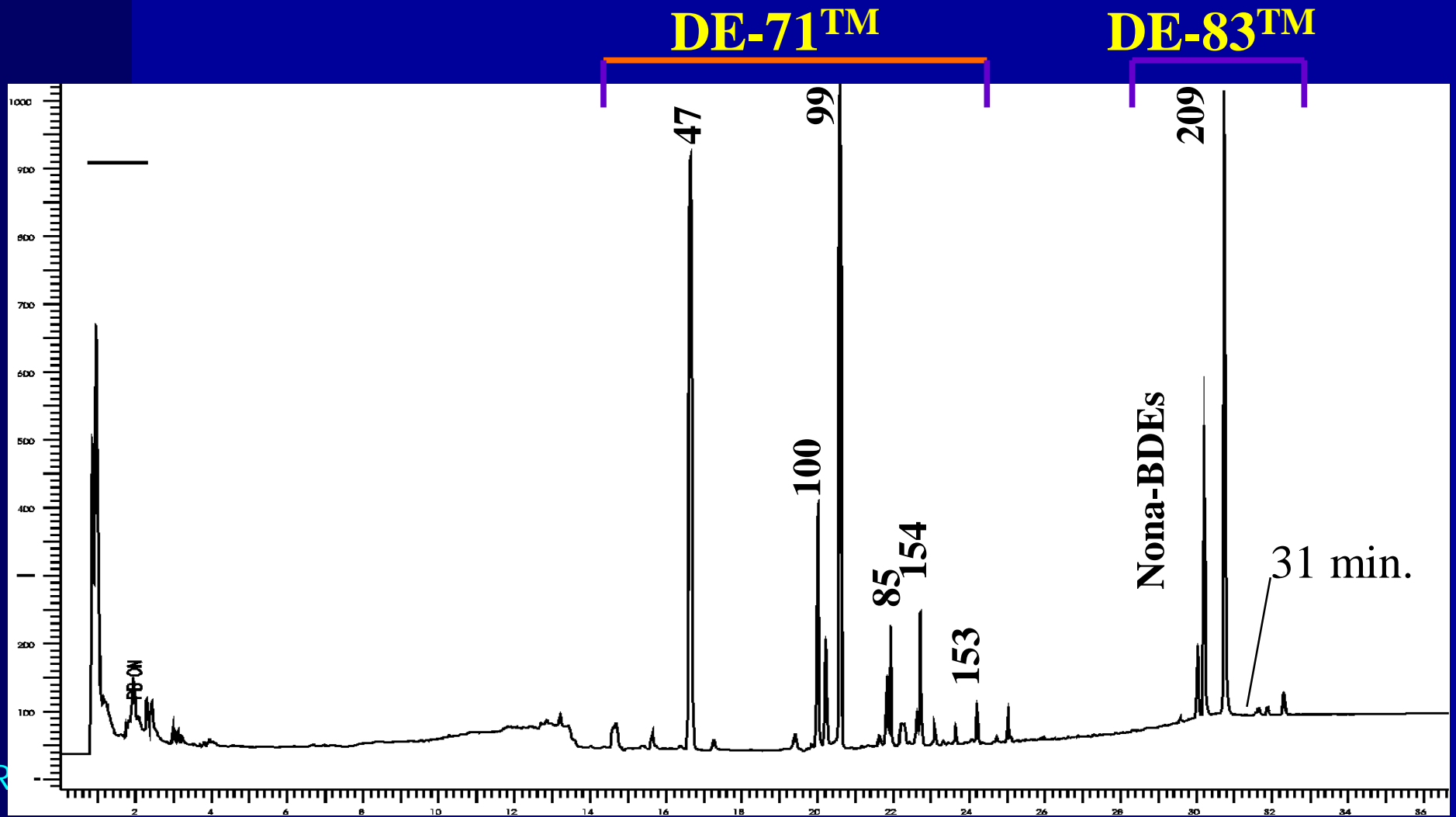
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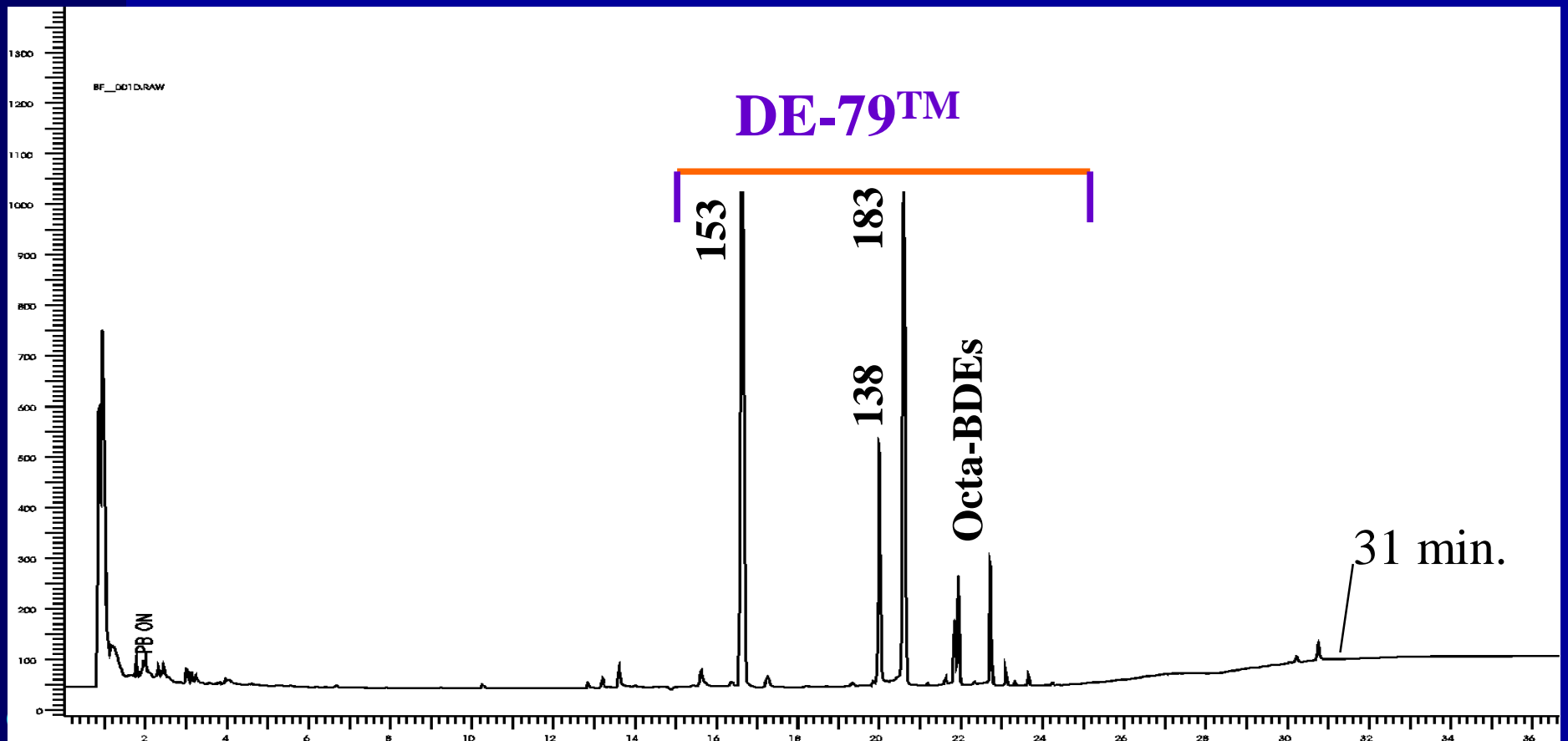
0.53 mm i.d. column partially resolves BDE 154 and 126 under these conditions



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.

Acknowledgements

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