Review of a Comprehensive, Alternate Approach for PCB Congener / Homolog Analysis

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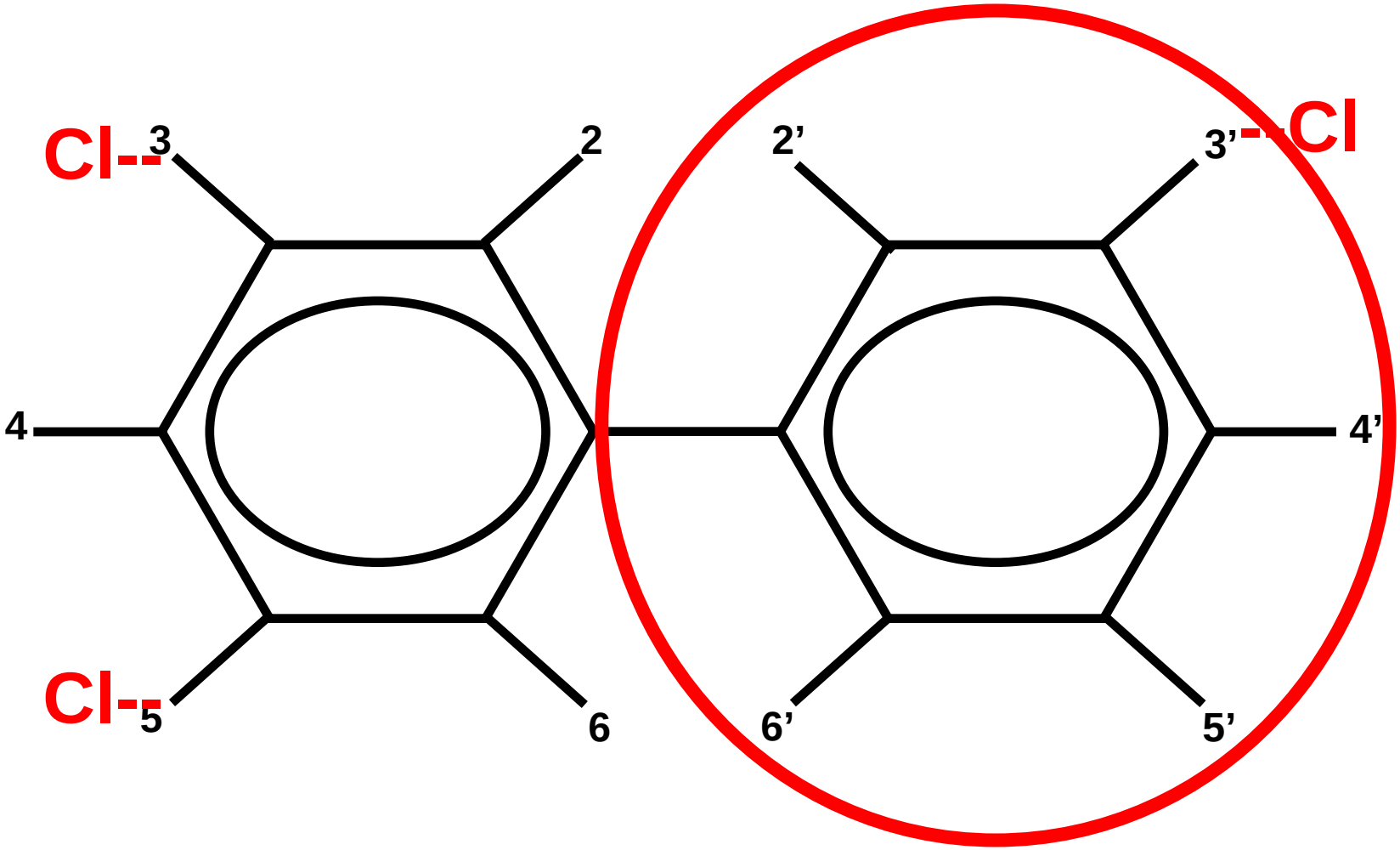
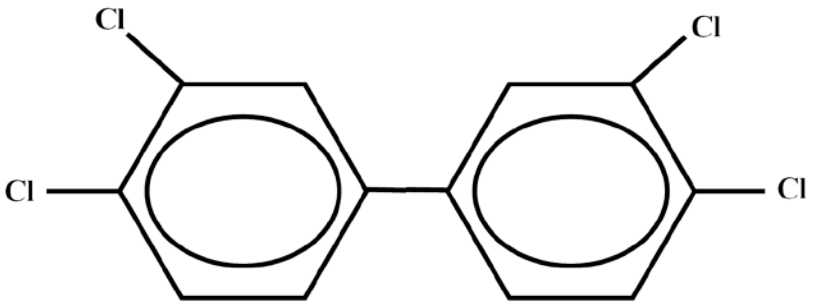
OVERVIEW
PCB Chemistry
Traditional Analytical Options
GC / LRMS Analysis
Concluding Remarks



Poly – Chlorinated - Biphenyls

PCB Chemistry Overview

- Biphenyl with 1 -10 chlorine atoms
  - 10 possible positions leads to 209 possible combinations
    - **209 individual PCB compounds – CONGENERS**



3,3',4,4' – Tetrachlorobiphenyl ***(IUPAC)***

BZ 77 ***(Ballschmiter & Zell)***

- PCBs can also be grouped according to the # of chlorine atoms
  - Level (or Degree) of chlorination
    - **10 HOMOLOGS (Homologues)**

Chlorinated Biphenyls by Homolog

Empirical Formula	Molecular Weight	# Isomers	
$C_{12}H_{10}$	154.1	1	
$C_{12}H_9Cl$	188.0	3	**Monochlorobiphenyls**
$C_{12}H_8Cl_2$	222.0	12	**Dichlorobiphenyls**
$C_{12}H_7Cl_3$	256.0	24	**Trichlorobiphenyls**
$C_{12}H_6Cl_4$	289.9	42	**Tetrachlorobiphenyls**
$C_{12}H_5Cl_5$	323.9	46	**Pentachlorobiphenyls**
$C_{12}H_4Cl_6$	357.8	42	**Hexachlorobiphenyls**
$C_{12}H_3Cl_7$	391.8	24	**Heptachlorobiphenyls**
$C_{12}H_2Cl_8$	425.8	12	**Octachlorobiphenyls**
$C_{12}H_1Cl_9$	459.7	3	**Nonochlorobiphenyls**
$C_{12}Cl_{10}$	493.7	1	**Decachlorobiphenyl**

Aroclors

Monsanto trade name

Technical grade mixtures of congeners, made by batch chlorination of biphenyl

Nine Aroclors:

1221, 1232, 1242/1016, 1248,

1254, 1260, 1262, 1268

Traditional PCB Analytical Options

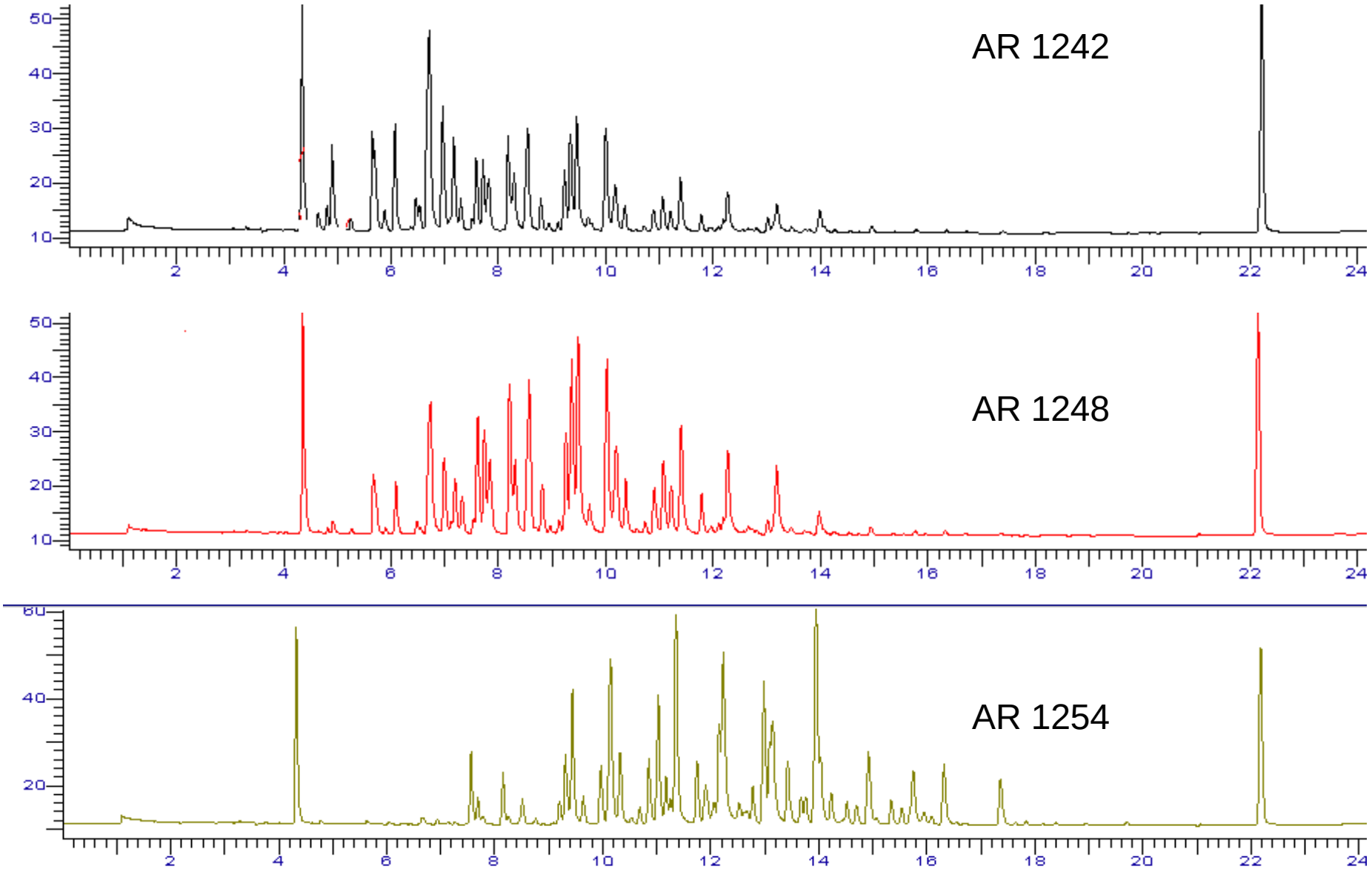
- Aroclor analysis
  - Gas chromatography w/electron capture detection (GC-ECD)
  - Most common PCB analysis
    - EPA 8082, 608
    - Aroclors only*

- Congener and/or homolog analysis
  - Gas chromatography / high resolution mass spectrometry (GC/HRMS)
    - Common methods – EPA 1668
  - Full 209 congener list, subsets & homologs

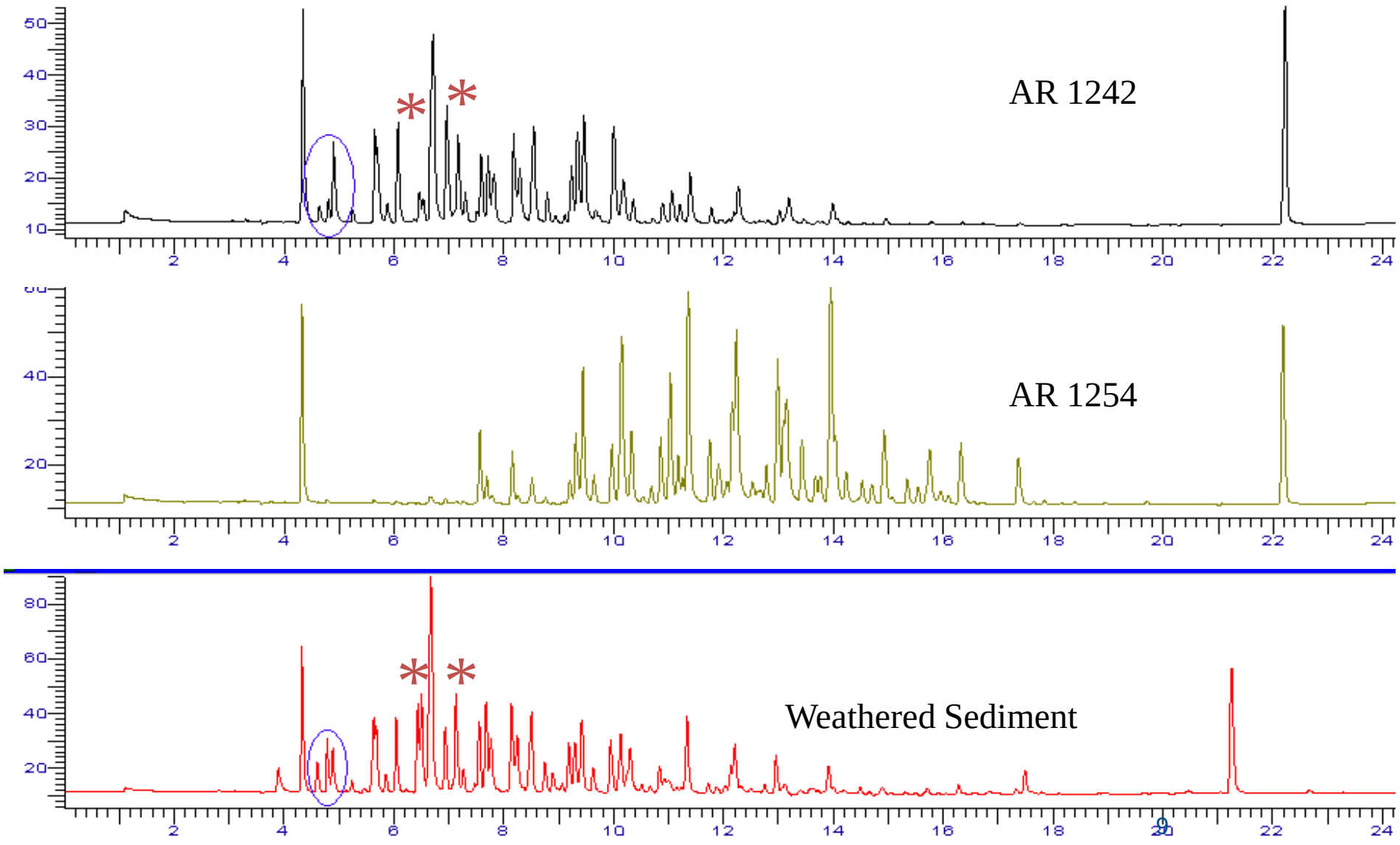
Analysis of PCB Aroclors by GC-ECD

- Qualitative analysis (identifying aroclors present)
  - GC retention time
    - characteristic patterns
    - Identification of unique aroclor peaks
    - Specific peak ratios
- Inexpensive and widely available
- Challenges
  - Mixtures, multi component analytes
  - Alteration of aroclor pattern in environment (i.e. “weathering”)
    - Some physical degradation, biological transformation
  - Quantitative issues:
    - Multiple aroclors… “double counting” ?
    - Other ECD-sensitive compounds can interfere

Aroclors by Method 8082



Qualitative ID



PCB Congeners/Homologs by GC / HRMS

- GC / HRMS – i.e. Method 1668
- Mass spectrometer provides qualitative certainty
  - Extremely sensitive
  - Costly w / longer turnaround times
  - Significant dilutions required for contaminated samples

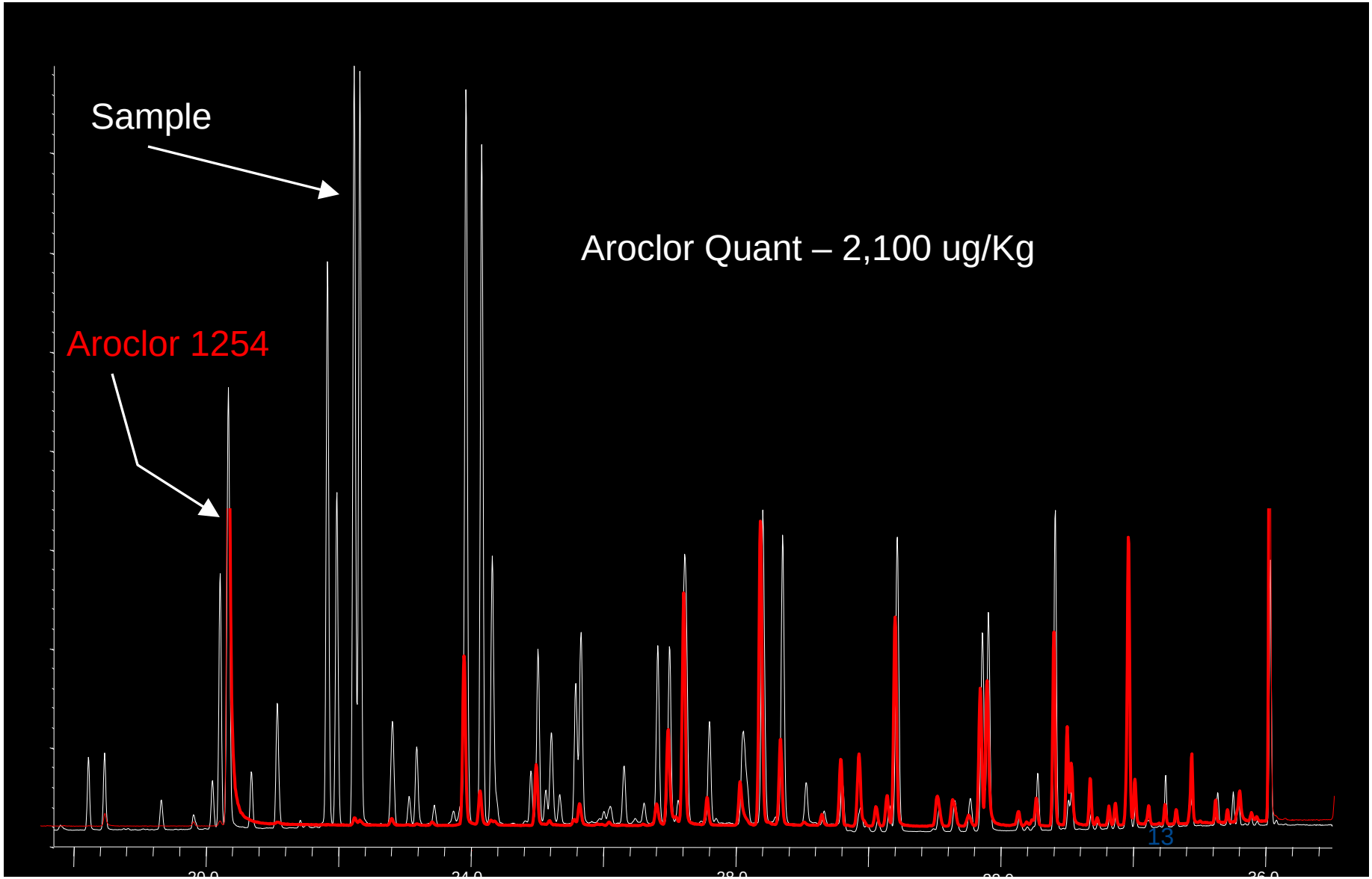
There is Another Way…

- PCB analysis by GC / LRMS
  - LRMS vs HRMS? Resolution
- GC / LRMS applications
  - When you need more than aroclors…
  - Representative “total” PCB concentrations
  - Priced between GC aroclor and HRMS analysis
- Homolog series
    - Cl_1 through $–Cl_{10}$
    - Total PCB
- Congeners
  - All 209, NOAA 18/22 list, or project specific subsets

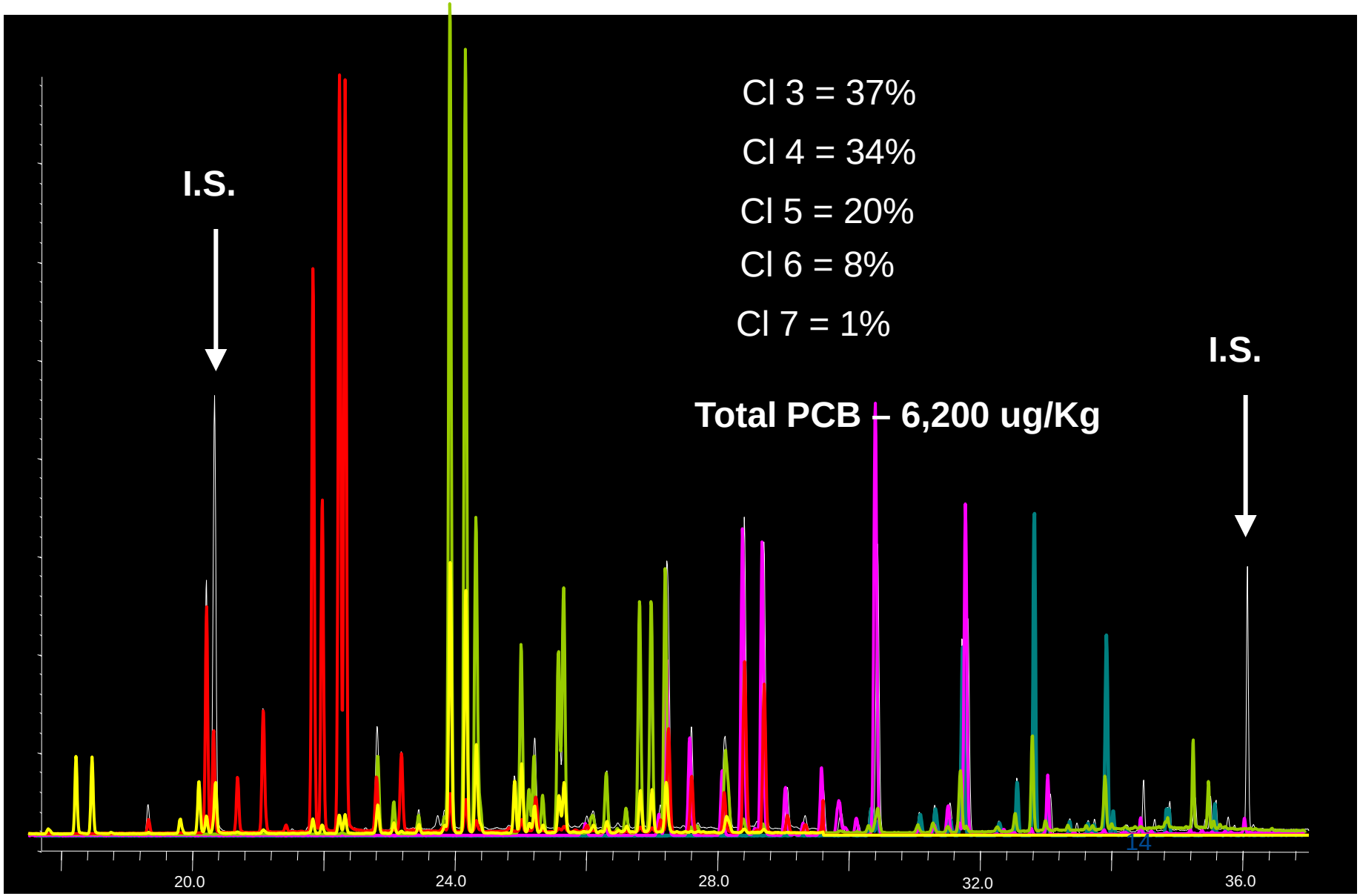
PCB Analysis by GC/LRMS - History

- Method 625 (acid / base-neutral extractables, SVOCs)
  - PCB aroclors listed as potential analytes
- Method 680
  - Adopts / modifies the approach introduced in Method 625
  - Method was not widely used at the time
- NOAA Technical Memorandum NMFS-NWFSC-59, 2004
  - Replaces earlier document utilizing GC-ECD
- Method 8270, performance based, modified

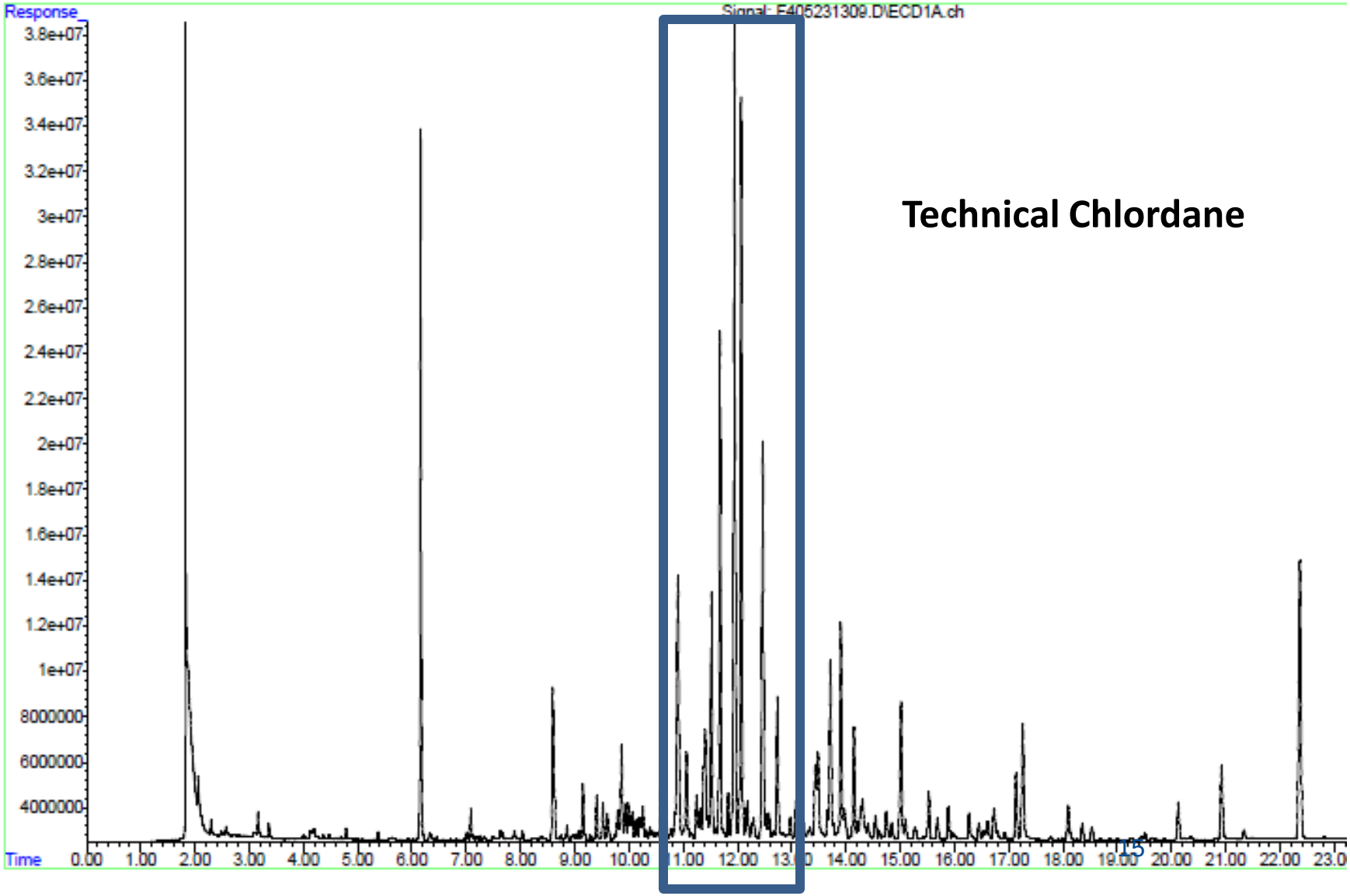
Quahog Quantitation – Aroclor Analysis



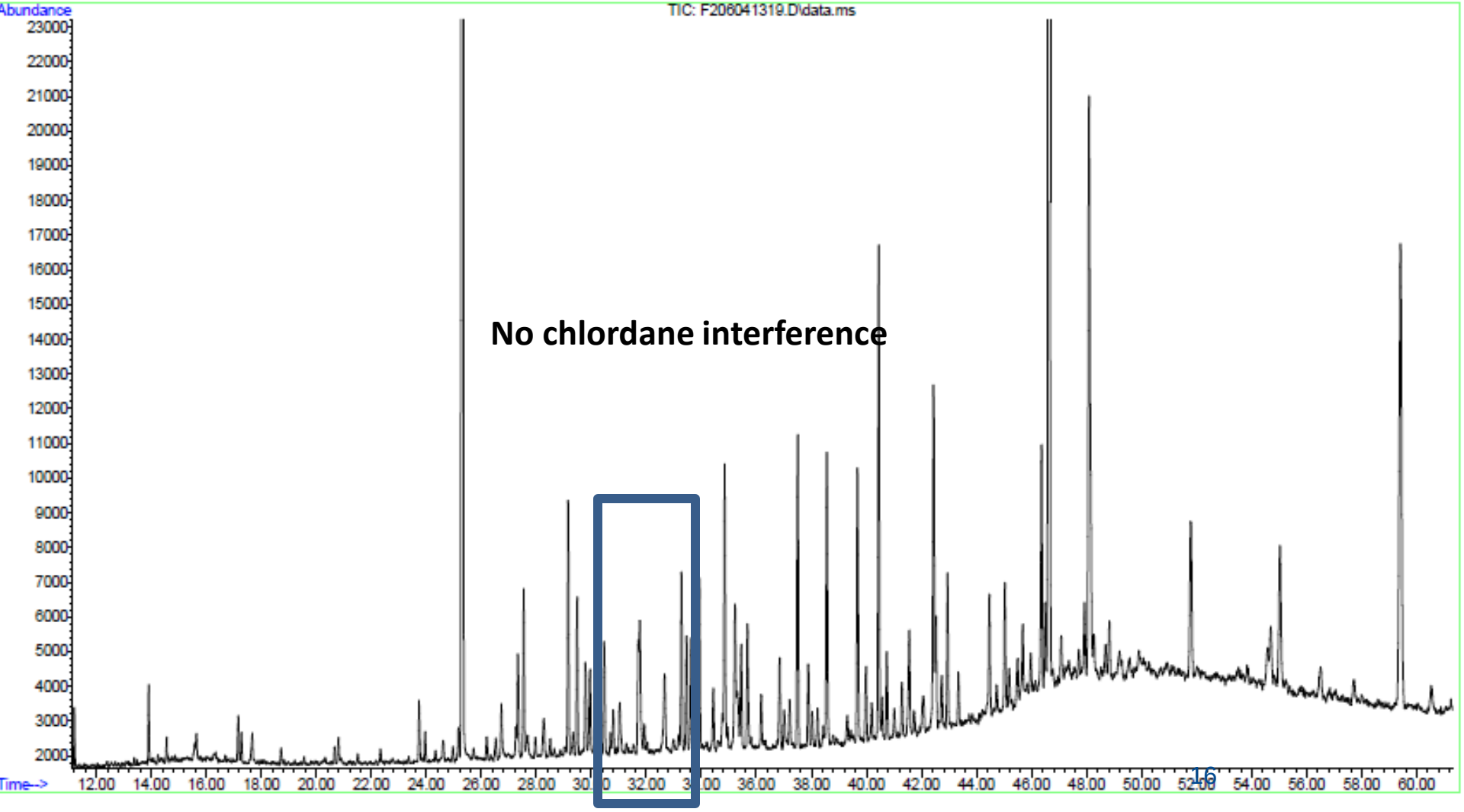
Quahog Quantitation – LRMS Homolog Analysis



Tissue Sample: GC-ECD Aroclor Analysis



Tissue Sample: GC-LRMS Analysis



PCB Analysis by GC/LRMS

- Applicable matrices
  - Air, water, soil, sediment, & tissue

- Sensitivity
  - Homologs
    - Aqueous: RL 0.5 ng/L
    - Soil/Sediment/Tissue: RL 0.4 ug/Kg

  - Congeners
    - Aqueous: RL 0.5 ng/L
    - Soil/Sediment/Tissue: RL 0.4 - 0.04 ug/Kg
    - Co-eluters

In Summary…

- For the right application, LRMS can be an attractive option
  - Comprehensive, cost effective, “middle ground”
- Eliminates the qualitative /quantitative bias that can be associated with GC aroclor analysis
  - “Weathering” & aroclor mixtures irrelevant
- Homolog analysis ideal for total PCB determination
- Can also simultaneously determine aroclors for comparison with historical aroclor data

Questions?

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