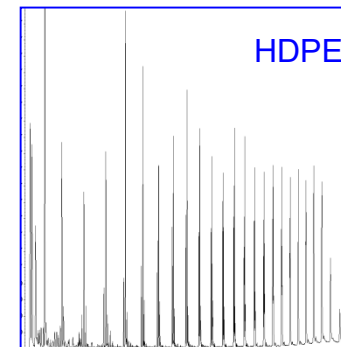
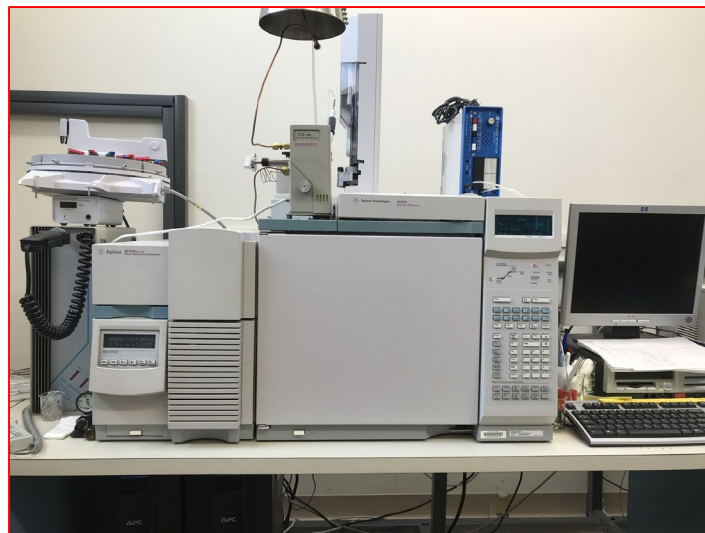
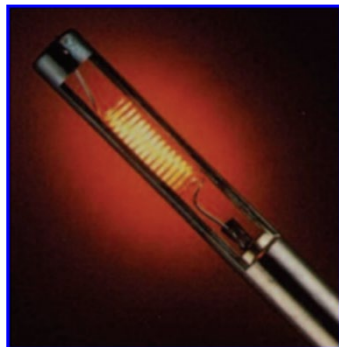


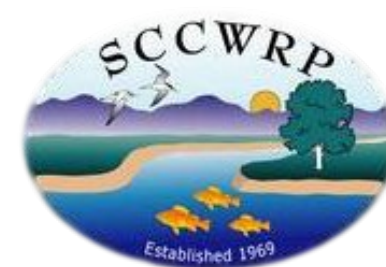
Microplastics Quest By Using Pyrolysis GC-MS



Ashok Deshpande
Research Chemist
NOAA-NMFS-NEFSC

Microplastics Methods Workshop

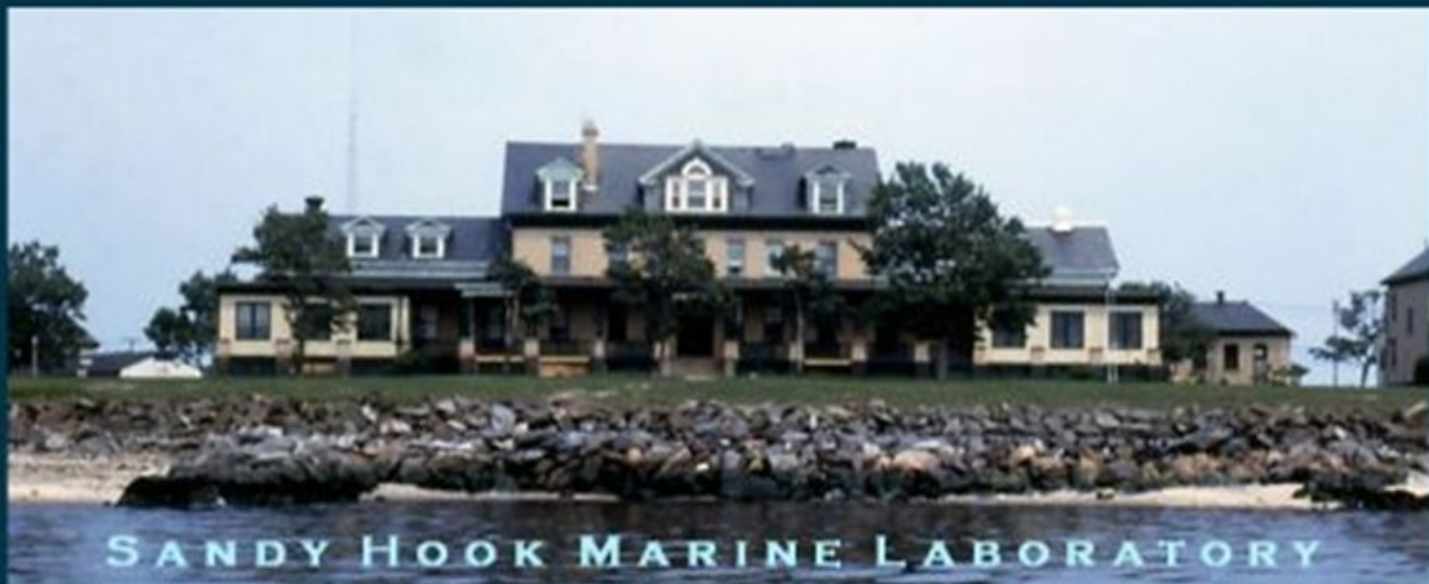
The Southern California Coastal Water Research Project
Costa Mesa, California Thursday, April 4-5, 2019





JAMES J. HOWARD MARINE SCIENCES LABORATORY

50 1961  2011
SANDY HOOK, NJ
YEARS OF FISHERY RESEARCH



SANDY HOOK MARINE LABORATORY

Raman Spectroscopy



Polymer Analysis



**TOOLS OF THE
TRADE**

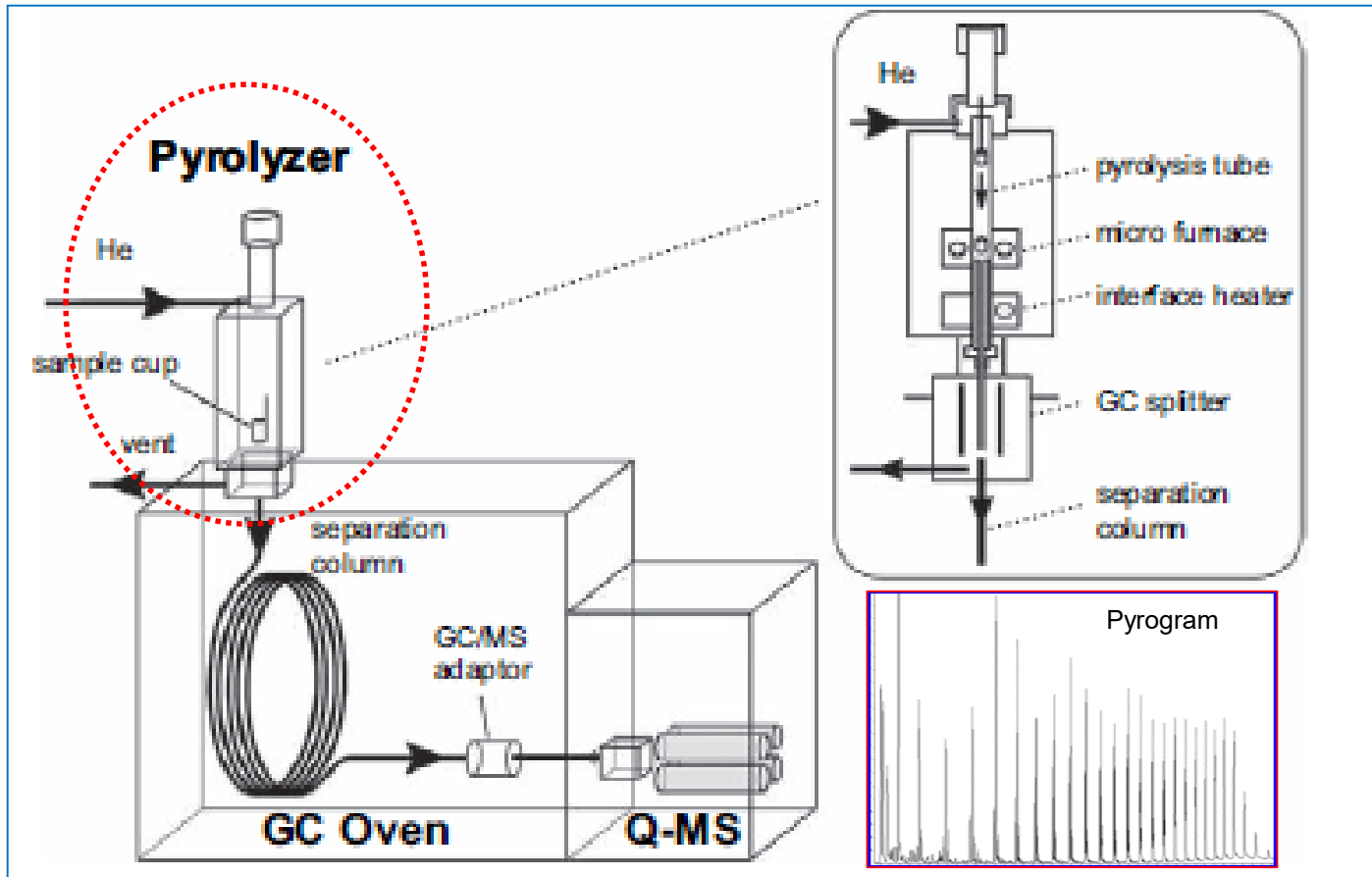


Infra-Red
Spectroscopy



Pyrolysis
GC-MS

PYROLYSIS-GC/MS



Credit: Tsuge, Ohtani and Watanabe

- Microplastic sample is heated at high temperature in the pyrolyzer.
- Thermal degradation results in a unique and reproducible signature of fragment molecules that is characteristic to a given polymer.

Anatomy of Pyrolysis GC-MS



CDS 2000 Pyroprobe

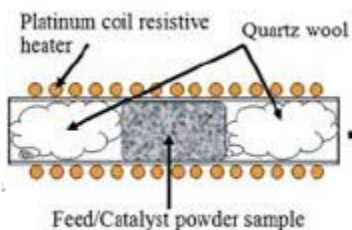
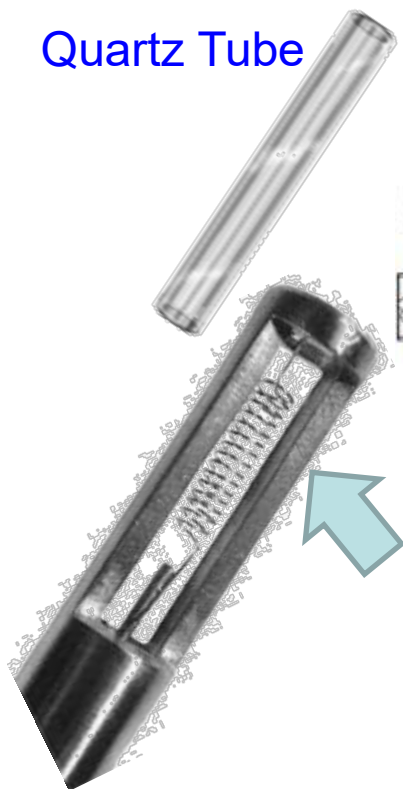


CDS 1500 GC-MS Interface



Agilent 5973 GC-MS

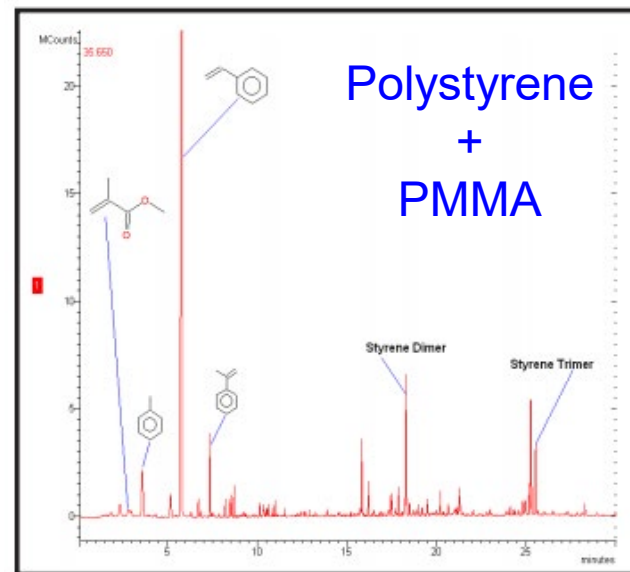
Quartz Tube



750°C
=
1382°F

Platinum Filament

Pyrogram



Credit: CDS Analytical

Going Above & Beyond
Just Peak Comparisons



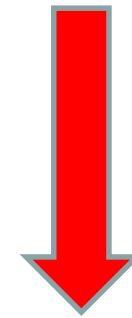
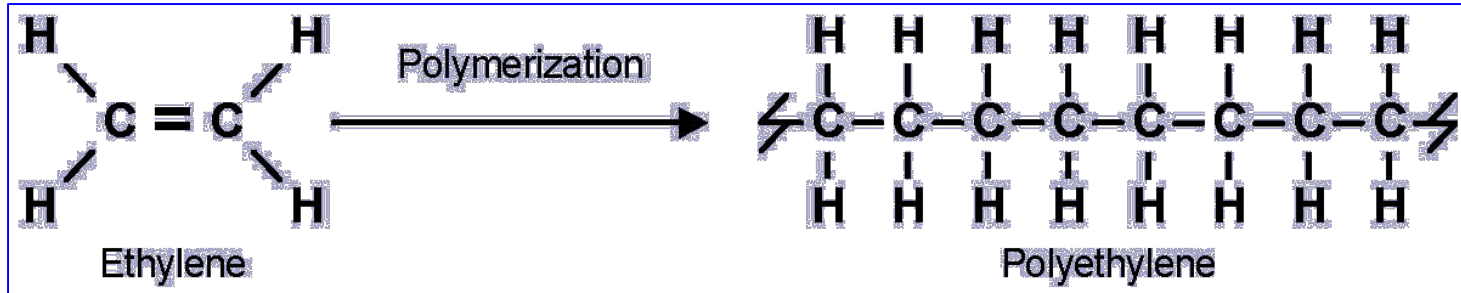
Creation of Pyrolysis
GC-MS Database



Involves



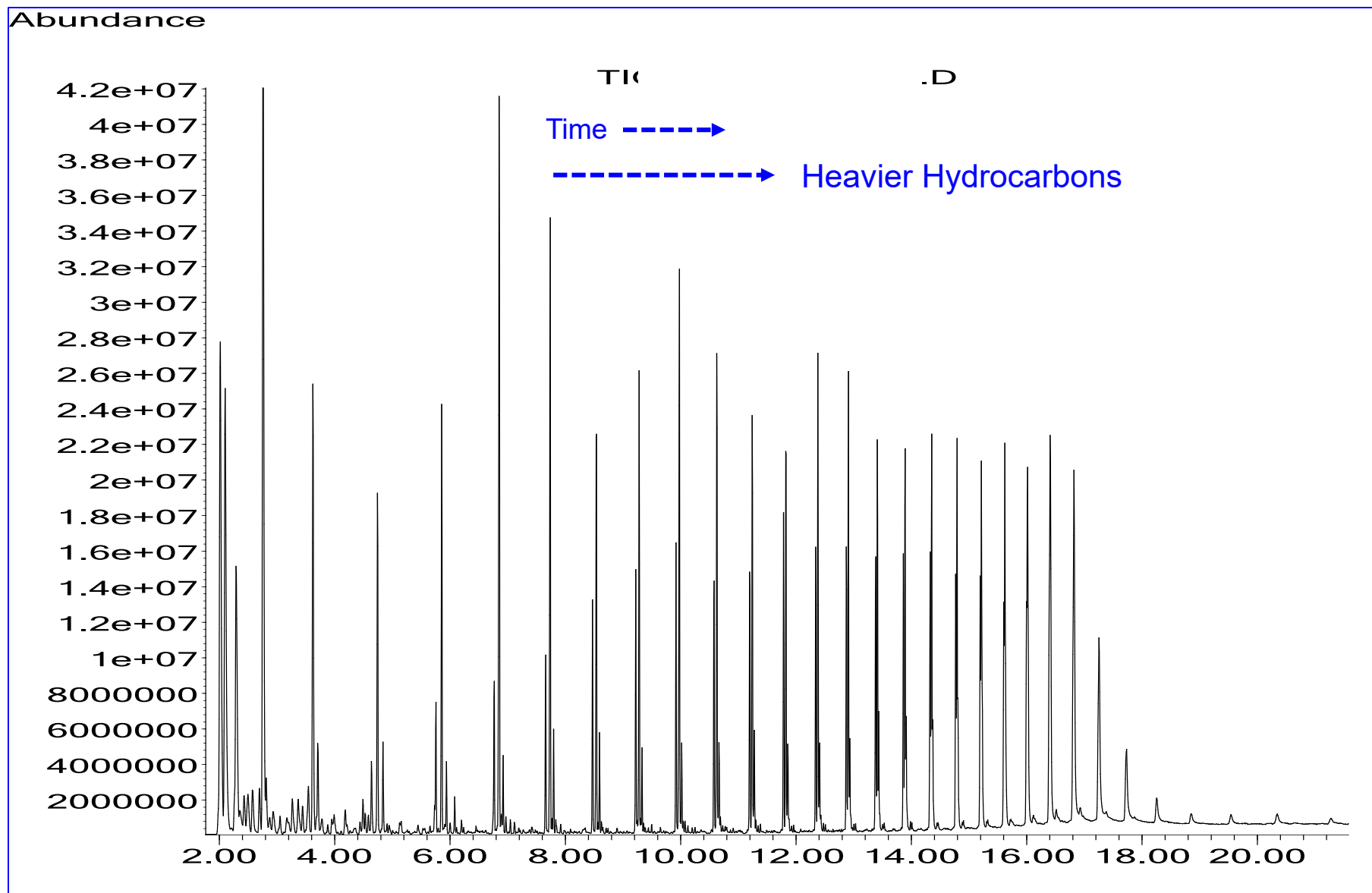
Systematic and Sequential
Identification of Marker Peaks
That can be later used for
Polymer Characterization



Pyrolysis

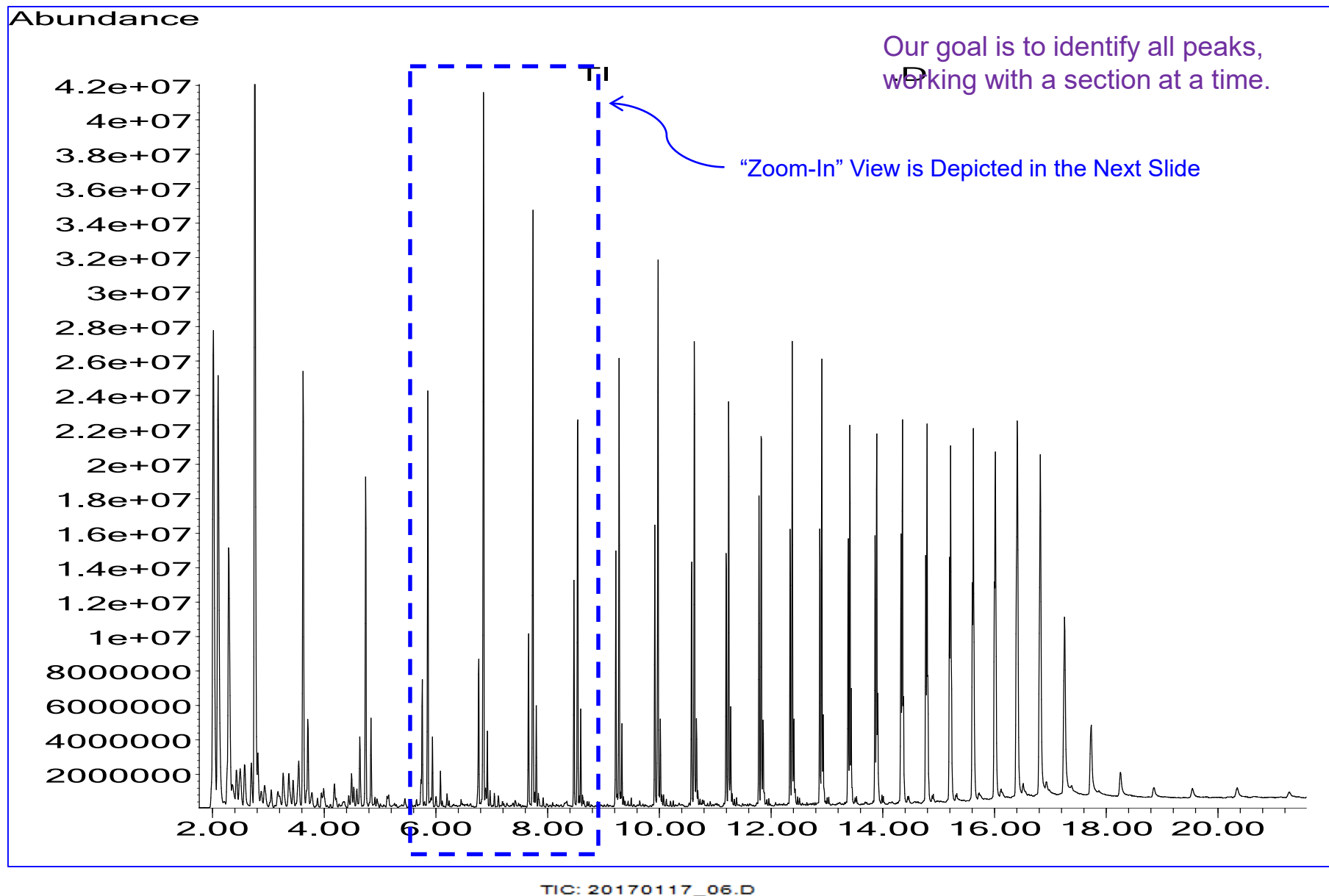
C-C bonds at different sites along the polymer chain break due to intense heat to yield a variety of short-chain molecules

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



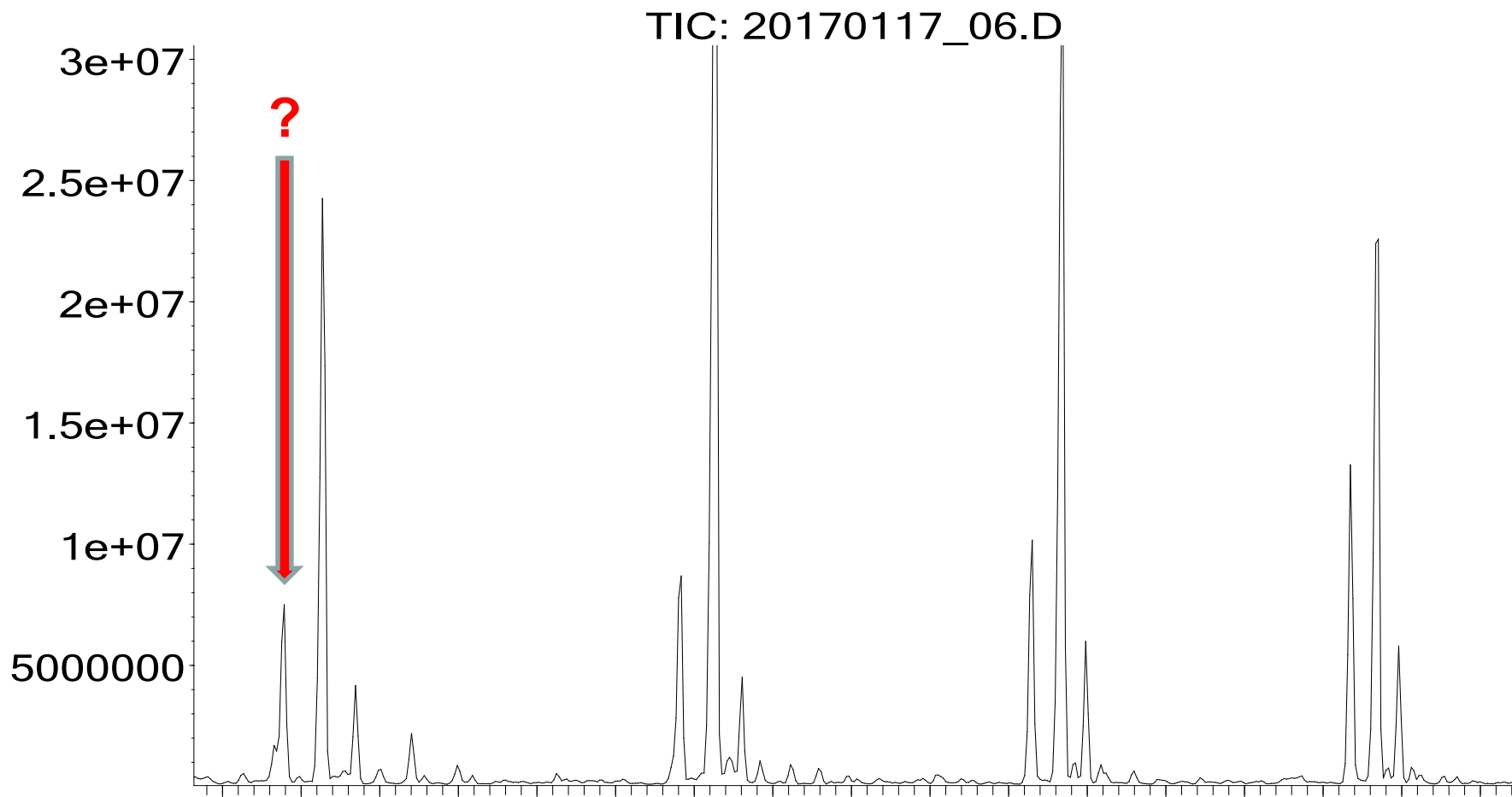
TIC: 20170117_06.D

Pyrogram of High-Density Polyethylene (HDPE)

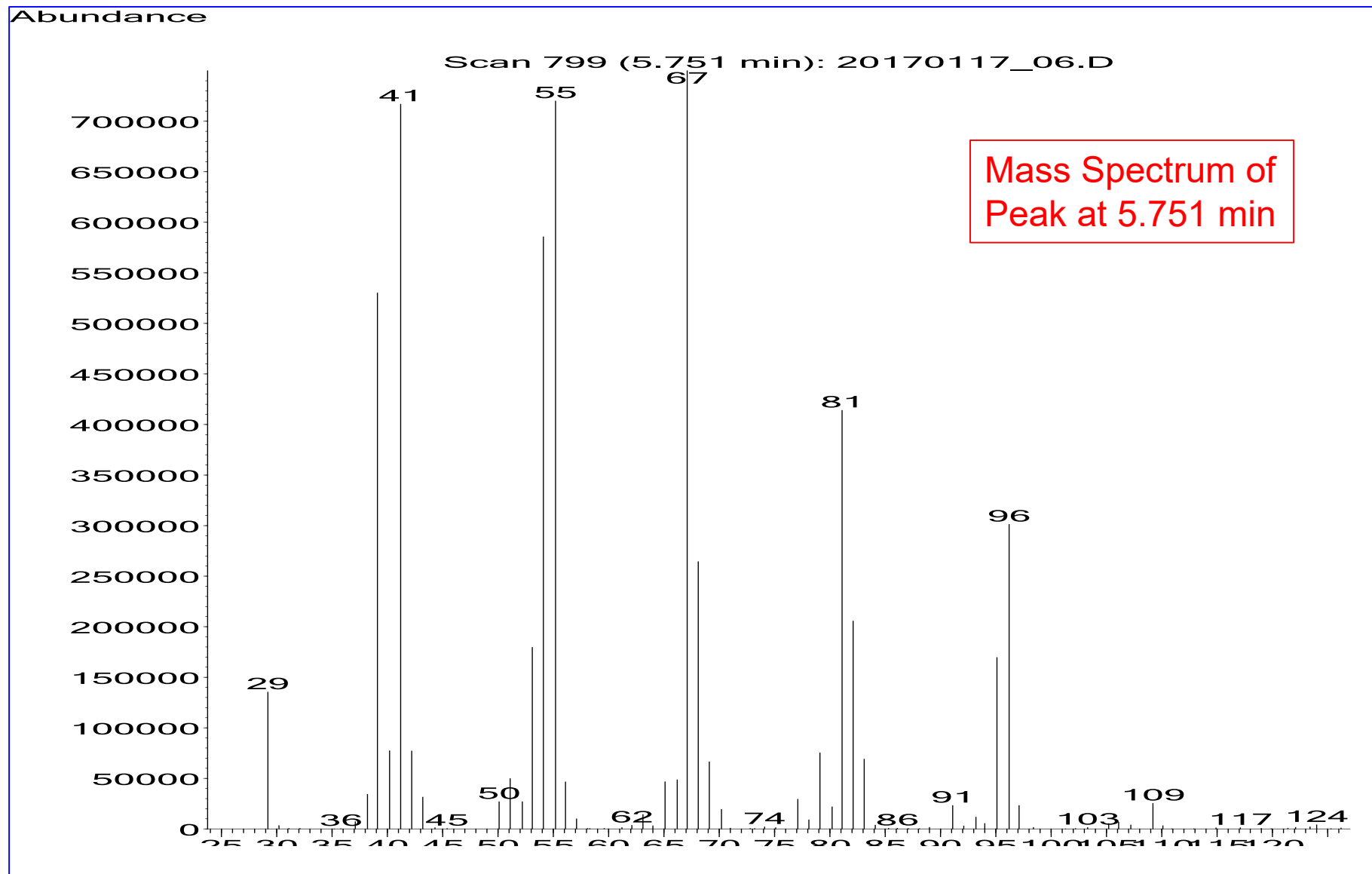


High-Density Polyethylene (HDPE): “Zoom-In” Part of the Pyrogram

Abundance These are not just any ordinary chromatographic peaks, they are 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

Go 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	Cyclohexan...
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: C₉H₁₆
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: H₂
Column Diameter: 0.25 mm

Lib. Search Other Search Names Compare Librarian MSMS

Ident Ident

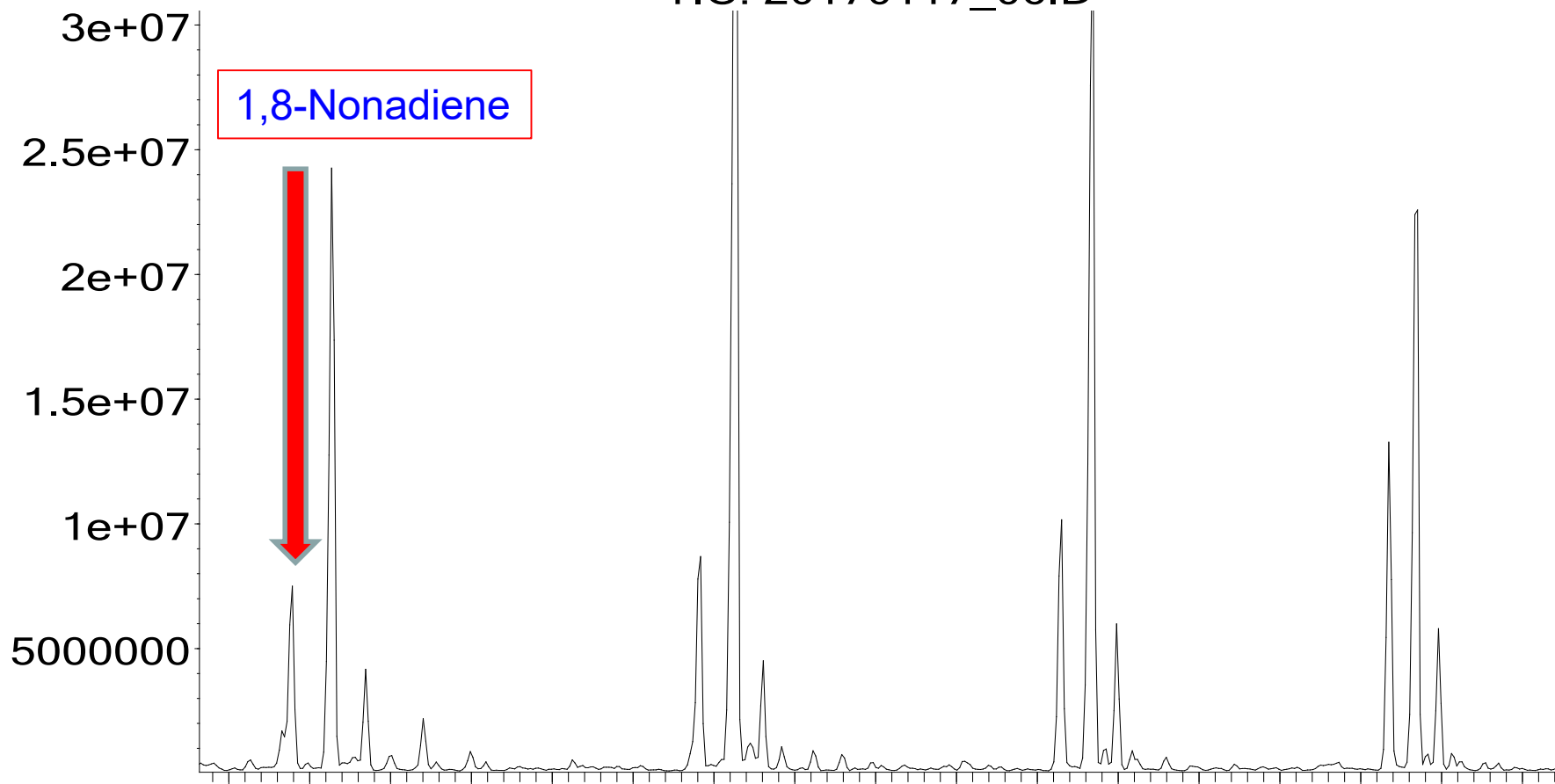
Start Instrum... Environ... Shin_Ts... Instrum... NIST M... F:\ Microso... 4:36 PM

High-Density Polyethylene (HDPE)

Abundance

Continue to identify other peaks in this section of the pyrogram..

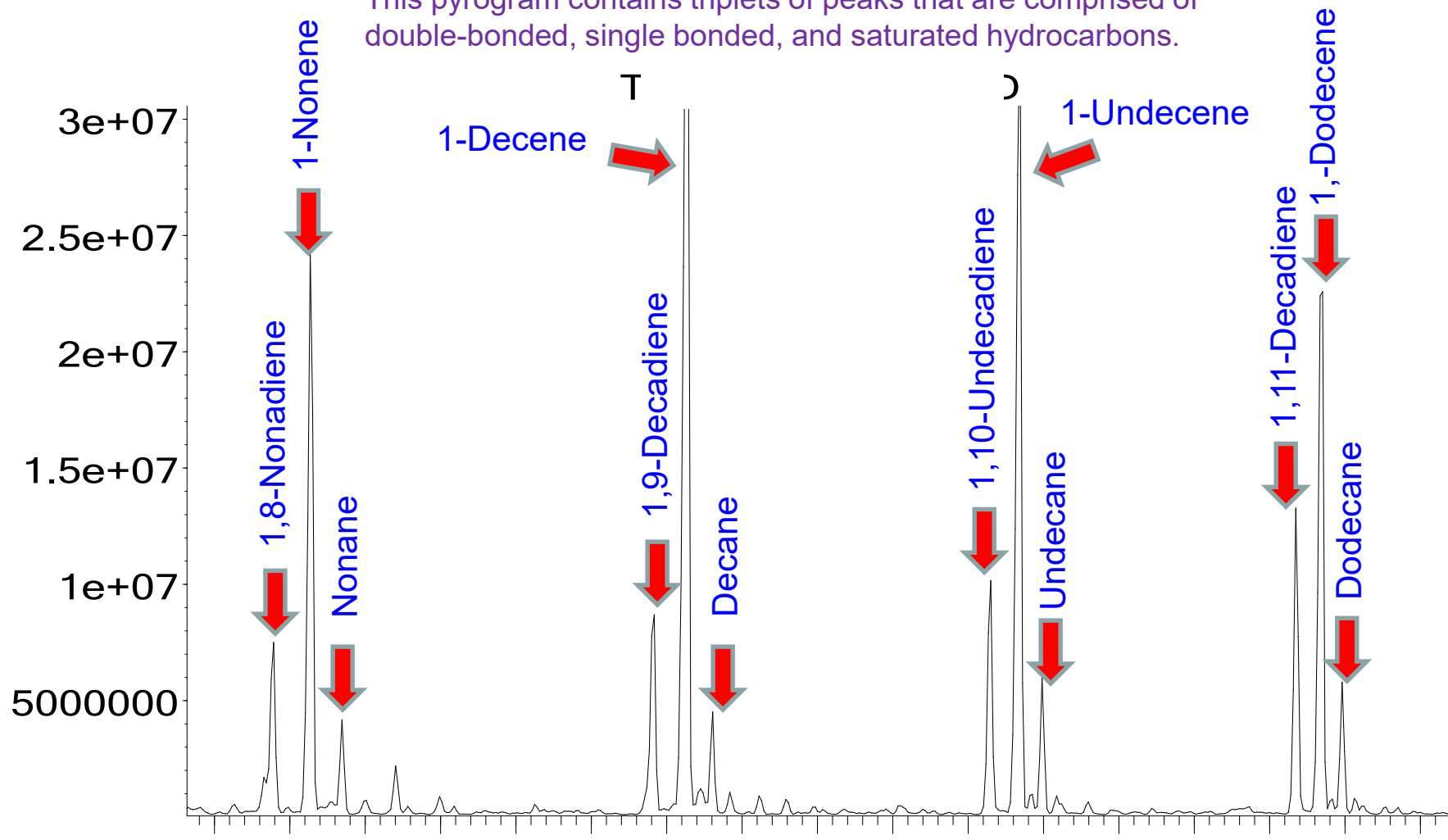
TIC: 20170117_06.D



High-Density Polyethylene (HDPE)

Abundance

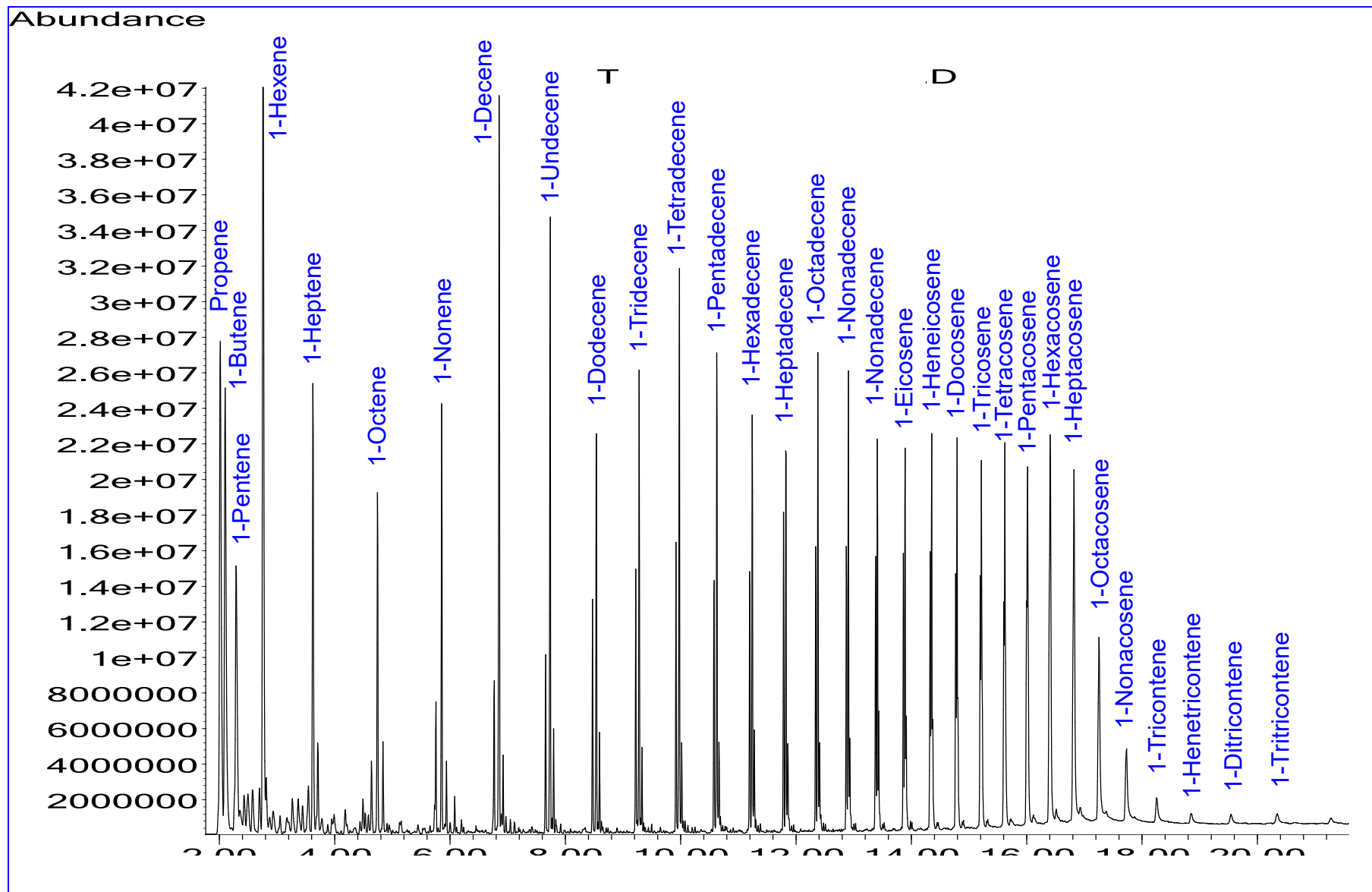
This pyrogram contains triplets of peaks that are comprised of double-bonded, single bonded, and saturated hydrocarbons.





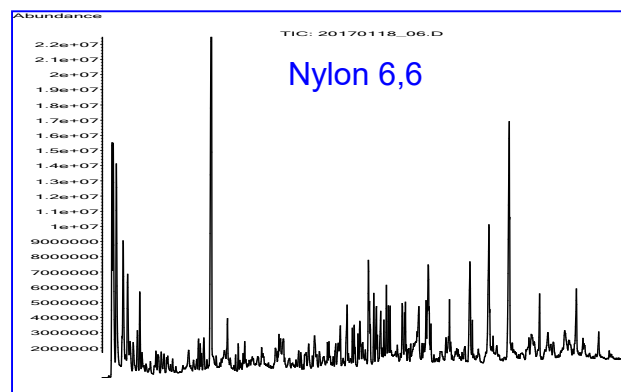
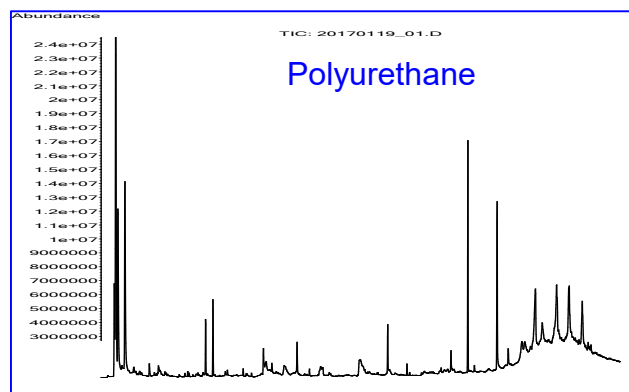
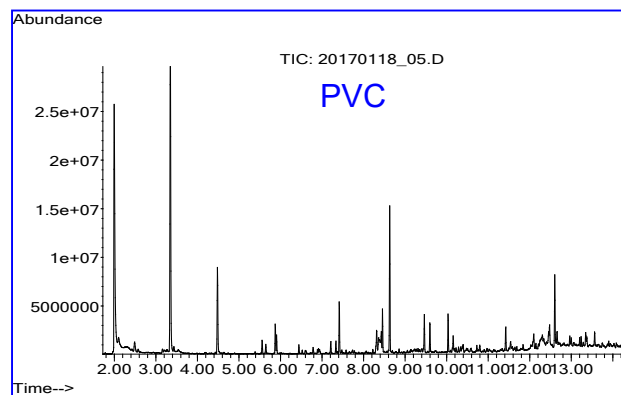
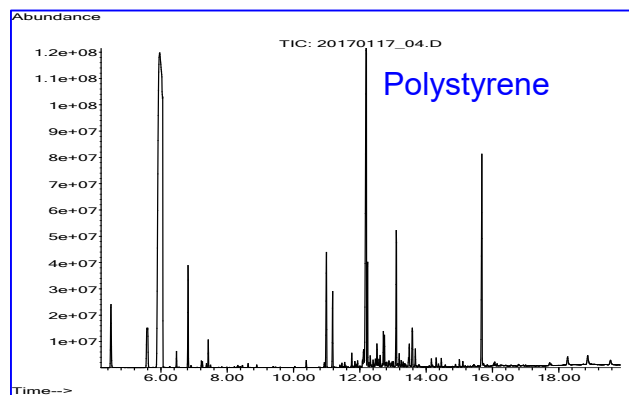
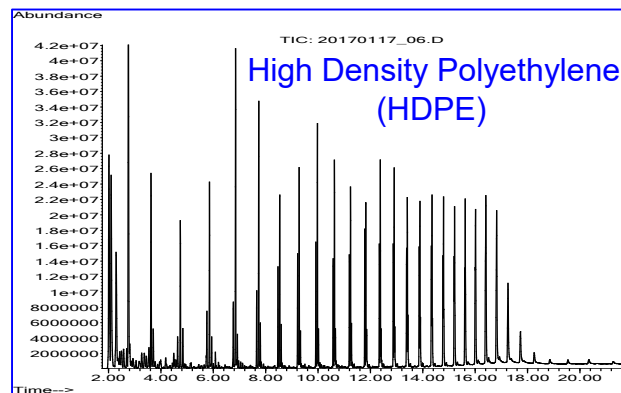
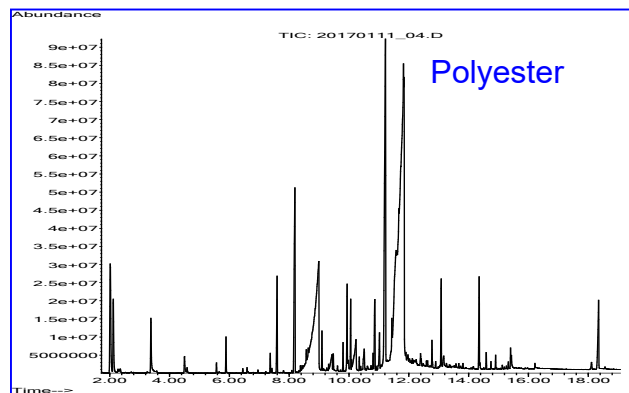
With a little more patience and perseverance,
characterize remaining peaks in the entire pyrogram..

High-Density Polyethylene (HDPE)



Examples of Pyrolysis GC-MS Pyrograms of Plastic Polymers

(Note that different polymers have different signatures)

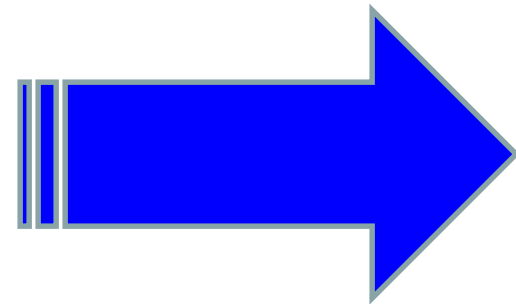


Good News!



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

COMMON PLASTIC ITEMS



12-Inch Hard Plastic Ruler

Abundance

1.1e+08

1e+08

9e+07

8e+07

7e+07

6e+07

5e+07

4e+07

3e+07

2e+07

1e+07

4.00

5.00

6.00

7.00

8.00

9.00

10.00

Styrene

Styrene Dimer

Polystyrene

Styrene Trimer



Micropipette Tip (100 μ l)

Abundance

TIC: 20161205_01.D

Polypropylene

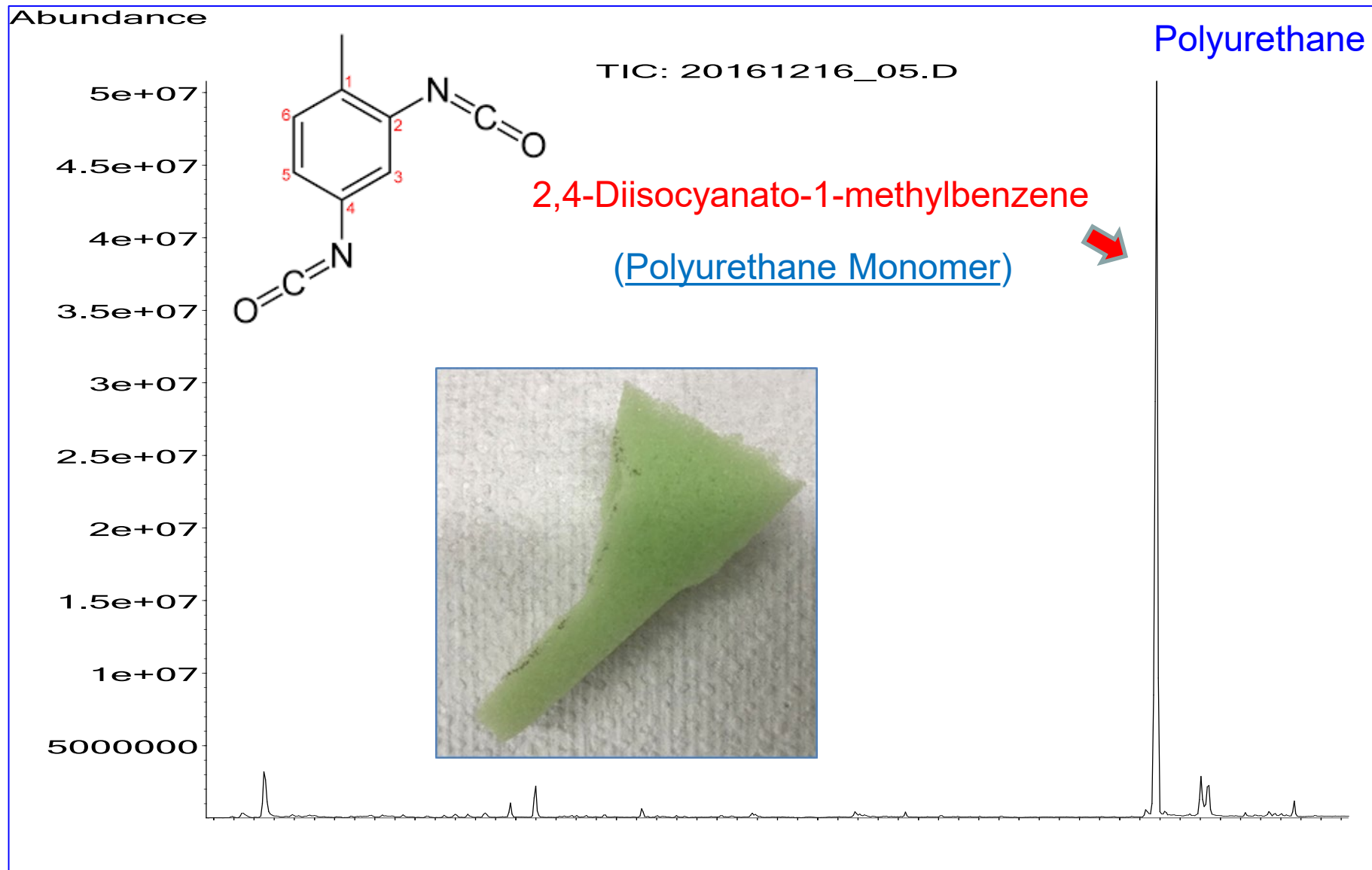
2,4-Dimethyl-1-heptene

(A Marker Compound of Polypropylene)

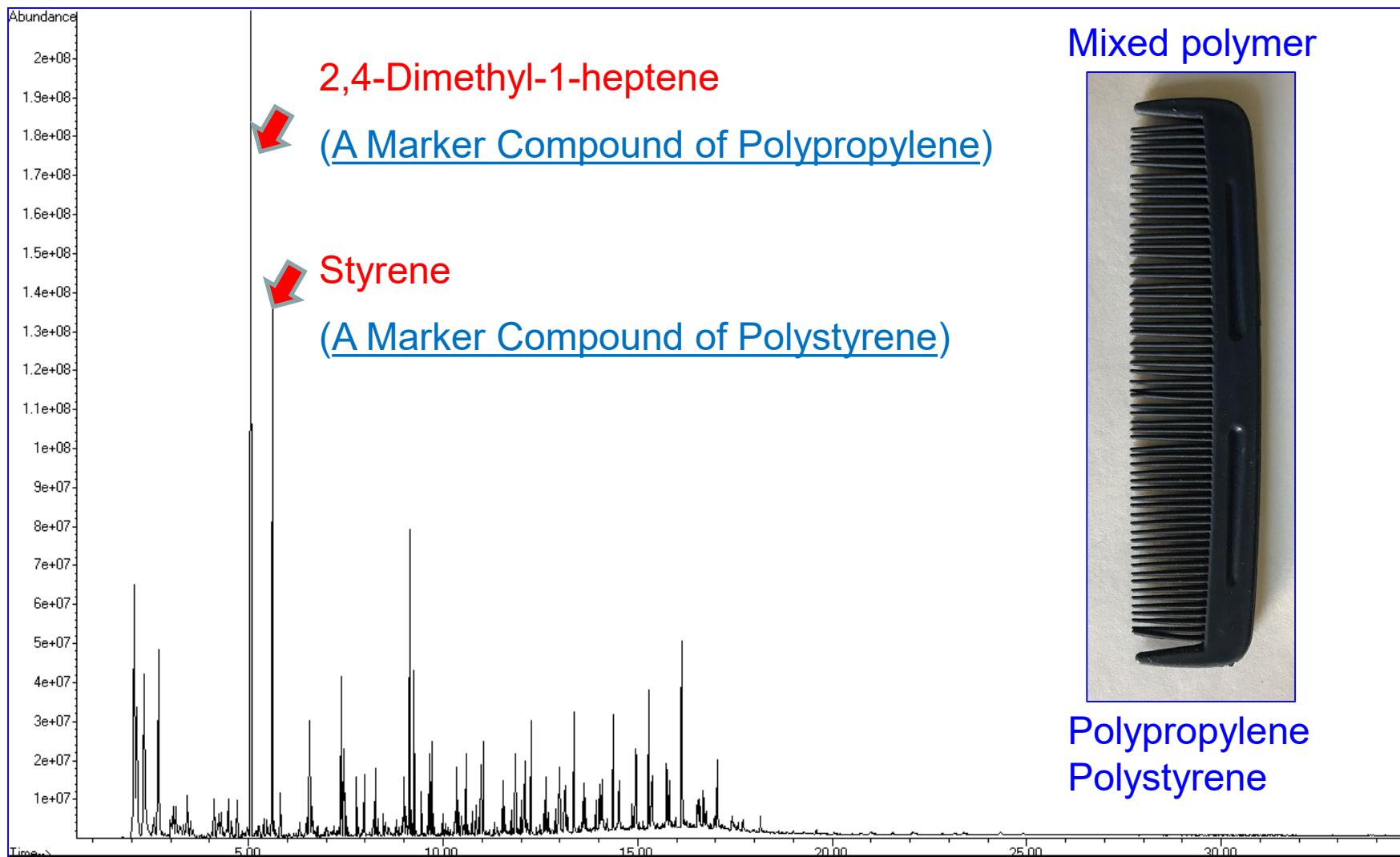
5e+07
4.5e+07
4e+07
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000



Foam

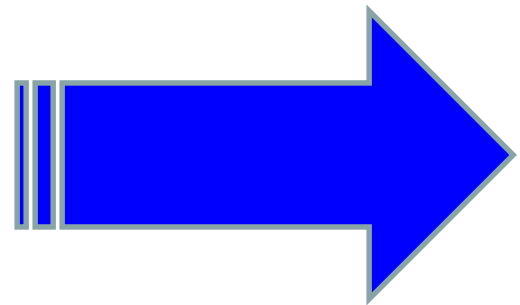


Hair Comb





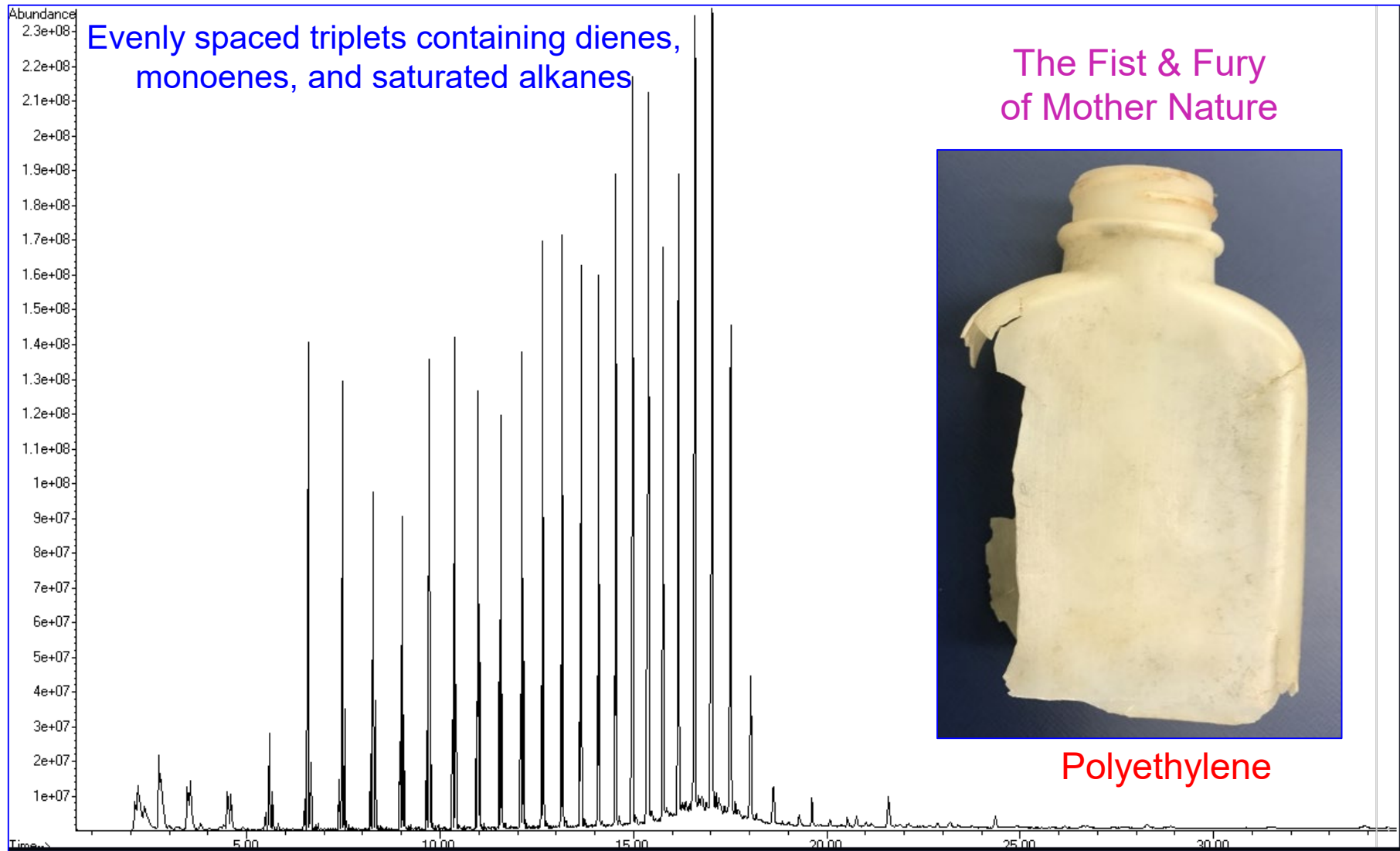
WEATHERED PLASTICS



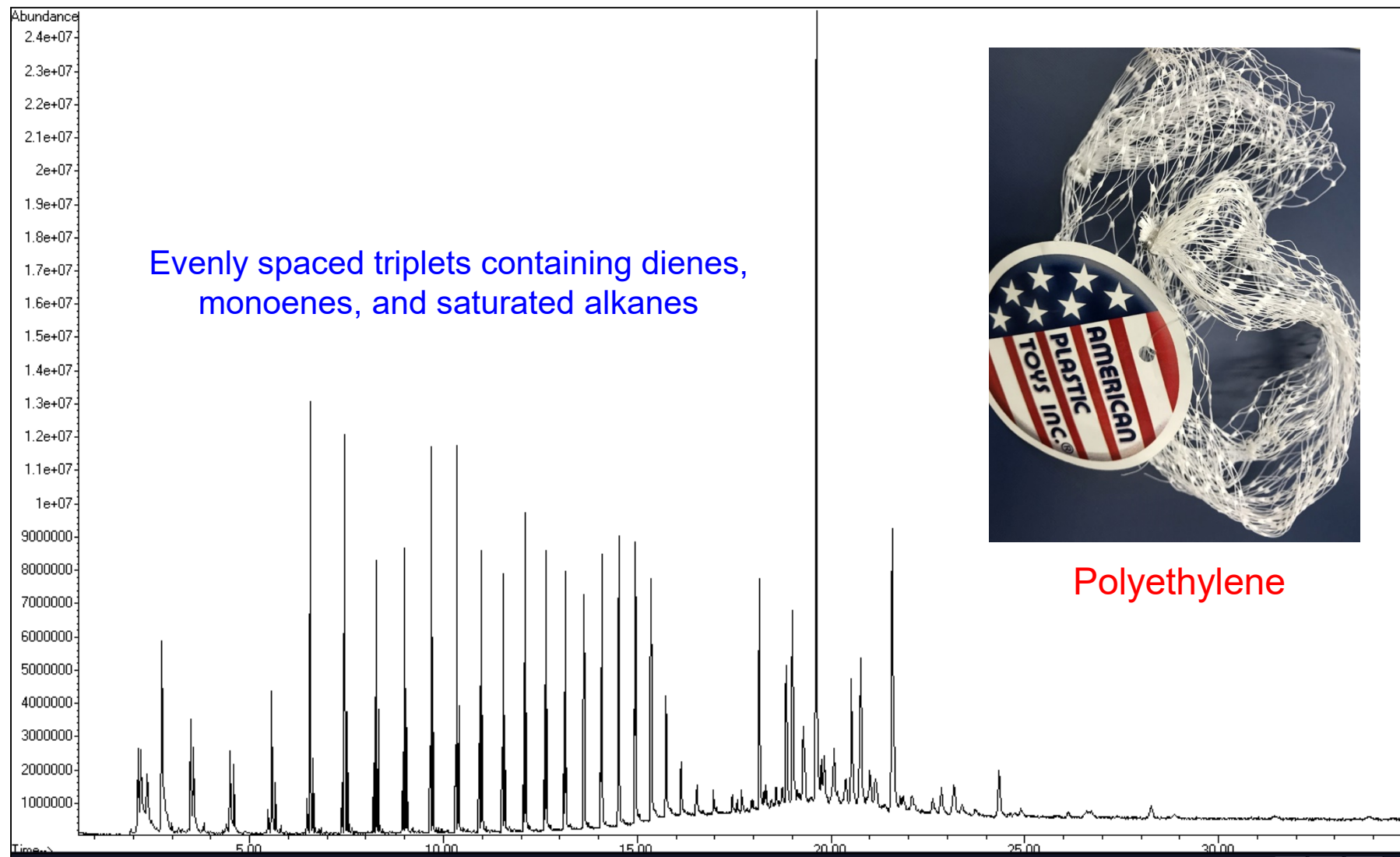
Plastic from the Beaches



Weathered Plastic bottle

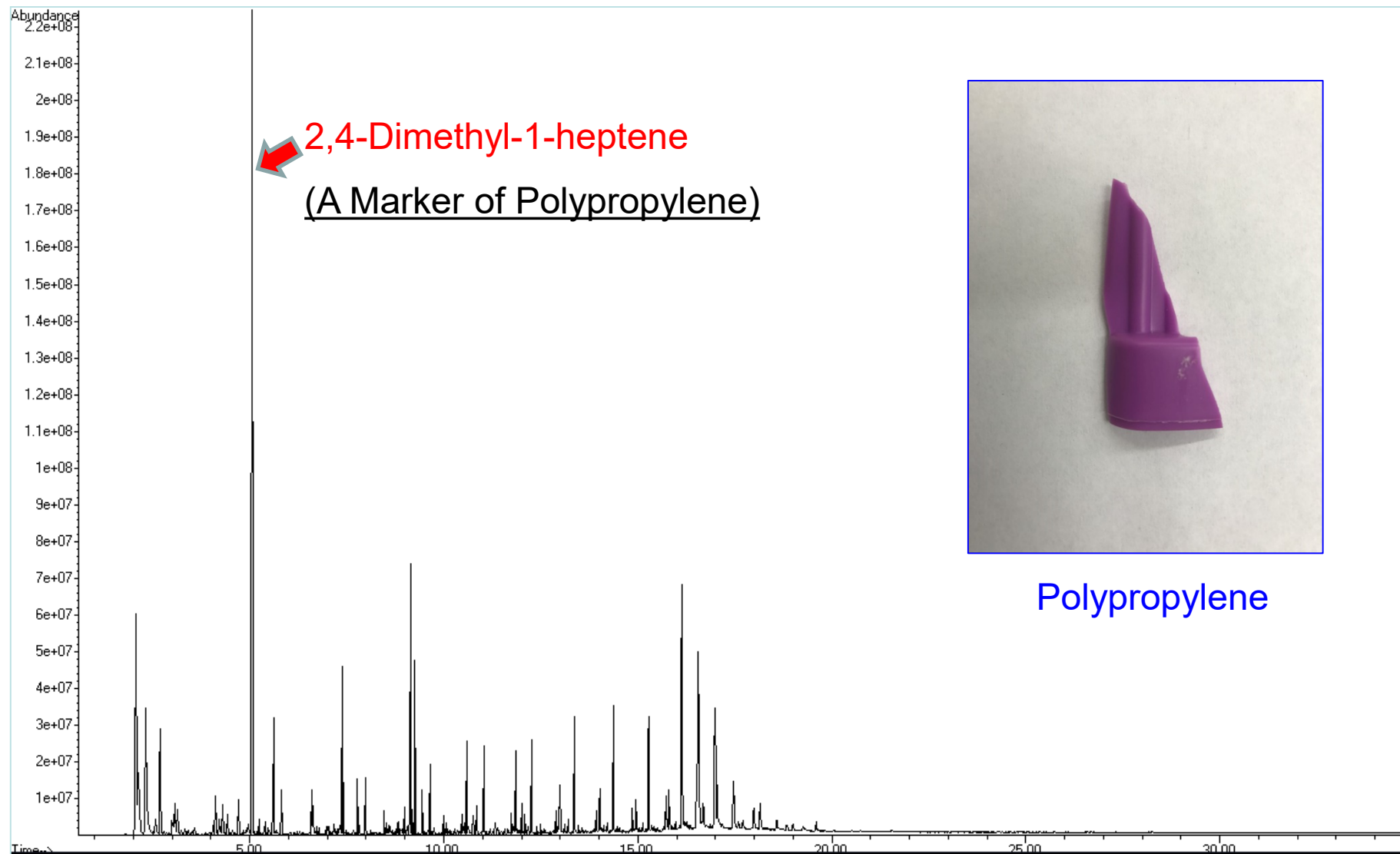


Toy Mesh Bag



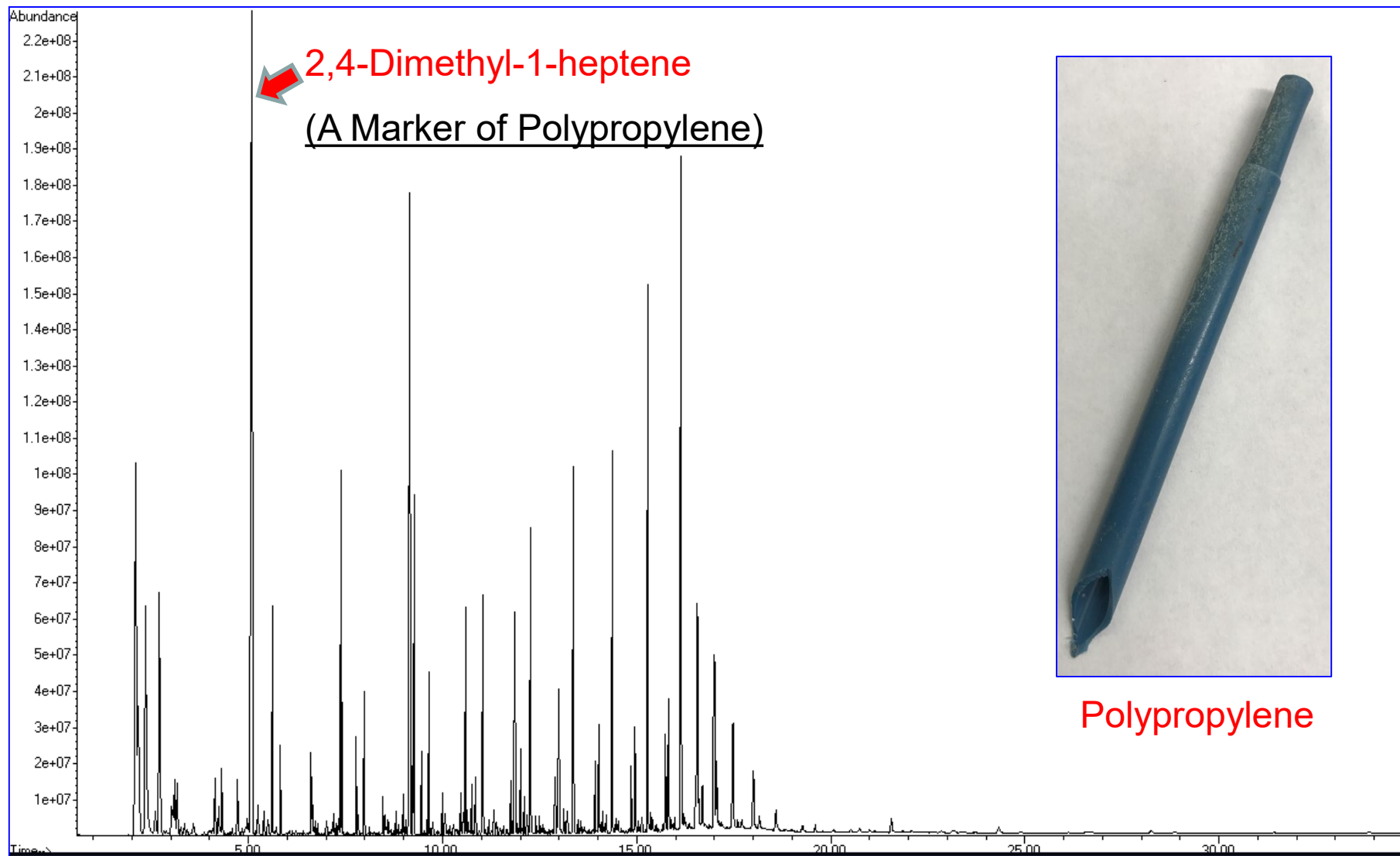
American Plastic Toy found in Long Branch, NJ

Purple piece of beach plastic



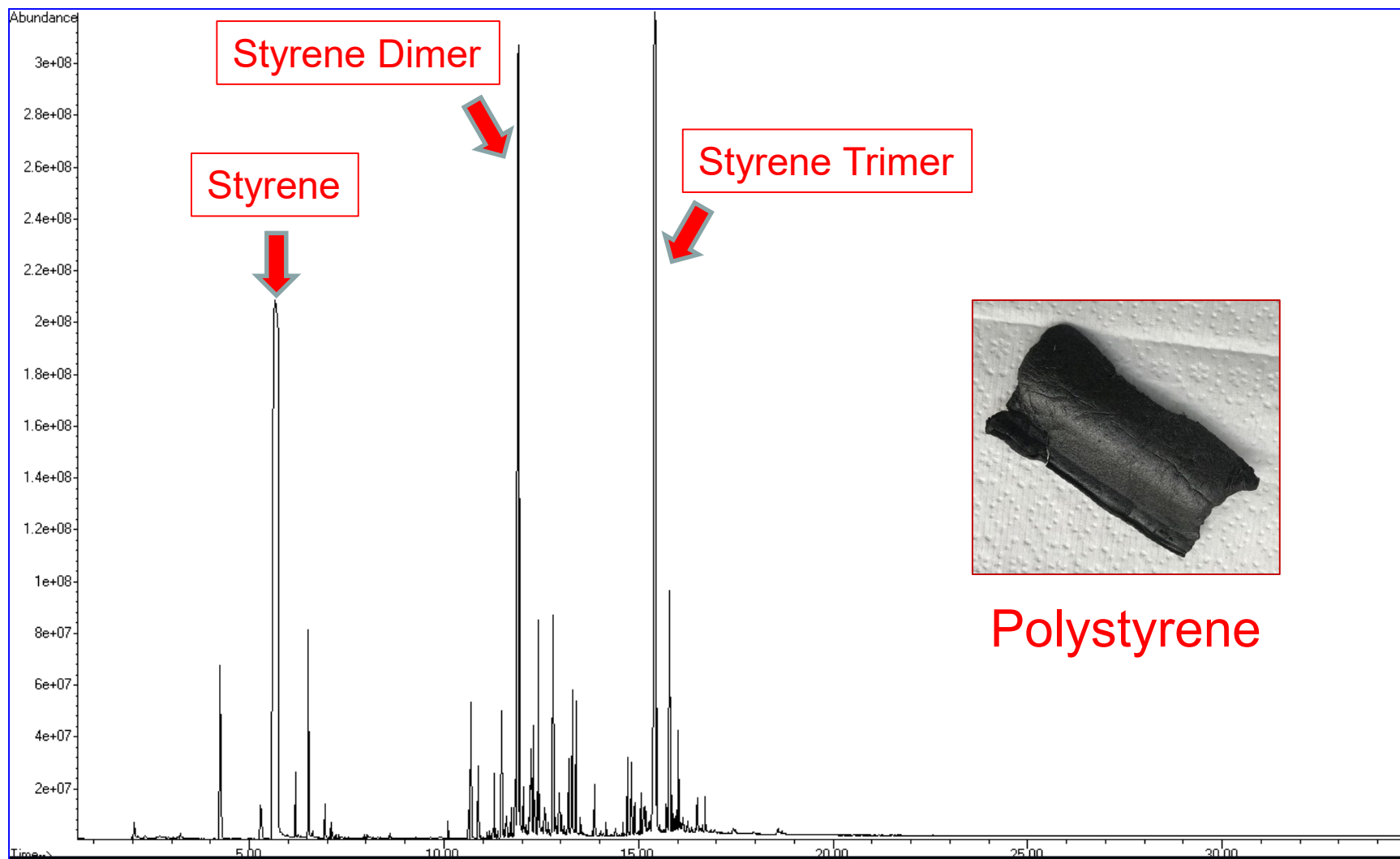
Found on Long Branch, NJ Beach

Weathered Pen Barrel

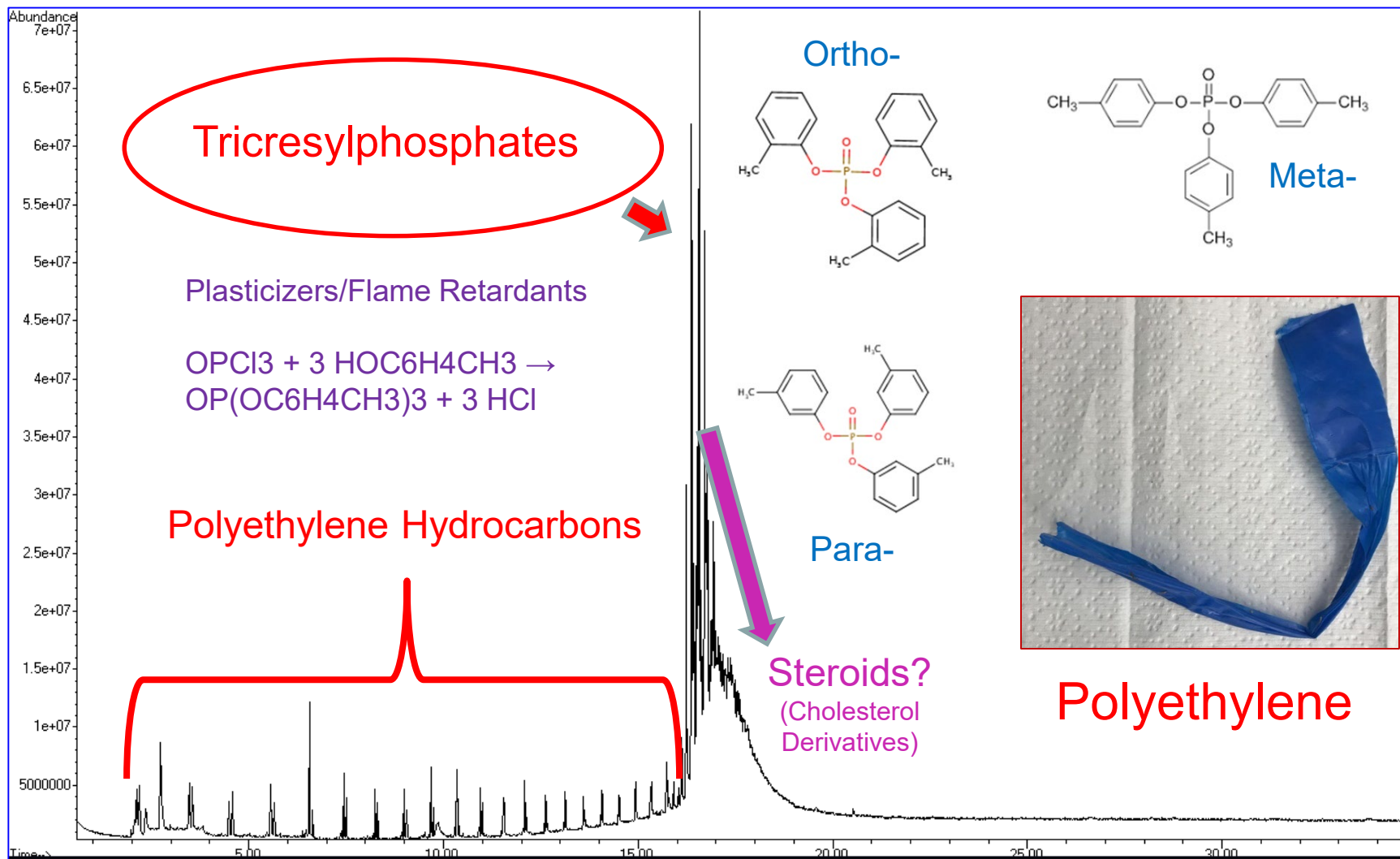


Found on the beach by Clean Ocean Action

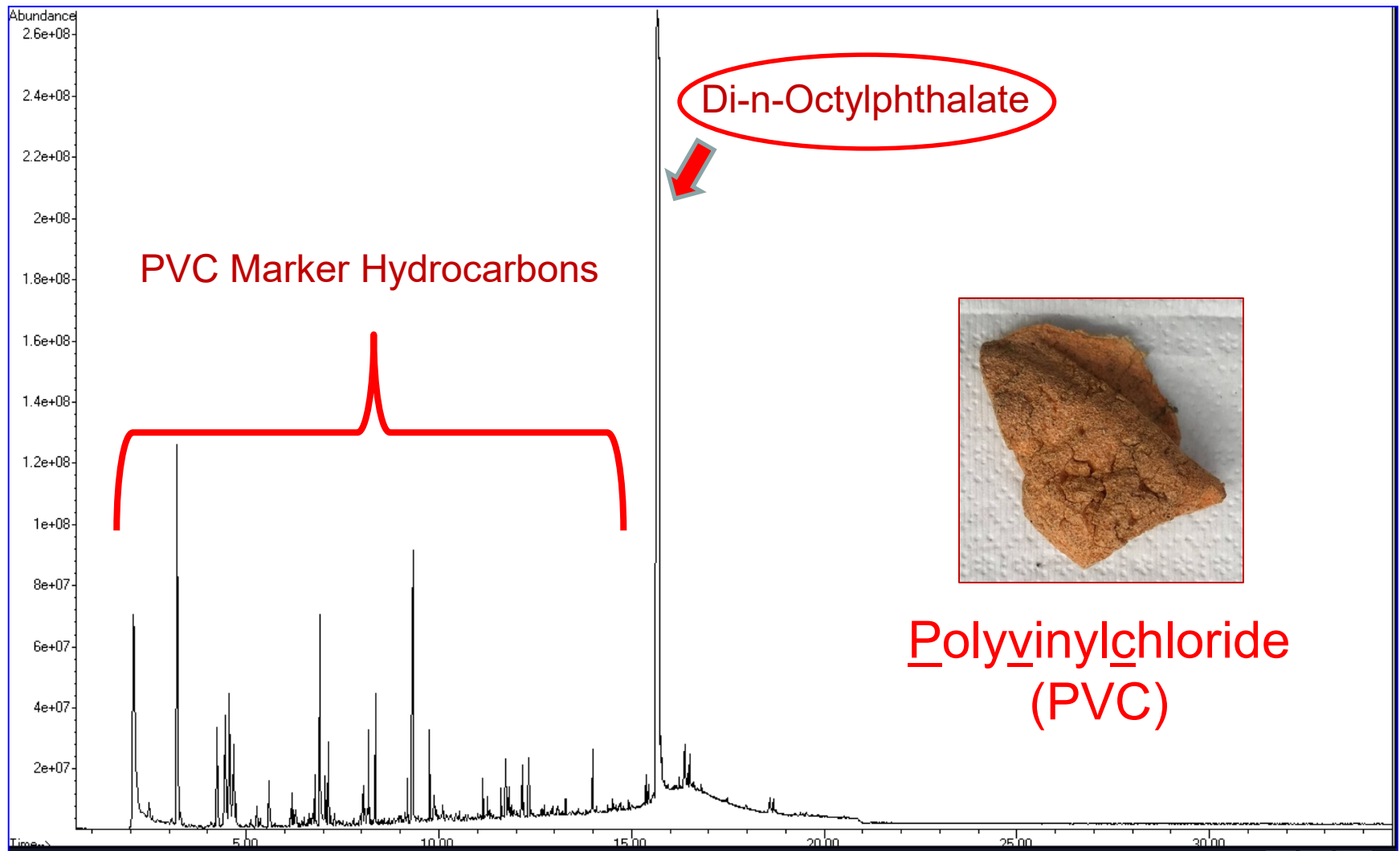
Alaska Beach - Black Foam



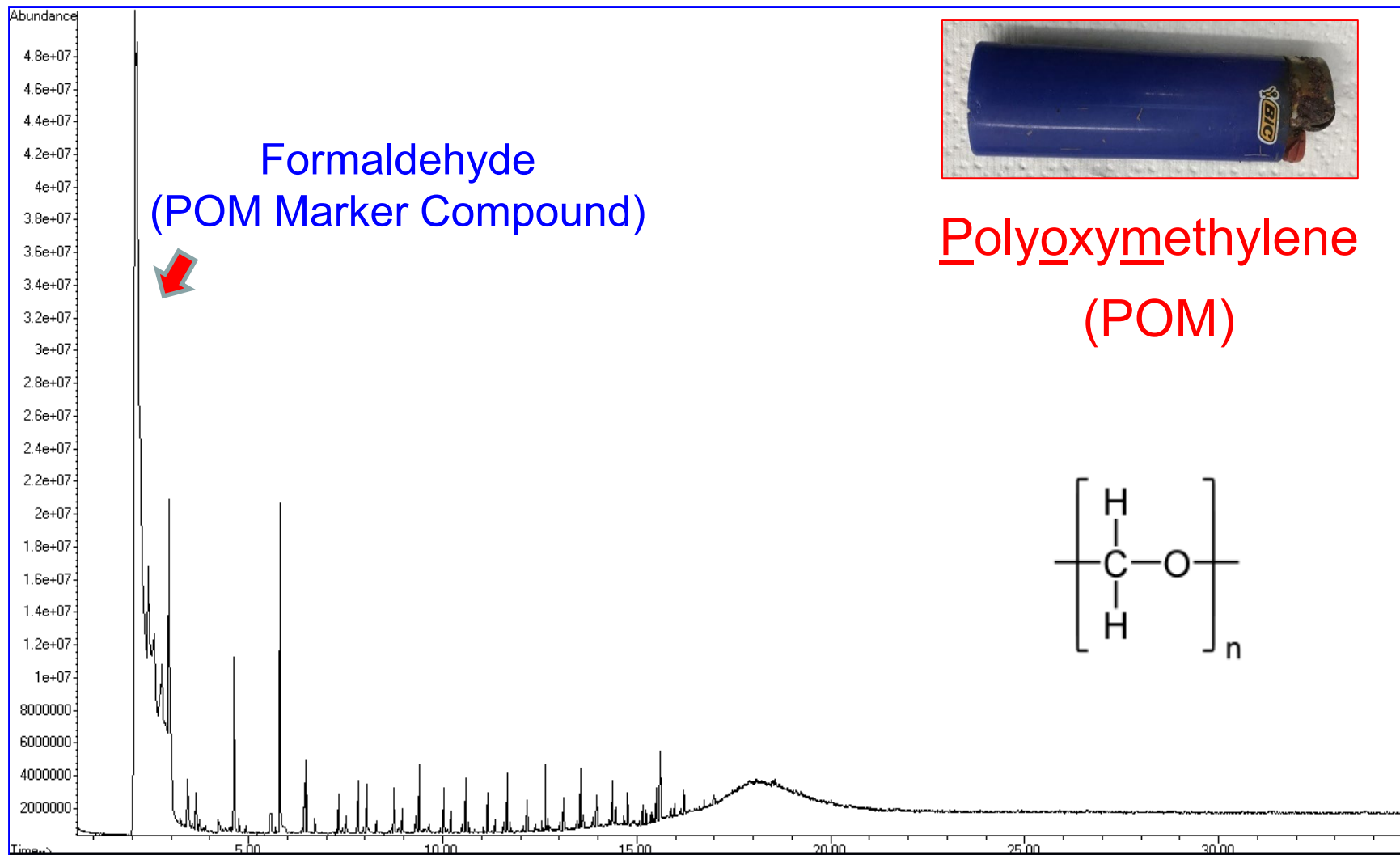
Alaska Beach - Blue Tape



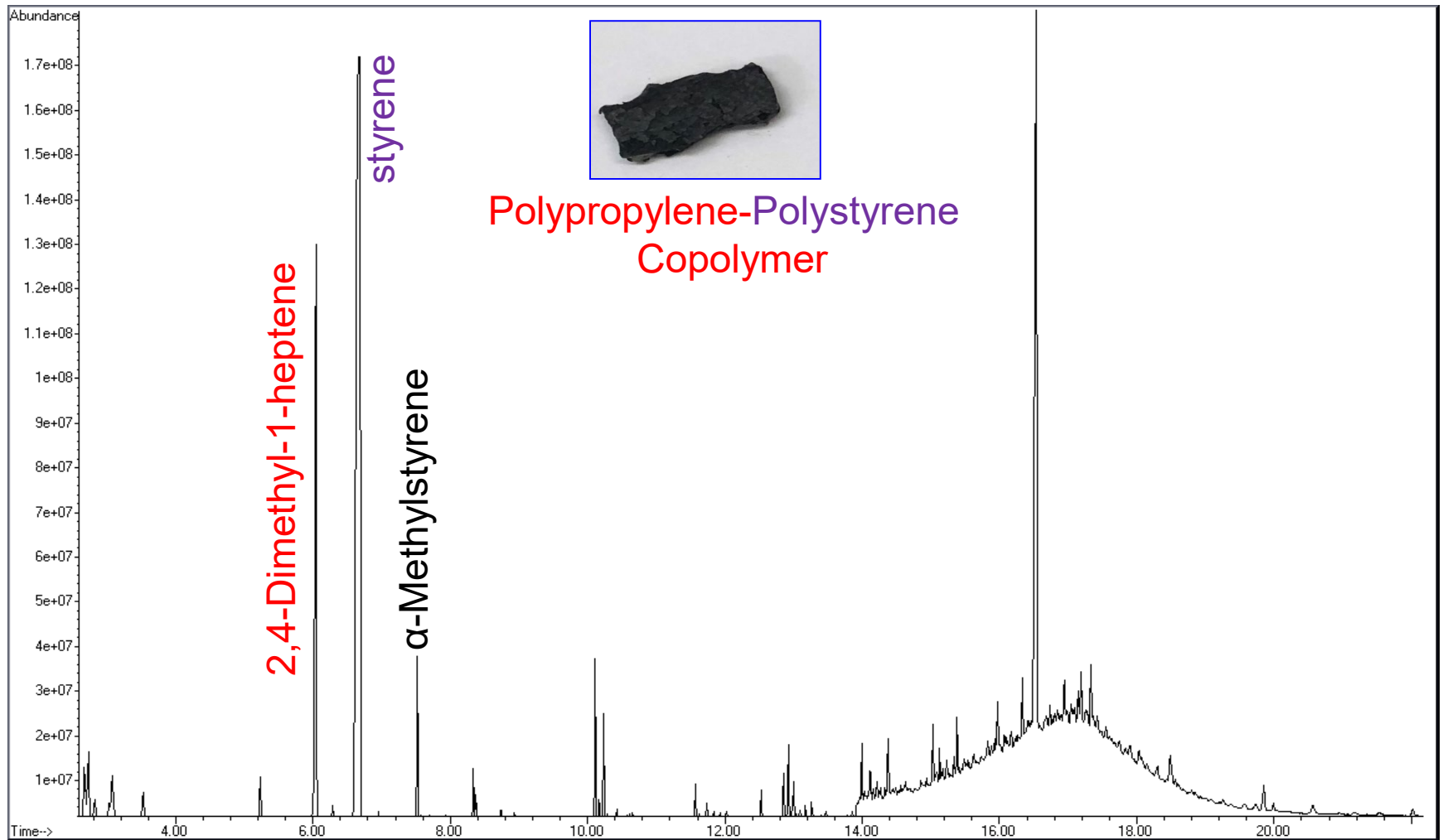
Alaska Beach - Orange Foam



Alaska Beach - BIC Lighter



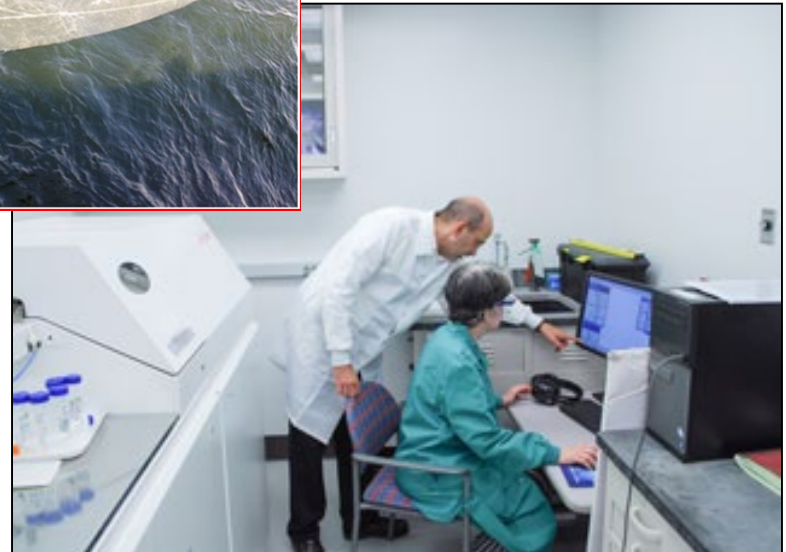
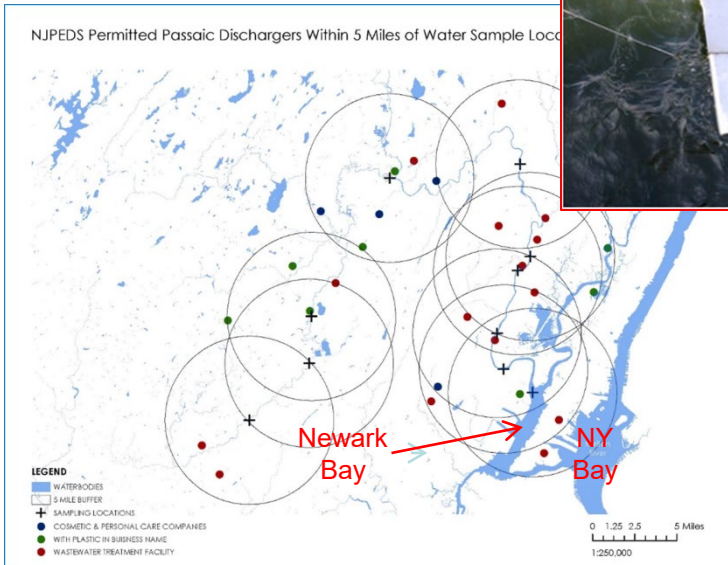
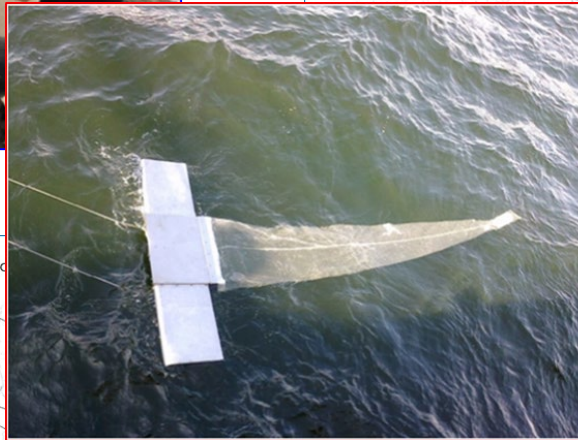
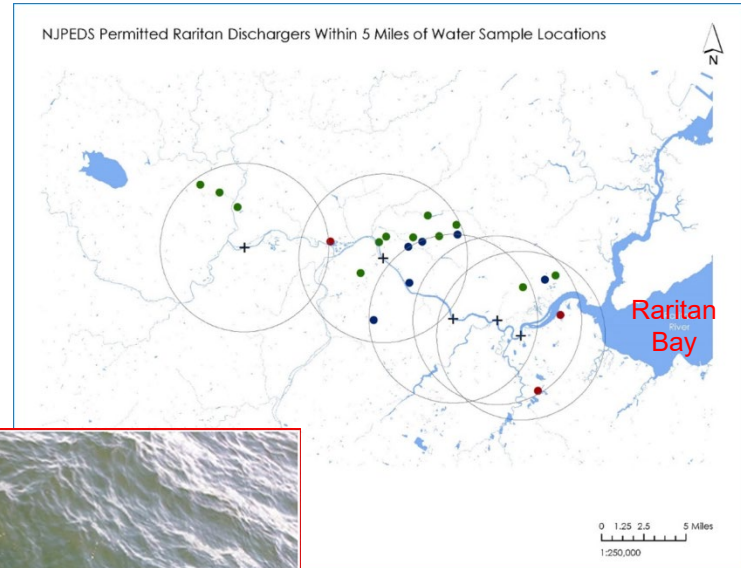
Hawaii-Lanai



Microplastics from the Raritan and Passaic Rivers in New Jersey



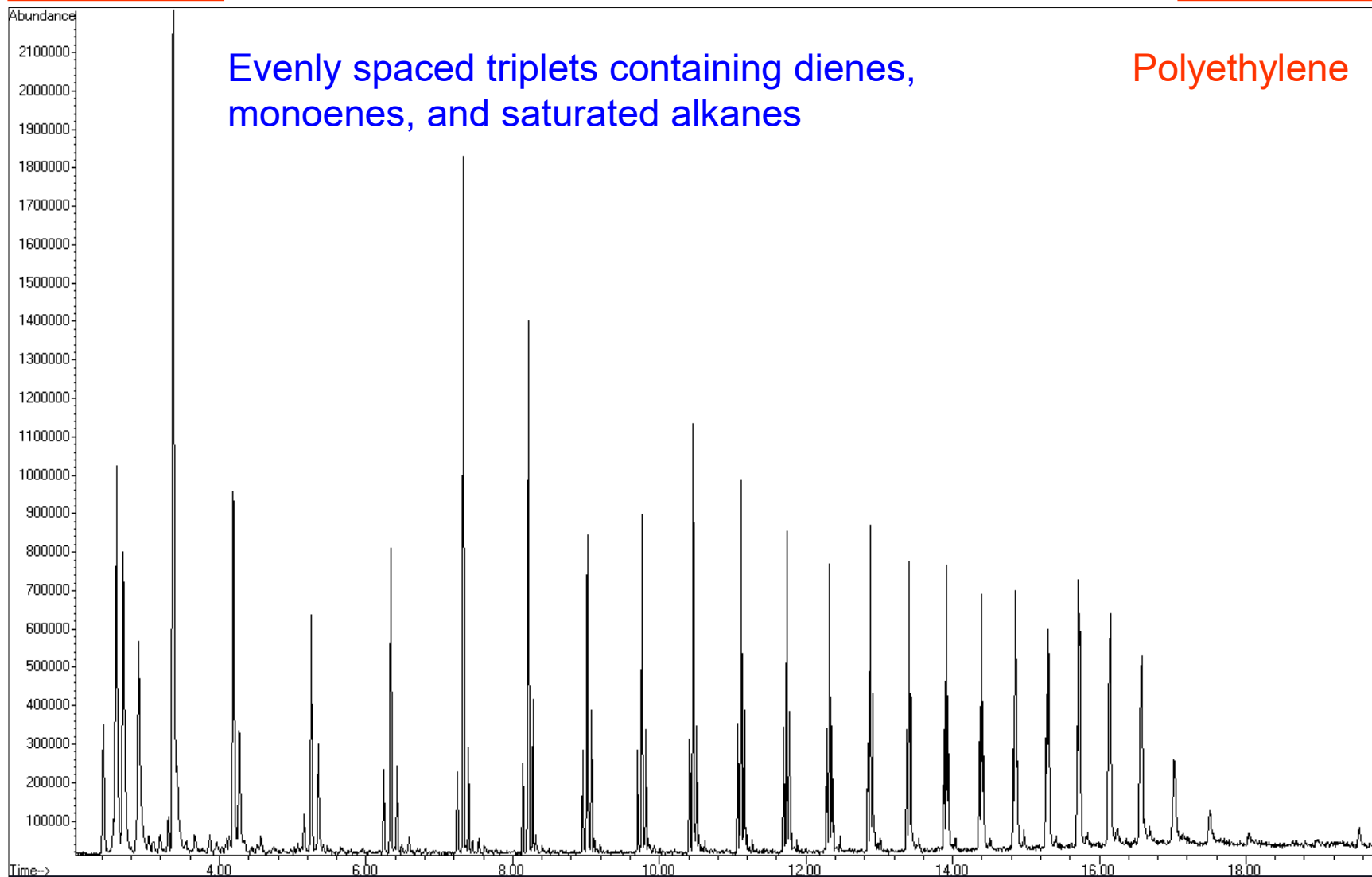
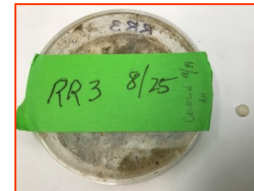
Dr. Keith Cooper and Dr. Beth Ravit



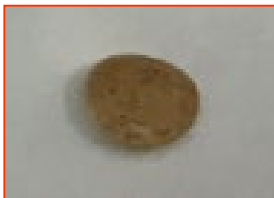
Dr. Brian Buckley



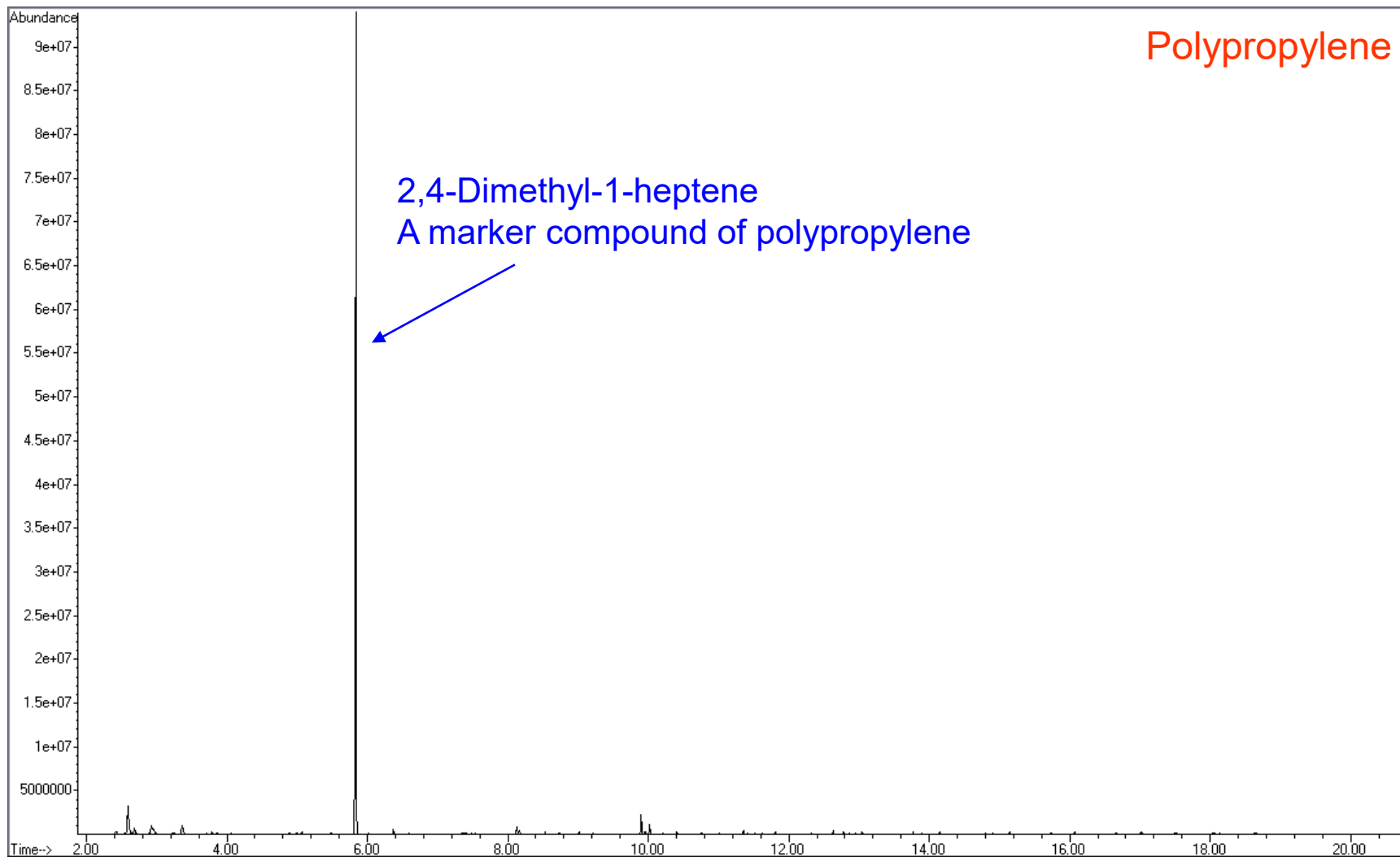
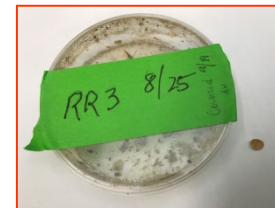
Rutgers Sample RR3 8/25
off-white nurdle



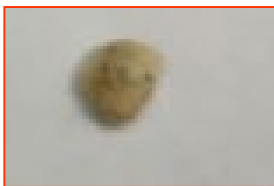
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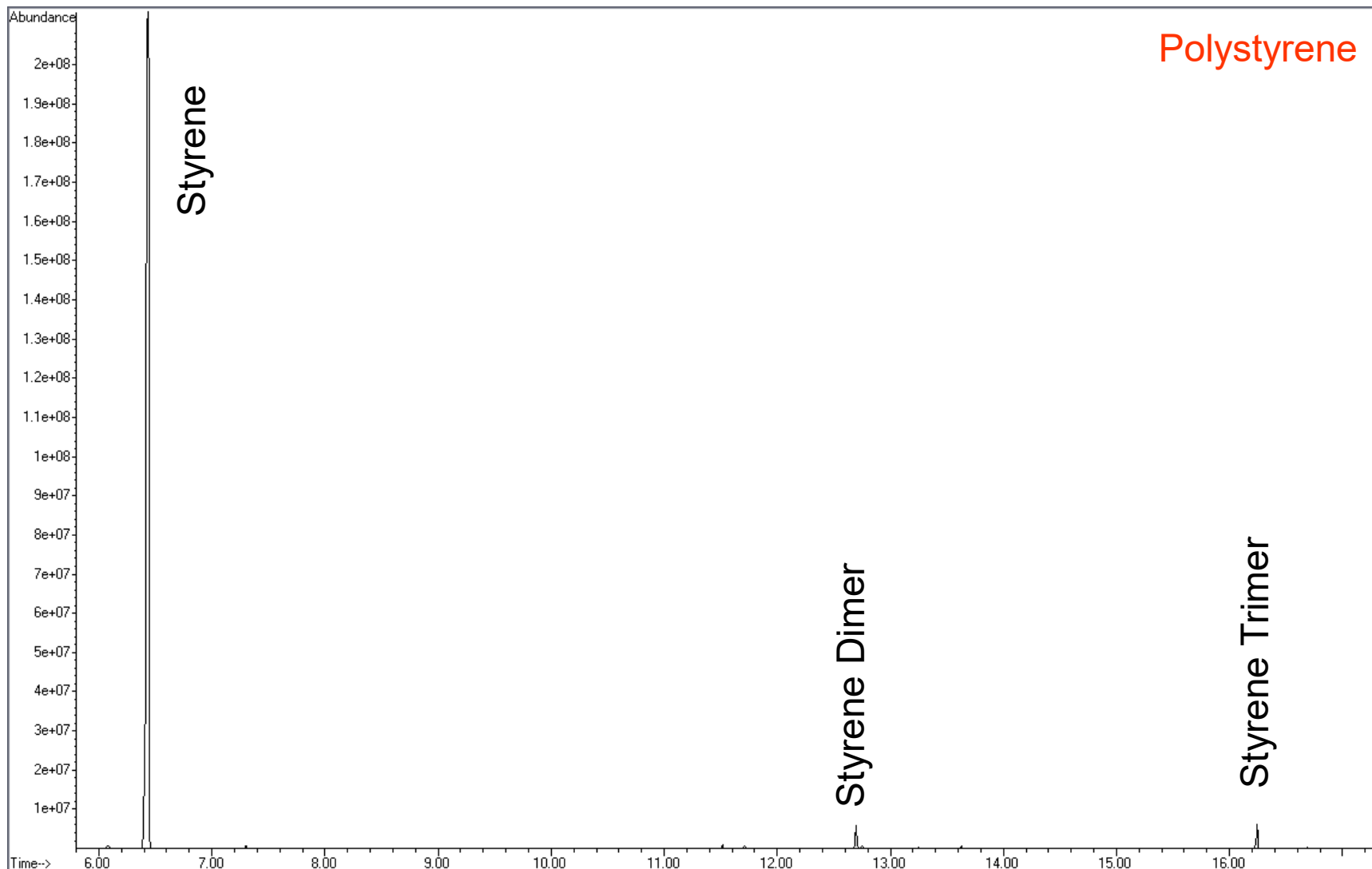
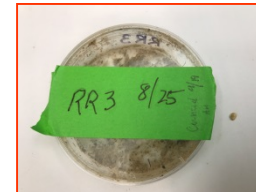
Rutgers Sample RR3 8/25
semi-transparent nurdle



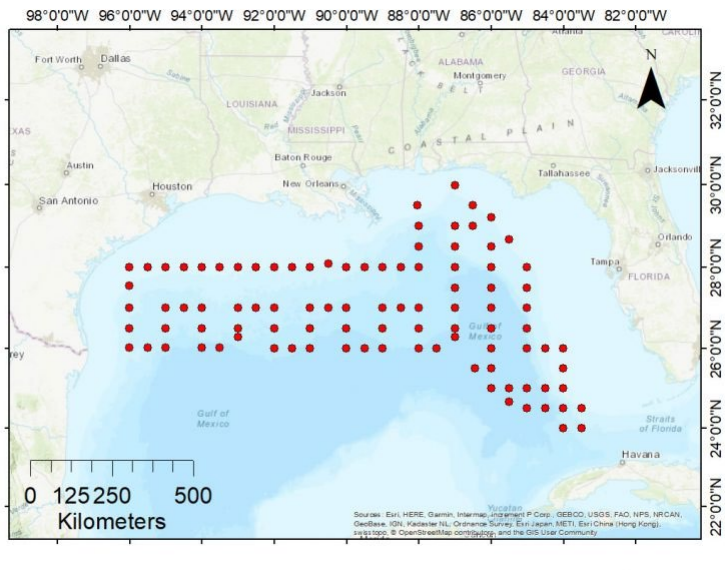
E:\Microplastics\Rutgers II\20180830_37.D



Rutgers Sample RR3 8/25
small round off-white foam



E:\Microplastics\Rutgers II\20180830_35.D



NOAA Restore Cruise Gulf of Mexico

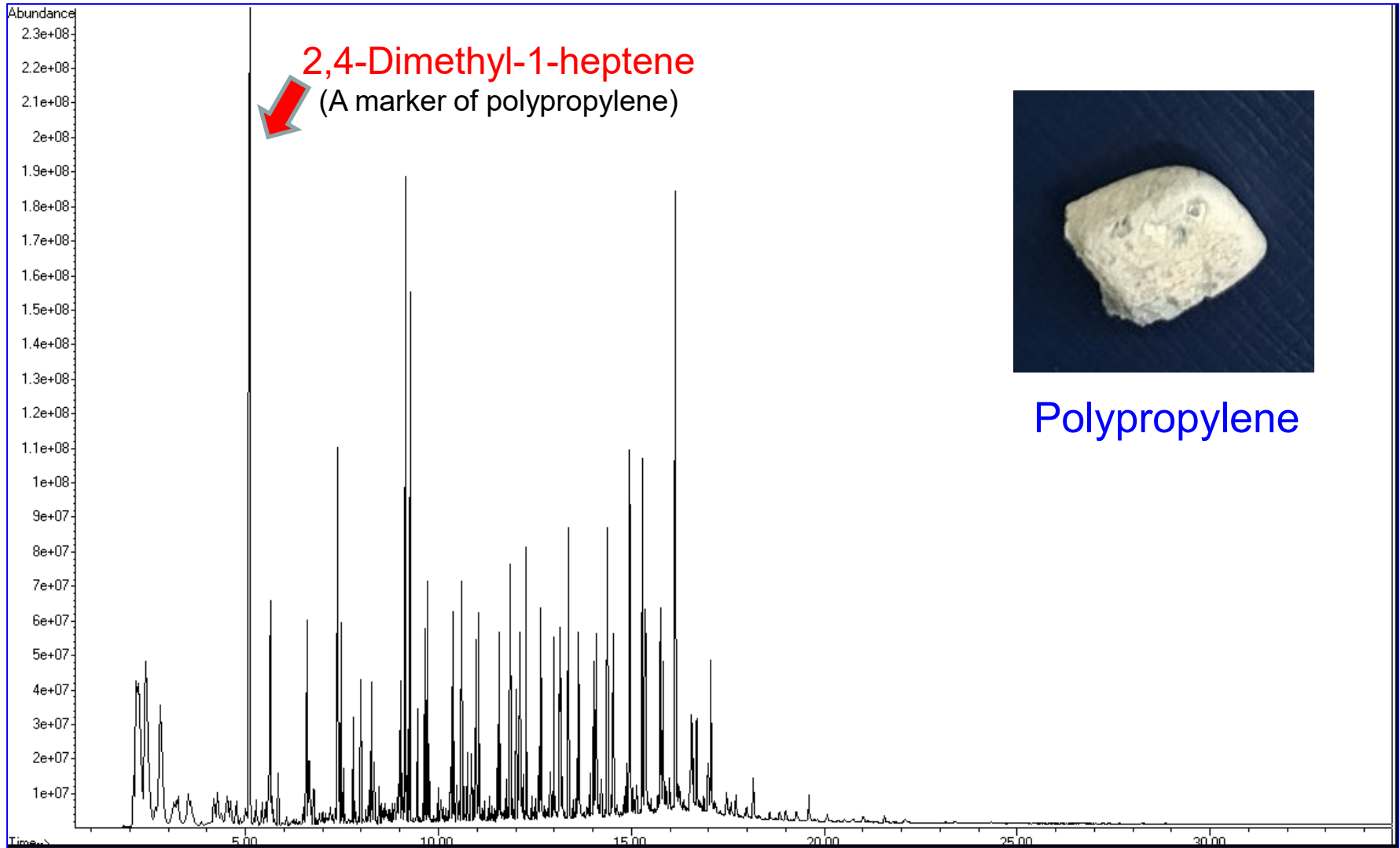


Microplastics in Sargassum Mats
(Proxy for Presence and Movement of Marine Debris)



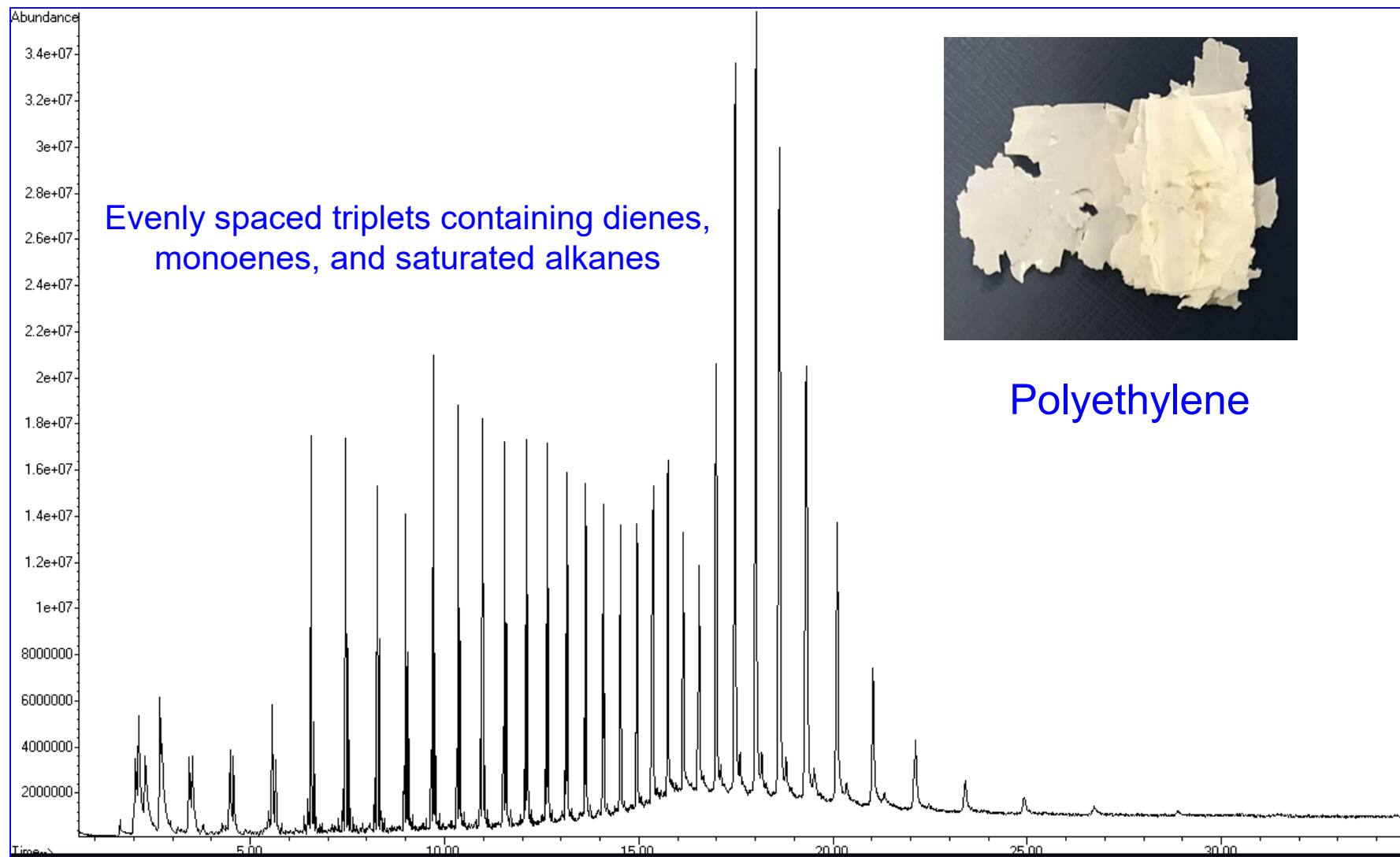
Dr. Frank Hernandez
University of Southern Mississippi

NOAA Restore Cruise PS-17-07 Sample 7



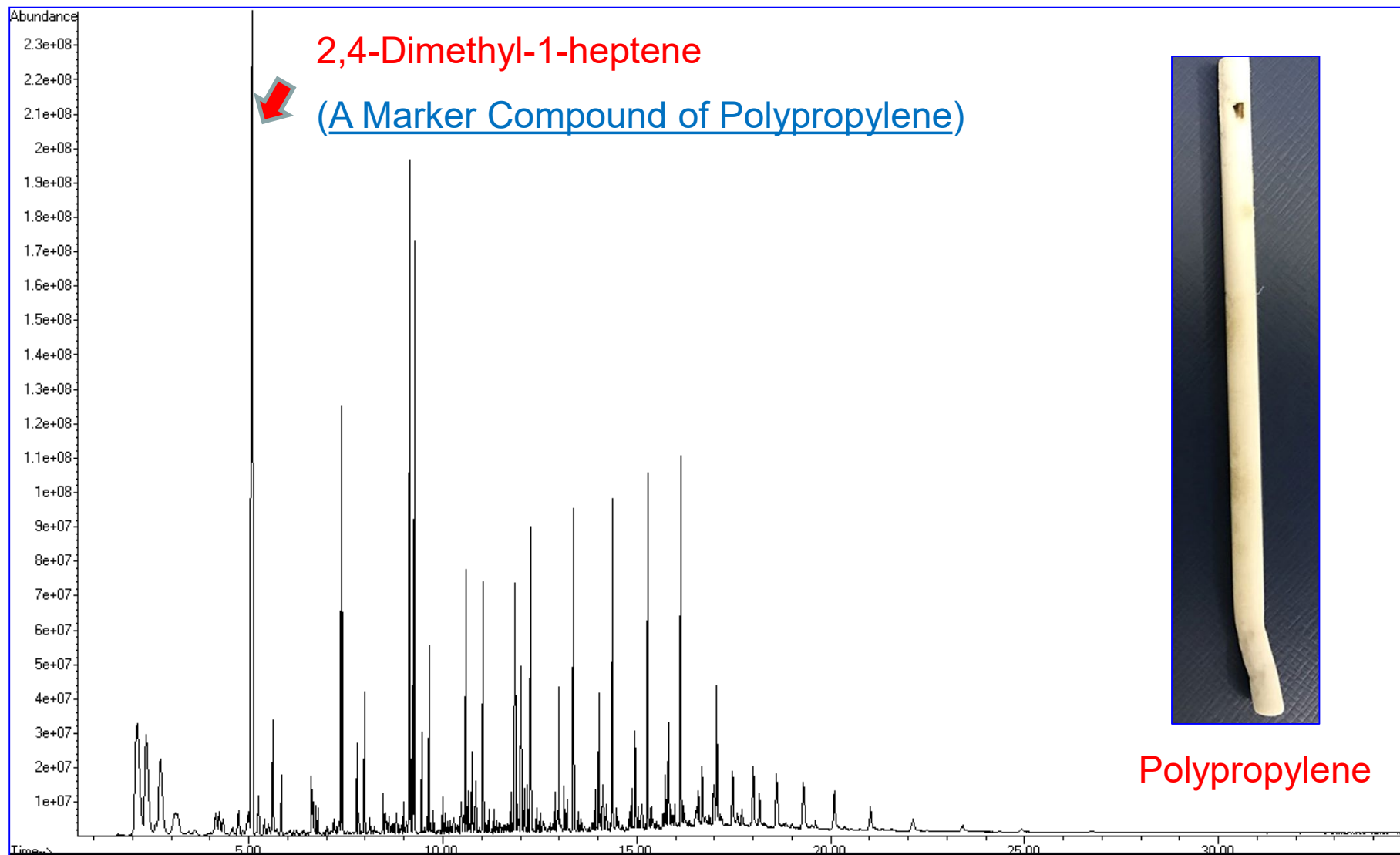
Gulf of Mexico Surface Water Dip Net

NOAA Restore Cruise PS-17-07 Sample 3



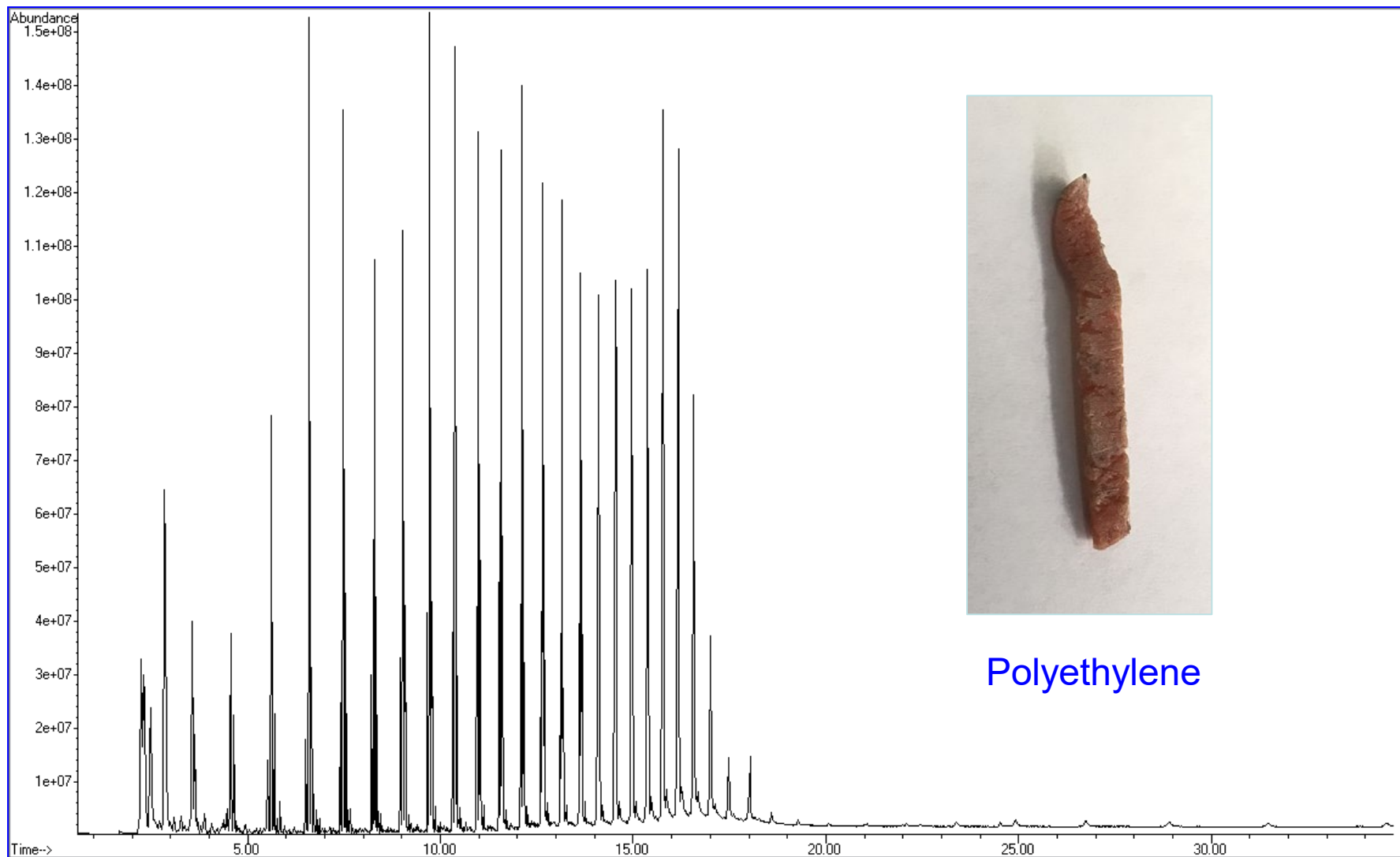
Gulf of Mexico Surface Water Dip Net

NOAA Restore Cruise PS-17-07 Sample 5



Gulf of Mexico Surface Water Dip Net

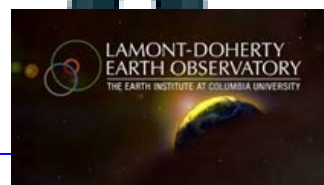
Gulf of Mexico Surface Water Dip Net



NOAA Restore Cruise PS-17-07 Sample 1

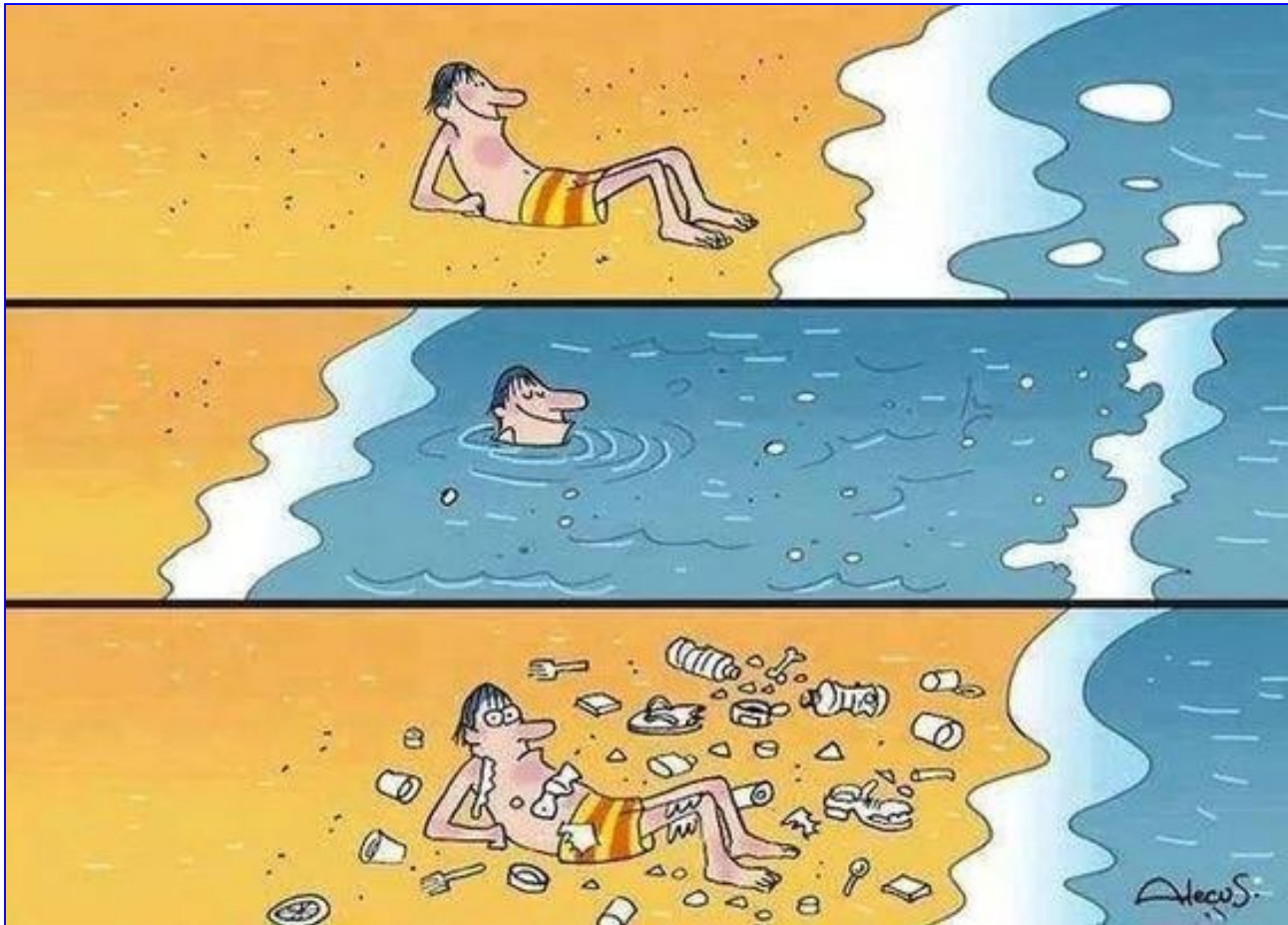


Collaborative Studies



It takes a village..





**Thank you
for your
attention**