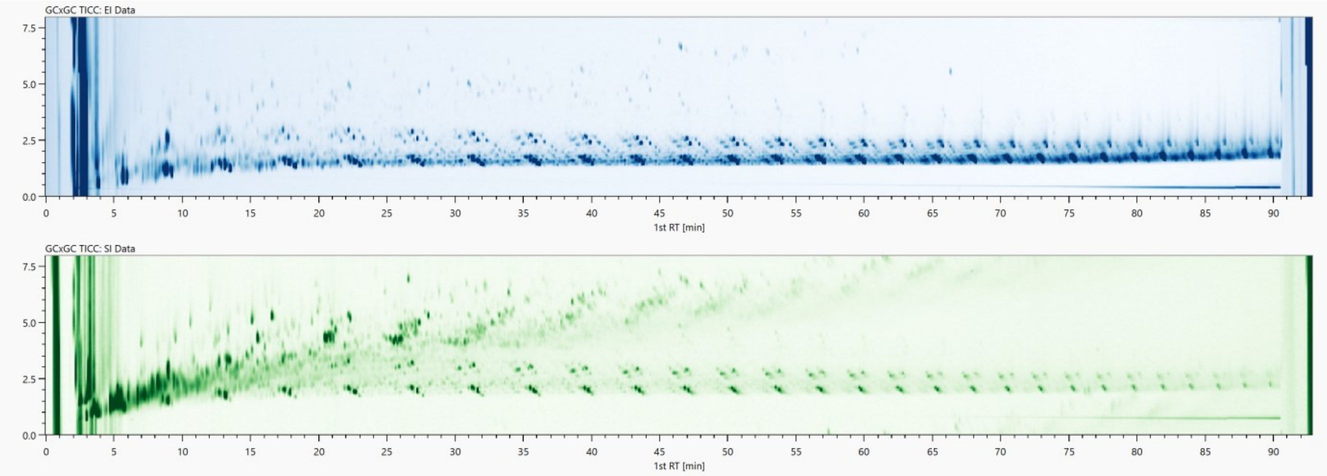



# Pyrolysis and GC×GC-MS. A hot topic!

## MDCW 2025, Liège

Robert (Chip) Cody

# AccuTOF GC-Alpha in our lab

**JEOL accessories**
- EI/CI/PI combination ion source
- EI/FI/FD combination ion source
- Direct insertion probe
- Escrime quantitative analysis software
- msFineAnalysis AI qualitative analysis software

**3rd-party**
- Agilent 8890 GC
- Frontier Lab Multi-shot pyrolyzer
- HTA 2800T autosampler (liquid, headspace, SPME)
- SepSolve thermal modulator for GCxGC-MS

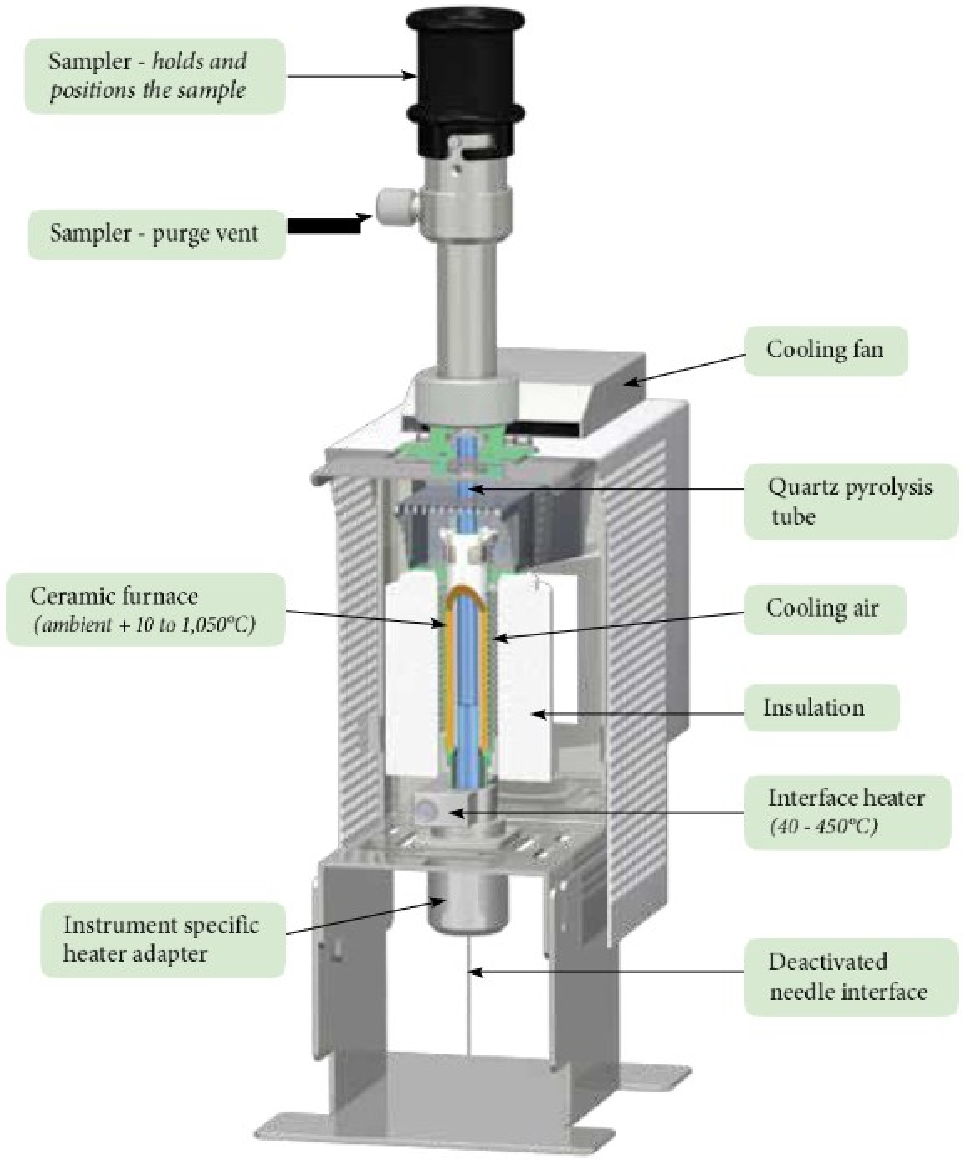
# Software for GCxGC-MS data analysis in our lab

- **ChromSpace (SepSolve)**
  - Primarily used for controlling our SepSolve Insight thermal modulator
  - Looking forward to learning more about capabilities for data analysis
- **AnalyzerPro XD (SpectralWorks)**
  - All-in-one software support for GC-MS, GCxGC-MS, and ambient ionization
  - Open Access through RemoteAnalyzer software
  - Peak detection incorporates deconvolution automatically
  - Best way to compare multiple batches of samples to find differences
- **GC Image (GC Image)**
  - Full-featured GCxGC software
  - Supports accurate-mass data
  - I like the graphic functions for making figures!
- **msFineAnalysis AI (JEOL)**
  - JEOL software for qualitative GC-MS analysis
  - Uses all available information from GC-MS measurements (EI, accurate mass, RI, and soft ionization)
  - **Unknown analysis with AI support and searchable AI-generated 130-million compound database**
  - **<u>Just updated with GCxGC support.</u>**

**Silver Sponsors of this workshop ☺**

# Sample introduction: Frontier Lab Multi-Shot Pyrolyzer (EGA/PY-3030D)

Pyrolysis is the key tool for qualitative polymer analysis by GC-MS and GCxGC-MS


- Furnace-based system
- Thermal desorption
- Pyrolysis
- Evolved gas analysis

# "Biodegradeable" plastic bag purchased online

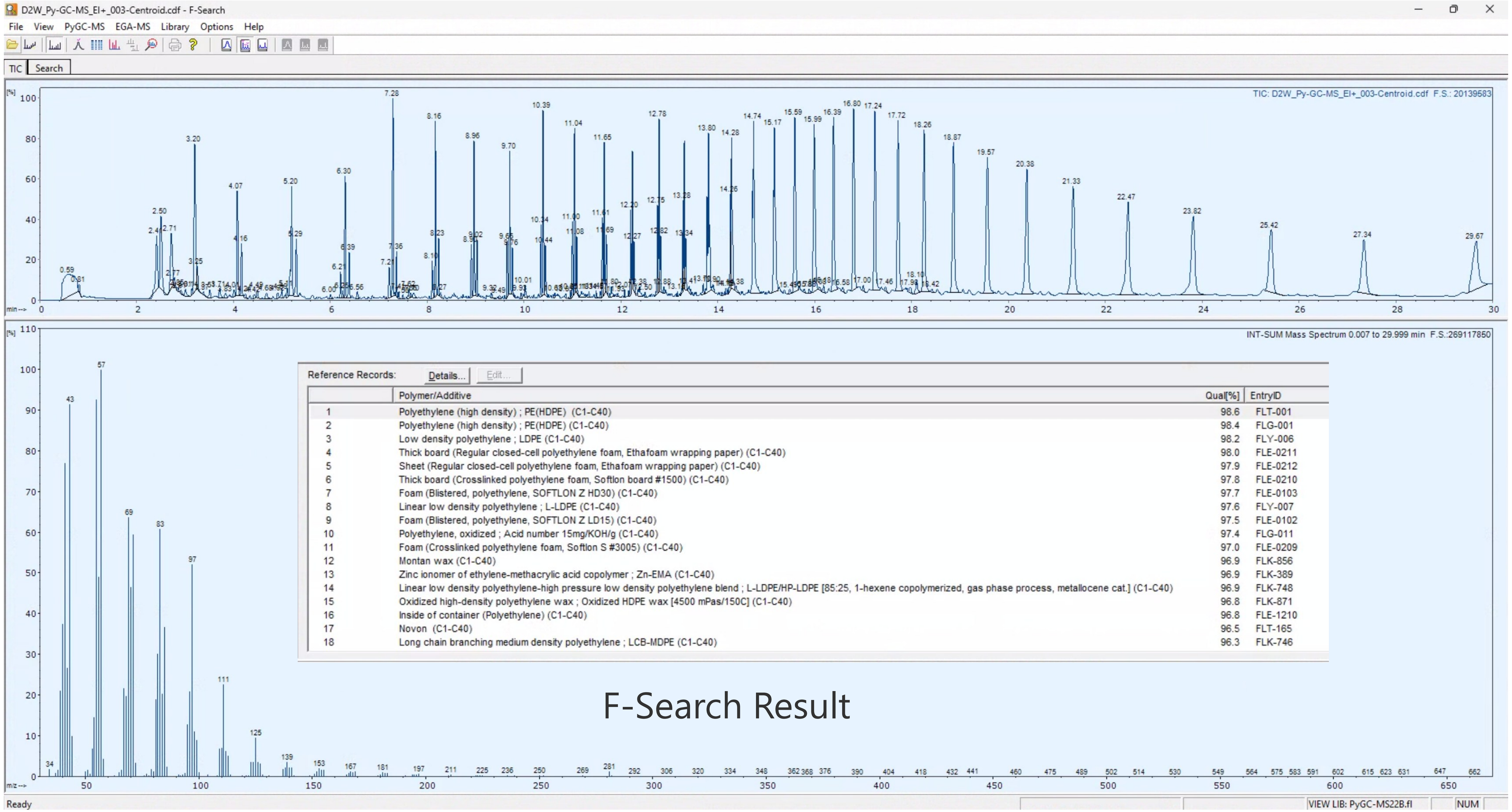
Inconsistent claims!


- Product description says that the bags are made from polylactic acid (PLA)
- Product description refers to ASTM standard D5511 "Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions"
- Label refers to a different ASTM standard: D6954-0 "Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation"

**About this item**

- Natural Materials: Our bags are constructed from PLA, which is made of 100% plant based resources like cornstarch. This also means our t shirt bag is BPA-free.
- Certified: Tested and proven to comply with the ASTM D5511 requirements for composting. Commercially compostable only*.

# The bags are not PLA: they're polyethylene!

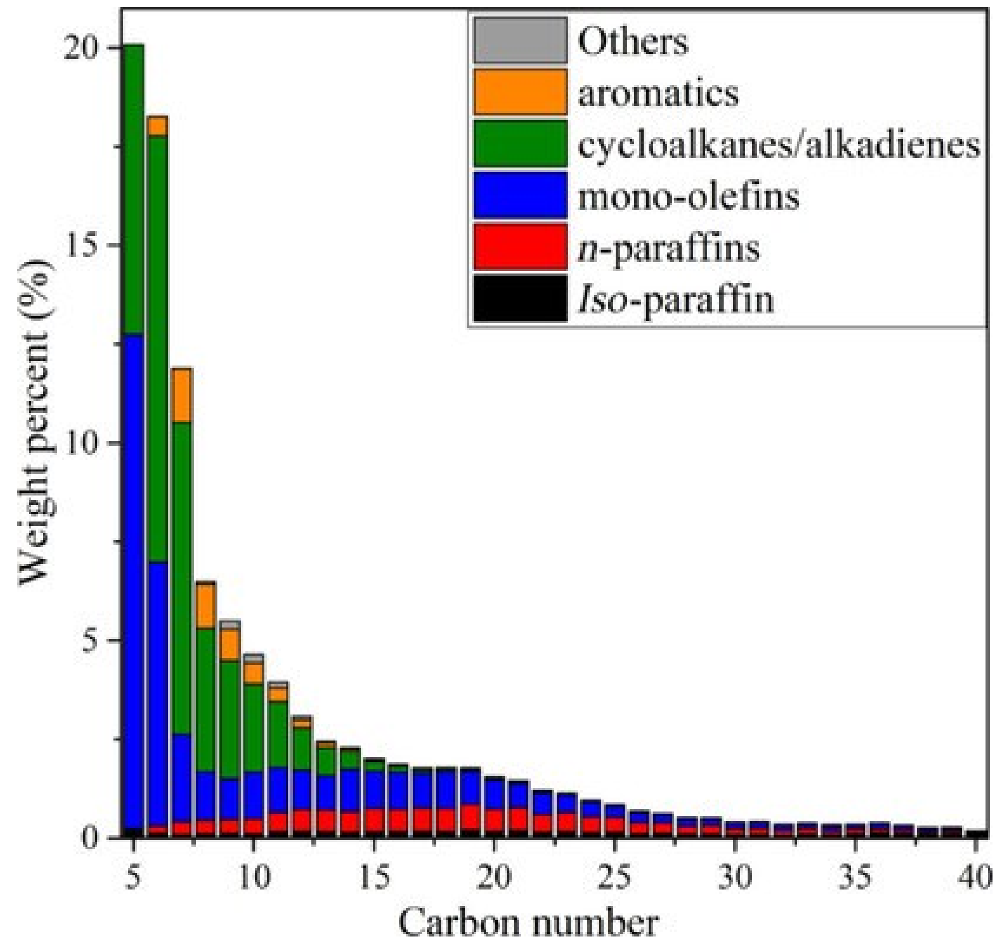



| | Polymer/Additive | Qual[%] | EntryID |
|---|---|---|---|
| 1 | Polyethylene (high density) ; PE(HDPE) (C1-C40) | 98.6 | FLT-001 |
| 2 | Polyethylene (high density) ; PE(HDPE) (C1-C40) | 98.4 | FLG-001 |
| 3 | Low density polyethylene ; LDPE (C1-C40) | 98.2 | FLY-006 |
| 4 | Thick board (Regular closed-cell polyethylene foam, Ethafoam wrapping paper) (C1-C40) | 98.0 | FLE-0211 |
| 5 | Sheet (Regular closed-cell polyethylene foam, Ethafoam wrapping paper) (C1-C40) | 97.9 | FLE-0212 |
| 6 | Thick board (Crosslinked polyethylene foam, Softlon board #1500) (C1-C40) | 97.8 | FLE-0210 |
| 7 | Foam (Blistered, polyethylene, SOFTLON Z HD30) (C1-C40) | 97.7 | FLE-0103 |
| 8 | Linear low density polyethylene ; L-LDPE (C1-C40) | 97.6 | FLY-007 |
| 9 | Foam (Blistered, polyethylene, SOFTLON Z LD15) (C1-C40) | 97.5 | FLE-0102 |
| 10 | Polyethylene, oxidized ; Acid number 15mg/KOH/g (C1-C40) | 97.4 | FLG-011 |
| 11 | Foam (Crosslinked polyethylene foam, Softlon S #3005) (C1-C40) | 97.0 | FLE-0209 |
| 12 | Montan wax (C1-C40) | 96.9 | FLK-856 |
| 13 | Zinc ionomer of ethylene-methacrylic acid copolymer ; Zn-EMA (C1-C40) | 96.9 | FLK-389 |
| 14 | Linear low density polyethylene-high pressure low density polyethylene blend ; L-LDPE/HP-LDPE [85:25, 1-hexene copolymerized, gas phase process, metallocene cat.] (C1-C40) | 96.9 | FLK-748 |
| 15 | Oxidized high-density polyethylene wax ; Oxidized HDPE wax [4500 mPas/150C] (C1-C40) | 96.8 | FLK-871 |
| 16 | Inside of container (Polyethylene) (C1-C40) | 96.8 | FLE-1210 |
| 17 | Novon (C1-C40) | 96.5 | FLT-165 |
| 18 | Long chain branching medium density polyethylene ; LCB-MDPE (C1-C40) | 96.3 | FLK-746 |

F-Search Result

# Oxidation and degradation of polyethylene?

**Degradation and pyrolysis of polyethylene is a topic of interest for recycling plastics.**




Zhao, D., Wang, X., Miller, J.B., Huber, G.W.: The Chemistry and Kinetics of Polyethylene Pyrolysis: A Process to Produce Fuels and Chemicals. ChemSusChem. **13, 1764-1774 (2020)**

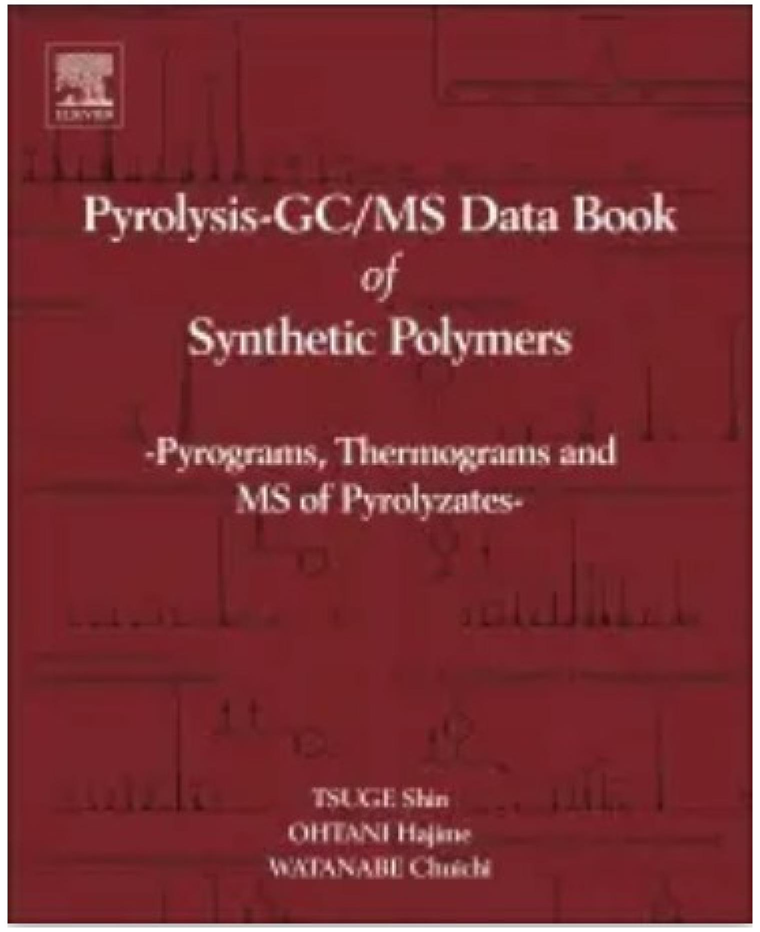
GC x GC-HRTOFMS can

- Monitor pyrolysis reactions on a small scale
- Characterize the products of pilot-plant pyrolysis

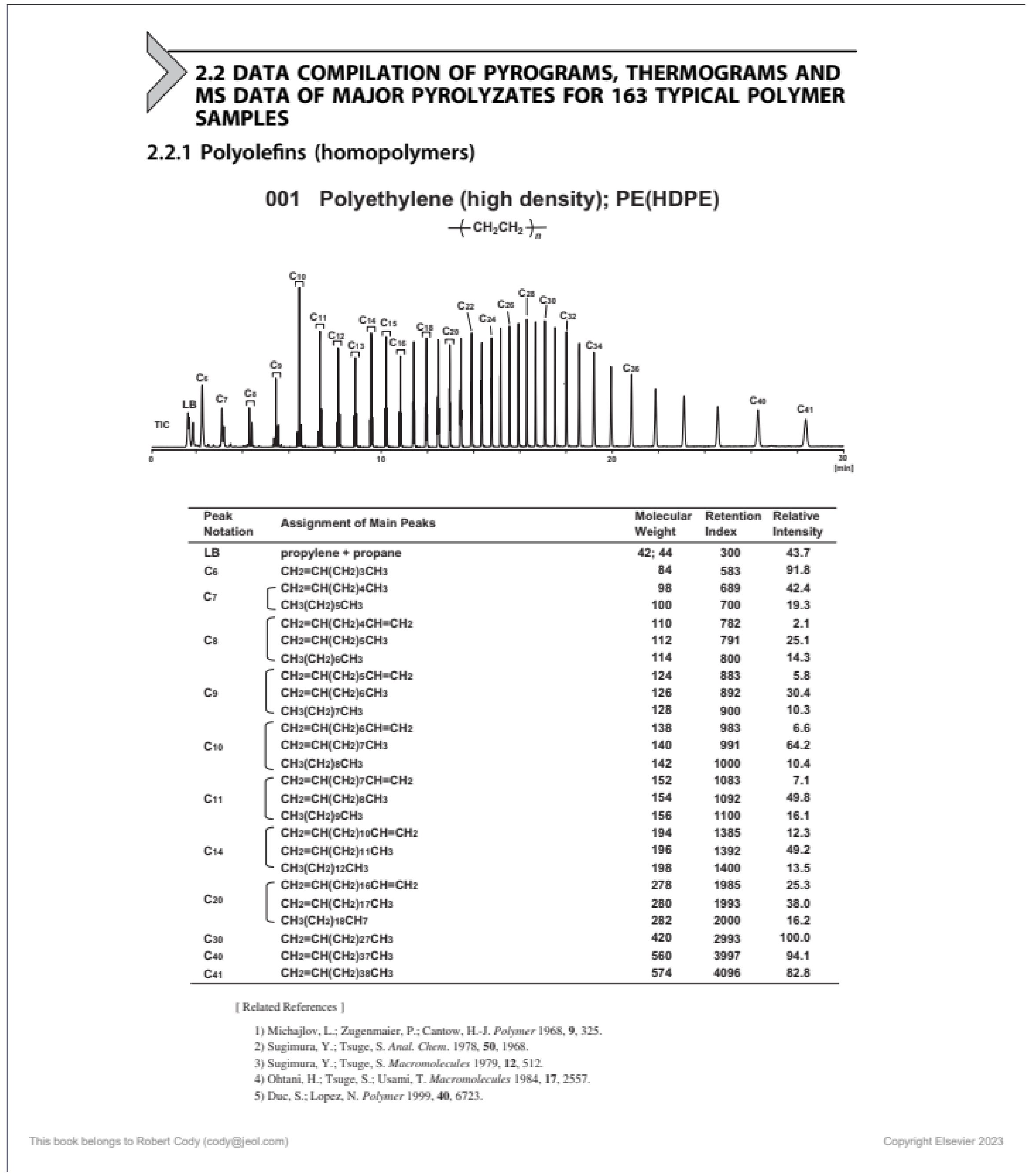
Important tools for this application:

- High-resolution MS
- Soft ionization (FI, PI, CI)

# Let’s look deeper at pyrolysis GC-MS for polyethylene




ISBN: 978-0-444-53892-5



**2.2 DATA COMPILATION OF PYROGRAMS, THERMOGRAMS AND MS DATA OF MAJOR PYROLYZATES FOR 163 TYPICAL POLYMER SAMPLES**

**2.2.1 Polyolefins (homopolymers)**

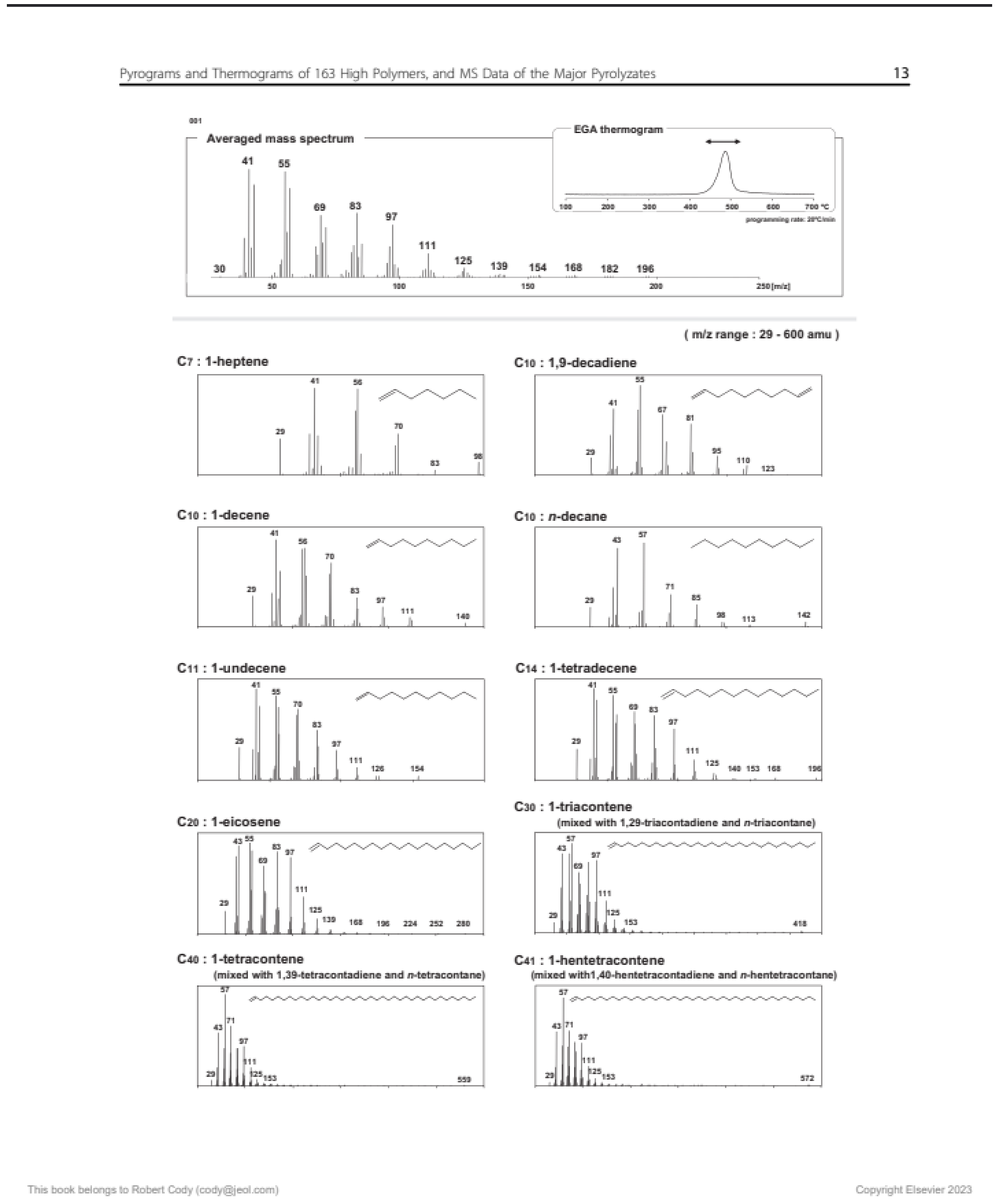
**001 Polyethylene (high density); PE(HDPE)**

| Peak Notation | Assignment of Main Peaks | Molecular Weight | Retention Index | Relative Intensity |
|---|---|---|---|---|
| LB | propylene + propane | 42; 44 | 300 | 43.7 |
| $C_6$ | $CH_2=CH(CH_2)_3CH_3$ | 84 | 583 | 91.8 |
| $C_7$ | $CH_2=CH(CH_2)_4CH_3$ | 98 | 689 | 42.4 |
| | $CH_3(CH_2)_5CH_3$ | 100 | 700 | 19.3 |
| $C_8$ | $CH_2=CH(CH_2)_4CH=CH_2$ | 110 | 782 | 2.1 |
| | $CH_2=CH(CH_2)_5CH_3$ | 112 | 791 | 25.1 |
| | $CH_3(CH_2)_6CH_3$ | 114 | 800 | 14.3 |
| $C_9$ | $CH_2=CH(CH_2)_5CH=CH_2$ | 124 | 883 | 5.8 |
| | $CH_2=CH(CH_2)_6CH_3$ | 126 | 892 | 30.4 |
| | $CH_3(CH_2)_7CH_3$ | 128 | 900 | 10.3 |
| $C_{10}$ | $CH_2=CH(CH_2)_6CH=CH_2$ | 138 | 983 | 6.6 |
| | $CH_2=CH(CH_2)_7CH_3$ | 140 | 991 | 64.2 |
| | $CH_3(CH_2)_8CH_3$ | 142 | 1000 | 10.4 |
| $C_{11}$ | $CH_2=CH(CH_2)_7CH=CH_2$ | 152 | 1083 | 7.1 |
| | $CH_2=CH(CH_2)_8CH_3$ | 154 | 1092 | 49.8 |
| | $CH_3(CH_2)_9CH_3$ | 156 | 1100 | 16.1 |
| $C_{14}$ | $CH_2=CH(CH_2)_{10}CH=CH_2$ | 194 | 1385 | 12.3 |
| | $CH_2=CH(CH_2)_{11}CH_3$ | 196 | 1392 | 49.2 |
| | $CH_3(CH_2)_{12}CH_3$ | 198 | 1400 | 13.5 |
| $C_{20}$ | $CH_2=CH(CH_2)_{16}CH=CH_2$ | 278 | 1985 | 25.3 |
| | $CH_2=CH(CH_2)_{17}CH_3$ | 280 | 1993 | 38.0 |
| | $CH_3(CH_2)_{18}CH_7$ | 282 | 2000 | 16.2 |
| $C_{30}$ | $CH_2=CH(CH_2)_{27}CH_3$ | 420 | 2993 | 100.0 |
| $C_{40}$ | $CH_2=CH(CH_2)_{37}CH_3$ | 560 | 3997 | 94.1 |
| $C_{41}$ | $CH_2=CH(CH_2)_{38}CH_3$ | 574 | 4096 | 82.8 |

[ Related References ]

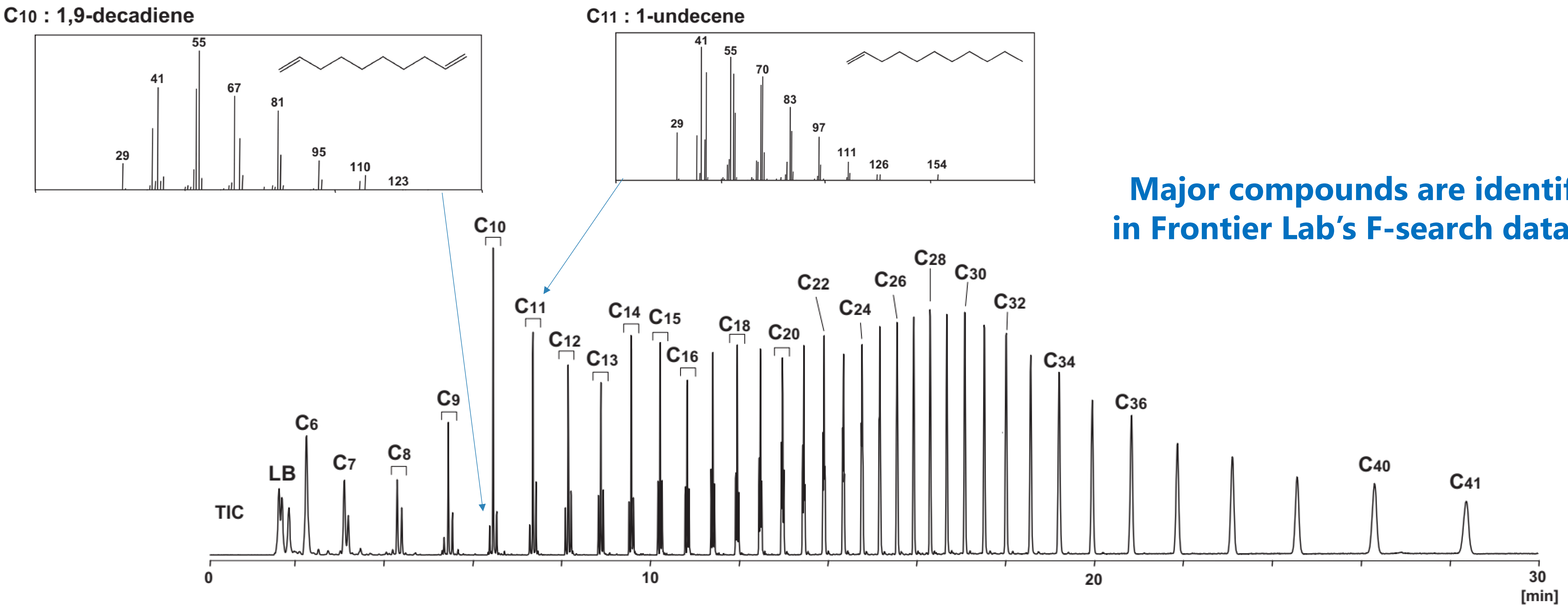

1) Michajlov, L.; Zugenmaier, P.; Cantow, H.-J. *Polymer* 1968, **9**, 325.
2) Sugimura, Y.; Tsuge, S. *Anal. Chem.* 1978, **50**, 1968.
3) Sugimura, Y.; Tsuge, S. *Macromolecules* 1979, **12**, 512.
4) Ohtani, H.; Tsuge, S.; Usami, T. *Macromolecules* 1984, **17**, 2557.
5) Duc, S.; Lopez, N. *Polymer* 1999, **40**, 6723.



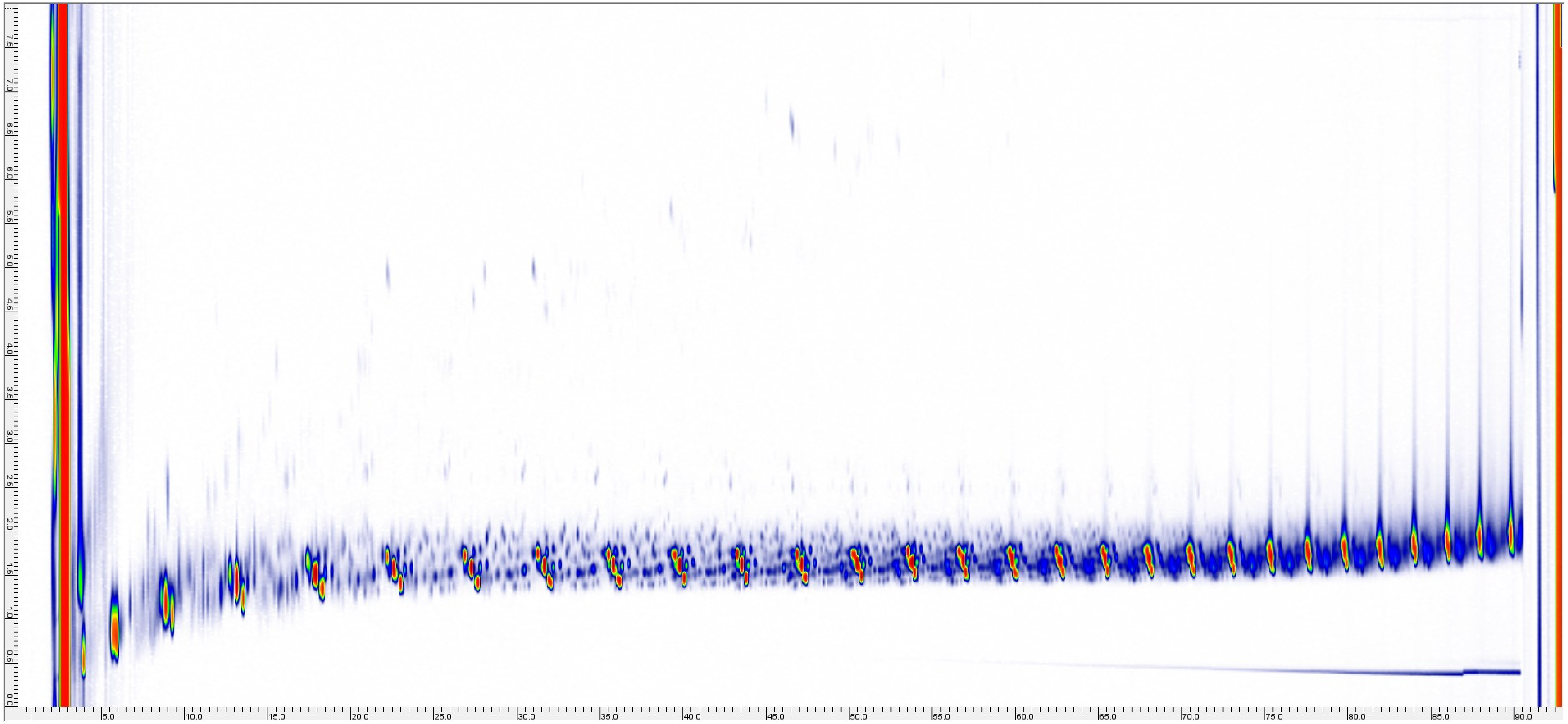

Here’s the reference book entry for pyrolysis 1D GC-MS of polyethylene

# Py HDPE chromatogram from the Pyrolysis GC/MS Data Book

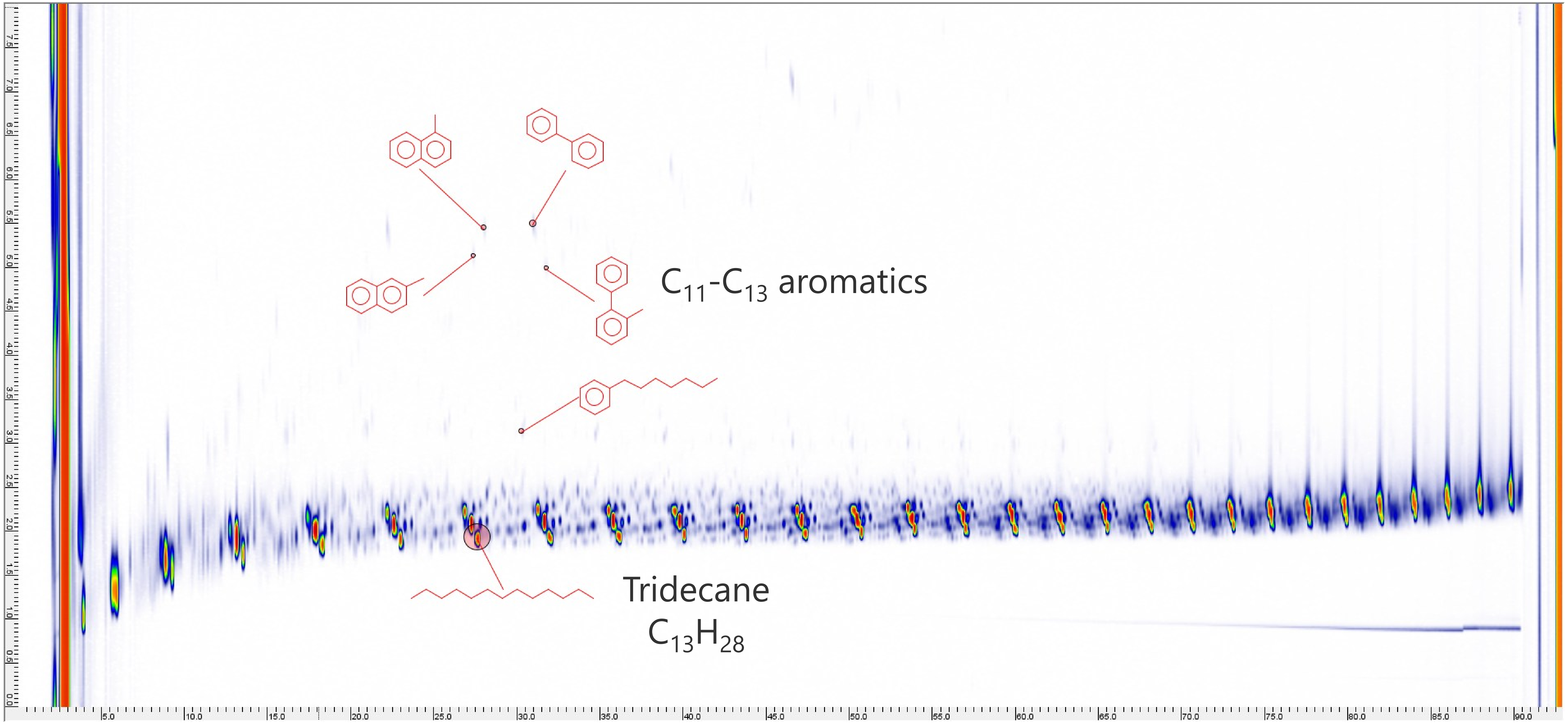



**Major compounds are identified in Frontier Lab's F-search database**

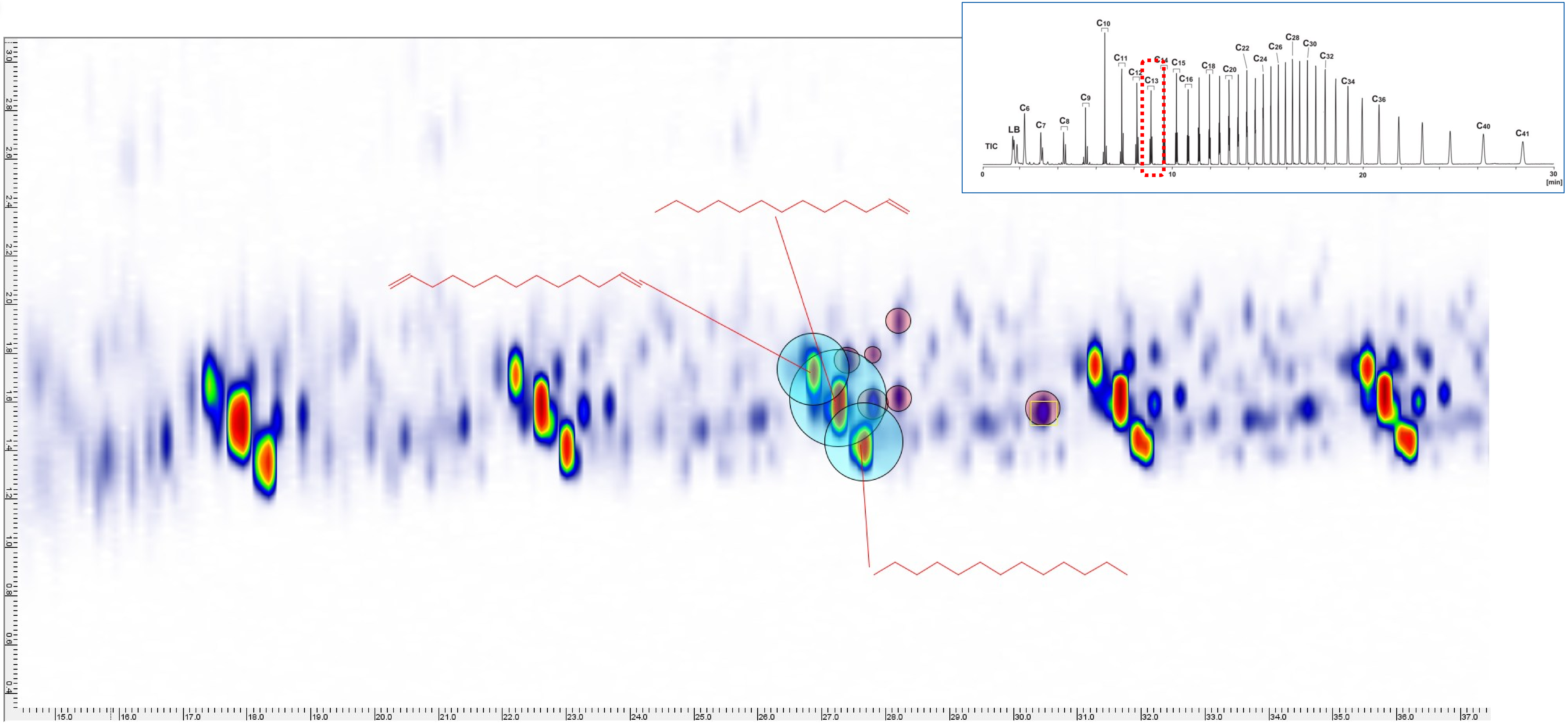
# Pyrolysis GCxGC-TOFMS for LDPE shows many more compounds



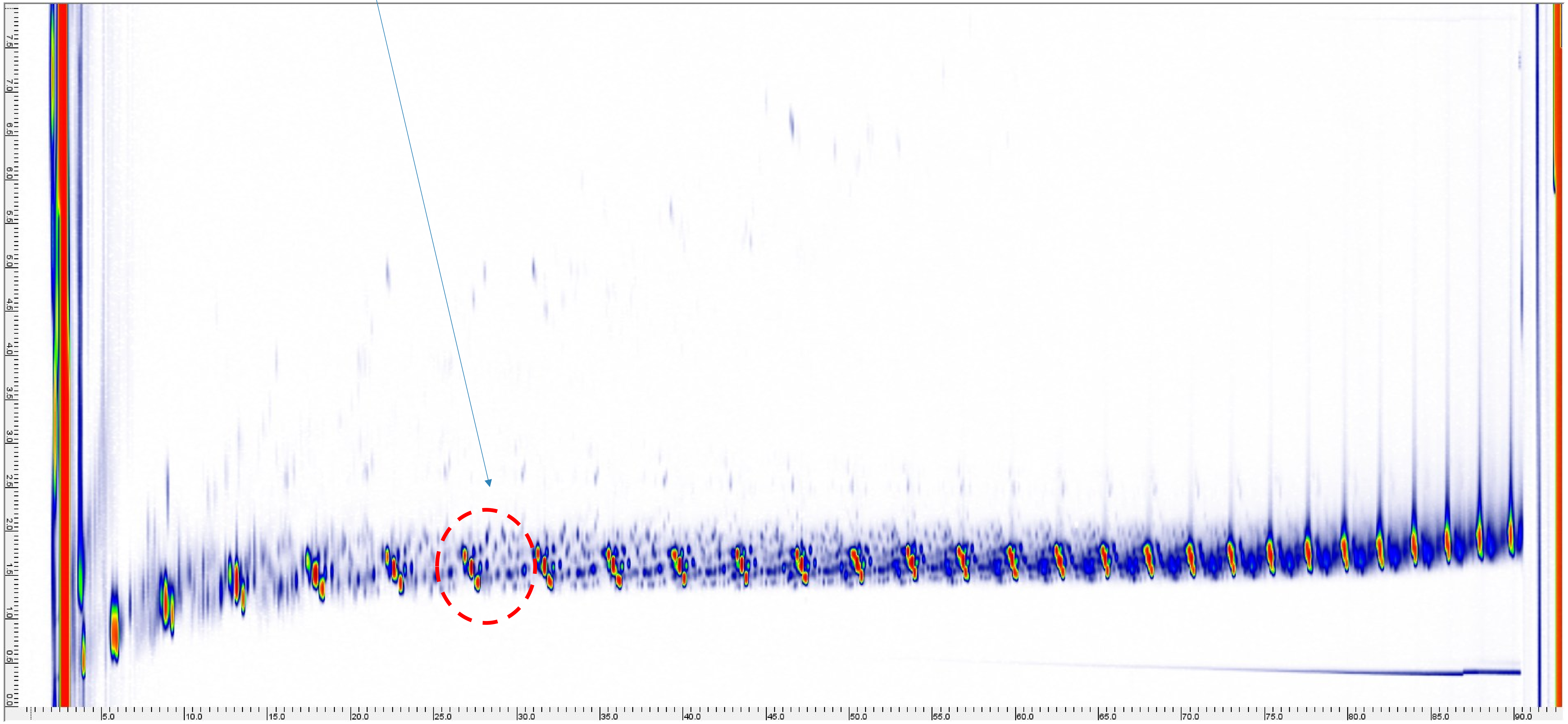
# Assignments for selected blobs



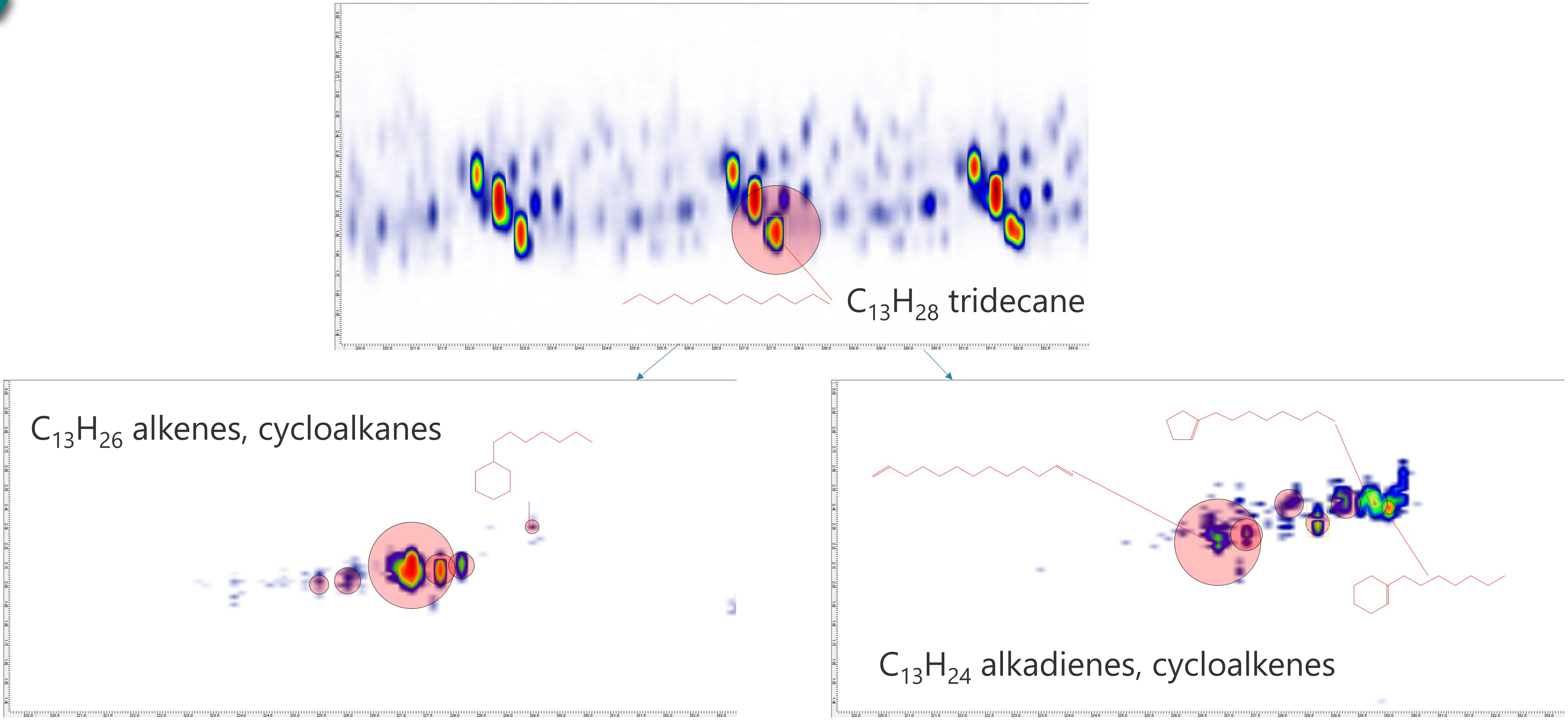
# Tridecane, 1-tridecane, and 1,12-tridecadiene



# Zoom in on this region

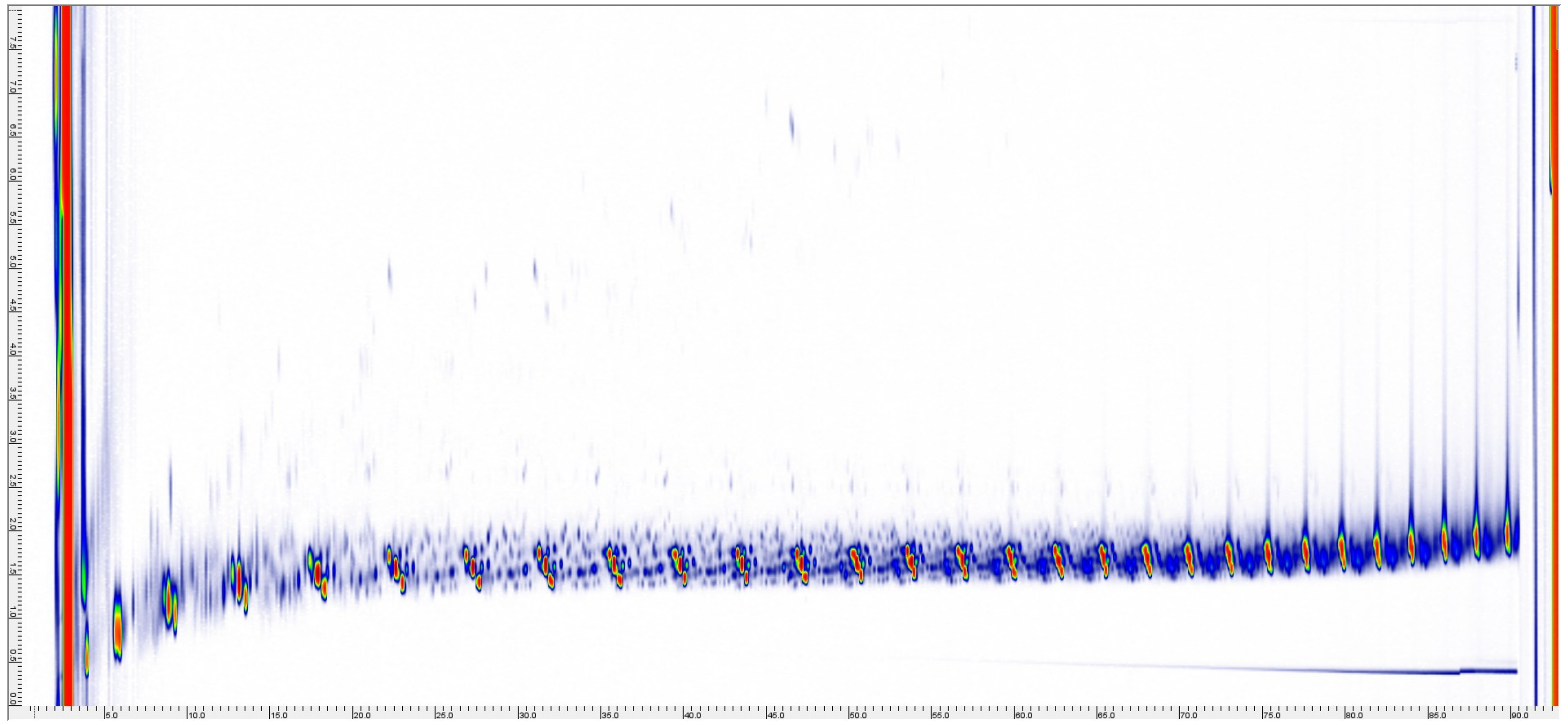


# $C_{13}$ $H_{2n-x}$ components in this region

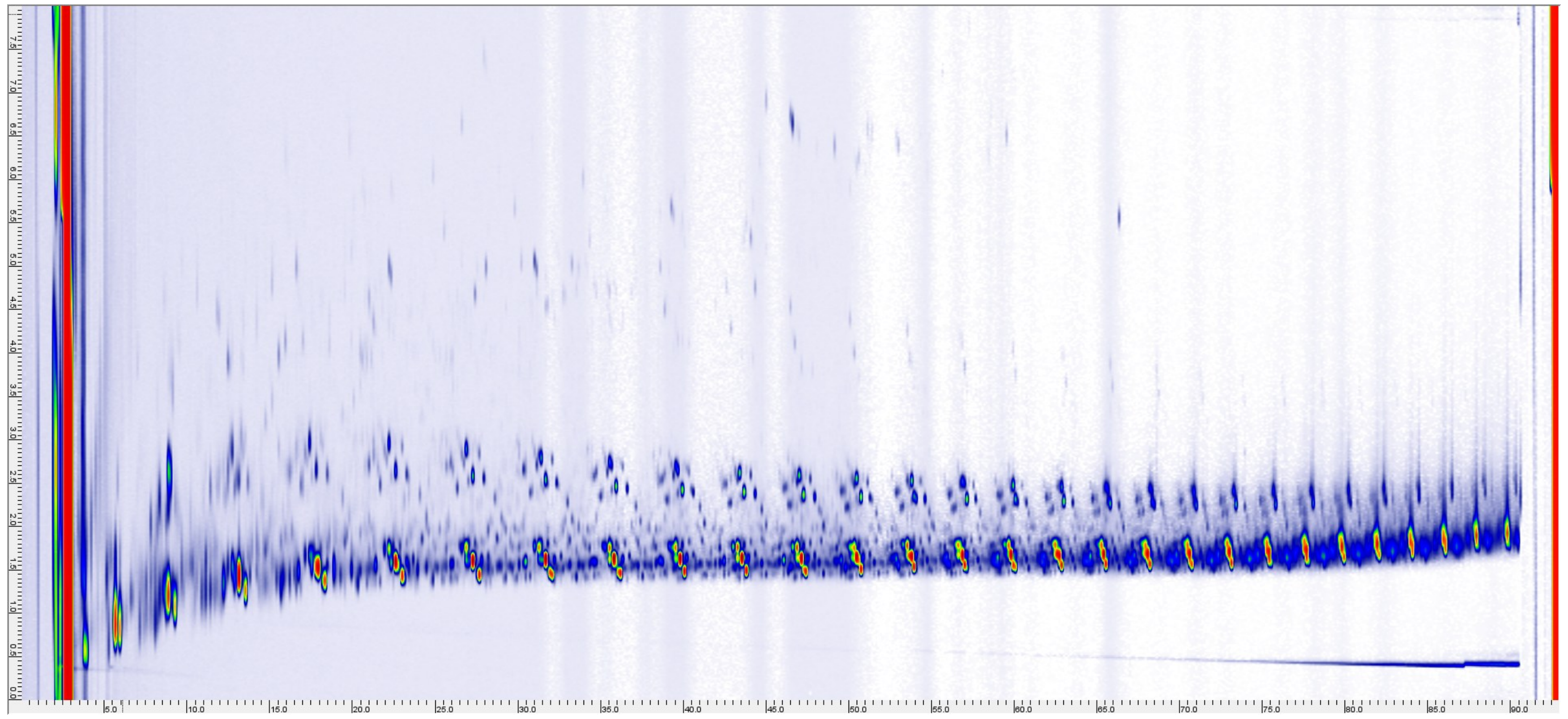


# How does oxidation change LDPE?

Low-density polyethylene (LDPE)

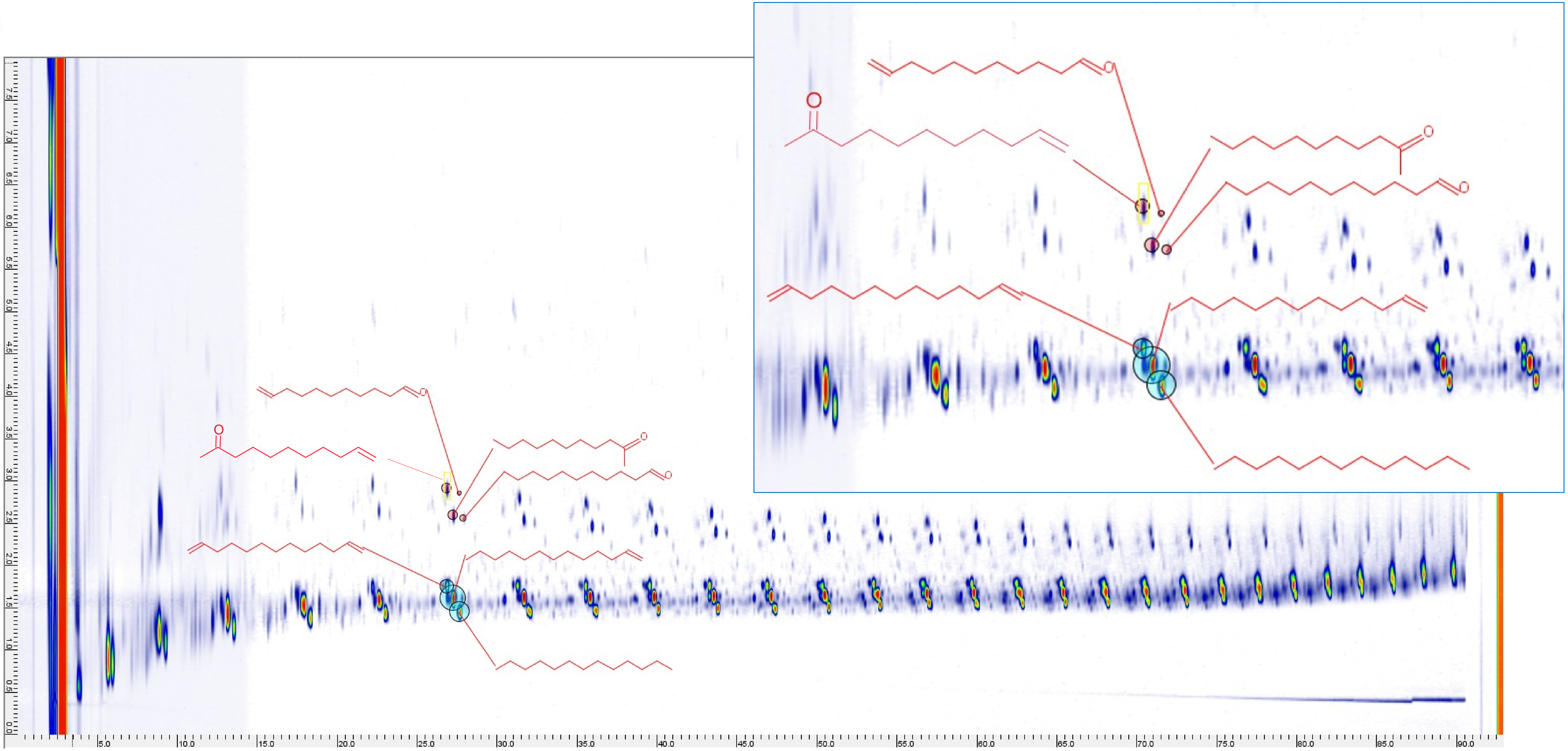


Polyethylene (oxidized)

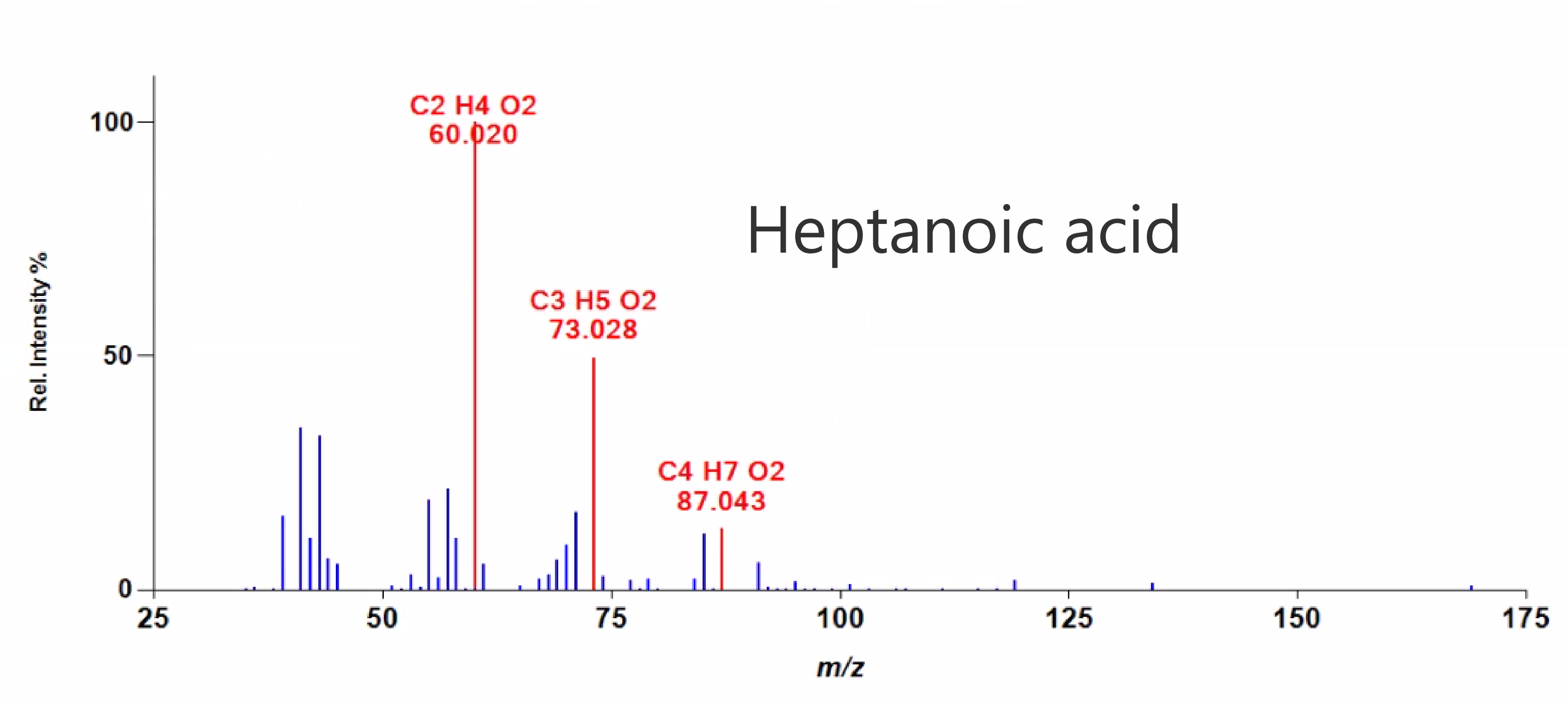


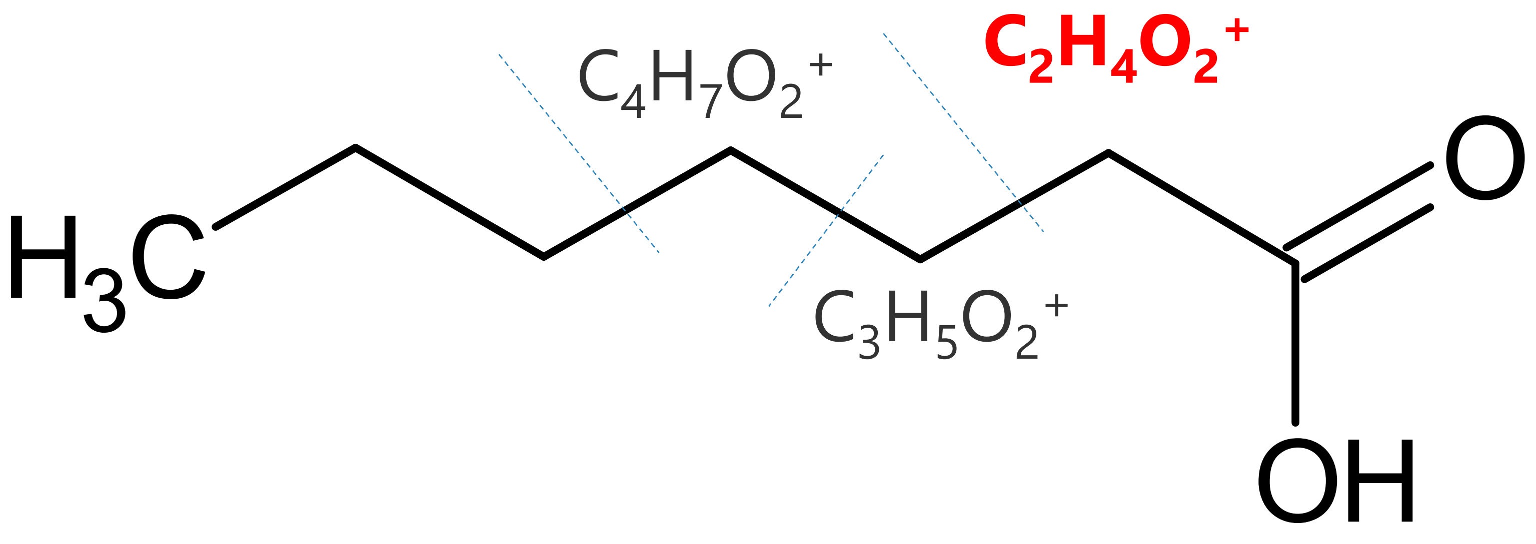
Scientific Polymer Products
Acid number 16 mg KOH/g

# Oxidized PE: ketones and aldehydes



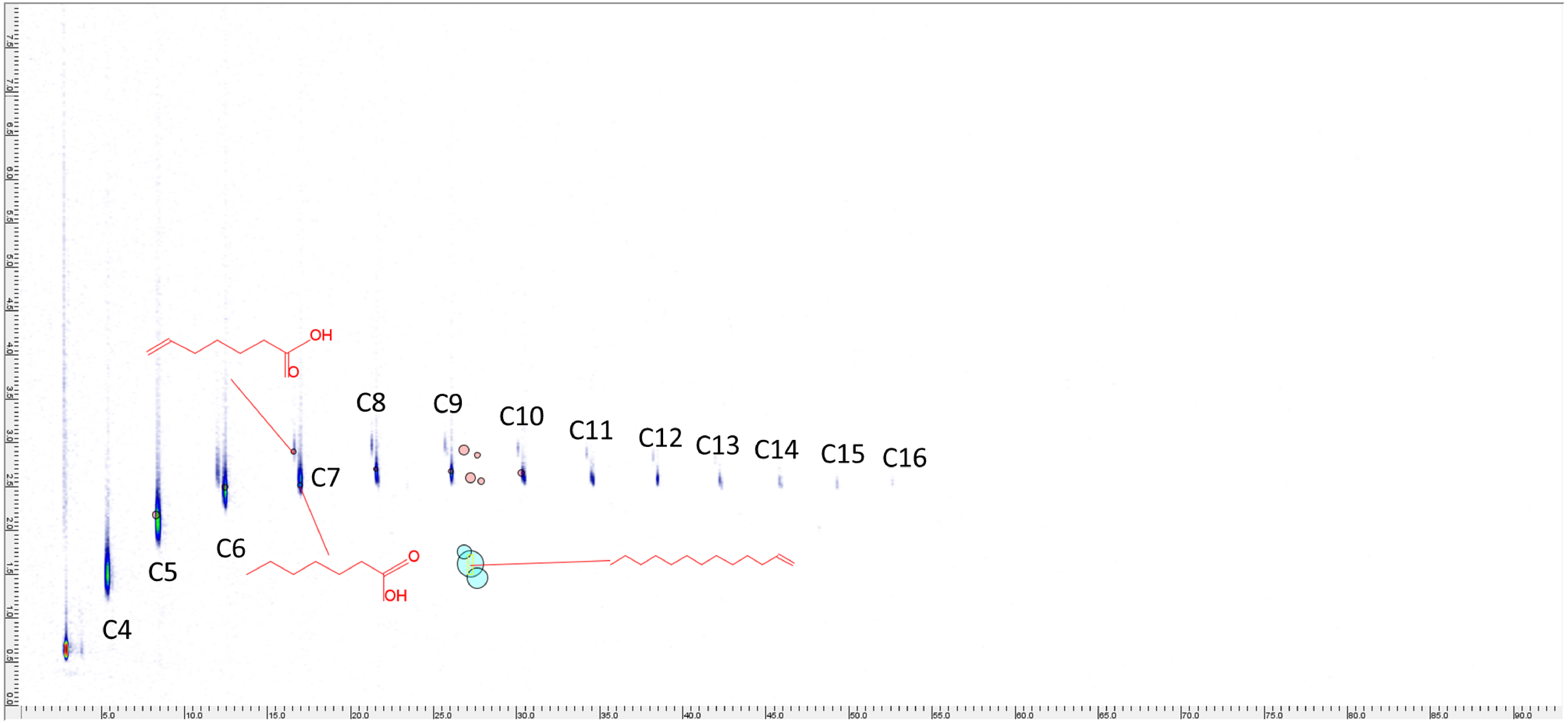
# Oxidized PE waxes are characterized by their acid number



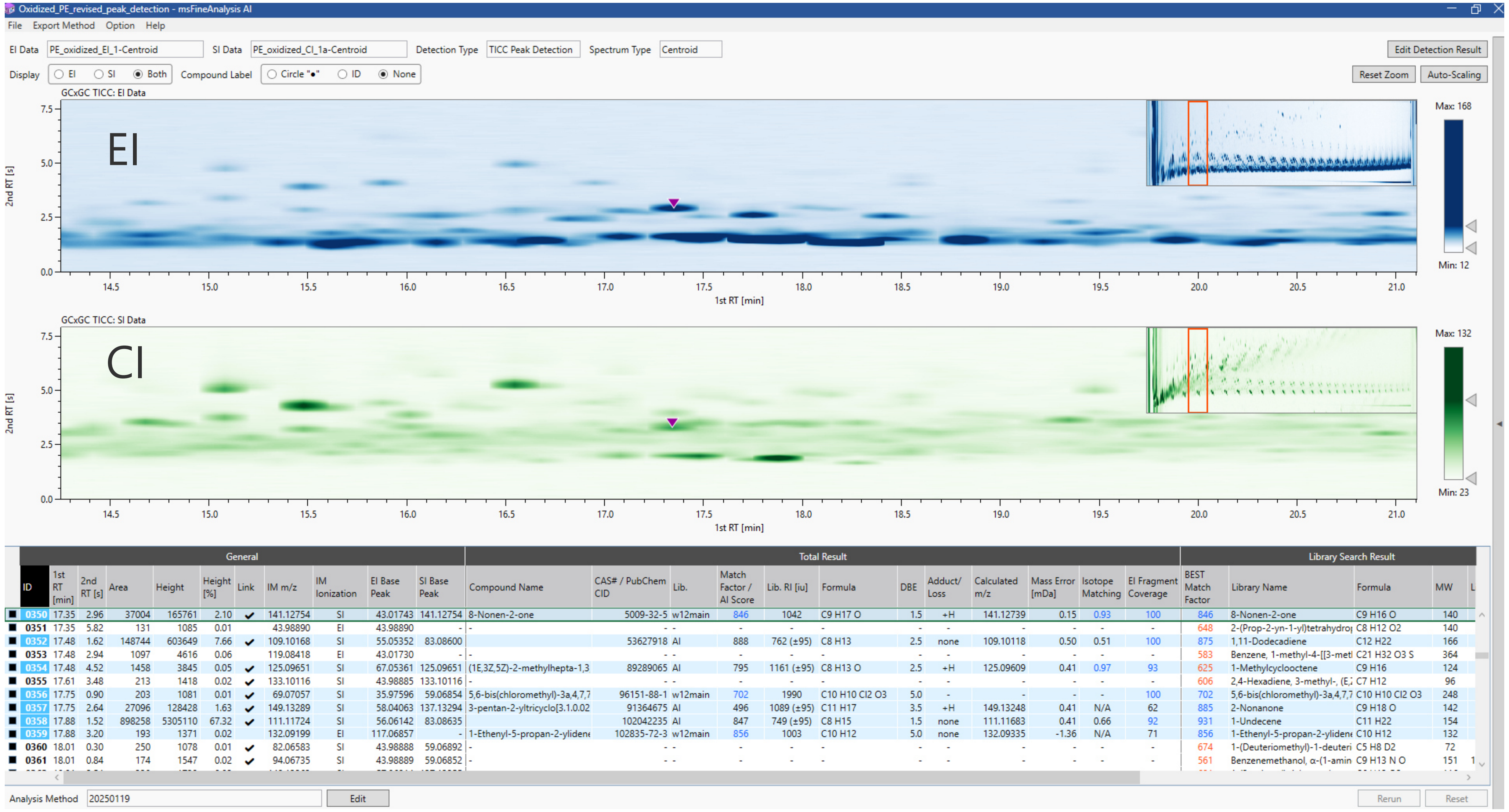

- The acid number relates to how oxidized PE waxes can form emulsions for coating agents and/or perform as lubricants.
- Determined by titration: This sample has an acid number of 16 mg KOH/g
- Carboxylic acids in the GCxGC-MS data are minor peaks in the TICC, but they can be identified by creating SICC's for the characteristic fragments in their EI mass spectra.
- Electron-capture negative-ion mass spectra would also identify the acids

# Carboxylic acids in the oxidized PE: SICC for $C_2H_4O_2^+$ fragment



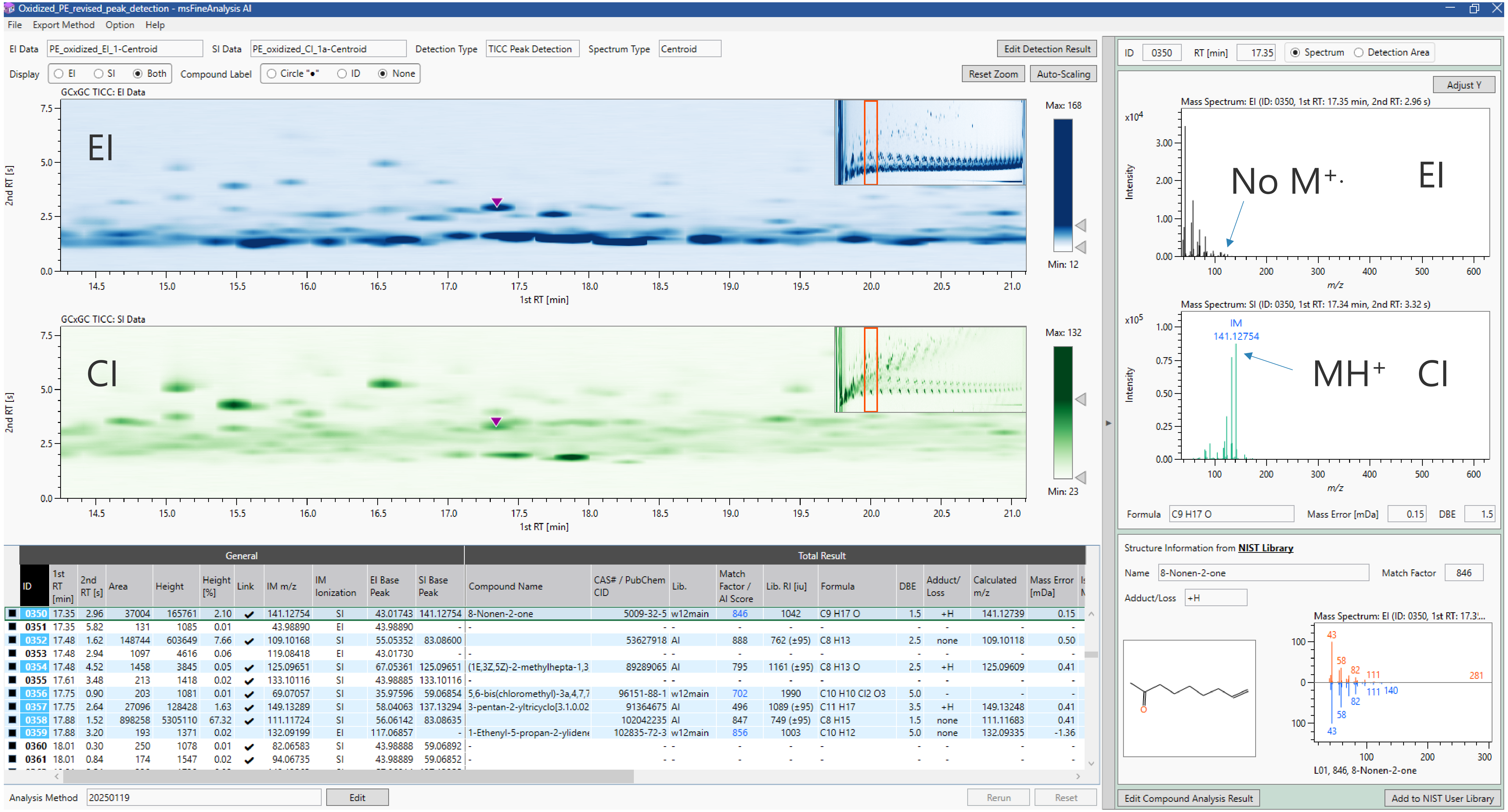
# New: msFineAnalysis AI adds support for GCxGC data

## Oxidized Polyethylene

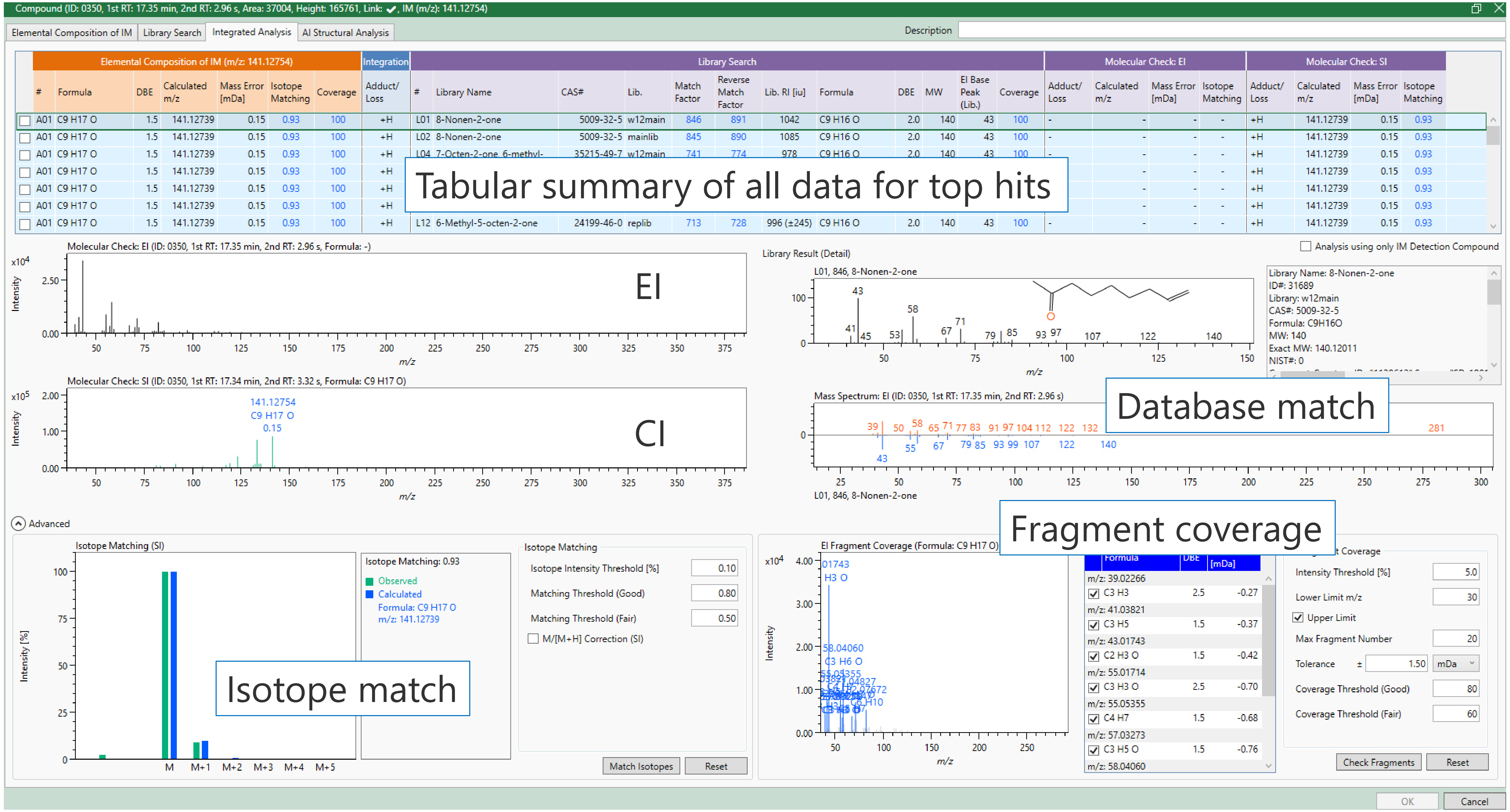



- Correlates EI and SI data
- Integrates all information
  - Elemental composition
  - Isotope match
  - Database search
  - Fragment coverage
  - RI matching
- AI database including pyrolysates
- Higher confidence in assignments

# 8-Nonene-2-one identification.

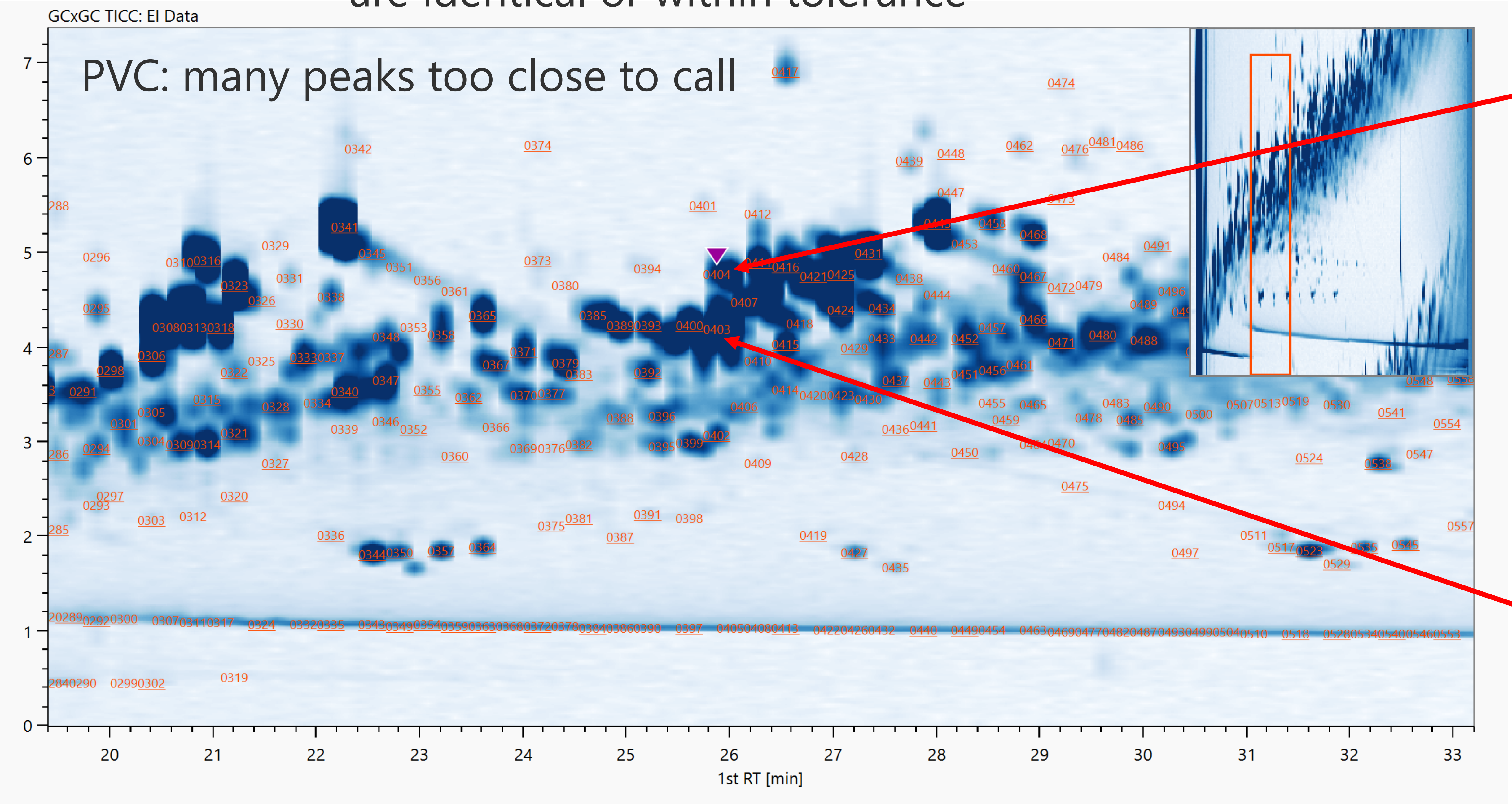


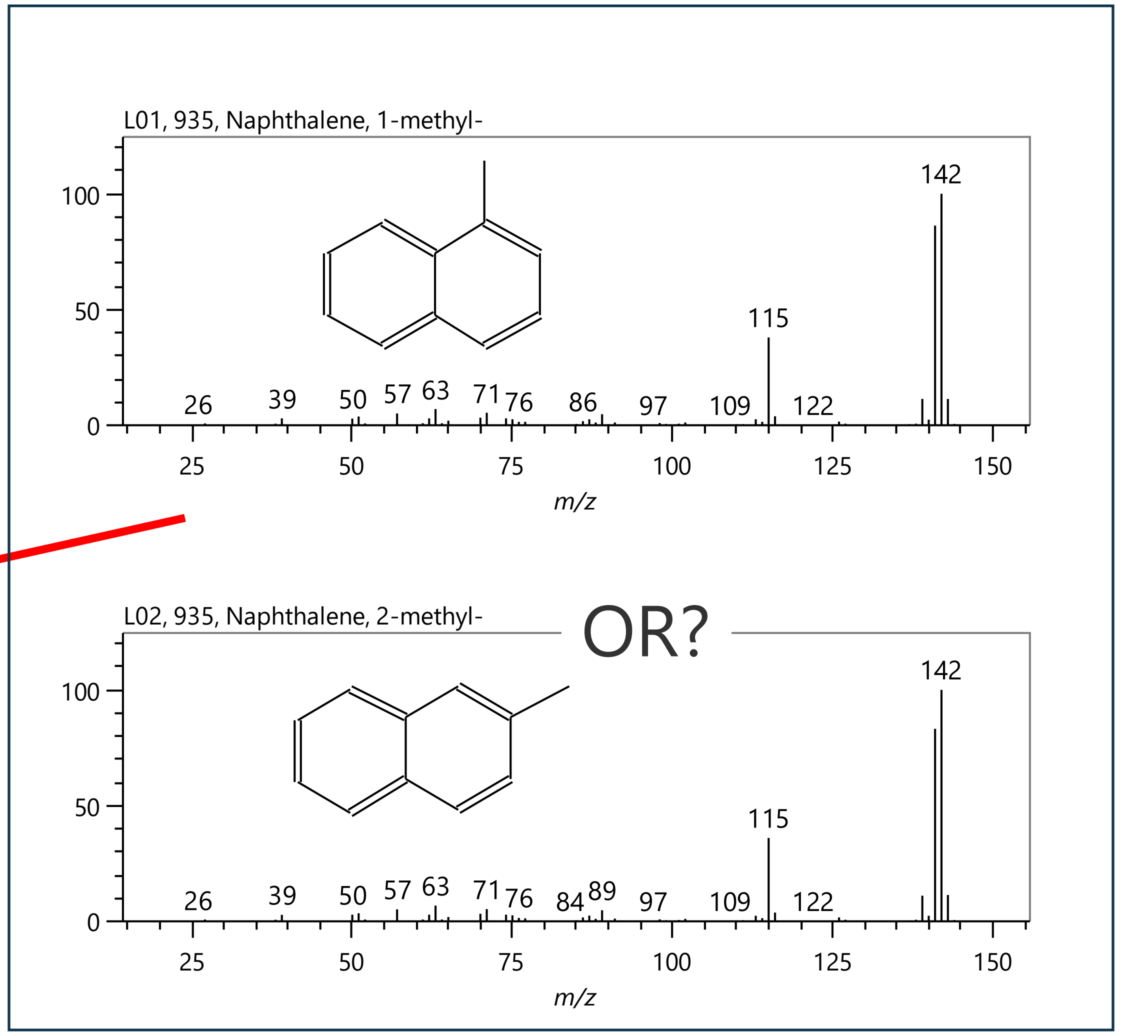
# Integrated Analysis tab

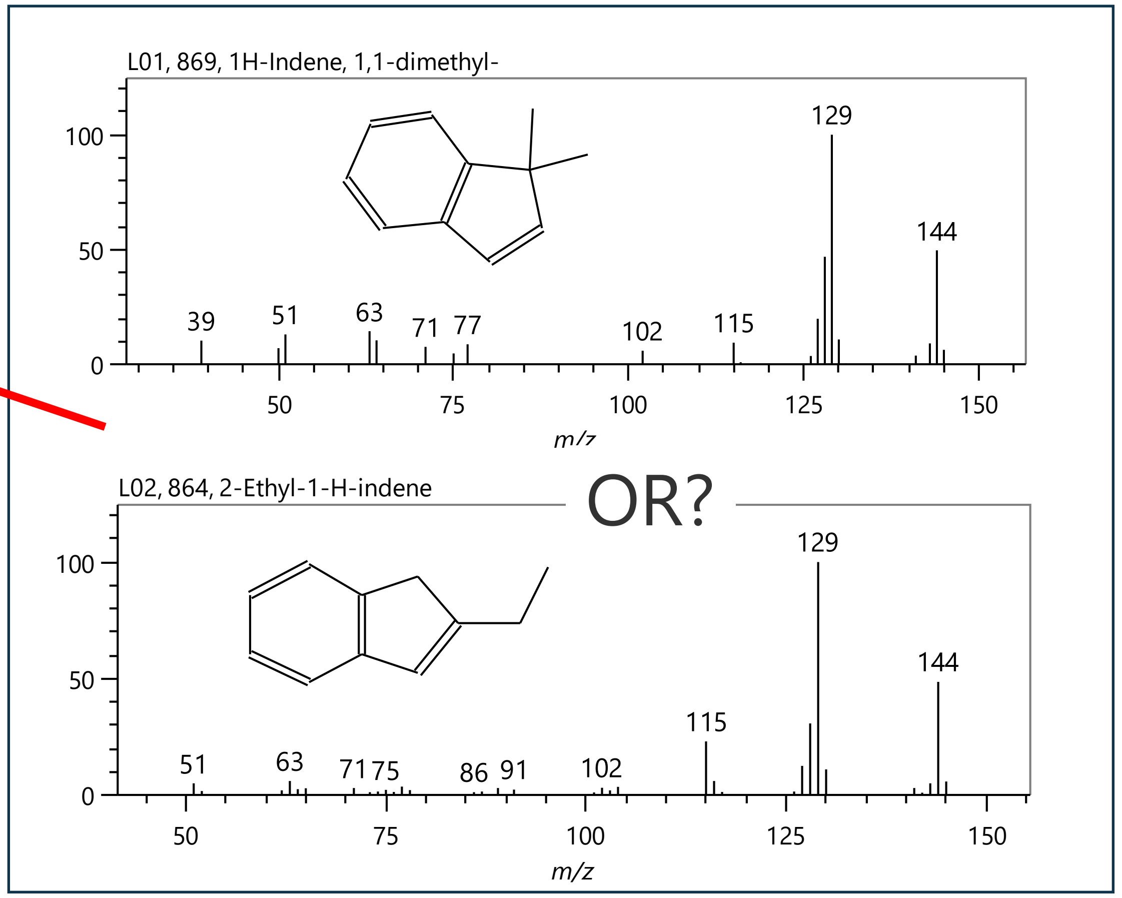


# A parting thought…

GCxGC separation OK, but RI’s and match factors are identical or within tolerance




It’s unlikely that we’ll ever ID every peak with 100% confidence, but we can get an idea of reasonable compositions.