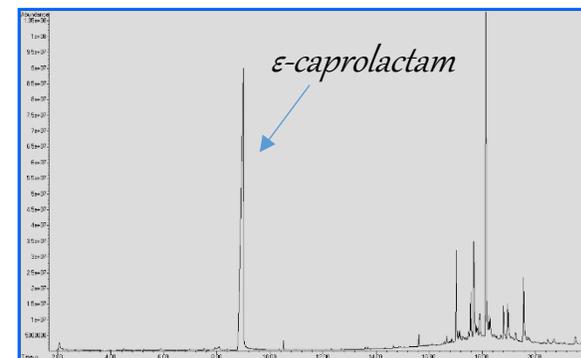
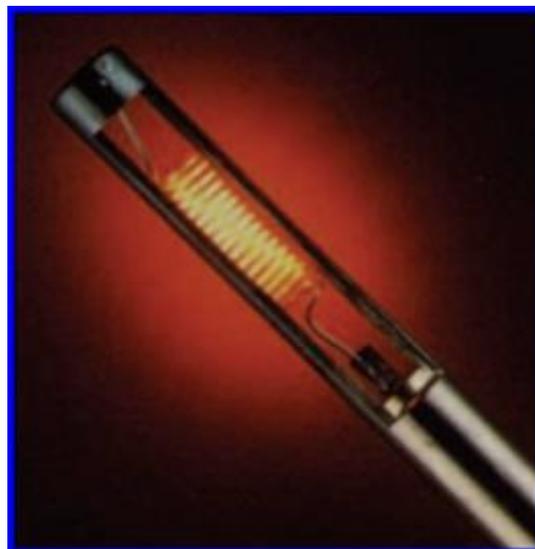


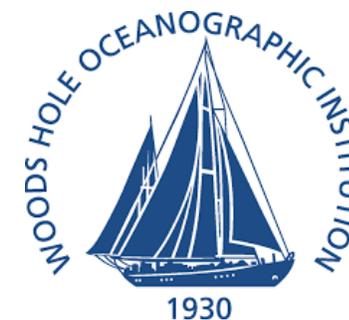
# Polymer Quest Using Pyrolysis GC-MS

Ashok Deshpande  
Research Chemist

NOAA-NMFS-NEFSC, Sandy Hook, New Jersey

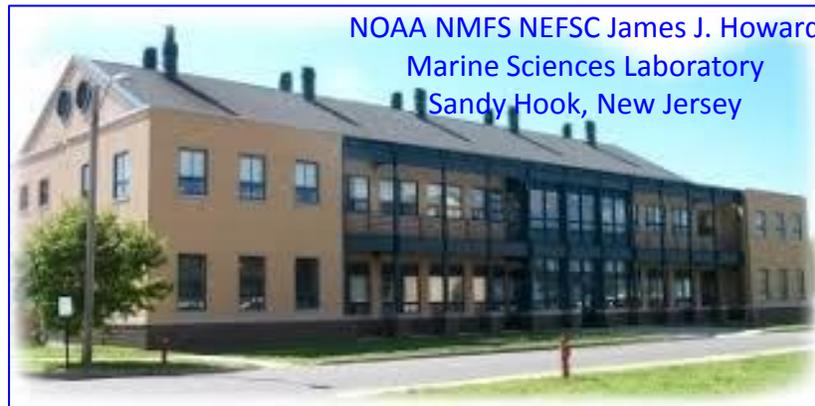


Fall Workshop: The Science of Microplastics in the World Ocean  
Woods Hole Oceanographic Institution  
October 15-18, 2019





Gateway National Recreational Area



1899: Guglielmo Marconi Chose the Twin Lights to Set Up History-Making Wireless Telegraph.



1841: The Towers Became the First Lighthouses in the U.S. to be Equipped with a Fresnel lens.



The Oldest Working Lighthouse in the United States: June 11, 1764

JAMES J. HOWARD MARINE SCIENCES LABORATORY

50 1961  2011  
SANDY HOOK, NJ  
YEARS OF FISHERY RESEARCH



SANDY HOOK MARINE LABORATORY



It is important to note that..



Plastic Codes								
CODE	 1 PETE	 2 HDPE	 3 V	 4 LDPE	 5 PP	 6 PS	 7 OTHER	
PLASTIC TYPE	Polyethylene Terephthalate	High-Density Polyethylene	Vinyl	Low-Density Polyethylene	Polypropylene	Polystyrene	Other plastics	Biodegradable plastics
EXAMPLES	Water bottle, Soda bottle, Peanut butter container.	Milk container, Shampoo bottle, Motor oil bottle	Detergent container, Clear food packaging, Piping.	Plastic food wraps, Squeezable bottle.	Yogurt container, Ketchup bottle, Syrup bottle.	Disposable plate & cups, Meat trays.	Baby bottle, 5-gallon water container	Bio-based plastic bottles
RECYCLABLE ?								

- ❖ Different Chemistries
- ❖ Different Properties and Applications
- ❖ Different Fates and Effects
- ❖ Different Management Practices

Raman  
Spectroscopy

Differential  
Scanning  
Calorimetry

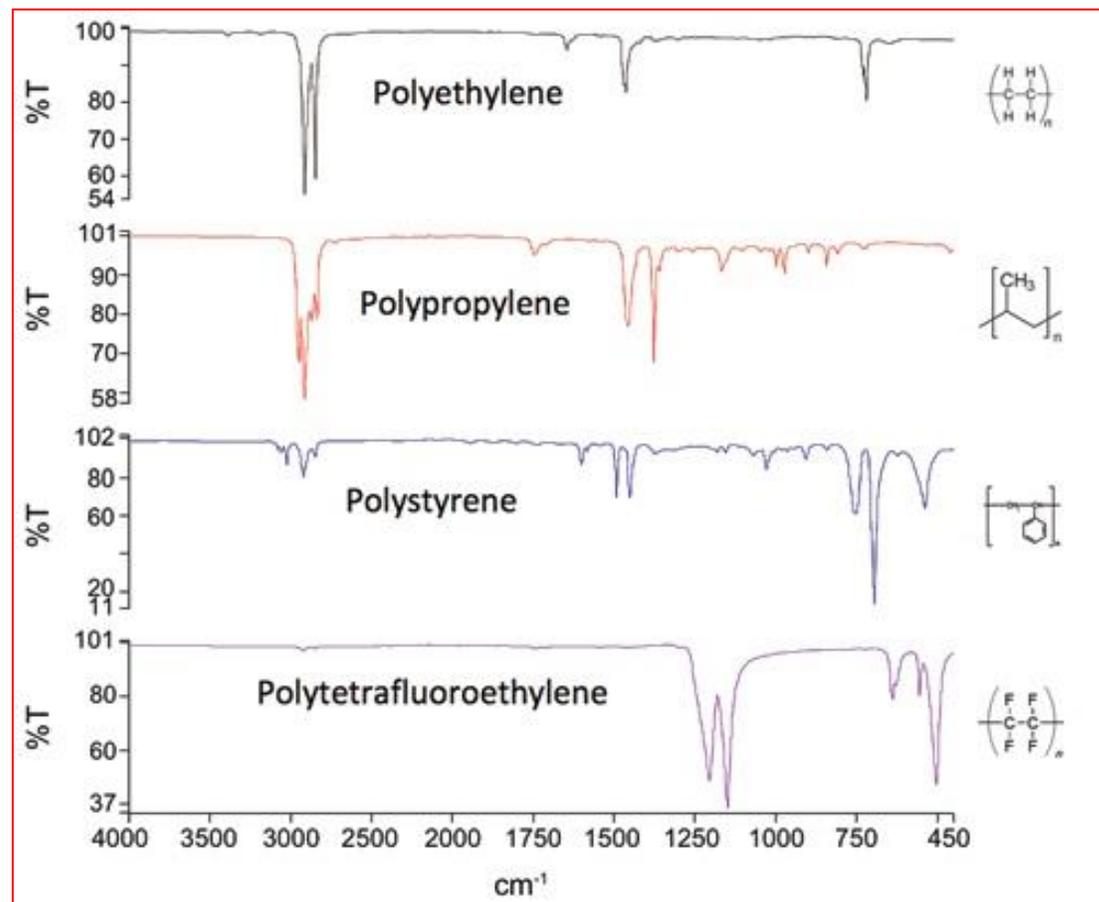
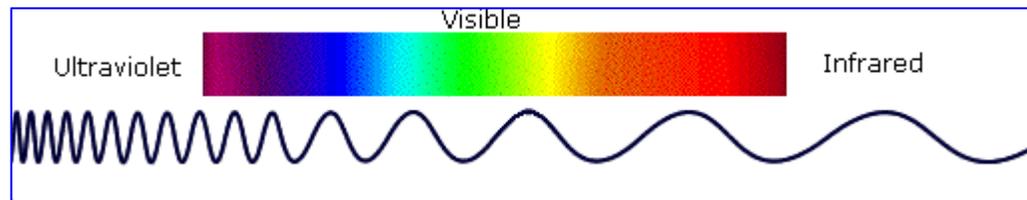
*Analytical*



Infra-Red  
Spectroscopy

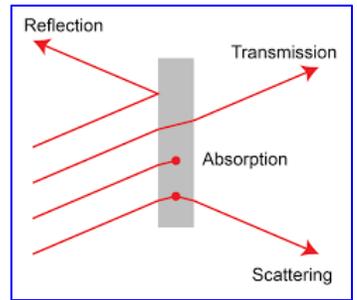
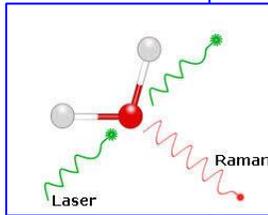
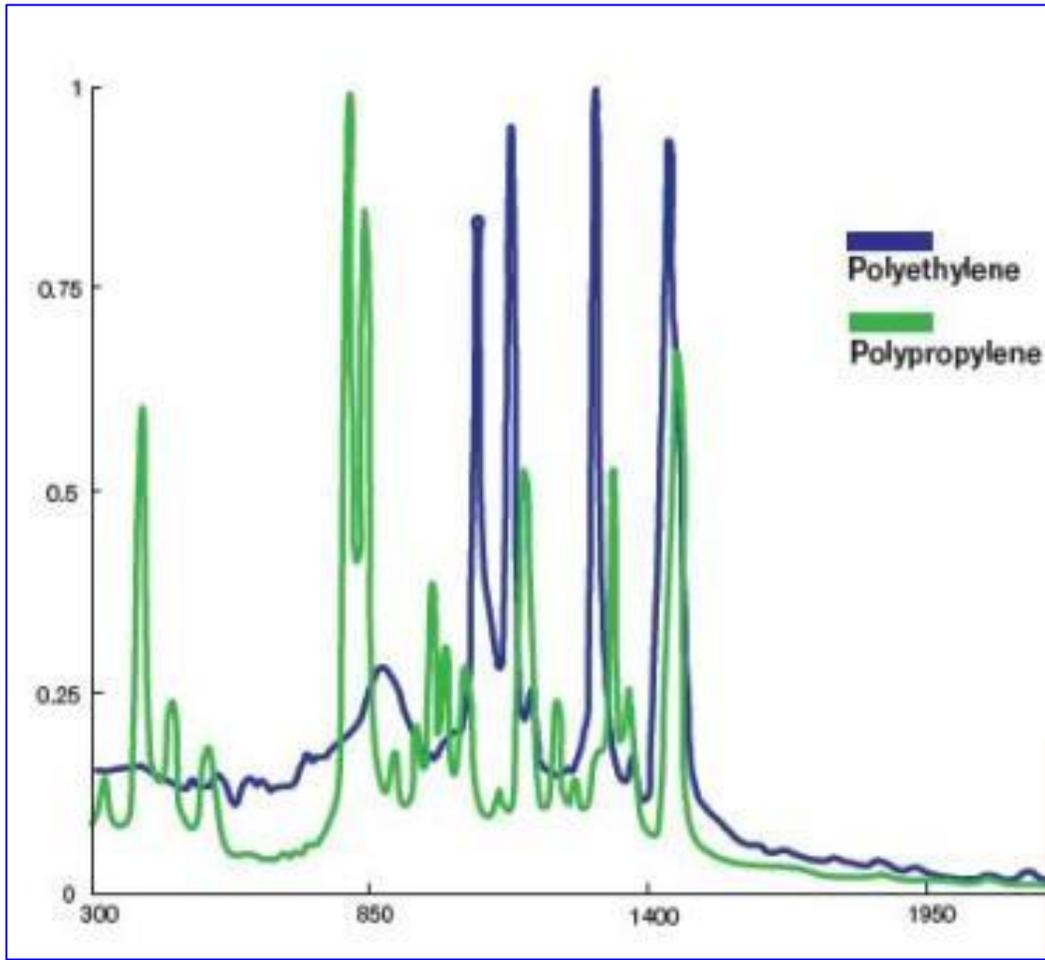
Mass  
Spectrometry

*Chemists*



## Infra-Red Spectroscopy

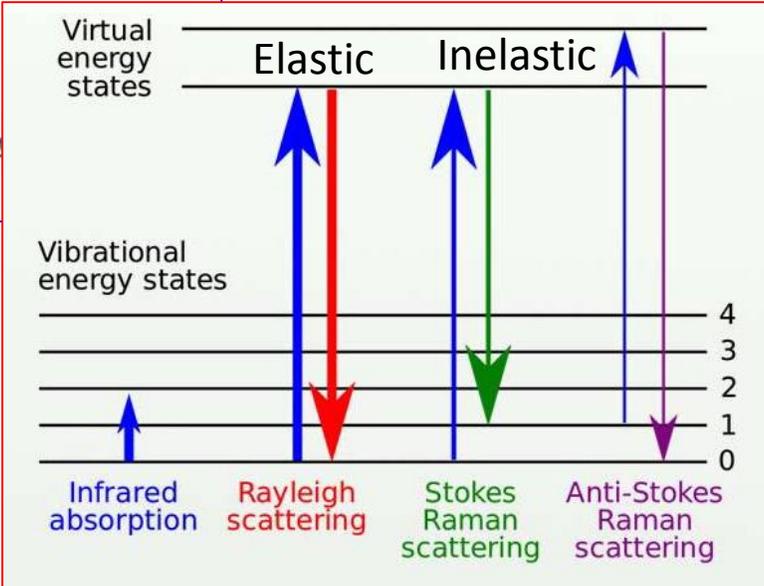
Vibrational excitation of covalently bonded atoms and groups.



Monochromatic Laser

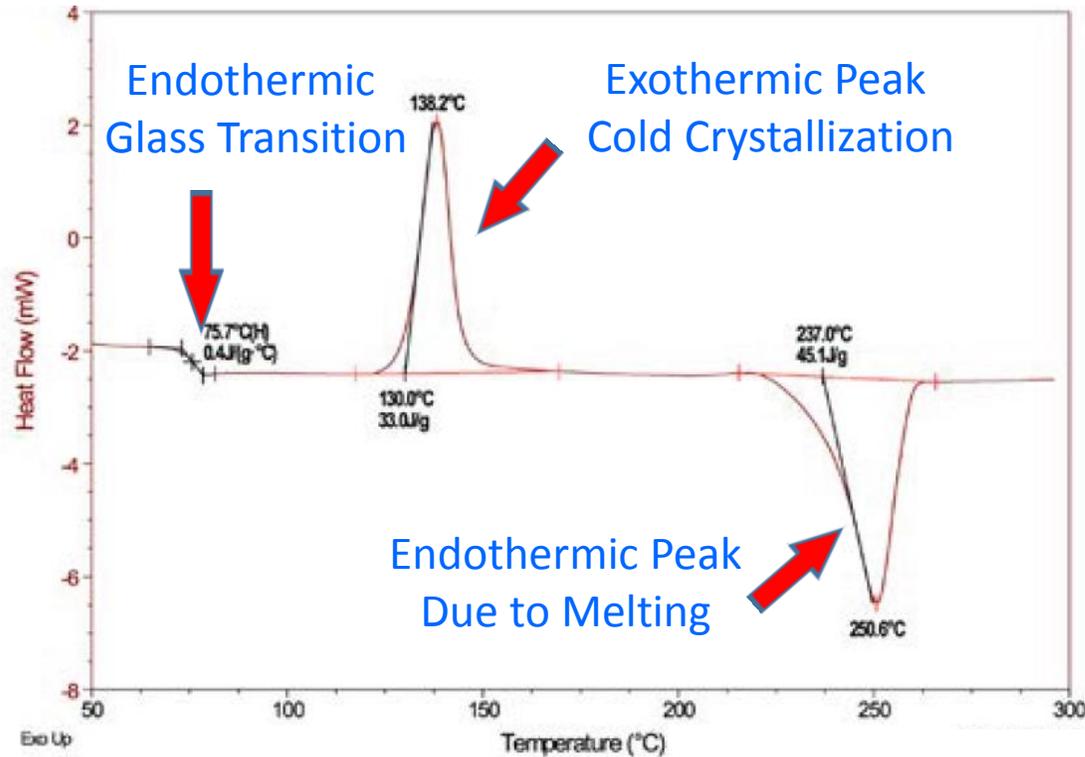
## Raman Spectroscopy

1 in  $10^7$  photons is scattered at frequencies different from, and usually lower than, the frequency of the incident photons.



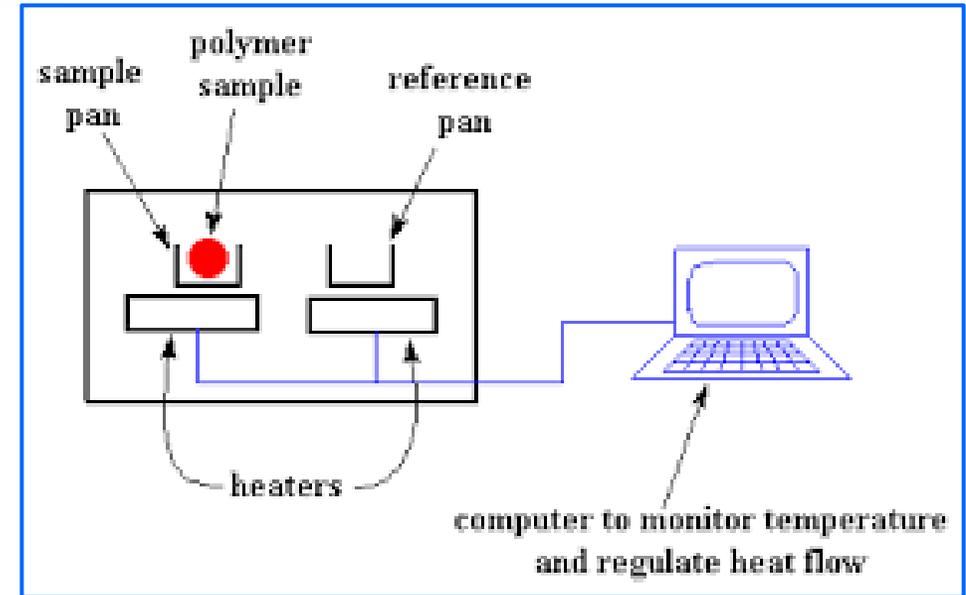
# Differential Scanning Calorimetry (DSC)

## Polyethylene Terephthalate



Heat Flow Versus Temperature

## Thermal Behavior of Polymers



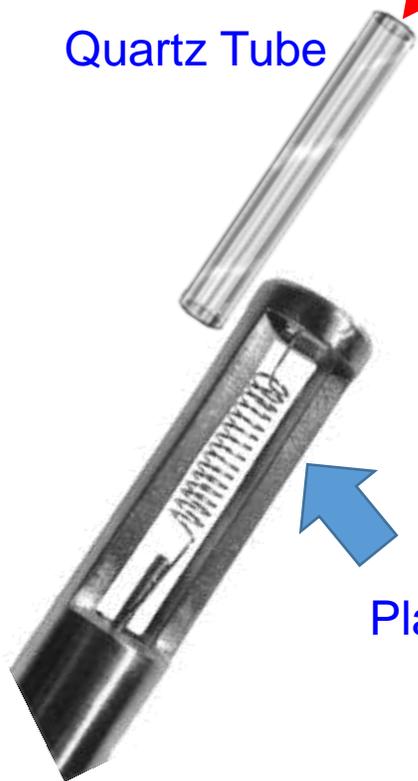
Heat flux DSC is comprised of a thermal cell with a sensor that registers temperature difference between sample filled pan and reference pan containing only air.

# Pyrolysis GC-MS Analysis

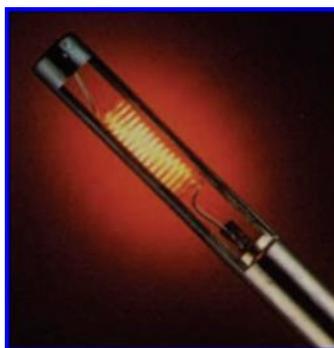


CDS-2000 Pyroprobe

Quartz Tube



Platinum Filament



750°C  
=  
1382°F

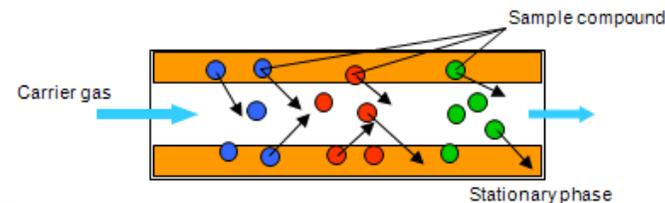


CDS-1500  
GC-MS Interface

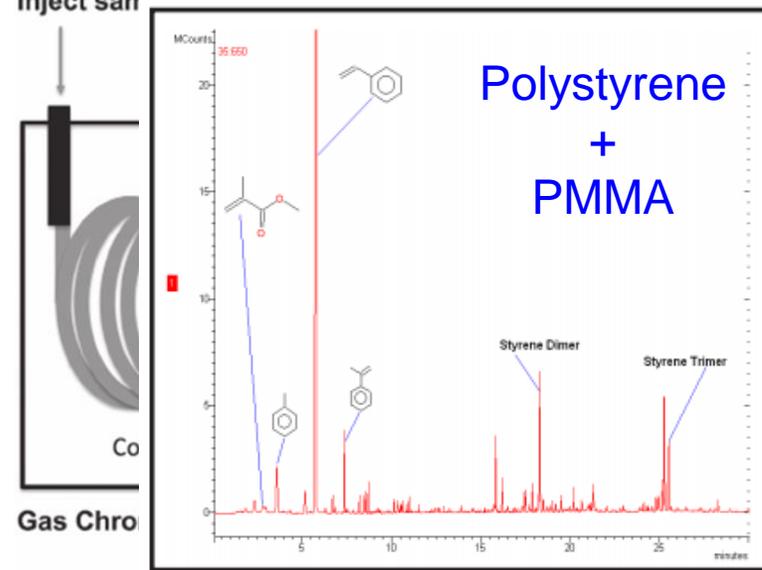
Pyroprobe



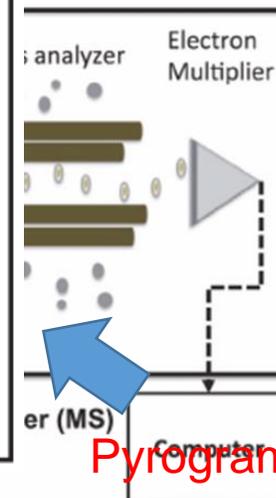
Agilent 5973  
GC-MS



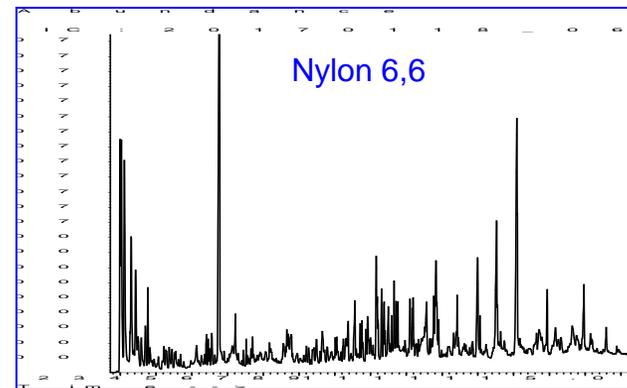
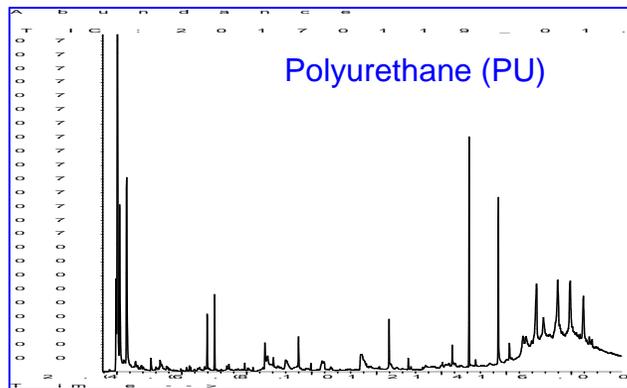
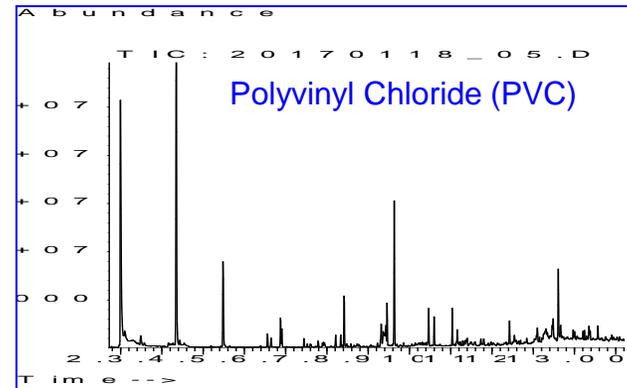
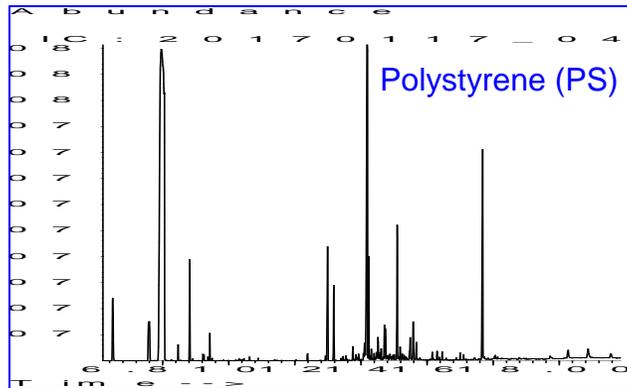
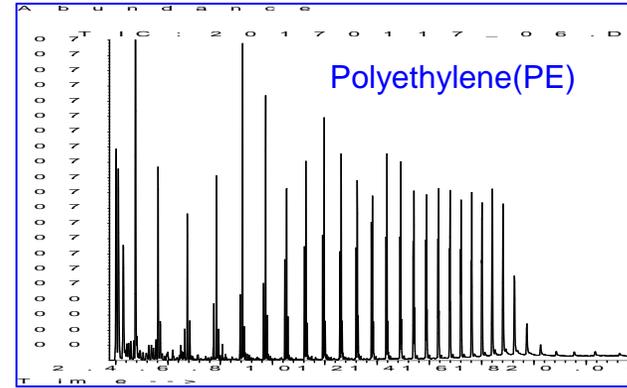
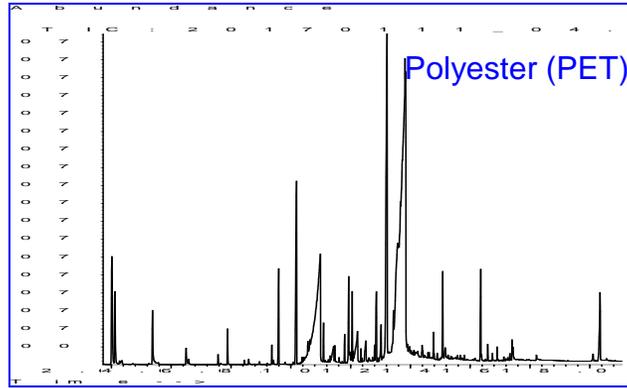
Inject sam



o-charge ratio will  
ratio of voltages.



# Example Pyrograms of a Few Commonly Used Plastic Polymers



## Observations:

- ❖ Pyrolysis GC-MS Pyrograms of commonly used plastic polymers are different.
- ❖ Similar to Infra-Red and Raman Spectroscopy, different GC-MS pyrogram signatures will allow differentiation between different plastic materials.
- ❖ Peak fingerprinting with Infra-Red, Raman, and Pyrolysis GC-MS appears to be qualitatively similar.

Why bother with ...  
so many techniques?

Does anyone else feel like we could ...?



Try Exploring the  
Power of  
Mass Spectroscopy



Check Out How We can  
Go Above & Beyond  
Just Peak Comparisons



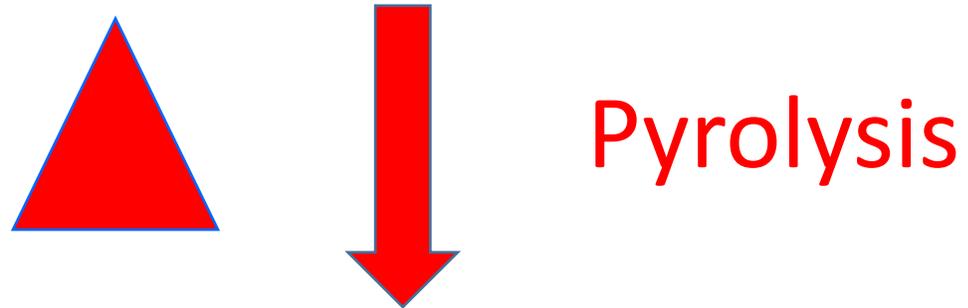
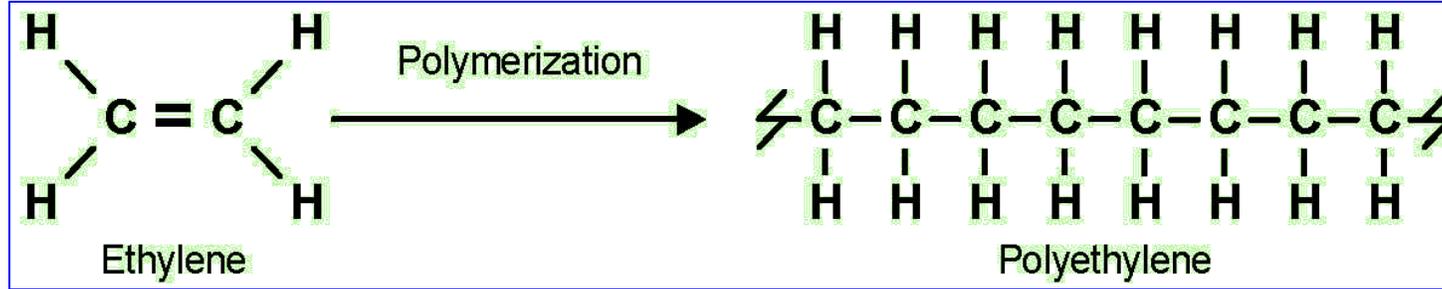
Creation of Pyrolysis  
GC-MS Database



Involves

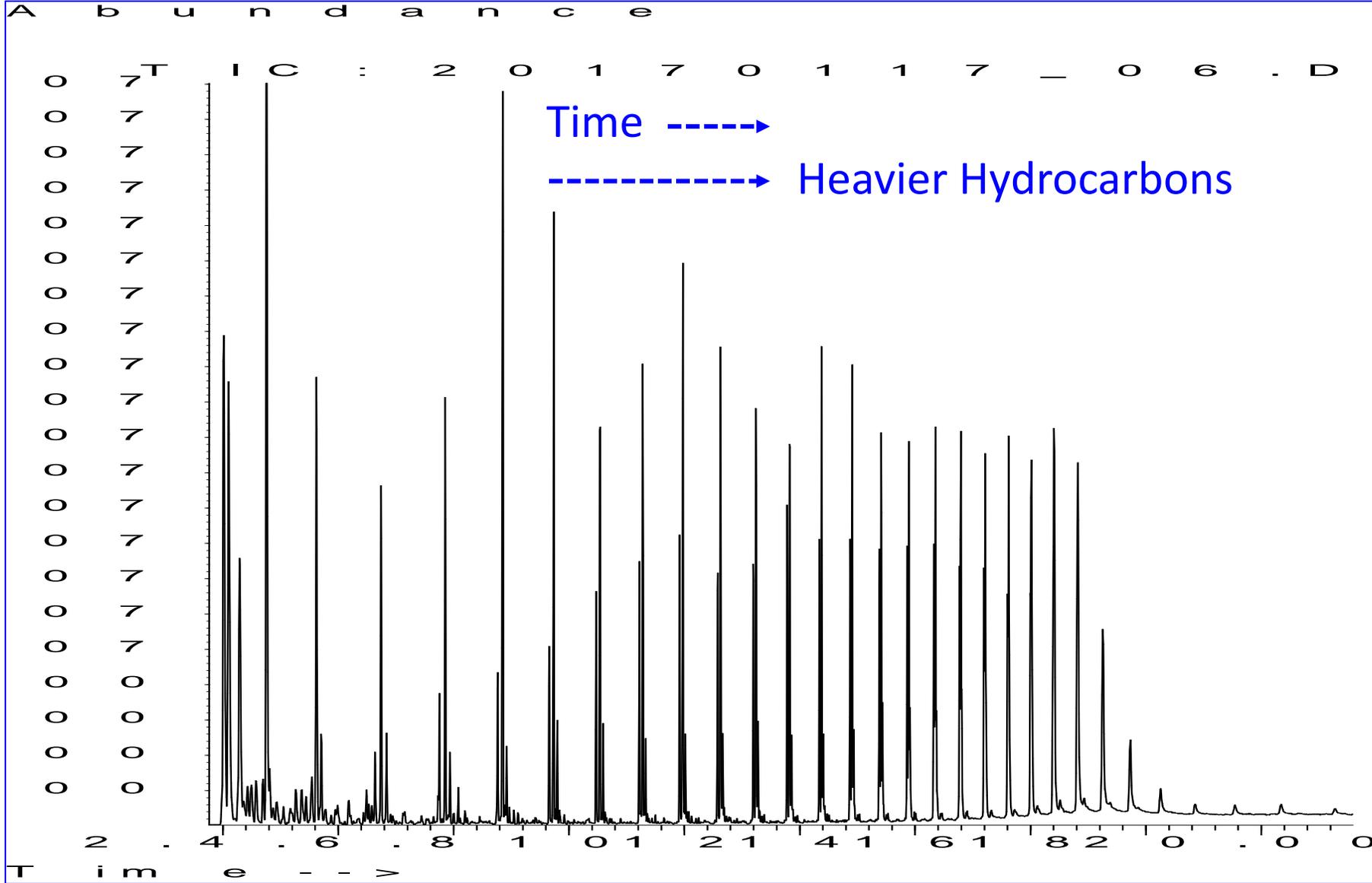


Systematic and Sequential  
Identification of Marker Peaks  
That can be Later used for Polymer  
Characterization



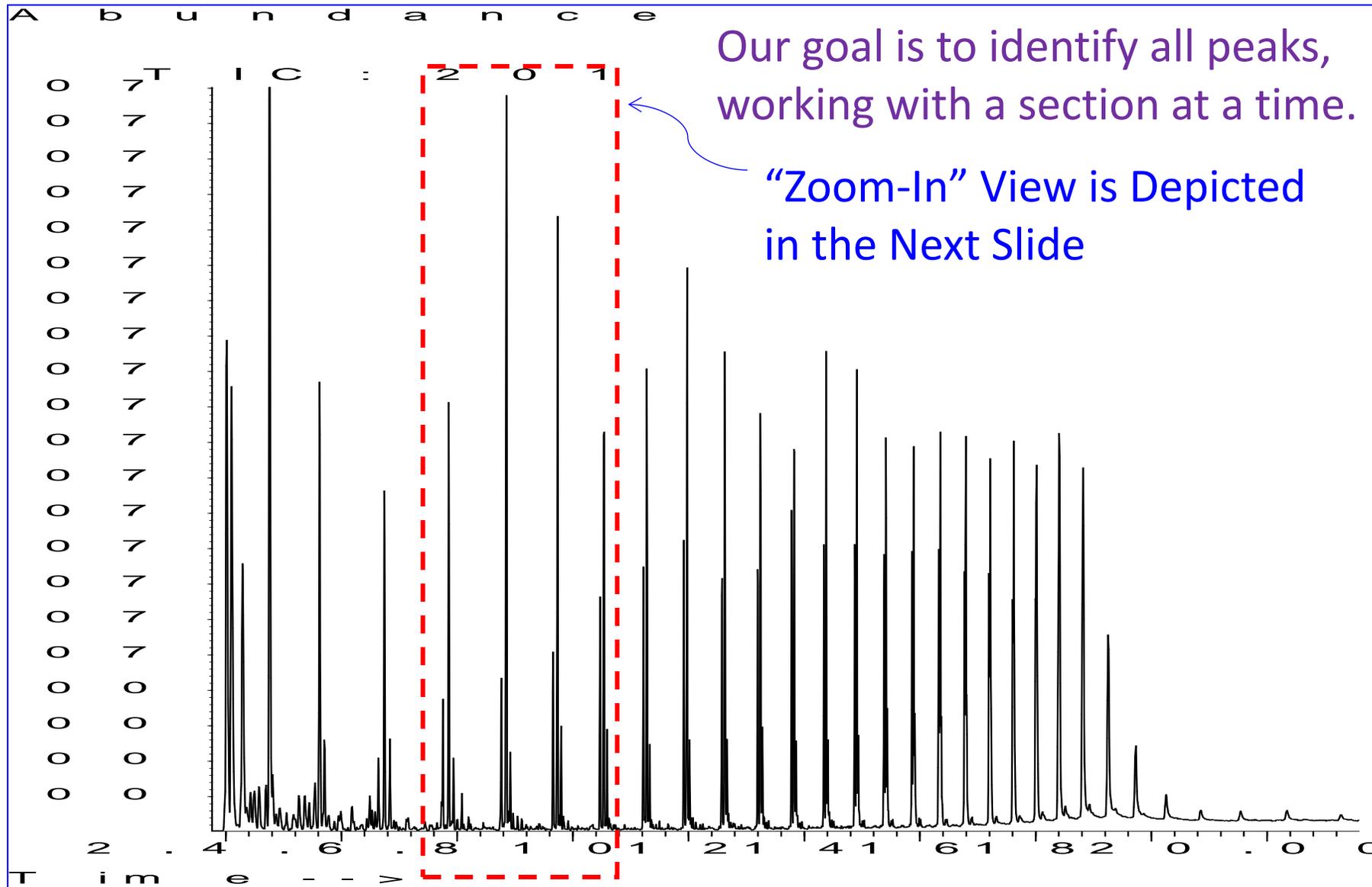
C-C bonds at different sites along the polymer chain break due to the intense heat to yield a variety of short-chain molecules.

# Total Ion Chromatogram (Pyrogram) of High-Density Polyethylene (HDPE)



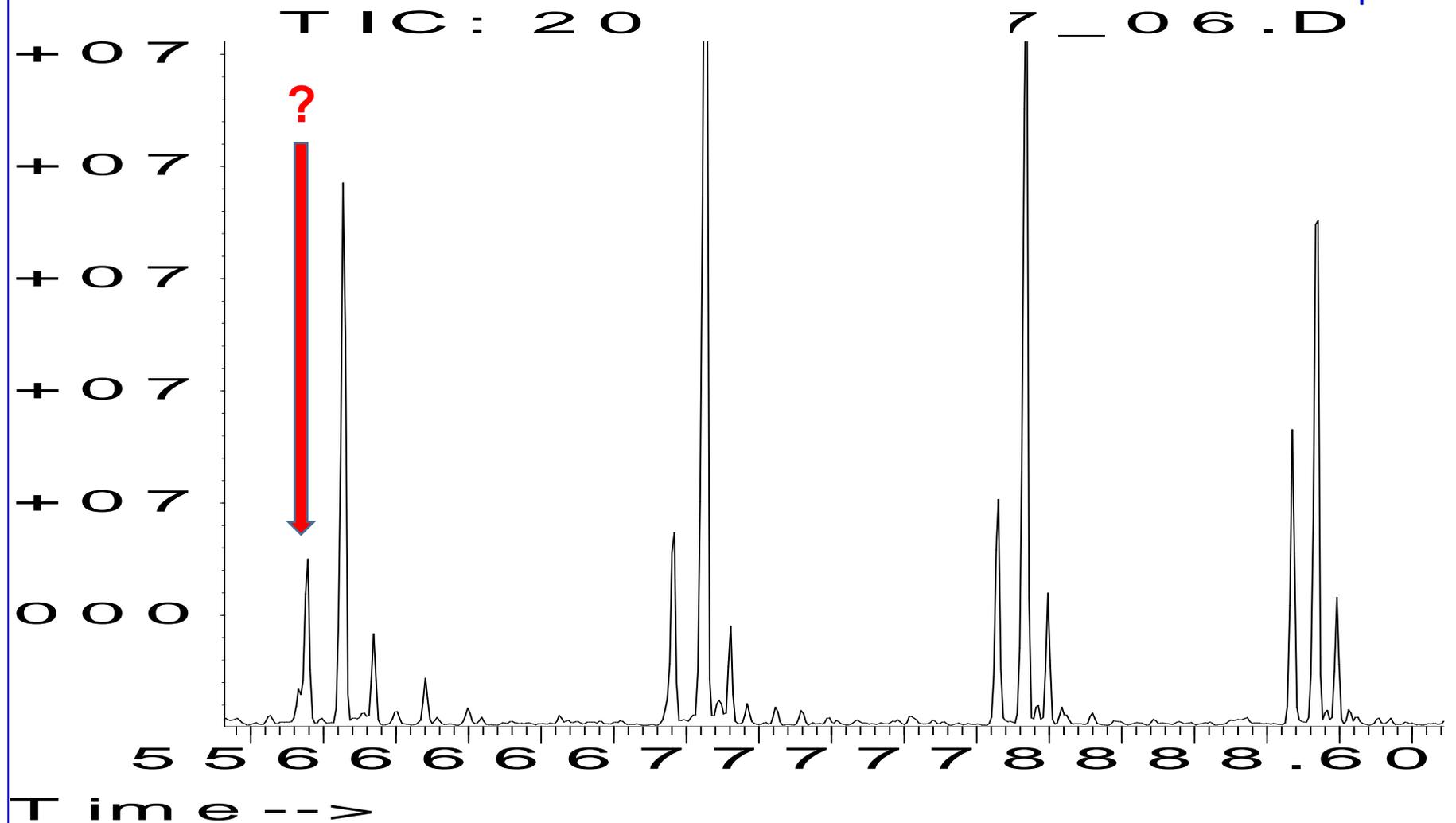
TIC: 20170117\_06.D

# Pyrogram of High-Density Polyethylene (HDPE)

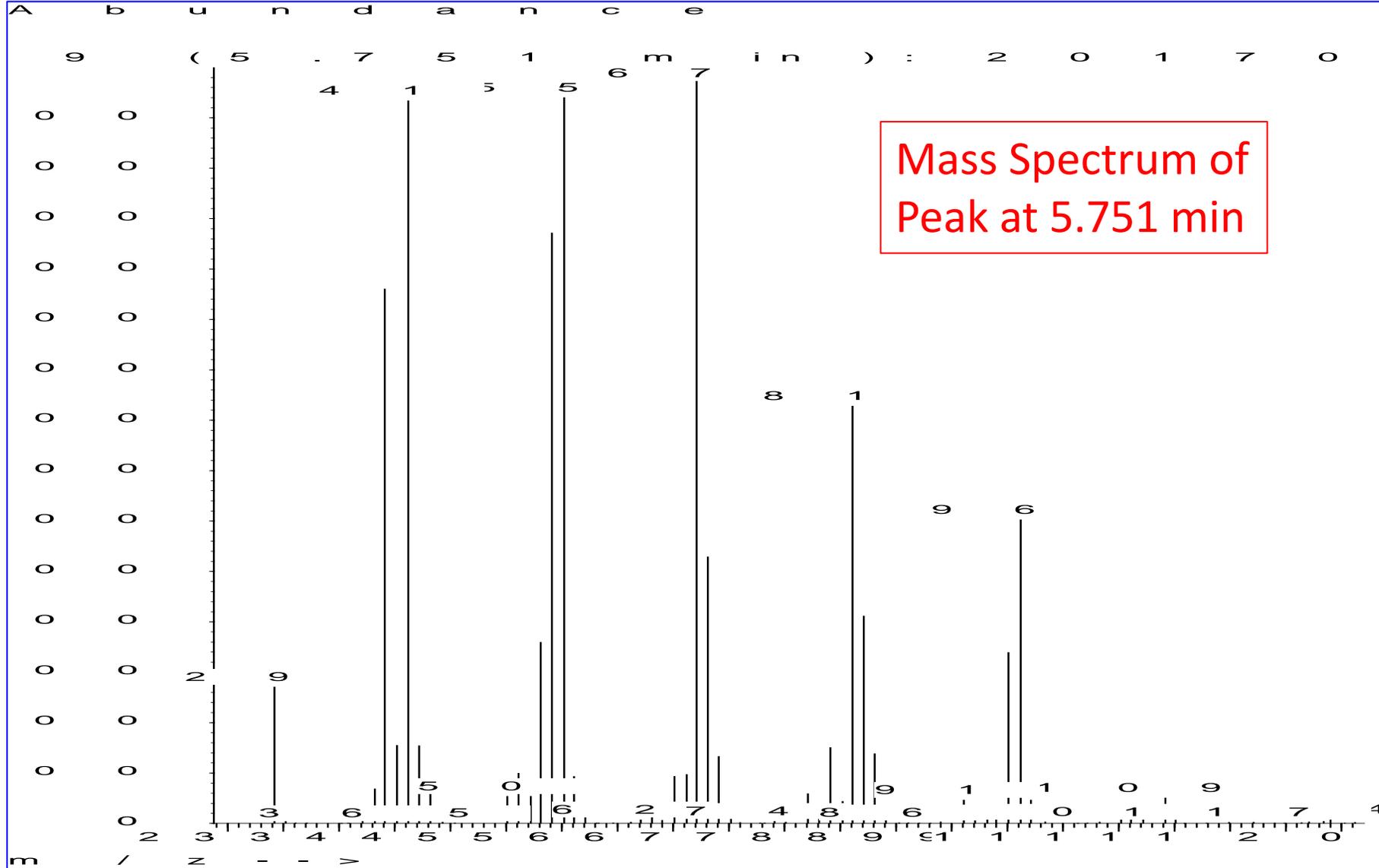


## High-Density Polyethylene (HDPE): “Zoom-In” Part of the Pyrogram

These are not just any ordinary chromatographic peaks, they are the ion chromatograms. There is a wealth of molecular structural information embedded underneath each peak.



# High-Density Polyethylene (HDPE)



# Library Search: Find Best Match for Mass Spectrum in the NIST Library

NIST MS Search 2.0 - [Ident, Presearch Default - InLib = 125, 73 spectra]

File Search View Tools Options Window Help

1. Scan 799 (5.751 min): 20170117\_06.D

mainlib;replib: 190825 total spectra

Mass Spectrum of Unknown Peak

Mass Spectrum in Library Database

Scan 799 (5.751 min): 20170117\_06.D

1,8-Nonadiene

Difference Head to Tail Side by Side Subtraction 915 918R 29.6P

#	Lib.	Match	R.Match	Name
1	R	915	918	1,8-Nonadie...
2	M	867	869	Cyclohexan...
3	M	867	869	Cyclohexan...
4	M	852	861	Cyclohexane
5	M	847	850	Z-1,8-Dode...
6	M	843	846	E-1,8-Dode...
7	R	841	845	1,9-Decadi...
8	M	836	855	1,10-Undec...
9	M	834	839	Spiropentan...
10	M	834	838	Z-1,6-Undec...
11	R	832	855	1,11-Dodec...
12	M	832	839	4,5-Nonadie...
13	M	831	860	Bicyclo[7.1...
14	R	831	839	Bicyclo[4.1...
15	M	830	833	E-1,6-Undec...
16	M	828	843	1-Methylcyc...
17	M	827	828	Pentalene, ...
18	M	825	833	1,1'-Bicyclo...
19	M	824	841	trans,trans-2...
20	R	823	843	Cyclohexan...

Library Match

1,8-Nonadiene

(replib) 1,8-Nonadiene

Plot/Text of Hit Plot of Hit

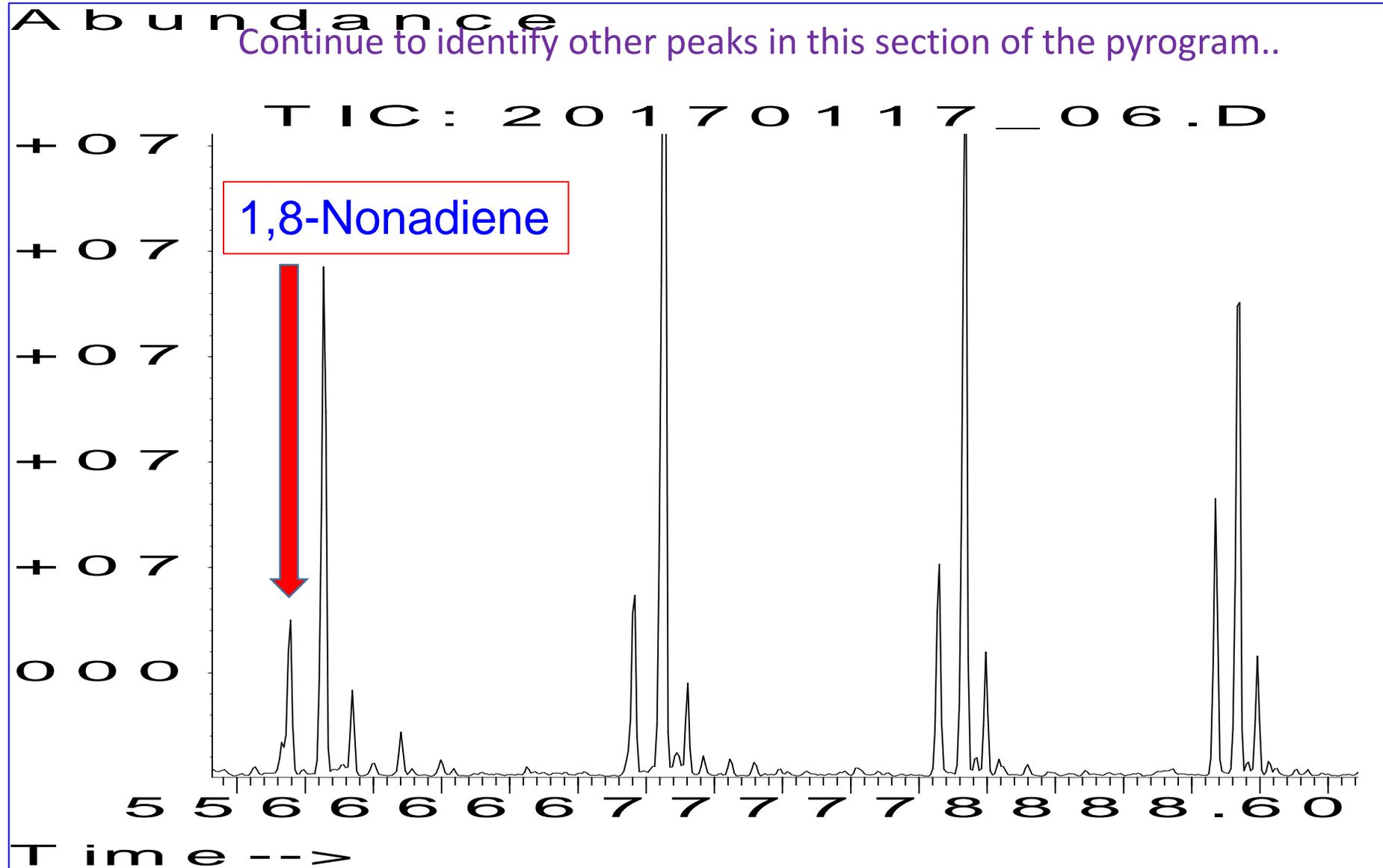
Name: 1,8-Nonadiene  
 Formula: C<sub>9</sub>H<sub>16</sub>  
 MW: 124 CAS#: 4900-30-5 NIST#: 107523 ID#: 1012 DB: replib  
 Other DBs: Fine, TSCA, HODOC, EINECS, IRDB  
 Contributor: Chuck Anderson, Aldrich Chemical Co.  
 10 largest peaks:  
 41 999 | 67 931 | 54 917 | 55 876 | 81 520 |  
 39 486 | 96 376 | 27 366 | 29 349 | 68 325 |  
 Synonyms:  
 no synonyms.  
 Estimated Kovats RI:  
 Value: 896 iu  
 Confidence interval (Hydrocarbons): 39(50%) 167(95%) iu  
 Kovats index  
 1. Value: 862.7 iu  
 Column Type: Capillary  
 Column Class: Semi-standard non-polar  
 Active Phase: Squalane  
 Column Length: 195 m  
 Carrier Gas: H<sub>2</sub>  
 Column Diameter: 0.25 mm

Lib. Search Other Search Names Compare Librarian MSMS

Ident Ident

Start Instrum... Environ... Shin\_Ts... Instrum... NIST M... F:\ Microso... 4:36 PM

# High-Density Polyethylene (HDPE)

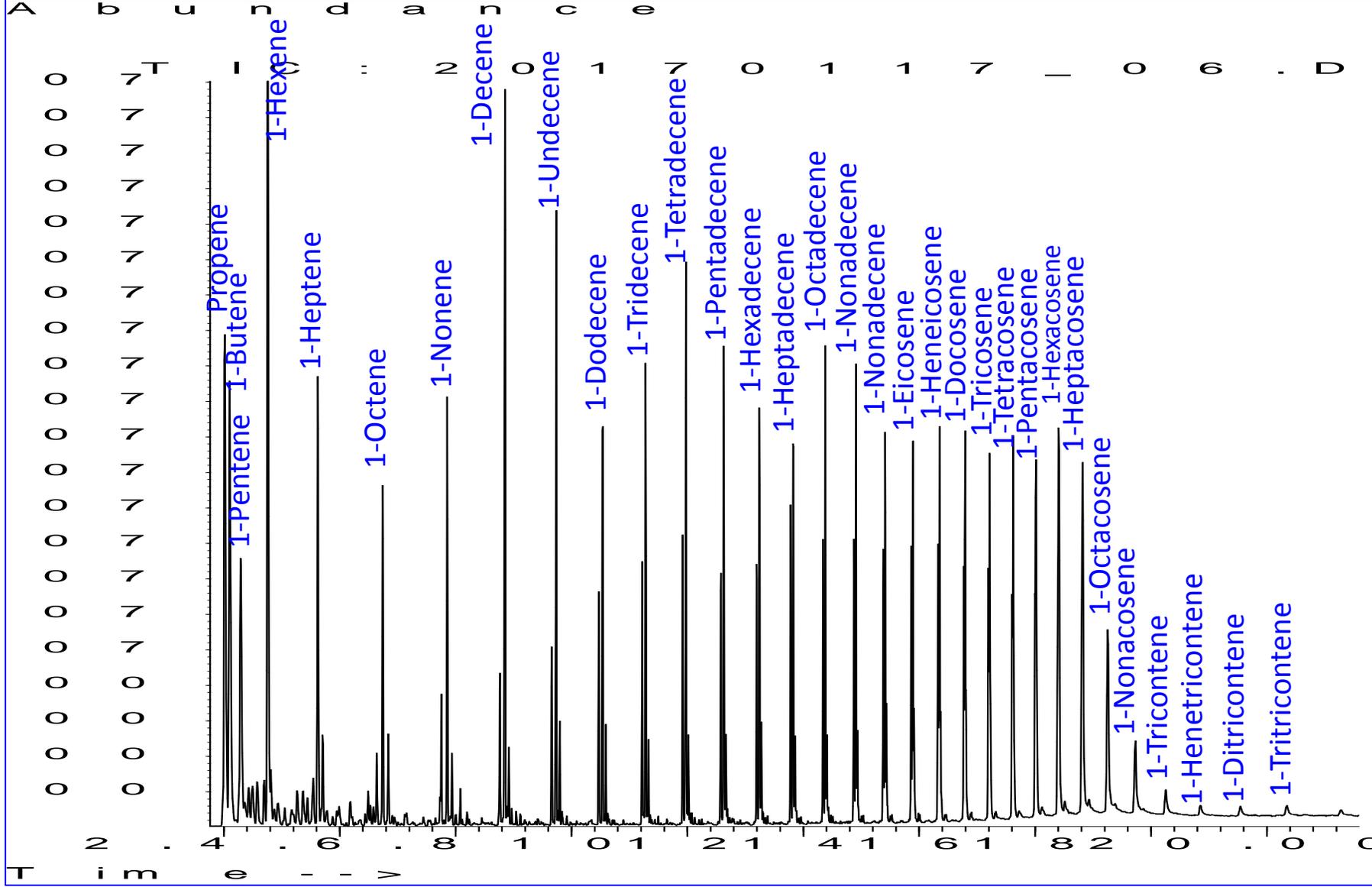




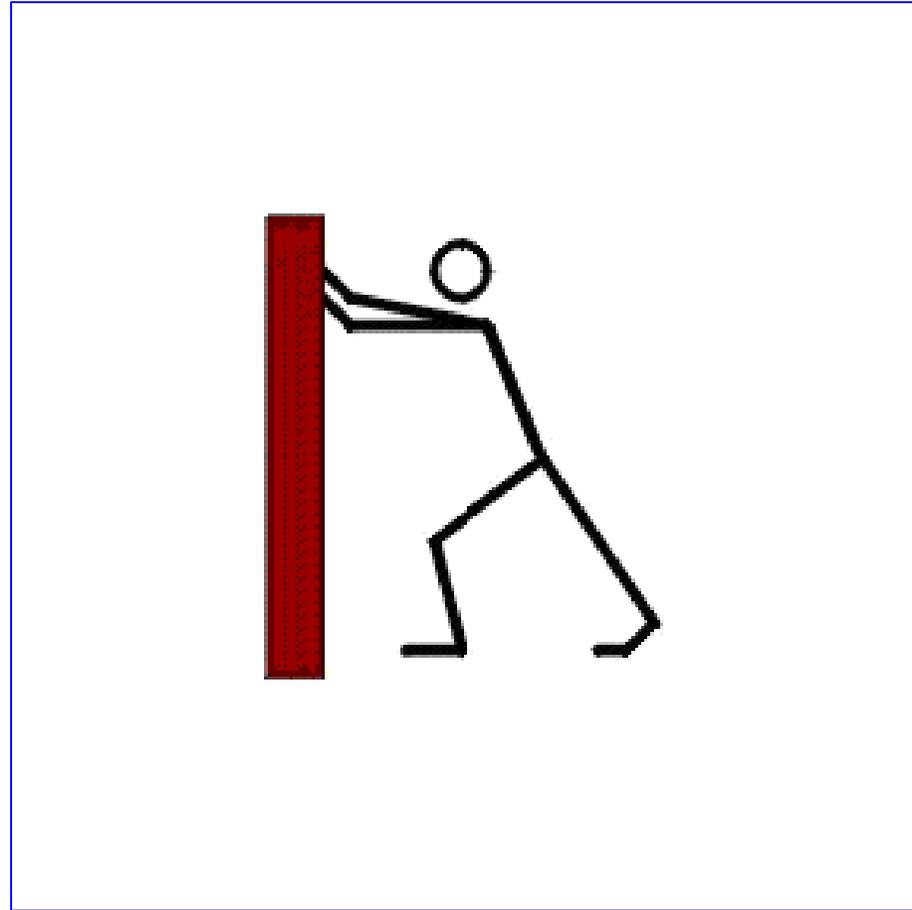


With a Little More Patience and Perseverance  
Characterize All Peaks in the Entire Program

# High-Density Polyethylene (HDPE)



HDPE Pyrogram Fully Characterized!!!



**Good News!**



We have to do this hard work only once to create the library!!!

# Applications of Pyrolysis GC-MS



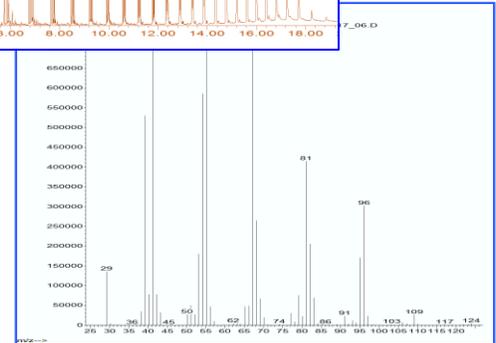
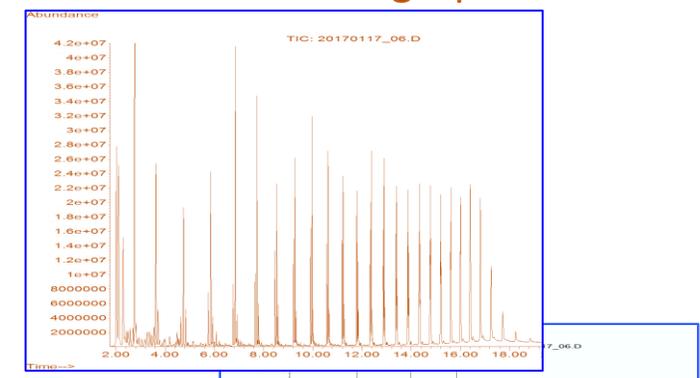
What is the polymer?  
What is the Co-Polymer?  
Any Chemical additives??

Hmm...

CM 11

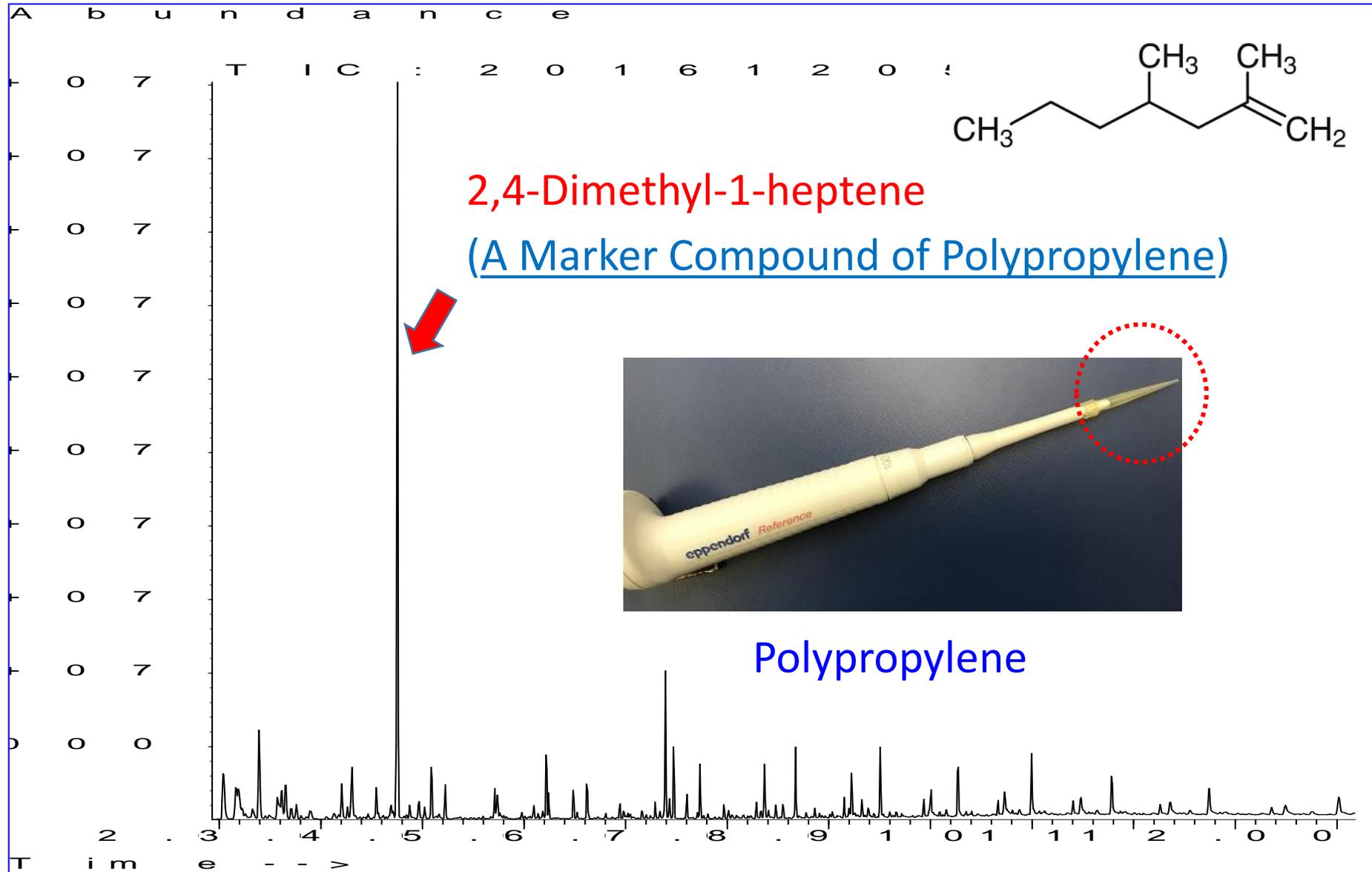
Microplastics

Peak Fingerprint

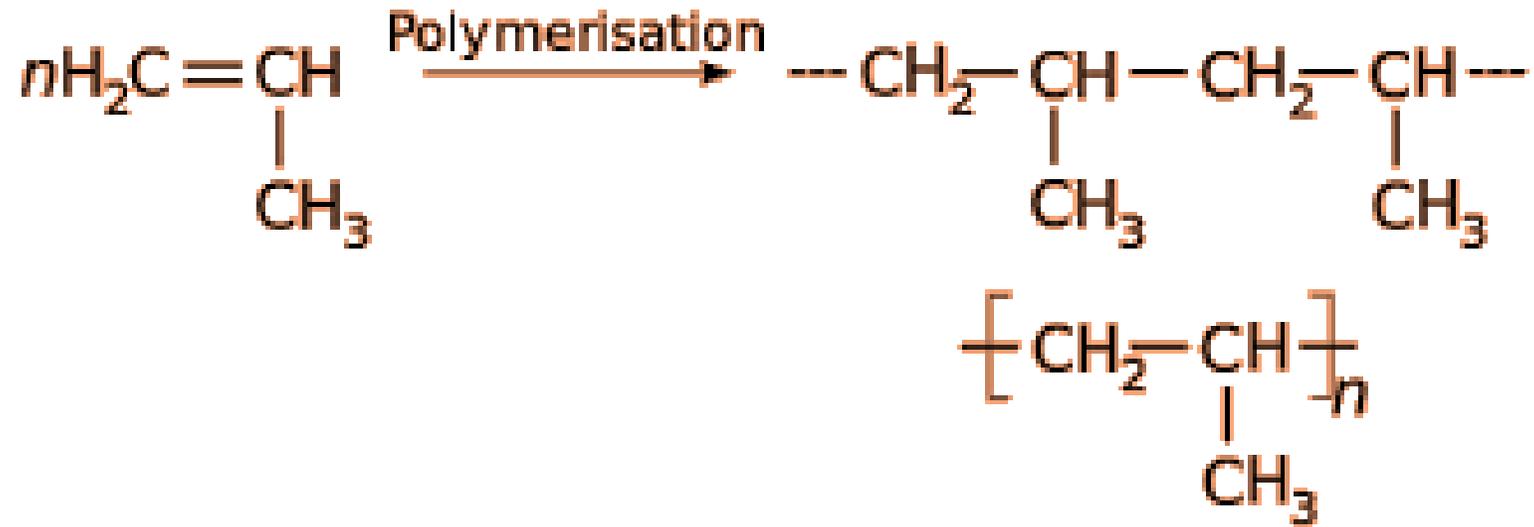


Mass Spectrum

# Micropipette Tip (100 µl)



## Polypropylene



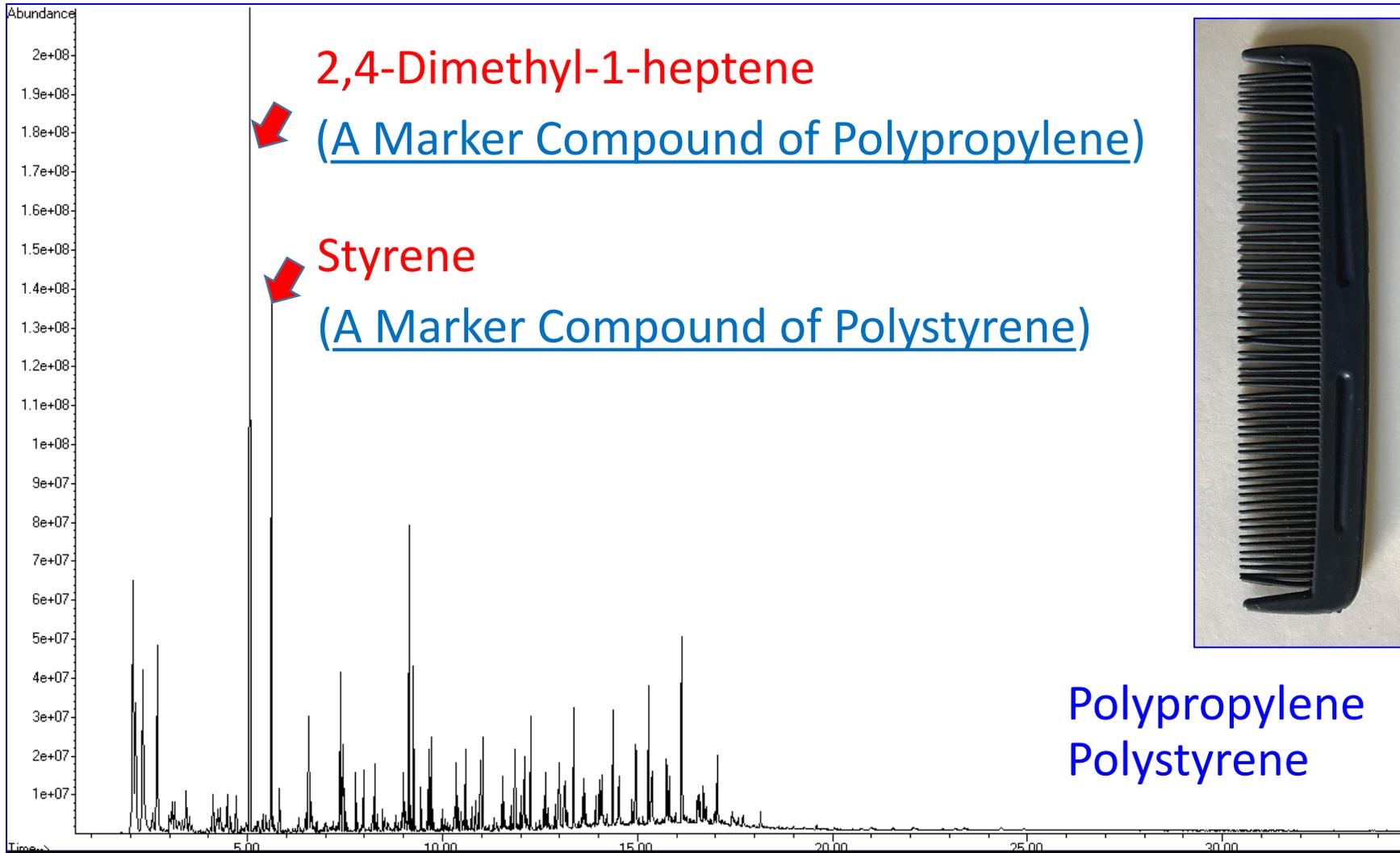
Monomer :  
propylene

Polymer :  
polypropylene

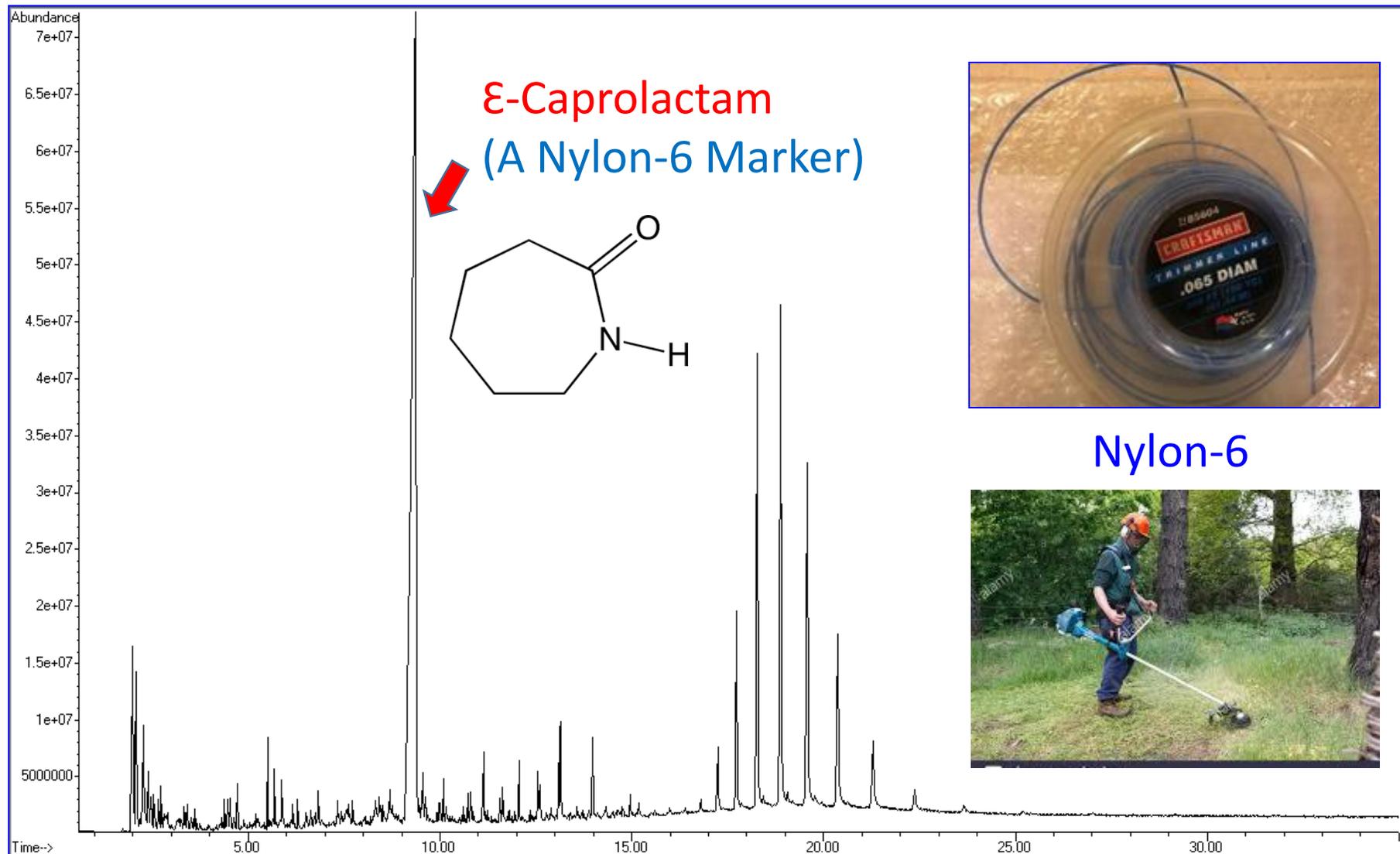




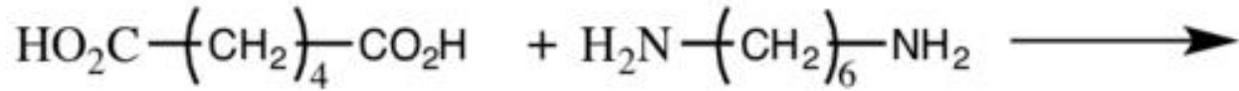
# Hair Comb



# Weed-Wacker Trimmer Line

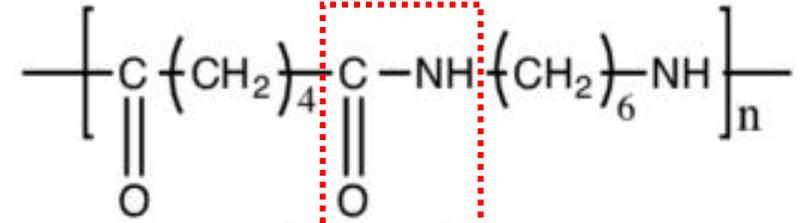


# Nylon Syntheses:



Adipic Acid

Hexamethylene diamine



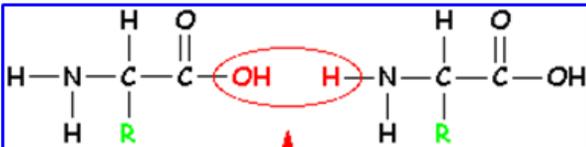
Nylon 66

Amide Linkage

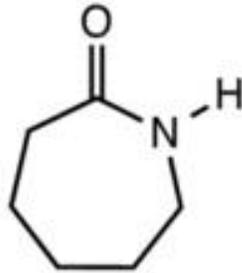
(a)

Amide Linkage

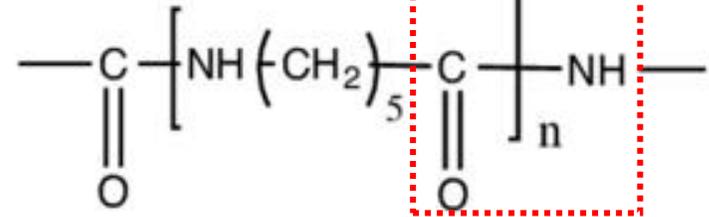
Proteins = Polyamides



These will be taken out to make H<sub>2</sub>O (water), and a new bond will form in their place.



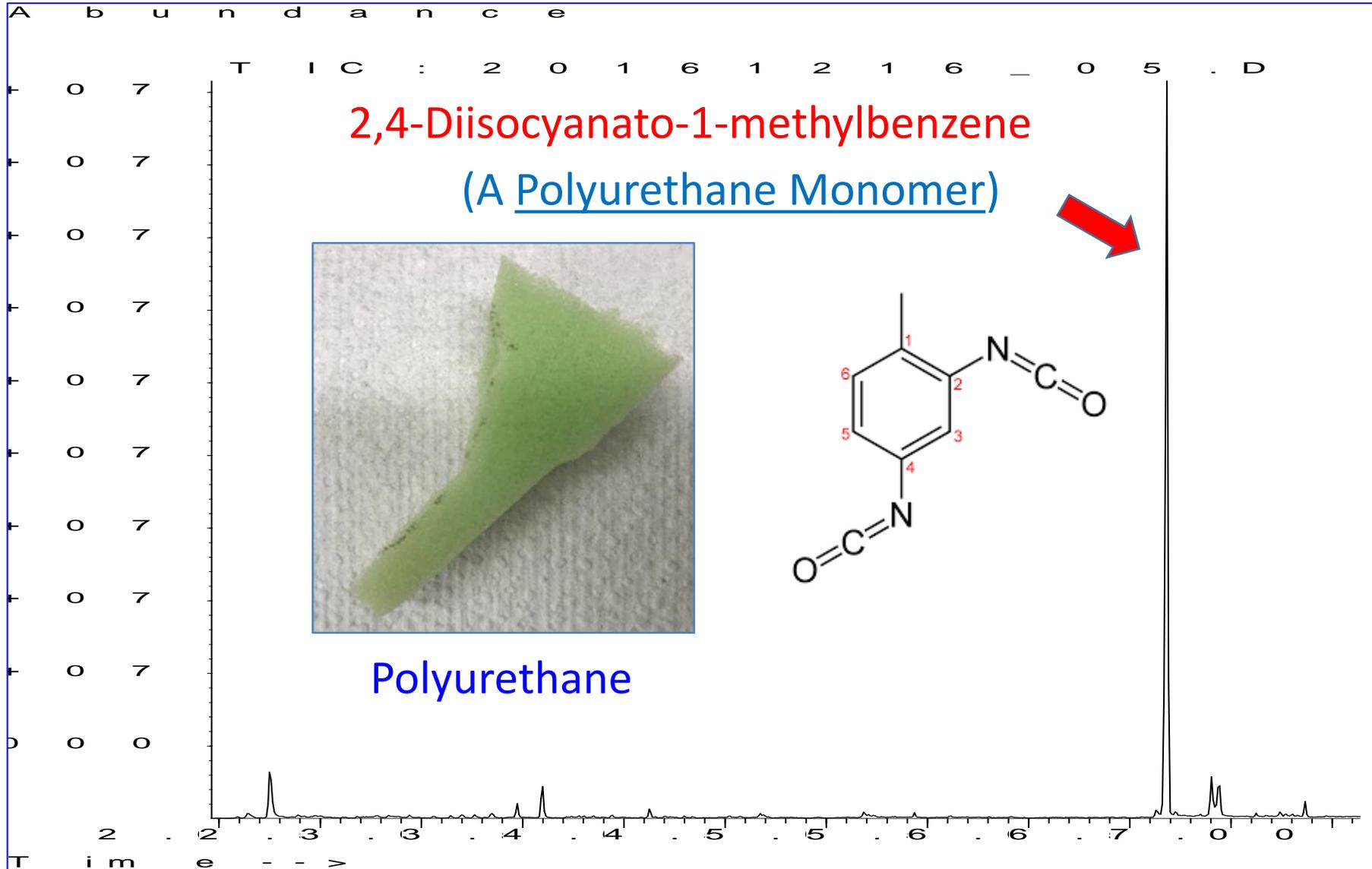
Caprolactam



Nylon 6

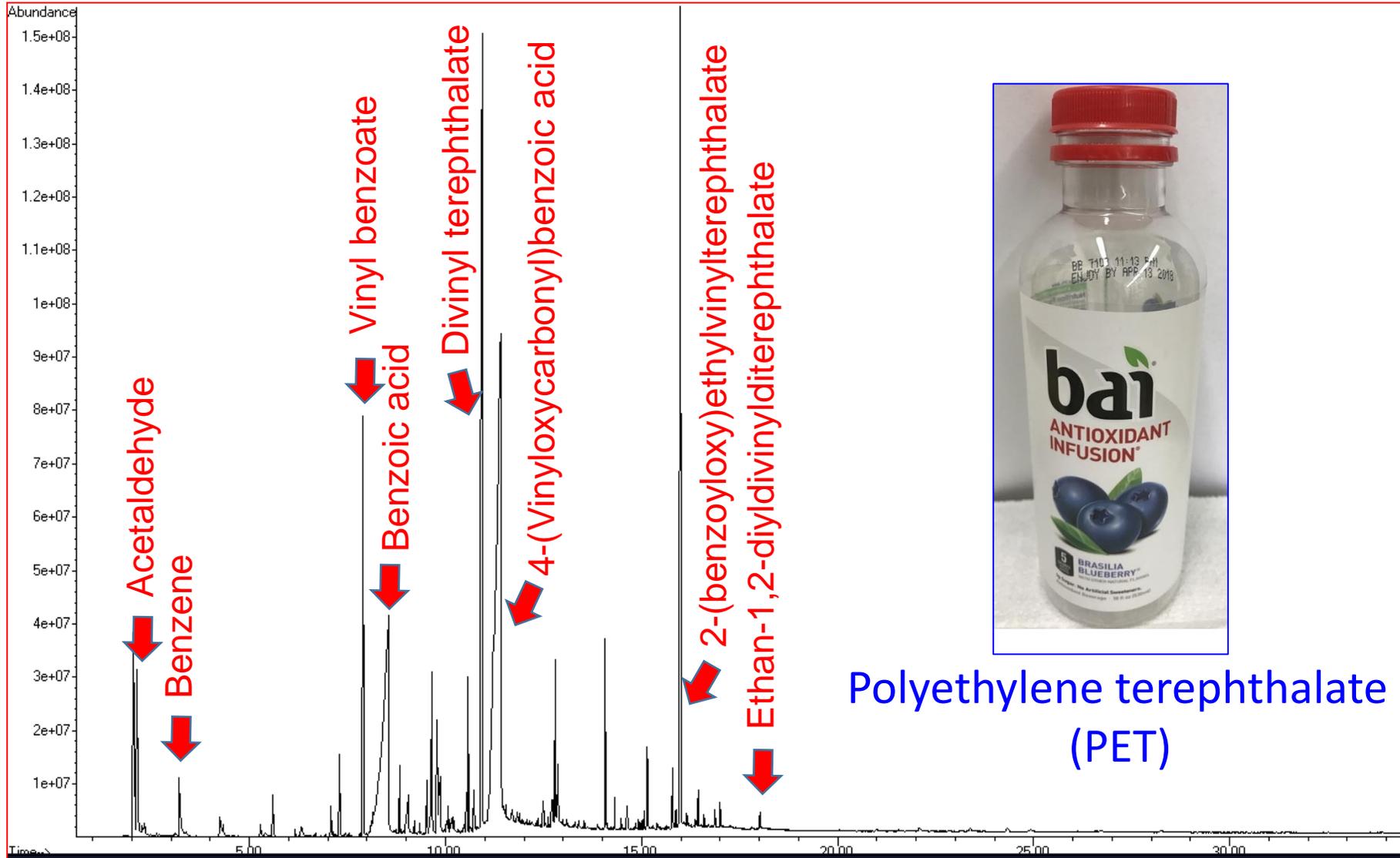
(b)

# Foam Sample





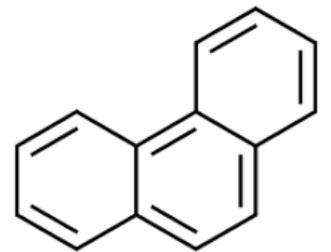
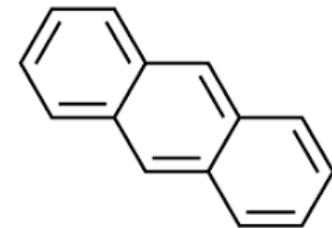
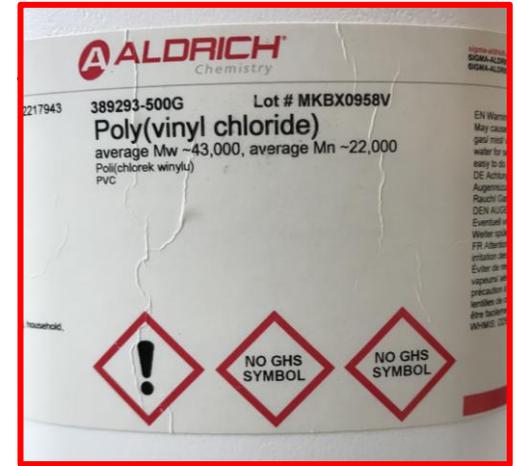
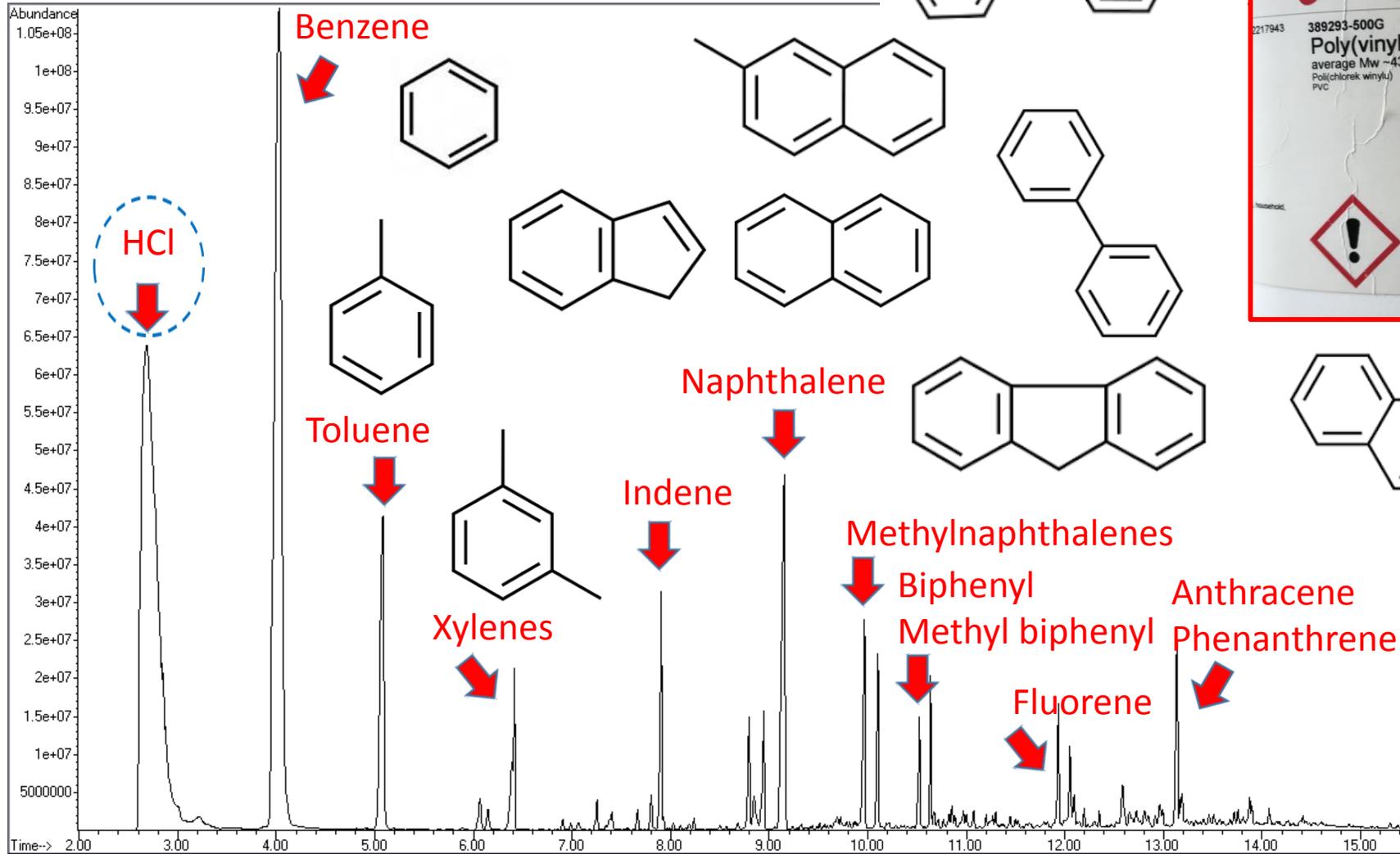
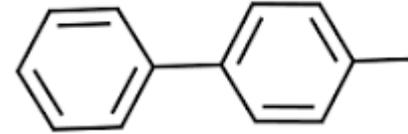
# bai Beverage Bottle



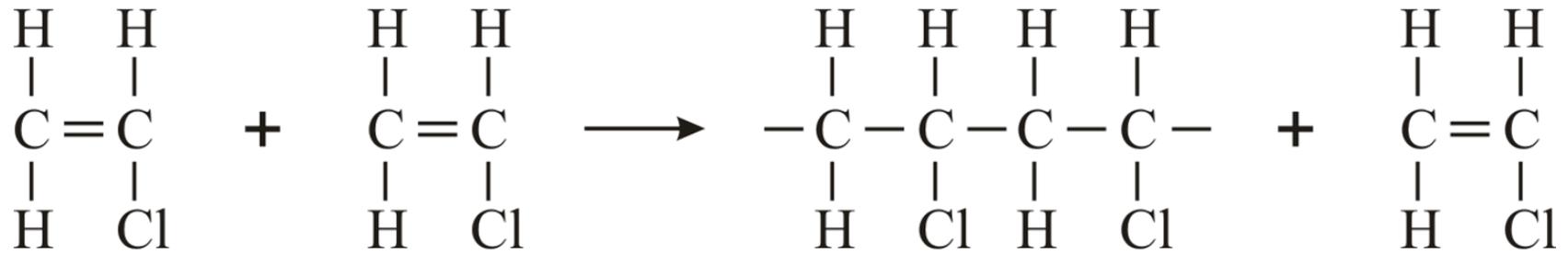
Polyethylene terephthalate  
(PET)



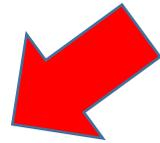
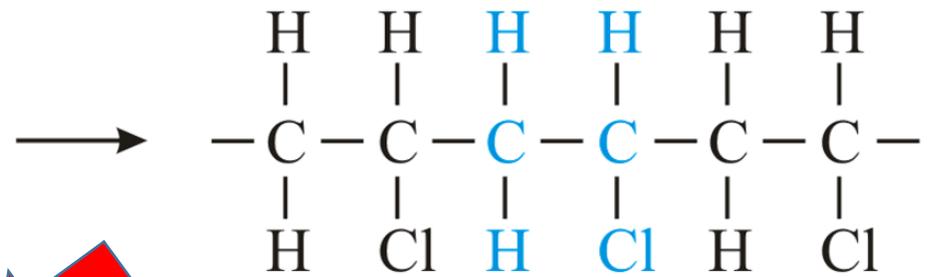
# PVC Standard



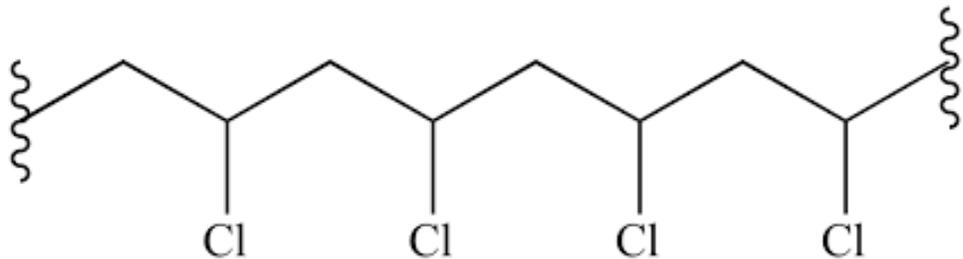
## Polyvinyl chloride (PVC)

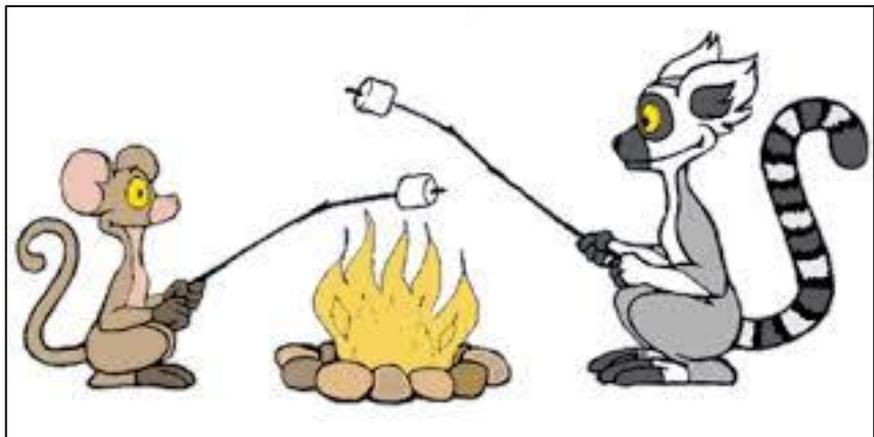


vinyl chloride monomers



poly(vinyl chloride)

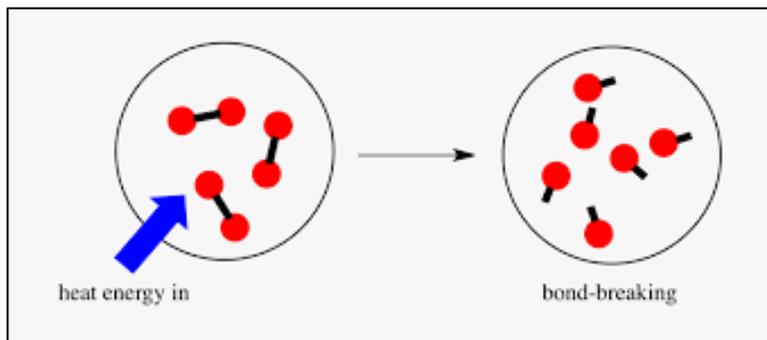




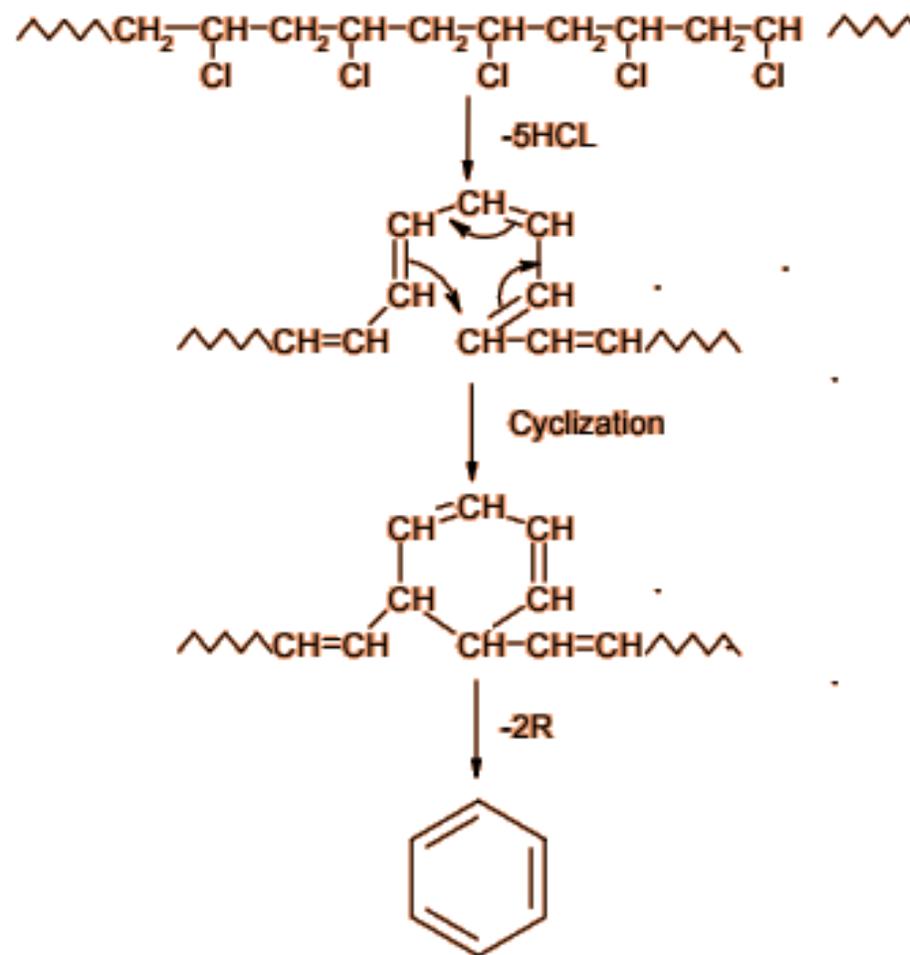
Pyrolysis = High Energy Environment



Plenty of Energy Available for the Breaking and Making of New Bonds



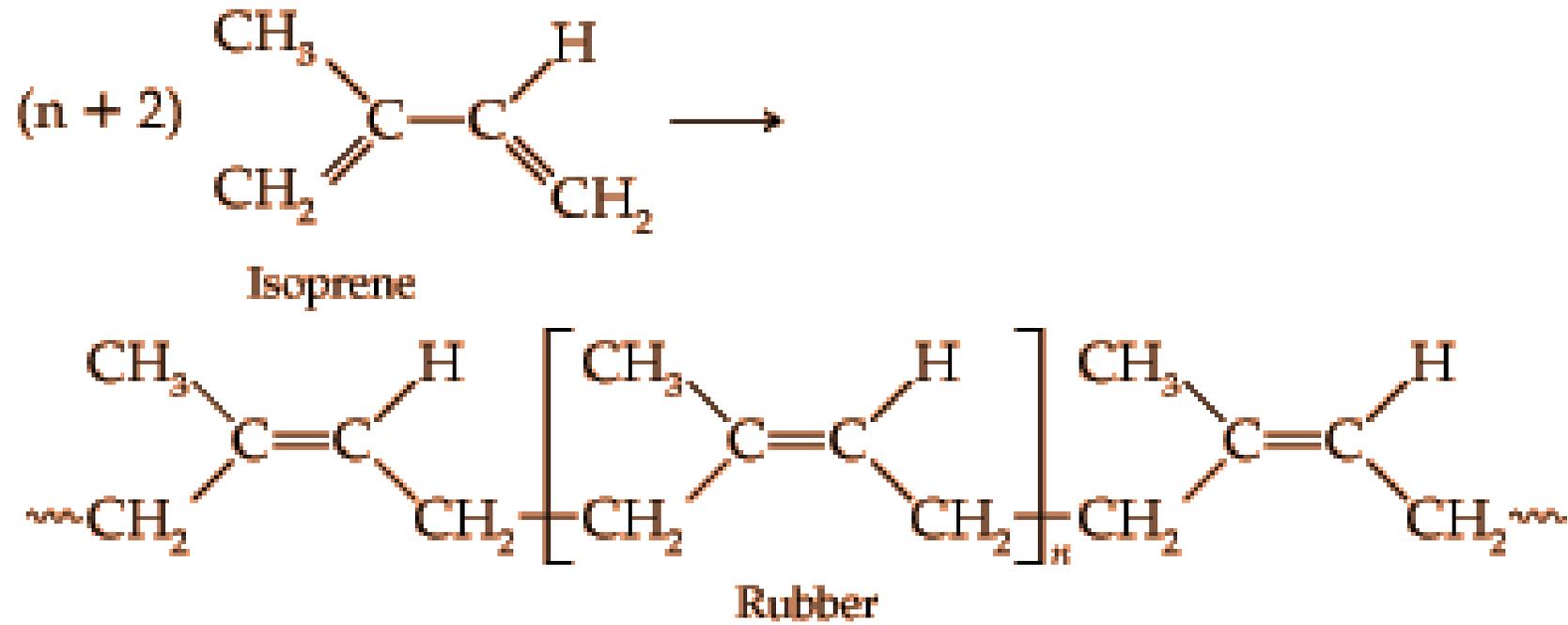
## Pyrolysis of PVC



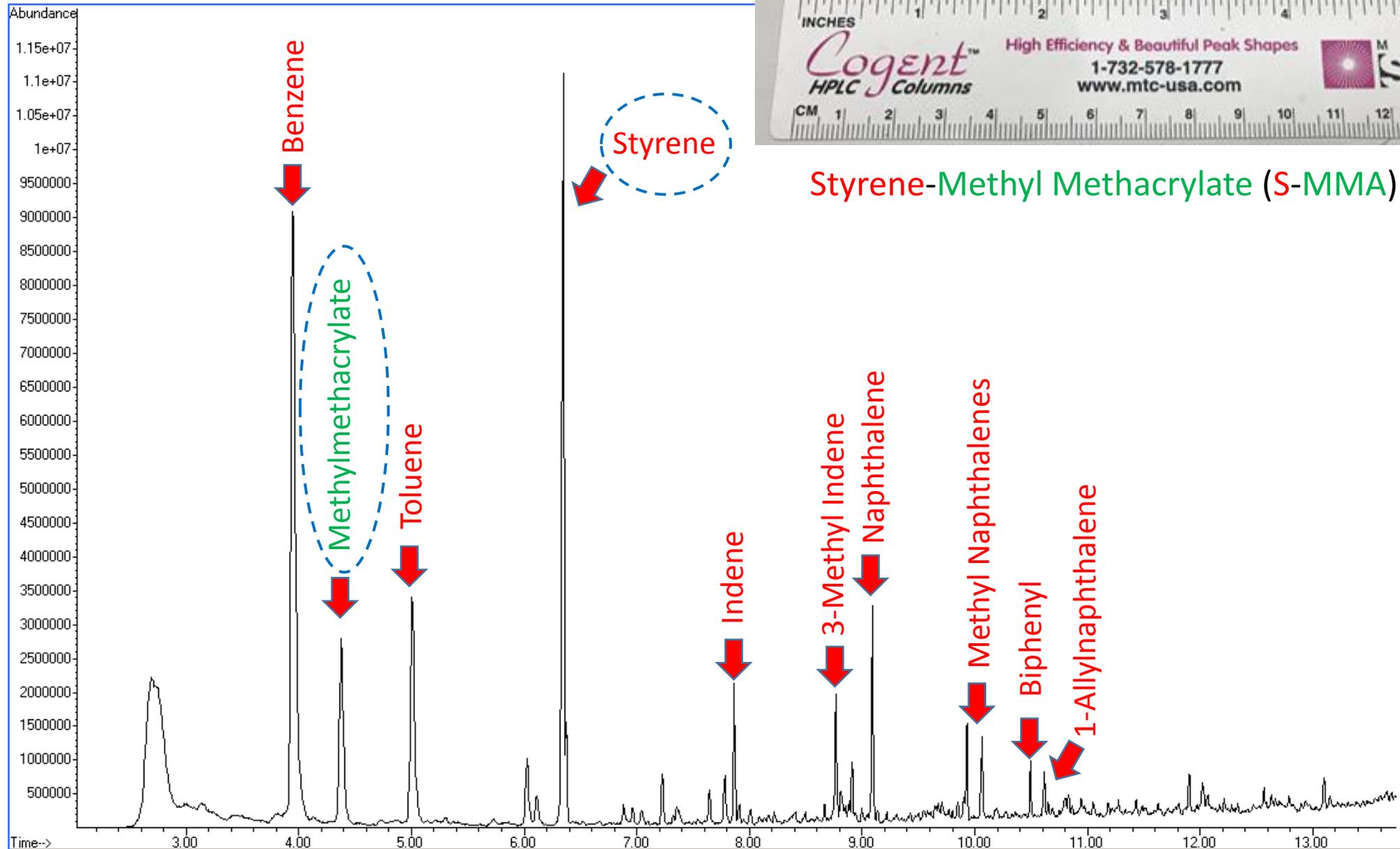
*Cyclization of PVC: a) removal of HCl, b) rearrangement and cyclization, c) elimination of side chains.*



## Natural Rubber



# Flexible Ruler



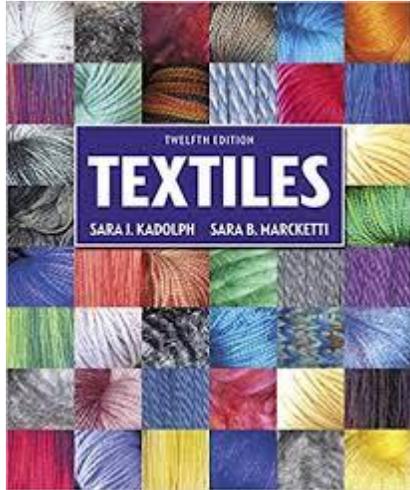
Styrene-Methyl Methacrylate (S-MMA)

## Collaborative Studies



It literally takes a village..

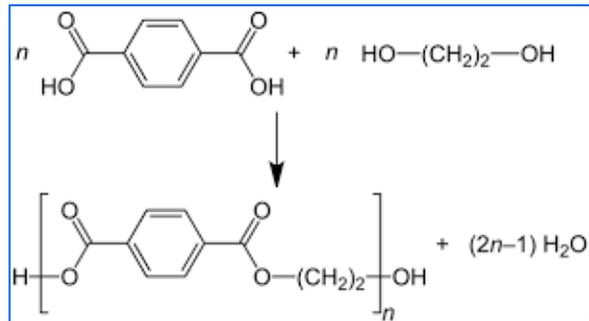
# Polymer IDs in Textiles



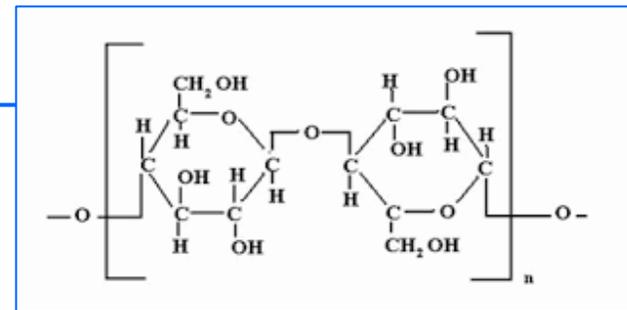
Dr. Steve Carr



# Fabric Sample 1



Polyethylene Terephthalate (PET)

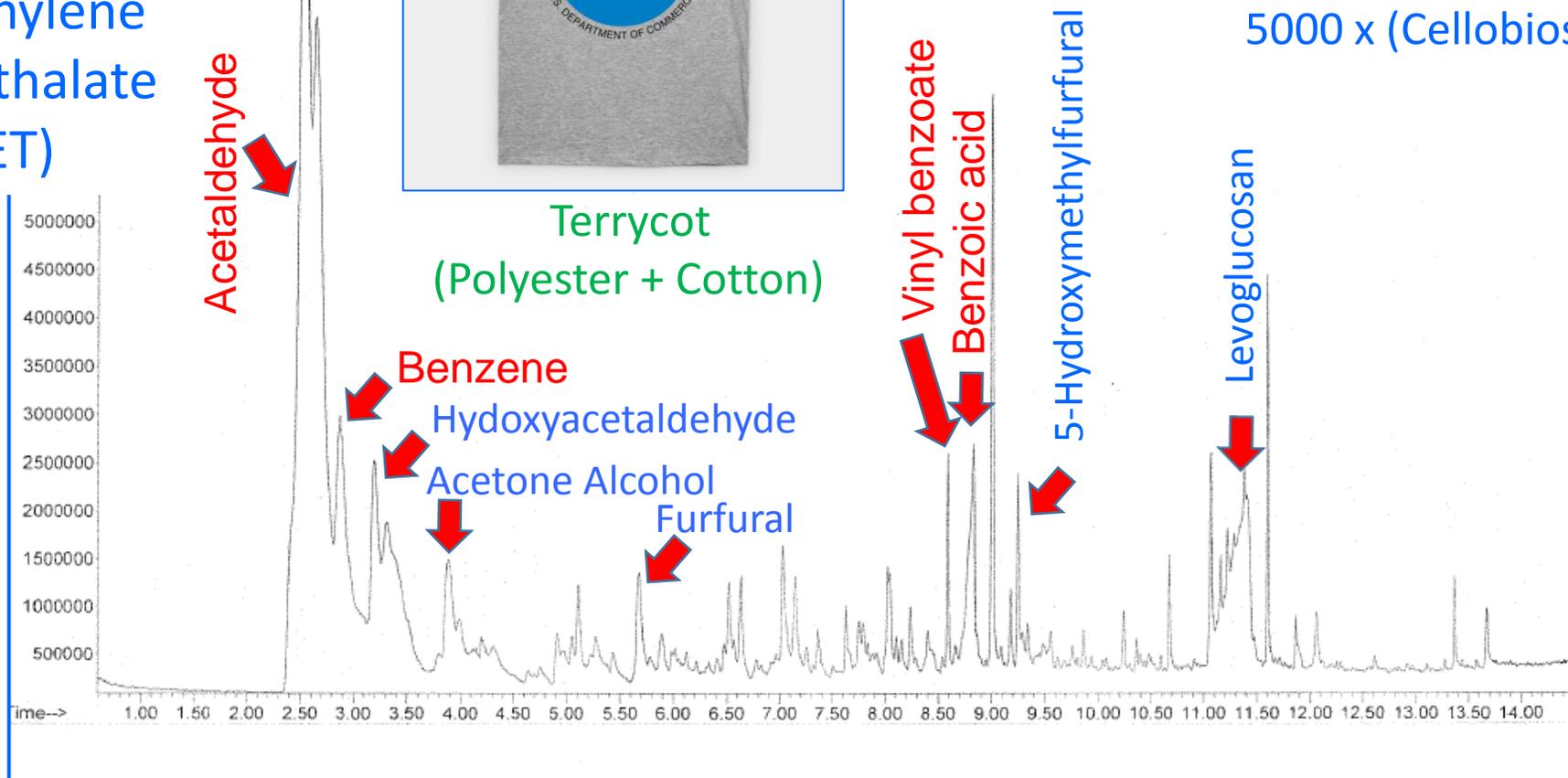


Cotton

5000 x (Cellobiose = 2 glucose units)



Terrycot (Polyester + Cotton)

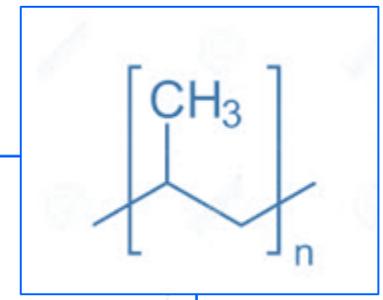


# Fabric Sample 2

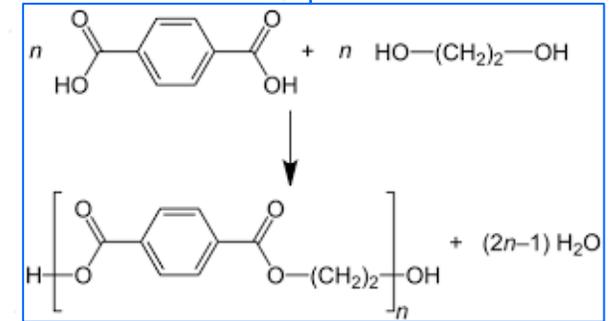
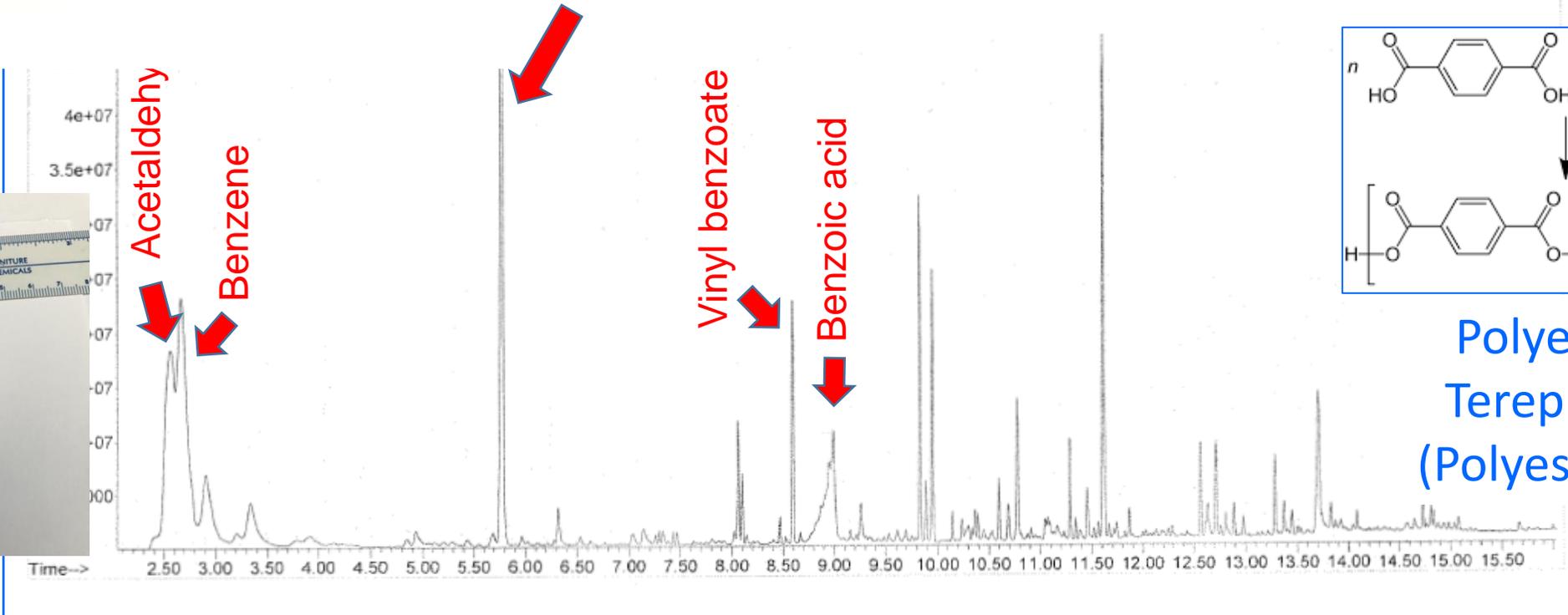


Sofa Coverings

{ Polypropylene  
Polyester (PET) } Fabric Blend

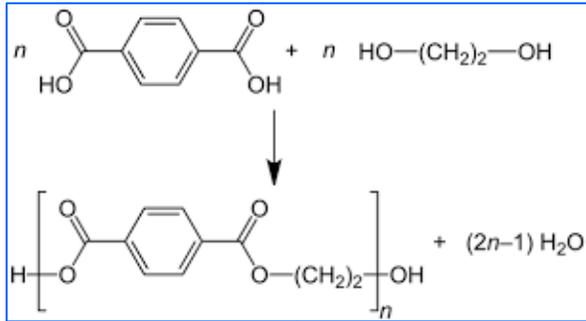


2,4-Dimethyl-1-heptene  
(A Marker Compound of Polypropylene)

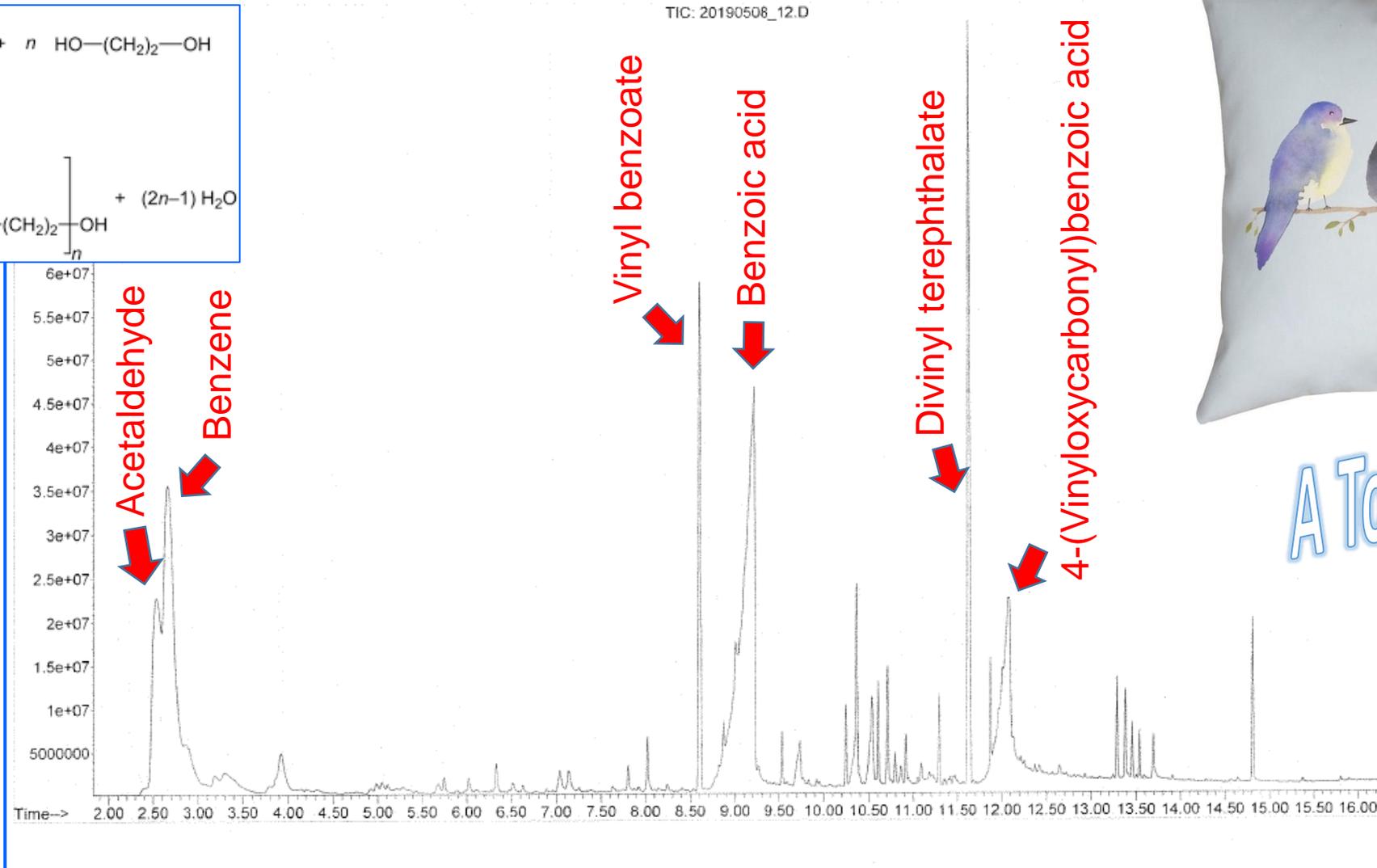


Polyethylene Terephthalate (Polyester) (PET)

# Polyethylene Terephthalate (PET)



# Fabric Sample 3



# Polyester (PET)



A Toss Pillow

Cindy Zipf



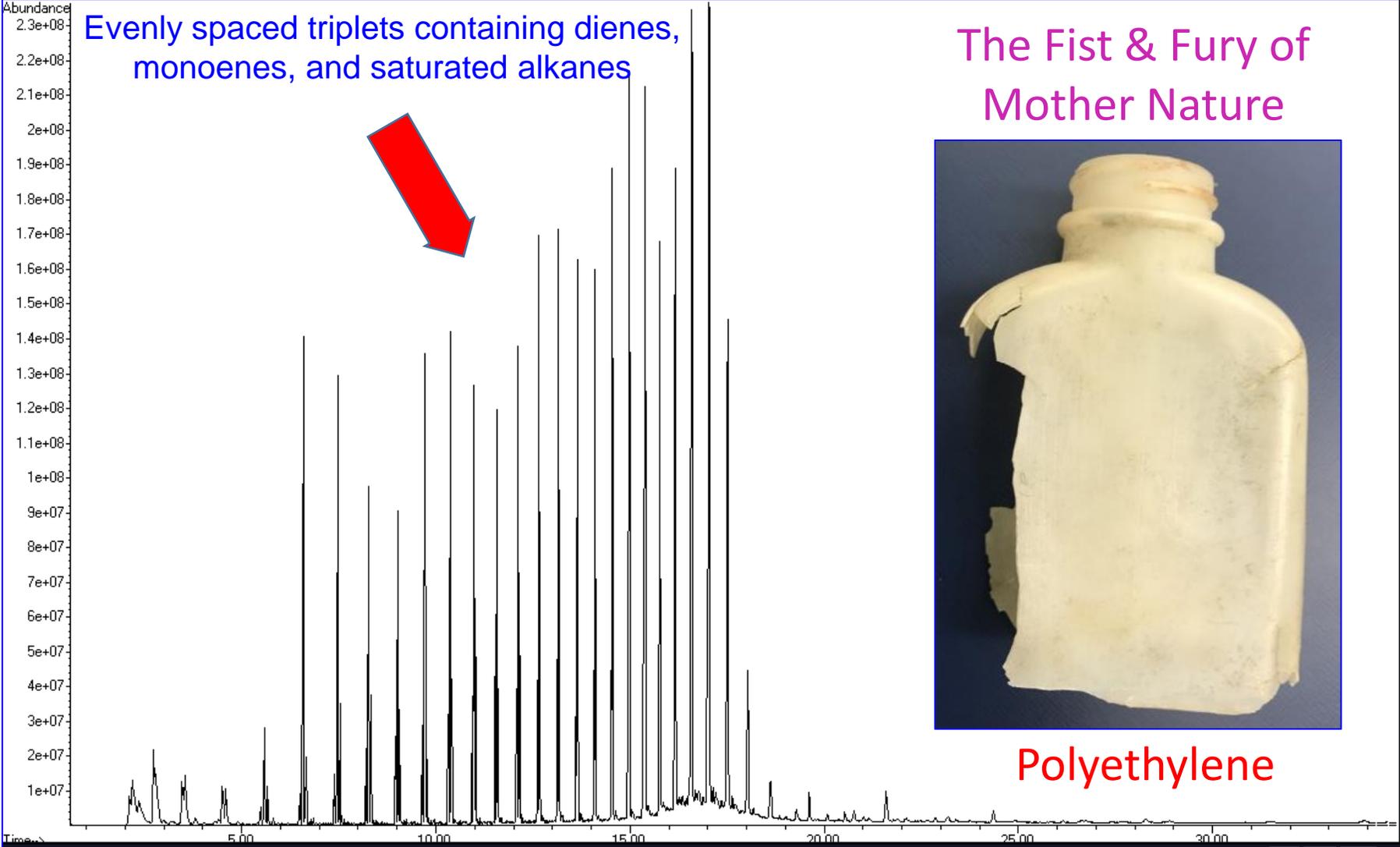
## Plastics from New Jersey



[Dr. Swarna Muthukrishnan](#)



# Weathered Plastic bottle



Evenly spaced triplets containing dienes, monoenes, and saturated alkanes

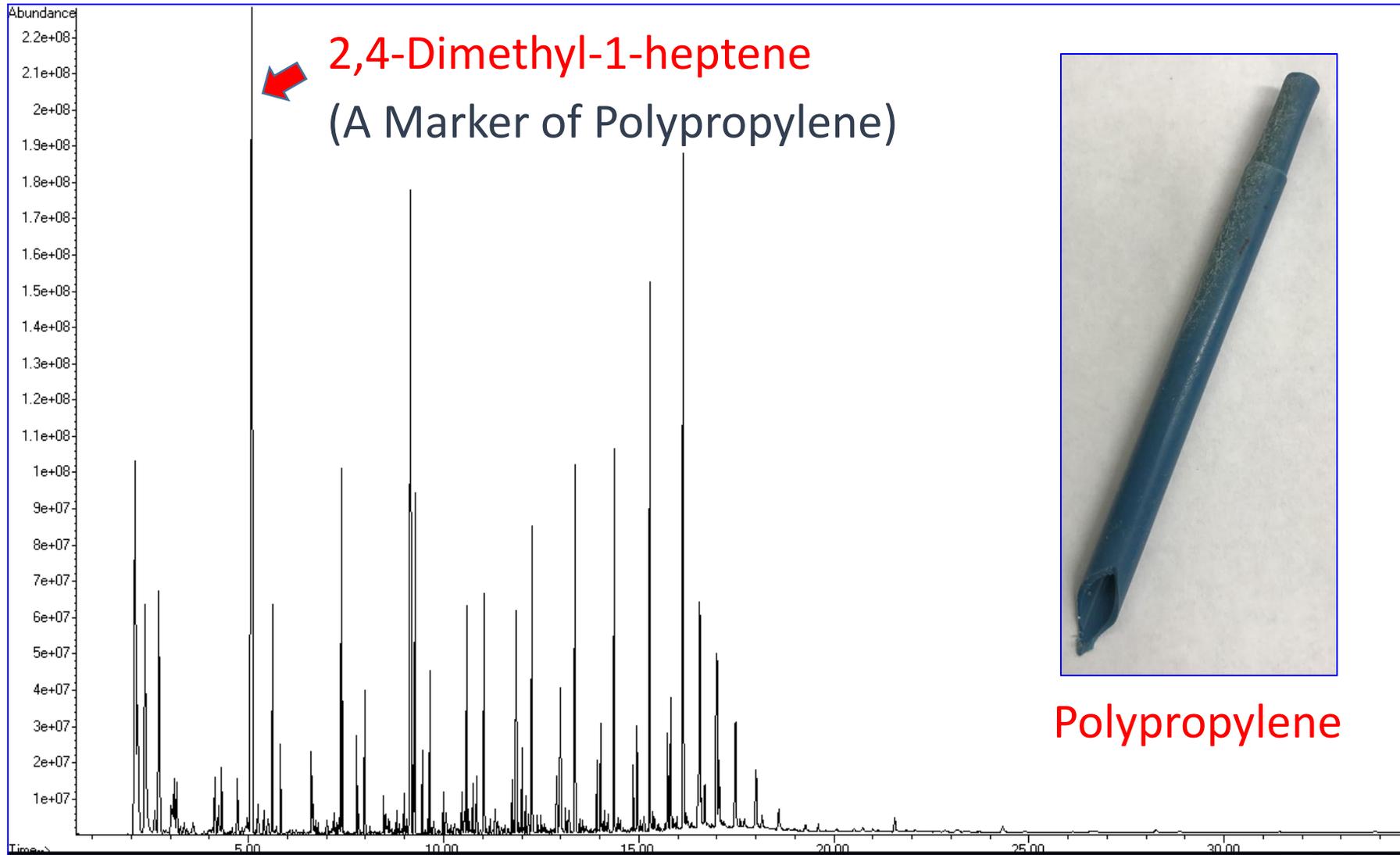
The Fist & Fury of Mother Nature



Polyethylene

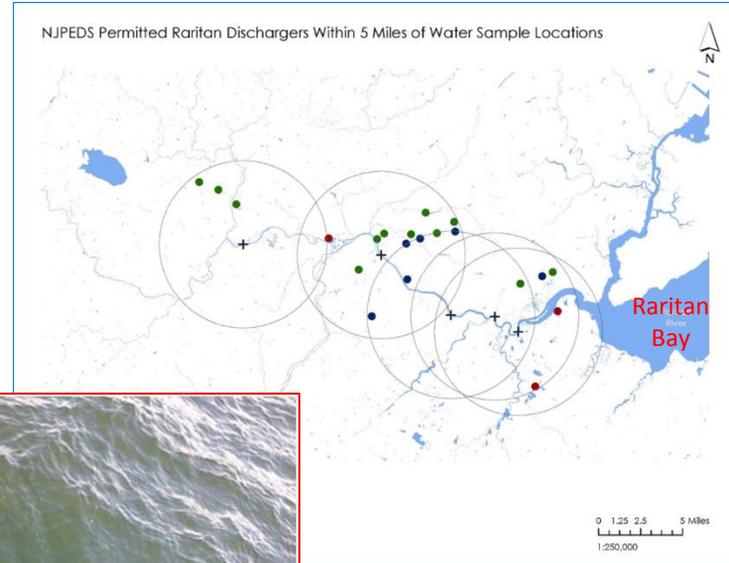
Found on the beach by Clean Ocean Action

# Weathered Ball Point Pen Barrel

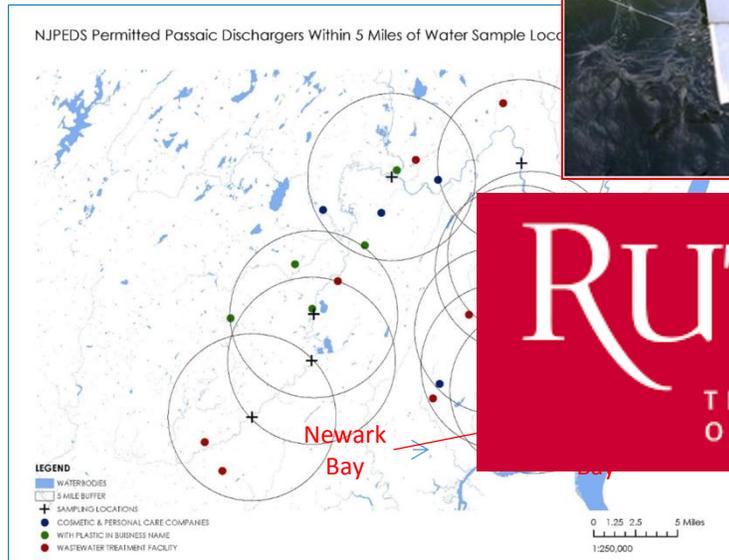


Found on the beach by Clean Ocean Action

# Microplastics from the Raritan and Passaic Rivers in New Jersey



Dr. Keith Cooper & Dr. Beth Ravit



Dr. Brian Buckley



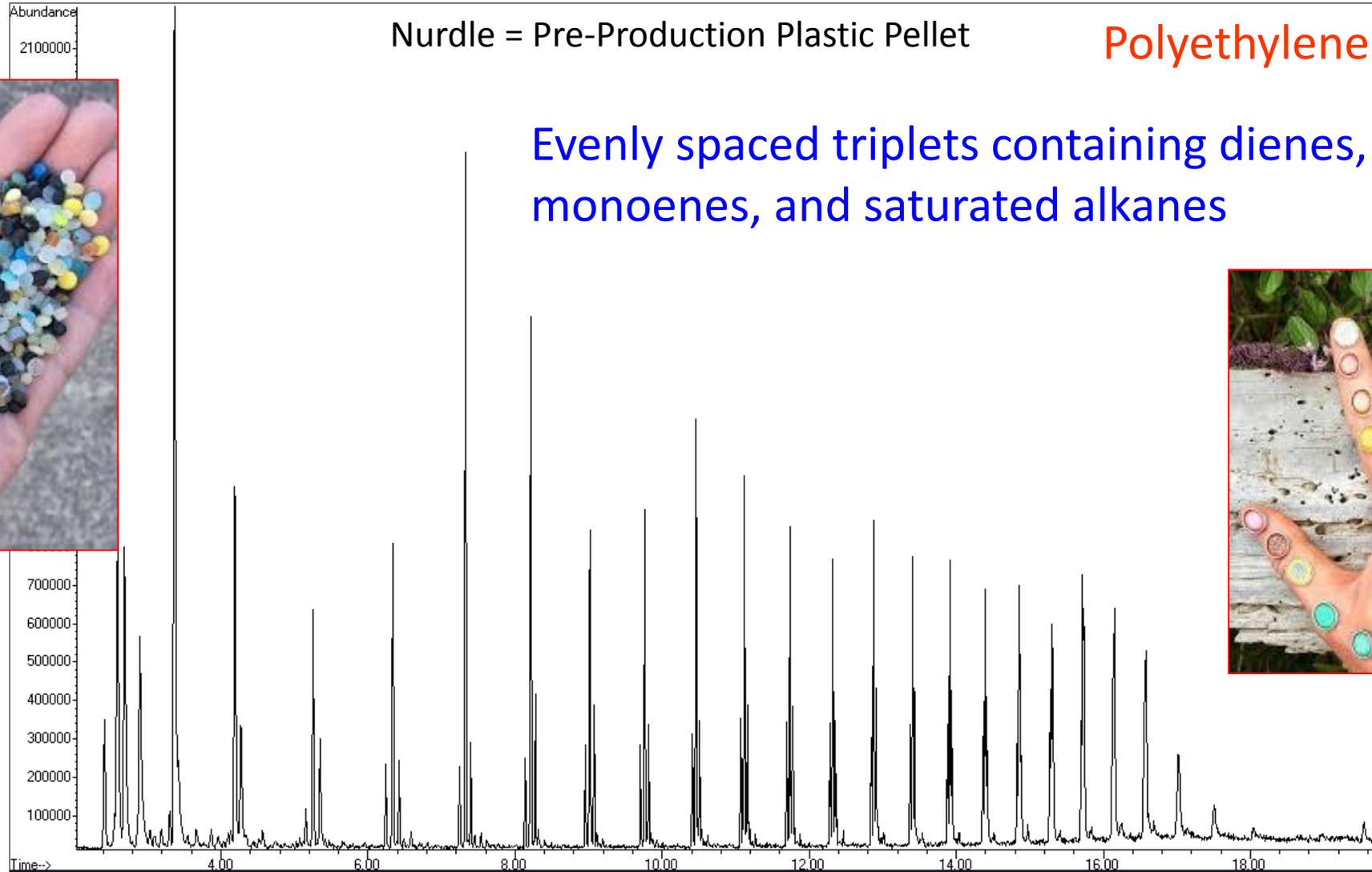
# Rutgers Sample RR3 8/25 Off-White Nurdle



Nurdle = Pre-Production Plastic Pellet

**Polyethylene**

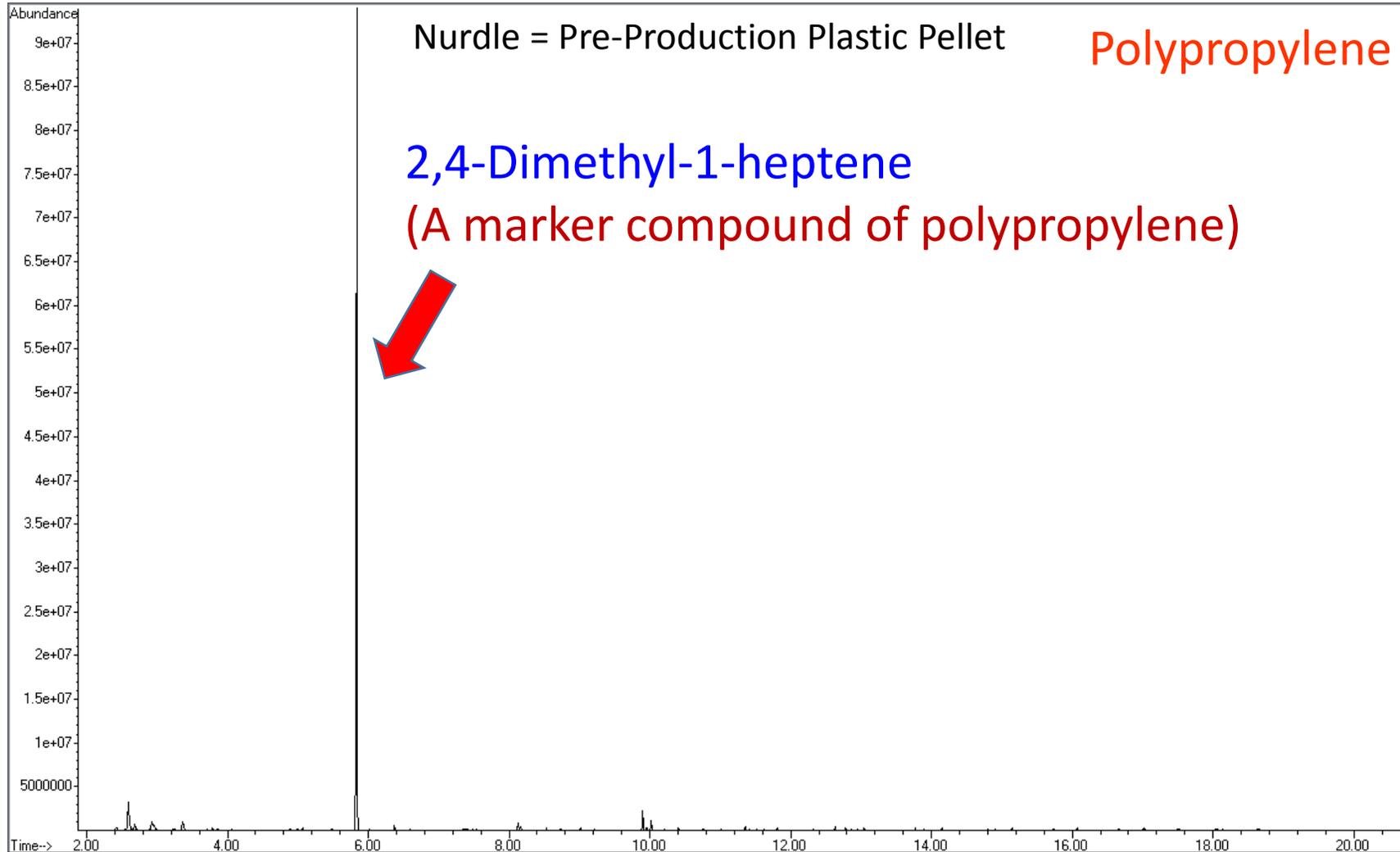
Evenly spaced triplets containing dienes, monoenes, and saturated alkanes



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# Rutgers Sample RR3 8/25 Semi-Transparent Nurdle

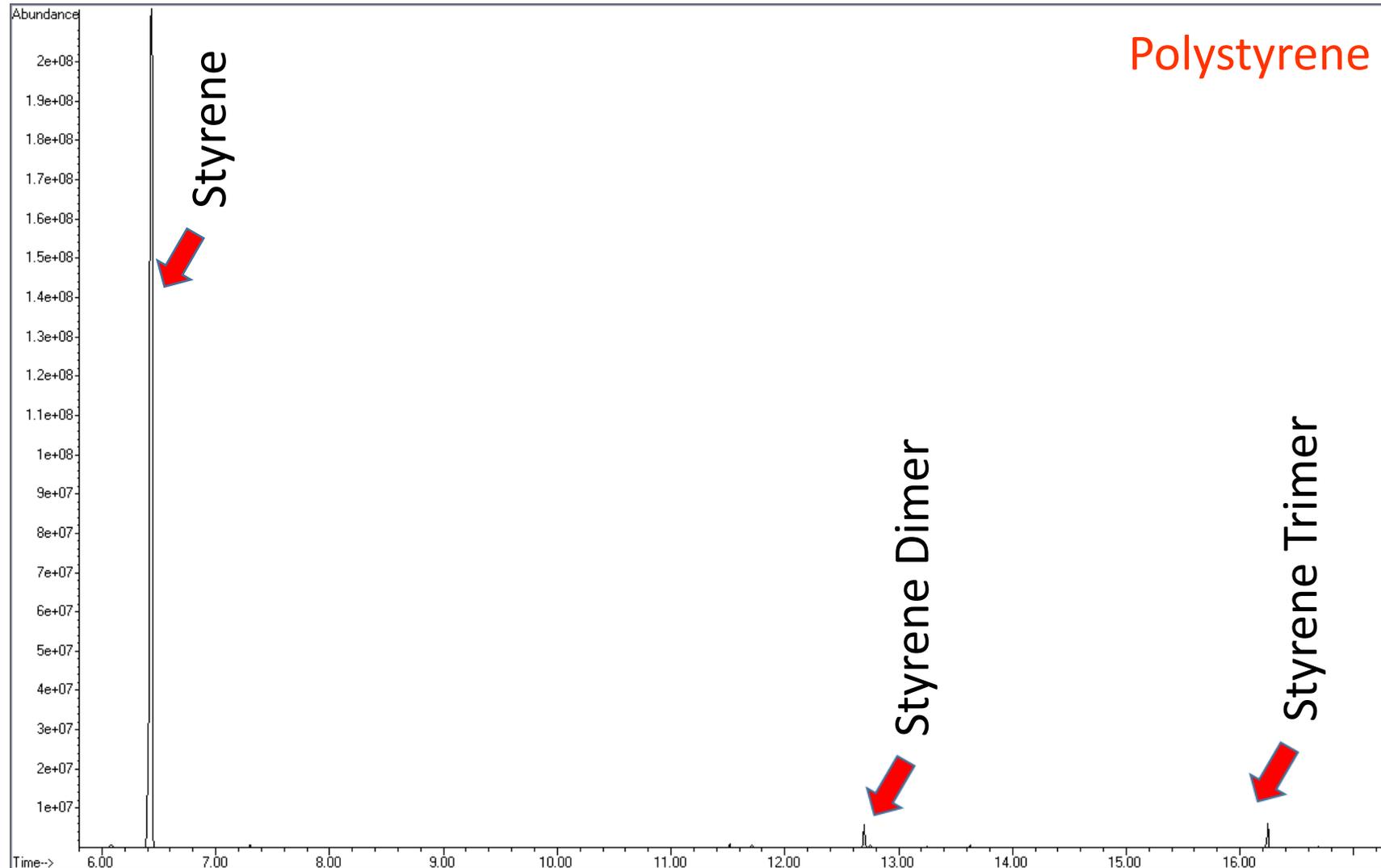


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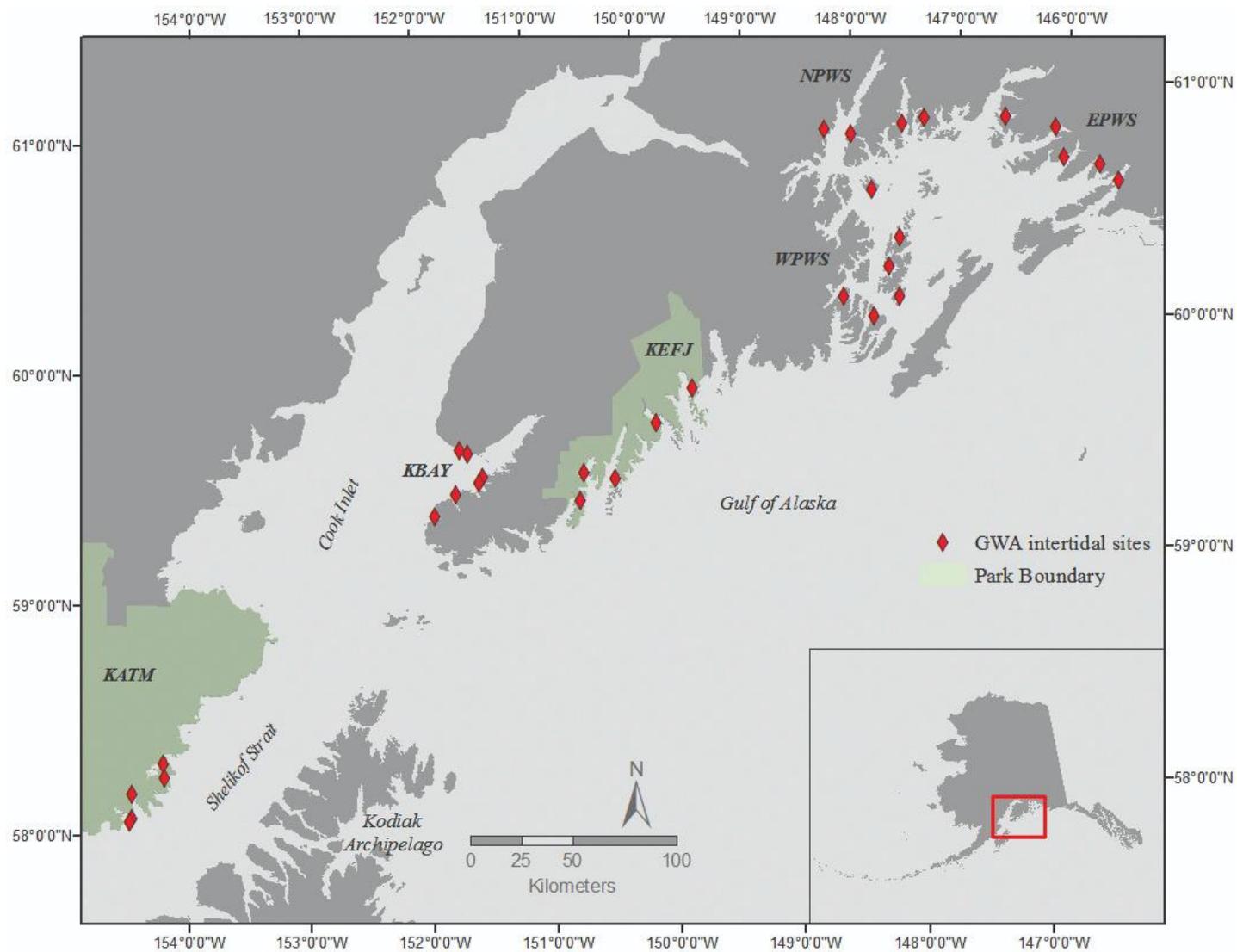
# Rutgers Sample RR3 8/25

## A Small, Round Off-White Foam



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# Plastics from the Remote Alaska Beaches

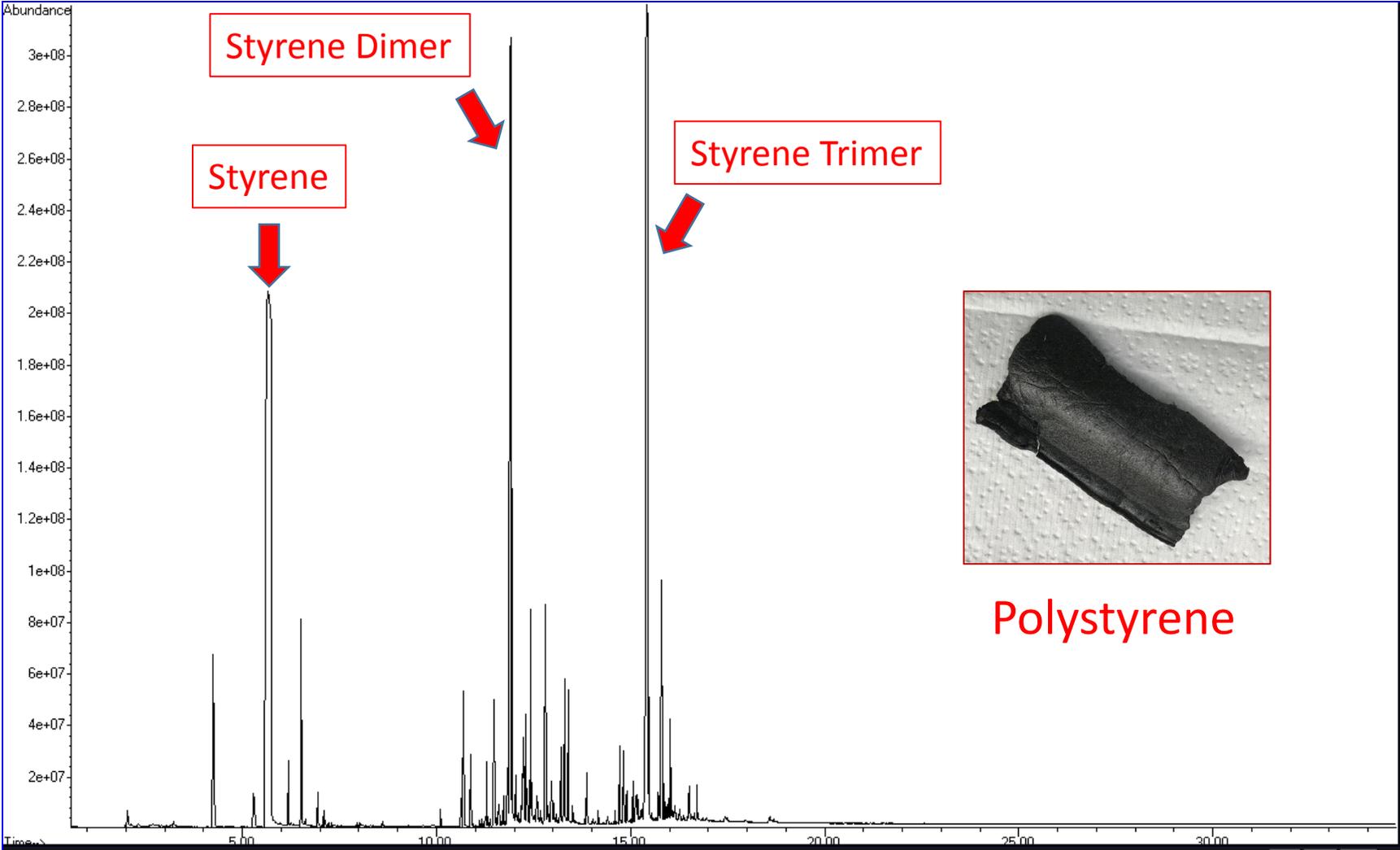


Kimberly A Kloecker

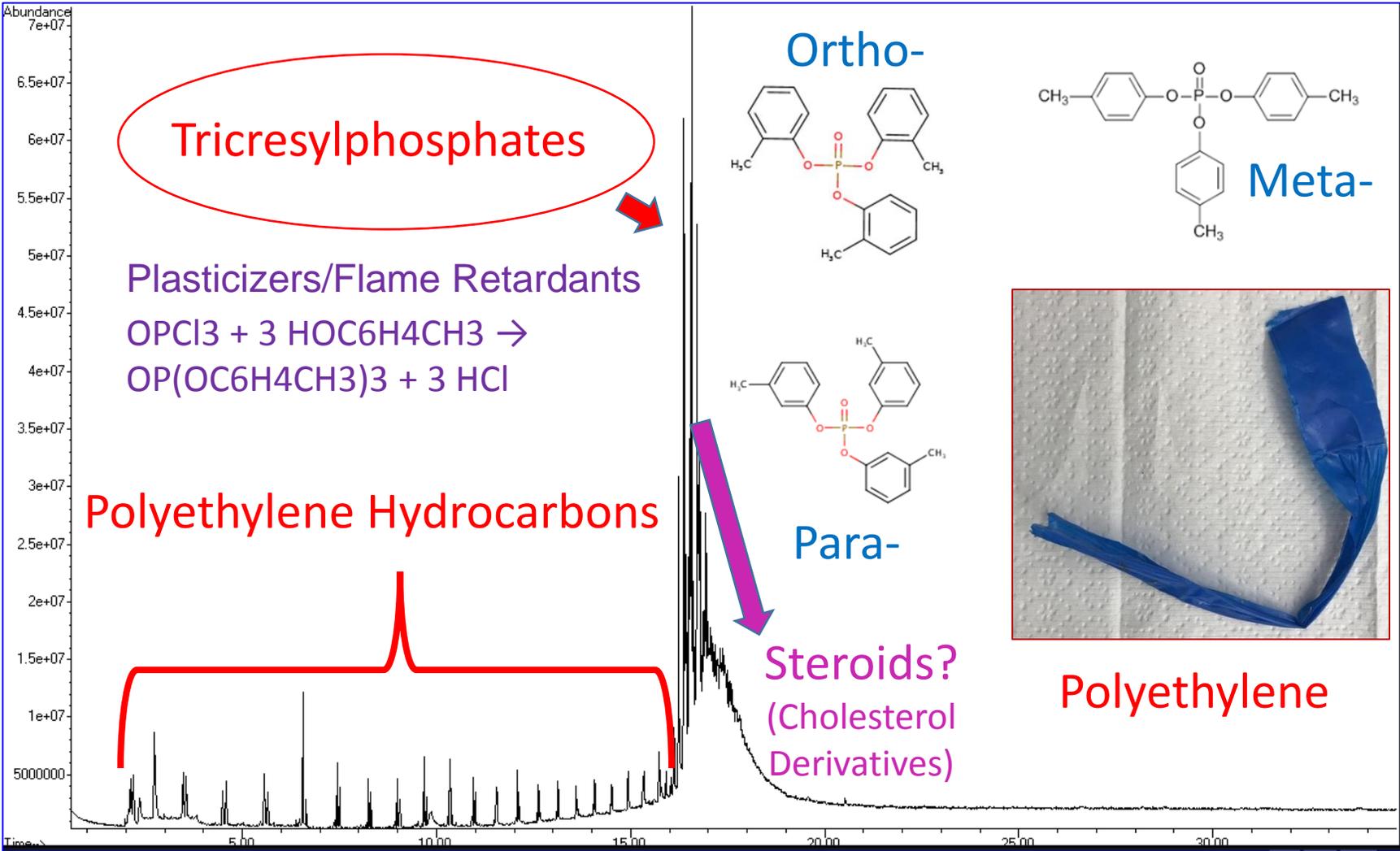


Ecologist, USGS  
Alaska Science Center  
Anchorage, Alaska

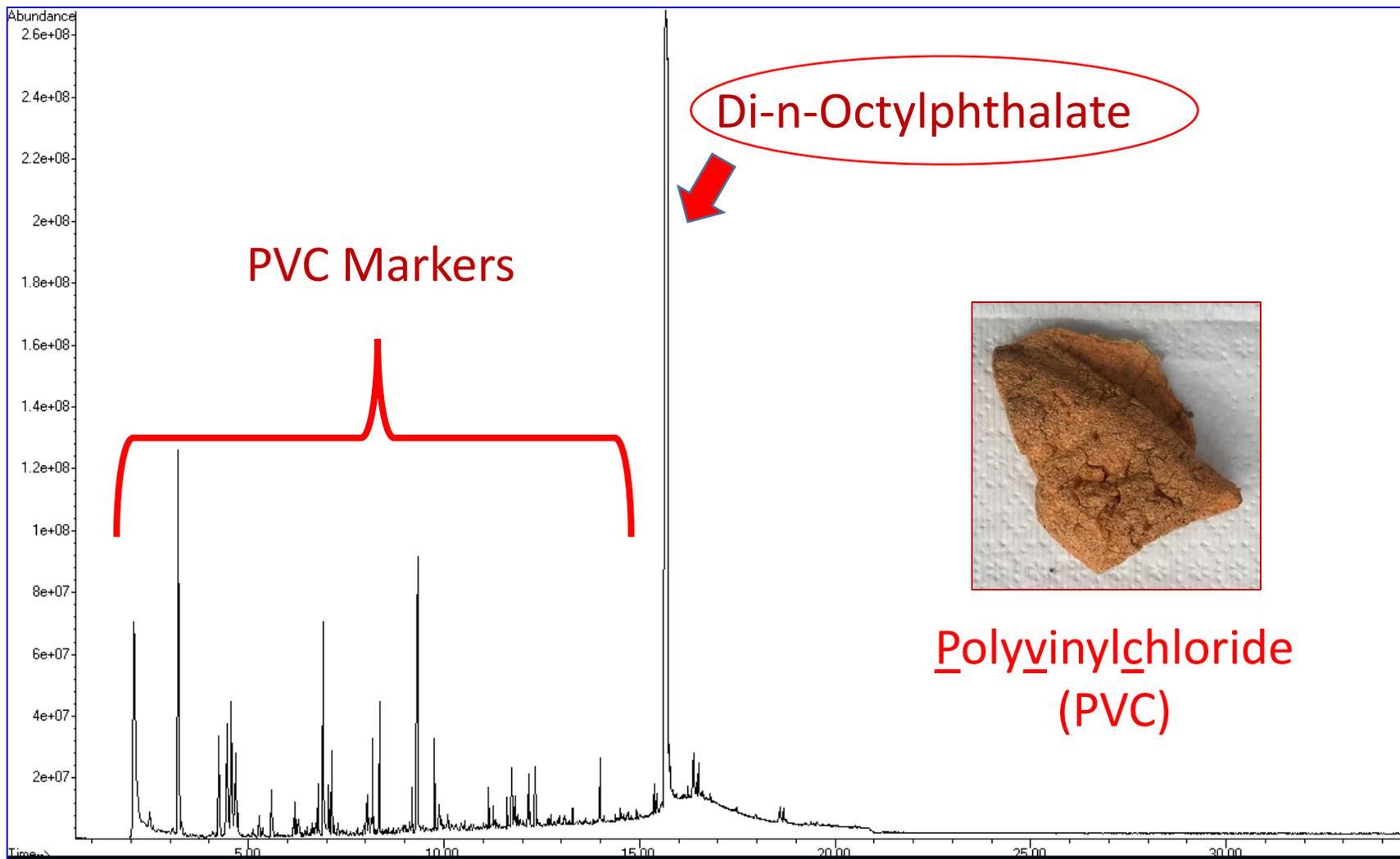
# Alaska Beach - Black Foam



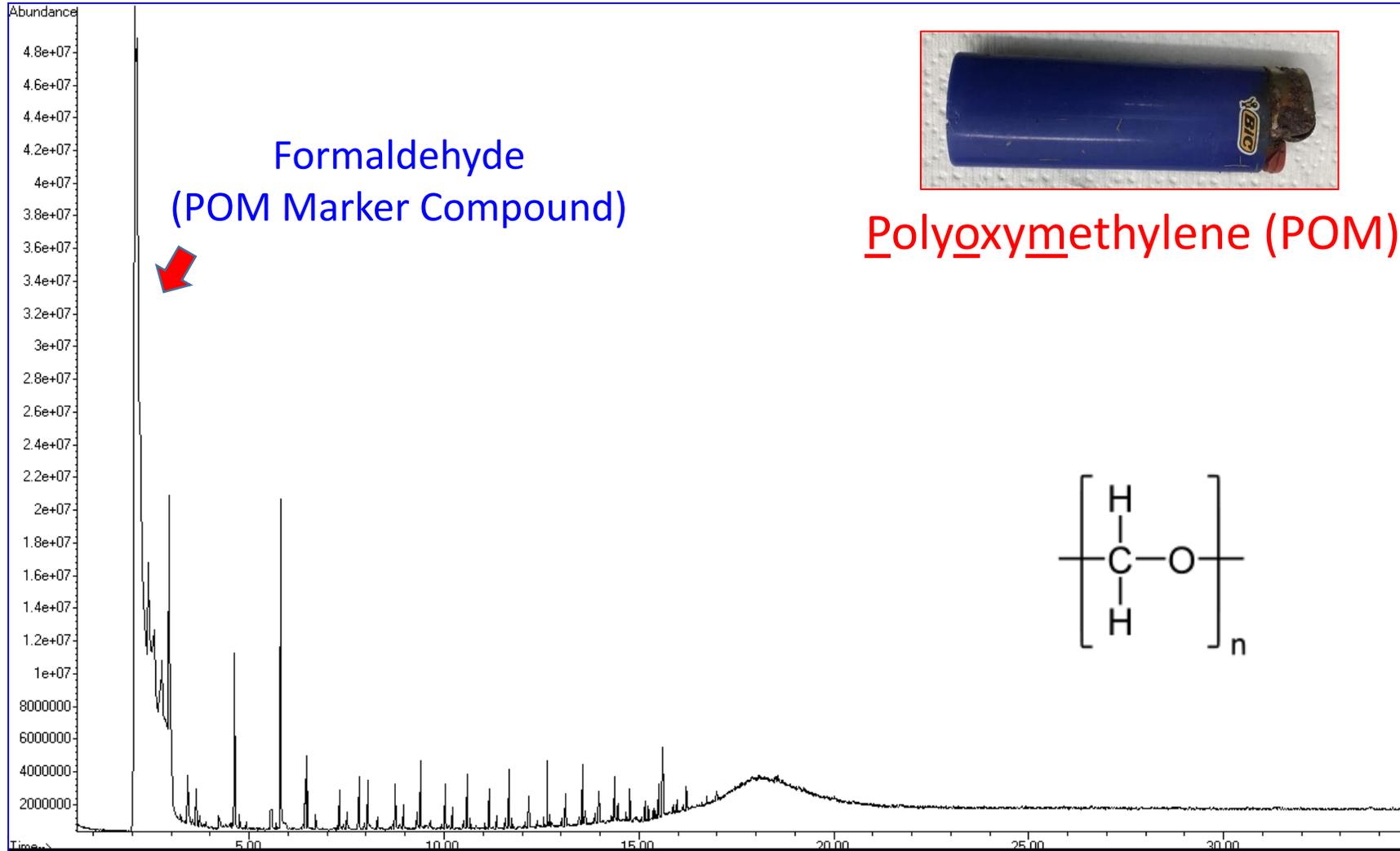
# Alaska Beach - Blue Tape



# Alaska Beach - Orange Foam

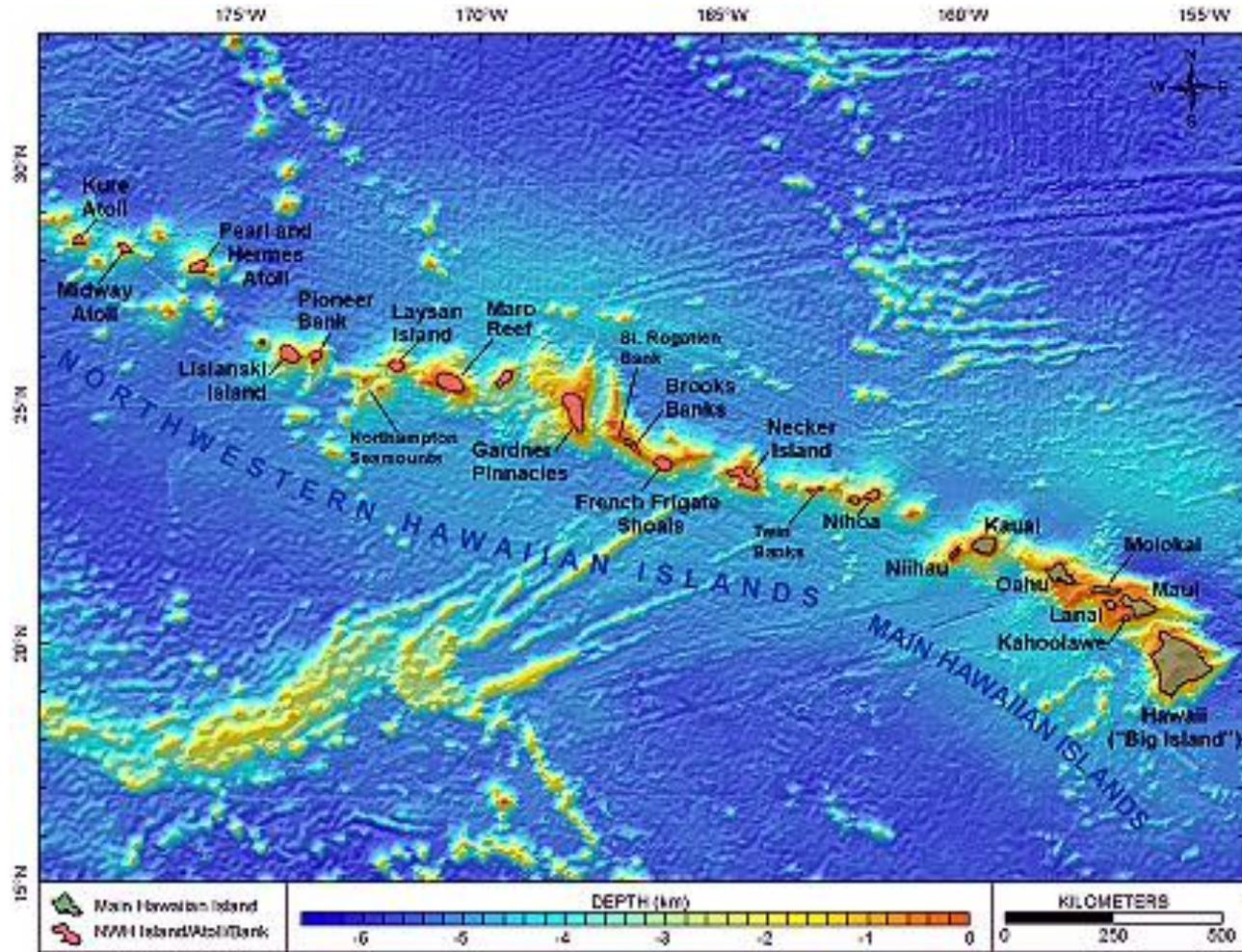


# Alaska Beach - BIC Lighter



# Plastics from the Hawaiian Beaches

Kayla Brignac



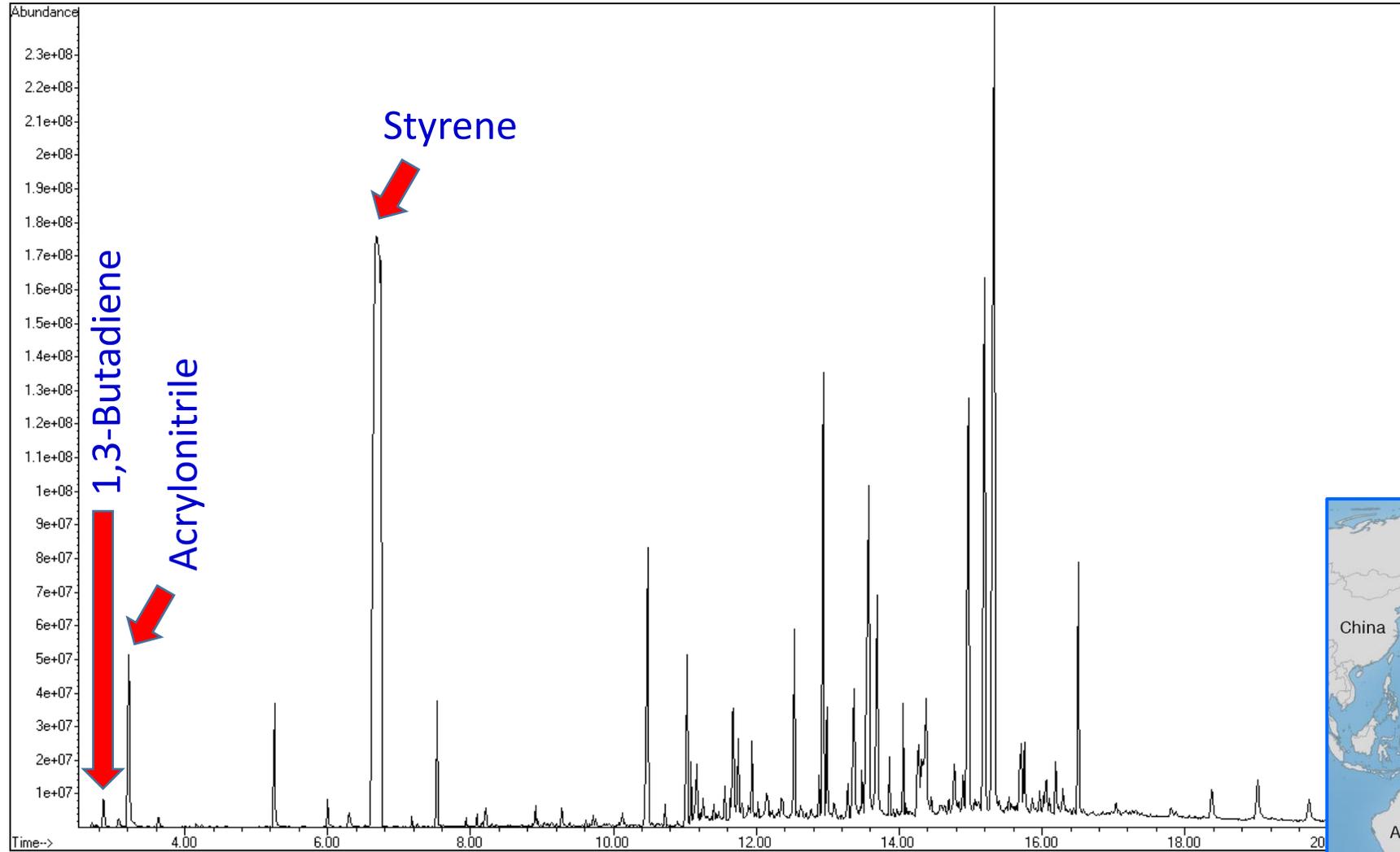
# NIST

Pacific Islands Program  
Island of Oahu

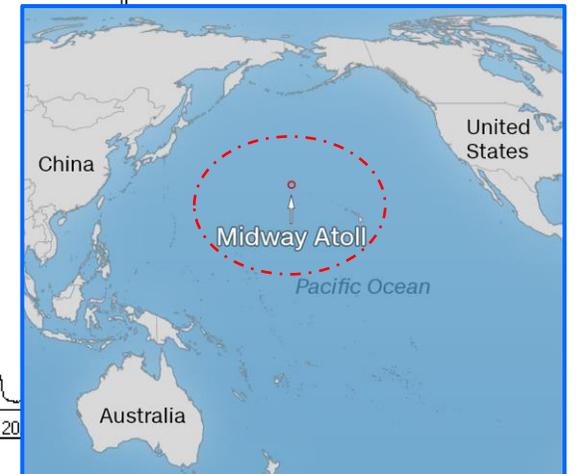
Dr. Jennifer M. Lynch



# Hawaii- Midway 30

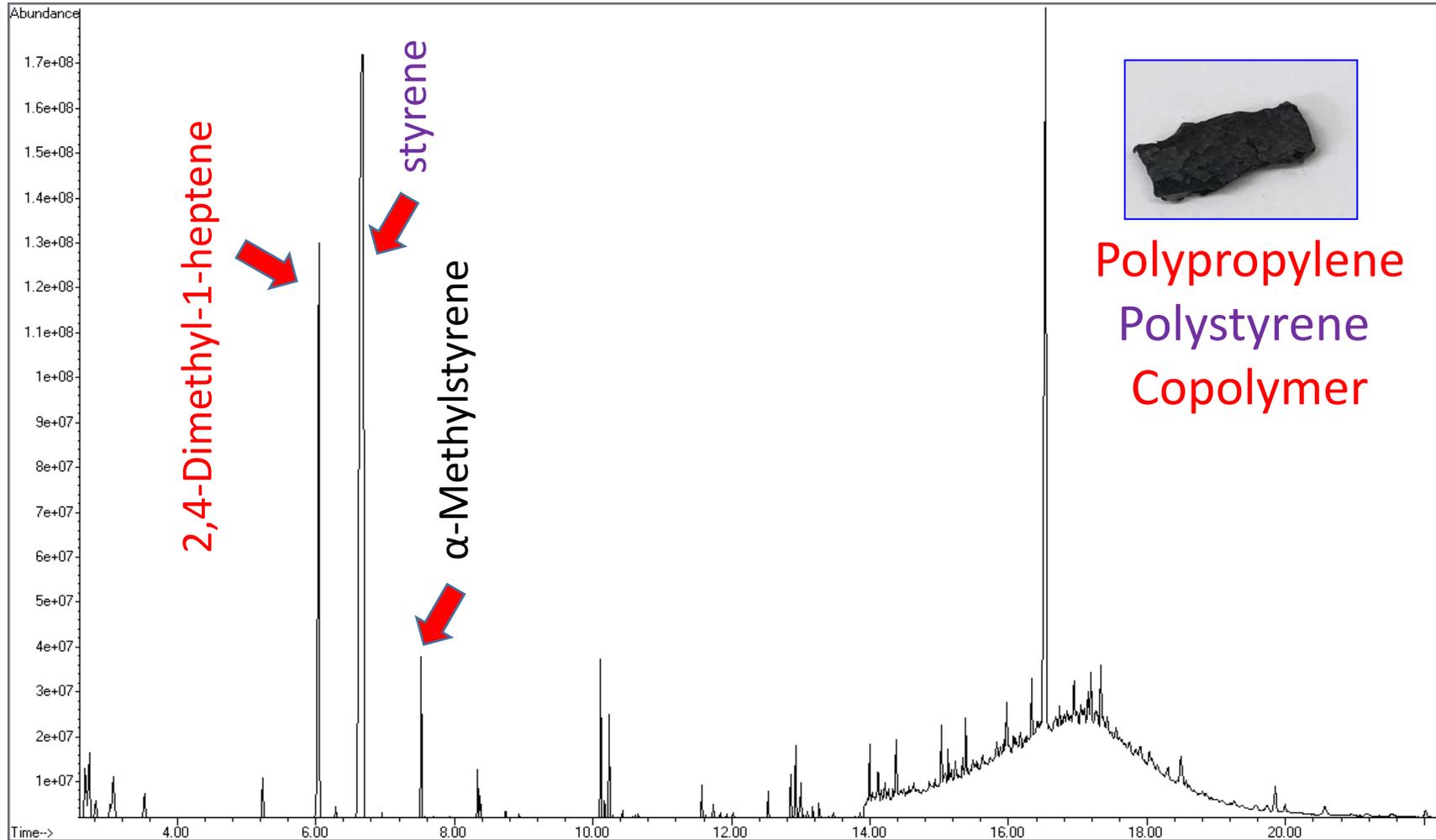


Acrylonitrile  
Butadiene  
Styrene  
Copolymer  
(ABS)



Sample 20180705\_04

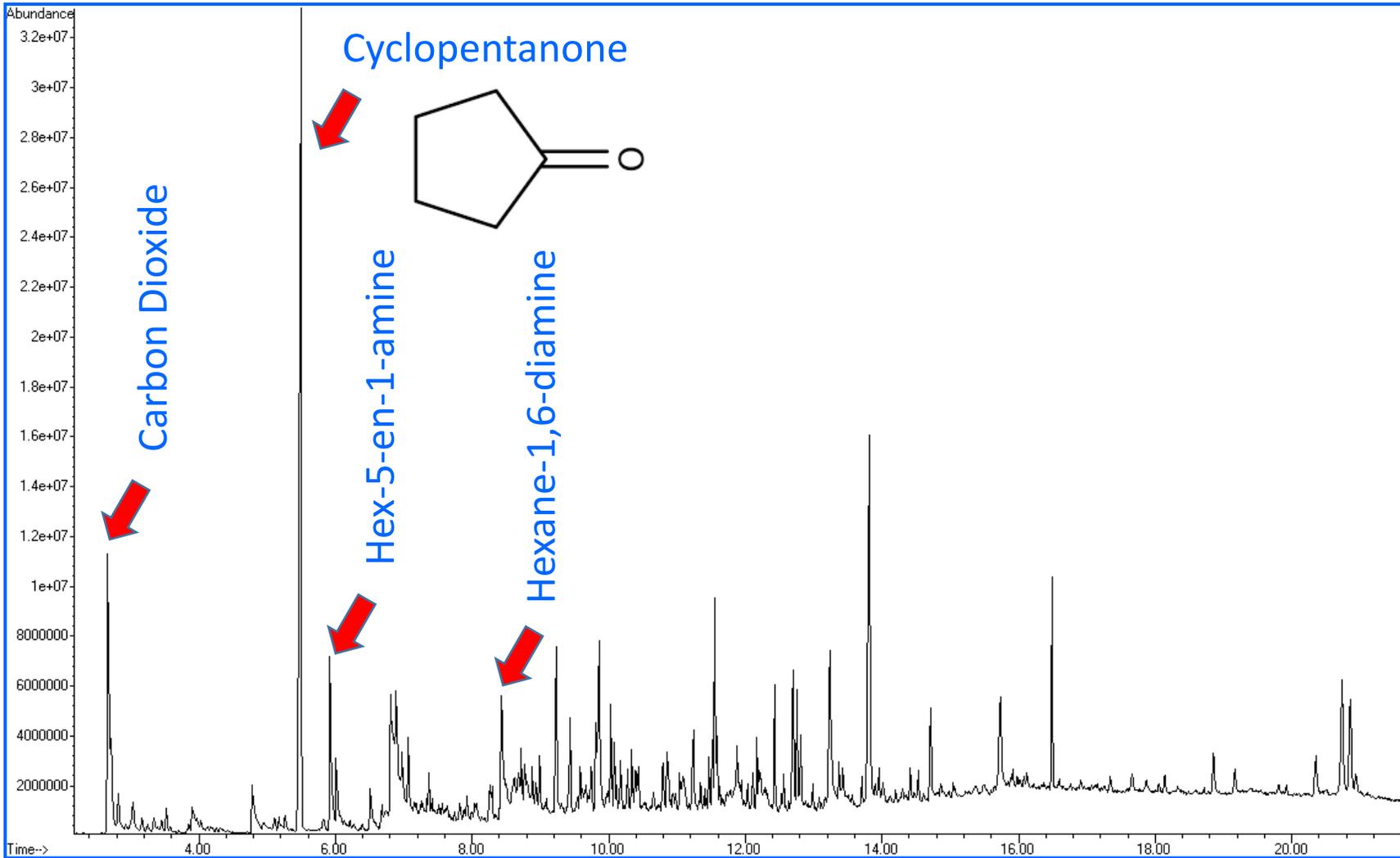
# Hawaii-Lanai



# Hawaii- Ka'ehu #1 31

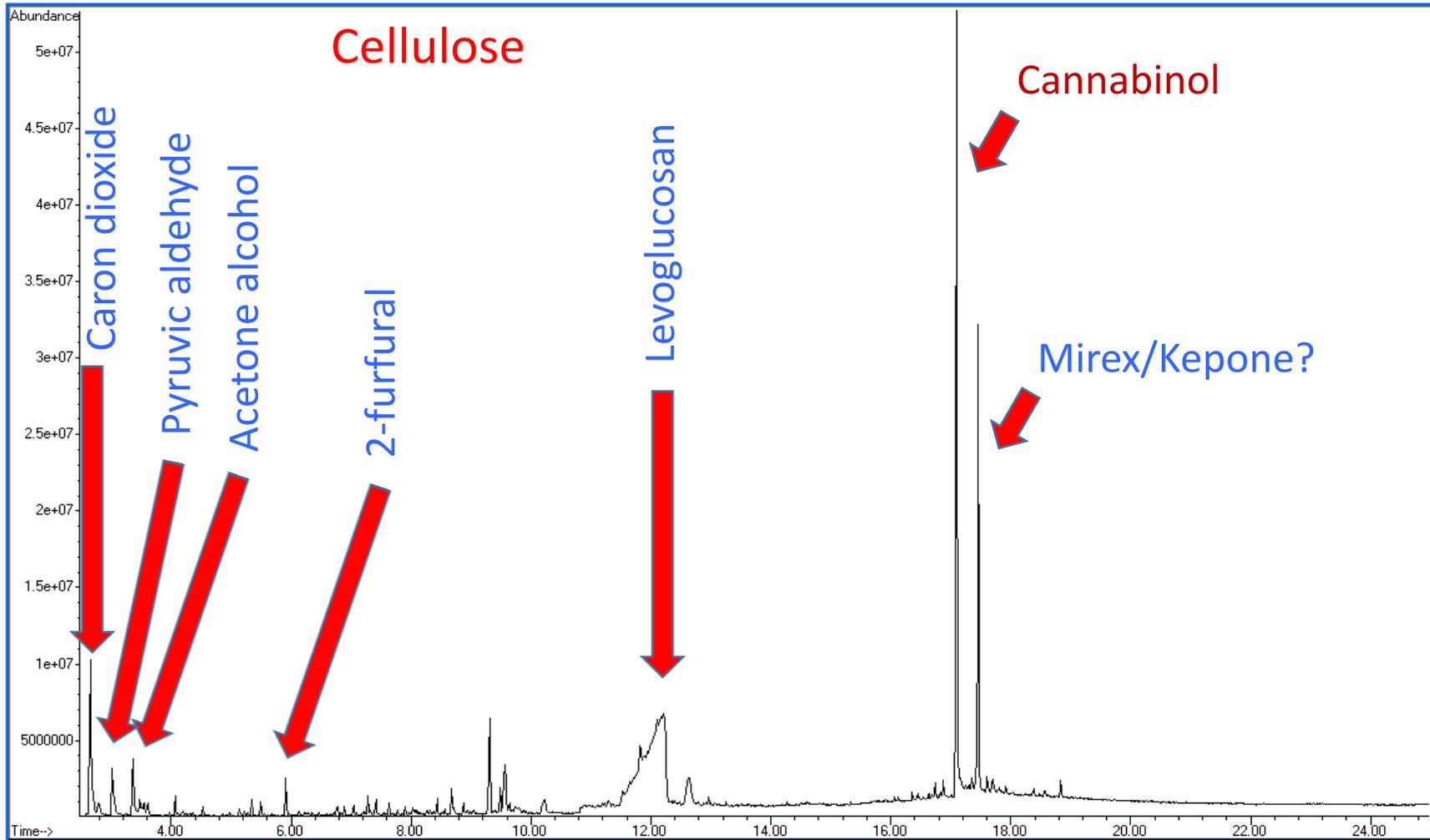


Nylon-6,6



Sample 20180706\_02

# Hawaii-Kiehei #1 15

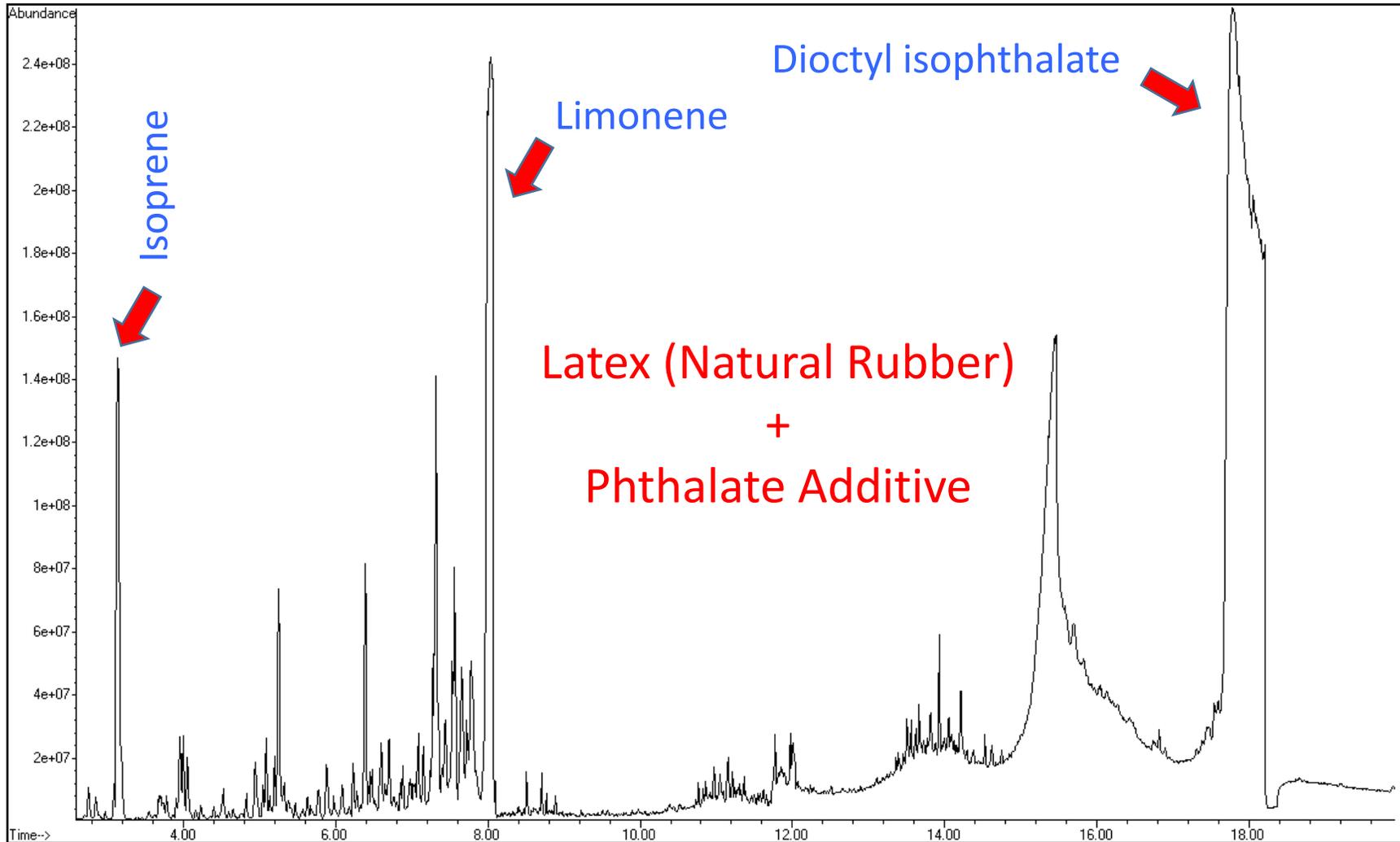


Cellulose  
with  
Cannabinol  
&  
(Mirex/Kepon?)

Sample 20180709\_03

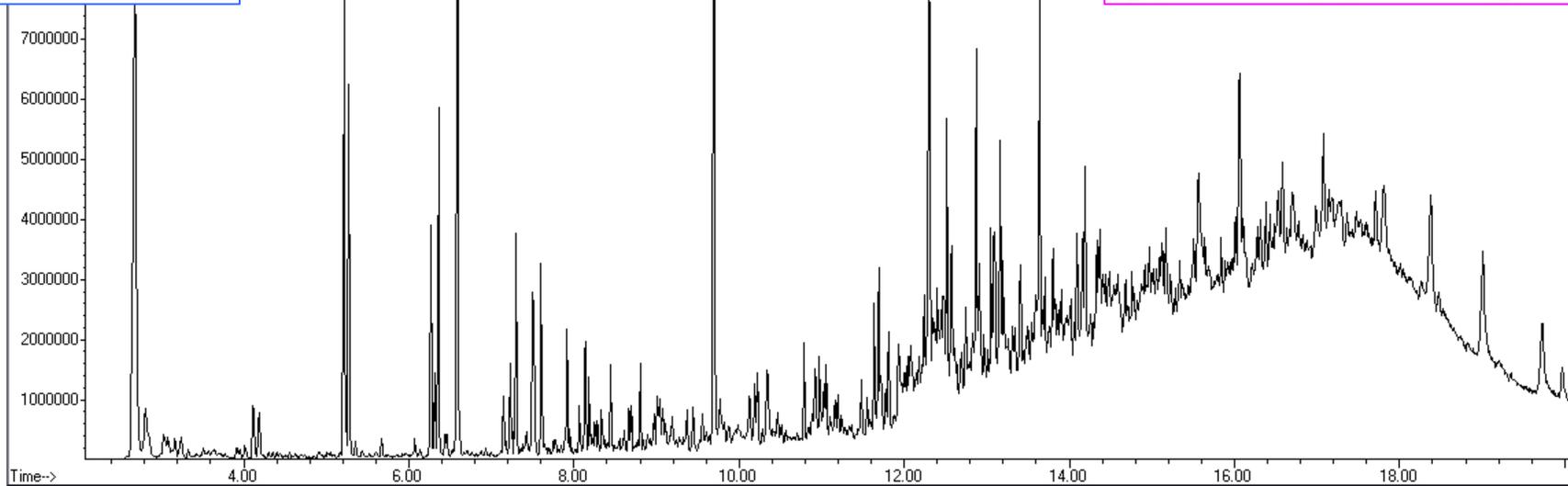
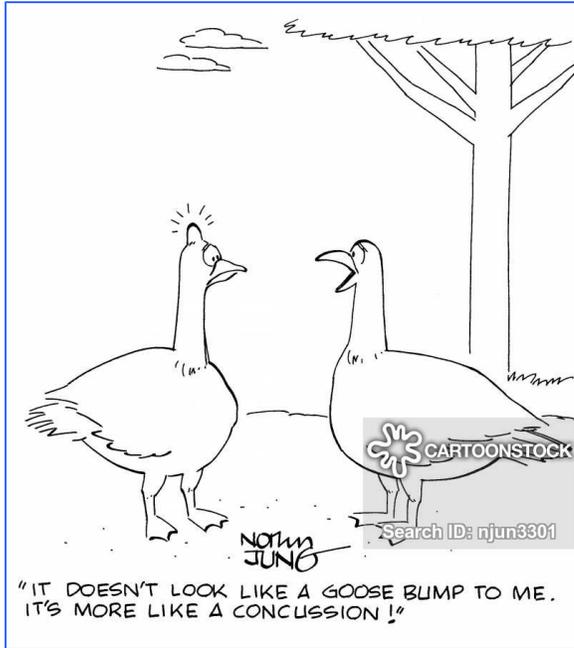


# Hawaii-Waikiki #3 2



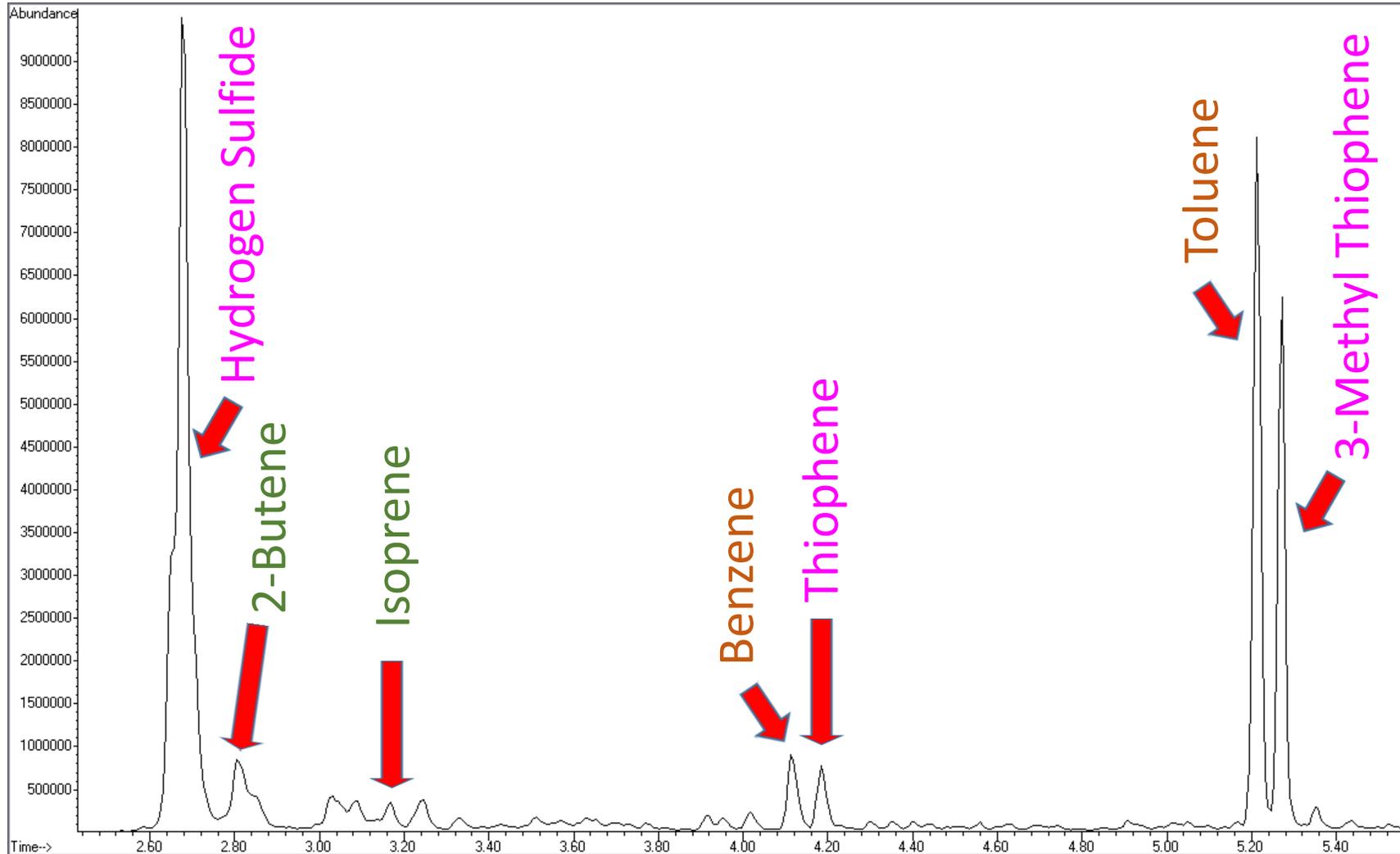
Sample 20180711\_03

# Kihei #1 27 Dark Red Foam

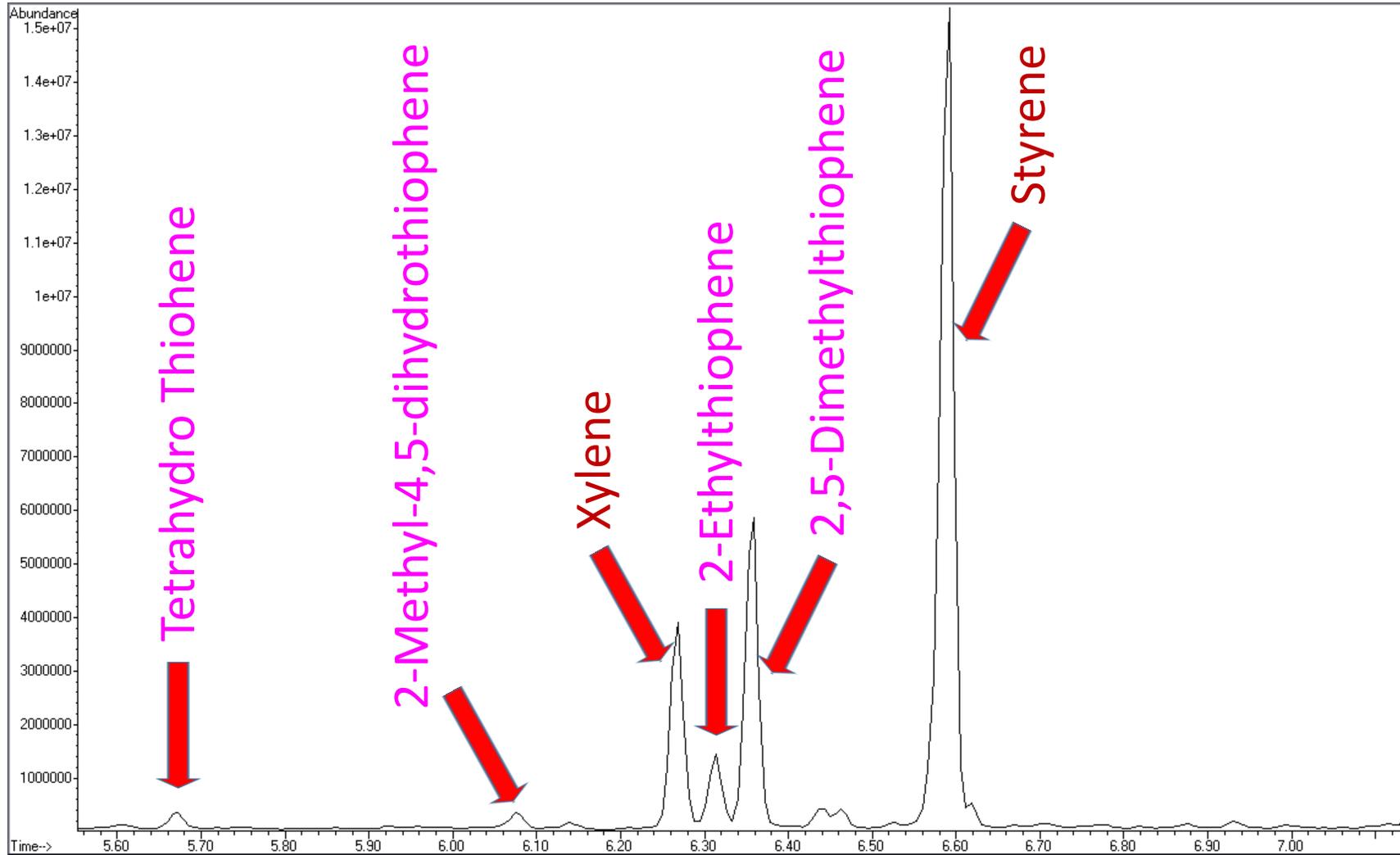


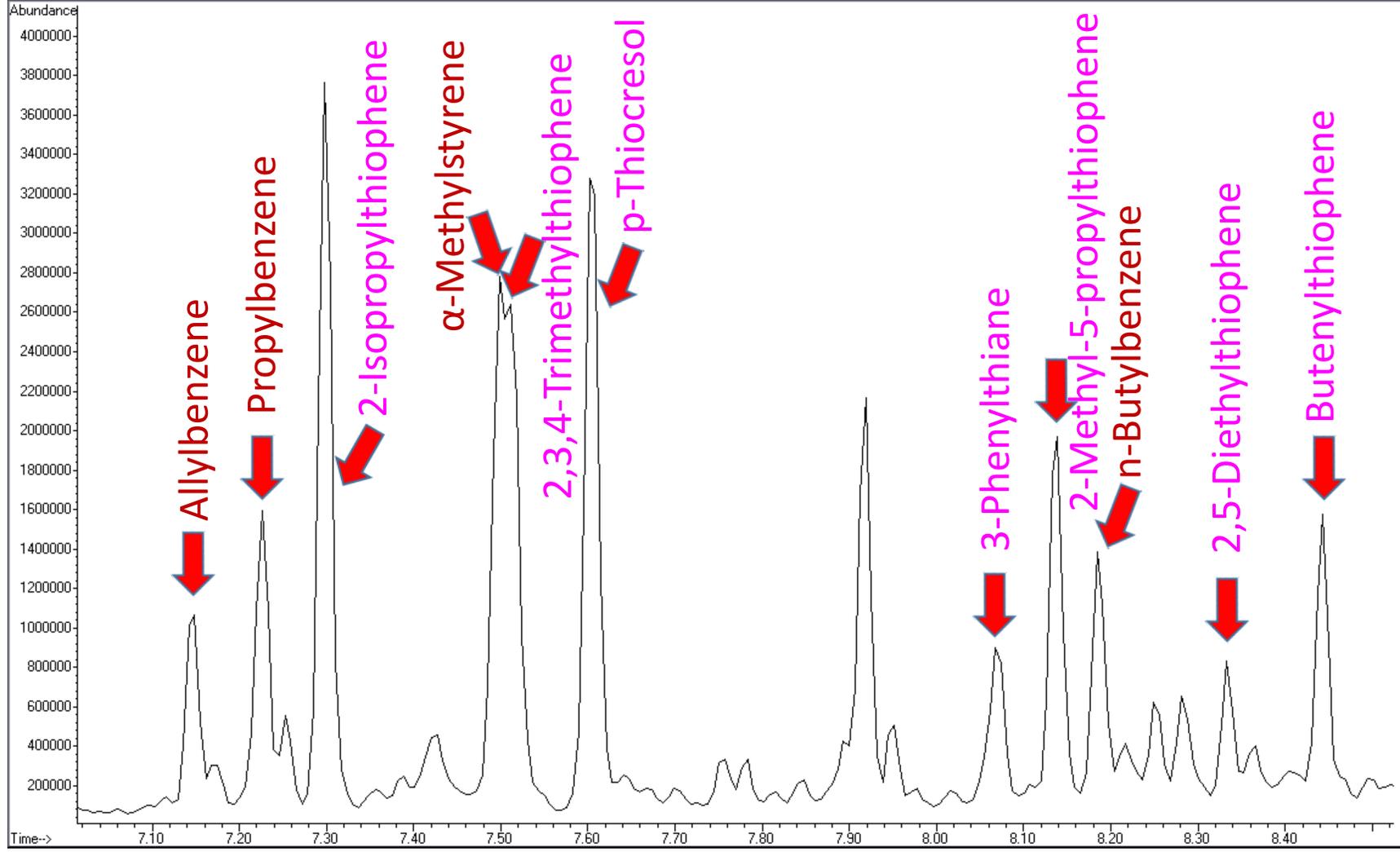
# Examine Different Sections of the Pyrogram

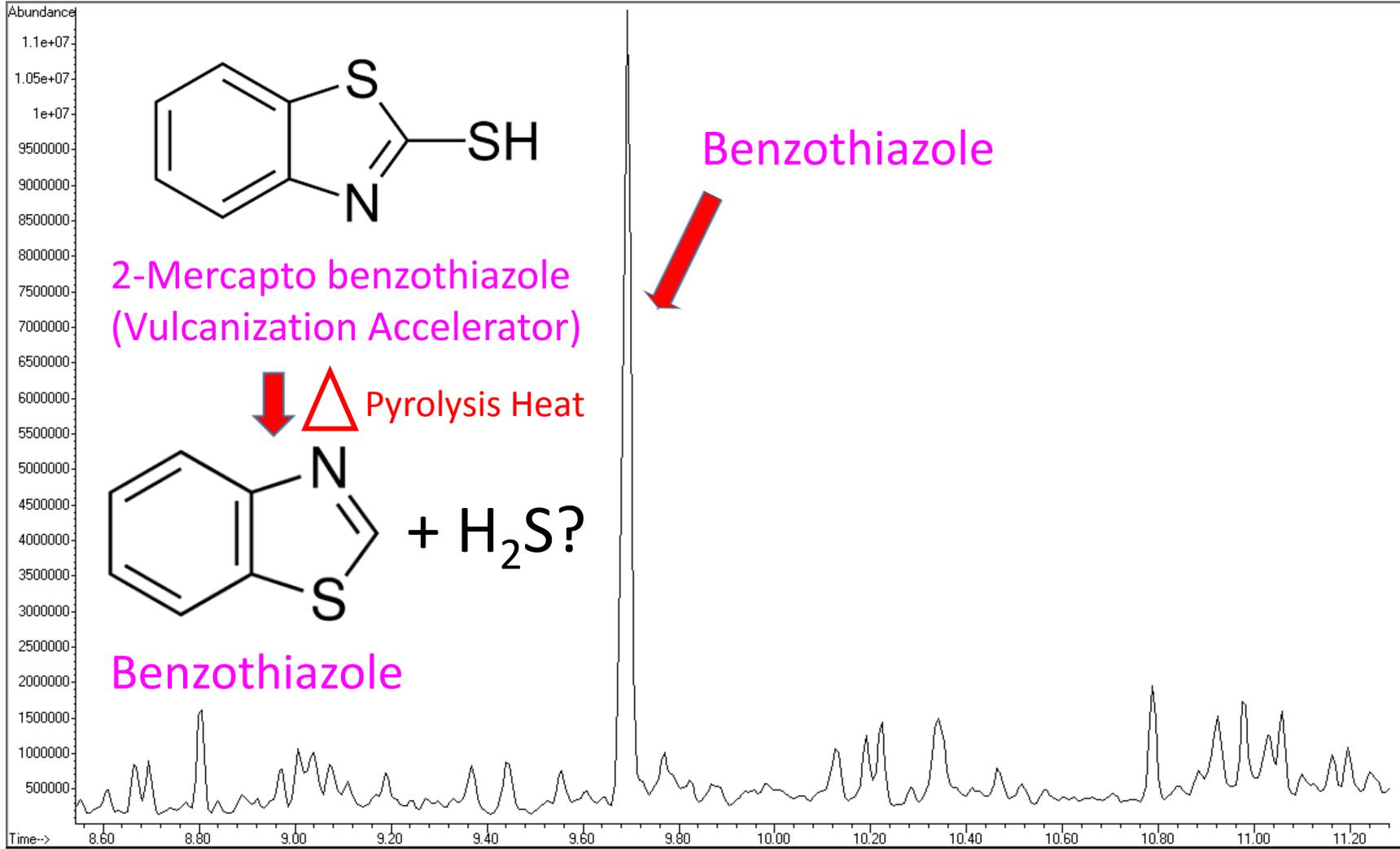
Kihei #1 27  
Dark Red Foam

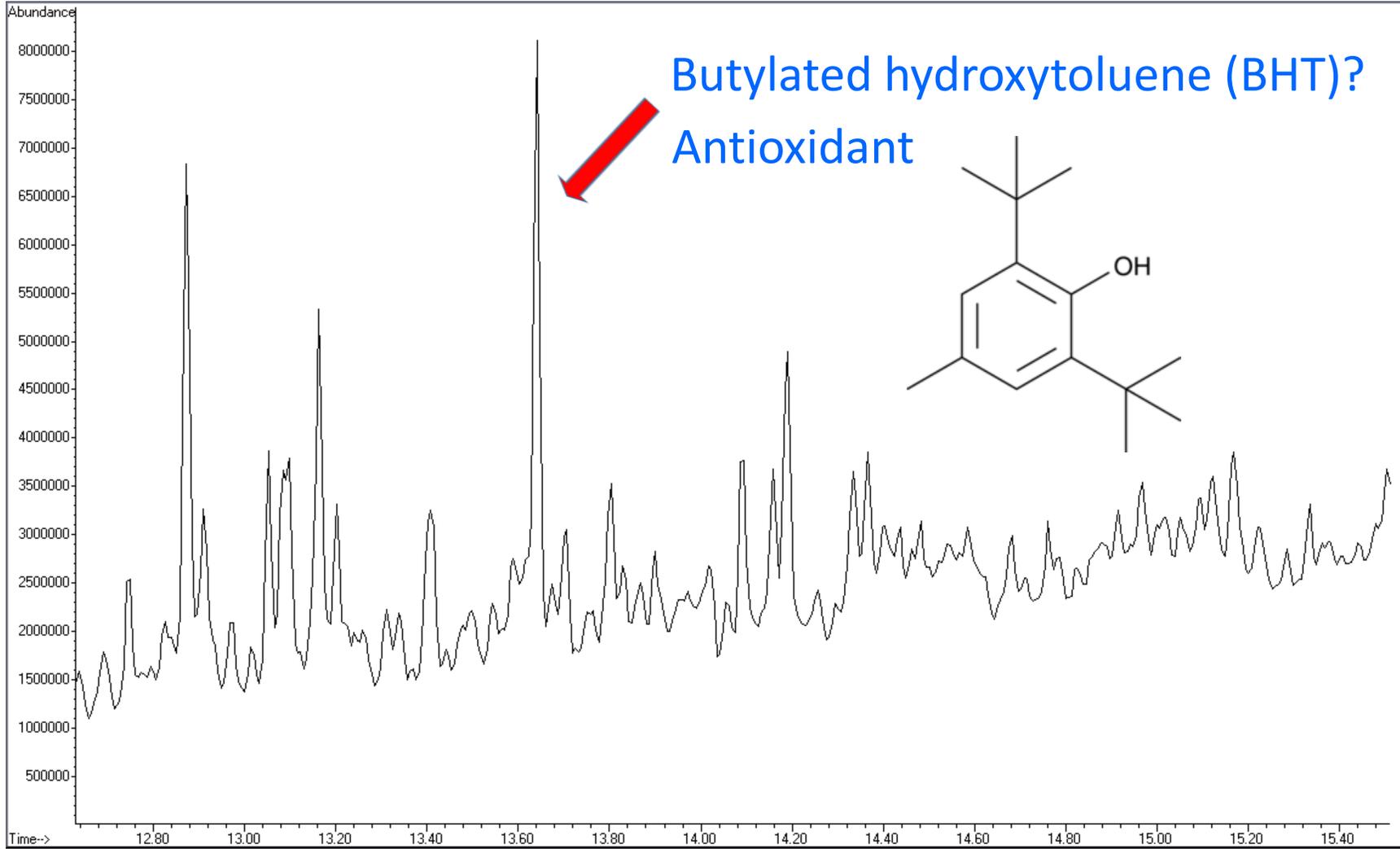


Kihei #1 27  
Dark Red Foam







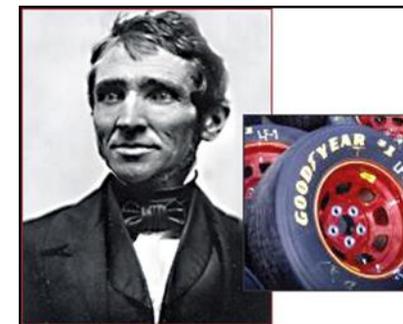




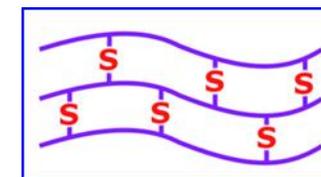
We think it is:

- ❖ Hydrogen Sulfide
- ❖ Isoprene – Isoprene Rubber
- ❖ Butene
- ❖ Thiophene & Other Sulfur Compounds
- ❖ Styrene & Other Aromatic Compounds
- ❖ Styrene-Butadiene Rubber
- ❖ Benzothiazole + possibly BHT?
- ❖ Presence of Vulcanized Rubber
- ❖ Vulcanized rubber
- ❖ Possibly: Styrene-Butadiene Rubber with Natural Rubber

Charles W. Goodyear

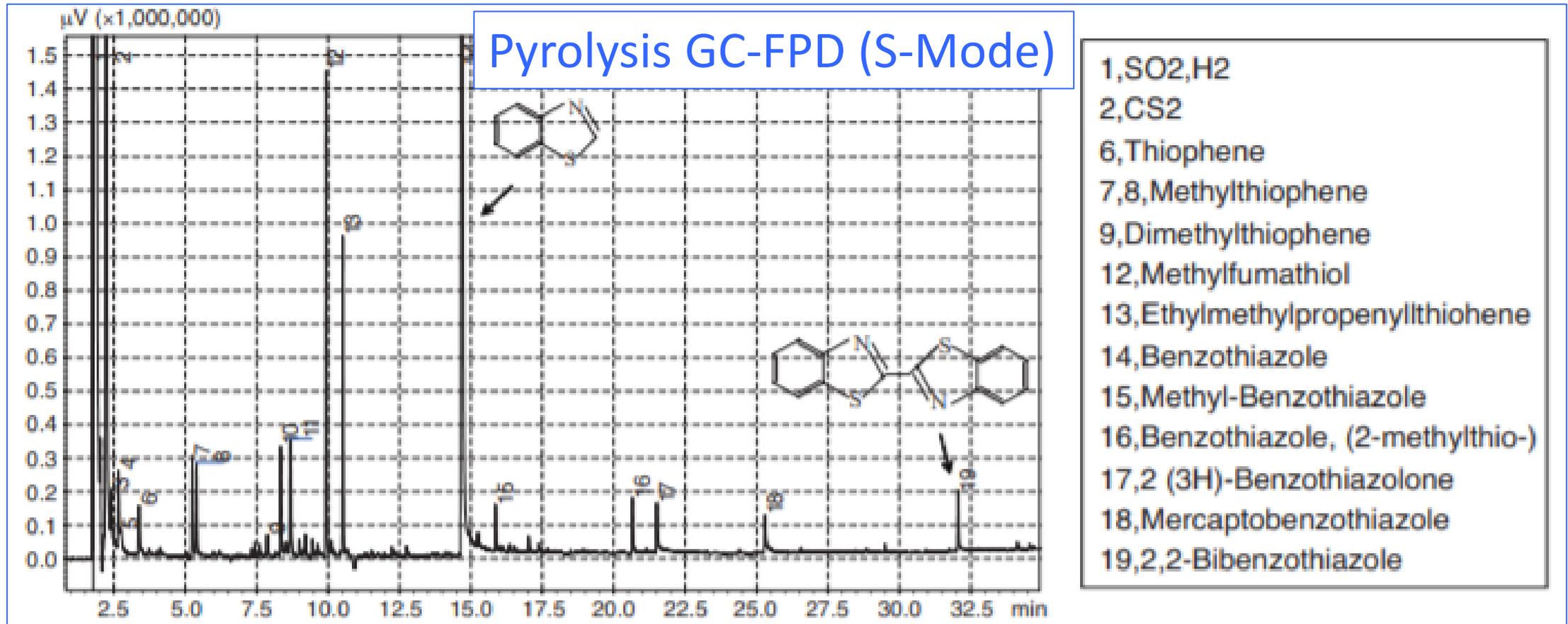


Inventor of Vulcanized Rubber



# Simultaneous Analysis of Sulfur Compounds in Rubber Using Detector Splitting System

## Pyrolysis GC-MS and Flame Photometric Detector in Sulfur Mode

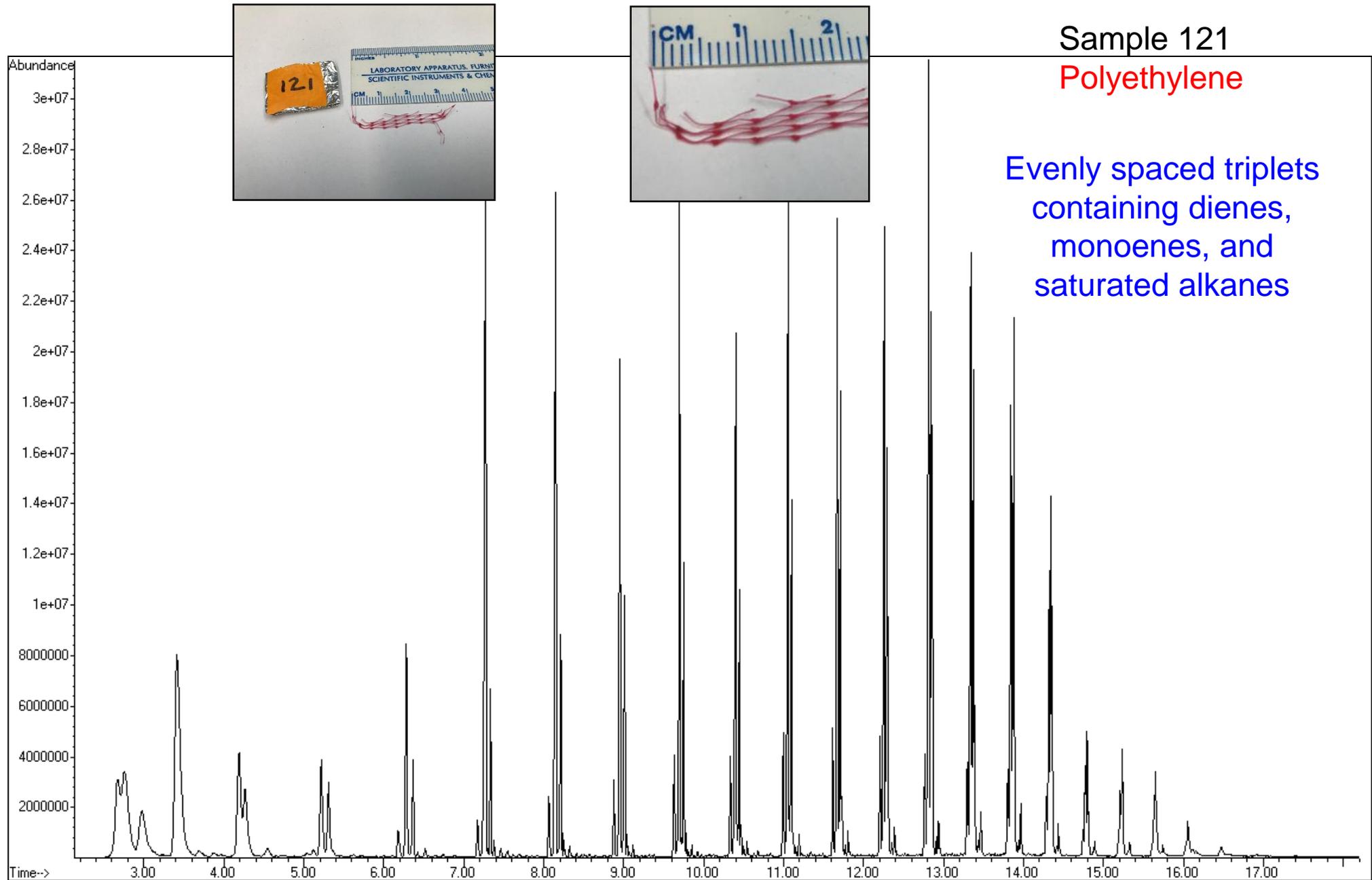


Application News: M257.N



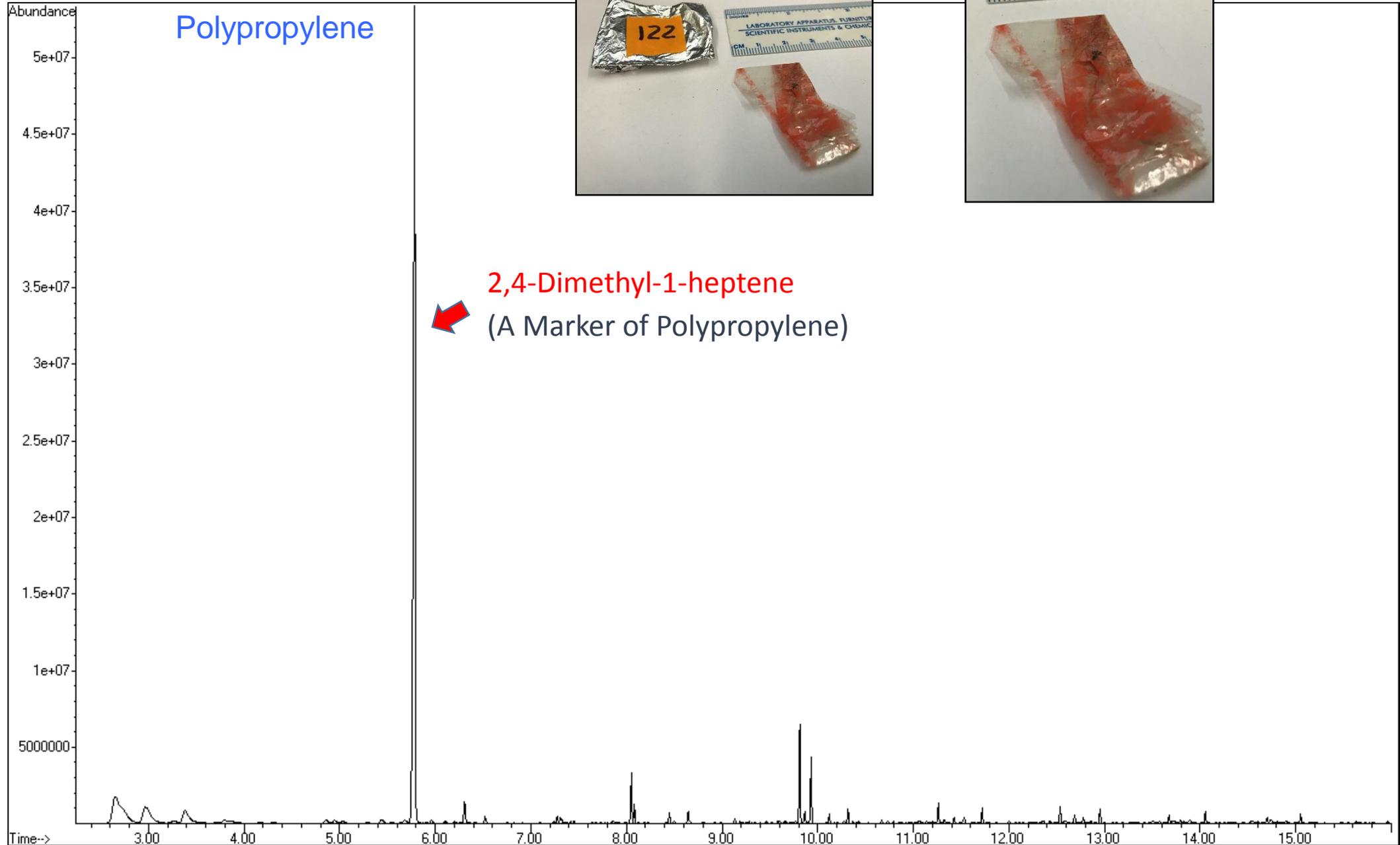
Sample 121  
Polyethylene

Evenly spaced triplets  
containing dienes,  
monoenes, and  
saturated alkanes



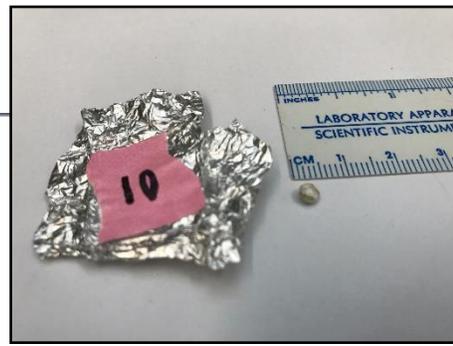
Sample 122

Polypropylene

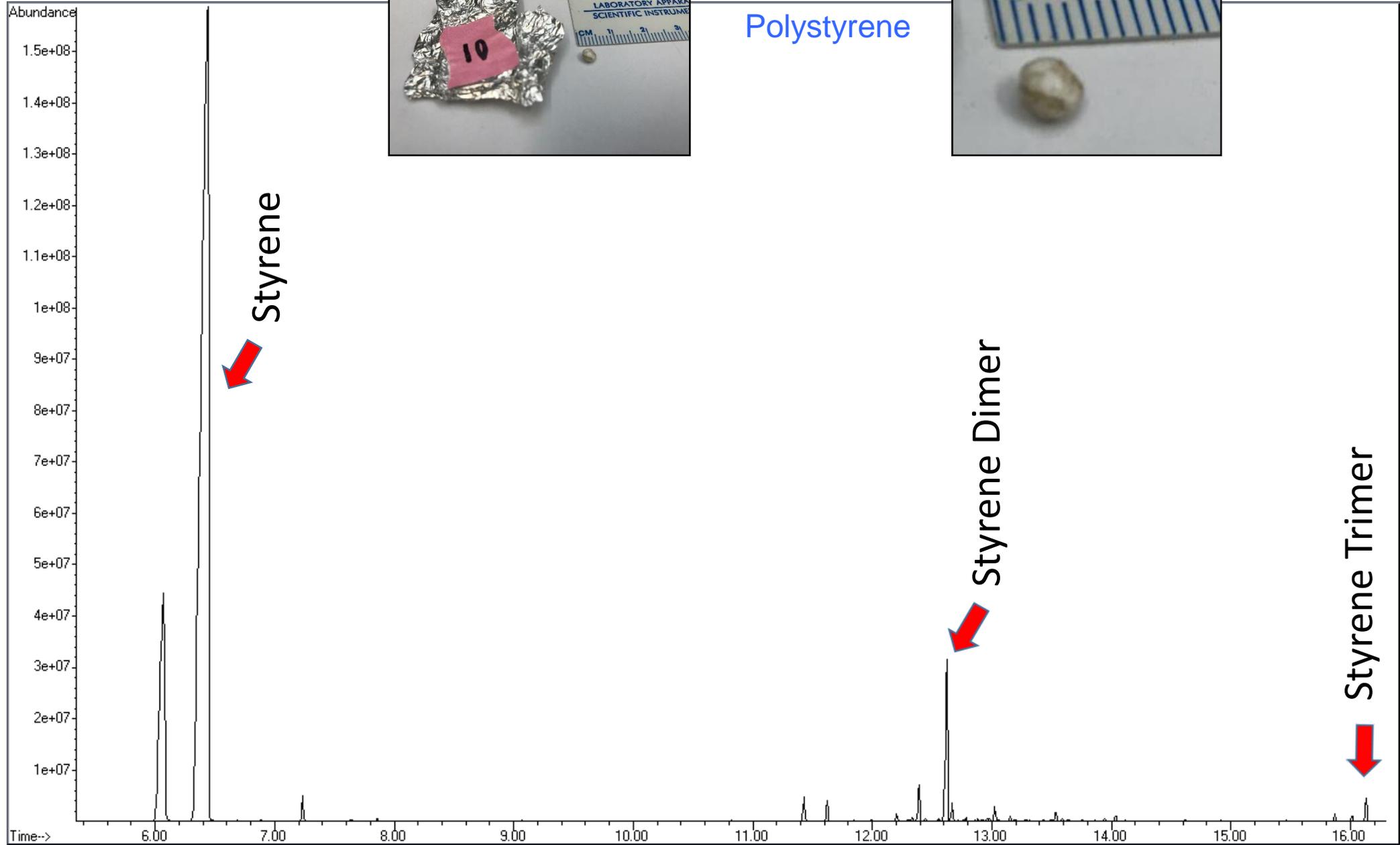


2,4-Dimethyl-1-heptene

(A Marker of Polypropylene)

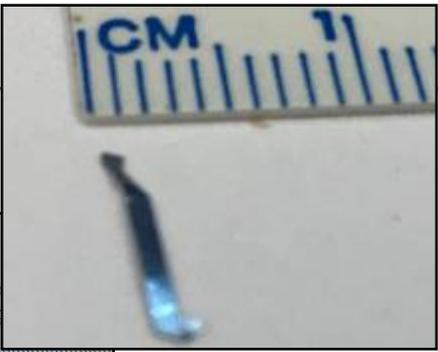
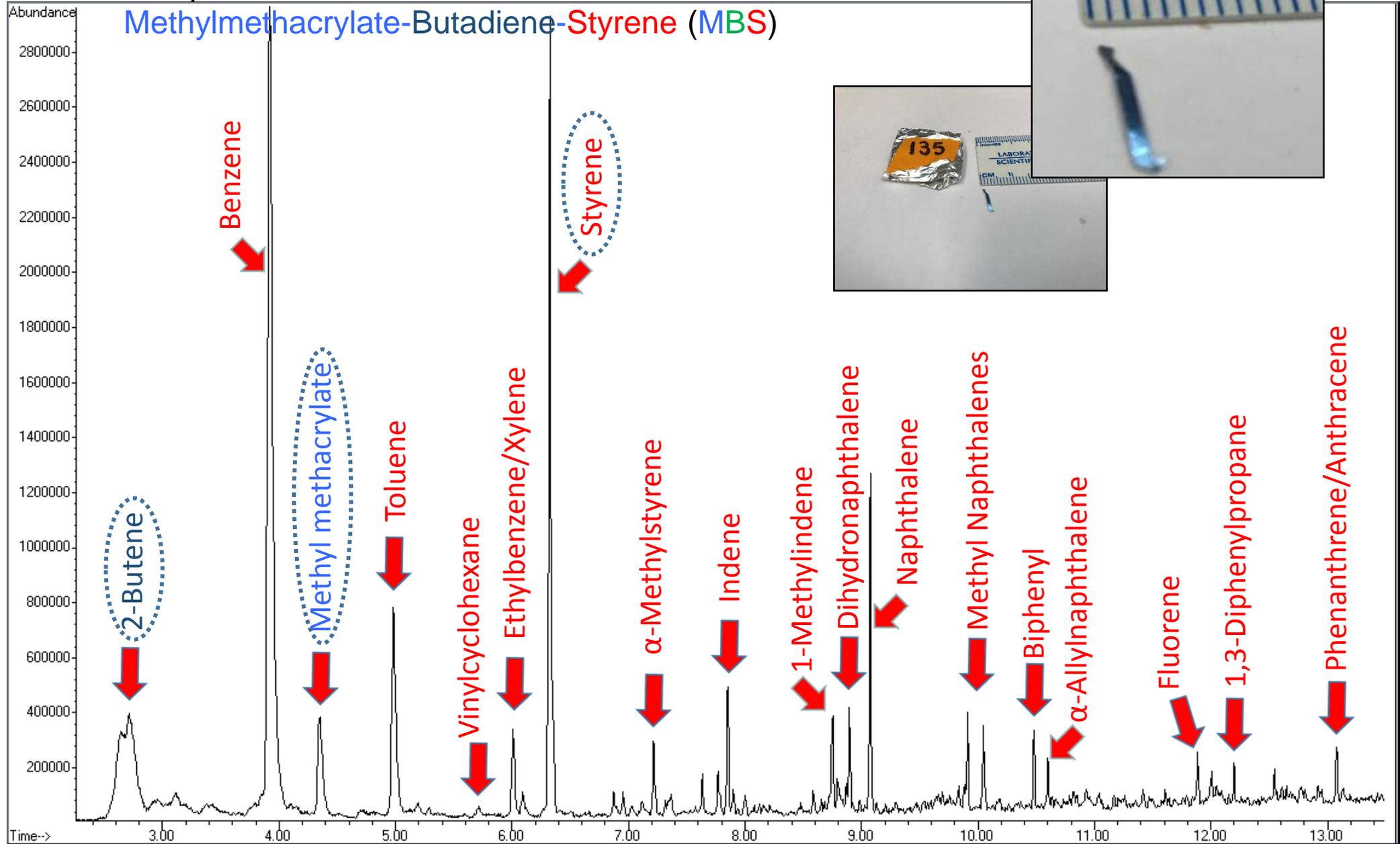


Sample 10  
Polystyrene



# Sample 135

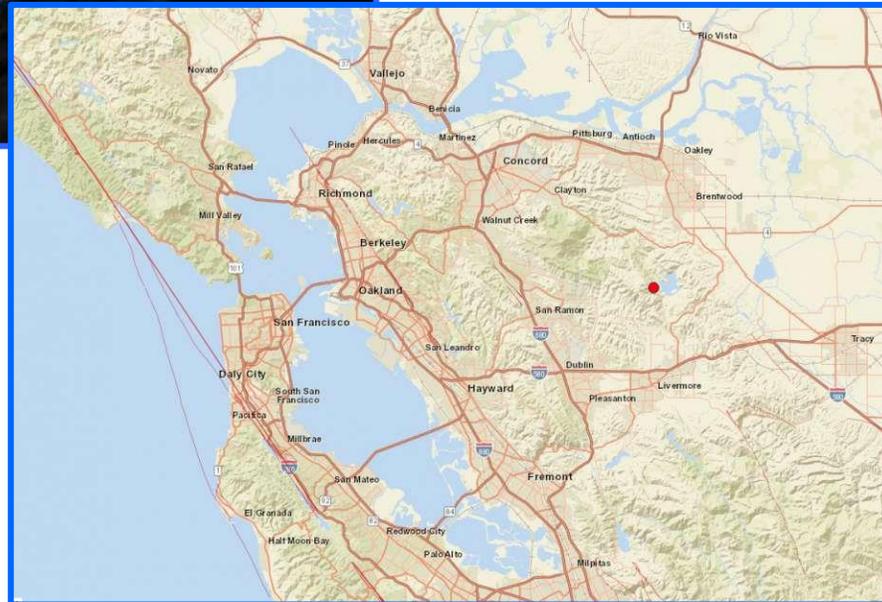
## Methylmethacrylate-Butadiene-Styrene (MBS)



## Particles in San Francisco Bay



Did the particles arise  
from the tire treads?



Dr. Chelsea M. Rochman



Department of Ecology &  
Evolutionary Biology  
University of Toronto, Canada

# TIRE TALK



The main polymers used for tires are as follows:

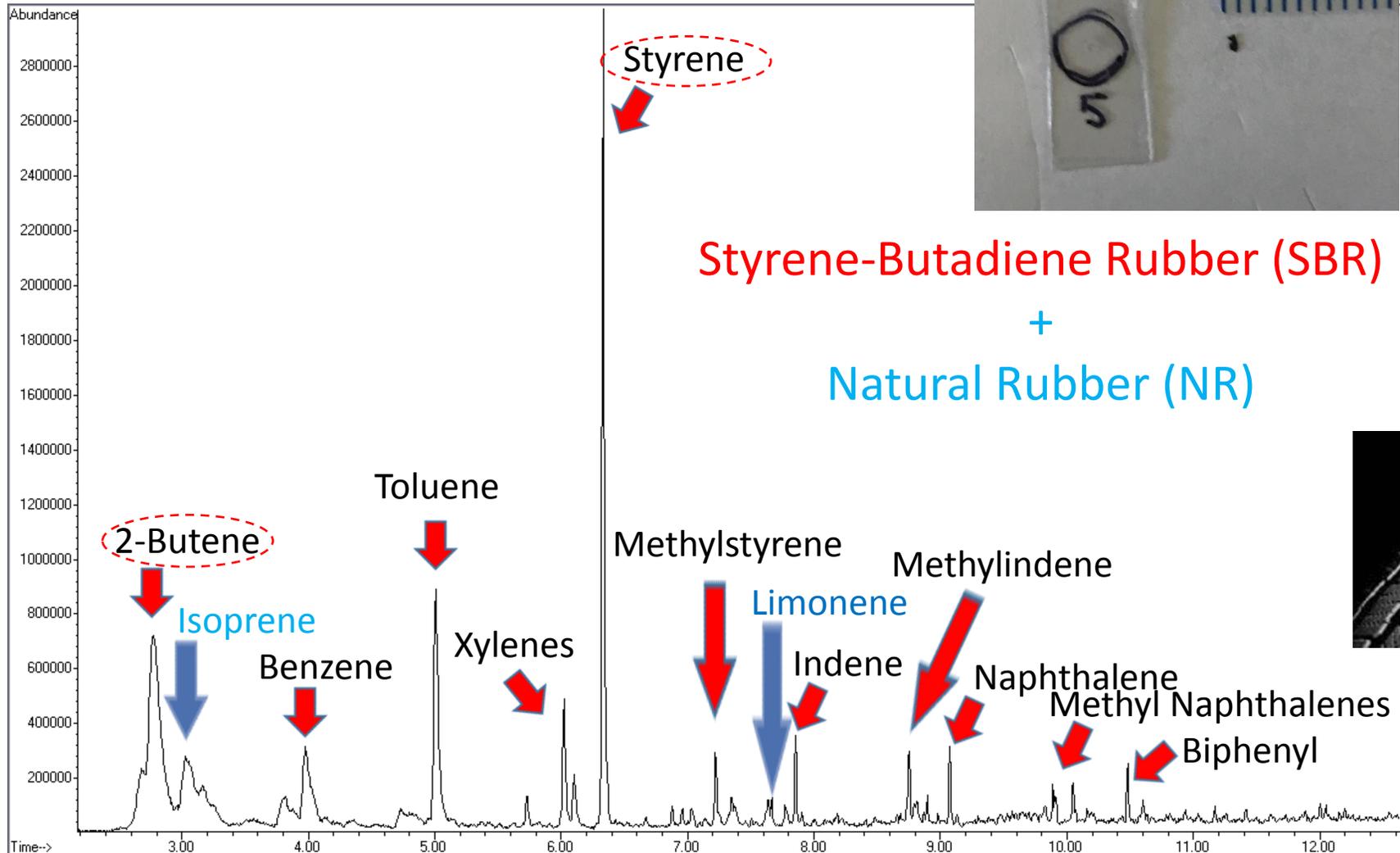
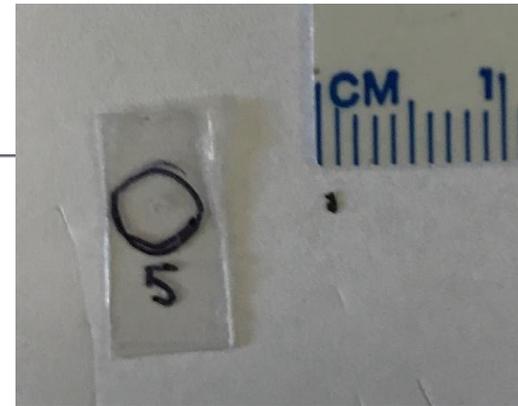
- ❖ Natural Rubber (NR)
- ❖ Styrene-Butadiene Rubber (SBR)
- ❖ Butadiene Rubber (BR)
- ❖ Isoprene Rubber (IR)
- ❖ Halogenated Butyl Rubber

All of the above are Synthetic Rubbers except for the Natural Rubber.

Main Use for Tire:

- ❖ Natural Rubber (NR) ...General Use, TB Tread
- ❖ Styrene-Butadiene Rubber (SBR) ...PC Tread
- ❖ Butadiene Rubber (BR) ...Sidewall
- ❖ Isoprene Rubber (IR) ...Partially Used to Replace NR
- ❖ Halogenated Butyl Rubber ...Inner Liner

# U Toronto Sample 5

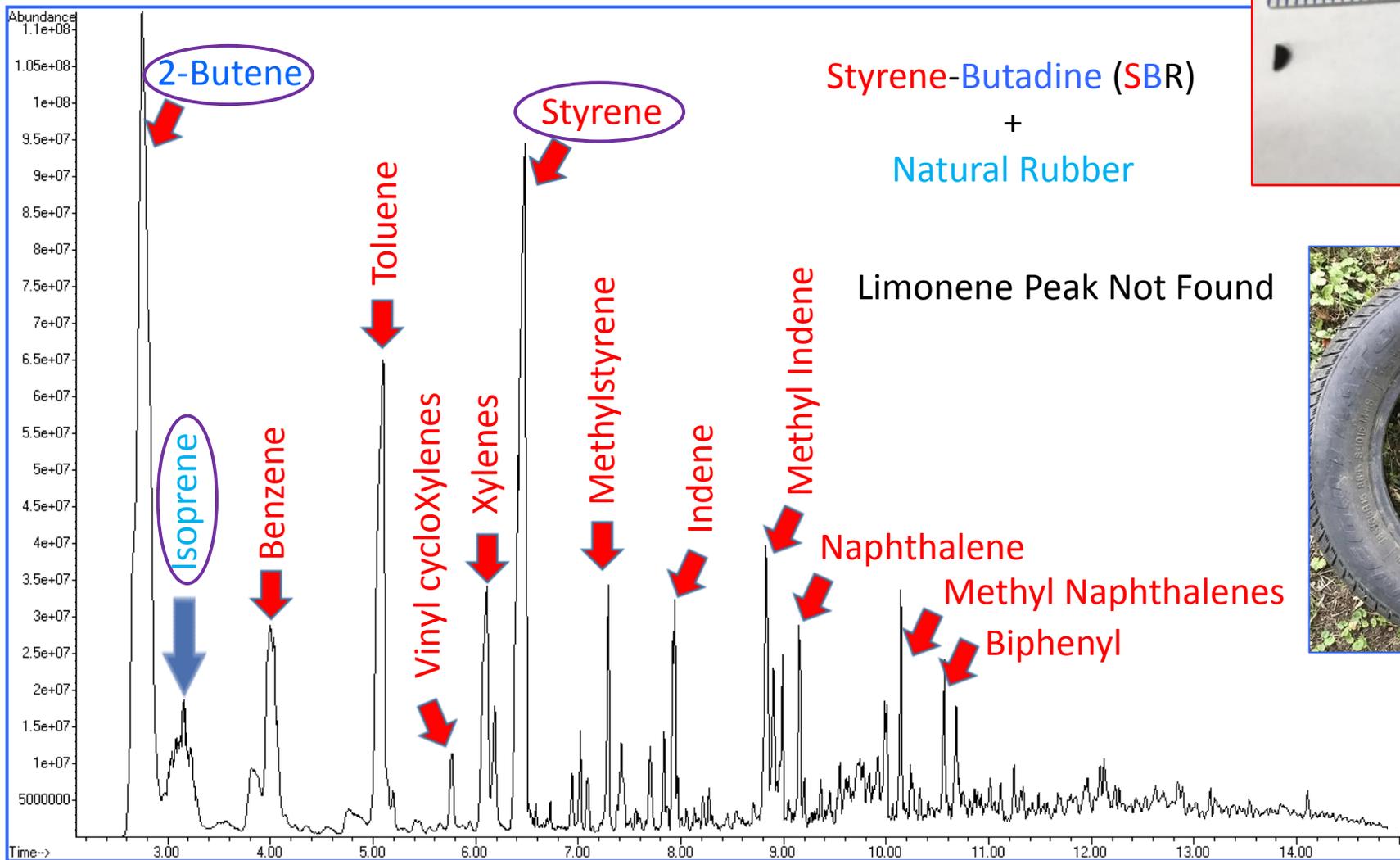


Styrene-Butadiene Rubber (SBR)  
+  
Natural Rubber (NR)

Tire Tread?



# Tire Tread Pieces Cut from a Used "Touring" Tire



Styrene-Butadine (SBR)  
+  
Natural Rubber

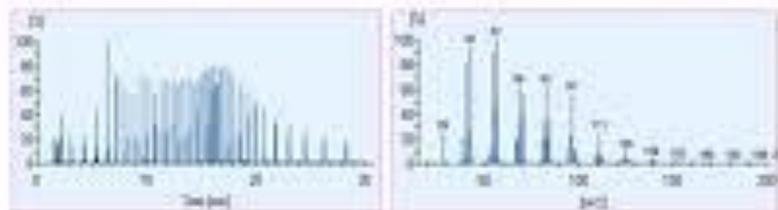
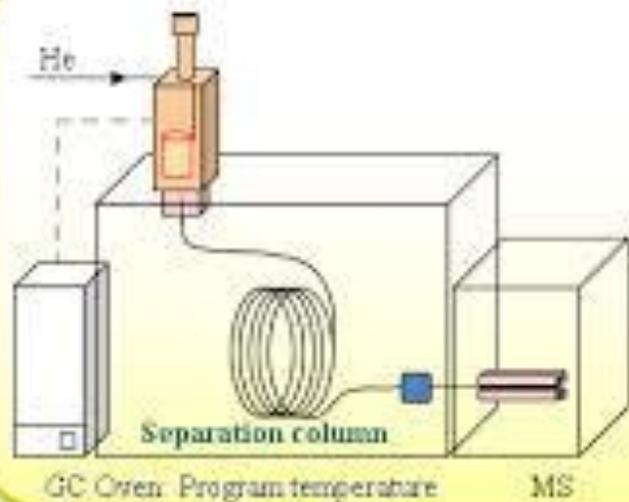


Used  
Weathered  
Tire



FAQ

### Py-GC/MS analysis



### 4. Limit of Detection & Limit of Quantitation

- Limit of Detection:
  - It is the lowest amount of analyte in a sample which can be detected but not necessarily quantitated.
- Limit of Quantitation:
  - It is the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.

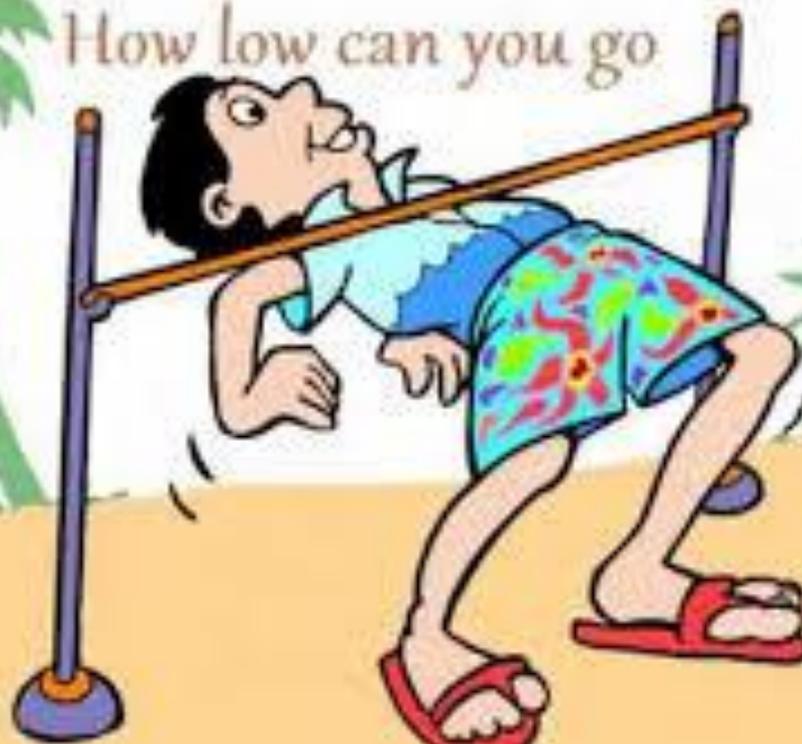


© Science 2018

Orbital Motion Education

27

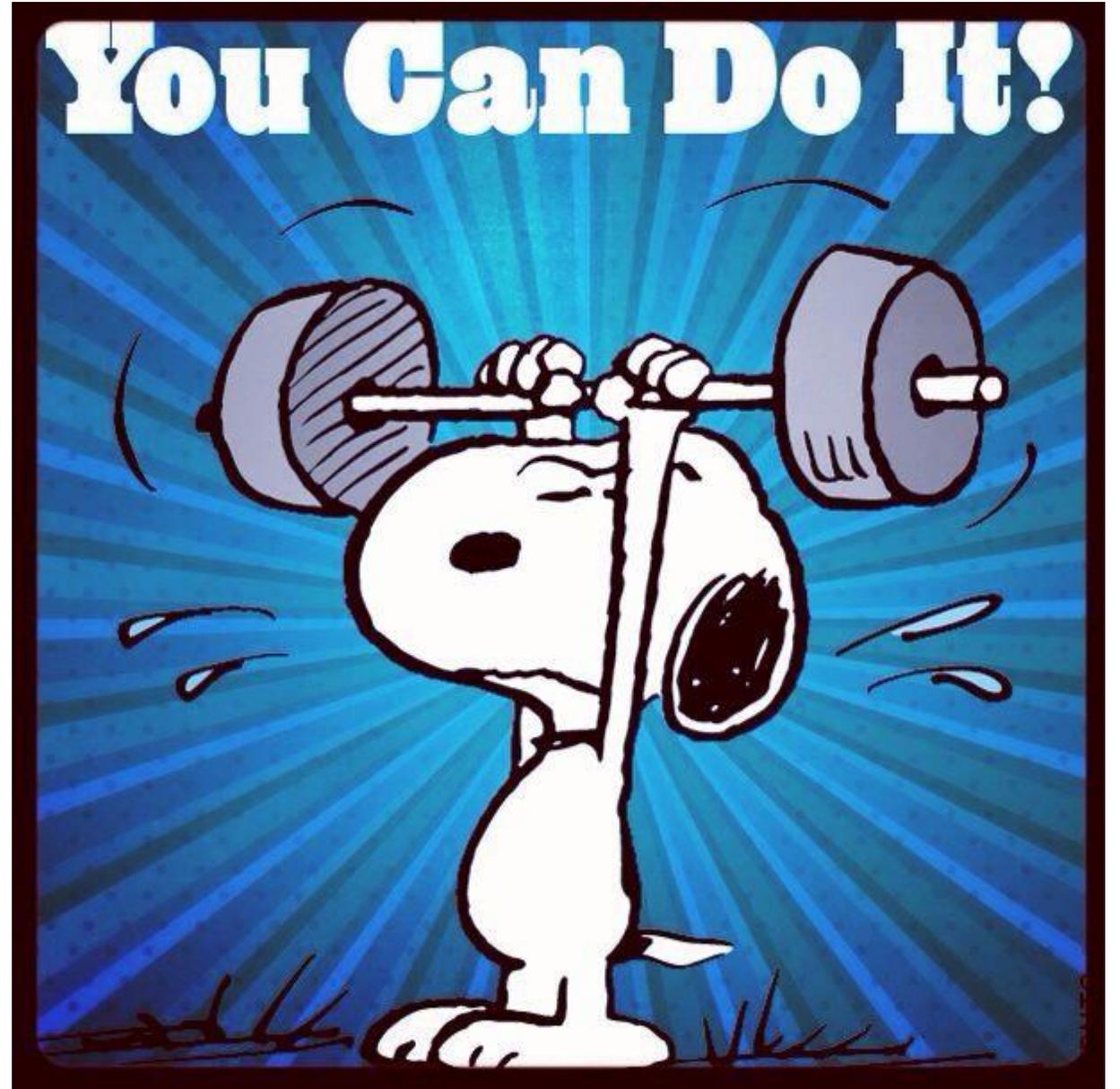
How low can you go



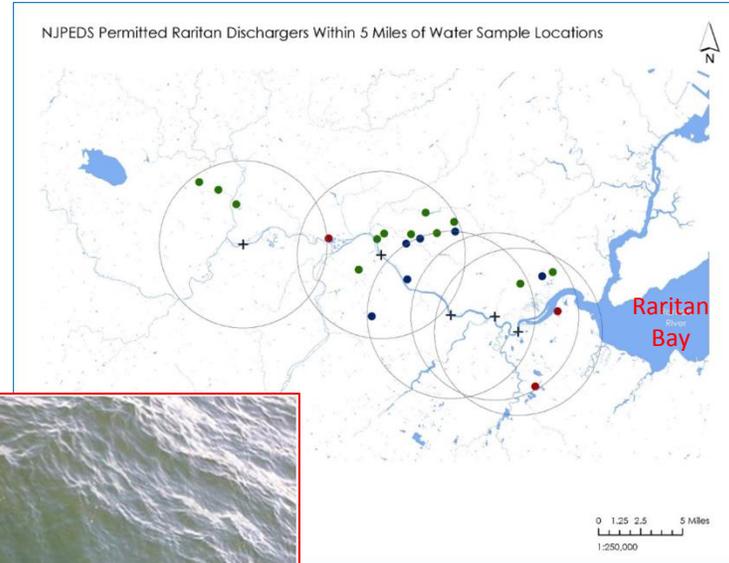
VERY *Simple*



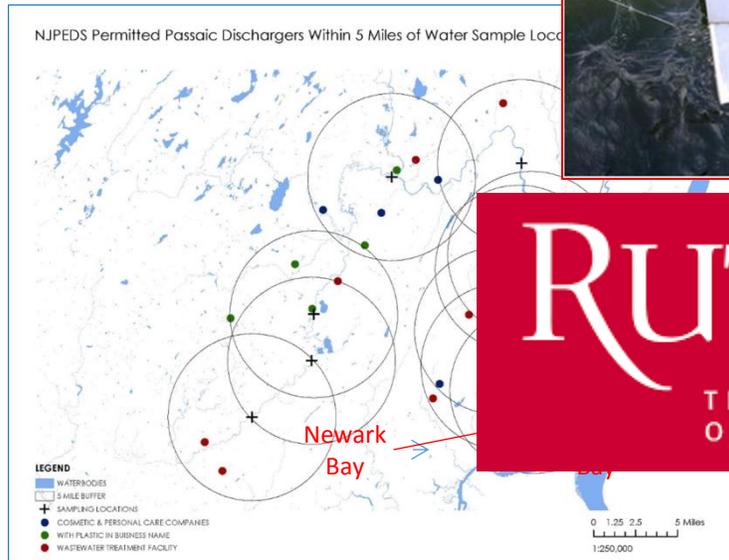
If you can see it..



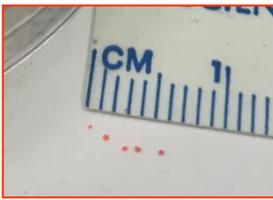
# Microplastics from the Raritan and Passaic Rivers in New Jersey



Drs. Keith Cooper & Beth Ravit

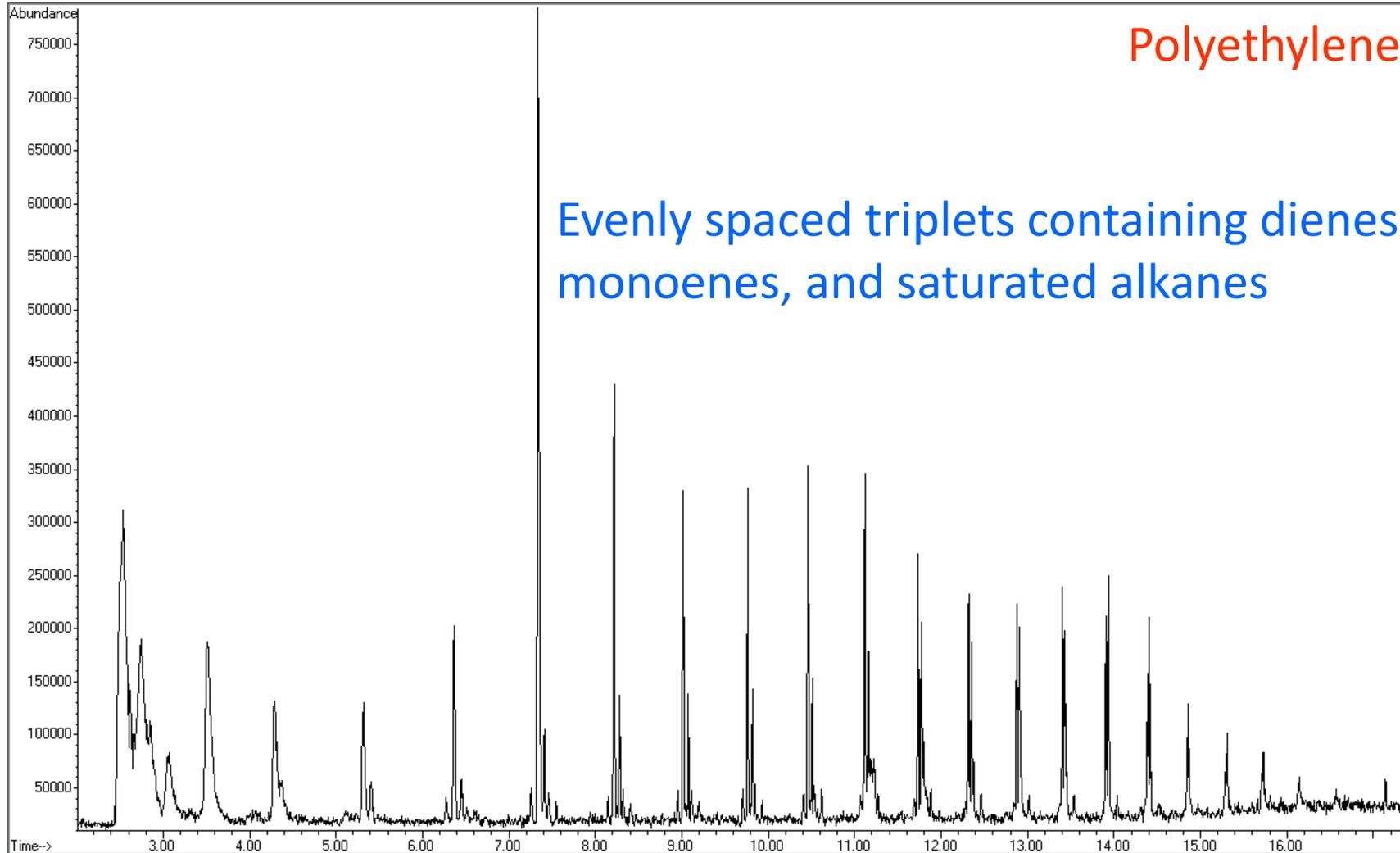


Dr. Brian Buckley

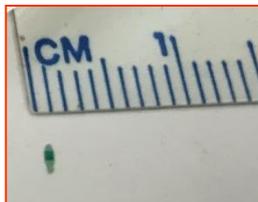


# Rutgers Sample RR6 6/29

Very tiny pink fragments

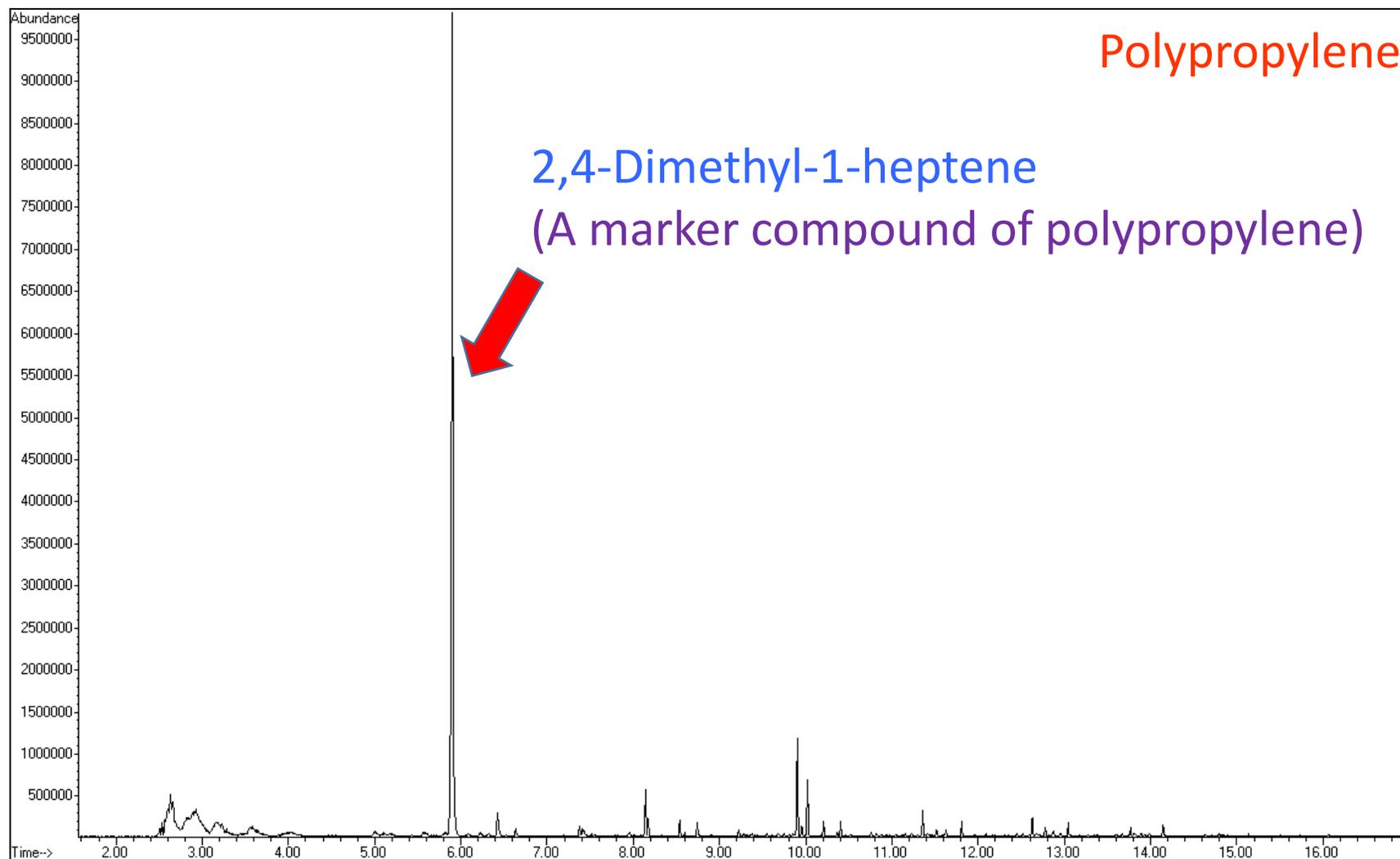


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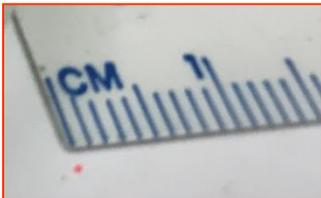


# Rutgers Sample RR4 5/17/17

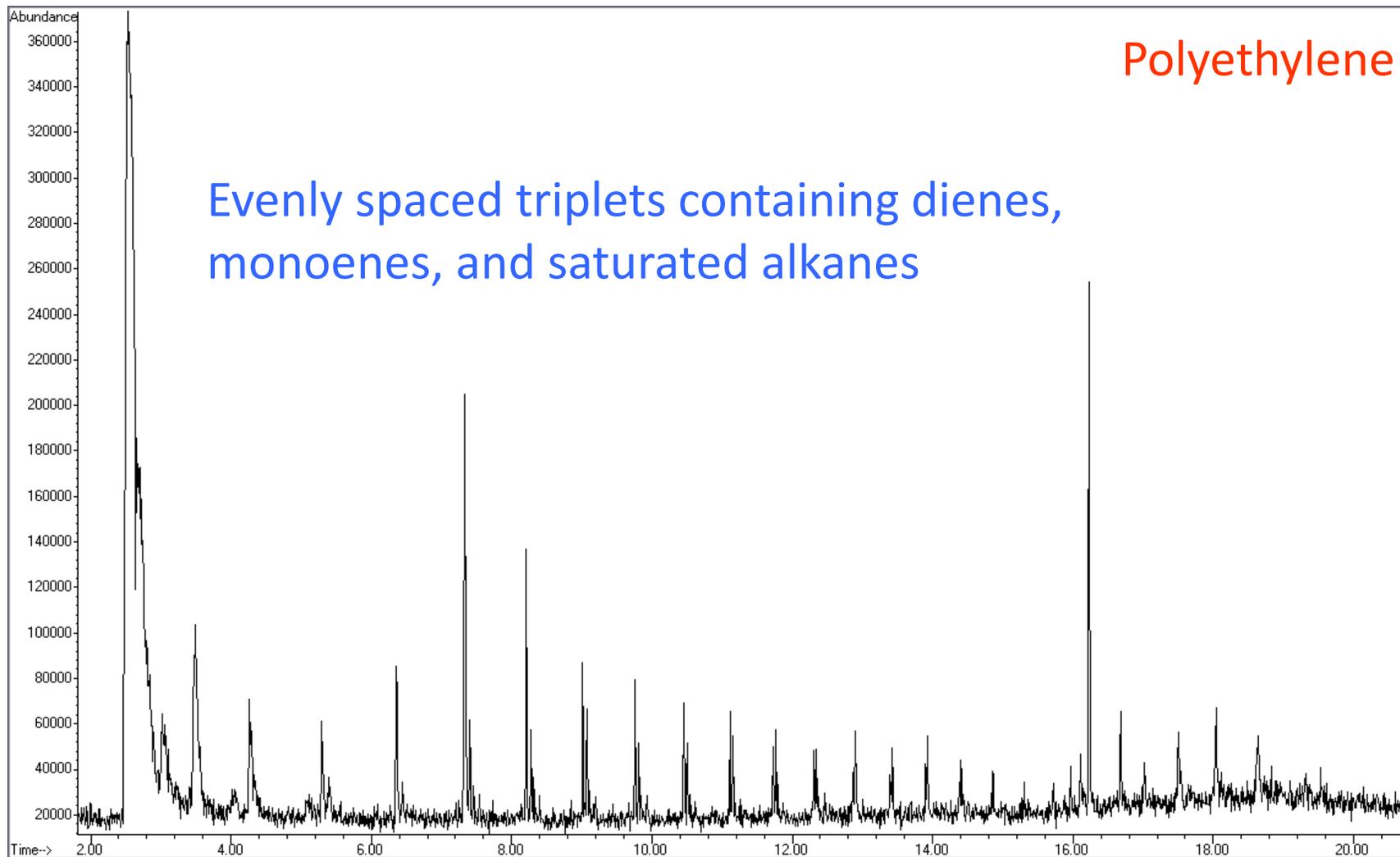
small green fragment



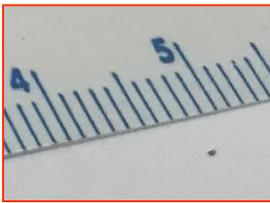
E:\Microplastics\Rutgers II\20180830\_74.D



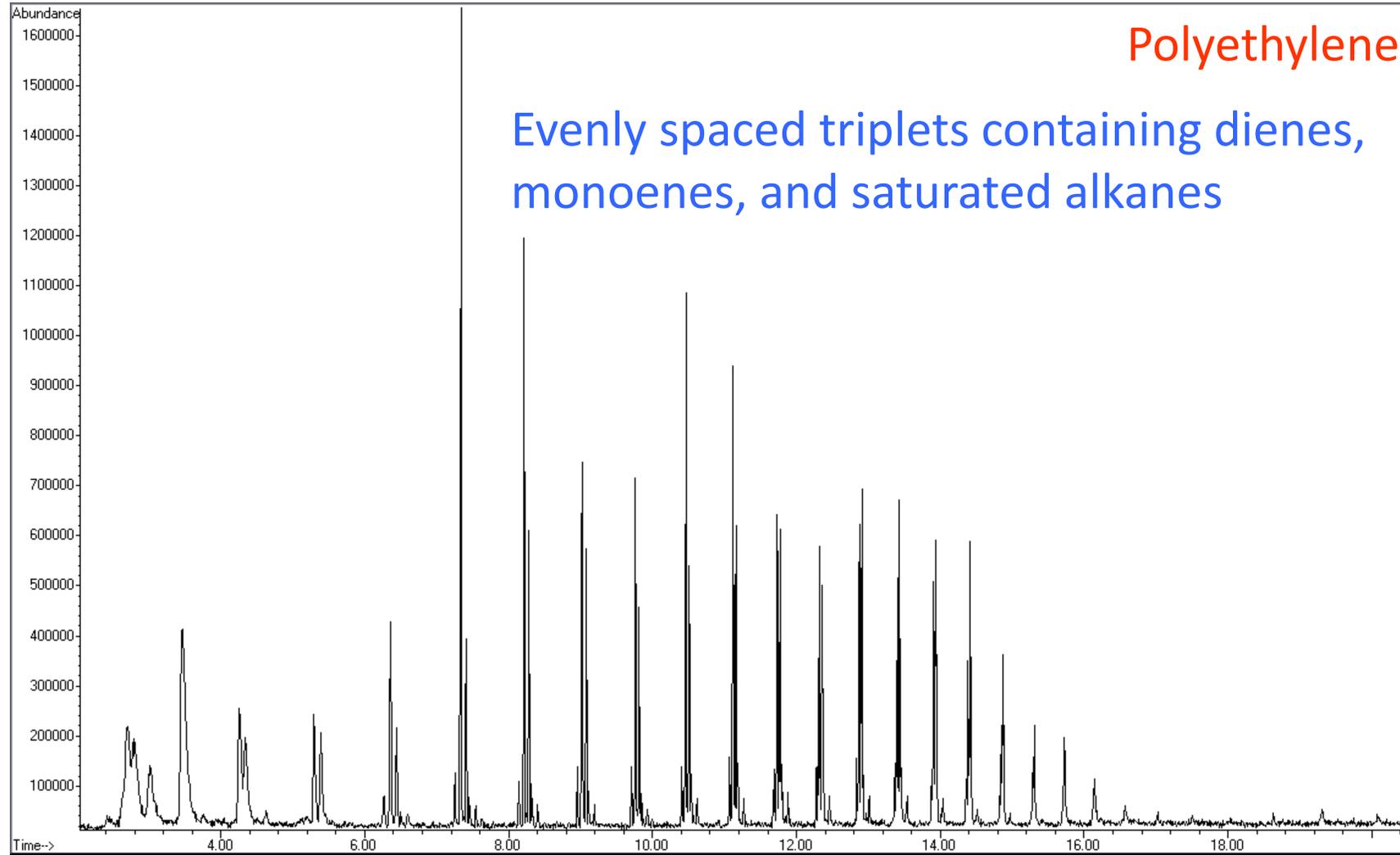
Rutgers Sample RR8 5/29/17  
very tiny pink fragment



E:\Microplastics\Rutgers II\20180830\_82.D



Rutgers Sample RR8 5/23/17  
dark blue fragment



E:\Microplastics\Rutgers II\20180830\_85.D

**Detection Limit**



**Fraction of a Millimeter**

## Benefits of Using Pyrolysis GC-MS:

- ❖ Mass Spectrometry is a gold-standard for the analytical chemistry data quality, and it provides the most accurate identification of chemical composition and structure.
- ❖ Many laboratories already have and routinely use the various GC-MS systems.
- ❖ No need to learn a new trade or find funds for the new instrument purchases.
- ❖ Addition of Pyrolysis component to the GC-MS is simple and cost-efficient.
- ❖ Inserting a sample in the quartz tube is as easy as threading a needle.
- ❖ Pyrolysis GC-MS provides a two-tier confirmation approach: (1) unique peak fingerprint of a given polymer, and (2) mass spectrum of each individual peak.
- ❖ Two-tier confirmation approach provides higher confidence in the data quality.
- ❖ No sample preparation is required except for cutting a tiny piece for the analysis.
- ❖ No effect of shape/size/density/texture/surface/color/brightness/opacity.
- ❖ Information on chemical additives can be obtained in the same sample run.
- ❖ Additional Distinct Benefit - MS Library is really really huge. NIST Library contains a mass spectral database on 267,376 unique compounds. Therefore, the identification of co-polymers, additives, and other chemicals is easily possible.

# New Challenges



Why should we care



Katama Bay Oyster

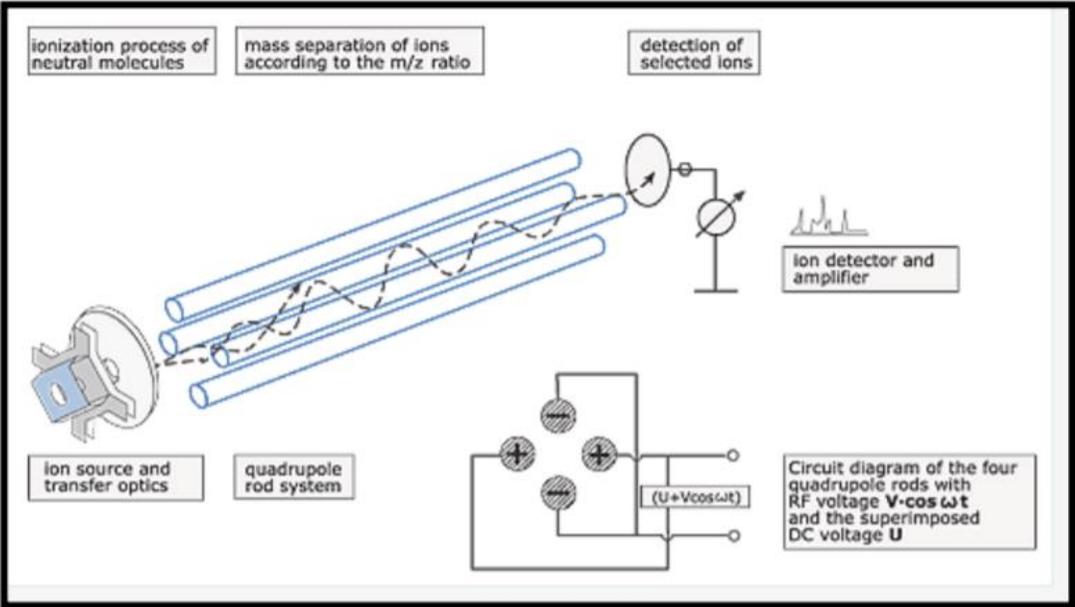
Katama Bay Oyster



Size Does Matter.



Not enough sample weight for pyrolysis GC-MS analysis?



Mass Spectrometry



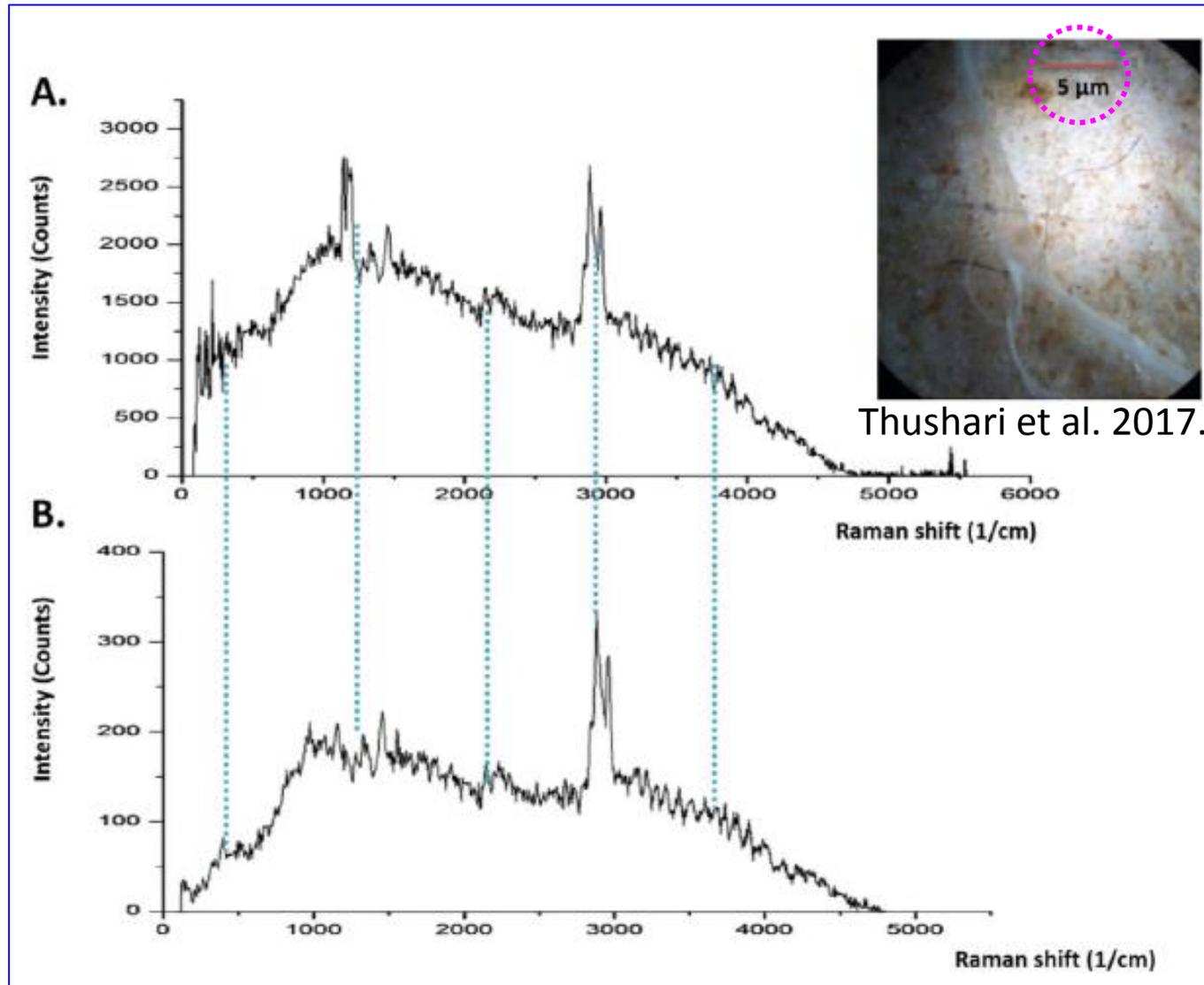


Suggestions on how to improve the detection limits:

- ❖ Increase the mass spectrometer autotune voltage.
- ❖ Experiment with the GC injector port split ratios.
- ❖ If accessible, switch the analyses from a single quadrupole to triple quadrupole mass spectrometer.
- ❖ For target polymer analyses and target additive analyses, switch from full-scan mass spectrometry to select ion monitoring mass spectrometry.
- ❖ If nothing works, then switch to FT-IR or Raman Spectroscopy as the potential exploratory tools.

**SUGGESTIONS**

# Polyethylene



A Great Potential!!!

Raman spectra showing the detection of polyethylene (PE). A) from the rock oyster (*Saccostrea forskalii*) collected from Bangsaen, B) from the reference library spectra.



# Unlimited Money



SUPER  
DUPER

High Resolution  
Mass Spectrometer

Figure 1. Instrumental setup: Multi-Shot Pyrolyzer (Frontier EGA/PY-3030D) with Auto-Shot Sampler (AS-1020E) coupled to an Exacte GC Orbitrap mass spectrometer

## Unlimited Money = 0.05 µg Detection Limit

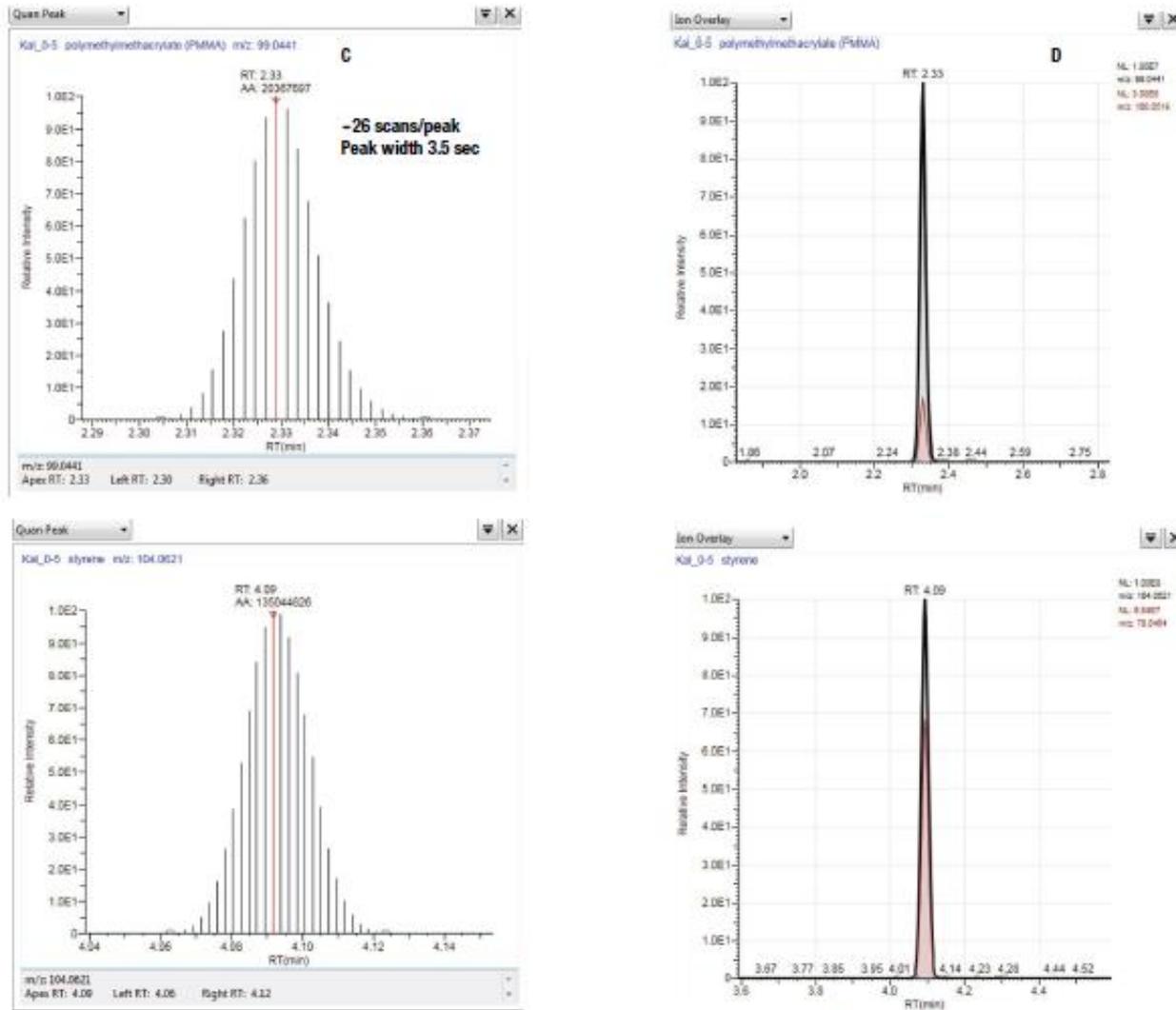


Figure 2-2. Chromatography and linearity of methyl methacrylate (top) and styrene (bottom) in a 0.05 µg standard. C shows integrated peak area of the quantification ion with corresponding scans/peak, and D shows an overlay of the quantification ion and the confirmation ion. Data were acquired in full-scan at 60,000 resolution [FWHM at  $m/z$  200]. Peak retention time (RT) as well as peak area counts (AA) are annotated. Peak smoothing (5x moving average) was applied.

Pyrolysis-GC-Orbitrap MS - a powerful analytical tool for identification and quantification of microplastics in a biological matrix

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