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

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Advantages of Fast GC

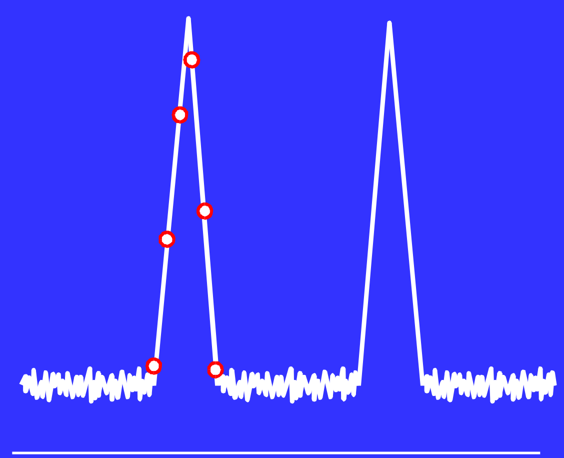
- Shorter Column lengths, faster ramp rates
  - Increased sample throughput
- Smaller column I.d., faster ramp rates
  - Narrower peak width
  - More plates/meter
  - Lower carrier flow rates
  - Higher column head pressures

Disadvantages of Fast GC

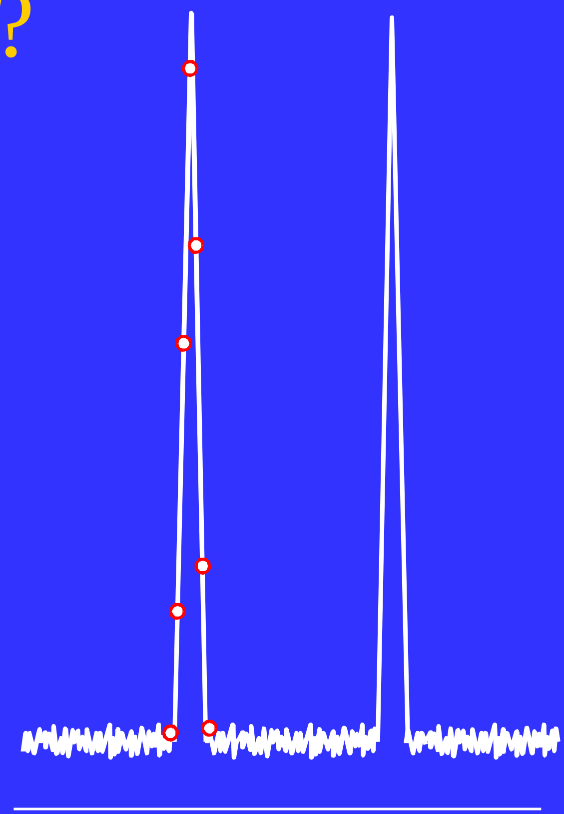
- Smaller column IDs
  - Lower column capacity – can require injection modification, and extract cleanup
- Narrower peak width
  - Places demands on detection systems

- 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?

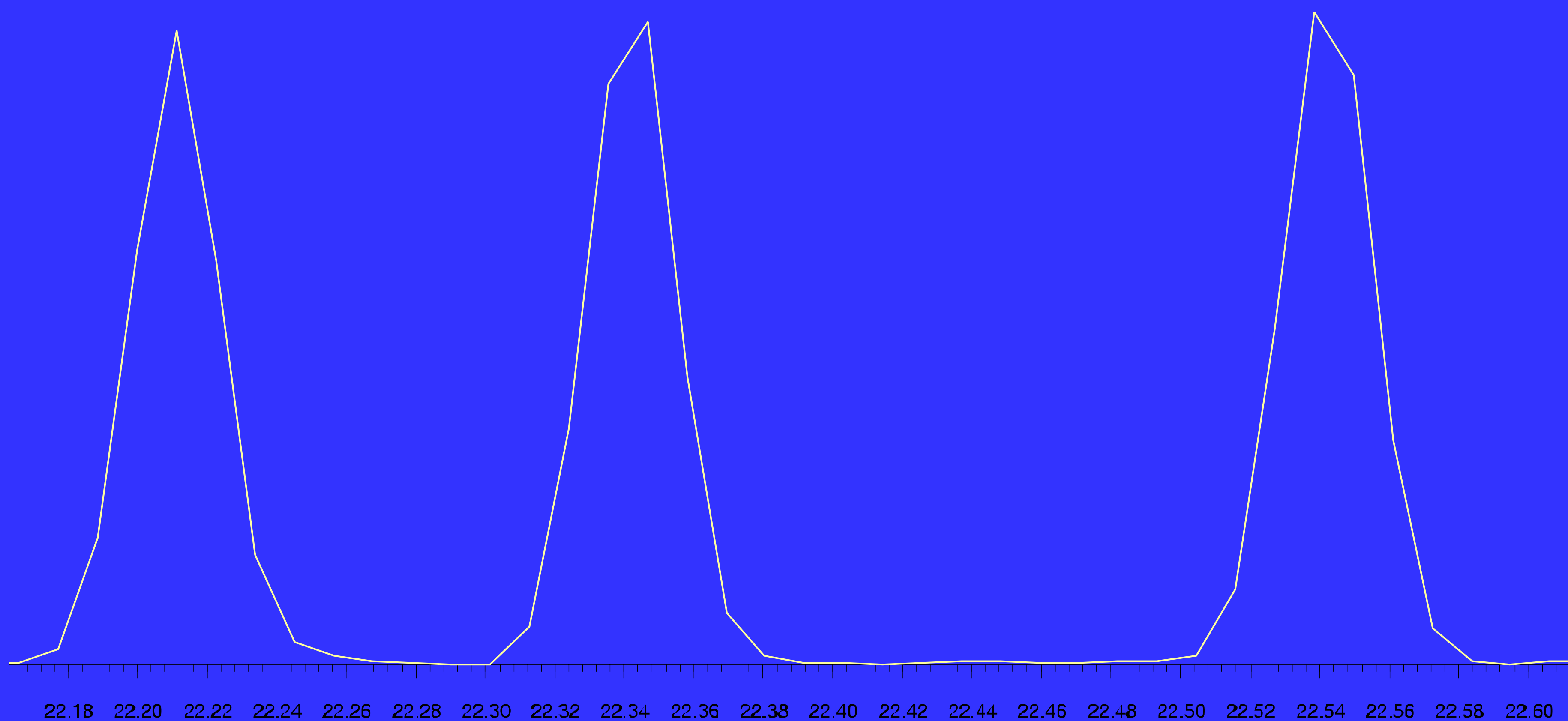


Minutes

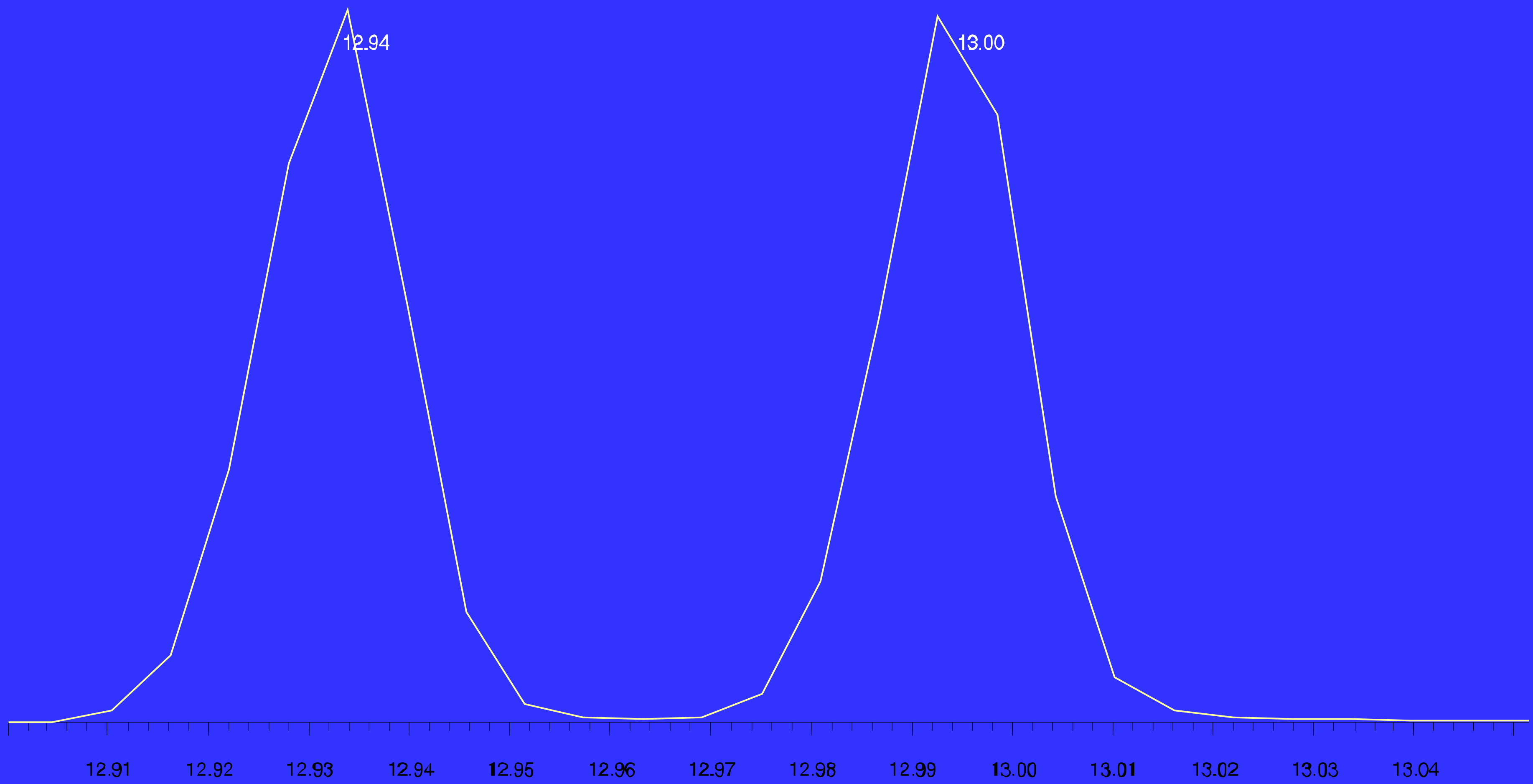


Seconds

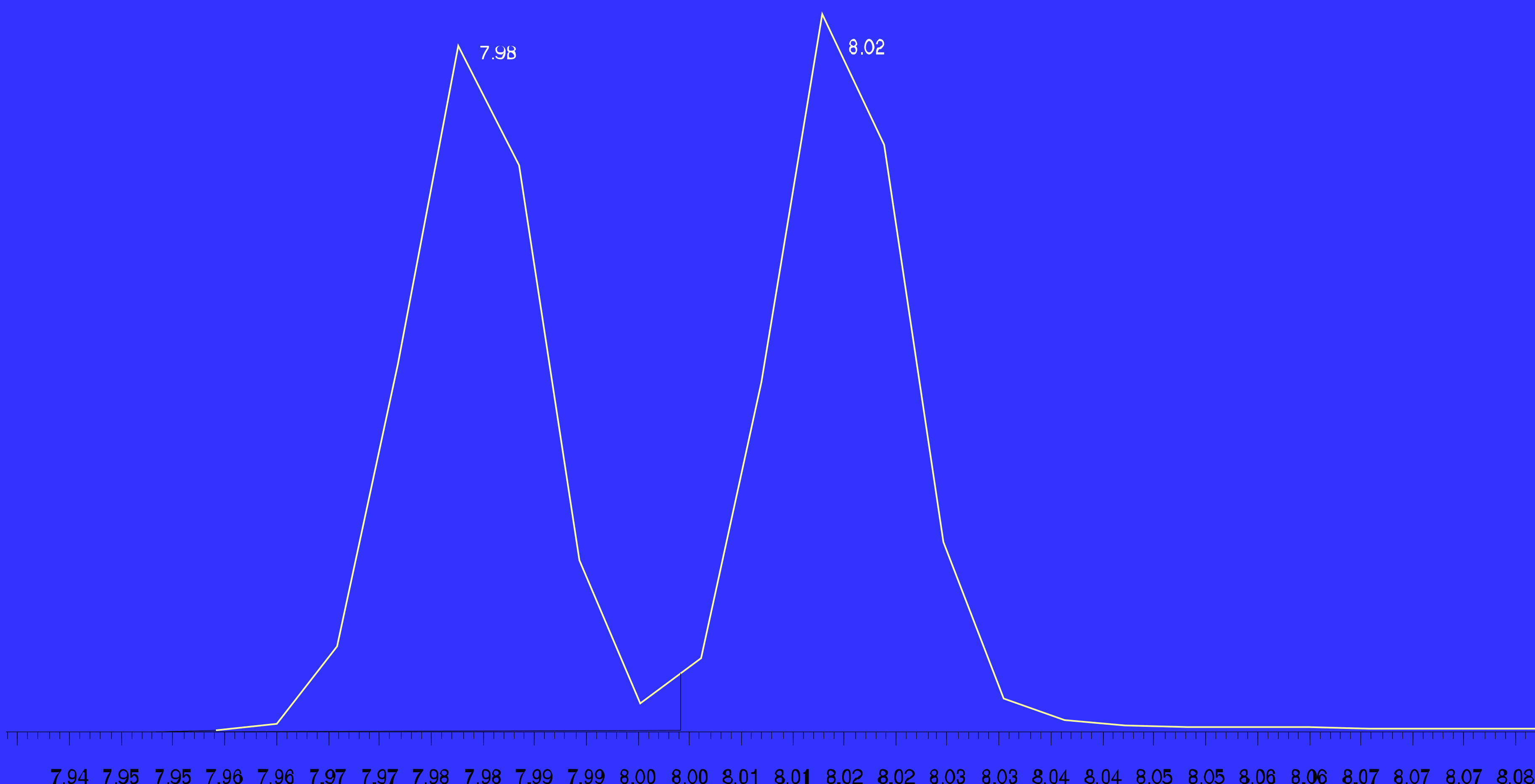
Sampling Frequency Limitations of Quadrupoles and Ion Traps Can Cause Peak Biasing



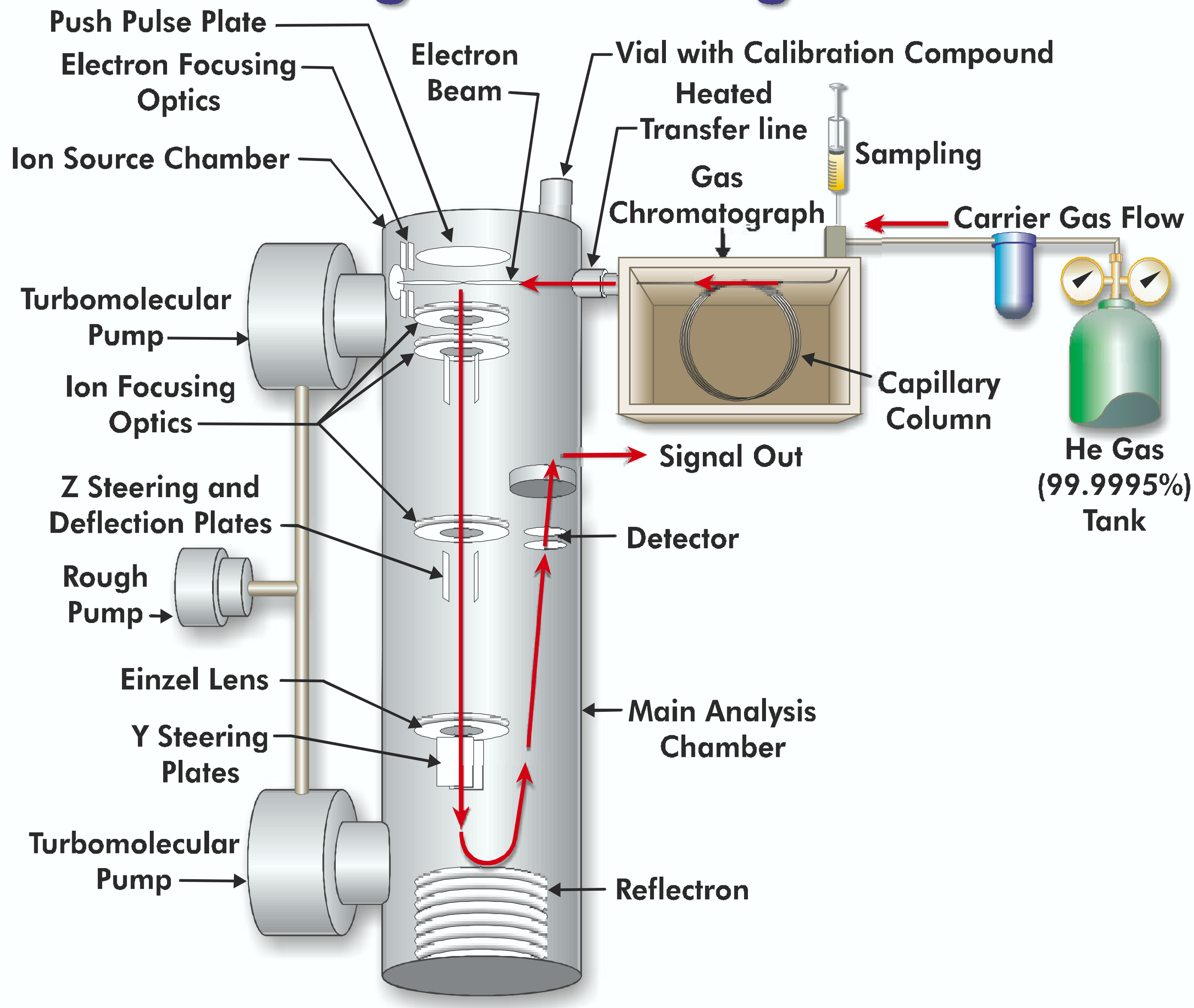
Peak Biasing...



Peak Biasing...

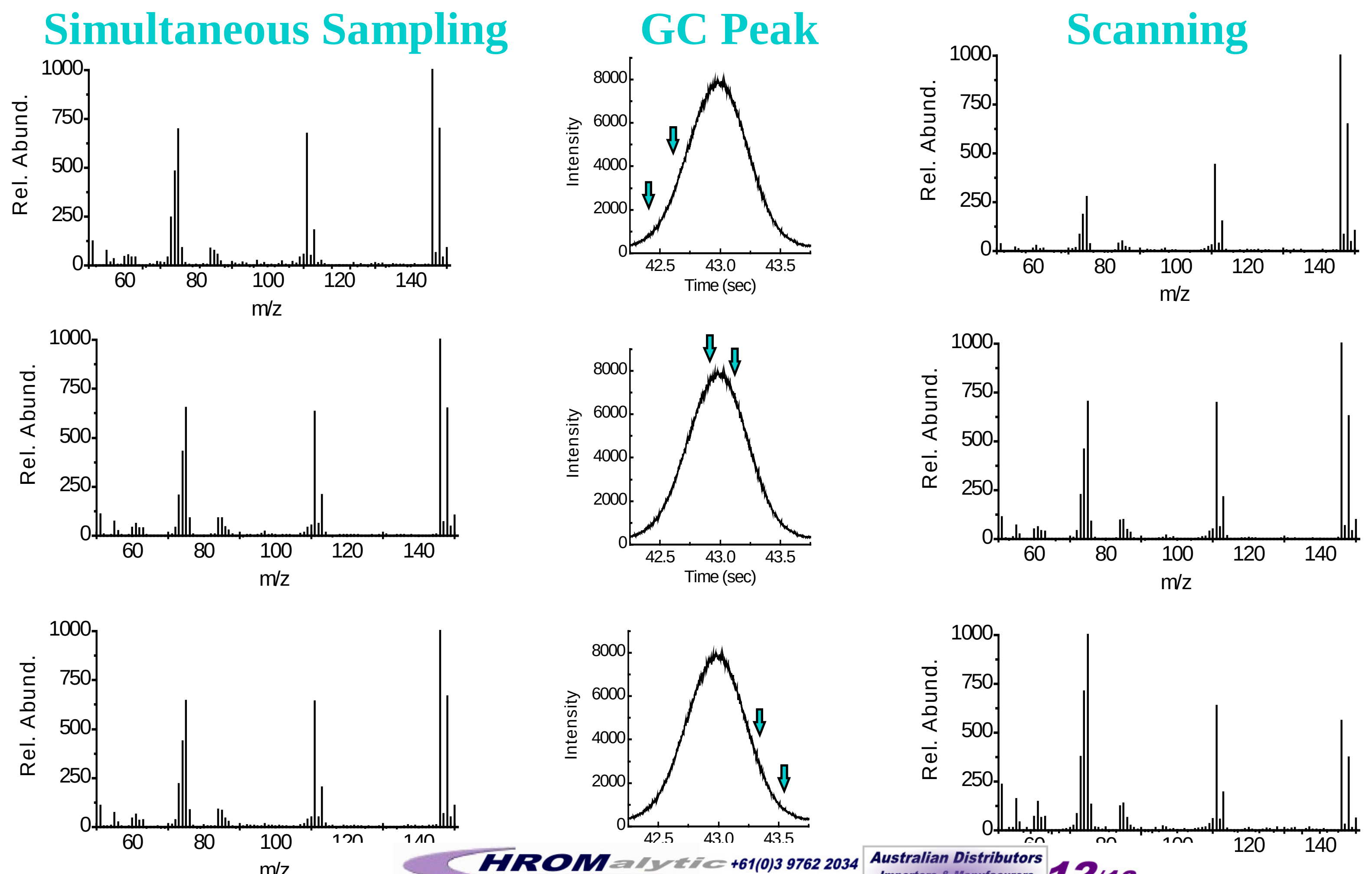


Pegasus II Diagram

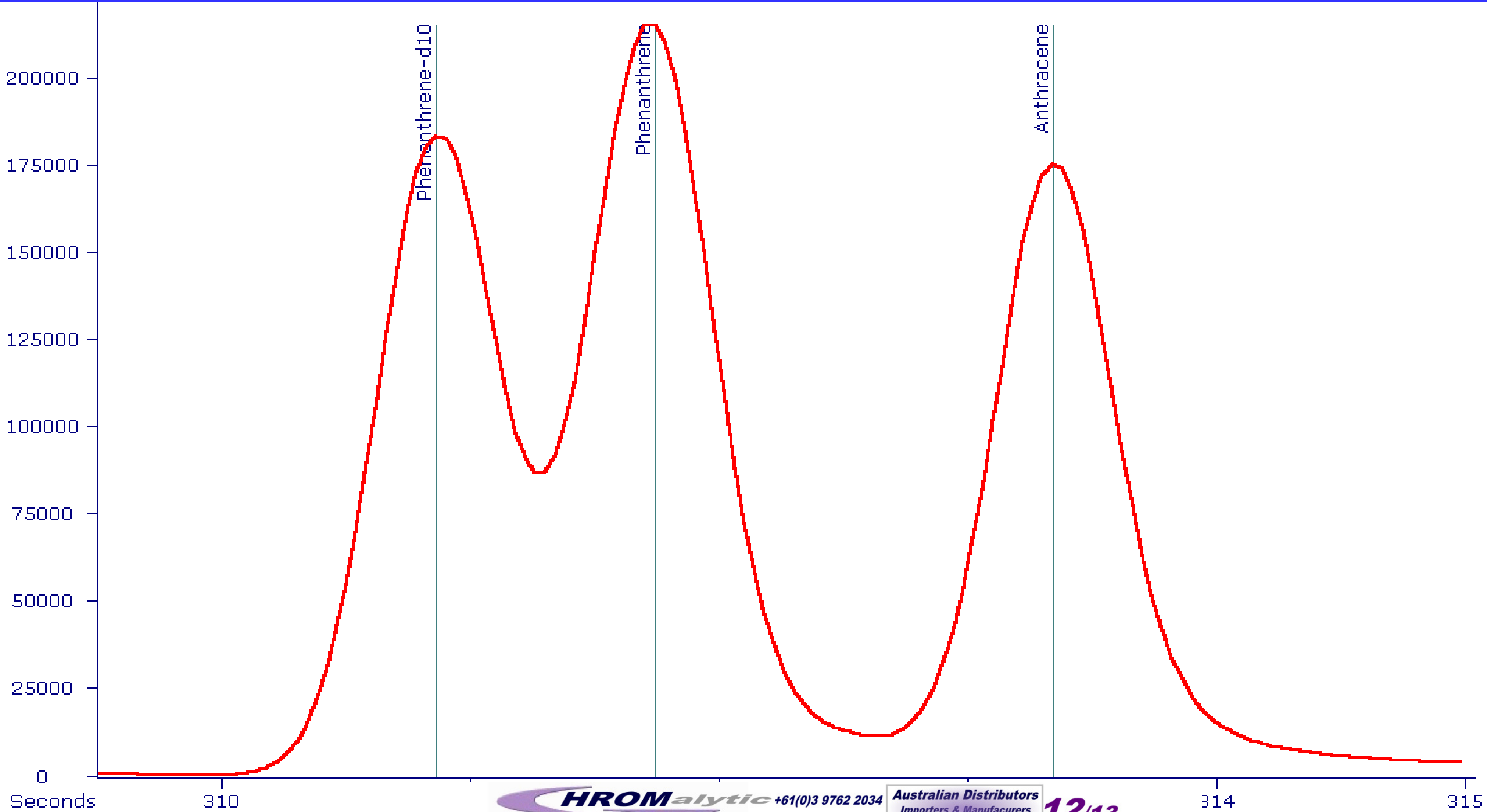


Spectra - TOF vs. Scanning MS

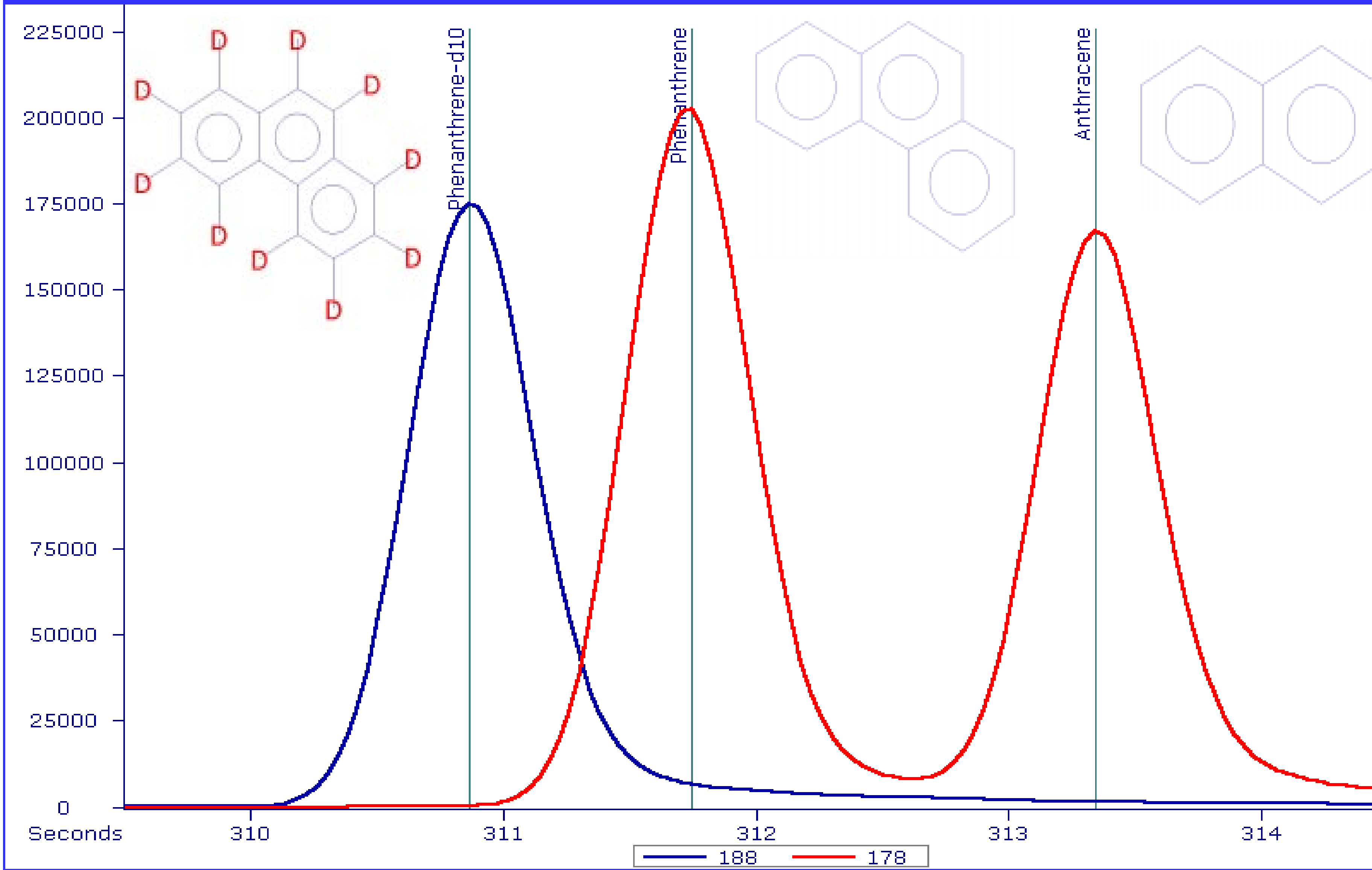
TOF Ion Ratios Vary Less Than 1% Across the Peak



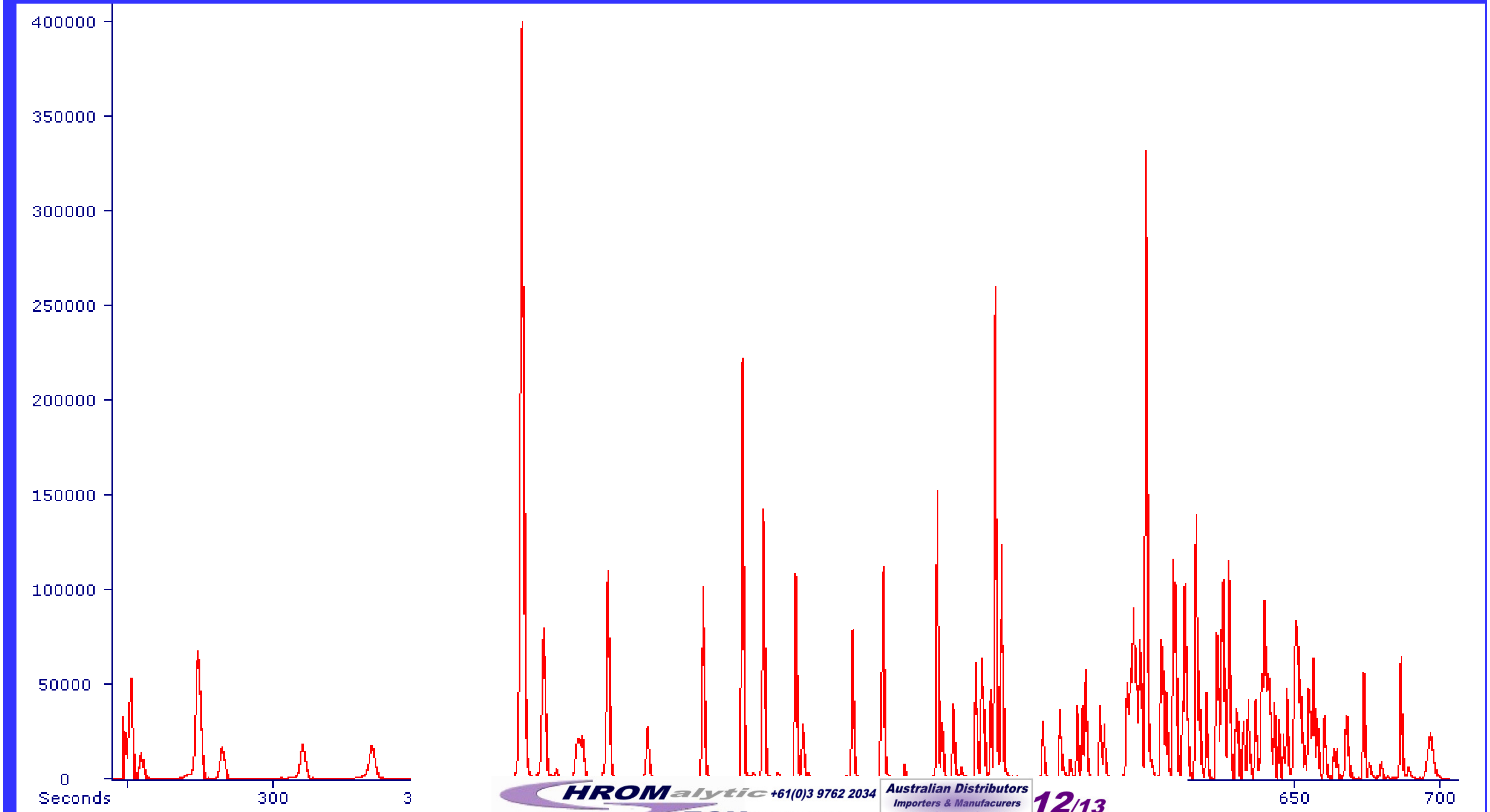
PAH Standard – AIC
D10-Phenanthrene, Phenenthrene, Anthracene



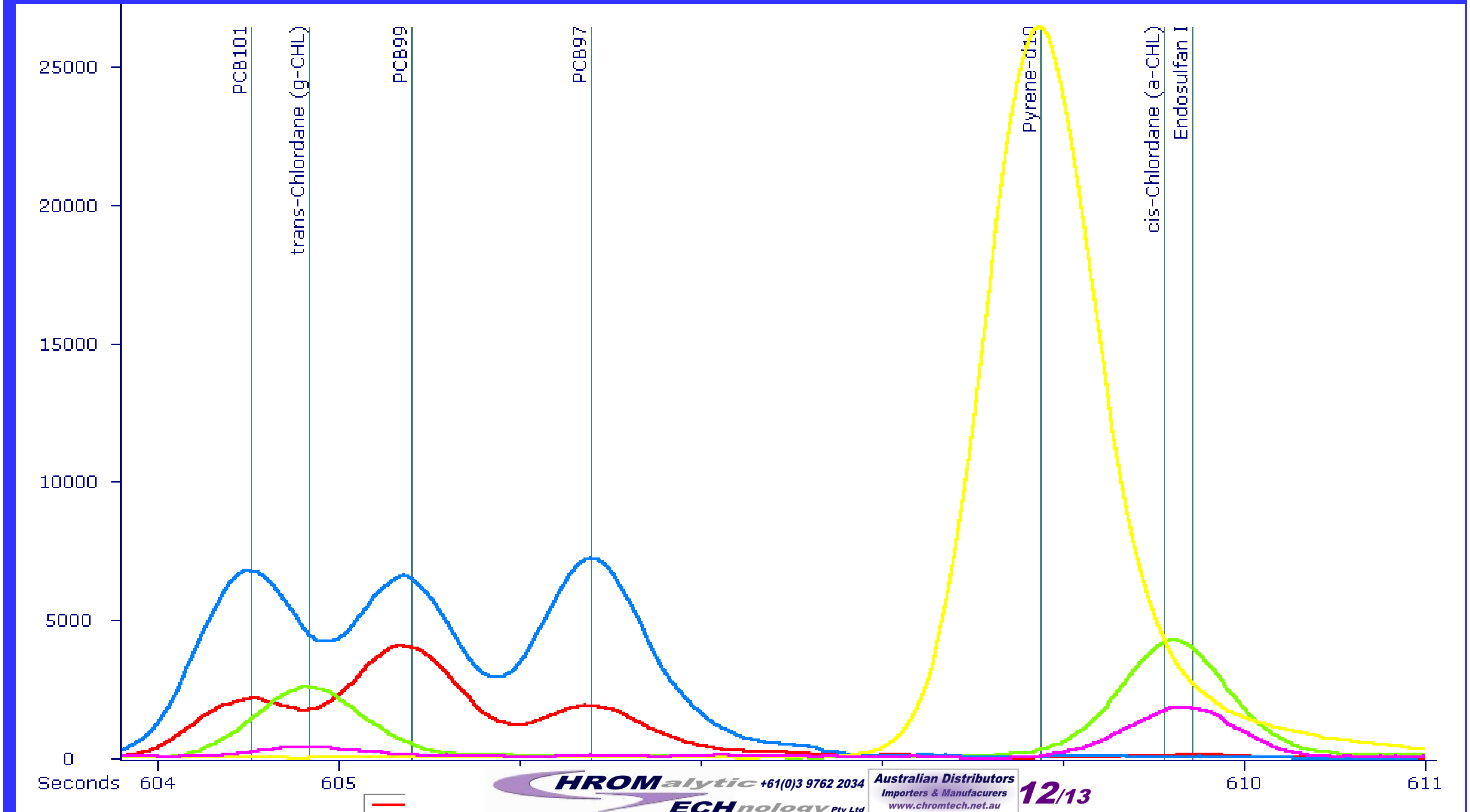
Peak #	Name	R.T.	Similarity	Reverse	Hit #	UniqueMass	S/N	Area	Library	CAS	Fo	Weight
6	Anthracene-d10	310.86	934	934	1	188	5993.3	2966200	MAINLIB	1719-06-8	C1	188
7	Phenanthrene	311.74	982	982	1	178	4412.7	3178700	MAINLIB	85-01-8	C1	178
8	Anthracene	313.34	977	977	1	178	3777.0	2847500	MAINLIB	120-12-7	C1	178



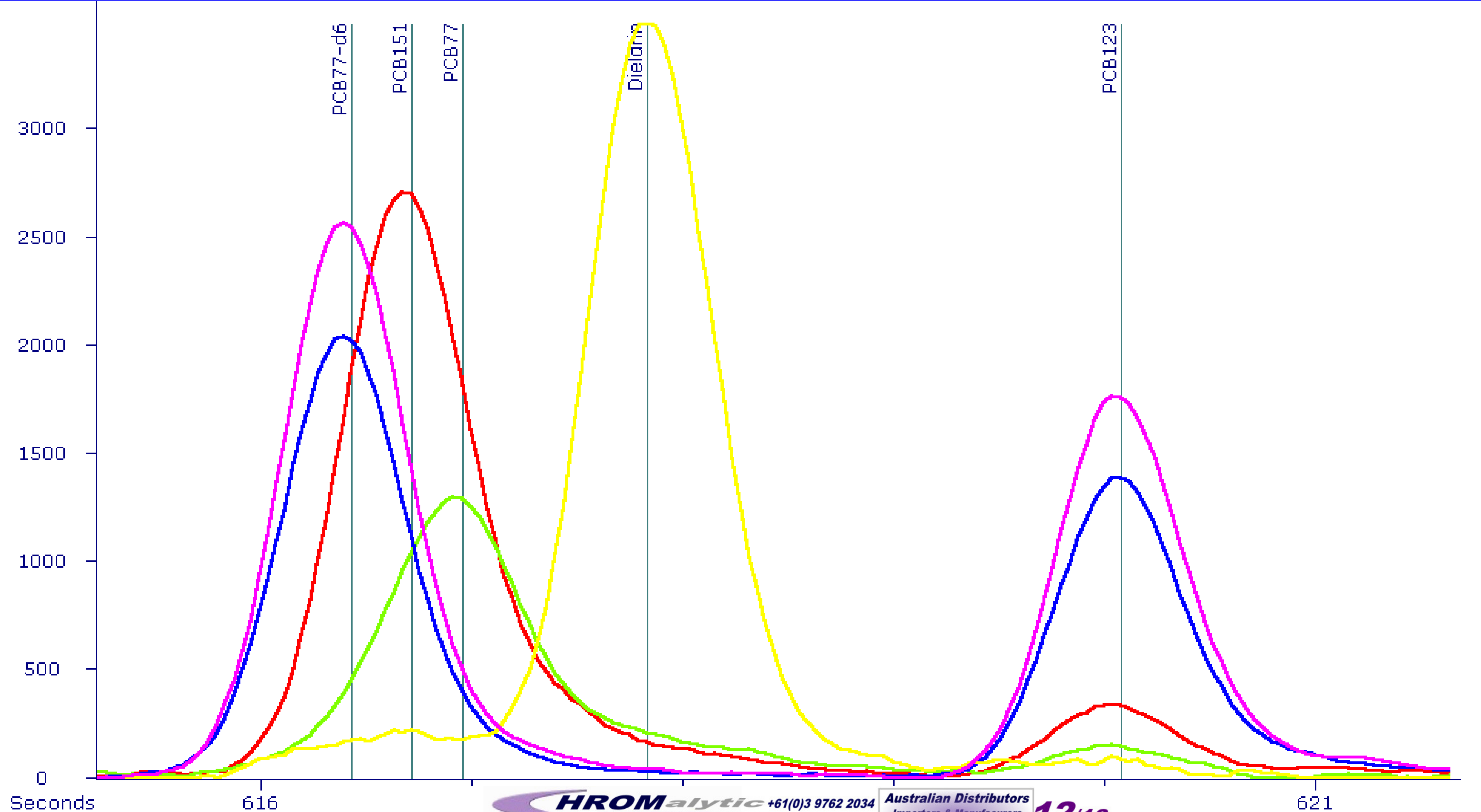
Sample D-0998
Analytical Ion Chromatogram (AIC)



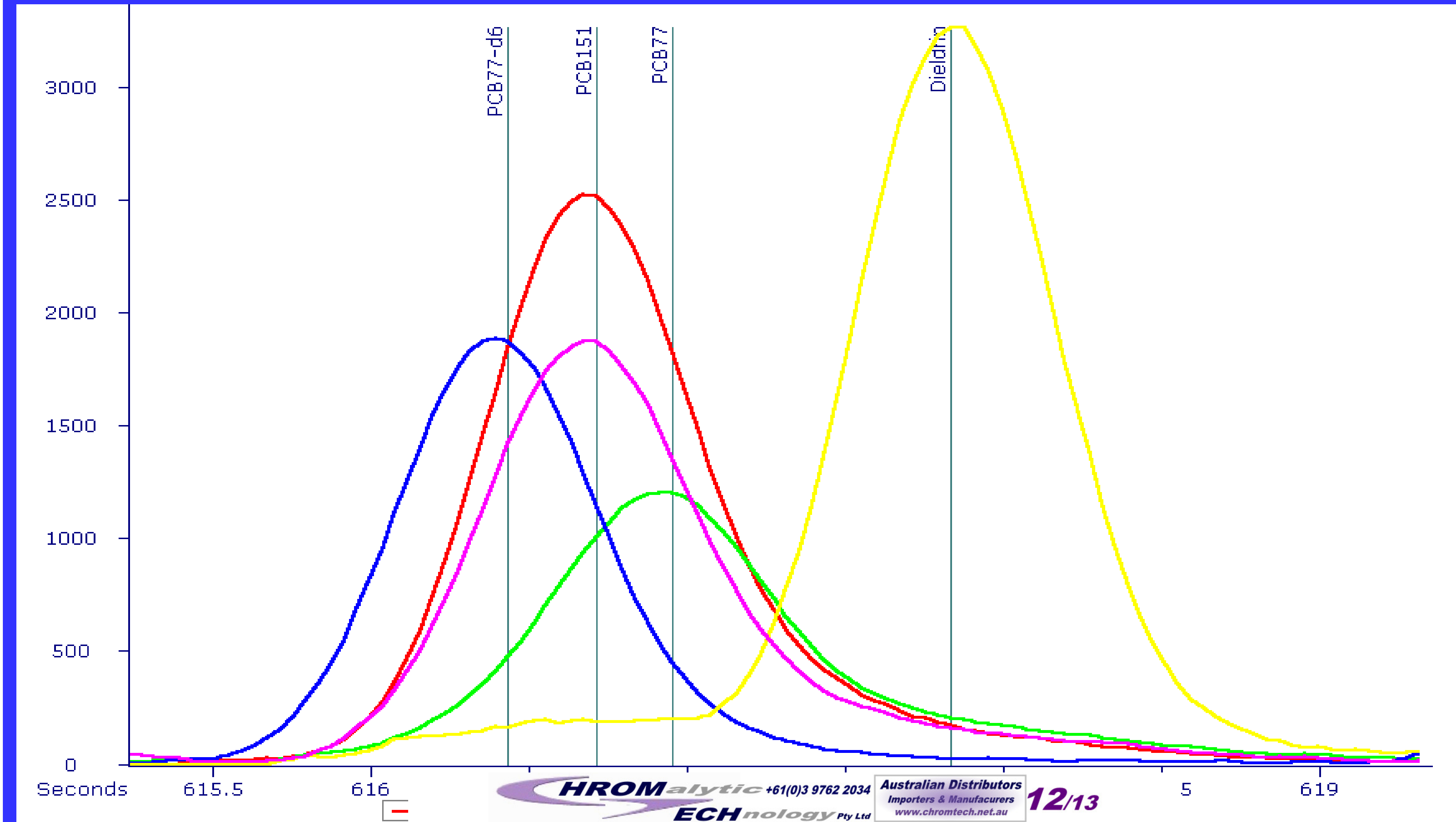
Sample D-0998



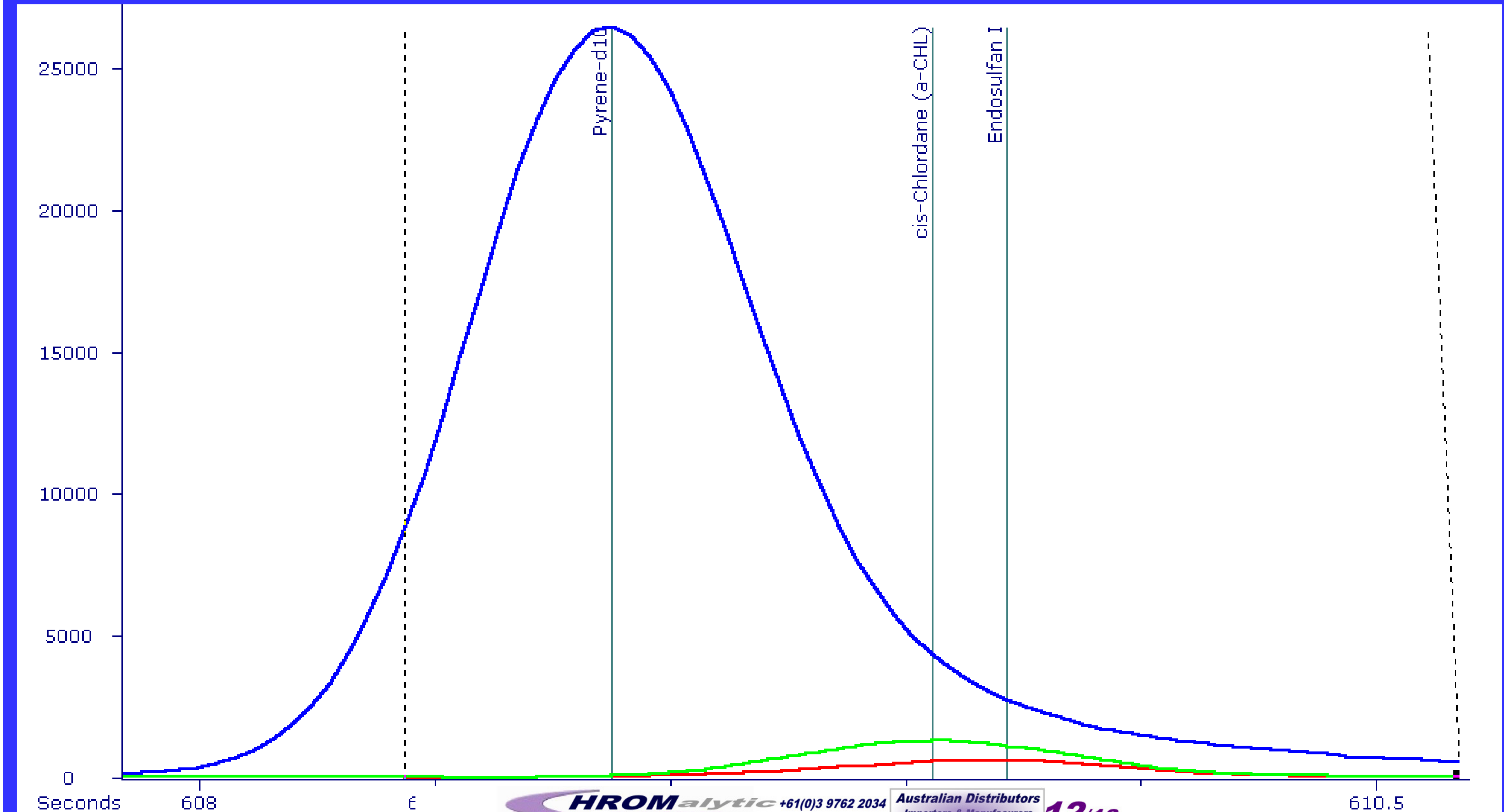
Sample D-0998
PCB77-d6, PCB151, PCB77, Dieldrin, PCB123



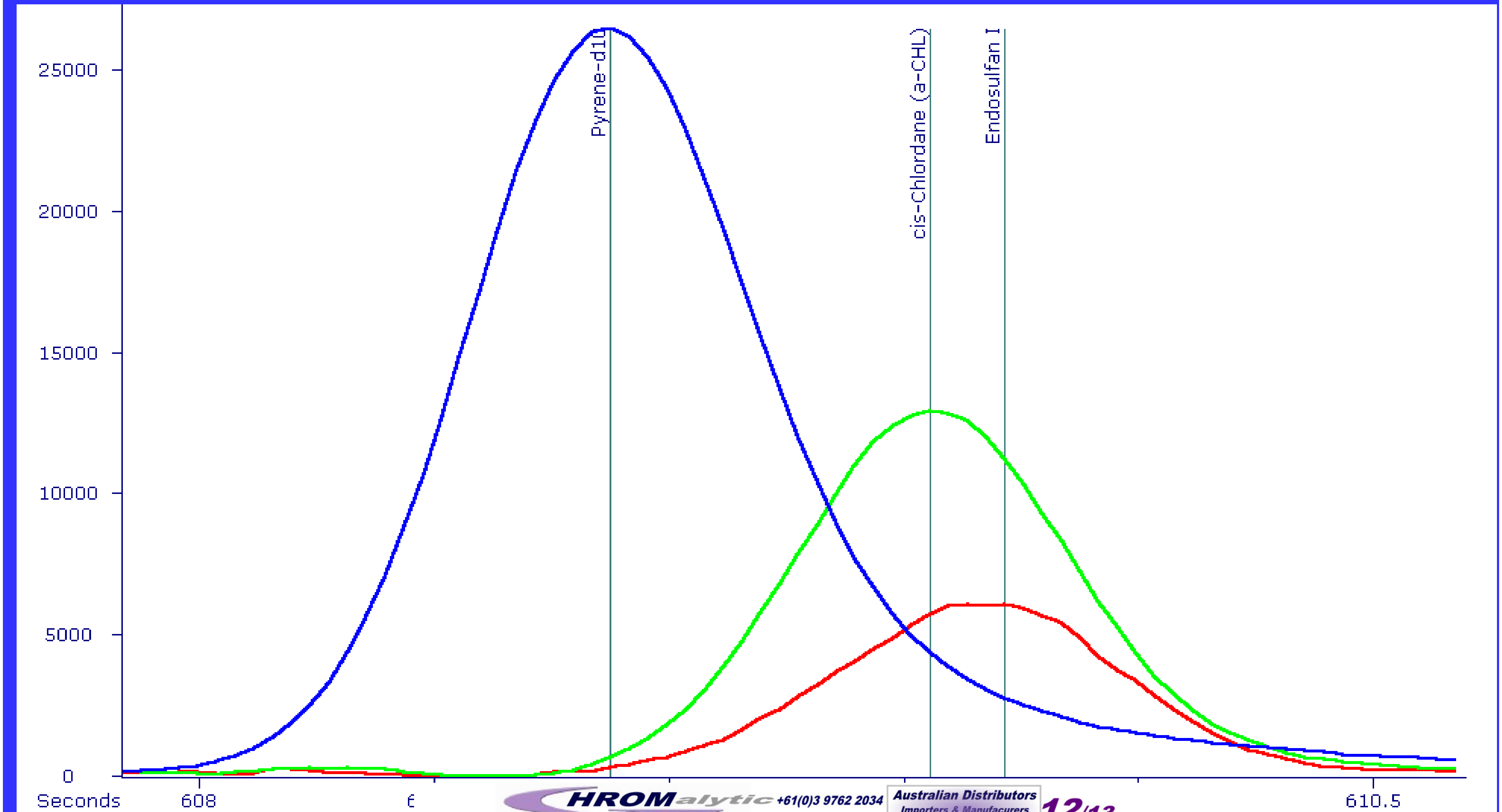
Sample D-0998
Analytical Ion Chromatogram (AIC)



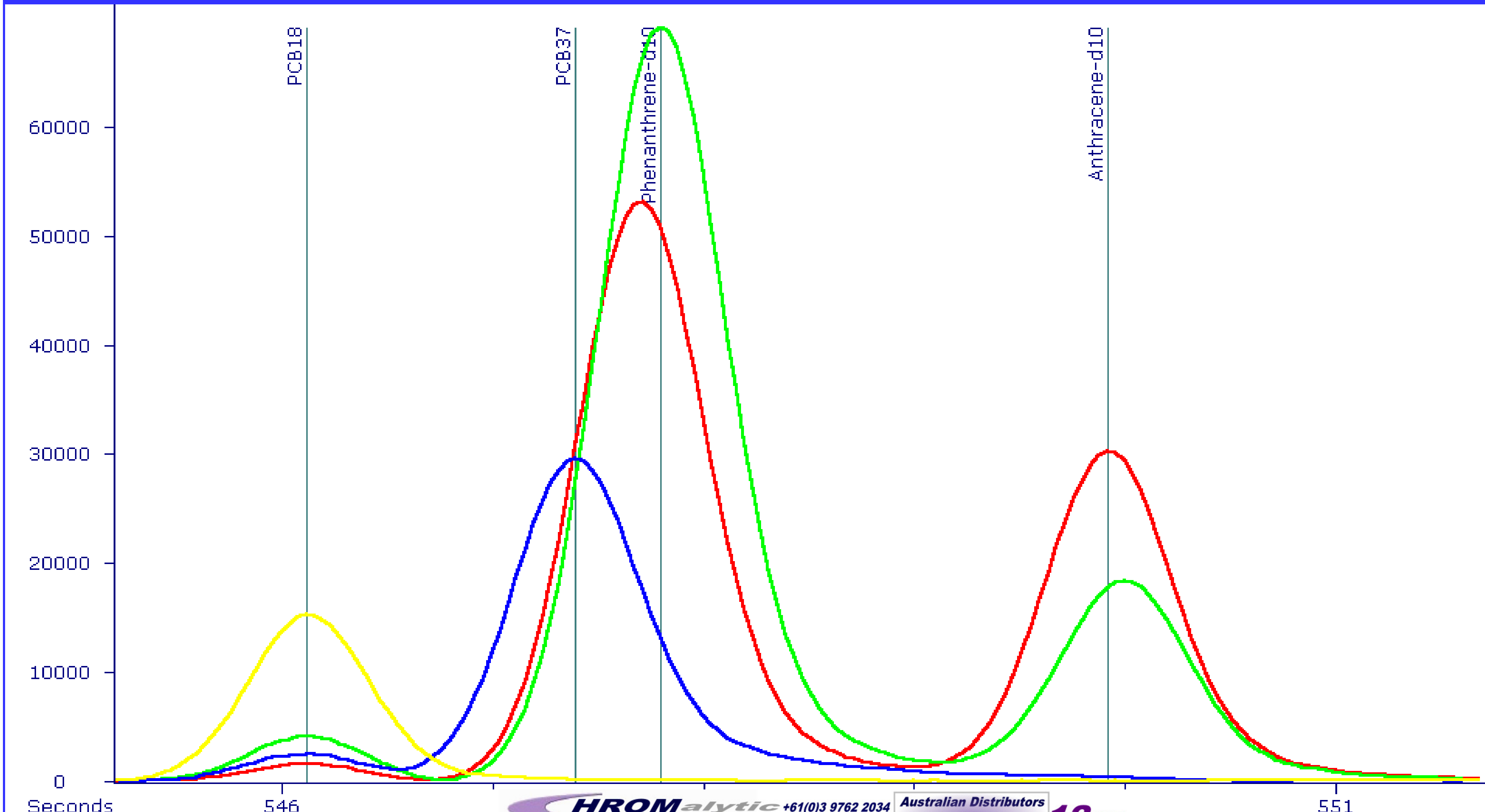
Sample D-0998
Pyrene-d10, a-CHL, Endosulfan I



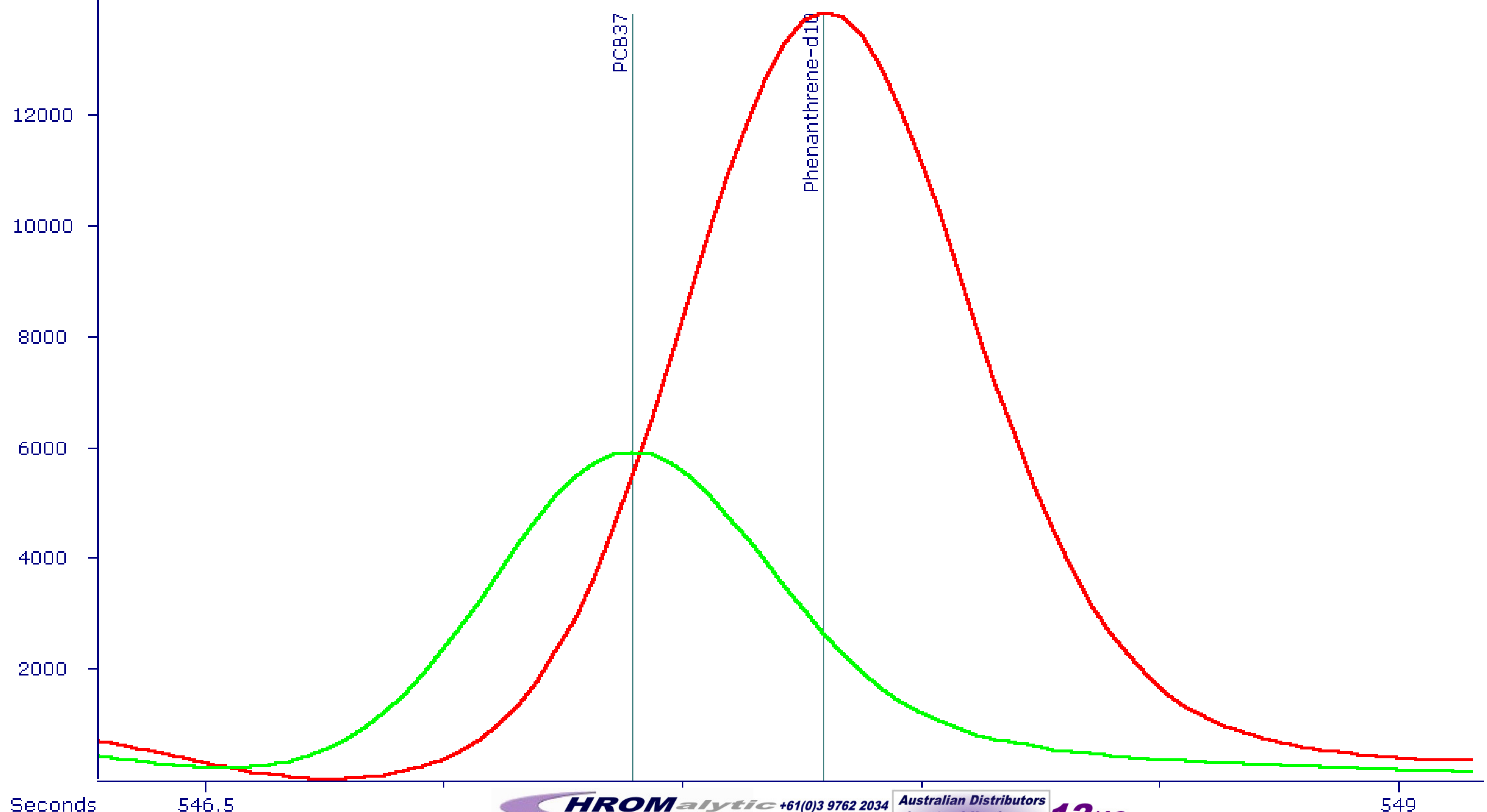
Sample D-0998
Pyrene-d10, a-CHL, Endosulfan I



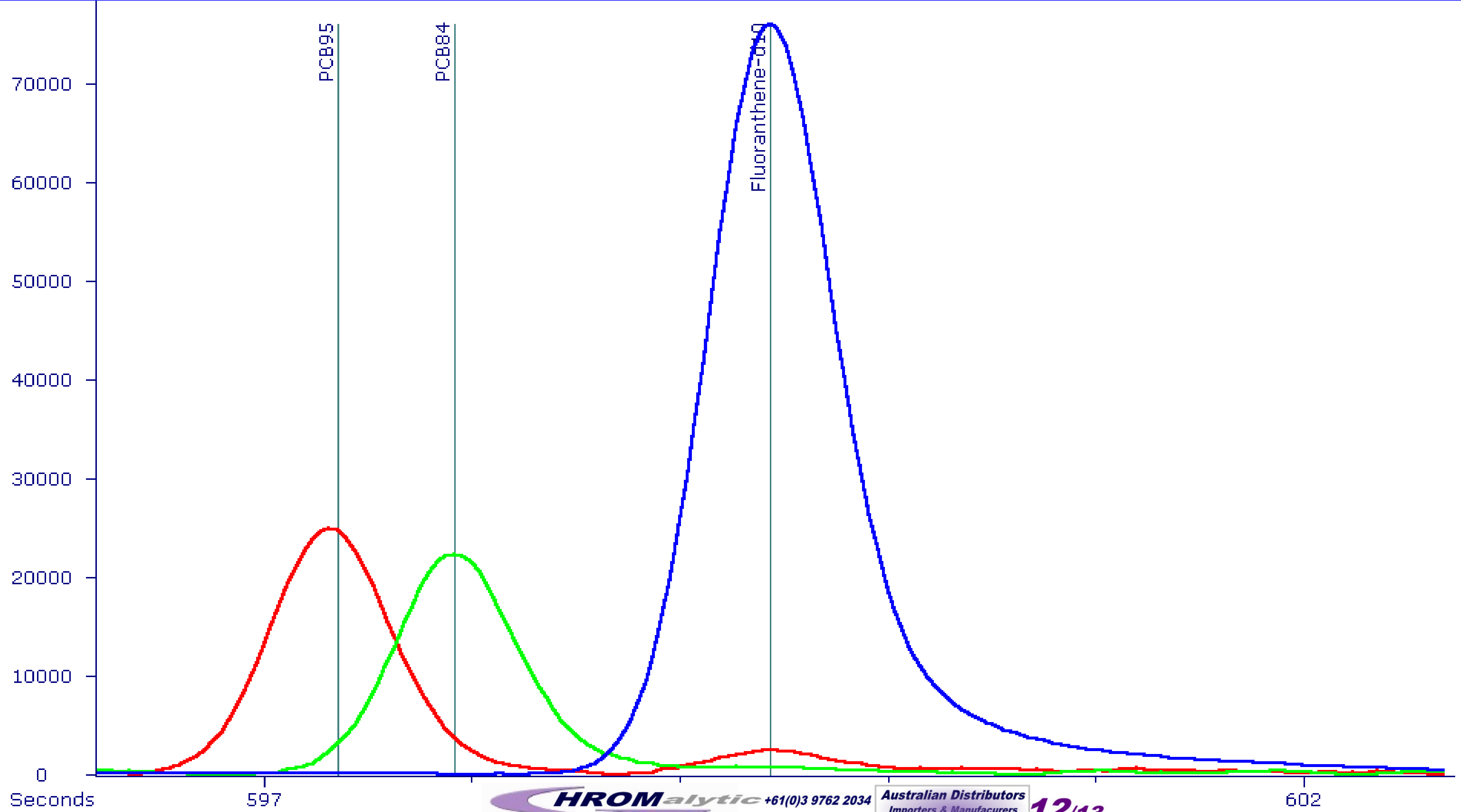
Sample D-0998
PCB18, PCB37, Phenanthrene-D10, Anthracene-D10



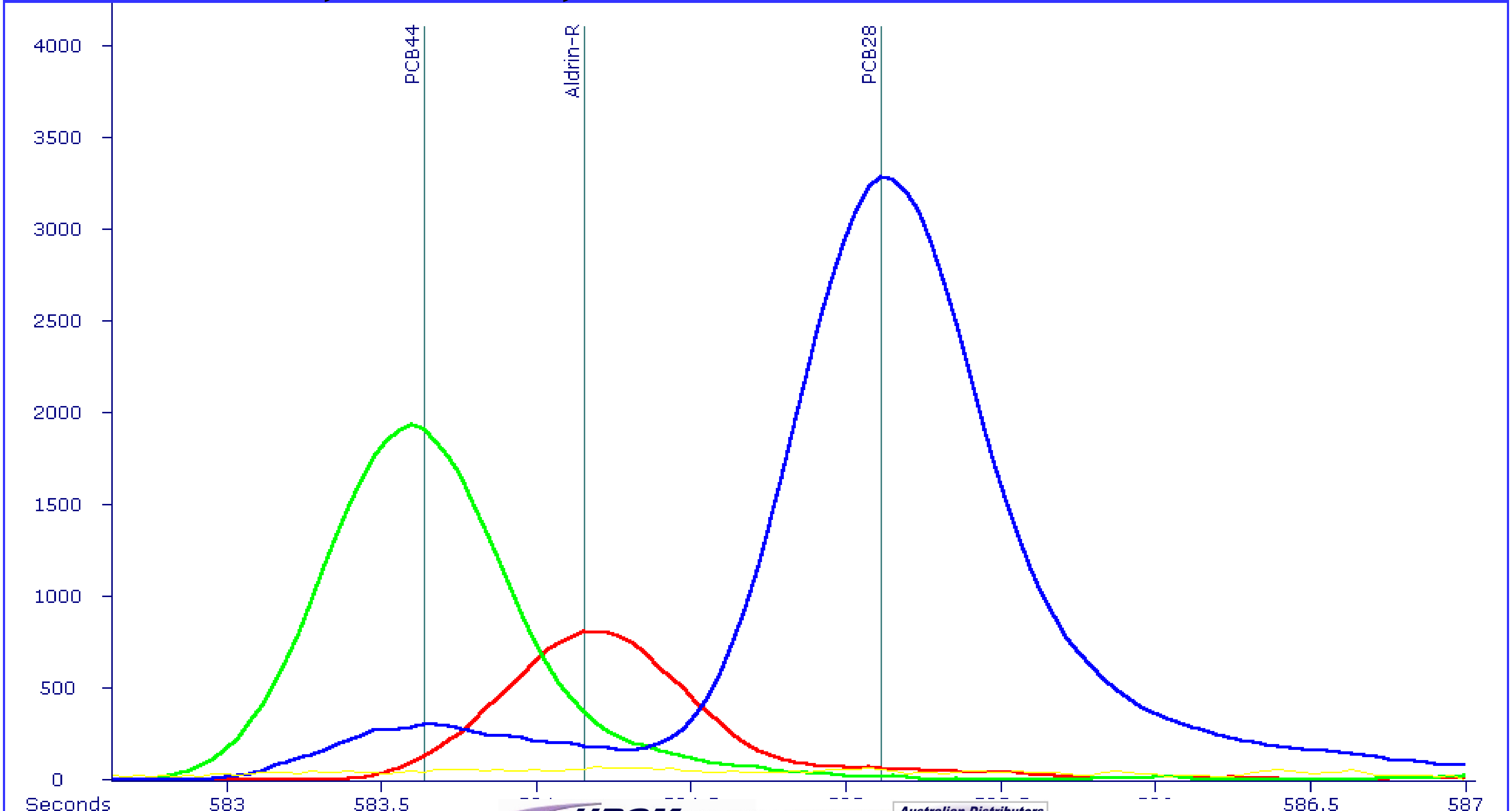
Sample D-0998
PCB37, Phenanthrene-d10



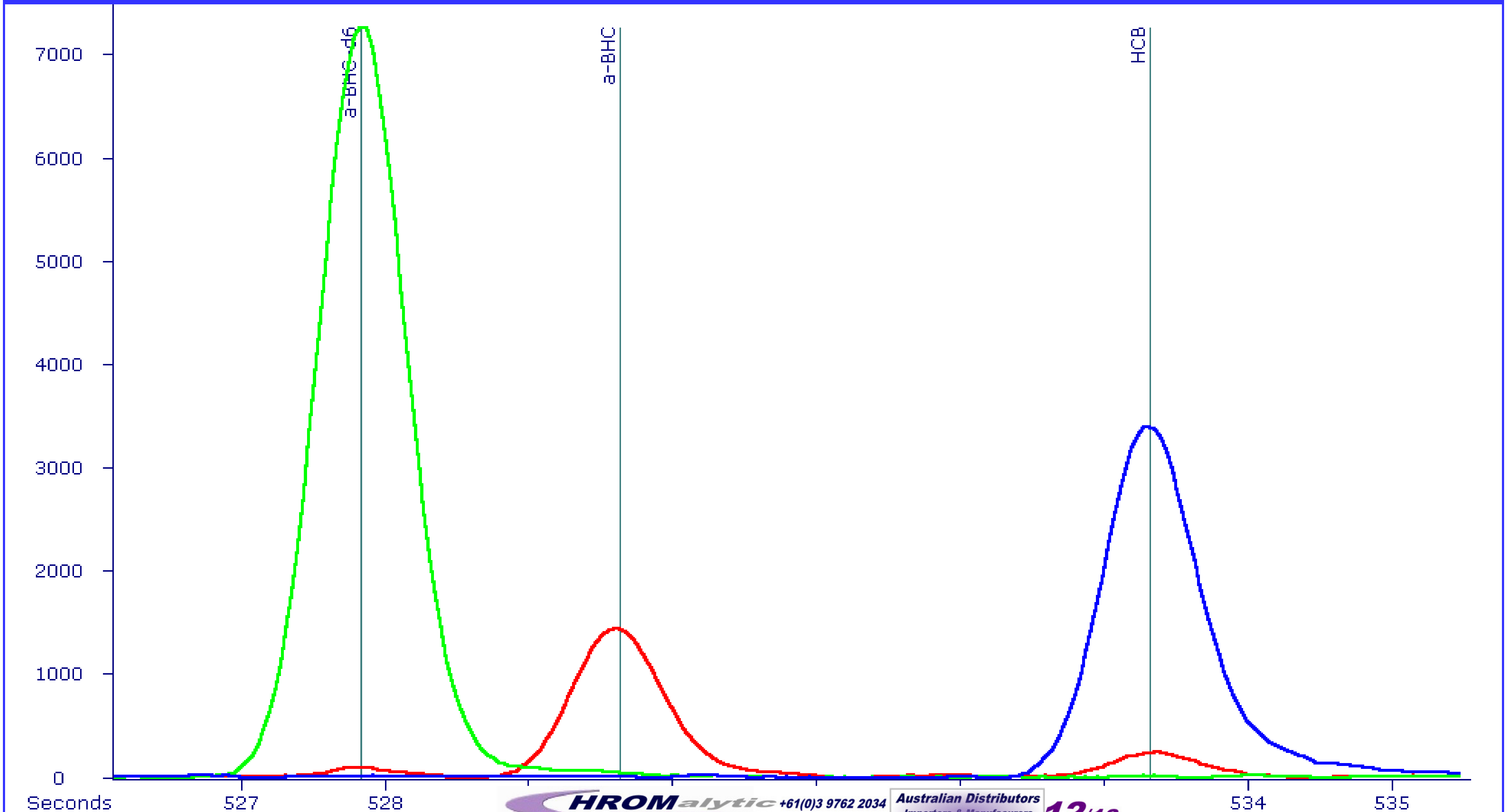
Sample D-0998
PCB95, PCB84, Fluoranthene-d10



Sample D-0998
PCB44, Aldrin-R, PCB28



Smaple 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

$$\alpha = k_2 / k_1$$

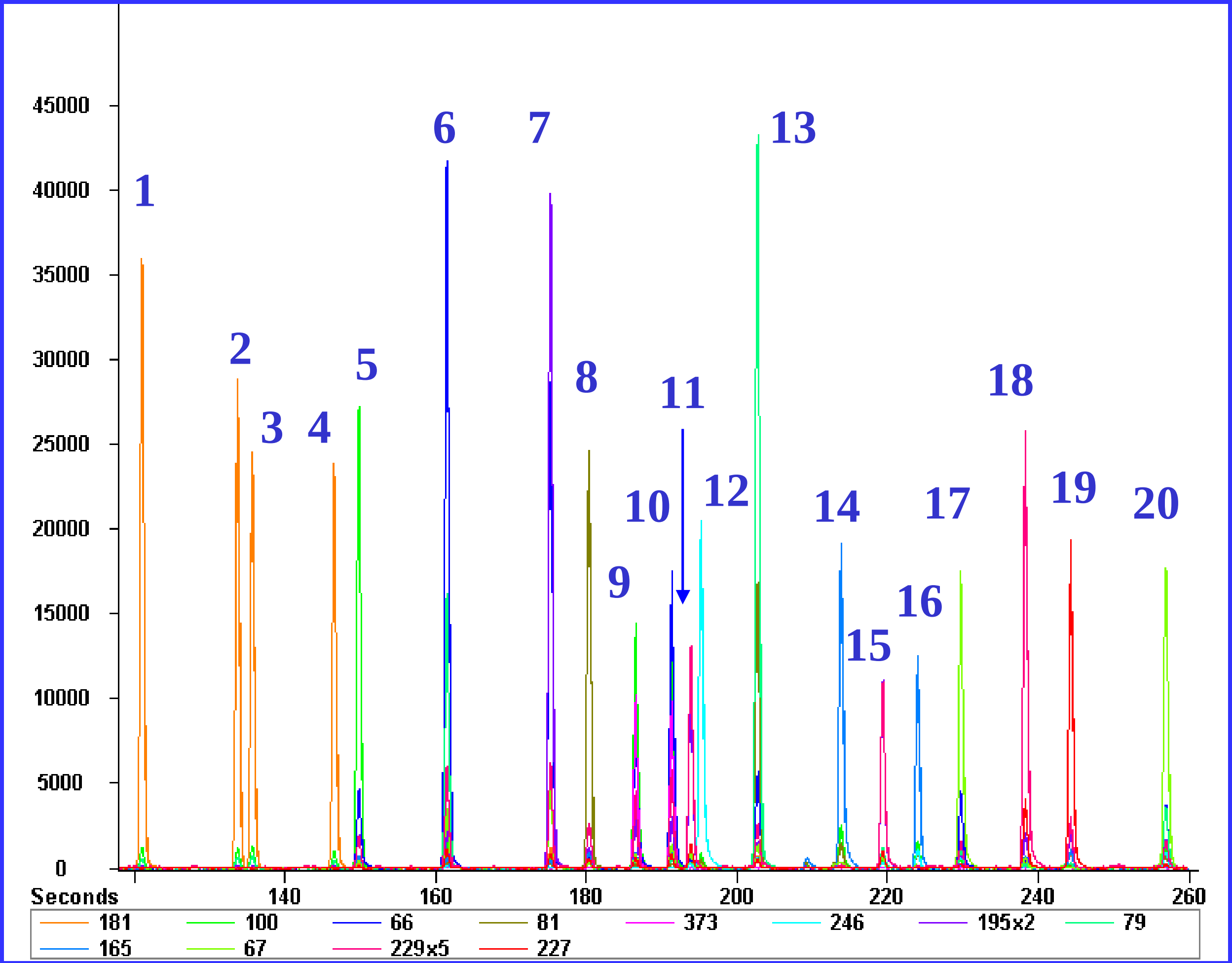
Coupling Tuned-Selectivity Phases to TOF-MS

- 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

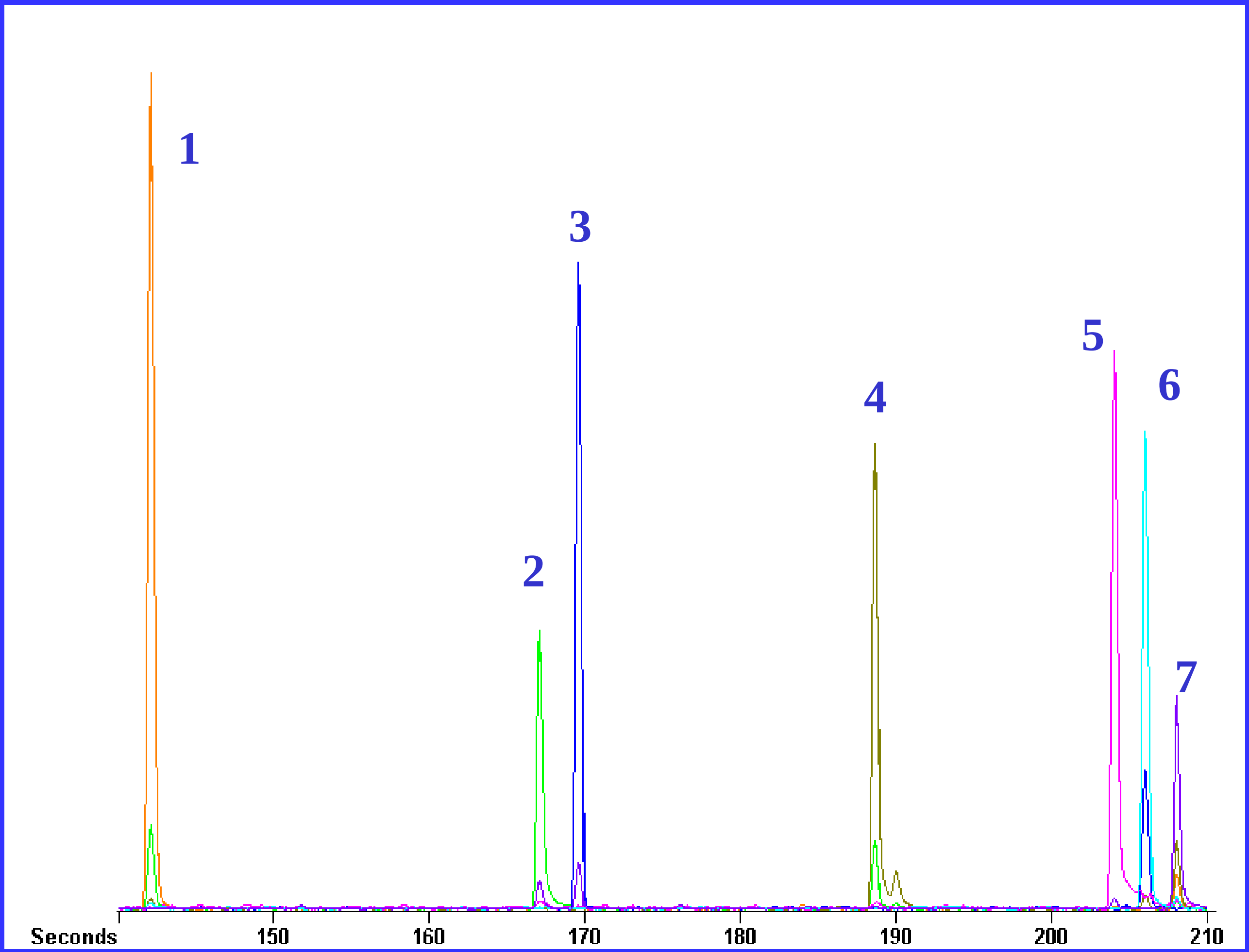
1. Alpha-BHC
2. Gamma-BHC
3. Beta-BHC
4. Delta-BHC
5. Heptachlor
6. Aldrin
7. Isodrin
8. Heptachlor epoxide
9. Gamma-Chlordane
10. Alpha-Chlordane
11. 4,4'-DDE
12. Endosulfan I
13. Dieldrin
14. 4,4'-DDD
15. Endosulfan II
16. 4,4'-DDT
17. Endrin aldehyde
18. Endosulfan sulfate
19. Methoxychlor
20. Endrin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



Baseline resolution in less than 4.5 minutes!

Fast GC/TOFMS of OC/OPPs on CLPII

LECO Pegasus II GC/TOFMS

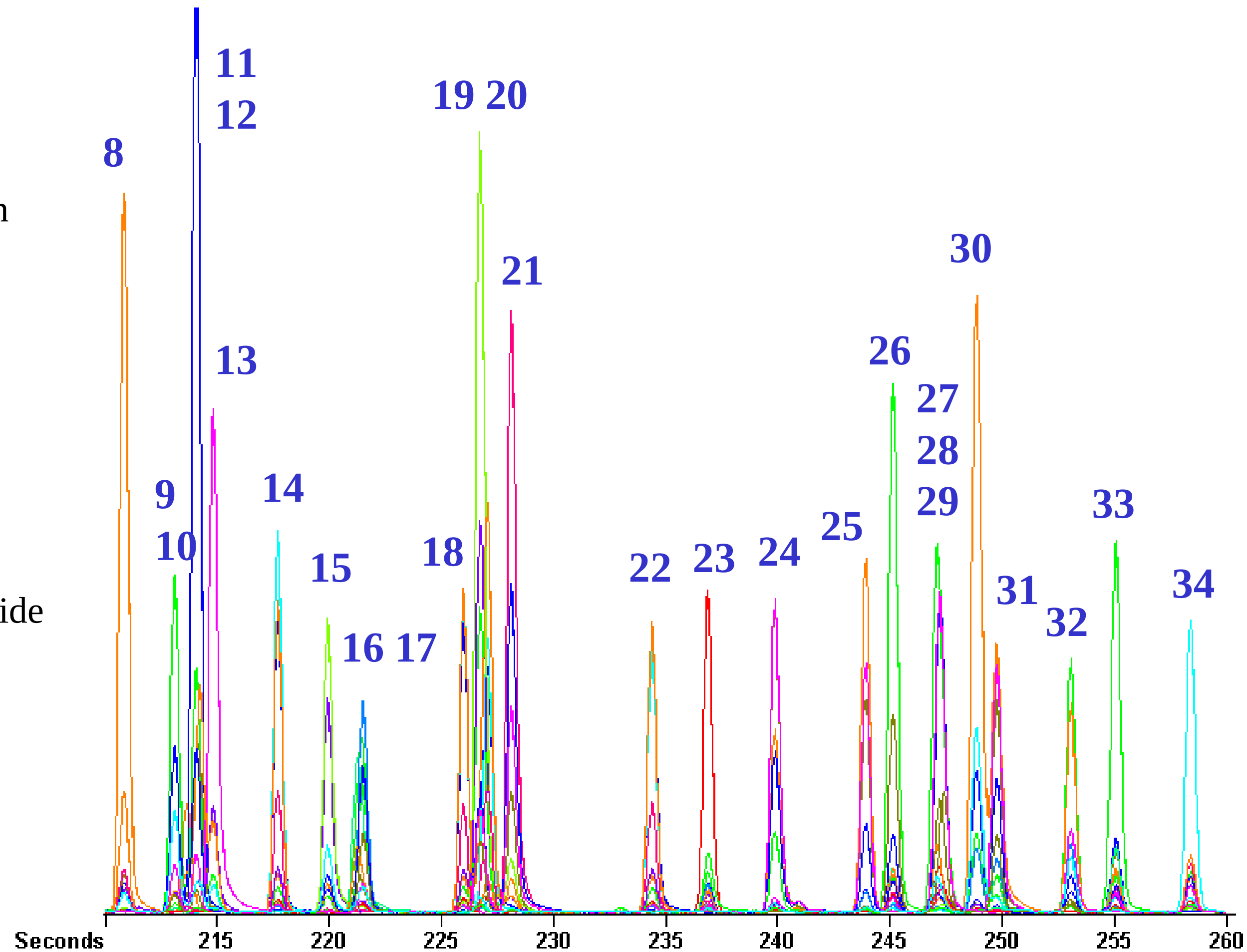


1. 1,2-Dibromo-3-chloropropane
2. Dichlorvos
3. Hexachlorocyclopentadiene
4. Mevinphos
5. Demeton O
6. TEPP
7. Ethoprop

Fast GC/TOFMS of OC/OPPs on CLPII

LECO Pegasus II GC/TOFMS

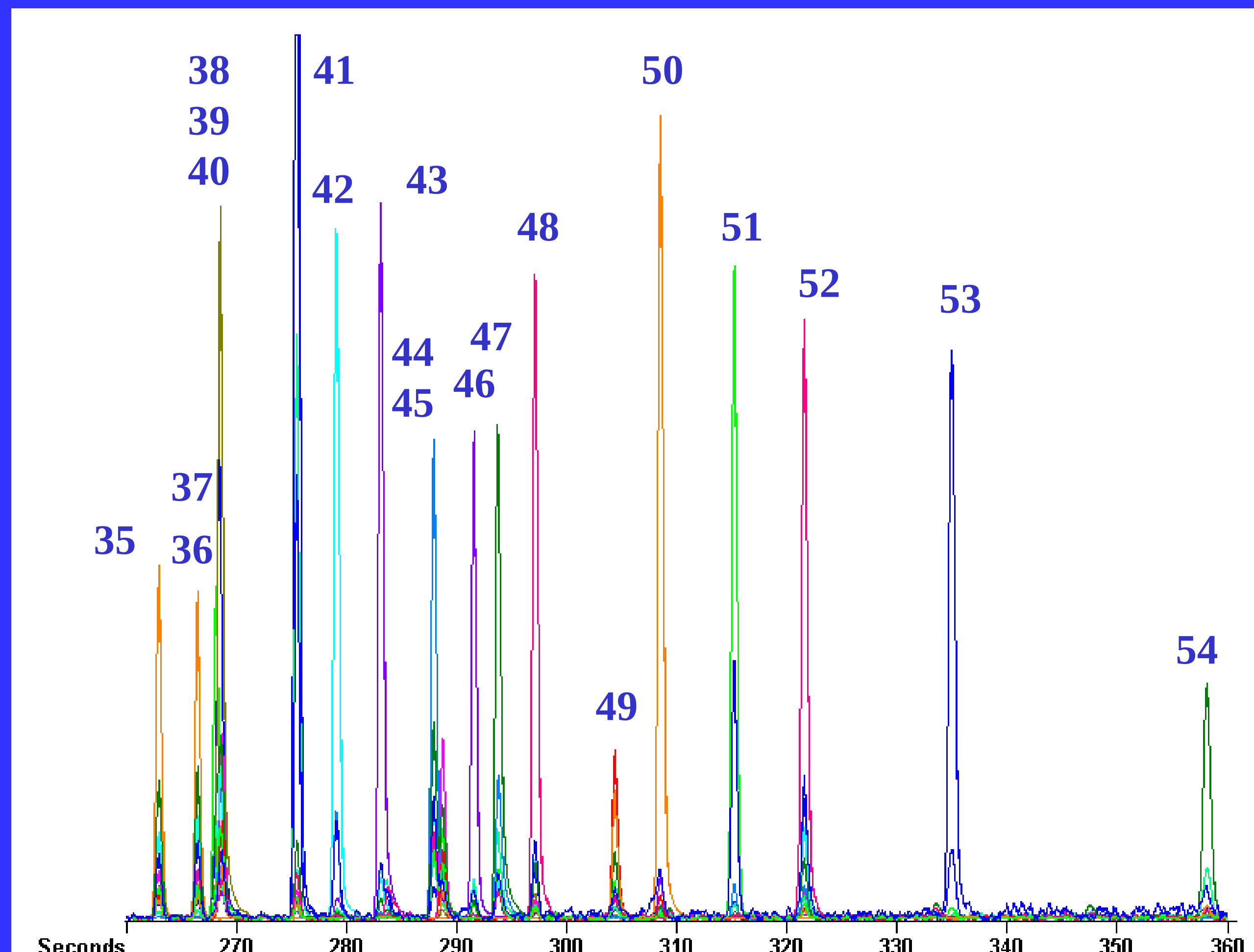
8. Trans-Diallate
9. Sulfotepp
10. Cis-Diallate
11. Phorate
12. Naled
13. Hexachlorobenzene
14. Alpha-BHC
15. Demeton S
16. Monocrotophos
17. Diazinon
18. Gamma-BHC
19. Disulfoton
20. Beta-BHC
21. Dimethoate
22. Delta-BHC
23. Heptachlor
24. Ronnel
25. Methyl parathion
26. Aldrin
27. Chlorpyrifos
28.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



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



utes!

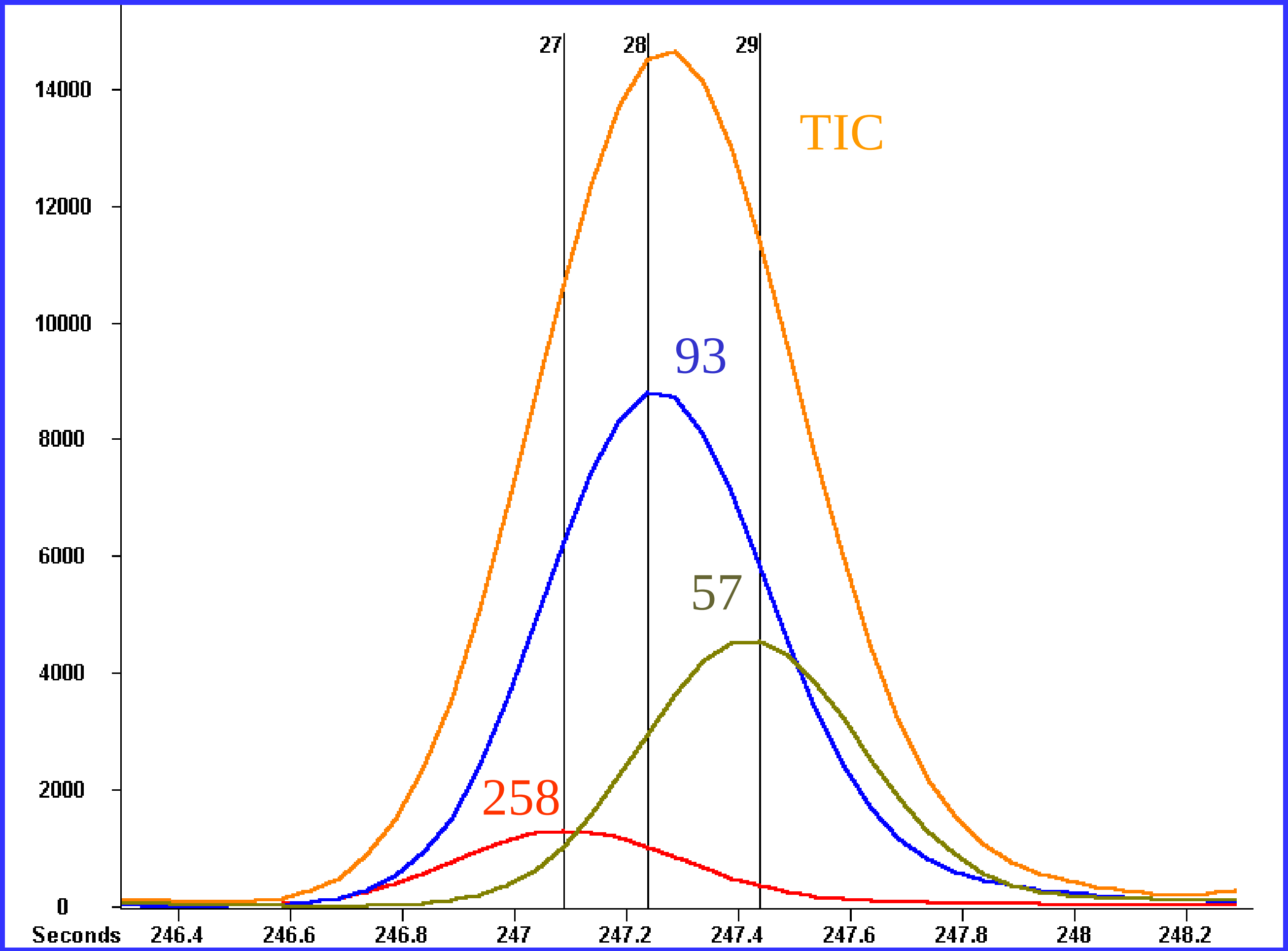
Automatic Peak Find Using TOFMS

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

LECO Pegasus II GC/TOFMS



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.

Acknowledgements

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  Leco Corporation - Las Vegas

For more information...

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