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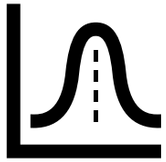
A Comprehensive Approach for Successful Microplastics Analysis

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Shimadzu Scientific Instruments, Inc.

NEMC 2024

ASTM D19 has developed and is developing several guides, practices, and methods for microplastics in water



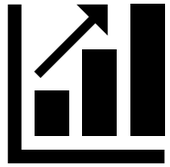
Reference materials D8402



Sample Collection D8332



Sample Preparation D8333



Analysis

DIA D8489

PY-GCMS D8401

IR Microscopy WK87463

D8332 describes how large volumes of the entire water column can be sampled

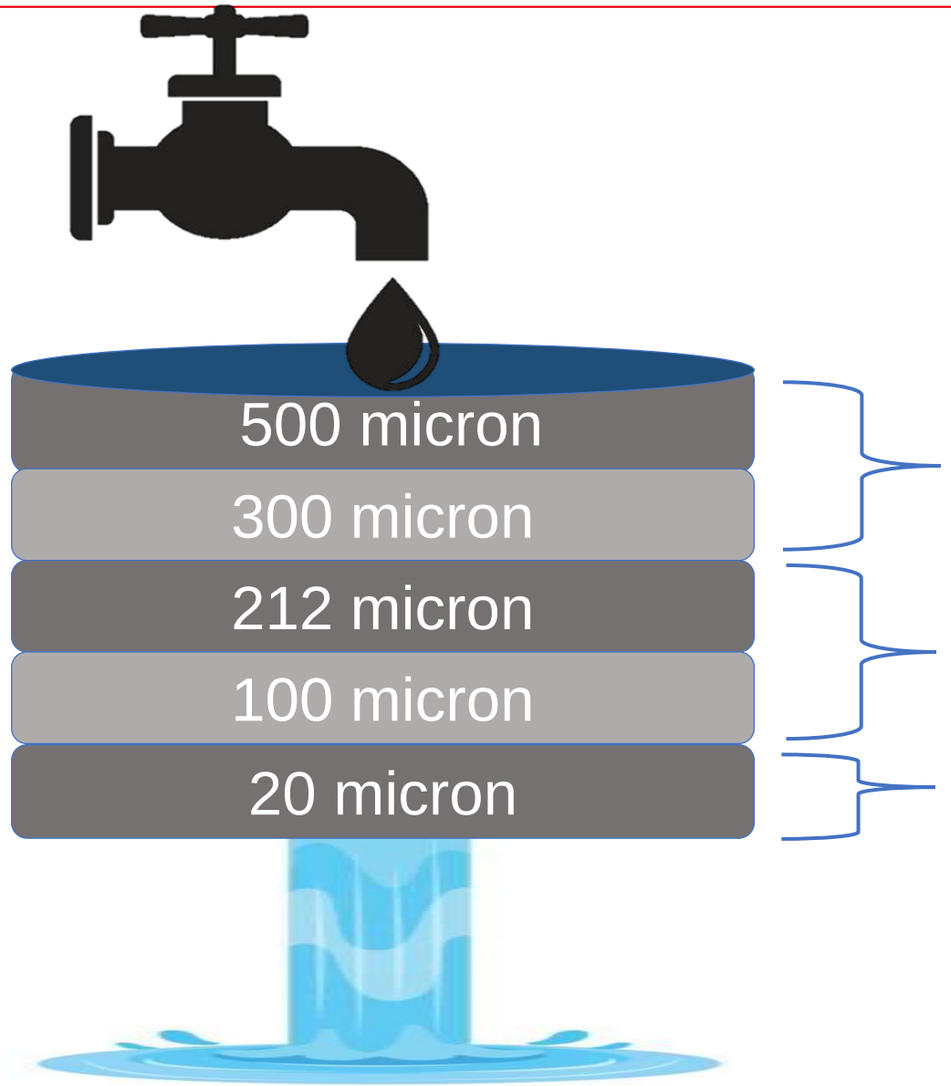




The key is a large volume through sieves

Jeremiah Bryksa ∗ ,Patric McGlashan ,Nadia Stelck ,Jon Wong , Andrew Anderson-Serson,Matthew Hart,Trace Malcom,Bob Battle,Paolo Mussone; High throughput application of ASTM D8332: Detailed prototype design and operating conditions for microplastic sampling of riverine systems; https://methods-x.com/article/S2215-0161(24)00134-1/fulltext

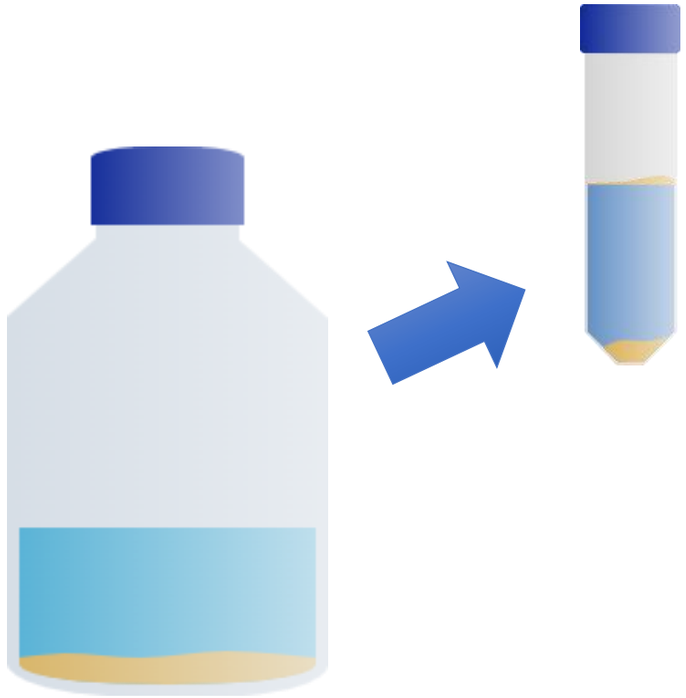
In addition, sample collection by D8332 presorts particles by sieve fraction





Separate sieve fractions can be digested and analyzed separately

Organic and other material (interferences) removed from each sieve fraction by sequential digestion using D8333 (only digest when needed)

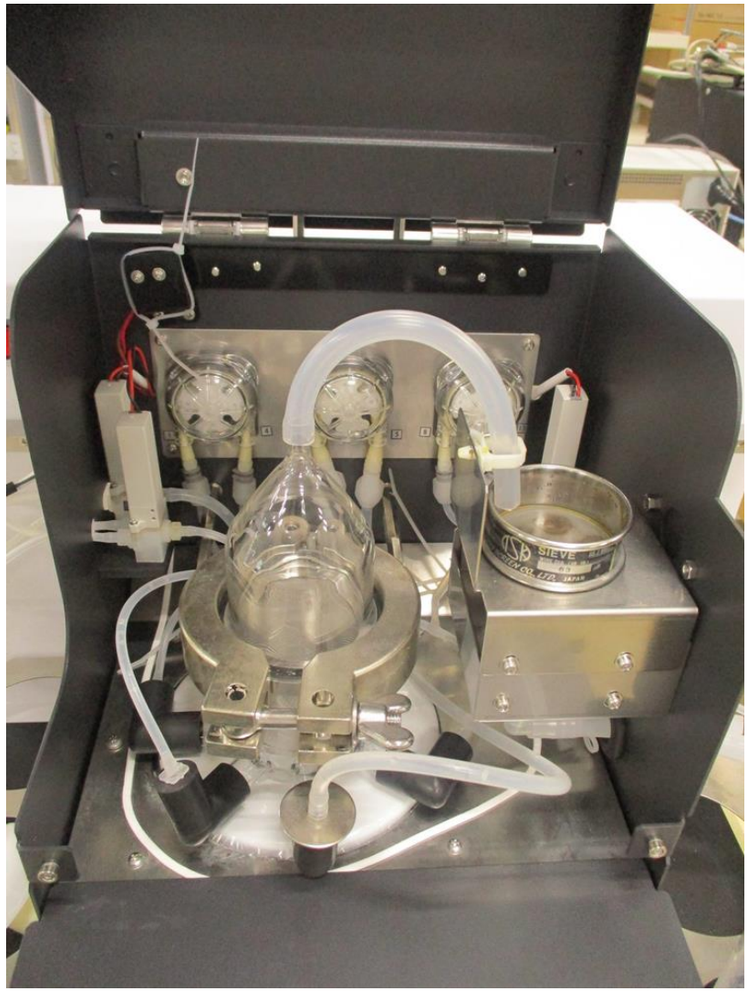


- H_2O_2
- Schweizer 5 minutes
- Ammonium Hydroxide 5 minutes
- Buffer
- Protease, buffer, lipase
- React 20 hours



Final sample = plastics suspended in methanol

Further prep may be needed after D8333, depending on the analysis method





Once the final sample is prepared each sieve fraction is ready for measurement



Pyrolysis GCMS

D8401



Dynamic Imaging

D8489



FTIR Microscopy



Manual IR Spectrometry

We developed ASTM D8489, a dynamic imaging method, to rapidly count particles in the < 100 µm sieve fractions

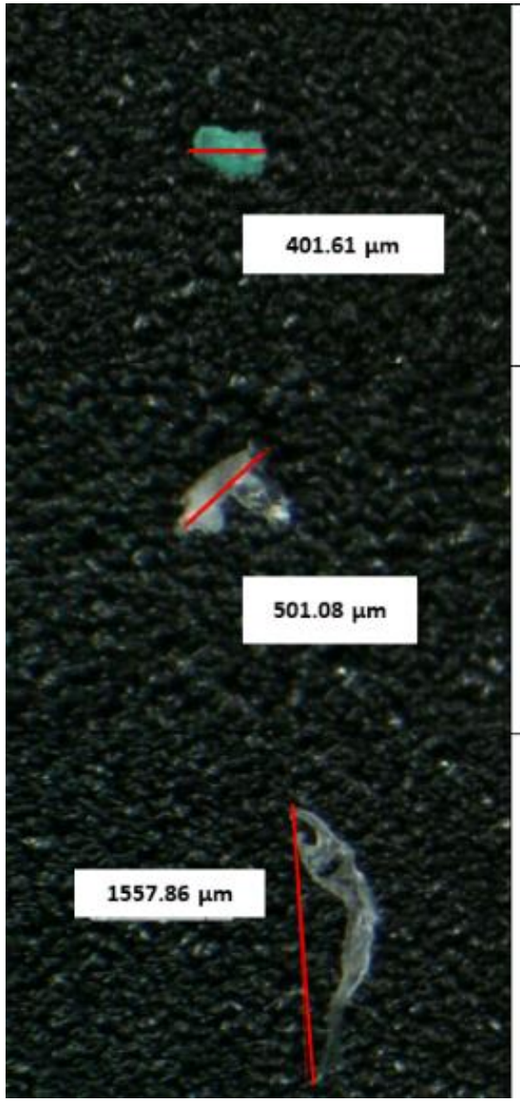
- The total number of particles, and size distribution is quickly obtained
- Data shows aliquots from the D8333 sample prep step are reproducible.
- You also get a size distribution
- Counting is much faster than by IR

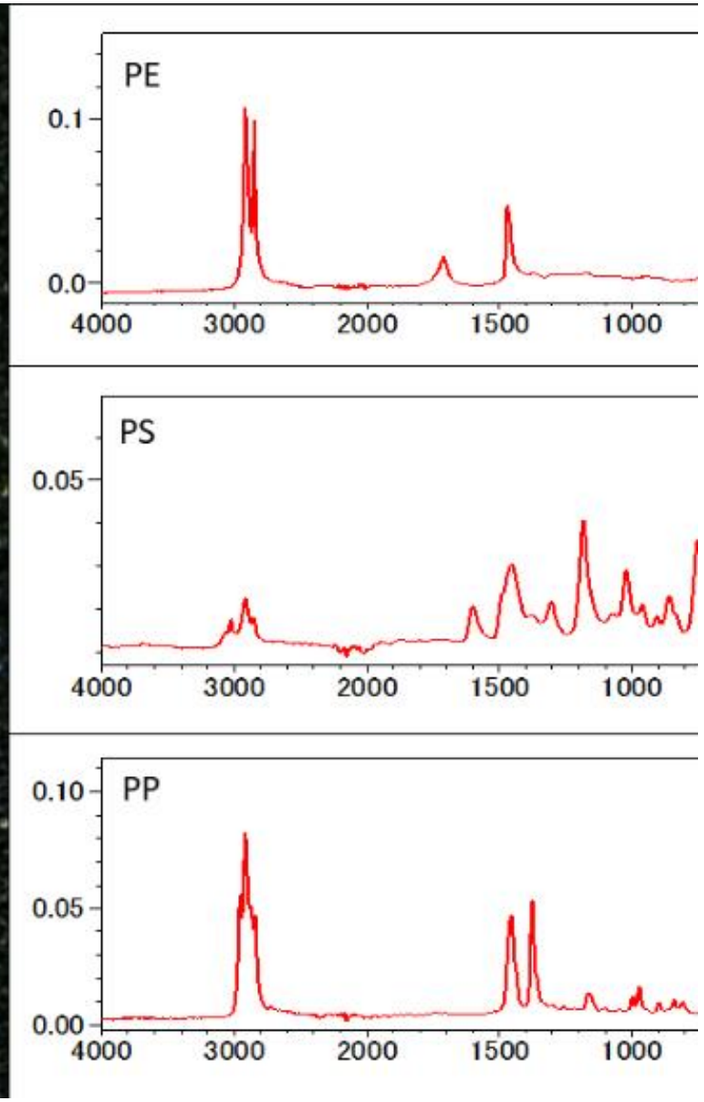


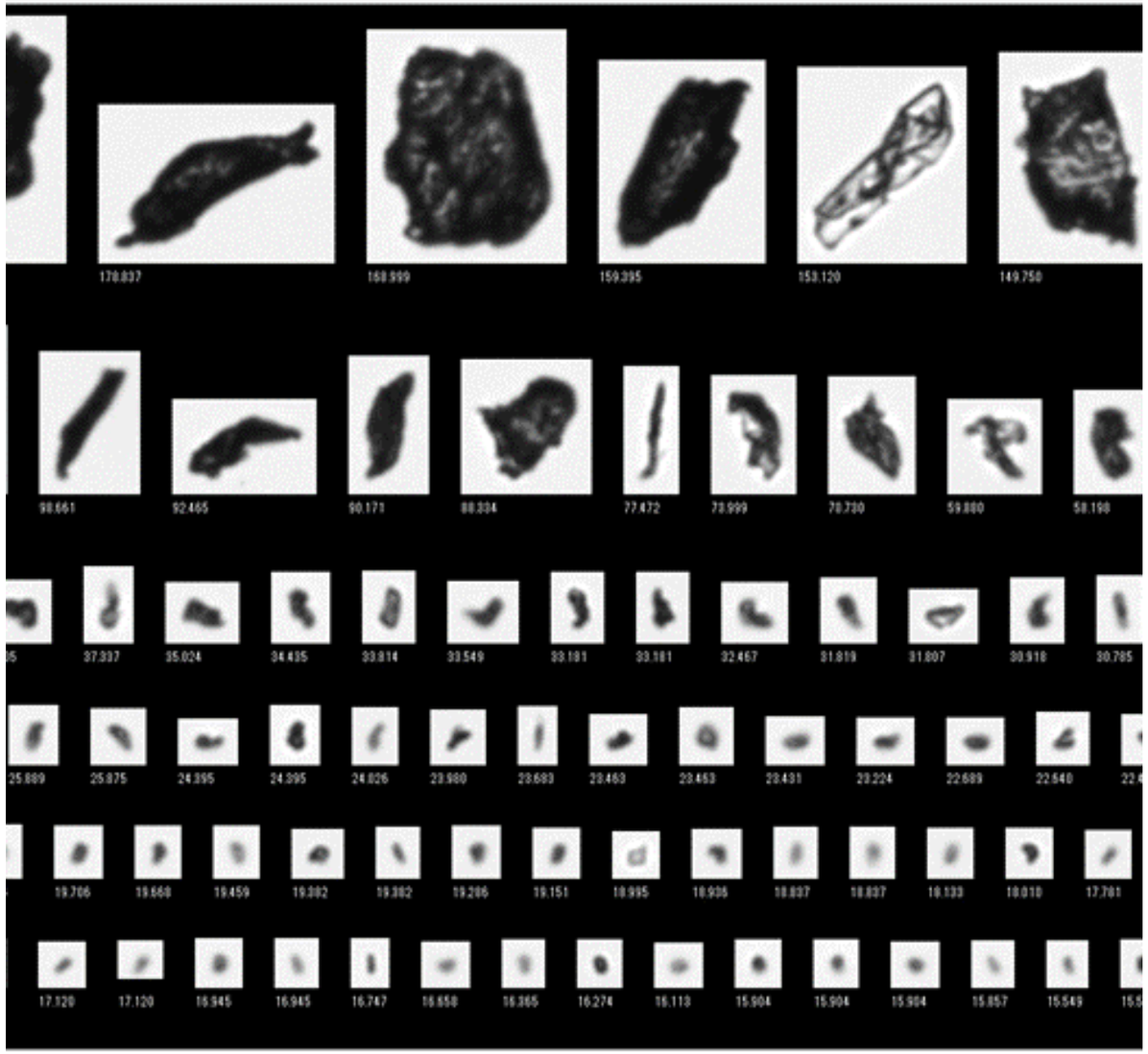
Replicate number	Concentration (count/mL)*					
	All	5-10 µm	10-25 µm	25-50 µm	50-100 µm	> 100 µm
1	3253	1623	1250	214	83	83
2	3667	2051	1140	283	69	124
3	3764	2037	1271	290	90	76
4	3640	2141	1140	228	76	55
5	3419	1837	1167	235	111	69
6	3508	2051	1105	242	76	35
7	3101	1761	1050	186	62	41
Average	3479	1929	1160	240	81	69
S.D.	238.4	190.1	77.9	36.7	15.8	30.1
RSD	6.85%	9.86%	6.72%	15.31%	19.54%	43.59%

* Concentration is calculated from Number of Particles, Number of Frames and flowcell volume.

Using ASTM D8489, you also get some morphology data that could be correlated with later IR analysis.







The D8489 data also shows that you can pipet the D8333 digestion within reasonable precision for individual measurement methods



Pyrolysis GCMS

D8401



Dynamic Imaging

D8489



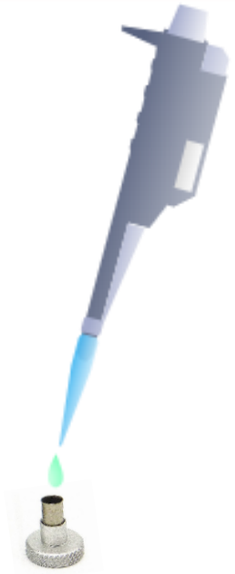


FTIR Microscopy

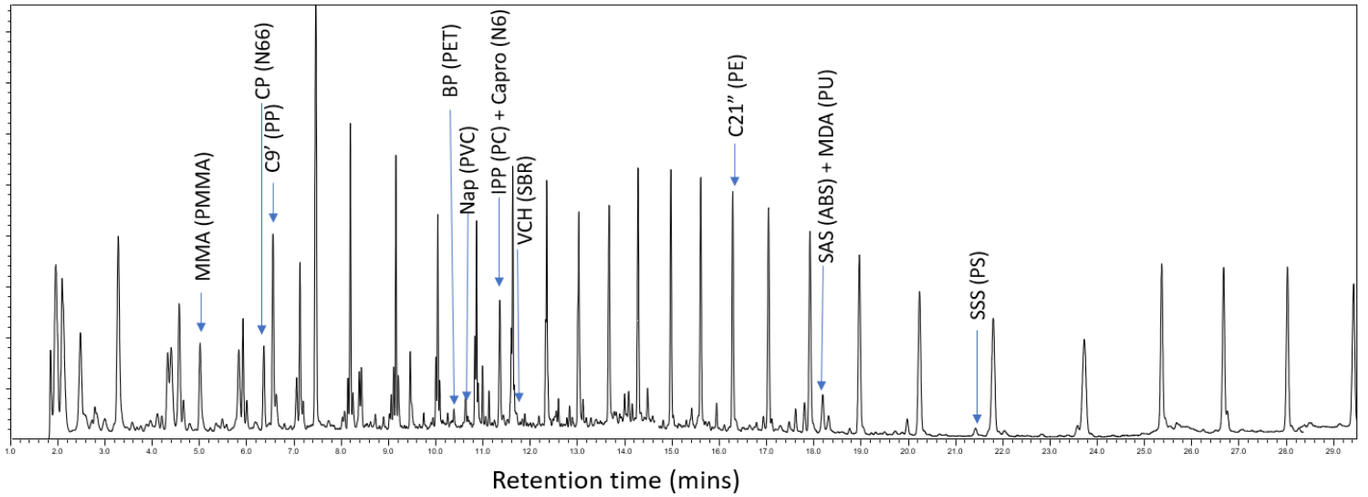


Manual IR Spectrometry

ASTM D8401 Microplastics by Pyrolysis GCMS

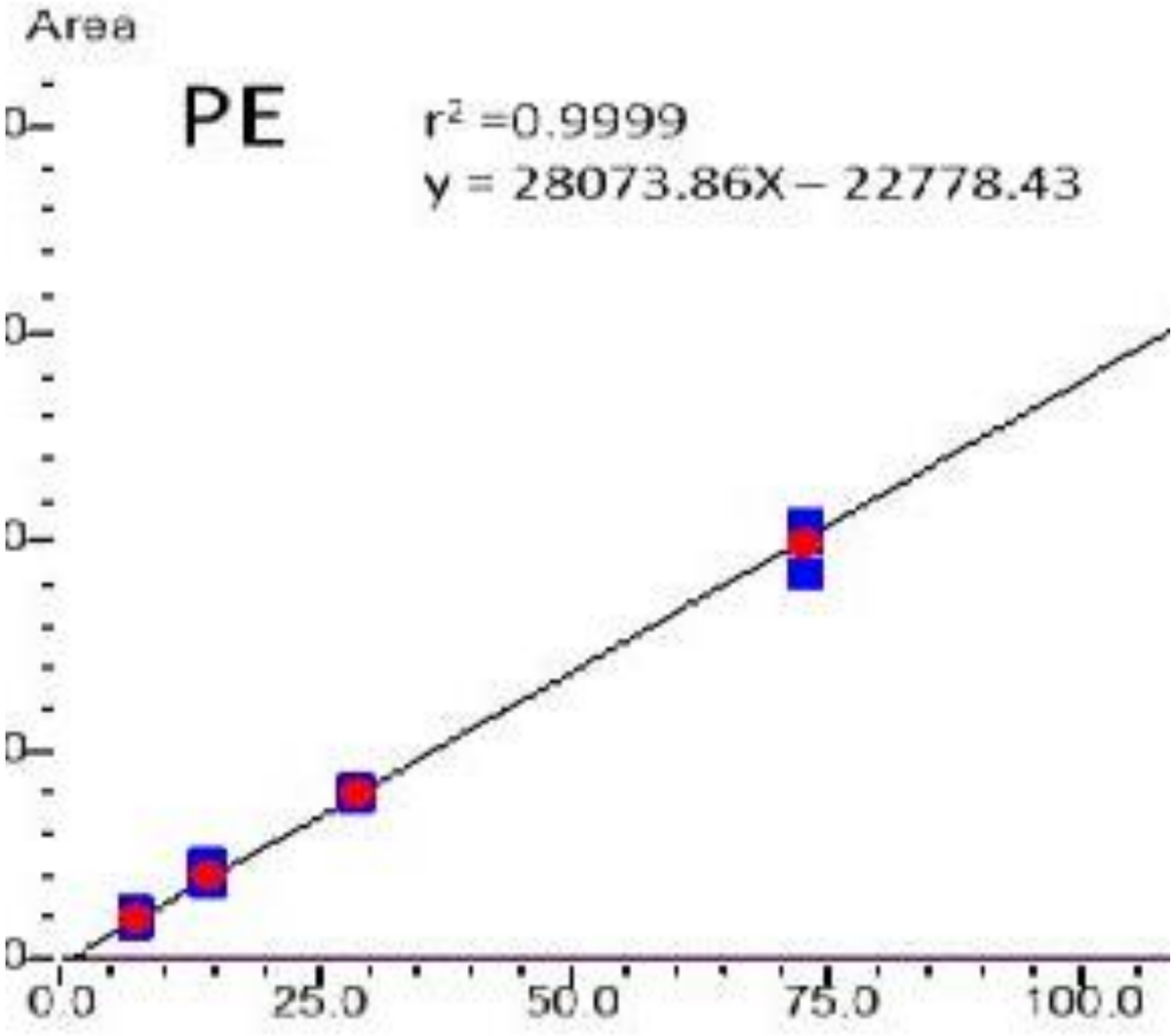


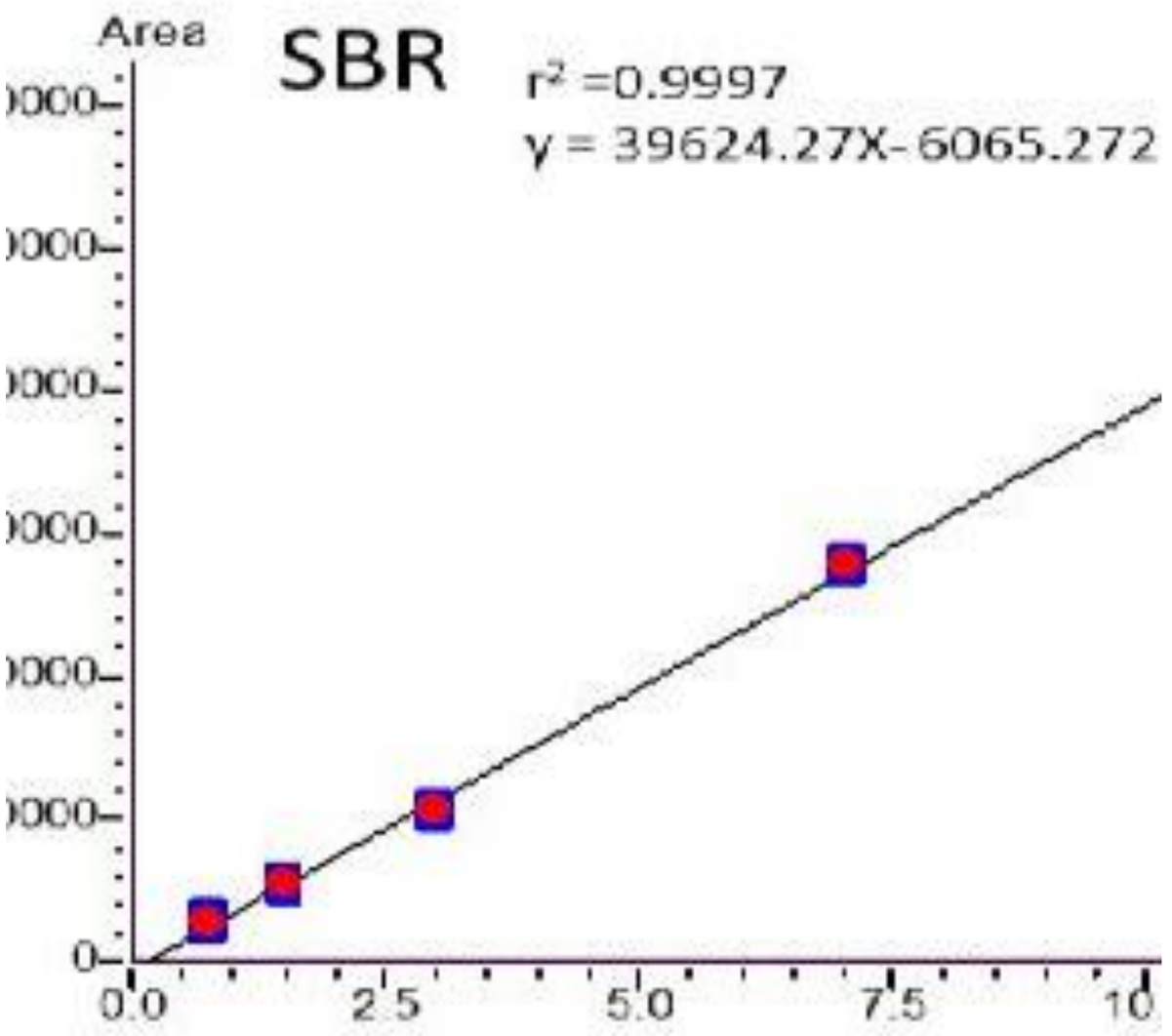




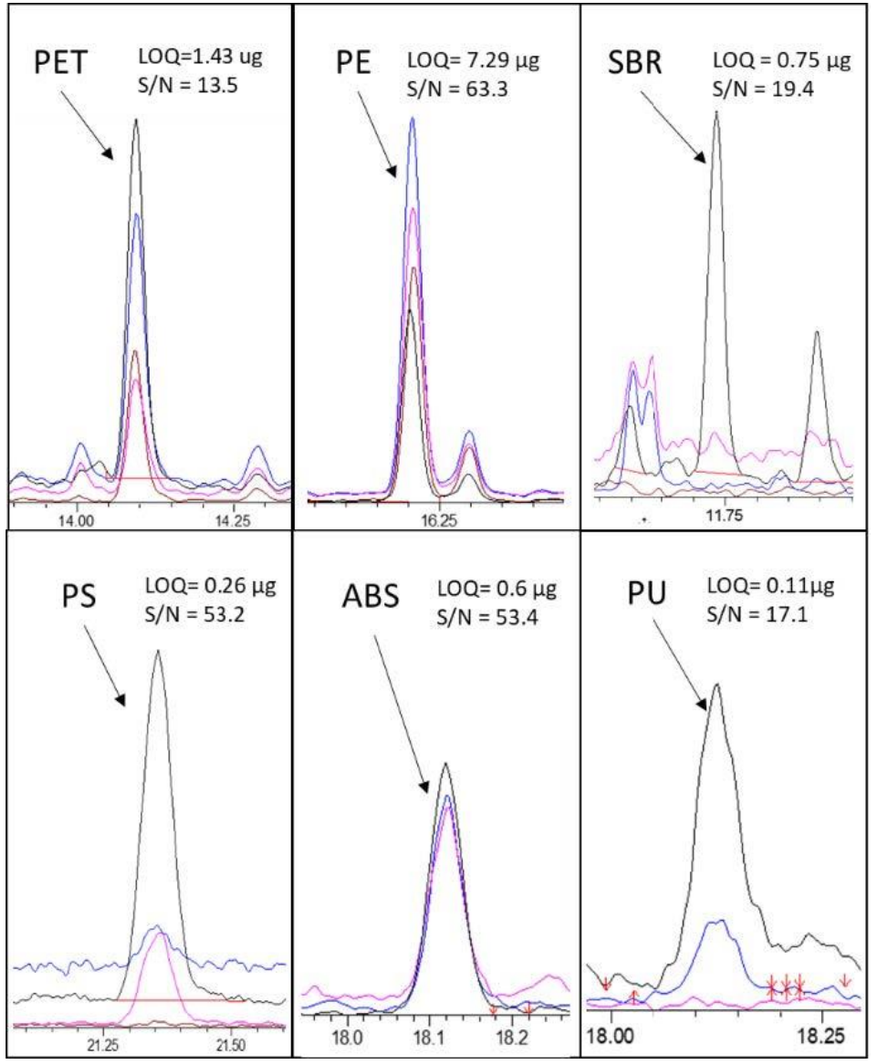
- Plastic particles from D8333 are transferred to PY cup and pyrozylates separated and identified.
- Pipet aliquot and evaporate, or dry crush and weigh
- 30-minute run time

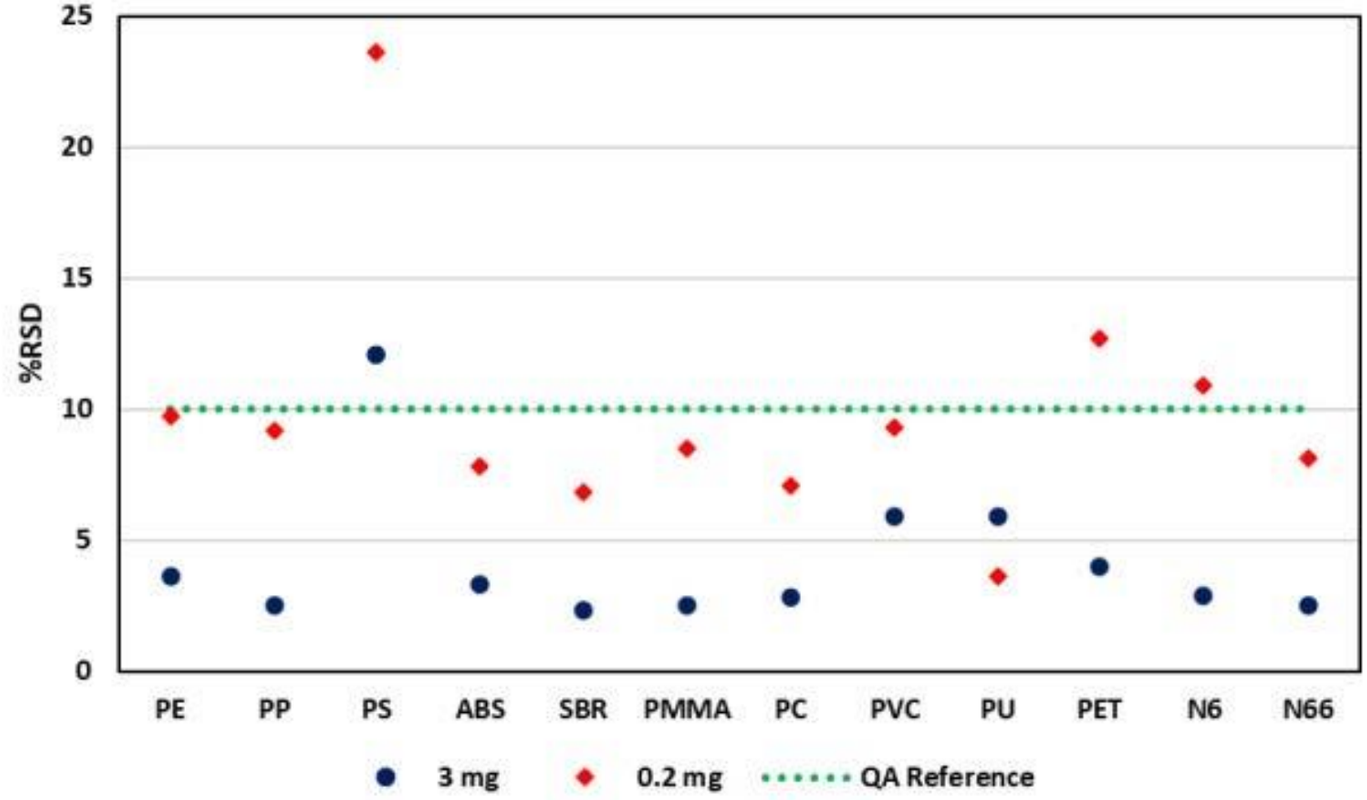
PY GCMS identifies and quantitates plastics and rubber by mass





PY-GCMS peaks and precision data





Single laboratory precision of 12 microplastics in CaCO3

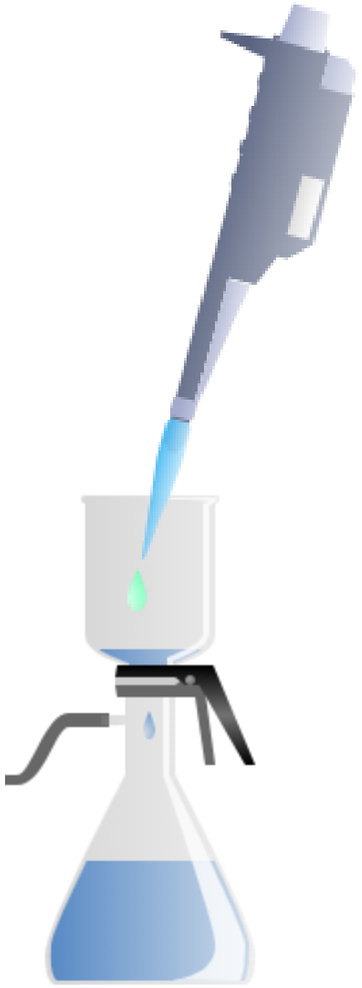
Single Laboratory Precision of 12 microplastics in 0.3 mg of a CaCO3 reference standard

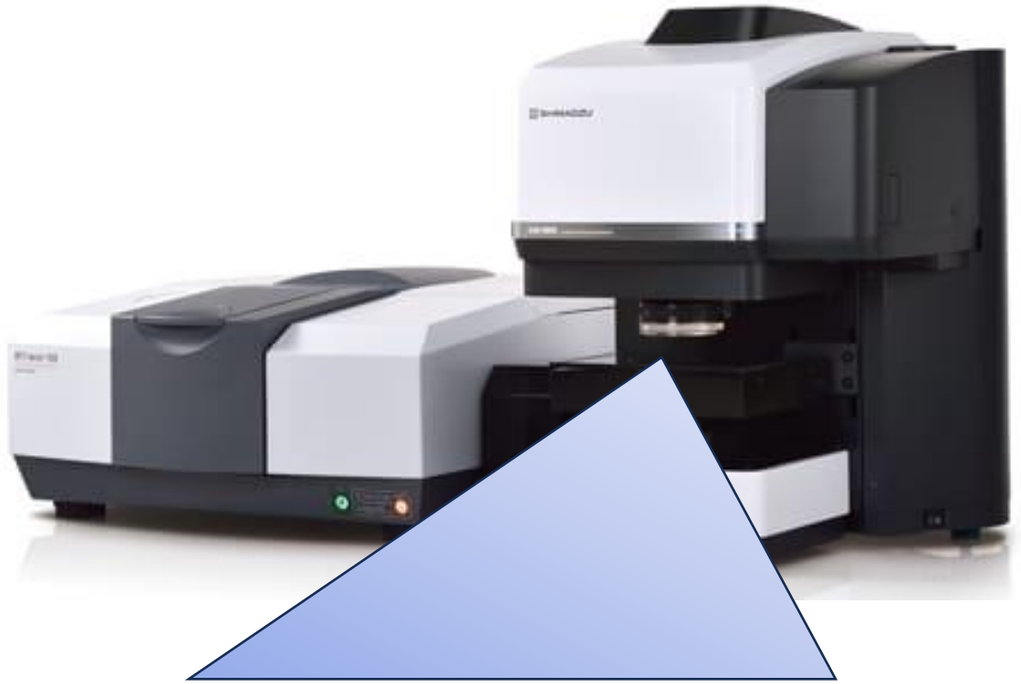
	#1	#2	#3	#4	#5	#6	#7	%RSD
PE	7.728	5.721	7.402	7.461	7.667	7.344	7.675	9.69
PVC	2.543	1.92	2.416	2.551	2.517	2.462	2.518	9.29
PP	2.074	1.643	1.976	2.104	1.959	1.947	2.227	9.17
PET	1.648	1.44	1.826	1.872	2.19	1.825	1.884	12.69
N66	1.244	1.032	1.272	1.303	1.295	1.273	1.343	8.12
SBR	0.926	0.785	0.985	0.93	0.947	0.906	0.913	6.81
ABS	0.694	0.543	0.664	0.655	0.642	0.624	0.685	7.84
PC	0.316	0.276	0.311	0.337	0.34	0.32	0.339	7.09
PMMA	0.283	0.24	0.256	0.294	0.31	0.282	0.292	8.55
N6	0.283	0.221	0.323	0.276	0.288	0.277	0.292	10.88
PU	0.164	0.148	0.16	0.164	0.159	0.158	0.164	3.58
PS	0.142	0.107	0.216	0.178	0.224	0.18	0.161	23.64

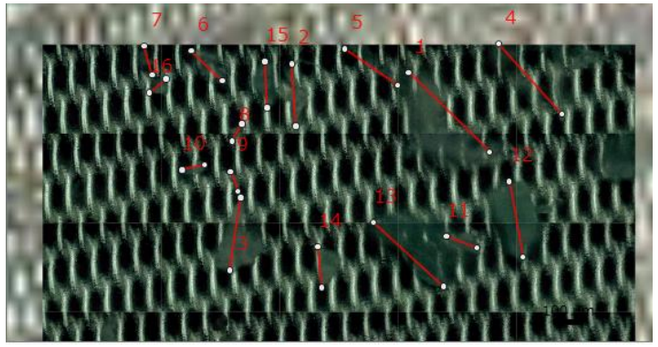
Single Laboratory Precision of 12 microplastics in 4 mg of a CaCO3 reference standard

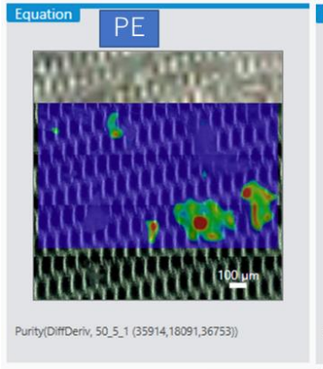
	#1	#2	#3	#4	#5	#6	#7	%RSD
PE	104.2	105.3	113.5	111.7	111.8	105.7	105.7	3.58
PVC	28.58	31.33	33.05	33.14	31.47	30.54	28.83	5.87
PP	26.36	25.92	27.37	27.72	26.82	26.34	26.1	2.52
PET	19.01	20.26	21.02	21.4	20.92	19.99	19.87	4.03
N66	15.04	15.58	16.21	15.98	15.79	15.62	15.34	2.50
SBR	10.3	10.83	11.08	10.95	10.92	10.8	10.69	2.33
ABS	8.433	8.737	8.633	8.269	8.218	8.703	8.013	3.27
PMMA	3.923	4.006	4.257	4.076	4.104	4.127	4.109	2.54
PC	3.651	3.778	3.881	3.742	3.767	3.636	3.578	2.78
N6	3.514	3.671	3.838	3.737	3.735	3.649	3.597	2.87
PS	3.243	4.116	3.754	3.087	3.391	4.208	3.383	12.12
PU	1.419	1.569	1.536	1.633	1.466	1.389	1.452	5.85

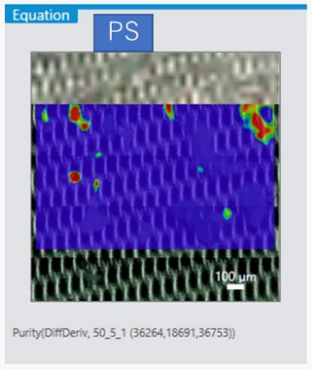
A portion of the D8333 digest sieve fractions can be filtered for analysis by IR Microscope

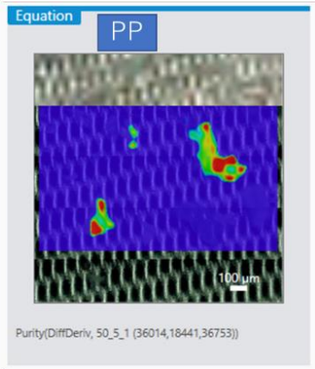






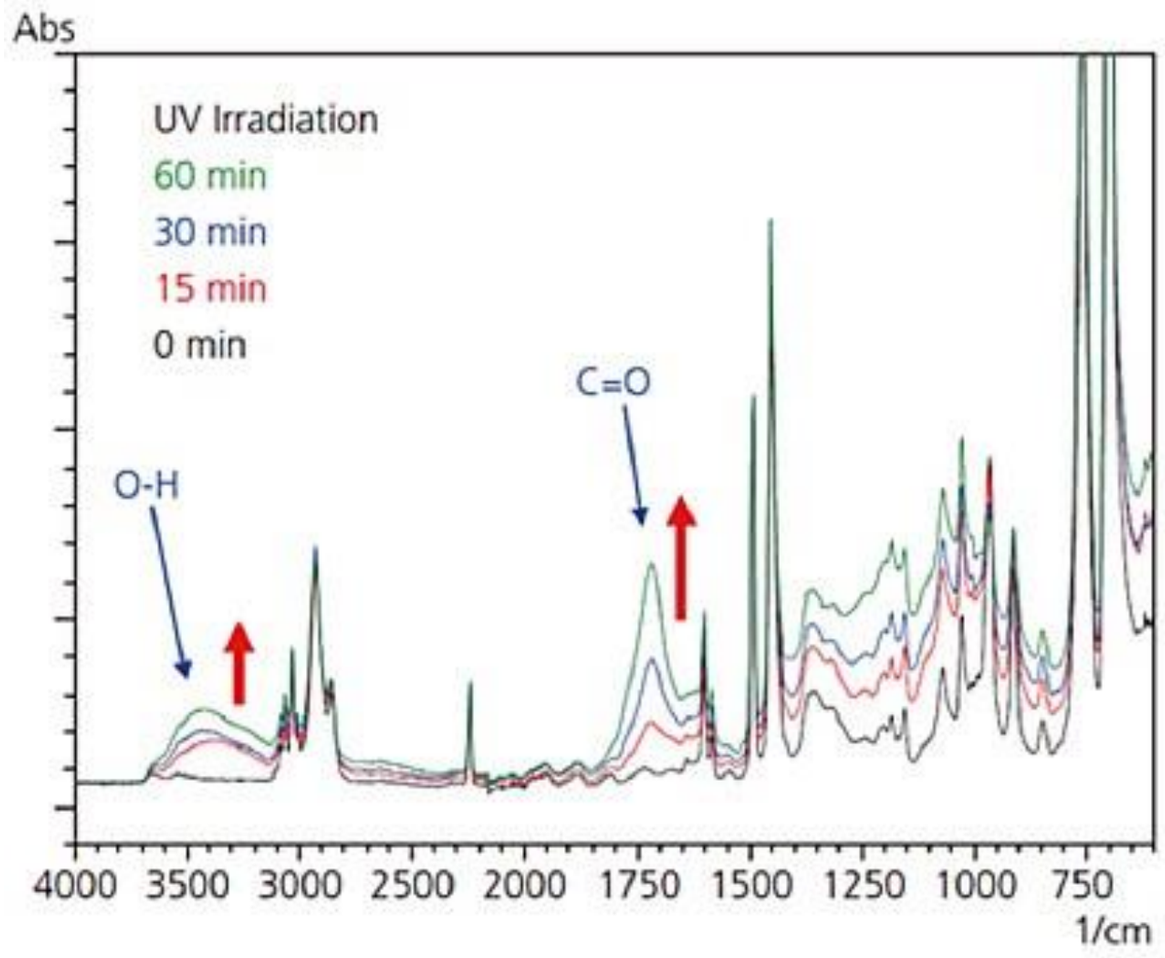




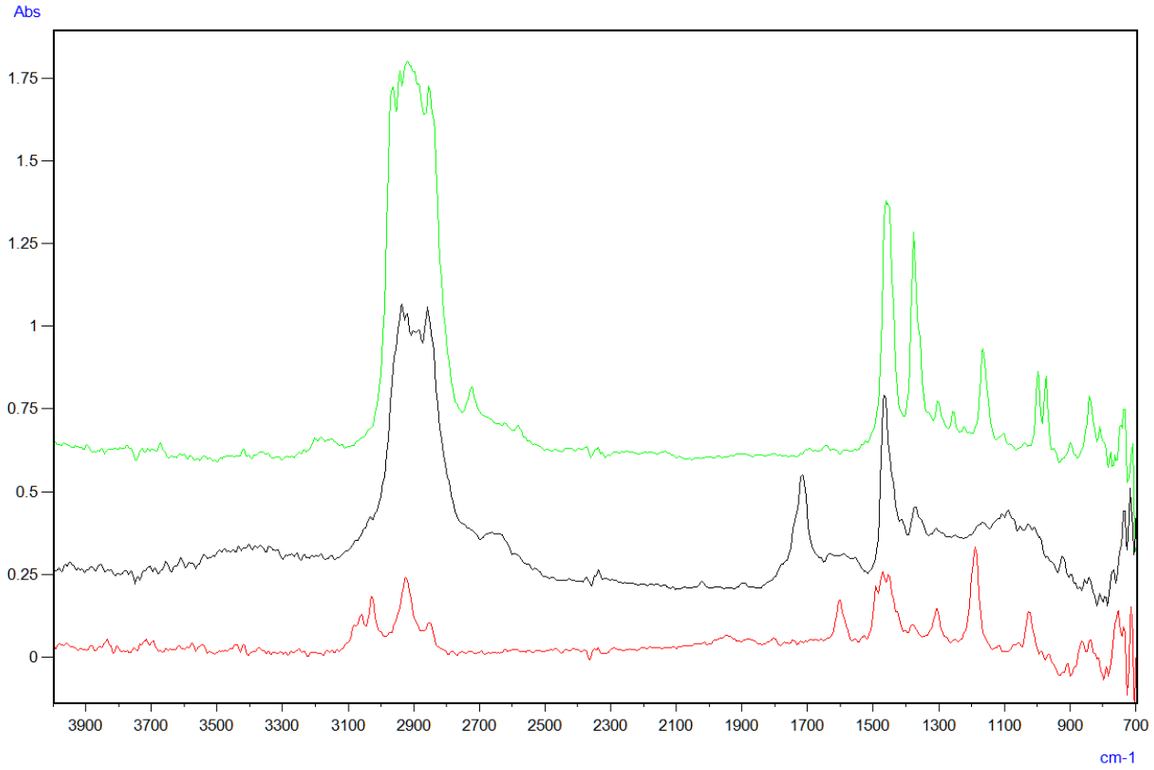


There are Interferences with microscopy and IR methods, so sample digestion more important than with PY-GCMS

- Undigested organic matter and inorganics obscure view
- Extra digestion or removal after D8333 may be needed
- May be limited to particles > 20 µm in diameter
- Surface contamination, such as oxide coatings
- Thermal and UV damage



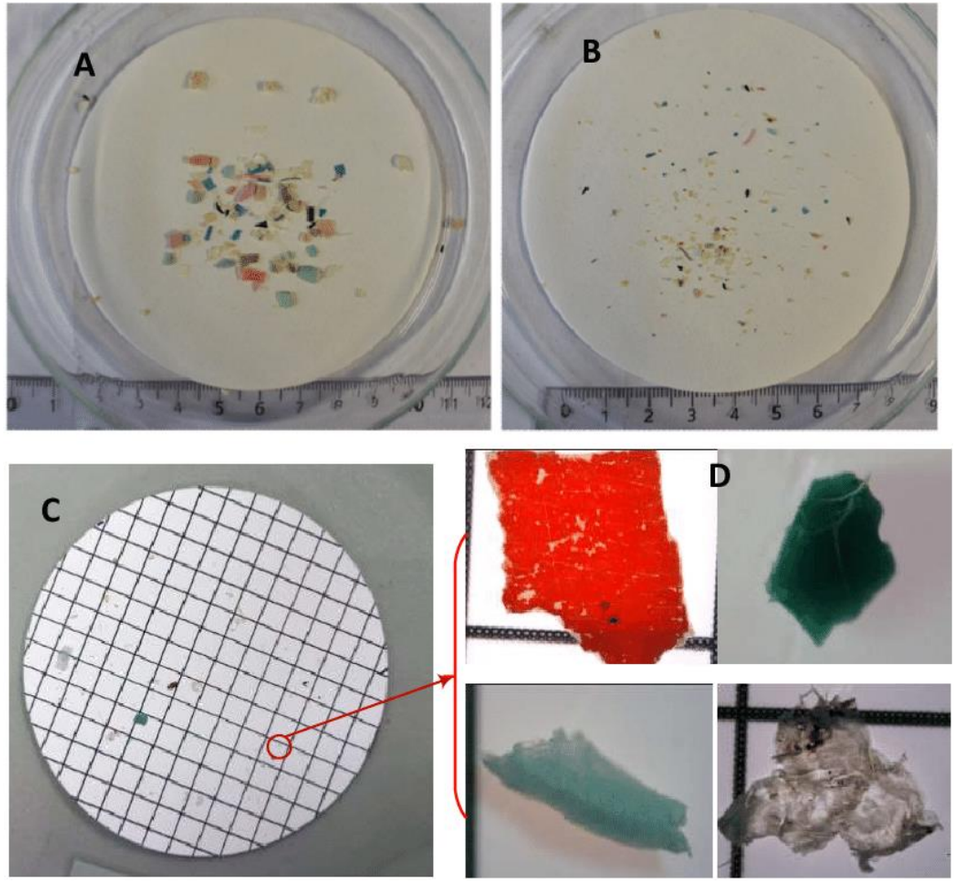
Spectra are obtained and microplastics identified by comparing to databases



	Sample 1				Sample 2			
	PE	PS	PP	Total	PE	PS	PP	Total
Average Particles per measurement area	4.3	3.3	2.3	10.7	5.3	1.3	1.7	8.3
Total Particles per filter	1725	1327	929	4246	2110	517	663	3317

- The identified plastics are counted, and total particles are calculated based on size of the filtered aliquot

Microplastics > 212 µm sieve fractions can be analyzed with a stereo scope and bench top IR



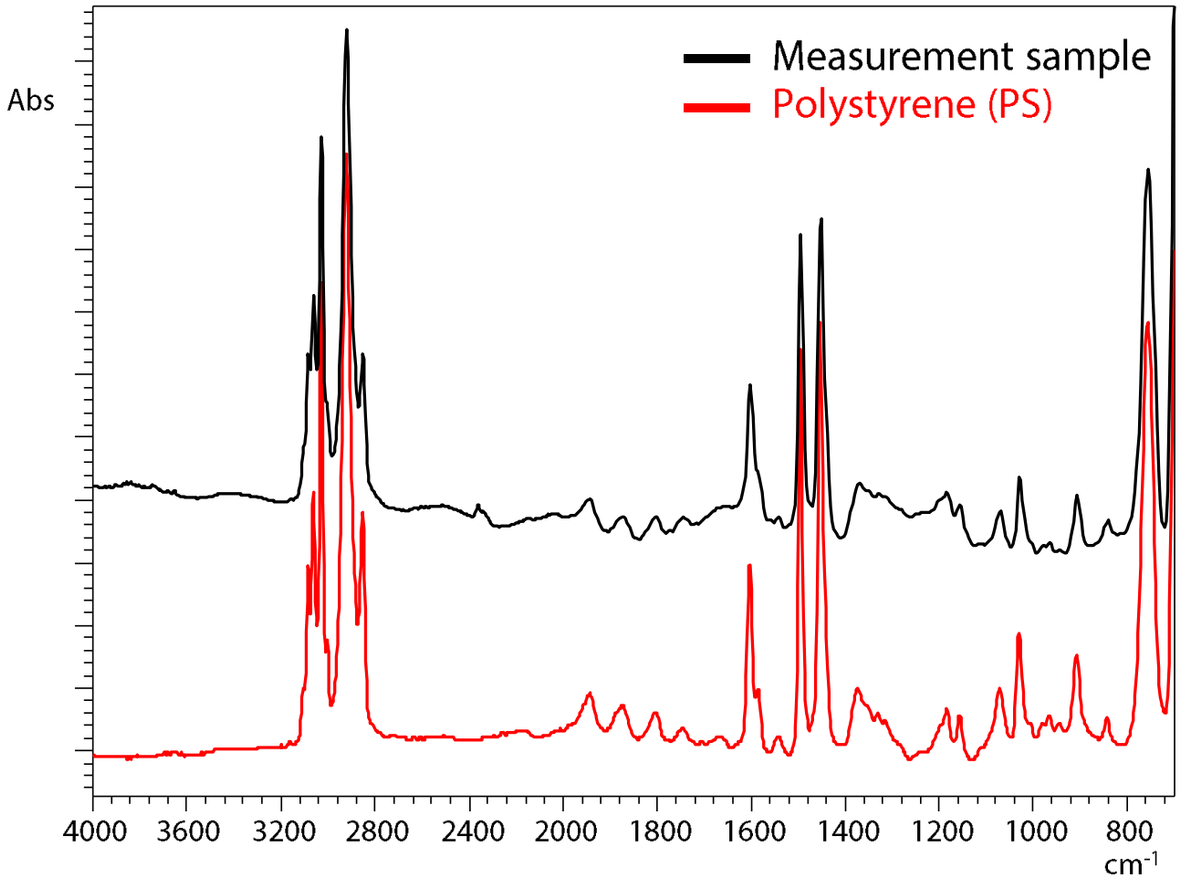


- The identified plastics are counted, and total particles are calculated based on size of the filtered aliquot
- Spectra are collected per particle and compared to database.



Microplastics Contamination in a High Population Density Area of the Chao Phraya River, Bangkok
June 2020Journal of Engineering and Technological Sciences 52(4):534-545
DOI:10.5614/j.eng.technol.sci.2020.52.4.6

Identify the various plastics by comparing spectrum to a library



- Generate a spectrum of each of the above selected particles.
- Use a commercial or laboratory generated library to compare spectrum with reference spectrum. Positive identification is made with a ≥60 % match.
- Less than 60 % may mean interferences are present.

Data from each technique can be used to fully characterize the plastics in the sample

- **D8332** samples large volumes and “pre-sorts” into various sieve fractions
- **D8333** removes interferences and maintains “pre-sorted” fractions
- Each digested fraction analyzed by pipetting aliquots
  - **D8489** rapidly count and obtains size distribution for smaller particles. Morphology can be correlated to optical and IR analysis.
  - **D8401** rapidly determines up to 12 microplastics, including rubber, and can be calculated as µg (mass).
  - IR Microscopy automates IR identification and counting of the smaller particles. Shapes and size distribution information is collected.
  - Optical characterization followed by manual IR Spectroscopy counts, sorts, and identifies the larger plastic particles.
  - The optical methods (including IR Microscopy) can estimate volume of the particles. With volume and identity, the mass of the particles can be estimated.
  - Mass from the IR and Microscopy data can be compared to mass obtained by pyrolysis GCMS

Questions?

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