

High-Speed Analysis of Pesticides Using Application-Specific Chromatographic Columns and Time of Flight Mass Spectrometry

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www.restekcorp.com



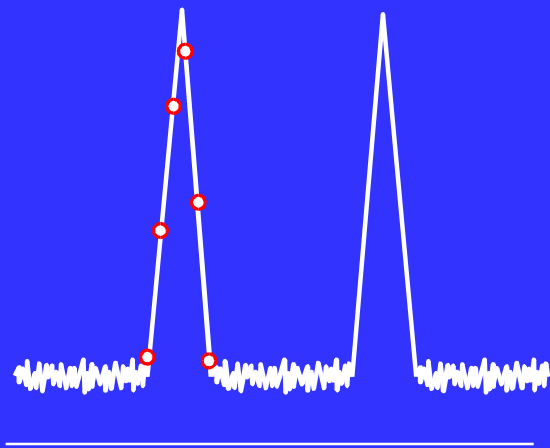
Advantages of Fast GC

- Shorter Column lengths, faster ramp rates
 - Increased sample throughput
- Smaller column I.d., faster ramp rates
 - Narrower peak width
 - More plates/meter
 - Lower carrier flow rates
 - Higher column head pressures

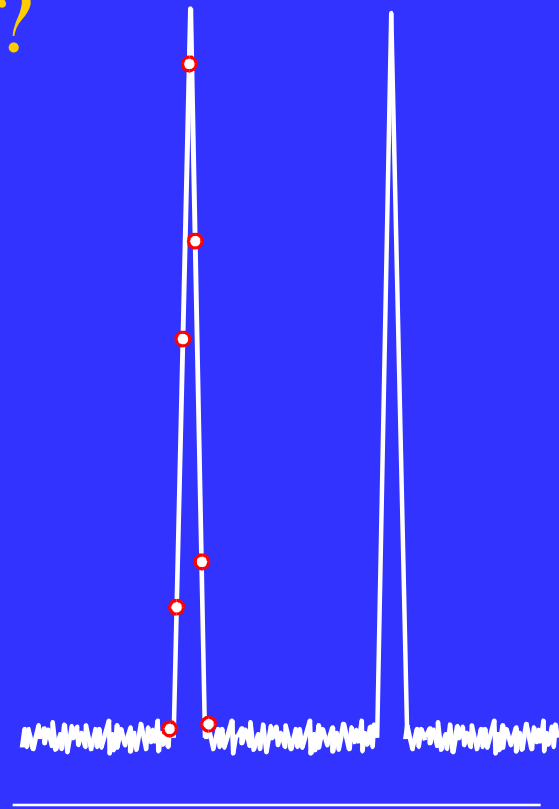
Disadvantages of Fast GC

- Smaller column IDs
 - Lower column capacity – can require injection modification, and extract cleanup
- Narrower peak width
 - Places demands on detection systems
- Fast GC has not been accepted as much as academic literature would imply, mainly due to limitations of detection systems

How many data points are necessary to correctly characterize a chromatographic peak?

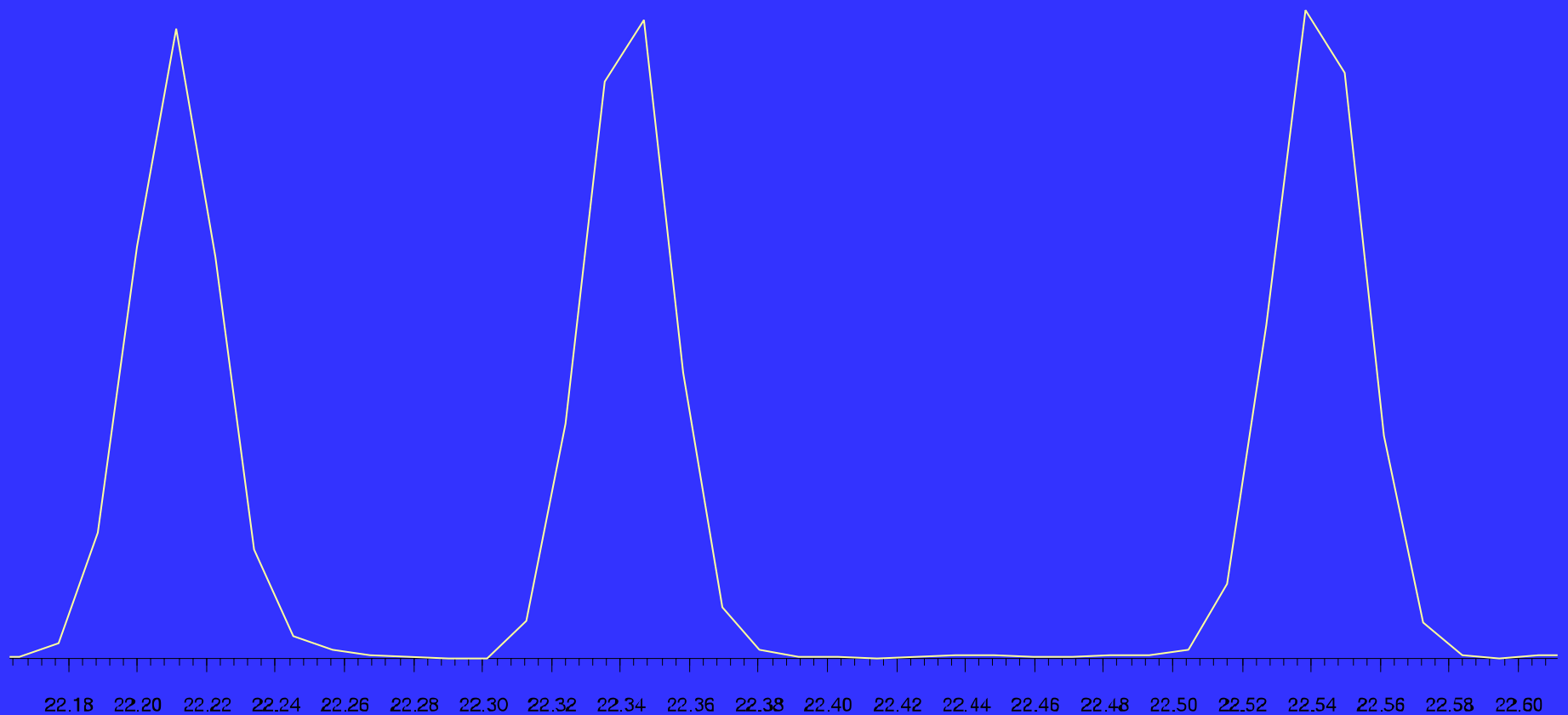


Minutes

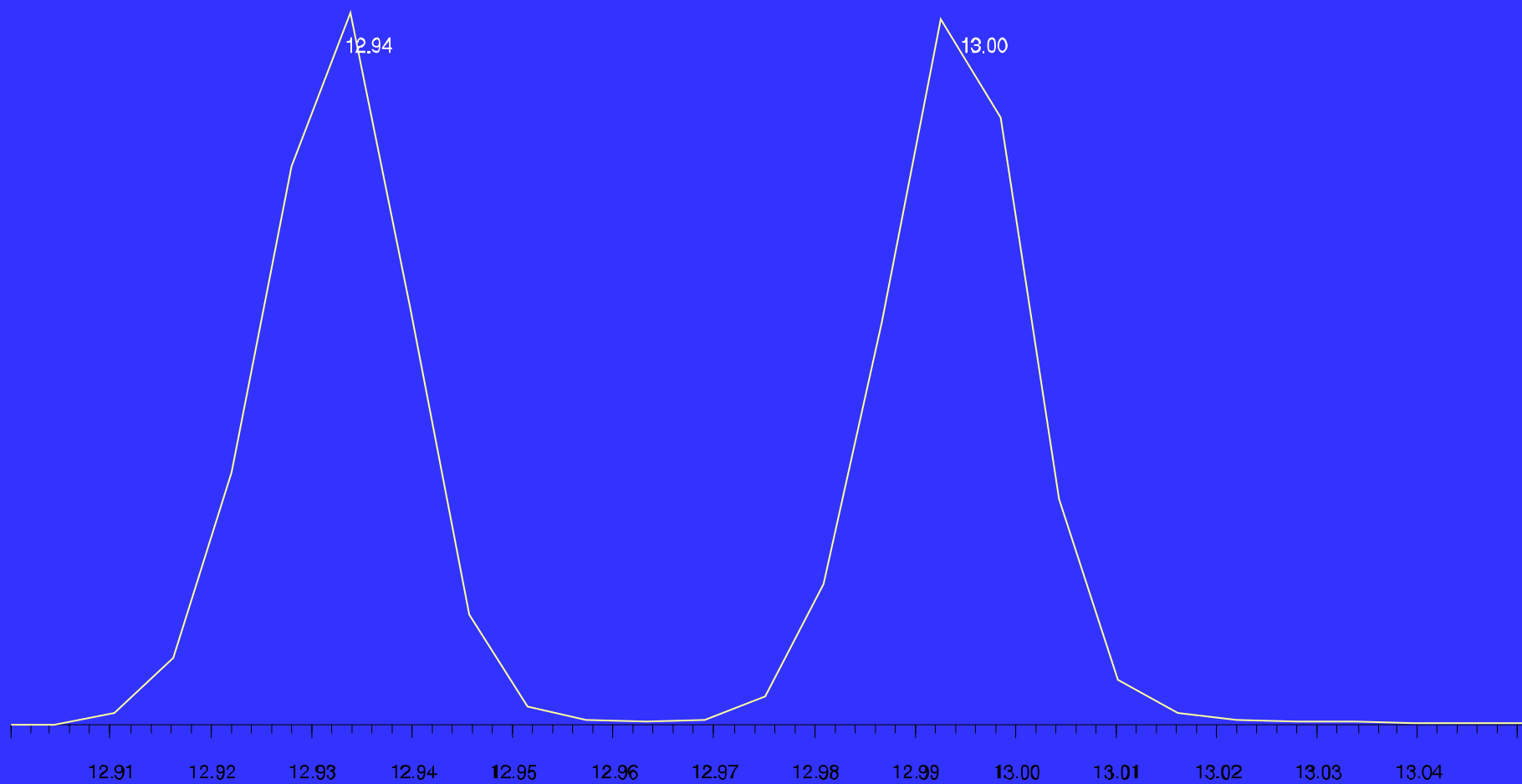


Seconds

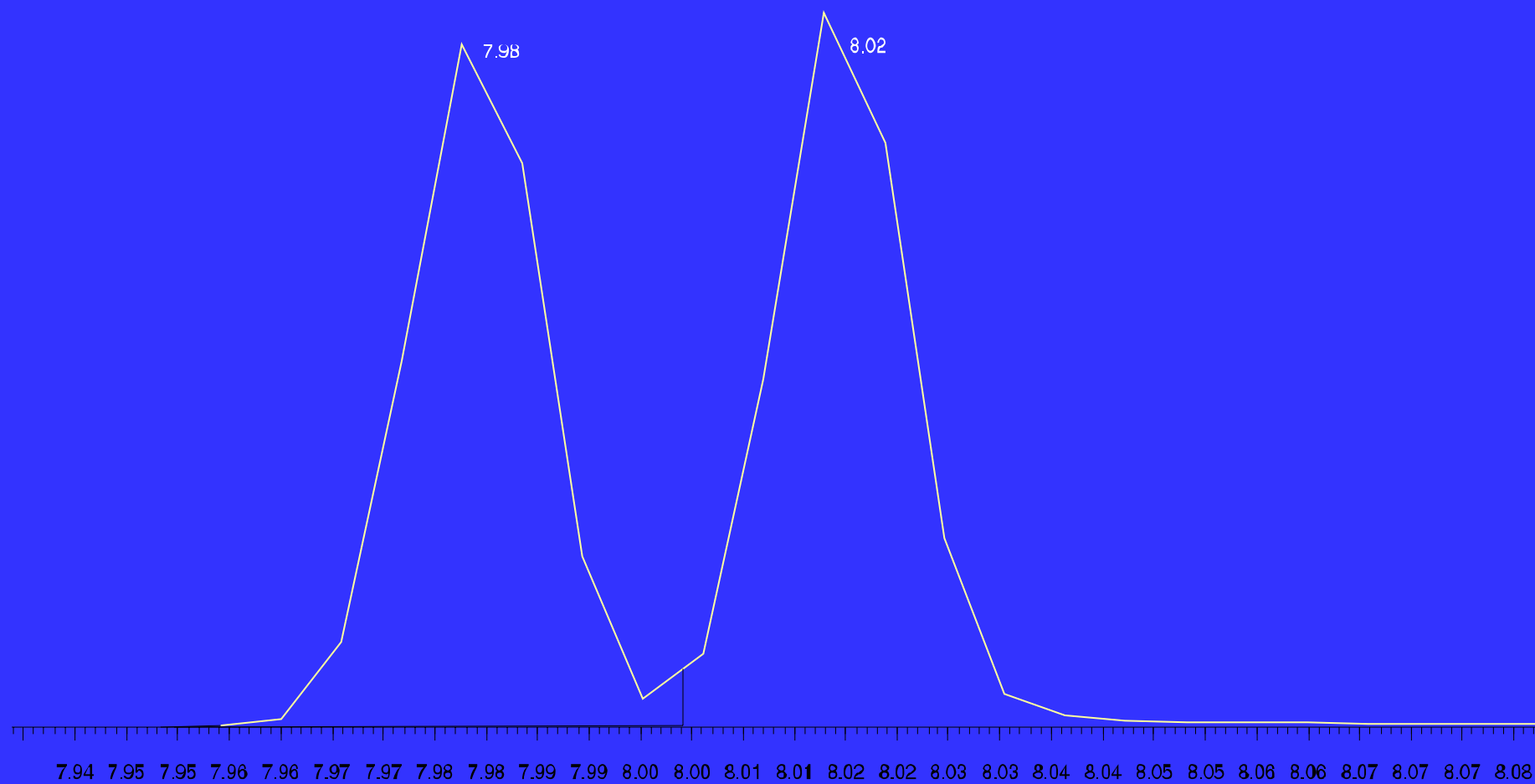
Sampling Frequency Limitations of Quadrupoles and Ion Traps Can Cause Peak Biasing



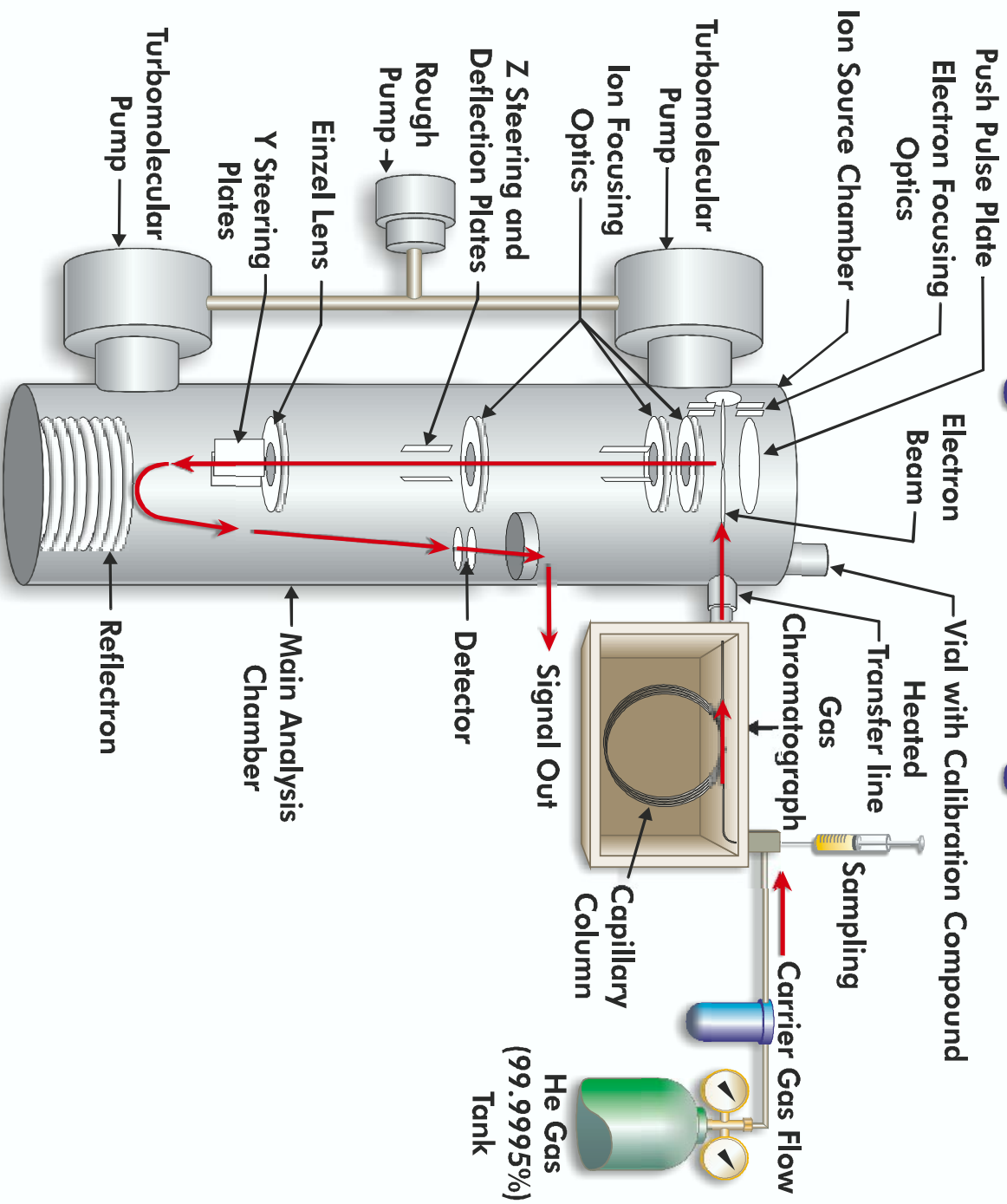
Peak Biasing...



Peak Biasing...



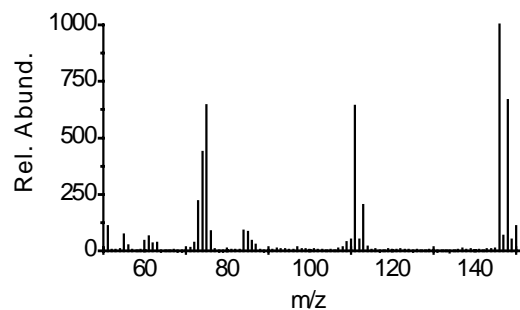
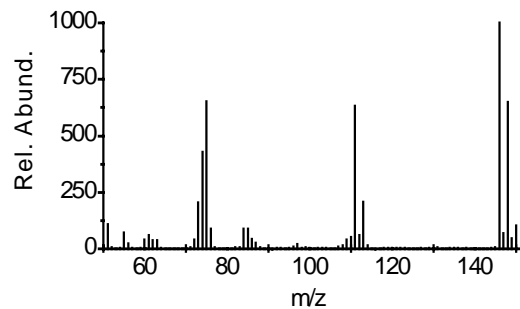
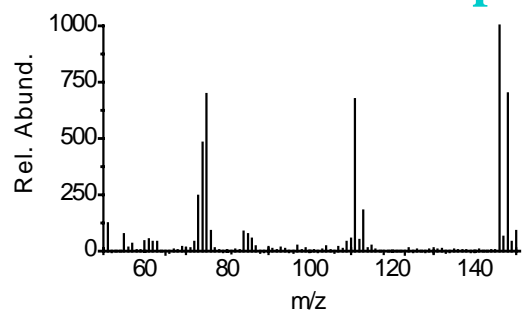
Pegasus II Diagram



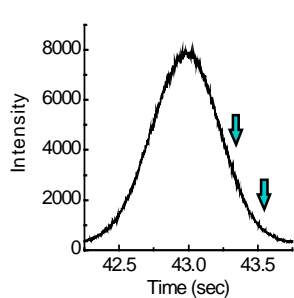
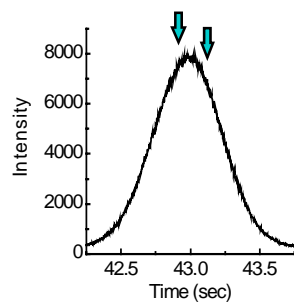
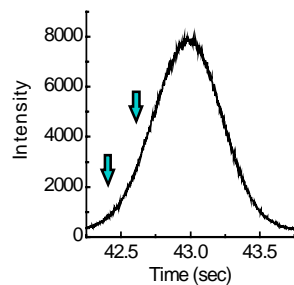
Spectra - TOF vs. Scanning MS

TOF Ion Ratios Vary Less Than 1% Across the Peak

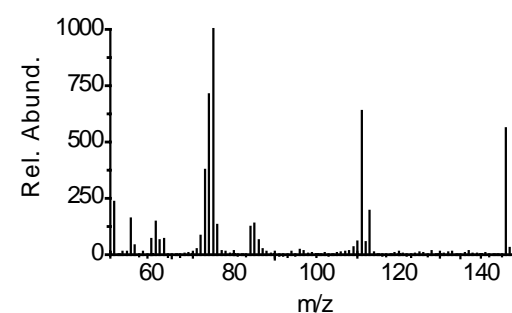
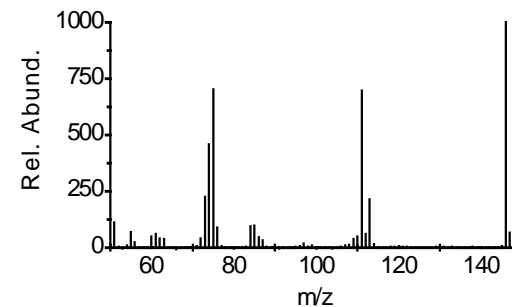
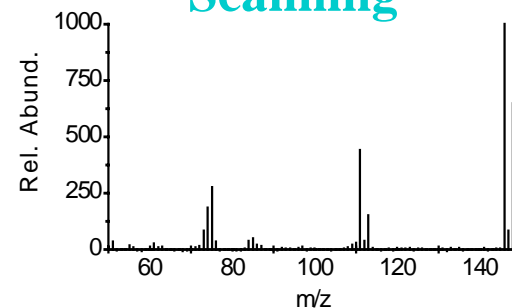
Simultaneous Sampling



GC Peak

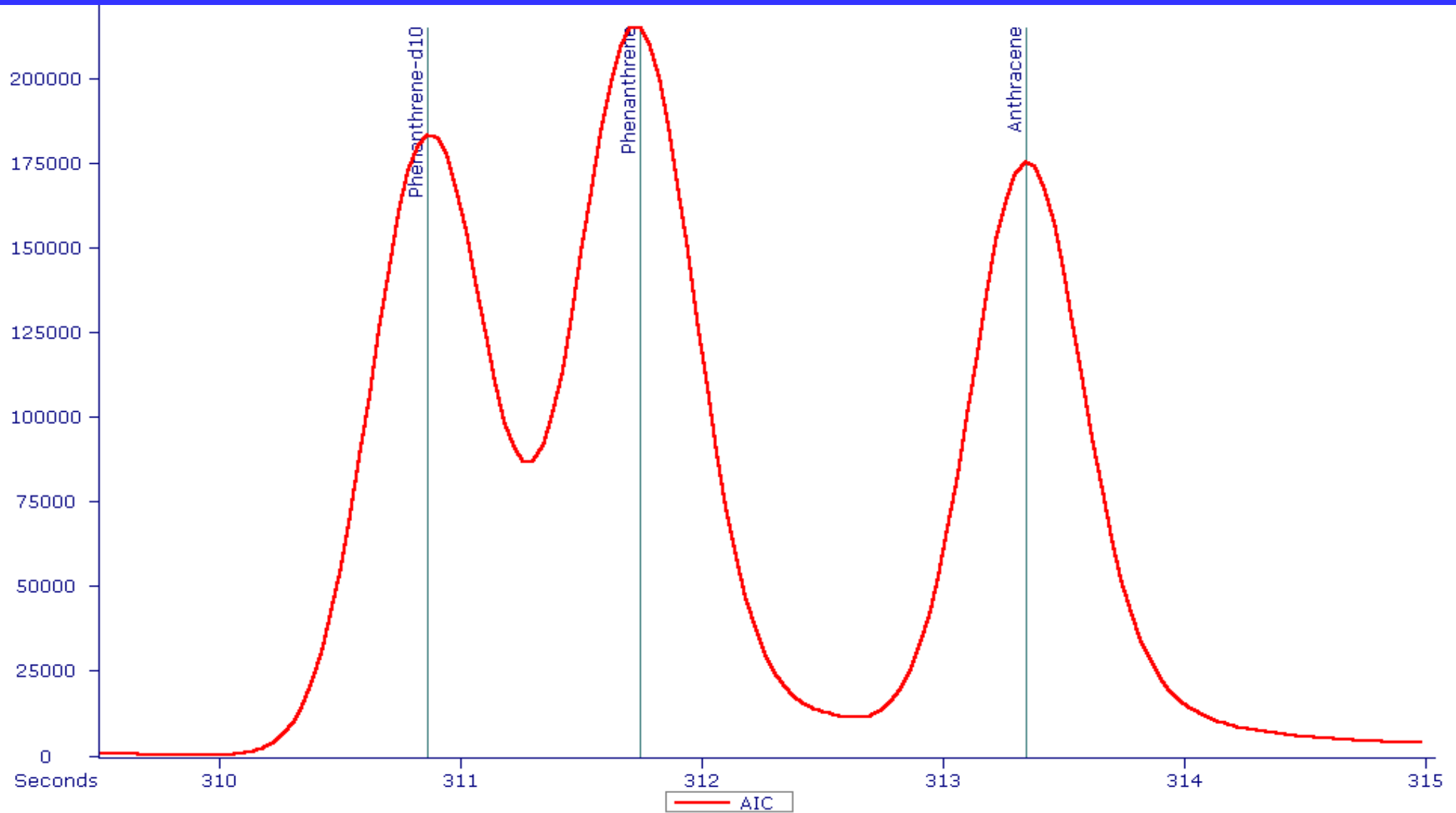


Scanning

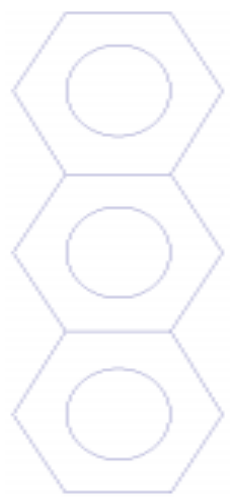
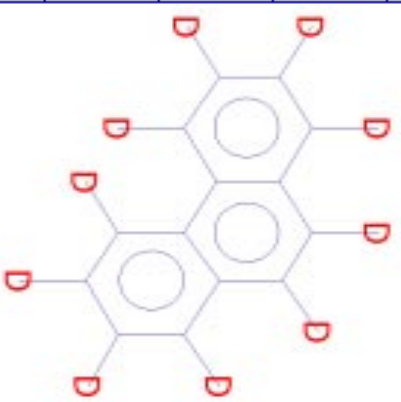
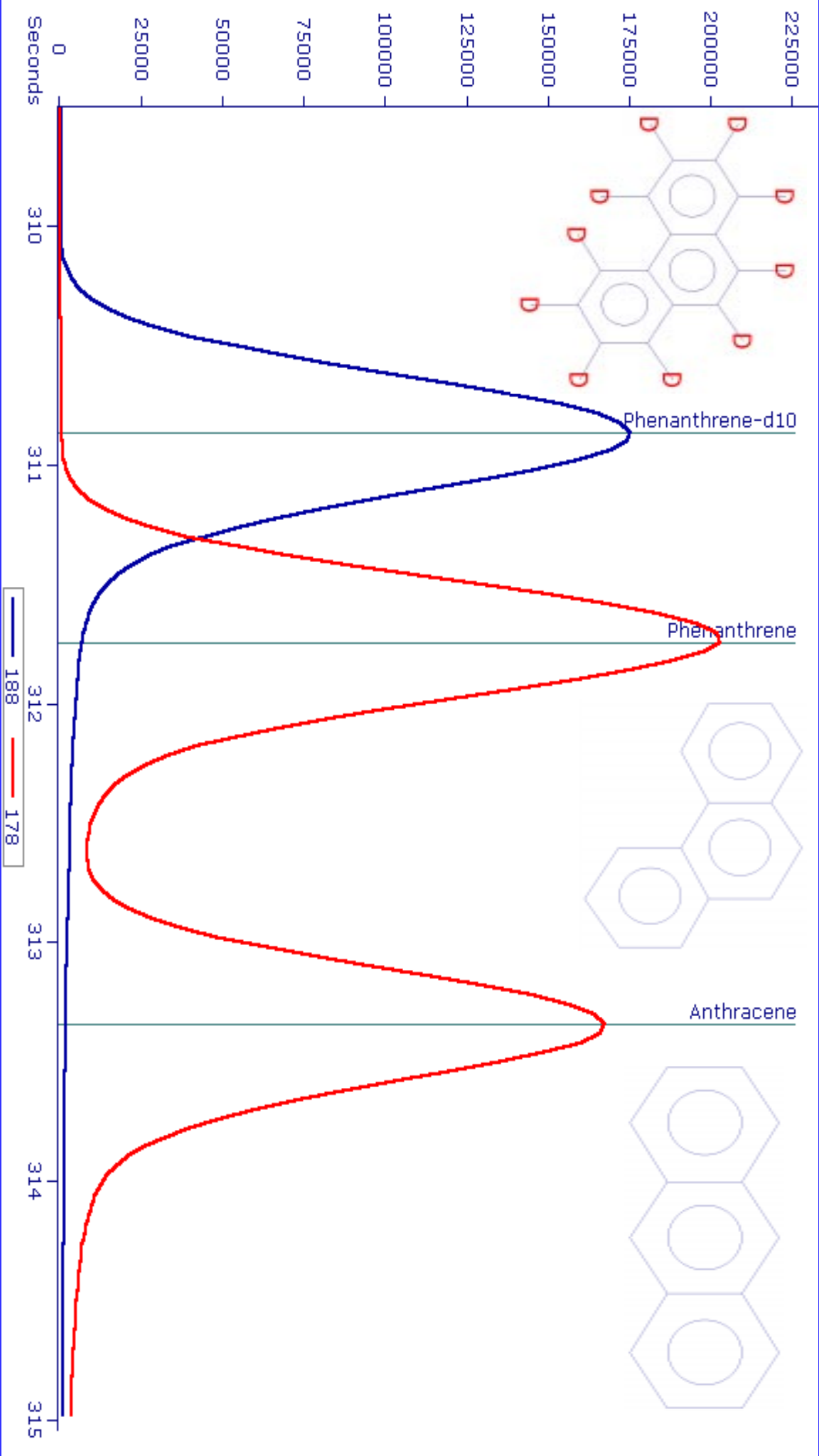


PAH Standard – AIC

D10-Phenanthrene, Phenanthrene, Anthracene

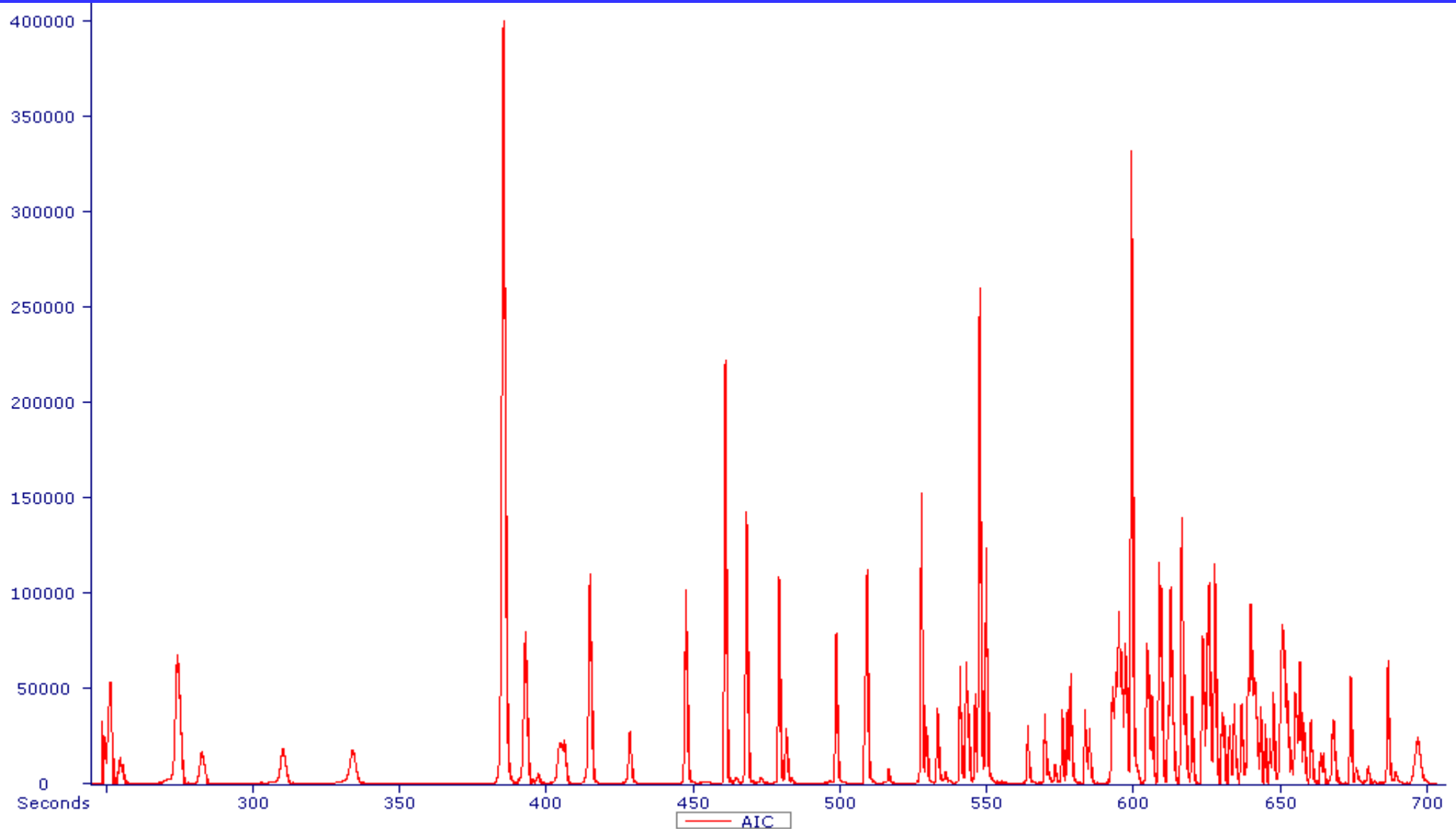


Peak #	Name	R.T.	Similarity	Reverse	Hit #	UniqueMass	S/N	Area	Library	CAS	Formula	Weight
6	Anthracene-d10	310.86	934	934	1	188	5993.3	2966200	MAINLIB	1719-06-8	C14D10	188
7	Phenanthrene	311.74	982	982	1	178	4412.7	3178700	MAINLIB	85-01-8	C14H10	178
8	Anthracene	313.34	977	977	1	178	3777.0	2847500	MAINLIB	120-12-7	C14H10	178

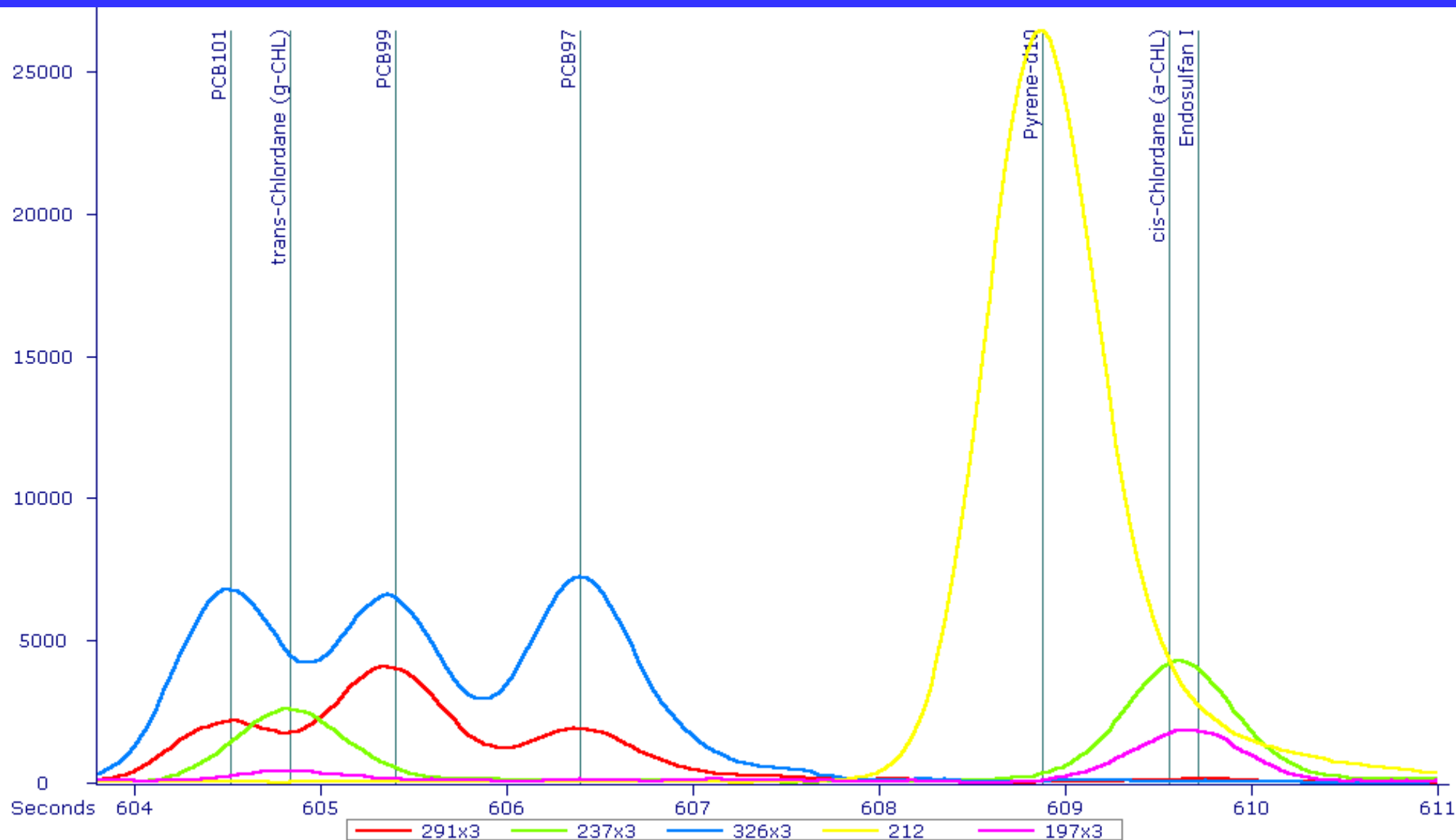


Sample D-0998

Analytical Ion Chromatogram (AIC)

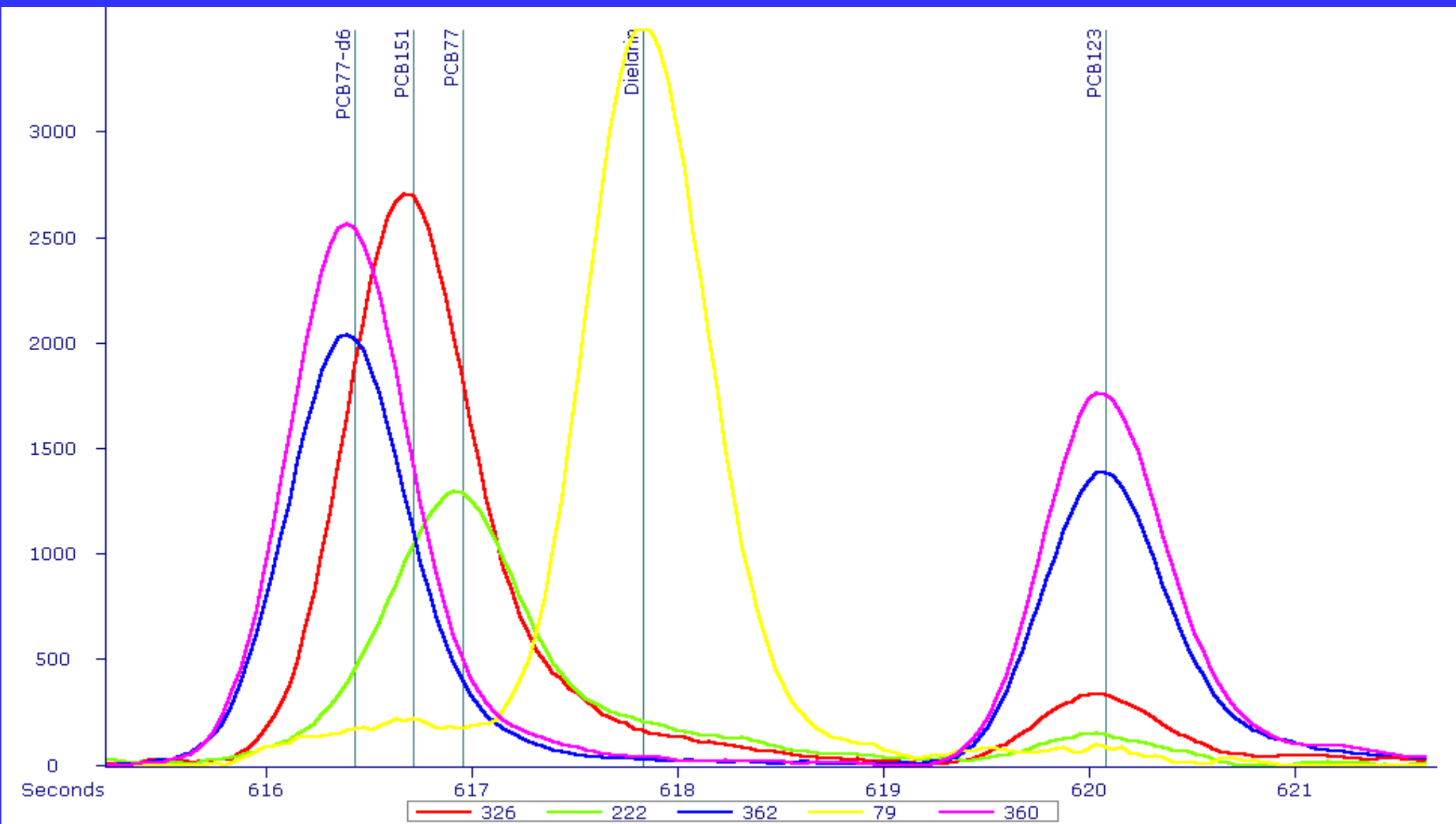


Sample D-0998



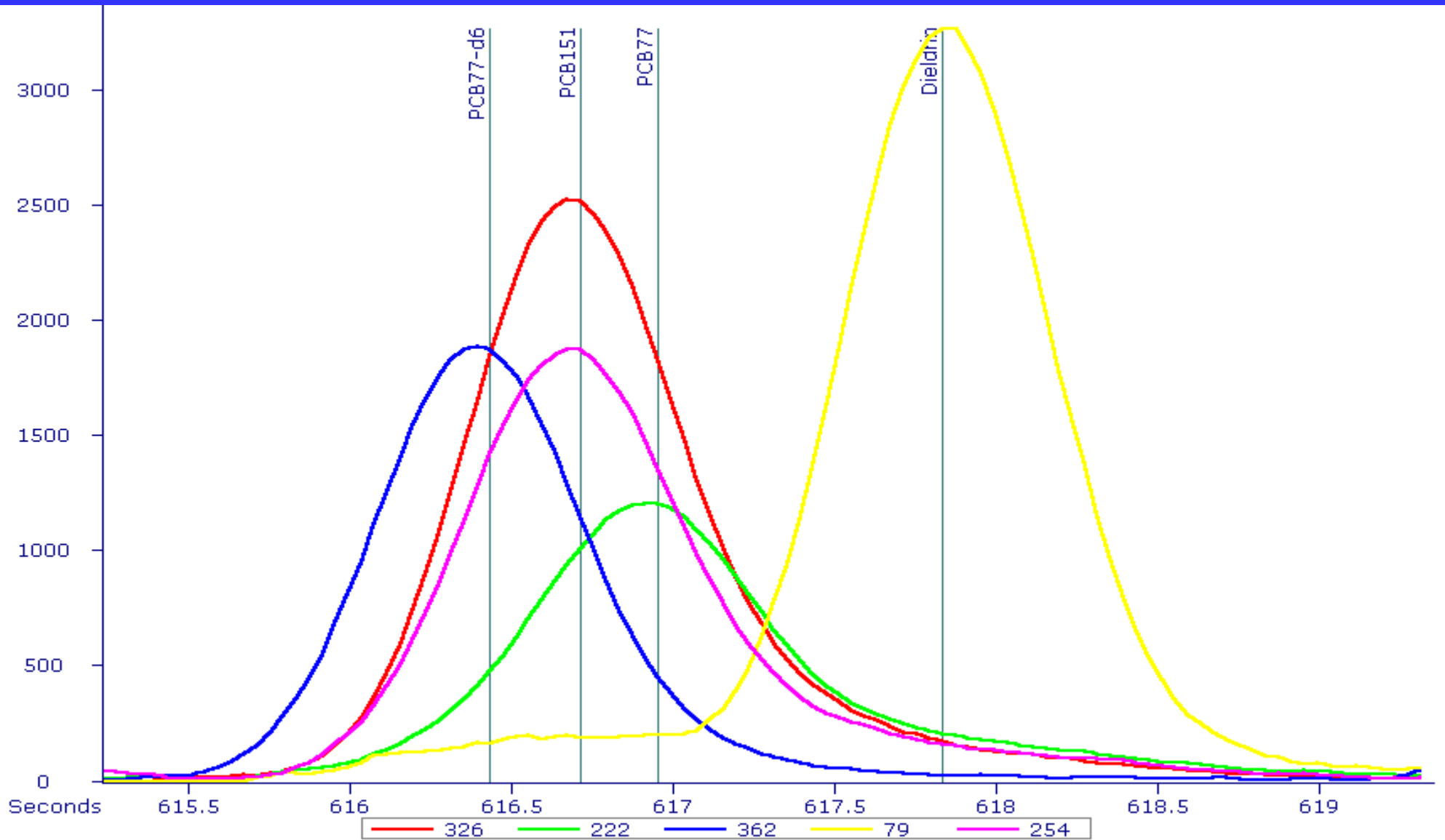
Sample D-0998

PCB77-d6, PCB151, PCB77, Dieldrin, PCB123



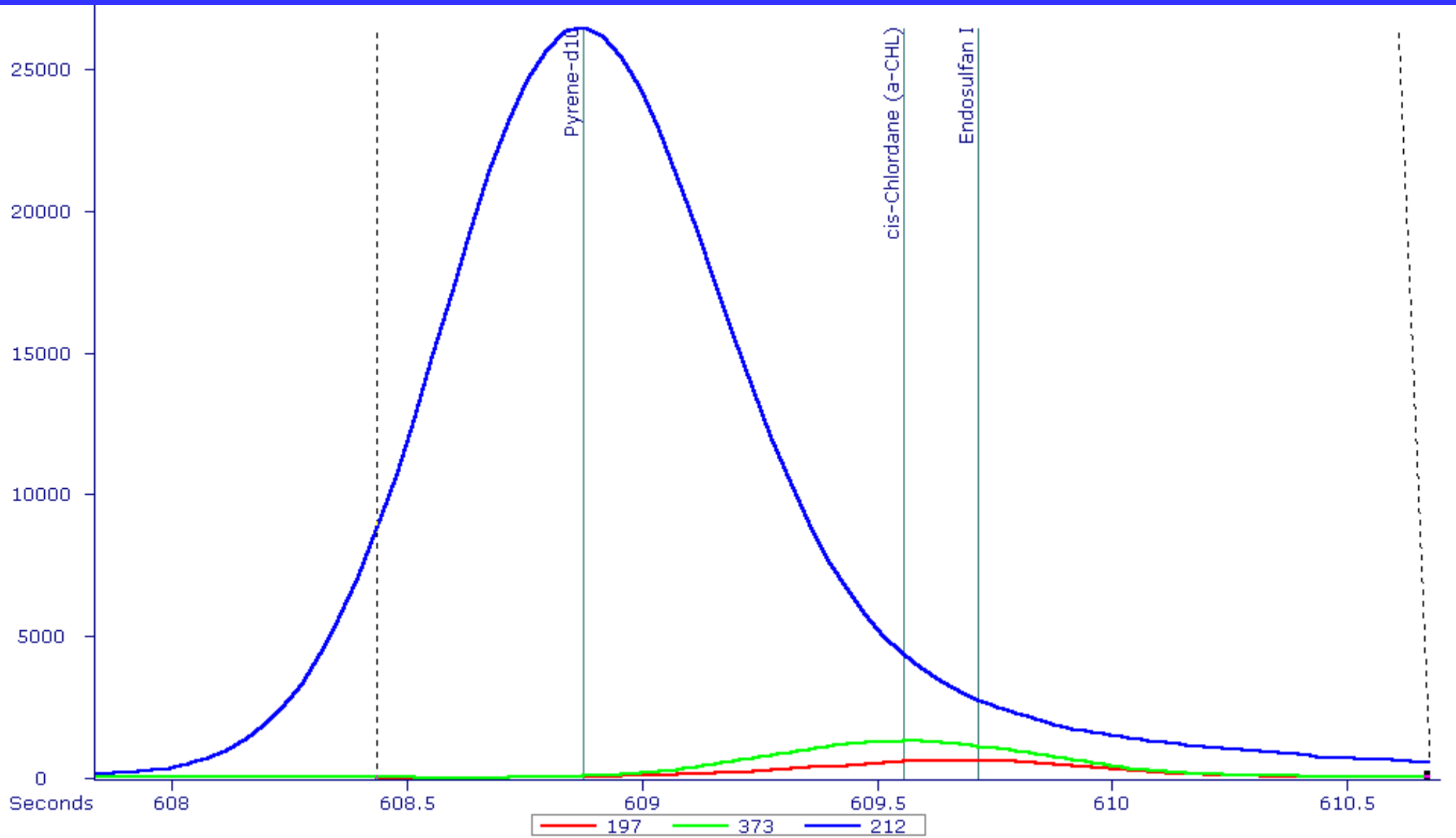
Sample D-0998

Analytical Ion Chromatogram (AIC)



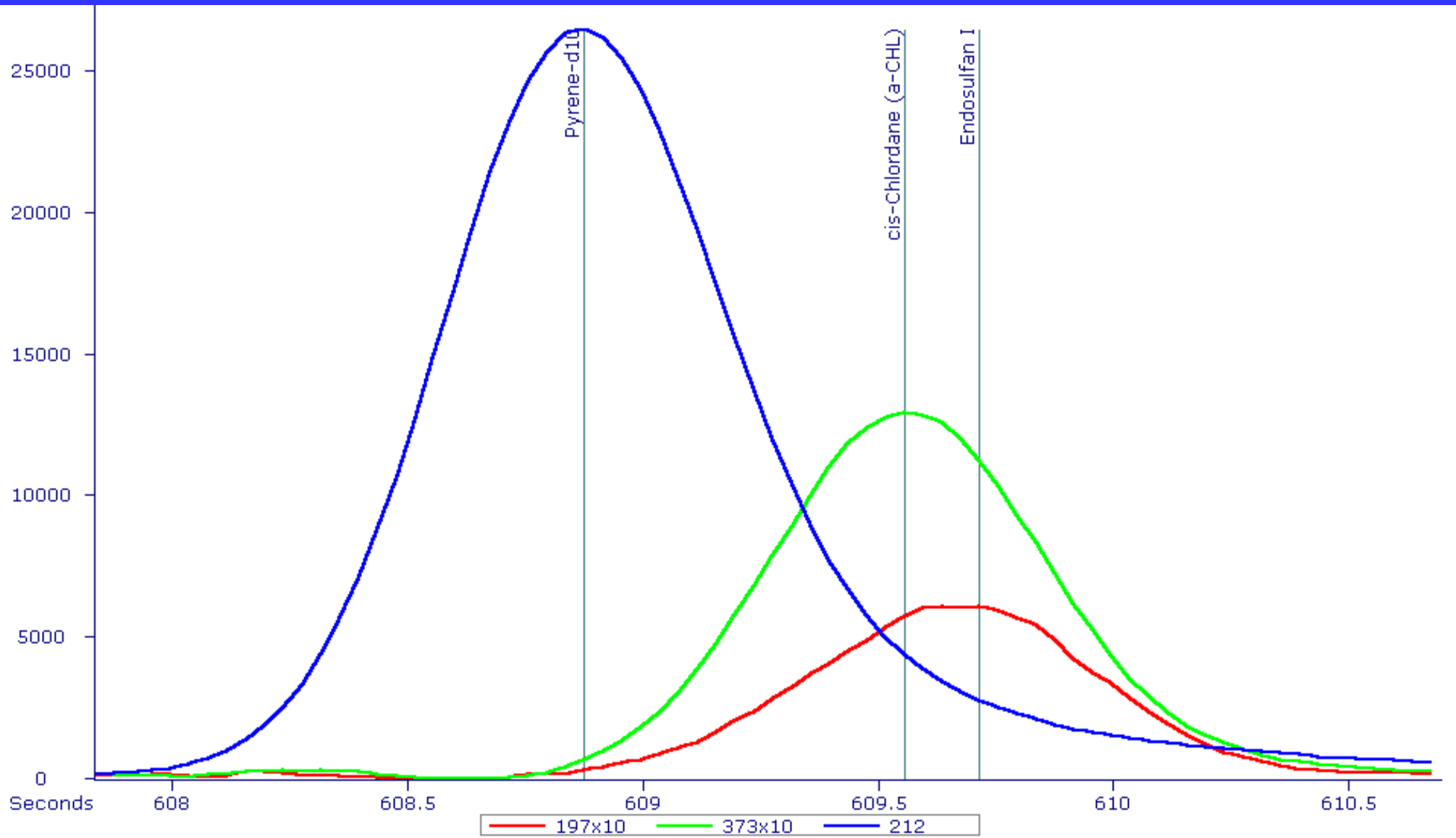
Sample D-0998

Pyrene-d10, α -CHL, Endosulfan I



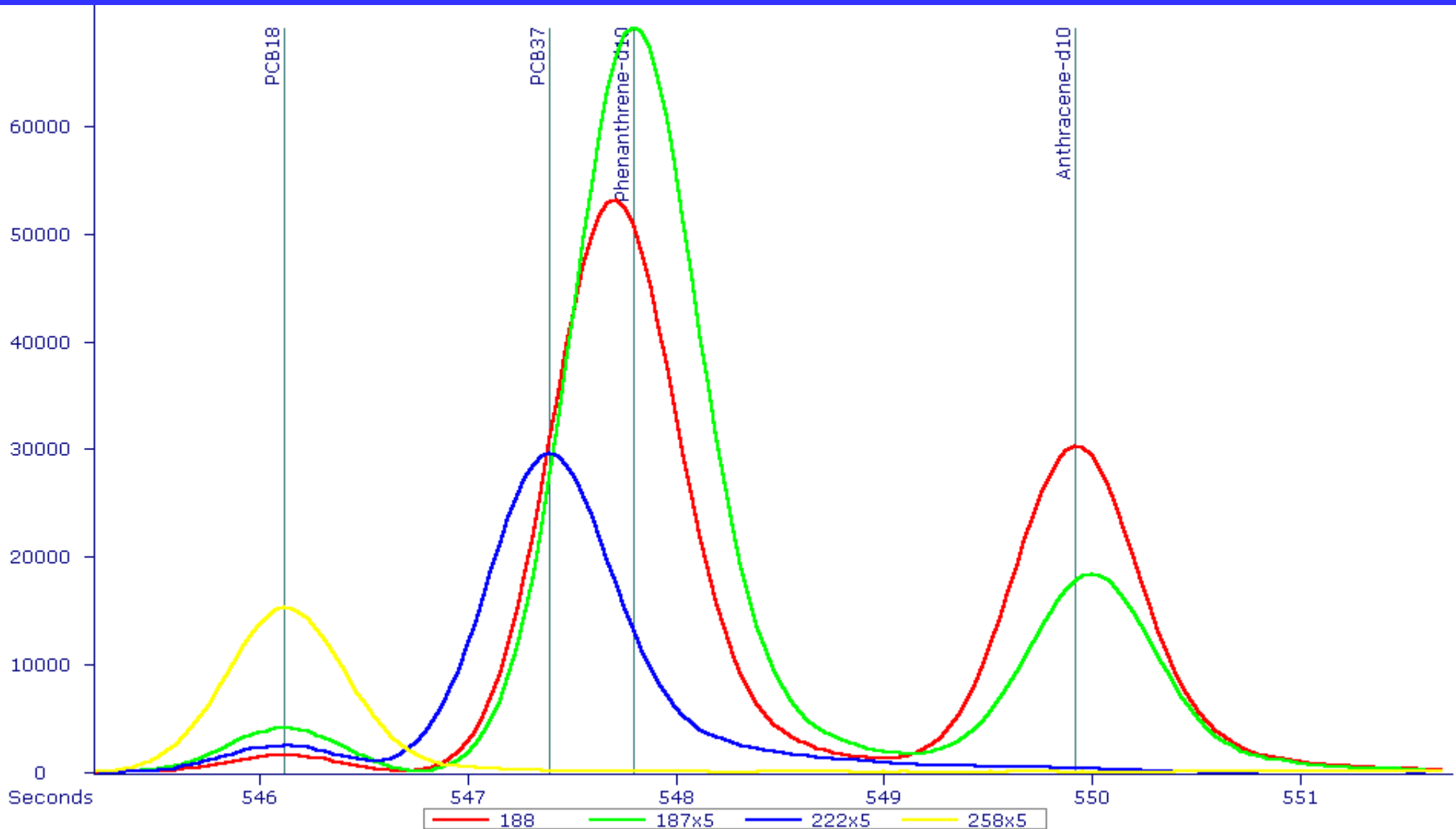
Sample D-0998

Pyrene-d10, α -CHL, Endosulfan I



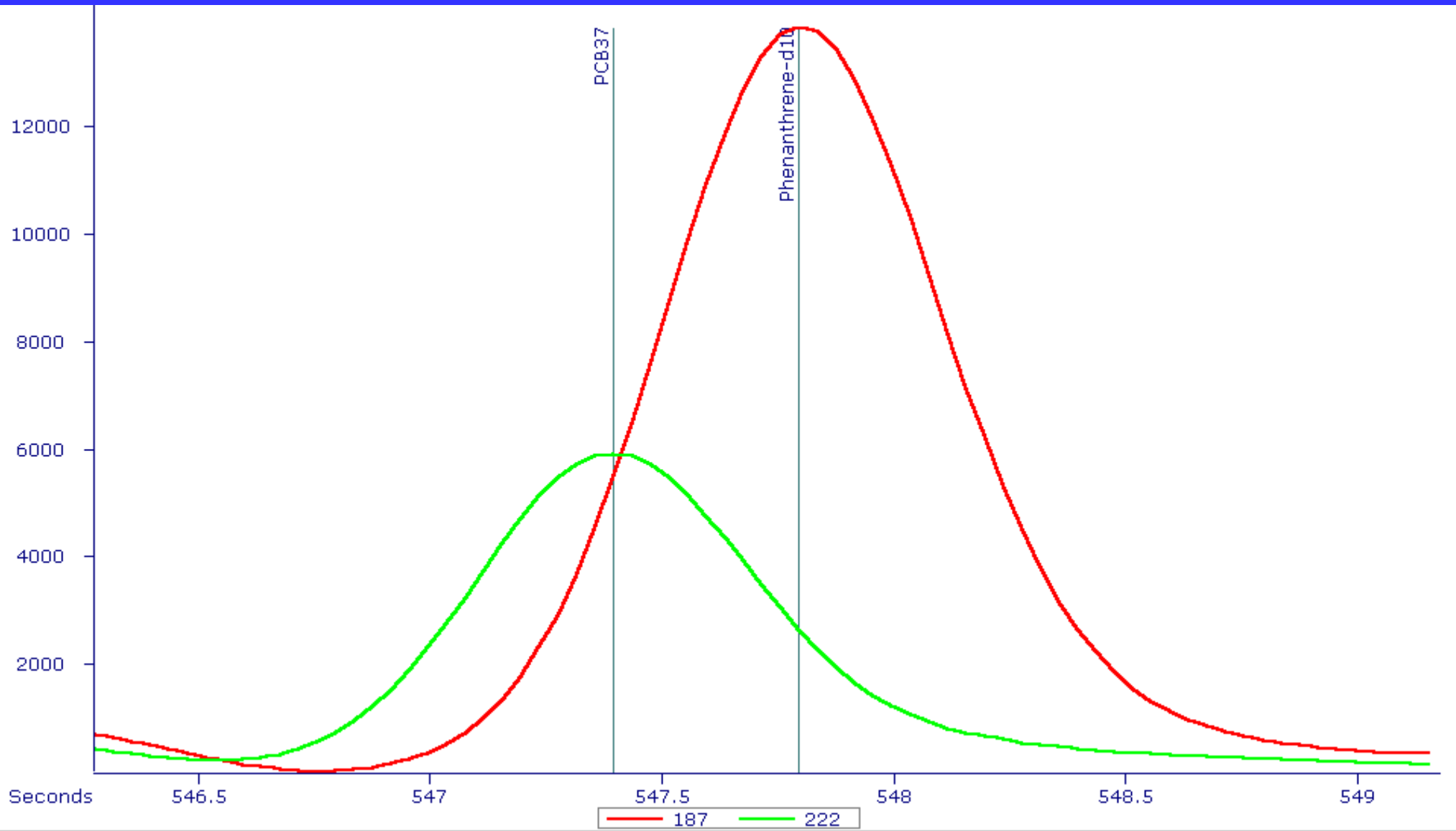
Sample D-0998

PCB18, PCB37, Phenanthrene-D10, Anthracene-D10



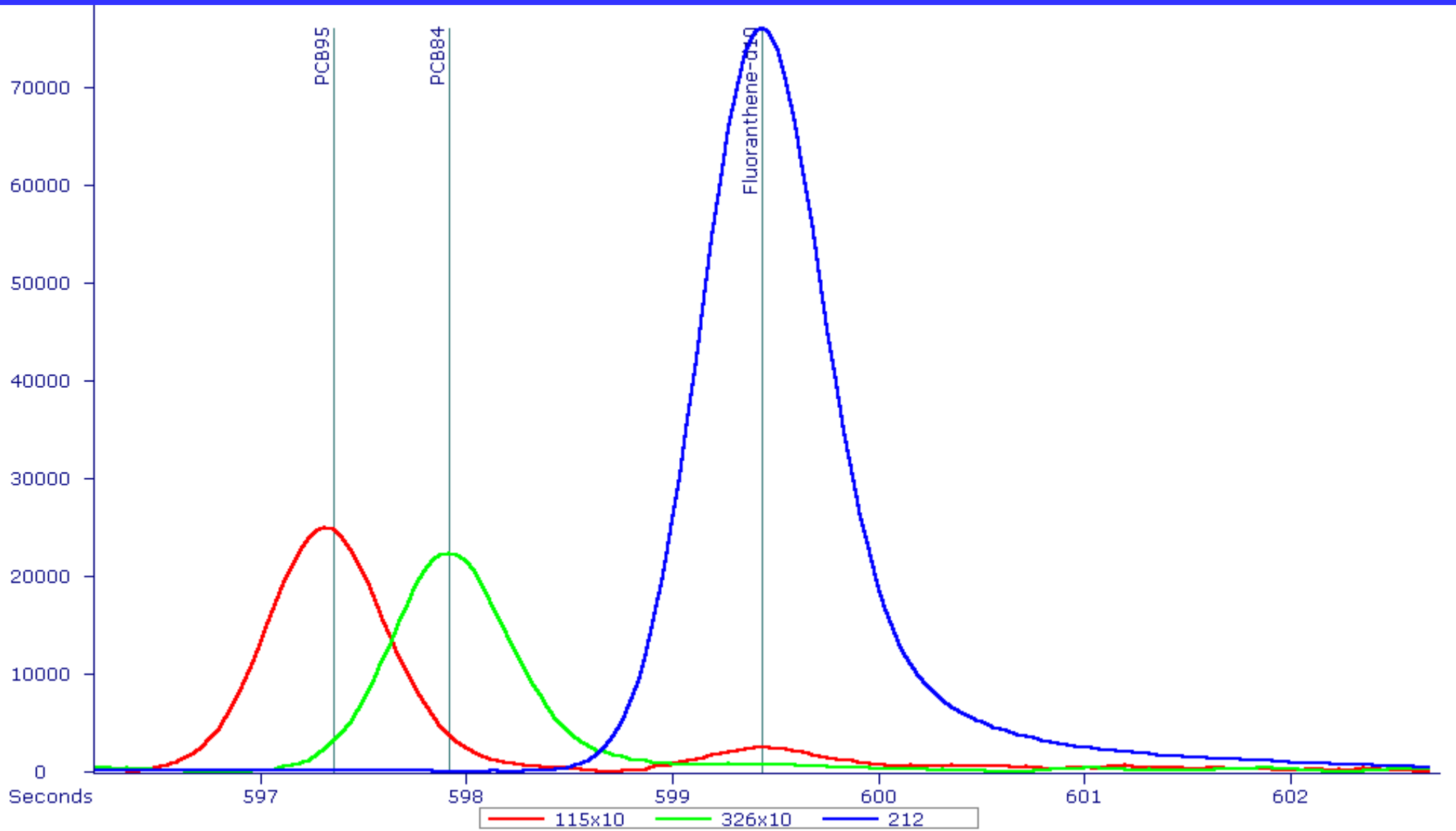
Sample D-0998

PCB37, Phenanthrene-d10



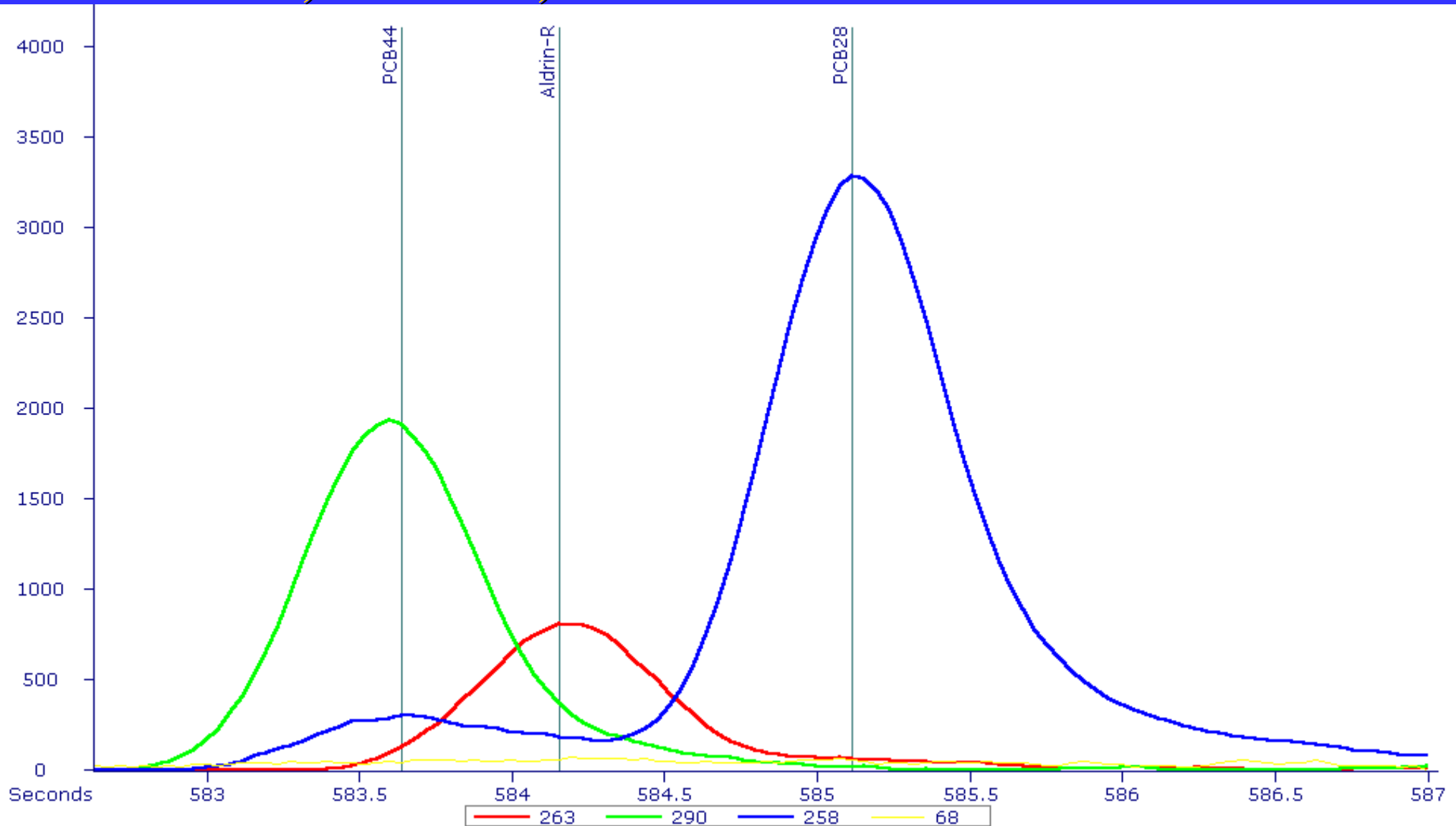
Sample D-0998

PCB95, PCB84, Fluoranthene-d10



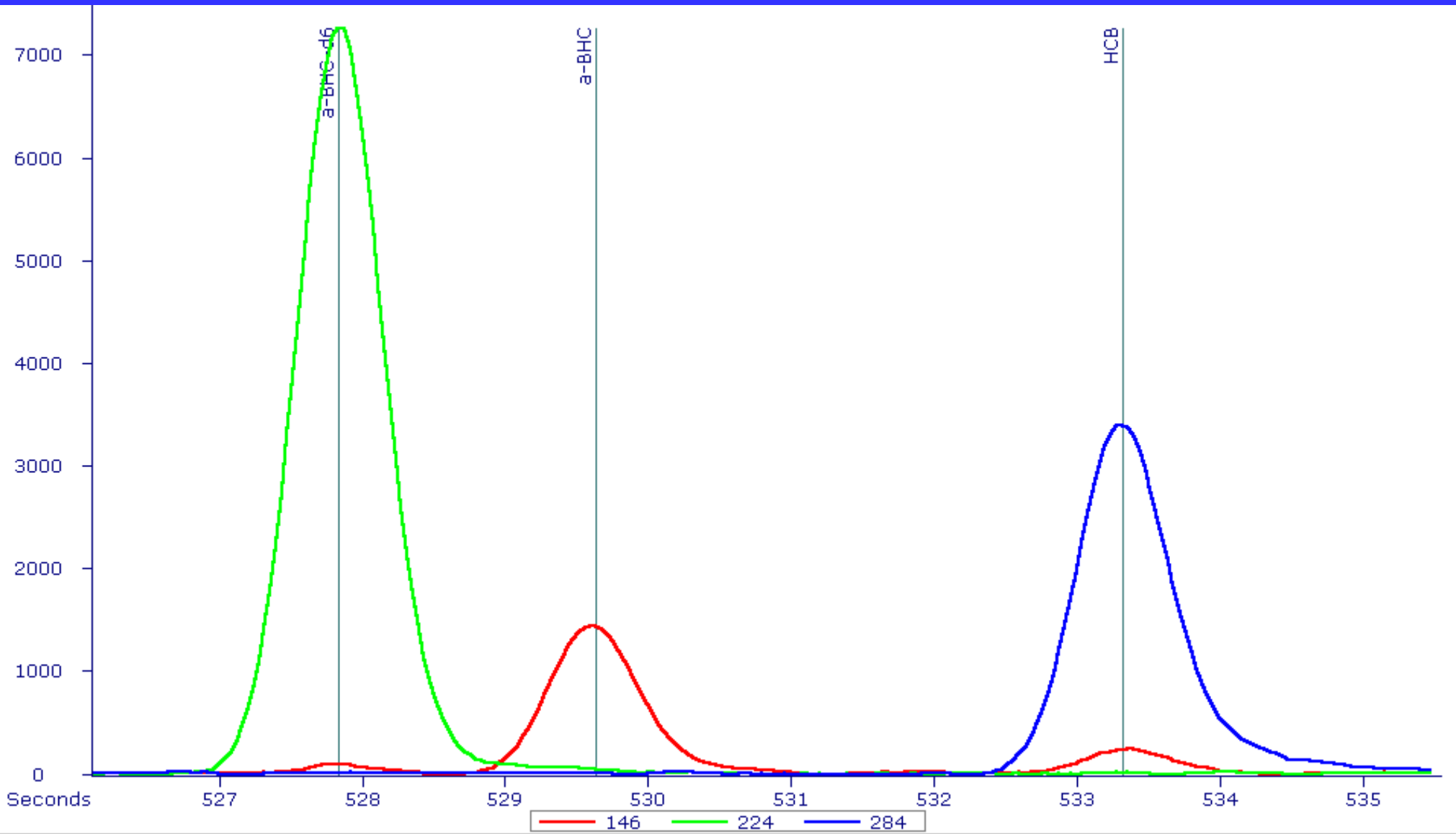
Sample D-0998

PCB44, Aldrin-R, PCB28



Smample D-0998

a-BHC-d6, a-BHC, HCB



Equations and Terms

Resolution

$$R = 1/4 \sqrt{L/h} \times (k/k+1) \times (\alpha-1/\alpha)$$

Capacity Factor

$$k = t_R - t_0 / t_0$$

Selectivity

$$\alpha = k_2 / k_1$$

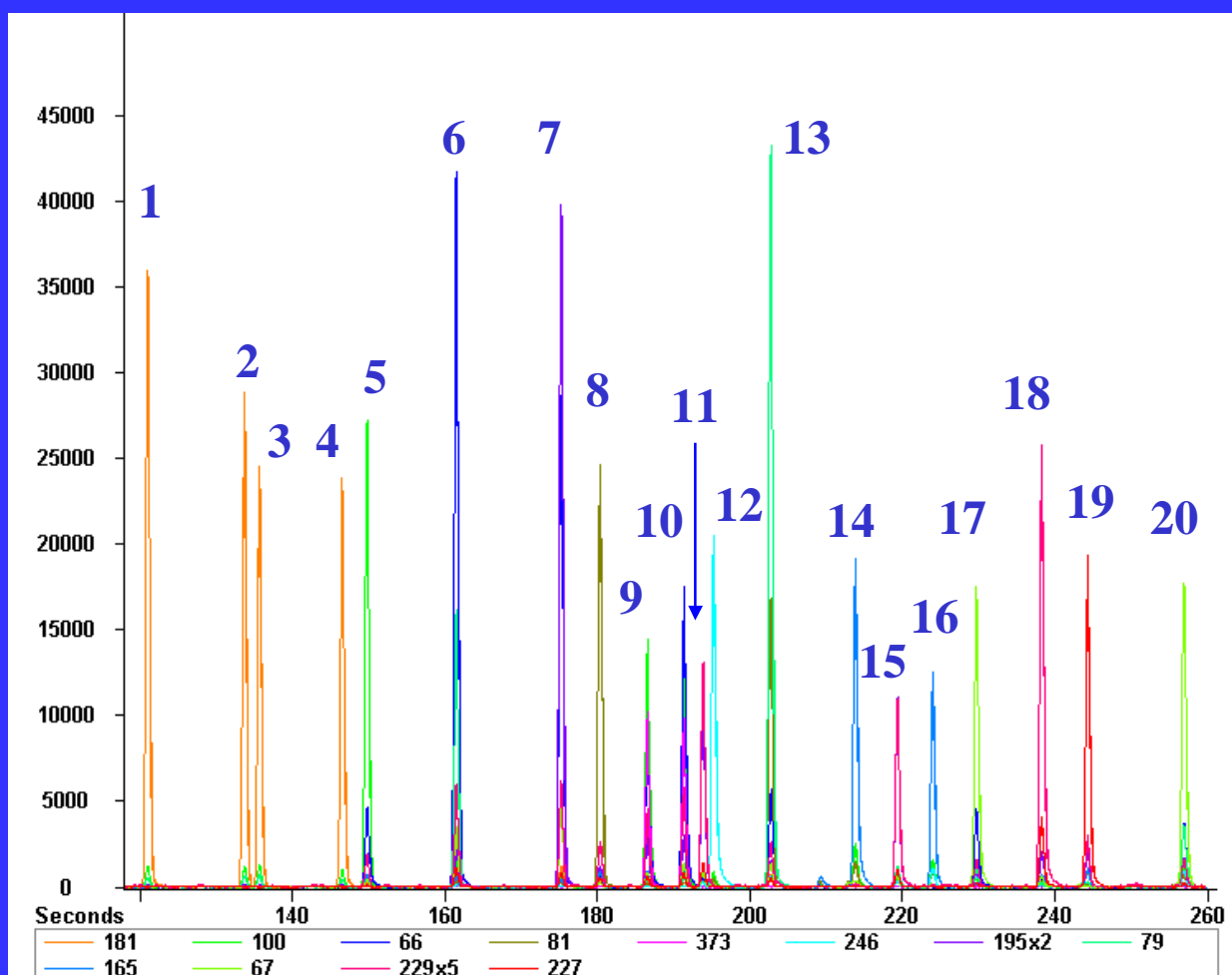
Coupling Tuned-Selectivity Phases to TOF-MS

- Do not need to rely as much on deconvolution procedures
- May be especially important for compounds with similar mass spectra
- More easily understood by auditors, and regulatory agencies?

Fast GC/TOFMS of OCPs on CLPII

LECO Pegasus II GC/TOFMS

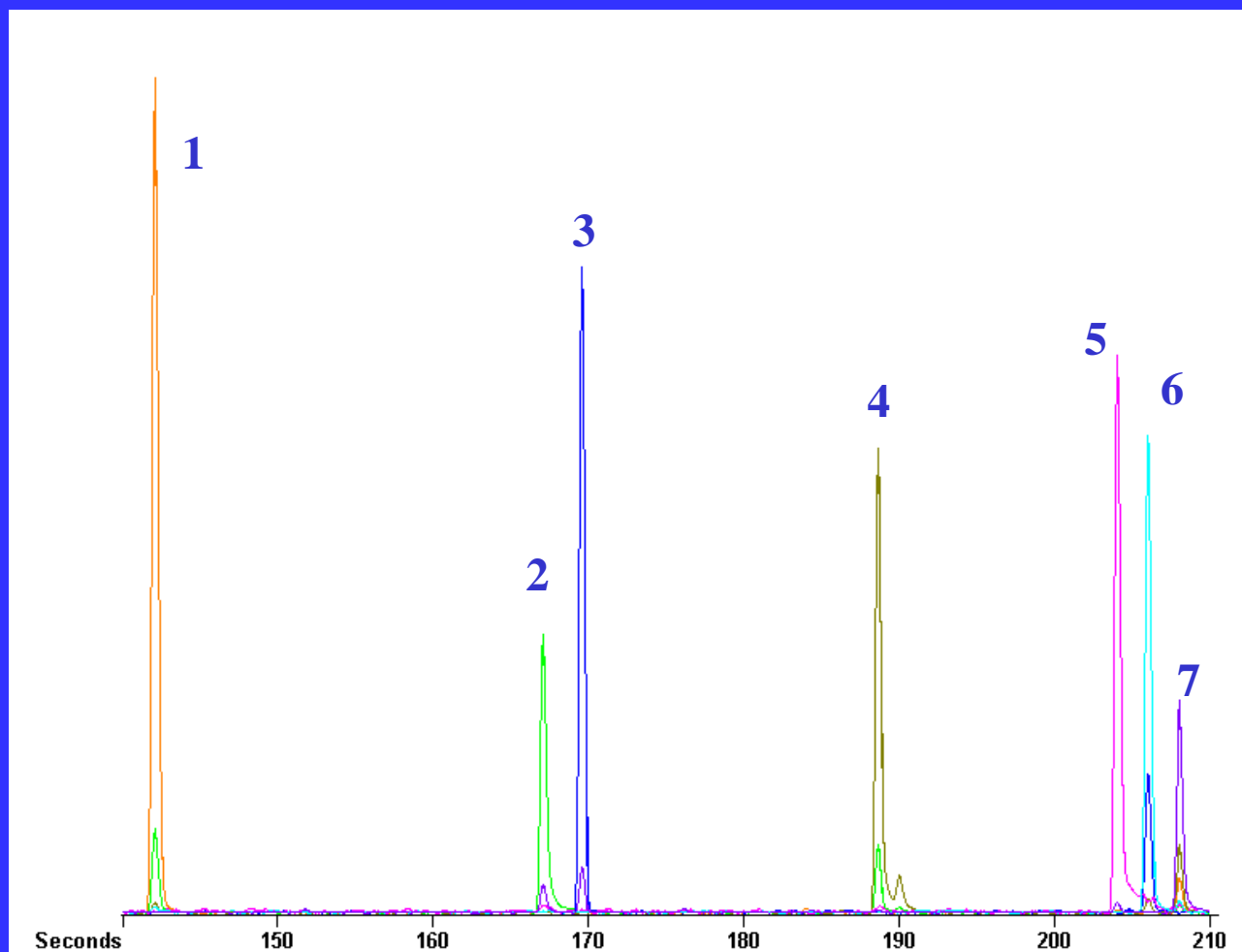
1. Alpha-BHC
2. Gamma-BHC
3. Beta-BHC
4. Delta-BHC
5. Heptachlor
6. Aldrin
7. Isodrin
8. Heptachlor epoxide
9. Gamma-Chlordane
10. Alpha-Chlordane
11. 4,4'-DDE
12. Endosulfan I
13. Dieldrin
14. 4,4'-DDD
15. Endosulfan II
16. 4,4'-DDT
17. Endrin aldehyde
18. Endosulfan sulfate
19. Methoxychlor
20. Endrin Ketone



Baseline resolution in less than 4.5 minutes!

Fast GC/TOFMS of OC/OPPs on CLPII

LECO Pegasus II GC/TOFMS

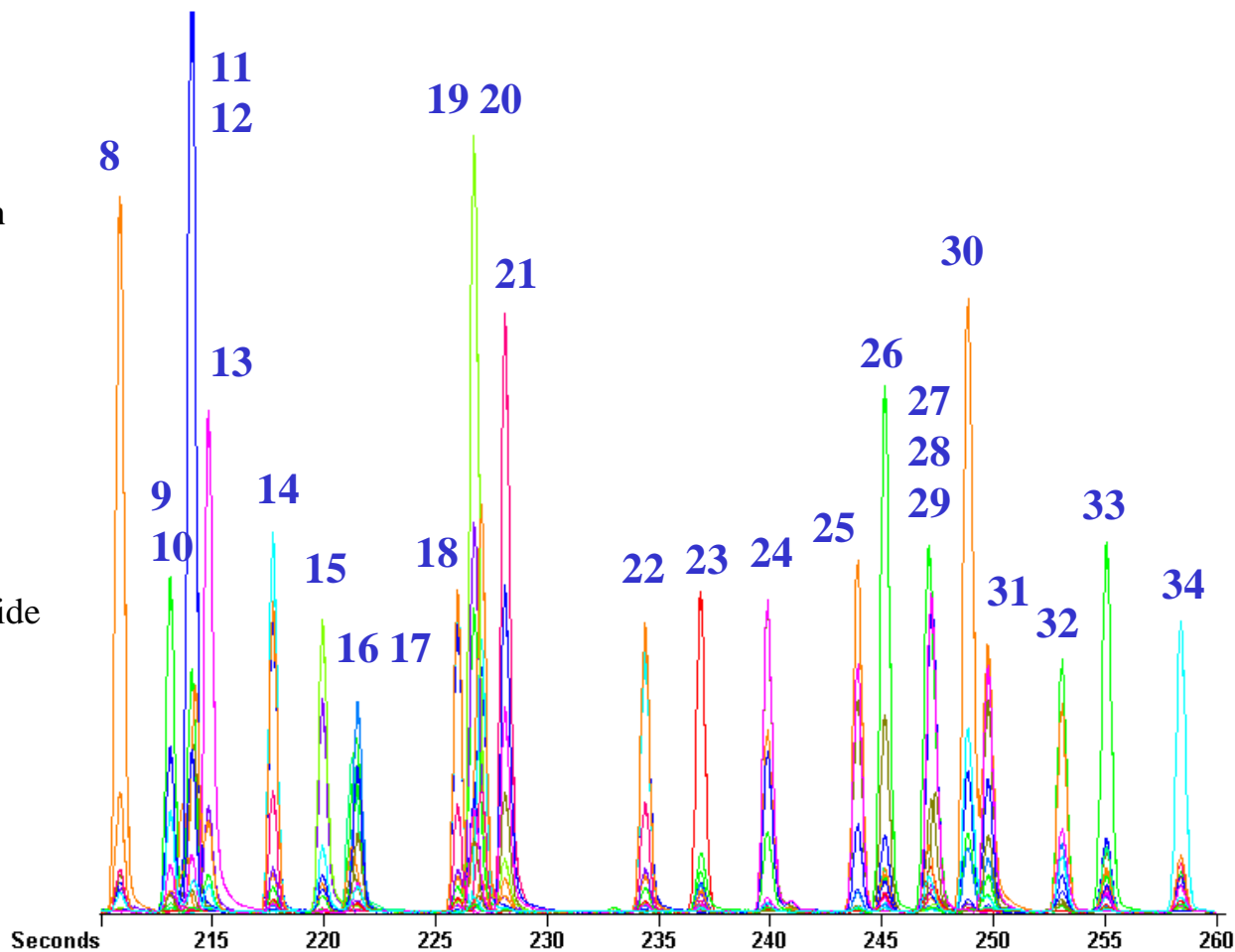


1. 1,2-Dibromo-3-chloropropane
2. Dichlorvos
3. Hexachlorocyclopentadiene
4. Mevinphos
5. Demeton O
6. TEPP
7. Ethoprop

Fast GC/TOFMS of OC/OPPs on CLPII

LECO Pegasus II GC/TOFMS

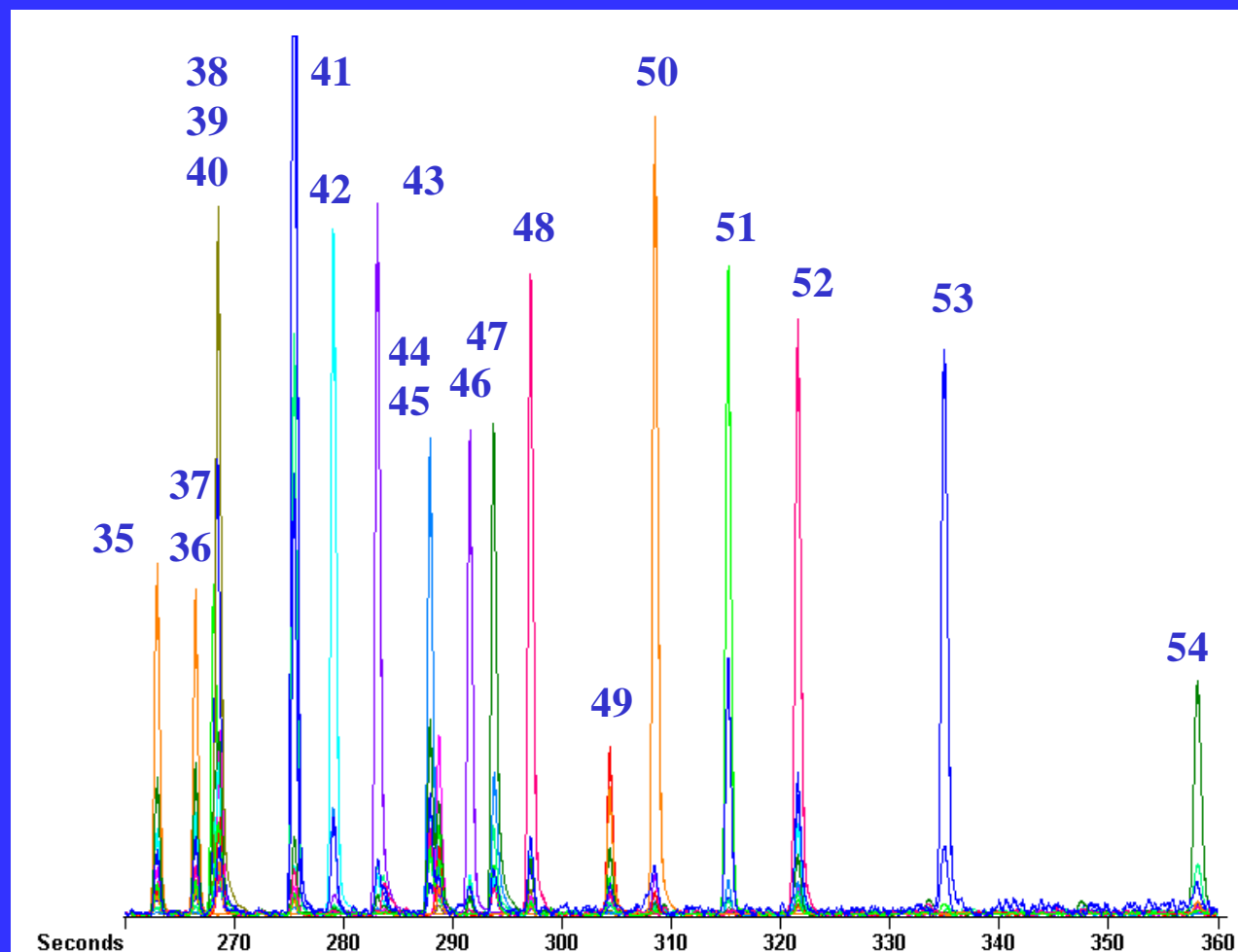
- | | |
|-----------------------|------------------------|
| 8. Trans-Diallate | 22. Delta-BHC |
| 9. Sulfotepp | 23. Heptachlor |
| 10. Cis-Diallate | 24. Ronnel |
| 11. Phorate | 25. Methyl parathion |
| 12. Naled | 26. Aldrin |
| 13. Hexachlorobenzene | 27. Chlorpyrifos |
| 14. Alpha-BHC | 28. Malathion |
| 15. Demeton S | 29. Merphos |
| 16. Monocrotophos | 30. Trichloronate |
| 17. Diazinon | 31. Fenthion |
| 18. Gamma-BHC | 32. Parathion |
| 19. Disulfoton | 33. Isodrin |
| 20. Beta-BHC | 34. Heptachlor epoxide |
| 21. Dimethoate | |



Fast GC/TOFMS of OC/OPPs on CLPII

LECO Pegasus II GC/TOFMS

- 35. Gamma-Chlordane
- 36. Alpha-Chlordane
- 37. Tokuthion
- 38. Stirofos
- 39. 4,4'-DDE
- 40. Endosulfan I
- 41. Dieldrin
- 42. Chlorobenzilate
- 43. 4,4'-DDD
- 44. Sulprofos
- 45. Endosulfan II
- 46. 4,4'-DDT
- 47. Fensulfothion
- 48. Endrin aldehyde
- 49. Endosulfan sulfate
- 50. Methoxychlor
- 51. EPN
- 52. Endrin ketone
- 53. Azinphos methyl
- 54. Coumaphos



54 compounds in 6 minutes!

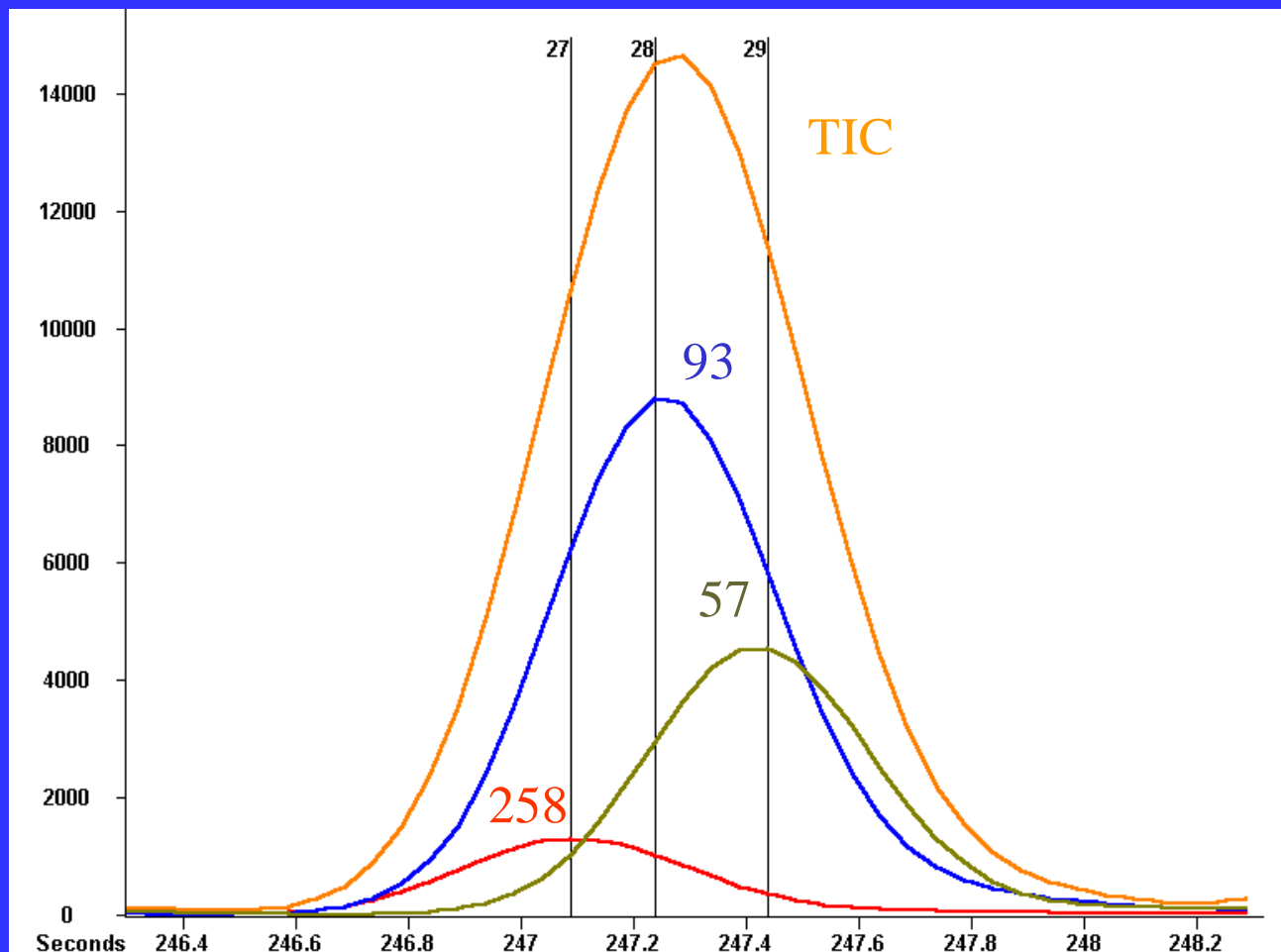
Automatic Peak Find Using TOFMS

LECO Pegasus II GC/TOFMS

- 27. Chlorpyrifos
- 28. Malathion
- 29. Merphos

Fast acquisition rate of TOFMS allows location of unique masses and subsequent deconvolution of mass spectra.

20 spectra/second



Three compounds located in a one-second wide peak.

Summary

- TOF-MS has “scan” speed required to accurately characterize peaks eluting from fast GC methods.
- Deconvolution procedures are further enhanced when some chromatographic separation is possible.
- Coupling tuned-selectivity phases with TOF-MS can lead to very powerful separation tool.

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For more information...

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