Endocrine disrupters in contaminated ground and surface water: Application of new technology (GCxGC/ToFMS) to the determination of nonylphenol isomers

[1]R. Eganhouse, [1]J. Pontolillo, [1]C. Zhang, [1]I. Cozzarelli, [2]Jason Masoner, [3]L. Barber
U.S. Geological Survey, [1]Reston, VA, [2]Oklahoma City, OK, and [3]Boulder, CO

R. Gaines, G. Frysinger
U.S. Coast Guard Academy, New London, CT

W. Giger, F. Gabriel, H.-P. Kohler
EAWAG, Dübendorf, Switzerland

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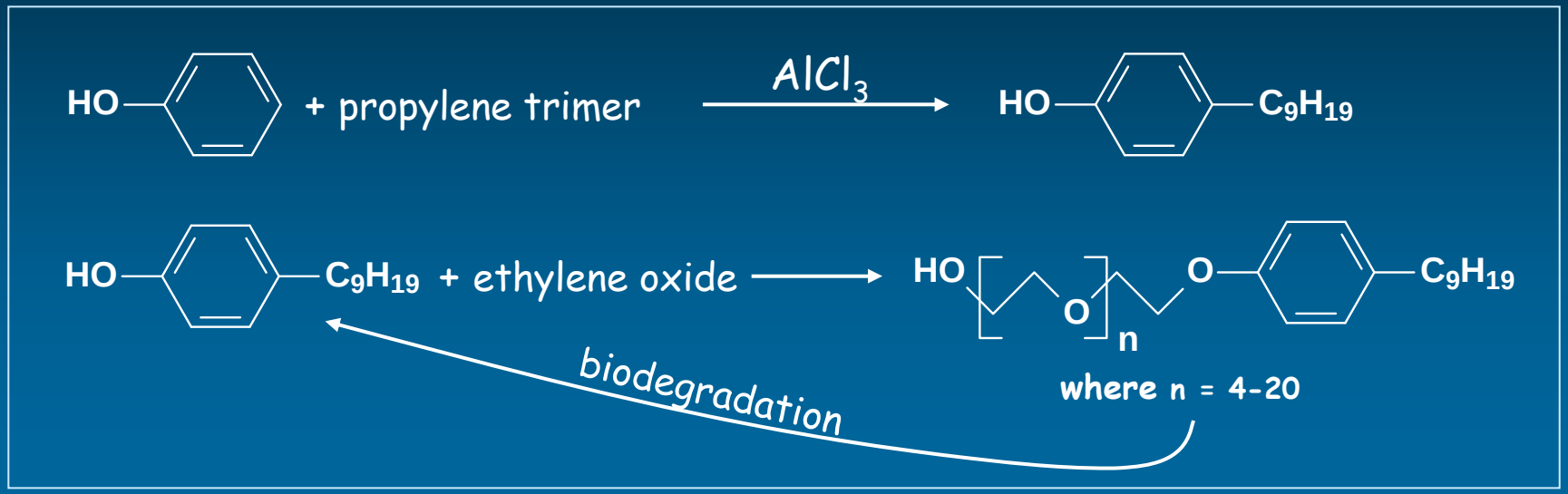
Synthetic nonylphenols (NPs)



- Complex mixture of isomers ($n \geq 550$).
- NPs → nonylphenol polyethoxylates (NPEOs).
- Introduced to the environment by discharge of wastewater effluent and/or disposal of biosolids, solid waste (NPEOs → NPs).
- NPs are known endocrine disruptors.
- Recent studies have shown: 1) environmental NP isomer compositions can differ from that of technical NP, 2) individual NP isomers degrade at different rates, and 3) NP isomers have physico-chemical properties that vary significantly (Log K_{ow} = 4.7-5.6).

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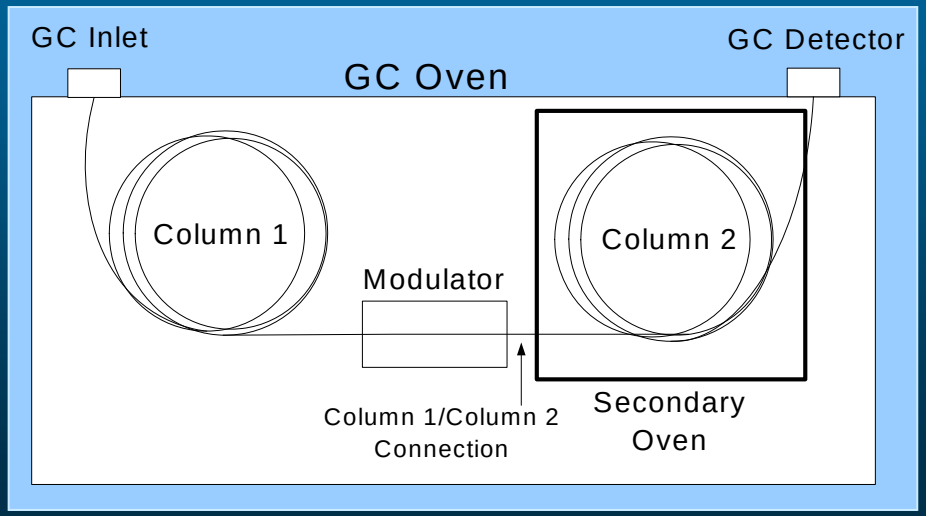
GCxGC/ToFMS basics

Two-Dimensional Gas Chromatography

1. Two GC columns with different phases (selectivities) provide improved separation. 2D peak capacity (PC) = $PC_{1°} \times PC_{2°}$.
2. Modulator transfers analytes step-wise as narrow pulses from 1st column to 2nd column.
3. All analytes should pass through 2nd column before introduction of next modulated peak to 2nd column. ∴ high speed chromatography!
4. The detector sees a series of 2nd column chromatograms, which are displayed as a 2D chromatogram (t_{r1}, t_{r2}).
5. The high resolution, high peak capacity separations of GCxGC are well suited to complex mixtures. S/N and ability to find clean baseline ↑. Can reduce prep time.



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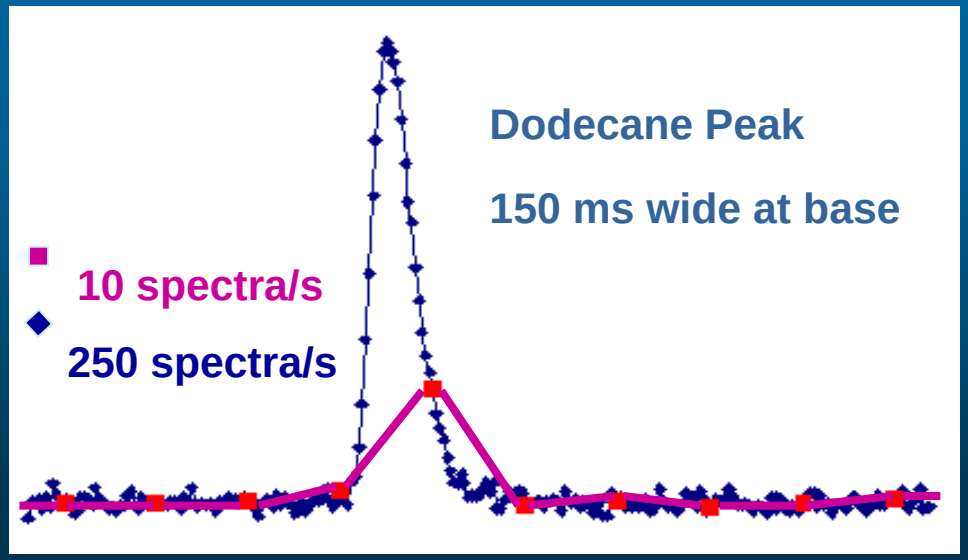
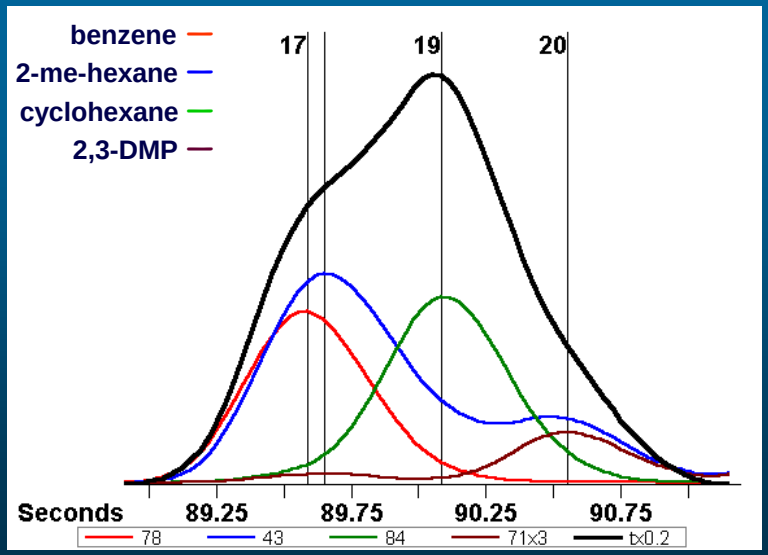
GCxGC/ToFMS basics

Time-of-Flight Mass Spectrometry

1. Fast data acquisition rates (50 – 500 spectra sec^{-1}) are necessary for narrow peaks of *GCxGC* (~50-250 msec).

2. Multichannel detection permits mass spectrum-based peak deconvolution (provided mass spectra of coeluting peaks possess unique ions). Full mass spectra can be acquired without sacrificing speed.





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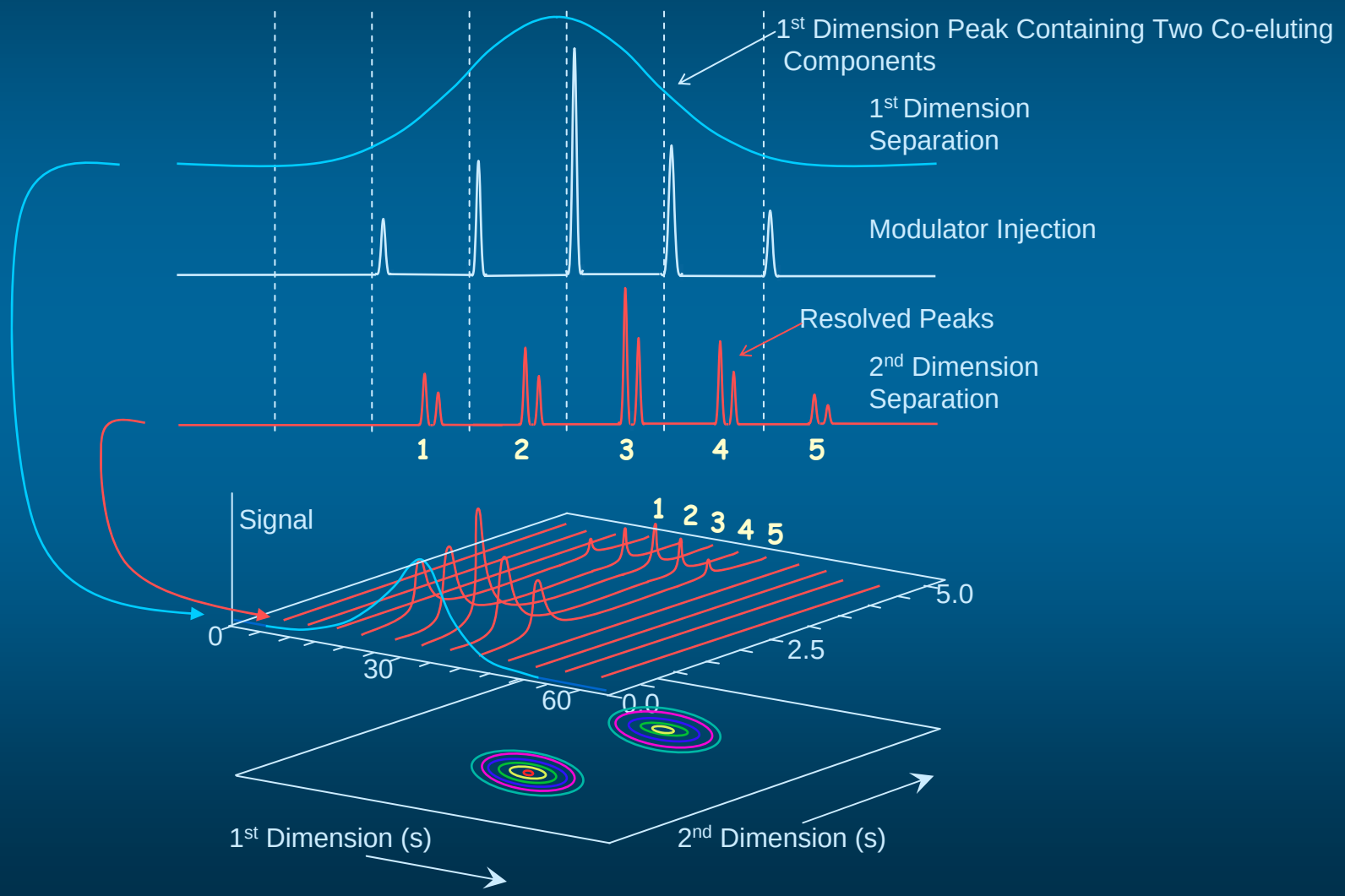
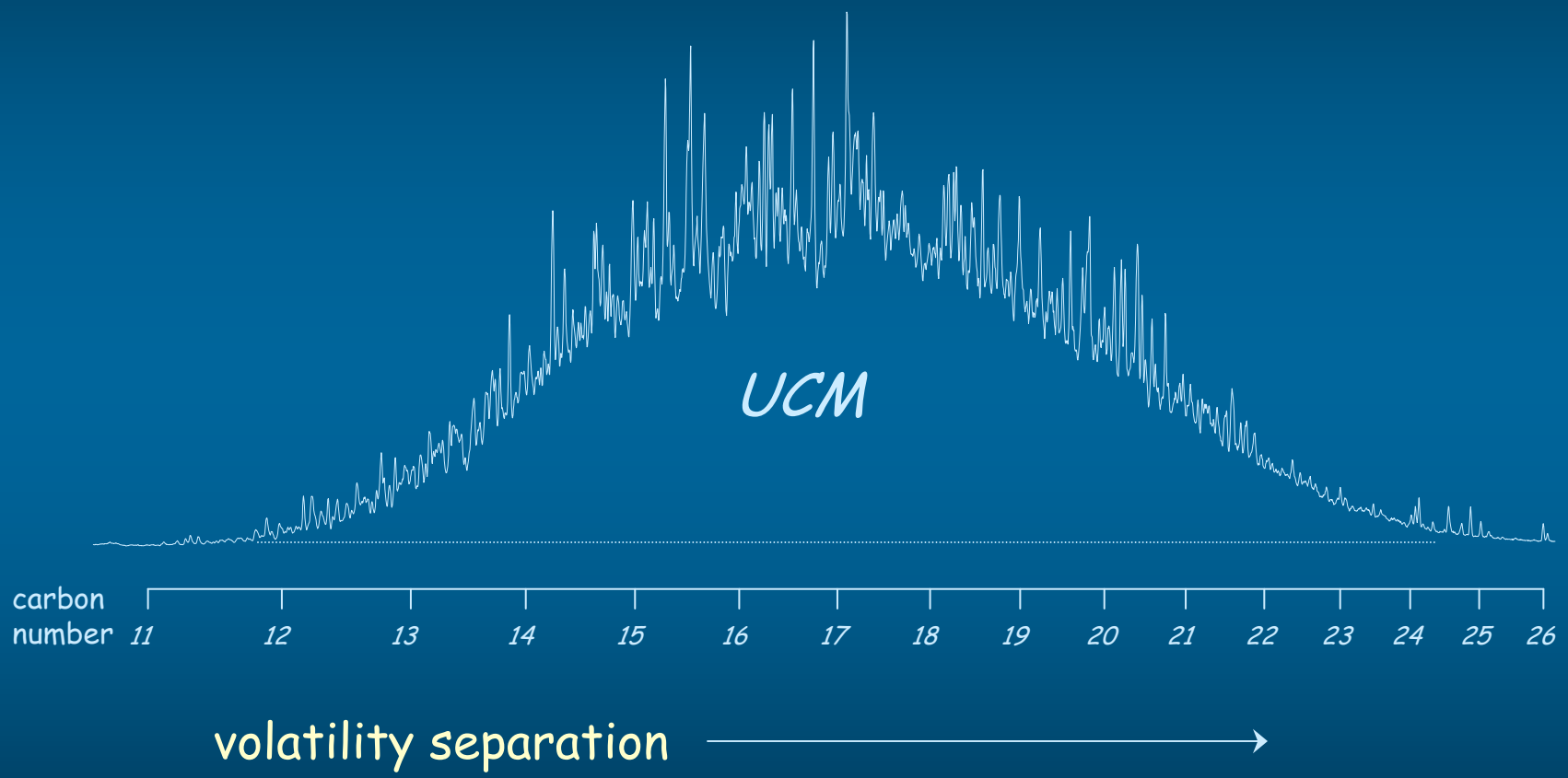
Graphics courtesy of LECO Corp. St. Joseph MI, USA

Peak modulation → Data visualization



Adapted from Frysinger *et al.* (2002)

One-Dimensional Gas Chromatography



30-year degraded No. 2 diesel fuel,
West Falmouth, MA, USA

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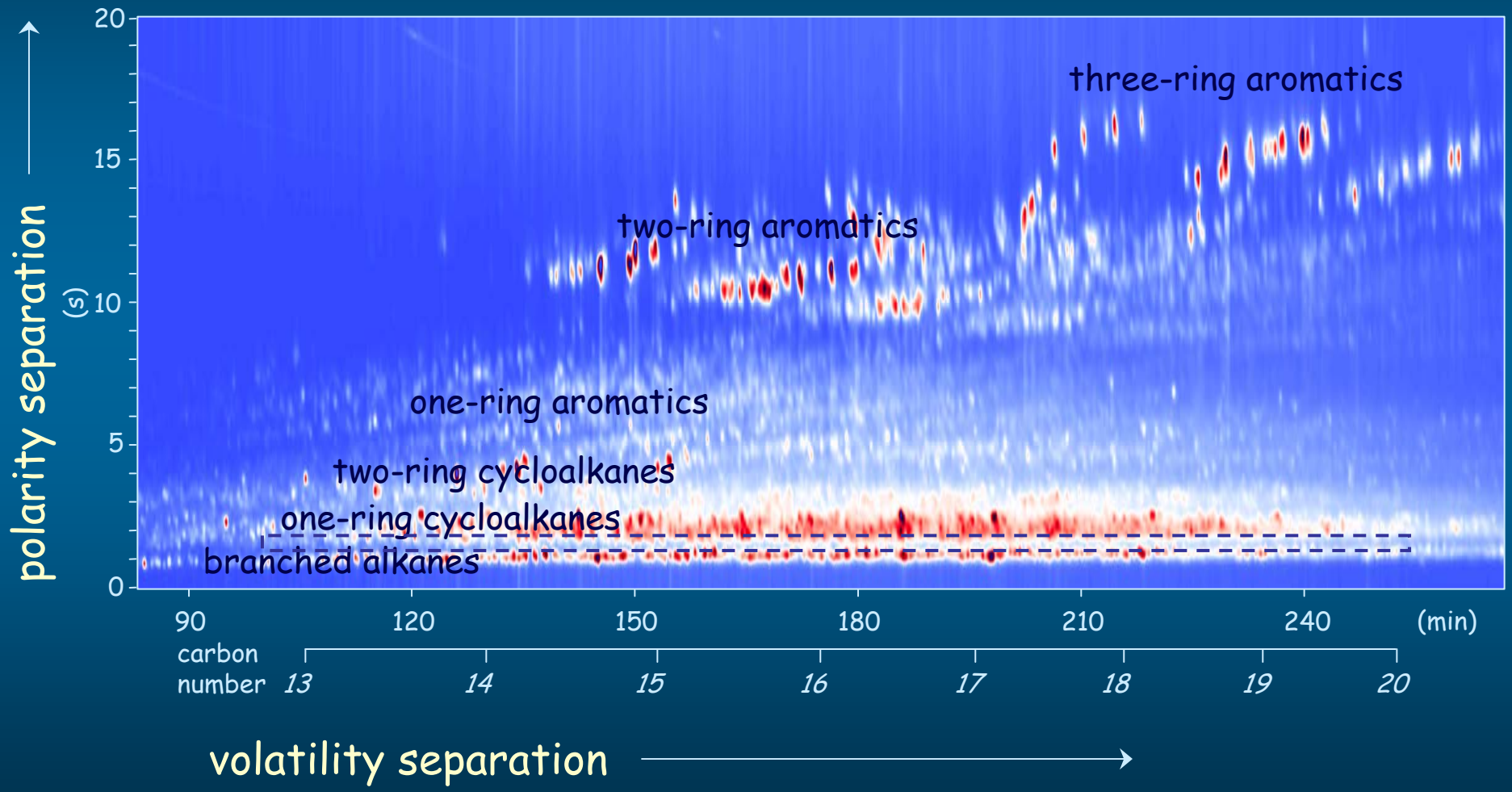
Comprehensive Two-Dimensional Gas Chromatography



30-year degraded No. 2 diesel fuel,
West Falmouth, MA, USA
From Frysinger *et al.* (2003)

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Current research

- Technical NP
  - Column set testing ✓
  - Optimization of best column set ✓
  - Characterization of technical NP….
  - Comparison of technical NP products from different suppliers ✓
- Analysis of field samples: some examples…
  - Cape Cod, MA ground water
  - Oklahoma landfills
  - Municipal wastewater (JWPCP, N. Canadian R.)
  - Degraded tech NP (microcosm expt.-Gabriel *et al.*, 2008)

✓-completed, …-in progress

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