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PY-GCMS Analysis of Microplastics Using Nitrogen as an Alternative Carrier Gas

August 5, 2024

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Today’s Agenda

- Review of MP Workflow
  - EGA-MS
  - Single Shot
  - Challenges Faced with Mixed Microplastics
  - System configuration for Quick Workflow
- Helium Data Review
  - Quantitative Analysis of Mixed Polymer Standards
  - Alternative Carrier Gases
- Expanding into Nitrogen
  - Overview of Nitrogen Data
  - Comparison between He and N_2

Steps in PY-GCMS Qualitative analysis of MP

1. Polymer Preparation

- Solid polymers are sliced or ground
- Placed into an eco cup with quartz wool

2. EGA-MS Analysis

- Thermal zone established
- Optimum PY furnace temp determined for Single Shot

3. Single Shot GCMS

- Pyrolyzates formed by flash pyrolysis
- Pyrogram obtained

4. Data Analysis and Comparison

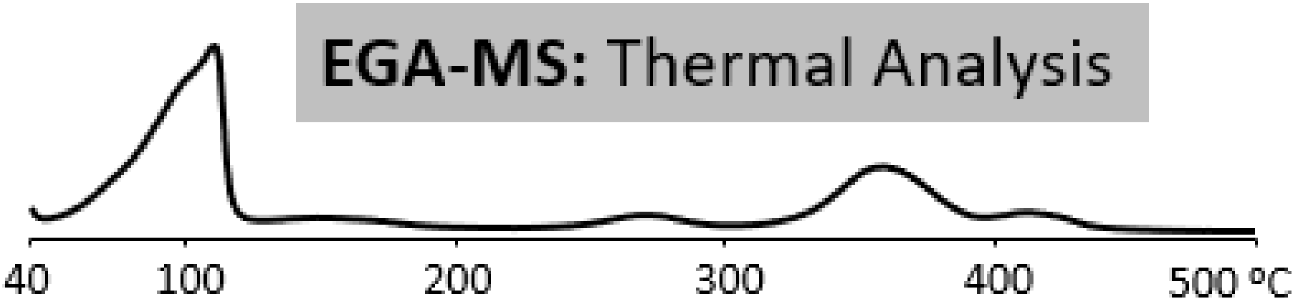
- All pyrolyzates identified via F-Search library
- Characteristic pyrolyzate determined via data comparison

Standard kit obtained from Hawaii Pacific University NIST

Evolve Gas Analysis

- **Imperative to understand the thermal zones of the polymers in question**
- **Initial spectral information for specific polymers**
  - Average mass spectrum can be matched against libraries
  - Thermograms can be complex requiring additional analysis
- **Major *m/z* could be prevalent for multiple polymers**

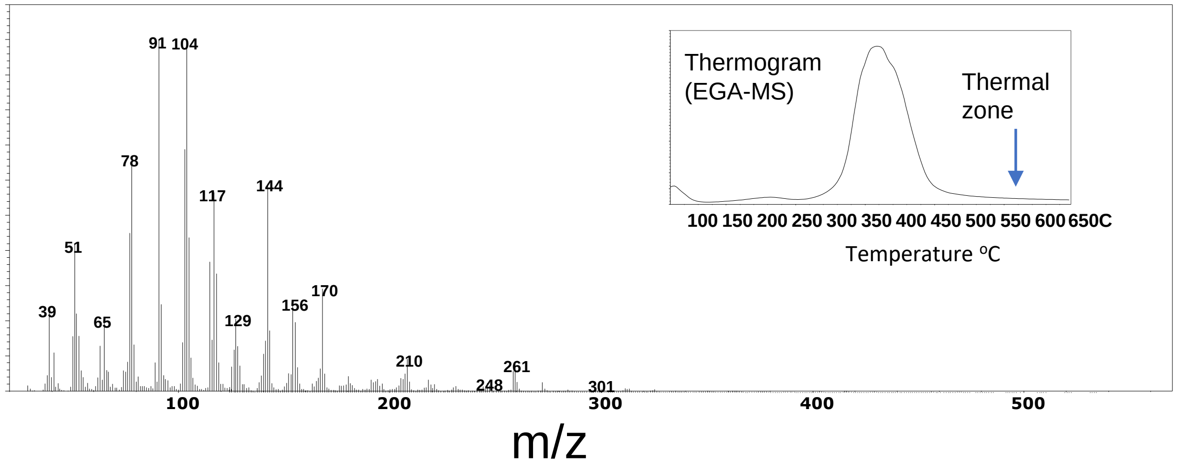
- **Heated from 100°C → 700 ° C**
- **2.5 M EGA tube**



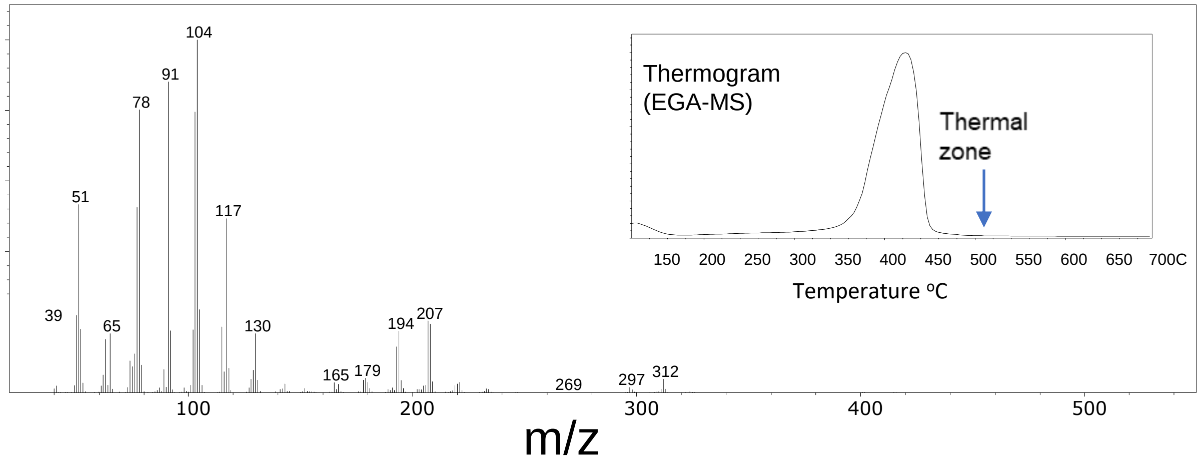
EGA of Acrylonitrile Butadiene Styrene (ABS) and Polystyrene (PS)

Compound name	Thermal zone, °C
Acrylonitrile-butadiene-styrene (ABS)	550
Nylon 6 (N6)	550
Nylon 6,6 (N6,6)	550
Polyethylene terephthalate (PET)	600
Polypropylene (PP)	600
Polystyrene (PS)	500
Polyvinylchloride (PVC)	600

ABS average mass spectrum

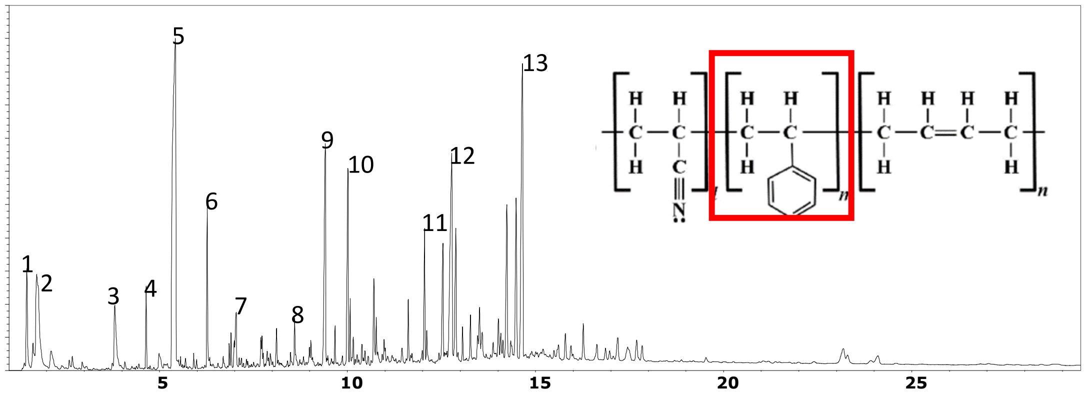


PS average mass spectrum



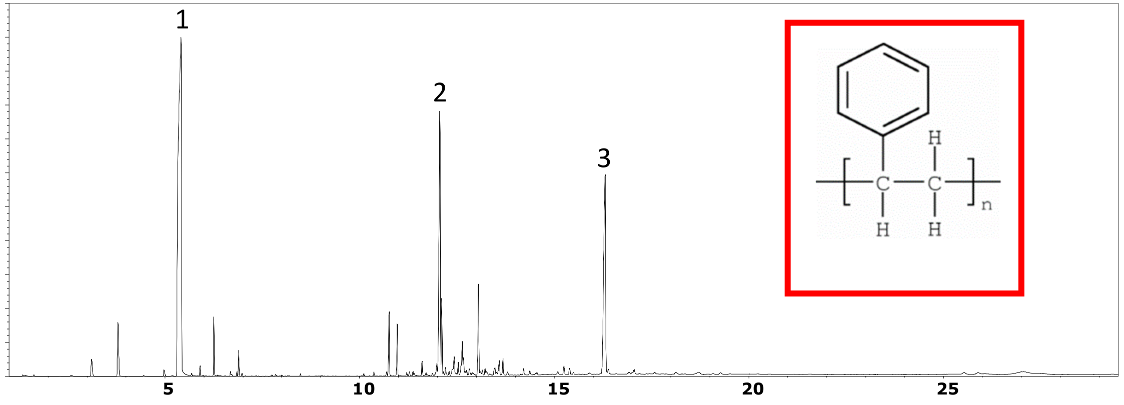
Challenges of Single Polymer Analysis

ABS pyrogram (600 °C)



Retention time (mins)

PS pyrogram (600 °C)



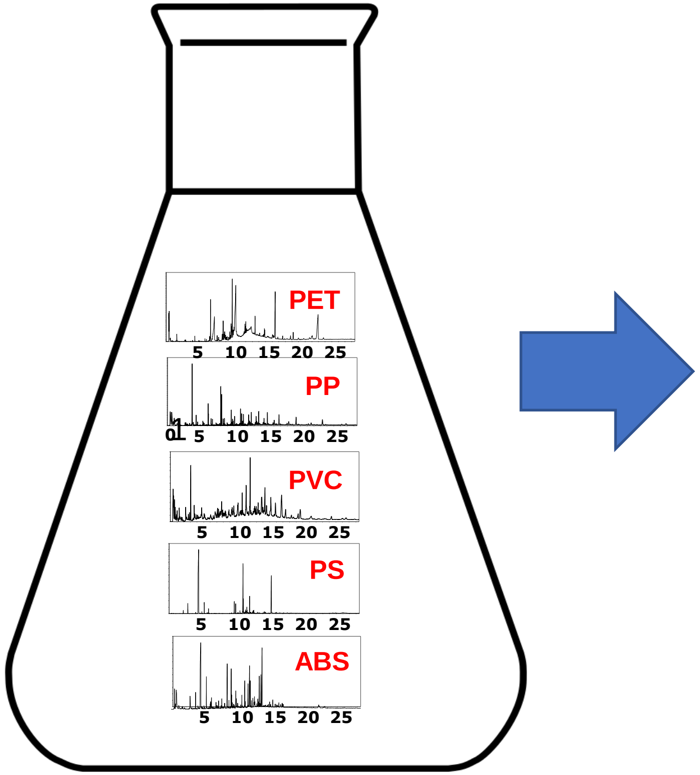
Retention time (mins)

Polymer analysis:

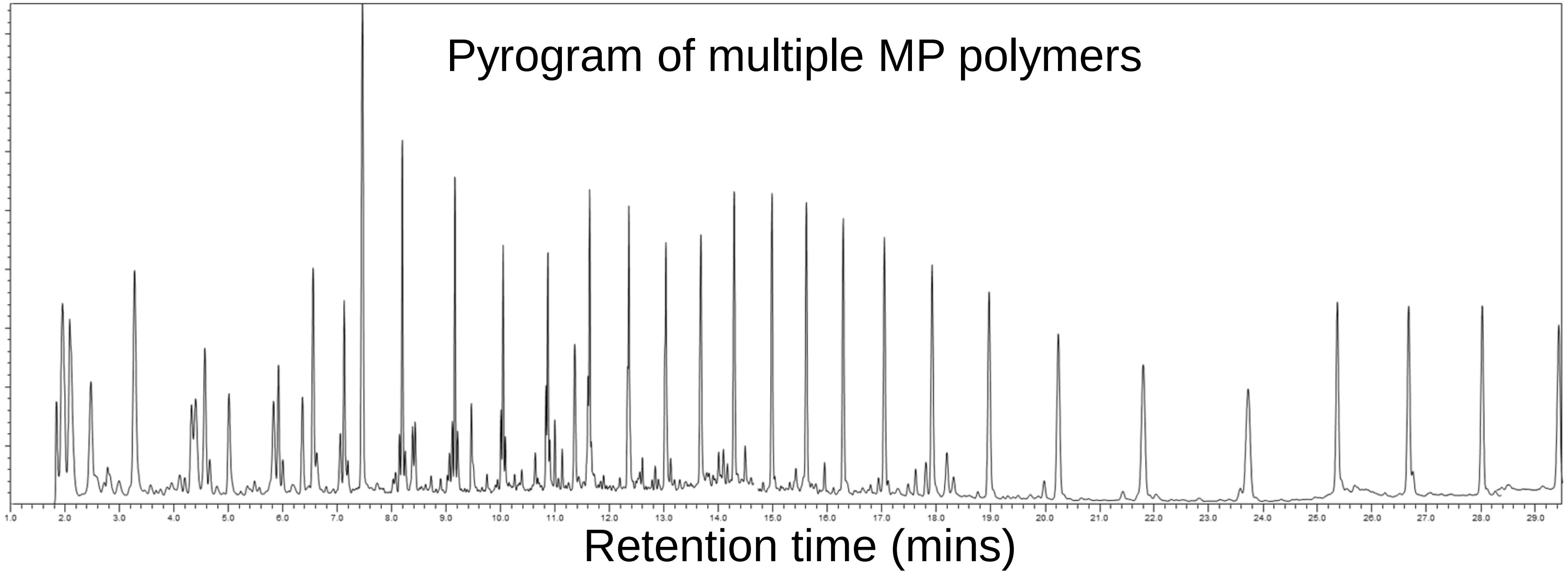
- Flash pyrolysis followed by mass spectrometry scan analysis of single analyte standard:
- Many polymer peaks (pyrolyzates) exist, additives may also be included.
- These pyrolyzates co-exist within other polymers and the chemical profile may look similar among many polymers.
- Not as easy to identify using standard libraries, such as NIST, recommended to use Py Handbook or specialized libraries such as F-search.

Challenges of Multiple Targeted Polymers Analysis

Sample containing multiple polymers



Py-GCMS MP analysis



MP analysis is challenging because these complicated polymers could all exist in the same matrix.
How do we identify and quantify individual polymers that share similar physiochemical properties??

Determination of unique pyrolyzates for identifying MPs in a multiple polymers mixture

Main pyrolyzates in ABS

2-Penyl-4-phenylpent-4-enenitrile (SAS) is unique to PS and is the characteristic pyrolyzate used to identify PS

Peak # ABS	F-Search Result
1	1,3-Butadiene
2	Acrylonitrile
3	Toluene
4	4-Vinylcyclohexane
5	Styrene
6	Alpha-Methylstyrene
7	2-Methylenepentanedinitrile (A dimer)
8	2-Methylene-4-phenylbutanenitrile (hybrid dimer)
9	4-Phenylbutanenitrile
10	4-Phenylpent-4-enenitrile (hybrid dimer)
11	3-Butene-1,3-diyldibenzene (styrene dimer)
12	2-Methylene-4-phenylheptanedinitrile (hybrid trimer)
13	2-Phenethyl-4-phenylpent-4-enenitrile (hybrid trimer)

Main pyrolyzates in PS

Styrene Trimer is unique to PS and is the characteristic pyrolyzate used to identify PS

Peak # PS	F-Search Result
1	Styrene
2	3-Butene-1,3-diyldibenzene (styrene dimer)
3	5-Hexene-1,3,5-triyltribenzene (styrene trimer)

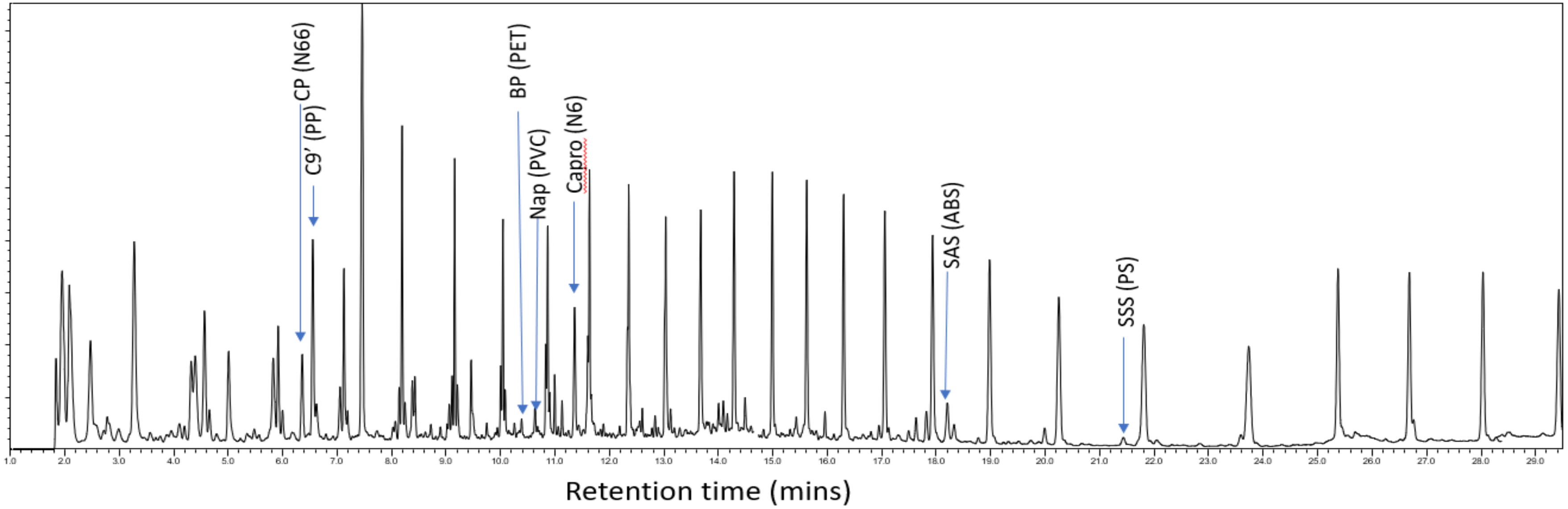
Overlapped pyrolyzate (red box)

Unique pyrolyzate (green box)

Characteristic Pyrolyzates for 6 Targeted Polymers

Compound name	Characteristic pyrolyzate	Quant ion	Qual ion
Acrylonitrile-butadiene-styrene copolymer (ABS)	2-Penyl-4-phenylpent-4-enenitrile (SAS)	170	91,115,118
Nylon-6 (N6)	ε -Caprolactam (Capro)	113	30,55,85
Nylon 6,6 (N66)	Cyclopentanone (CP)	84	39,55,56
Polyethylene terephthalate (PET)	Benzophenone (BP)	182	51,77,105
Polypropylene (PP)	2,4-Diemethyl-1-heptene (C9')	126	43,55,70
Polystyrene (PS)	Styrene trimer (SSS)	91	117,207,312
Polyvinylchloride (PVC)	Naphthalene (Nap)	128	102

Pyrogram of multiple MP polymers

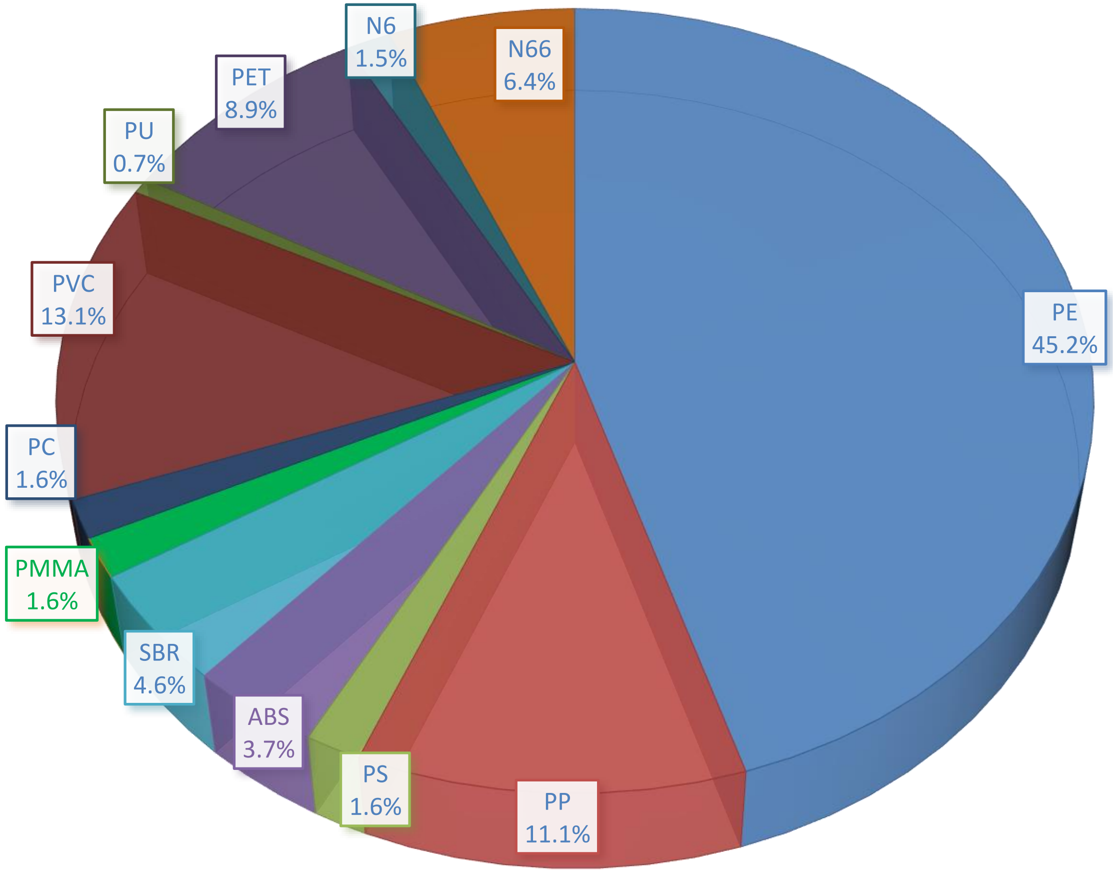


Providing a fast workflow in the measurement of MPs.

- Shimadzu and Frontier lab provide a fast workflow solution that is accurate, sensitive and precise
- Frontier MP kit includes 12 polymers mix in $CaCO_3$ or SiO_2
- F-Search software is seamless and processes data from Shimadzu GC-MS
- Target compounds are readily identified using retention indices and calibration curves are quickly built

Percent polymer composition and mass of each analyte in 4 mg MPS-CaCO3

MPS-$CaCO_3$



Polymer	Mass (µg) in 4 mg standard
Polyethylene (PE)	145.8
Polypropylene (PP)	35.7
Polystyrene (PS)	5.2
Acrylonitrile-butadiene-styrene copolymer (ABS)	12.1
Styrene-butadiene rubber (SBR)	15.0
Polymethyl methacrylate (PMMA)	5.3
Polycarbonate (PC)	5.1
Polyvinylchloride (PVC)	42.4
Polyurethane (PU)	2.1
Polyethylene terephthalate (PET)	28.6
Nylon-6 (N6)	4.9
Nylon 6,6 (N66)	20.7

Operational process by F-Search MPs 2.1

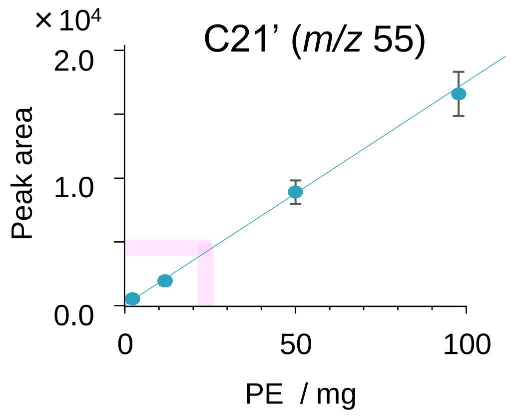
Step 1 Adjustment of retention index (RI)

RI is created based on the pyrolyzates of MPCS

Step 2 Creating a calibration file (QFL)

Calibration file is created based on pyrograms of MPCS

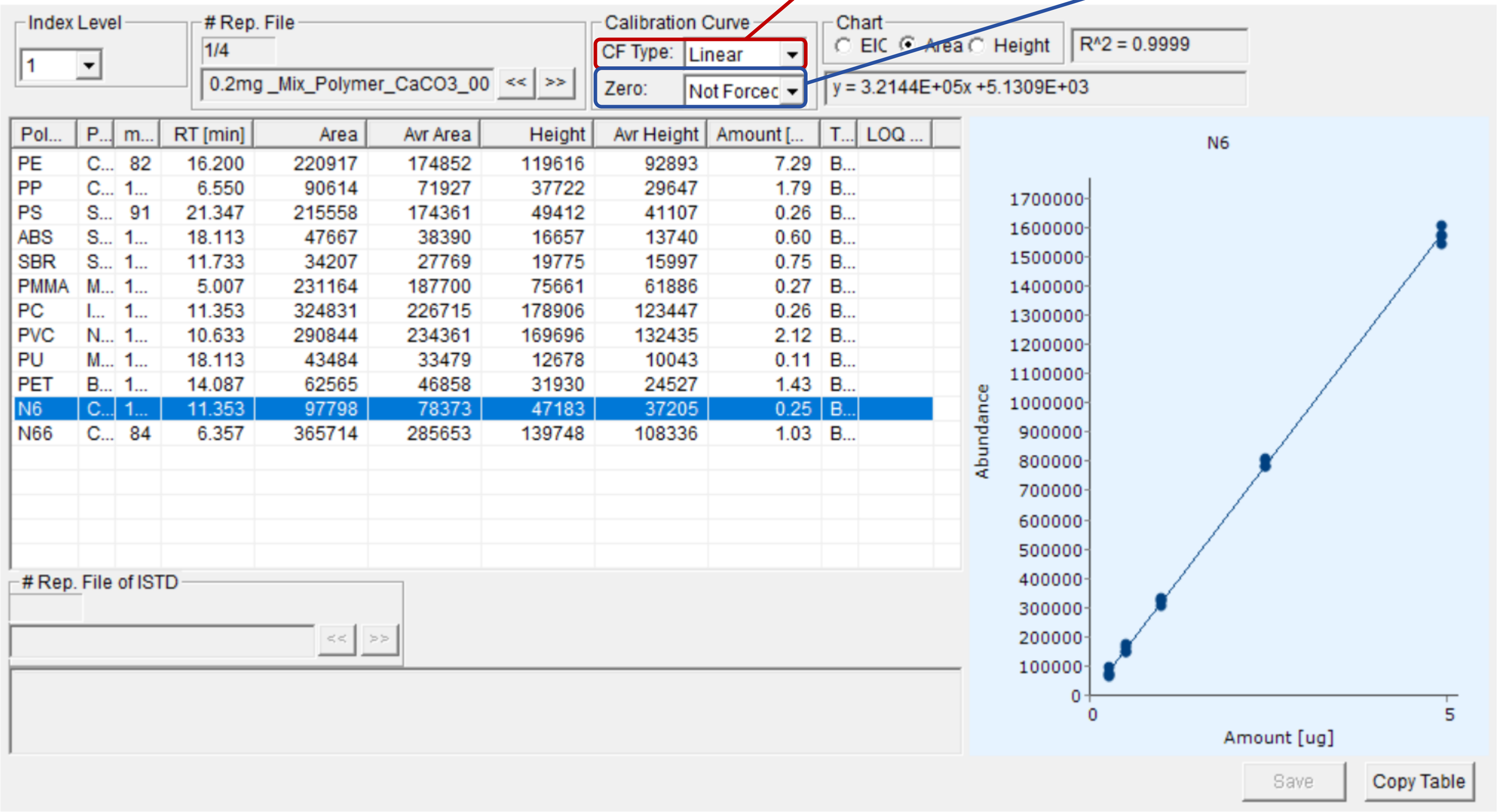
Step 3 Qualitative/quantitative analysis of actual MPs analysis data



Step 4 Interpretation/review of results

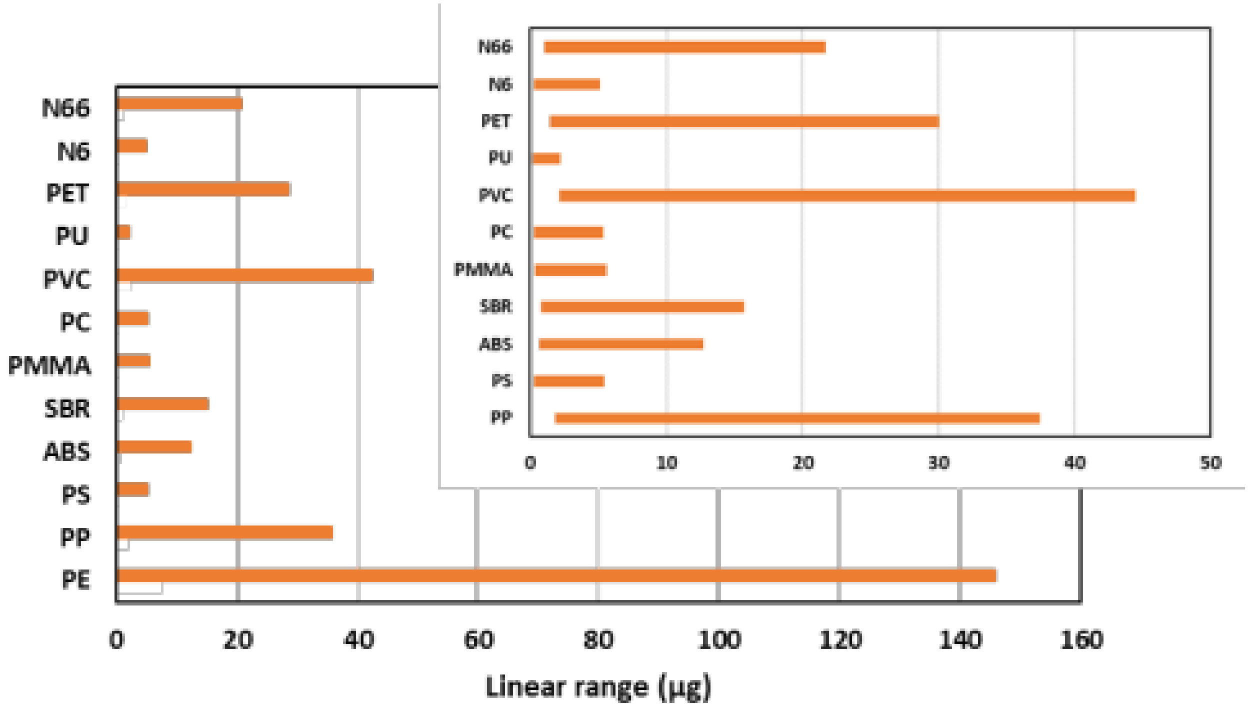
F-Search MP Quantitative calibration view

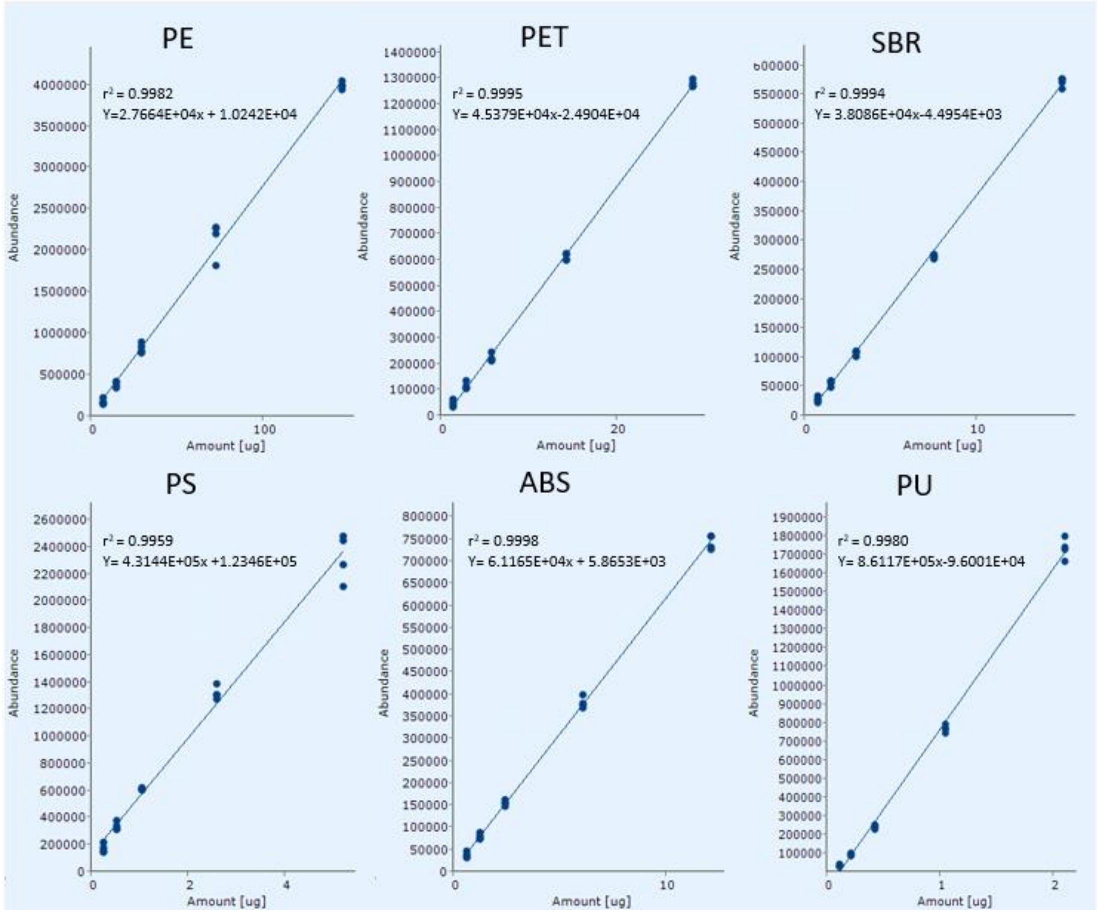
The Calibration curve is selected from linear/quadratic and with/without forced zero intercept.



Pol...	P...	m...	RT [min]	Area	Avr Area	Height	Avr Height	Amount [...	T...	LOQ ...
PE	C...	82	16.200	220917	174852	119616	92893	7.29	B...	
PP	C...	1...	6.550	90614	71927	37722	29647	1.79	B...	
PS	S...	91	21.347	215558	174361	49412	41107	0.26	B...	
ABS	S...	1...	18.113	47667	38390	16657	13740	0.60	B...	
SBR	S...	1...	11.733	34207	27769	19775	15997	0.75	B...	
PMMA	M...	1...	5.007	231164	187700	75661	61886	0.27	B...	
PC	I...	1...	11.353	324831	226715	178906	123447	0.26	B...	
PVC	N...	1...	10.633	290844	234361	169696	132435	2.12	B...	
PU	M...	1...	18.113	43484	33479	12678	10043	0.11	B...	
PET	B...	1...	14.087	62565	46858	31930	24527	1.43	B...	
N6	C...	1...	11.353	97798	78373	47183	37205	0.25	B...	
N66	C...	84	6.357	365714	285653	139748	108336	1.03	B...	

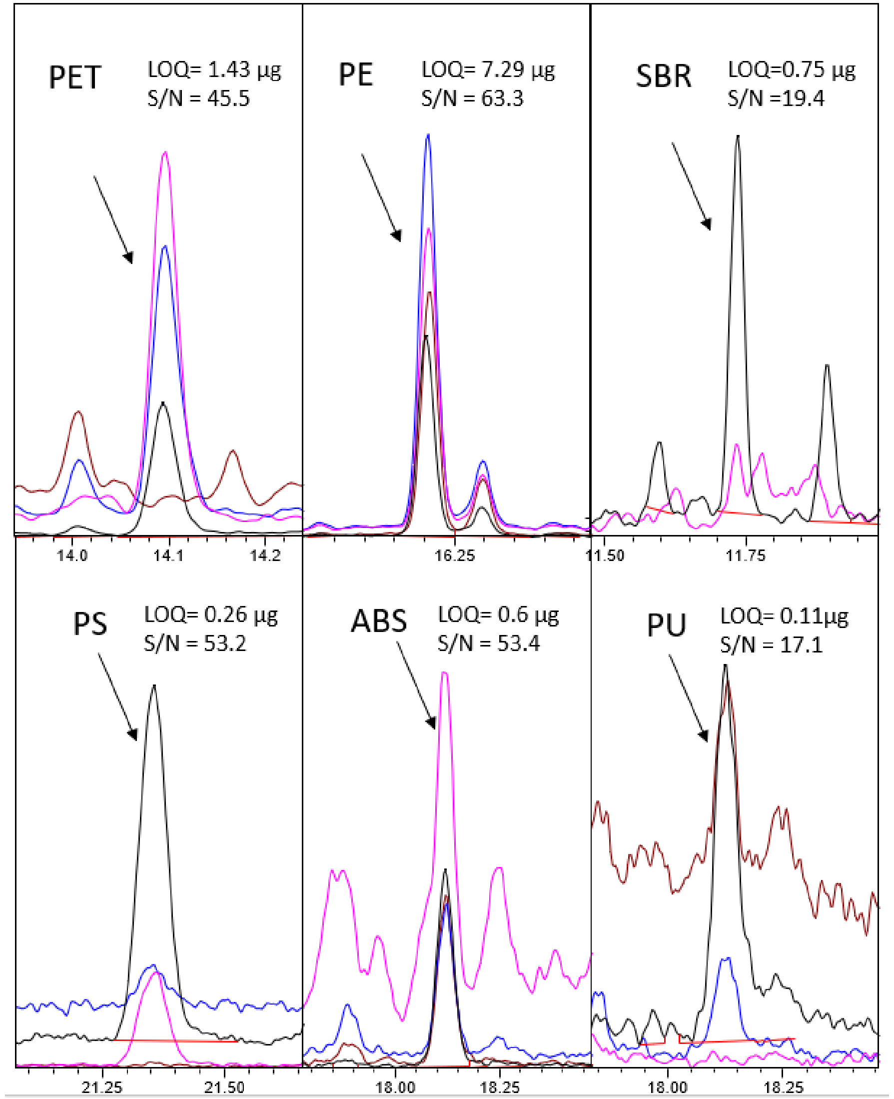
Helium Data Review





Lower Limit of Quantification (LLOQ)

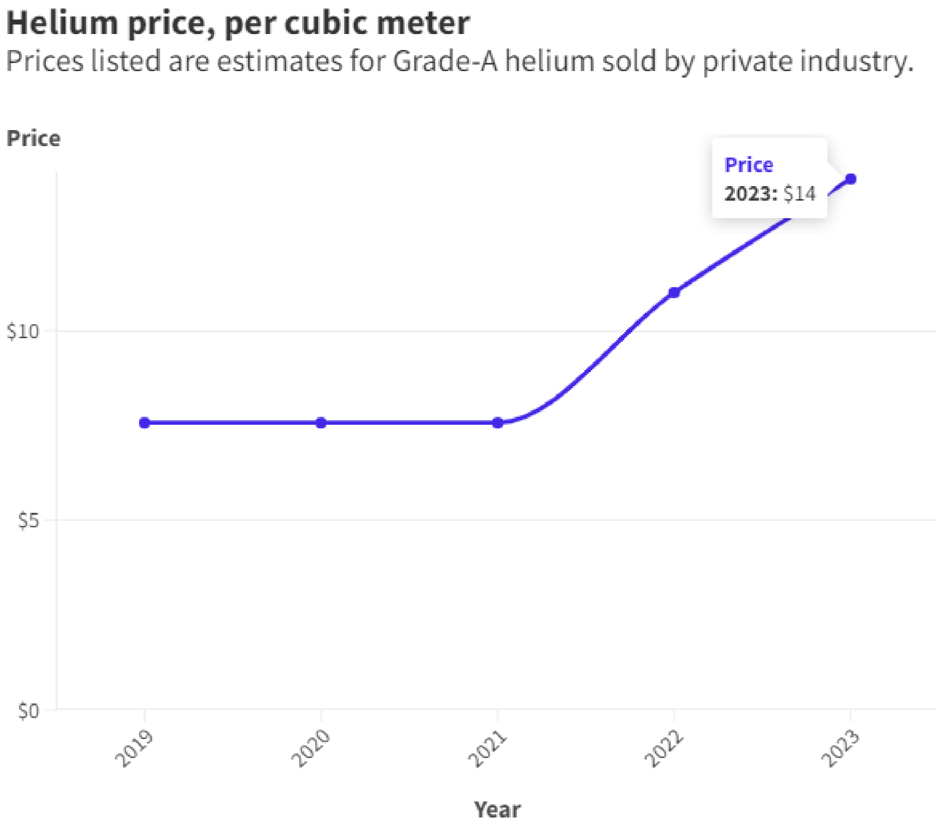
- Limit of quantitation for representative polymers in this study.
- Based on polymer concentration in MP-$CaCO_3$ standard, 2 mg standard weight is required to obtain Pseudo LLOQ for each compound.



Polymer	Recovery % (n=7)		Retention Time (min)	LLOQ (µg)	% Drift (at 0.8 mg)
	3 mg	0.2 mg			
PE	99.0	99.9	16.2	7.3	-16.9
PP	99.6	111.2	6.6	1.8	-11.4
PS	92.2	66.4	21.3	0.3	-9.3
ABS	92.9	107.3	18.1	0.6	-18.1
SBR	96.0	121.8	11.7	0.8	-8.7
PMMA	102.8	103.6	5.0	0.3	-6.5
PC	97.2	123.0	11.4	0.3	-10.8
PVC	97.5	114.1	10.6	2.1	-9.6
PU	94.9	145.1	18.1	0.1	-19.8
PET	95.0	126.7	14.1	1.4	-18.2
N6	100.1	112.0	11.4	0.3	-11.0
N66	100.8	121.5	6.4	1.0	-7.2

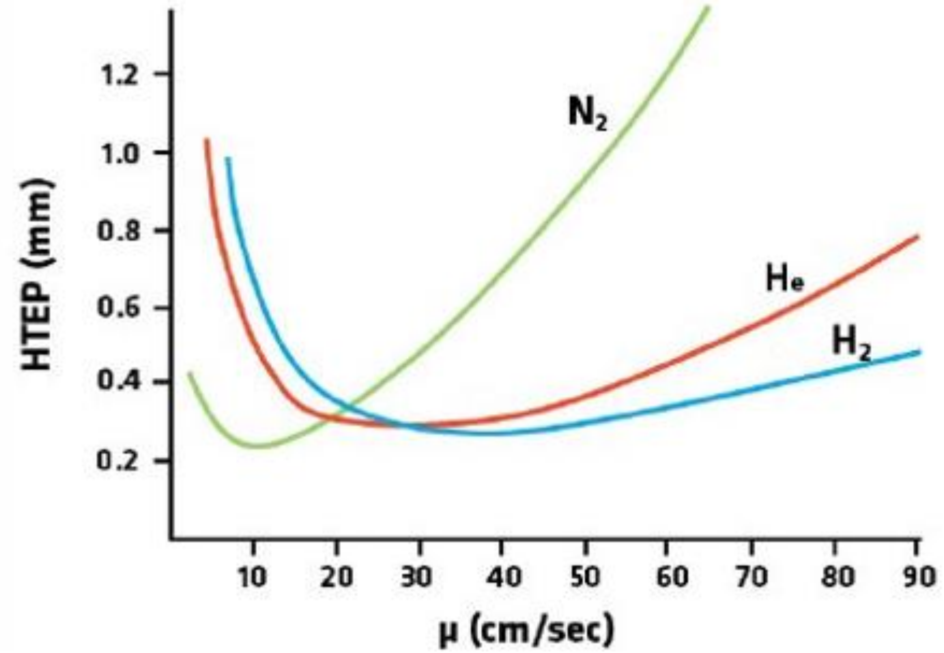
Helium vs. Nitrogen

Helium



- Cost of He continues to rise with unequal rates of production
- H2 difficult alternative for Pyrolysis

Nitrogen

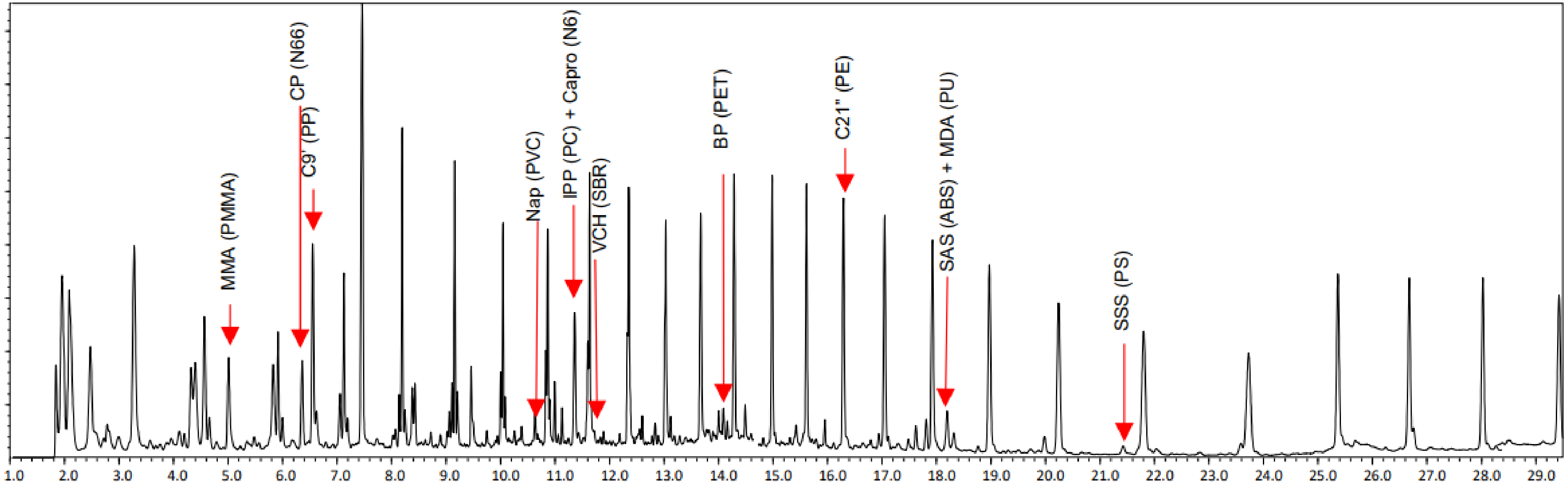


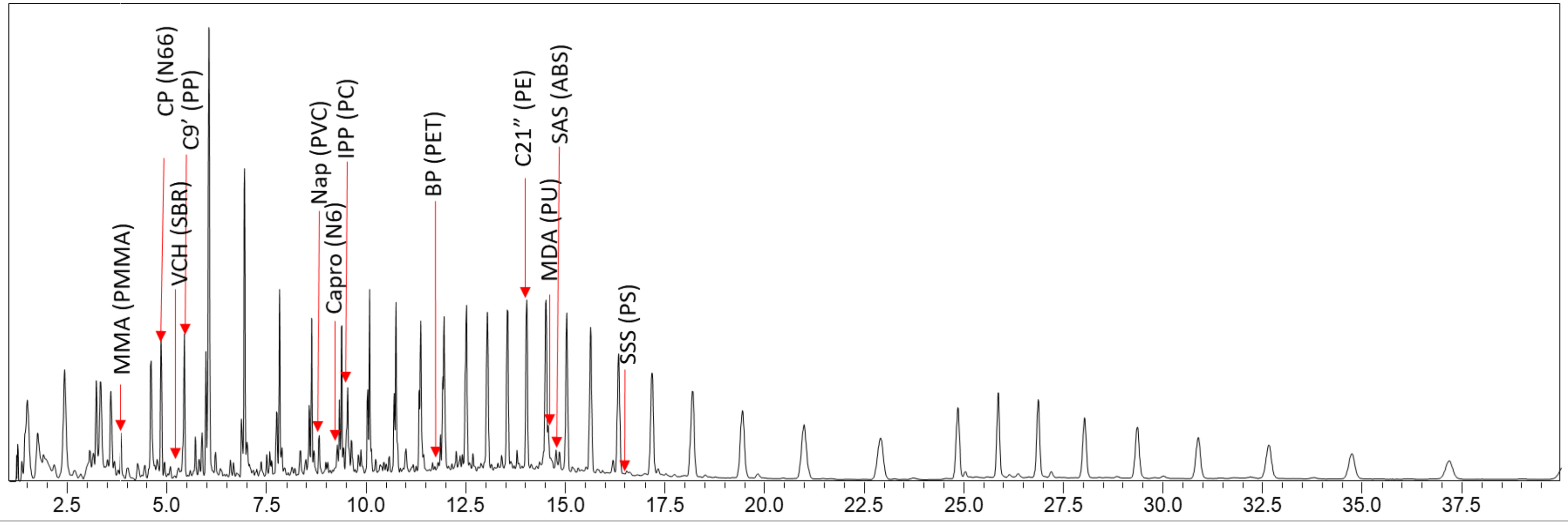
- Best Efficiency and Inert
- Can be unforgiving with unoptimized linear velocities

Nitrogen Configuration

Gas Chromatography	Nexis GC-2030
Injection port mode	Split mode; 35:1 split ratio
Injector pressure	94.1 kPA
Carrier gas	Nitrogen
Injection port temperature	300 °C
Column: Frontier Lab UAMP column	Restek Mxt-5 (20 m x 0.18 mmID x 0.40 µm
Flow control mode	Linear velocity
Oven Temperature	40 °C (2 mins. hold), 20 °C /mins. to 280 °C (10 mins. hold), 40 °C /min to 320 °C (60 mins. Hold)
Mass Spectrometer	**QP2020 NX**
Interface Temperature	300 °C
Ion Source Temperature	230 °C
Detector Voltage	Relative to Tune 0 kV
Threshold	0
Acquisition mode Scan Range SIM ions	Scan/SIM m/z 29 to 350; Event time 0.2 s Listed in table 2
Pyrolyzer	**EGA/PY-3030D**
Single Shot Furnace Temp	600 °C
Interface Temp	300 °C
Auto sampler flushing gas	Nitrogen
Auto sampler Purge Time	10 sec

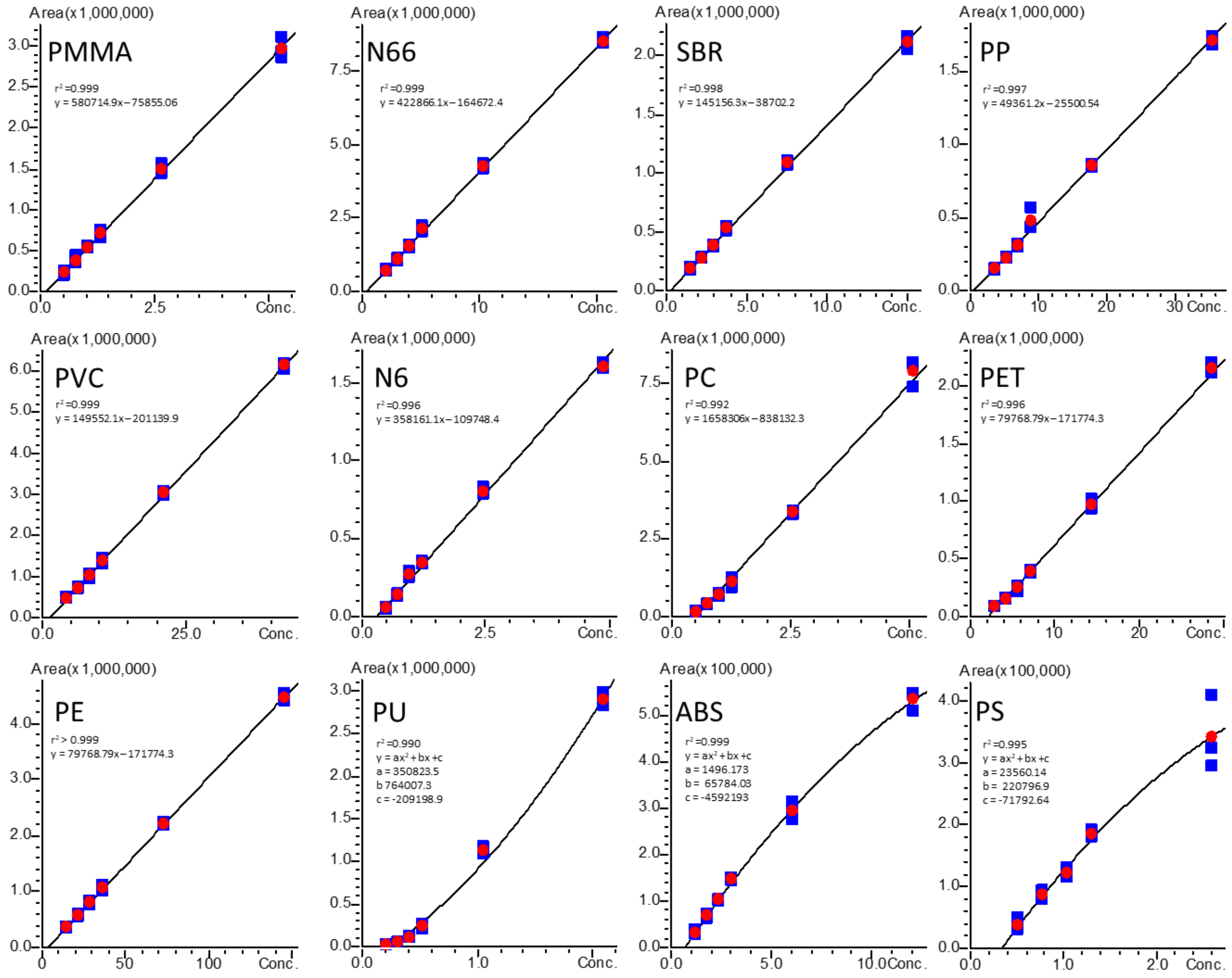
Nitrogen Results – Runtime





Nitrogen Results – Linearity Comparison

Nitrogen Results

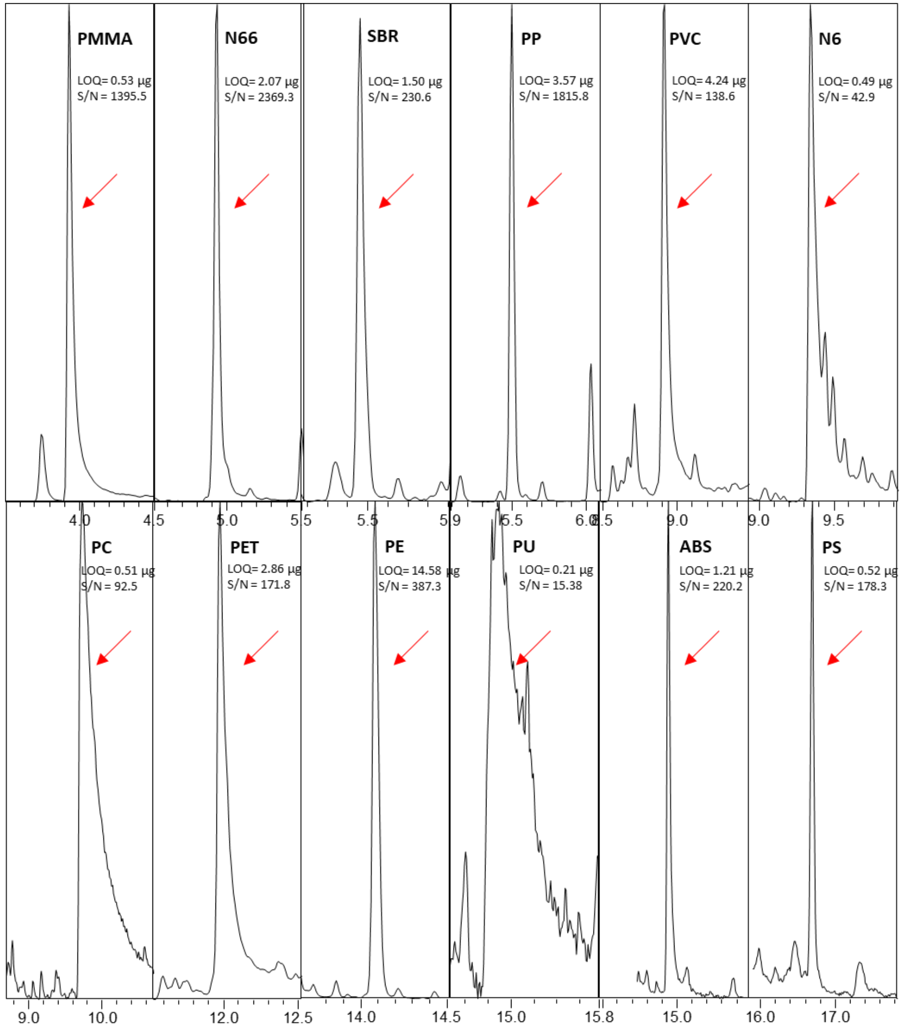


Helium Results

Polymer	Linearity (r^2)
PE	0.9982
PP	0.9997
PS	0.9959
ABS	0.9998
SBR	0.9994
PMMA	0.9988
PC	0.9999
PVC	0.9999
PU	0.9980
PET	0.9995
N6	0.9999
N66	> 0.9999

LLOQ – Sensitivity

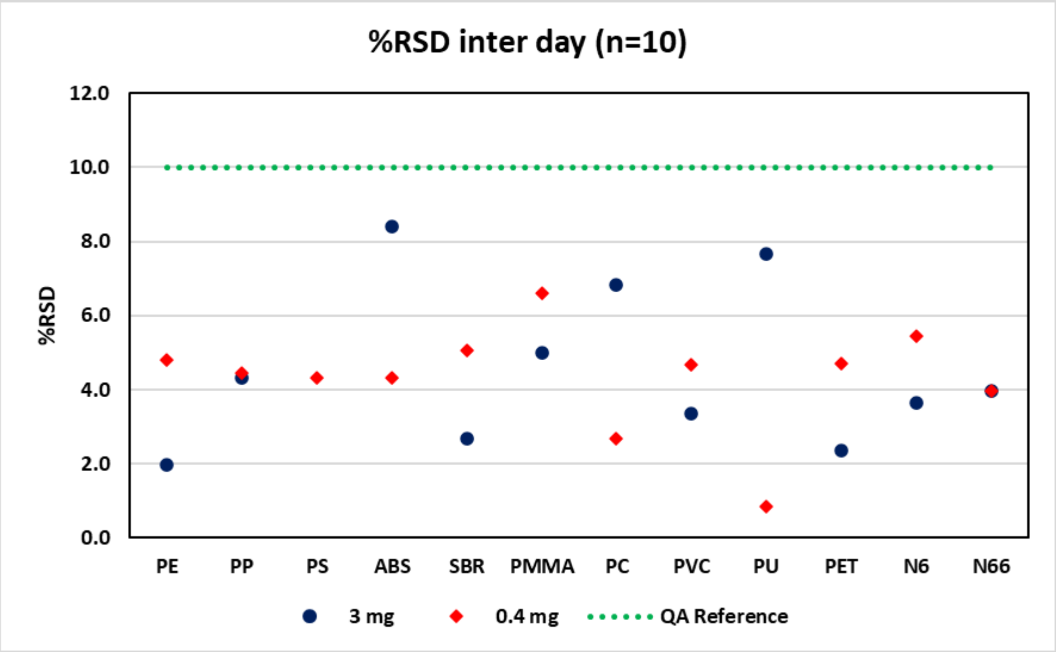
Nitrogen Results



Helium Results

Polymer	LLOQ (µg)
PE	7.3
PP	1.8
PS	0.3
ABS	0.6
SBR	0.8
PMMA	0.3
PC	0.3
PVC	2.1
PU	0.1
PET	1.4
N6	0.3
N66	1.0

Nitrogen Results – Precision



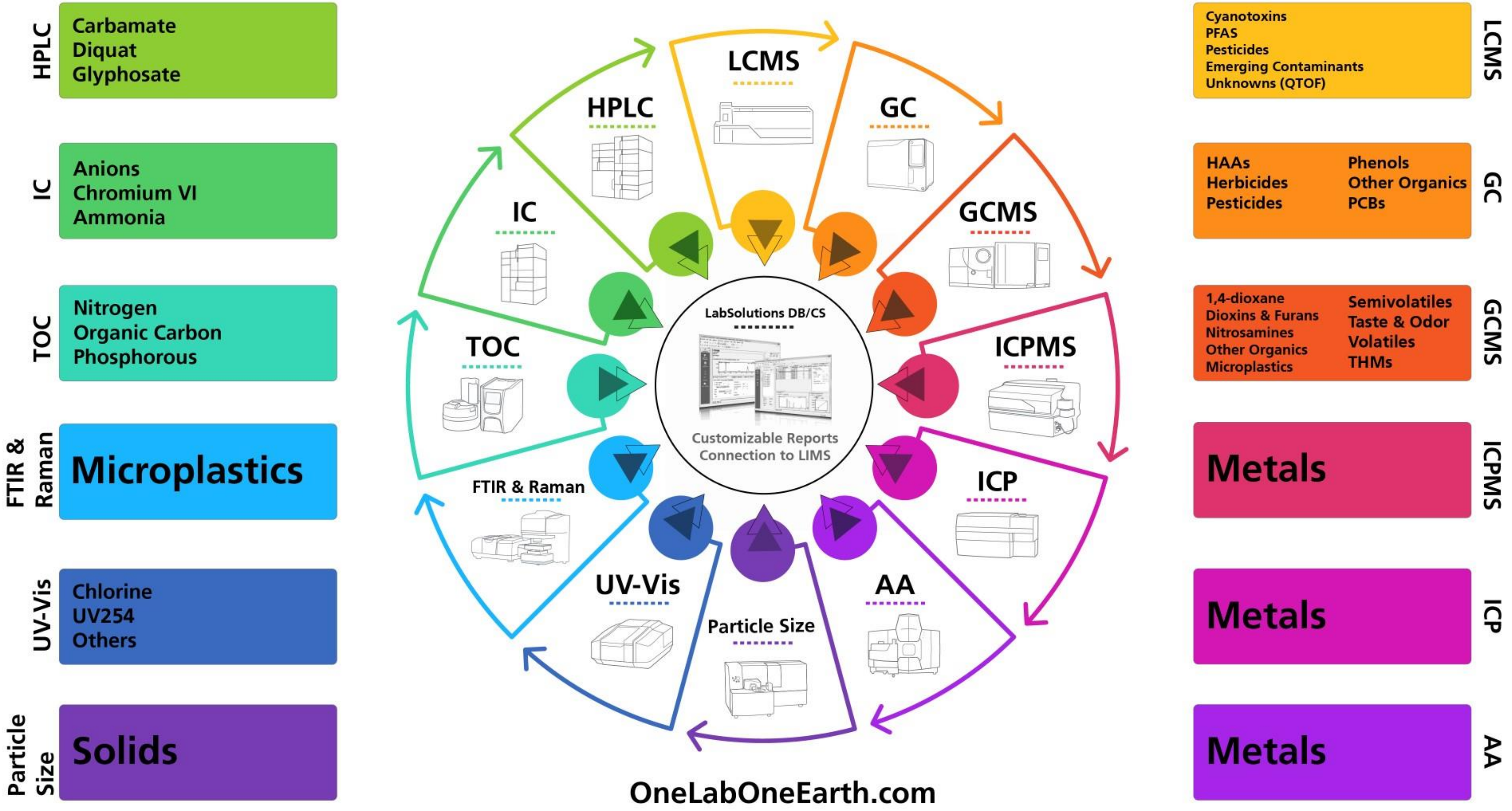
Polymer	Recovery % (n=10)		Retention Time (min)	LOQ (µg)	Linearity (r^2)	% Drift (0.8mg)
	3 mg	0.4 mg				
PE	109.2	112.8	14.0	14.58	0.999	23.3
PP	103.8	109.2	5.6	3.57	0.993	12.7
PS	N/A	103.7	16.8	0.52	0.997 [a]	-5.5
ABS	108.1	104.9	15.0	1.21	0.999 *	9.0
SBR	106.7	116.6	5.6	1.5	0.998	13.3
PMMA	105.1	115.3	4.0	0.53	0.999	22.6
PC	107.9	122.0	9.7	0.51	0.992	23.0
PVC	101.3	114.8	9.0	4.24	0.999	16.3
PU	102.1	125.0	14.8	0.21	0.990 *	12.7
PET	103.1	133.8	12.0	2.86	0.996	23.3
N6	104.2	102.6	9.4	0.49	0.996	31.0
N66	104.5	111.1	5.0	2.07	0.999	19.9

Special Thanks and Conclusion!

- PY-GCMS is an effective tool for identifying and quantifying mixed polymer samples at low levels
- Nitrogen maintains sensitivity and throughput while reducing operating cost when compared to helium.

- Andy Sandy – Applications Scientist of ADC
- Evelyn Wang – Application Manager of ADC
- Okamura Yoshiyuki – GM of Application Development Center
- Ruth Marfil-Vega – Sr. Environmental Marketing Manager

Questions?


HPLC
Carbamate
Diquat
Glyphosate
IC
Anions
Chromium VI
Ammonia
TOC
Nitrogen
Organic Carbon
Phosphorous
FTIR & Raman
Microplastics
UV-Vis
Chlorine
UV254
Others
Particle Size
Solids
LCMS
HPLC
GC
IC
GCMS
TOC
ICPMS
LabSolutions DB/CS
Customizable Reports
Connection to LIMS
FTIR & Raman
ICP
UV-Vis
AA
Particle Size
OneLabOneEarth.com
Cyanotoxins
PFAS
Pesticides
Emerging Contaminants
Unknowns (QTOF)
LCMS
HAAs
Herbicides
Pesticides
Phenols
Other Organics
PCBs
GC
1,4-dioxane
Dioxins & Furans
Nitrosamines
Other Organics
Microplastics
Semivolatiles
Taste & Odor
Volatiles
THMs
GCMS
Metals
ICPMS
Metals
ICP
Metals
AA