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Excellence in Science

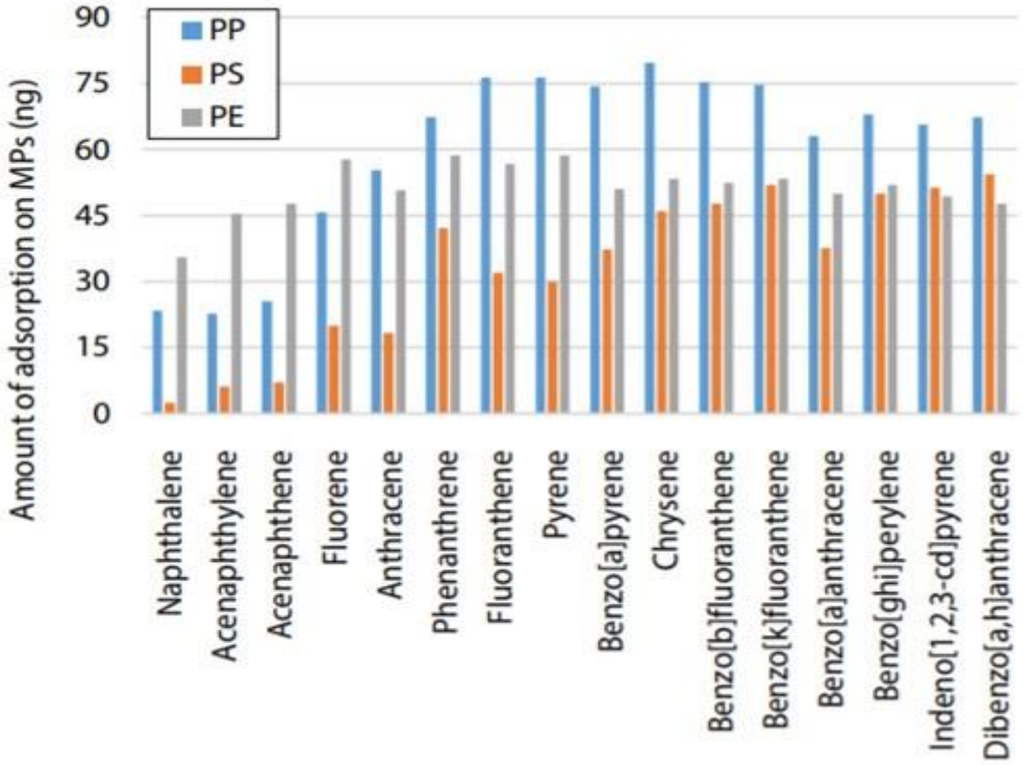
Determination of Microplastics in Water and Wastewater Using IR Spectroscopy

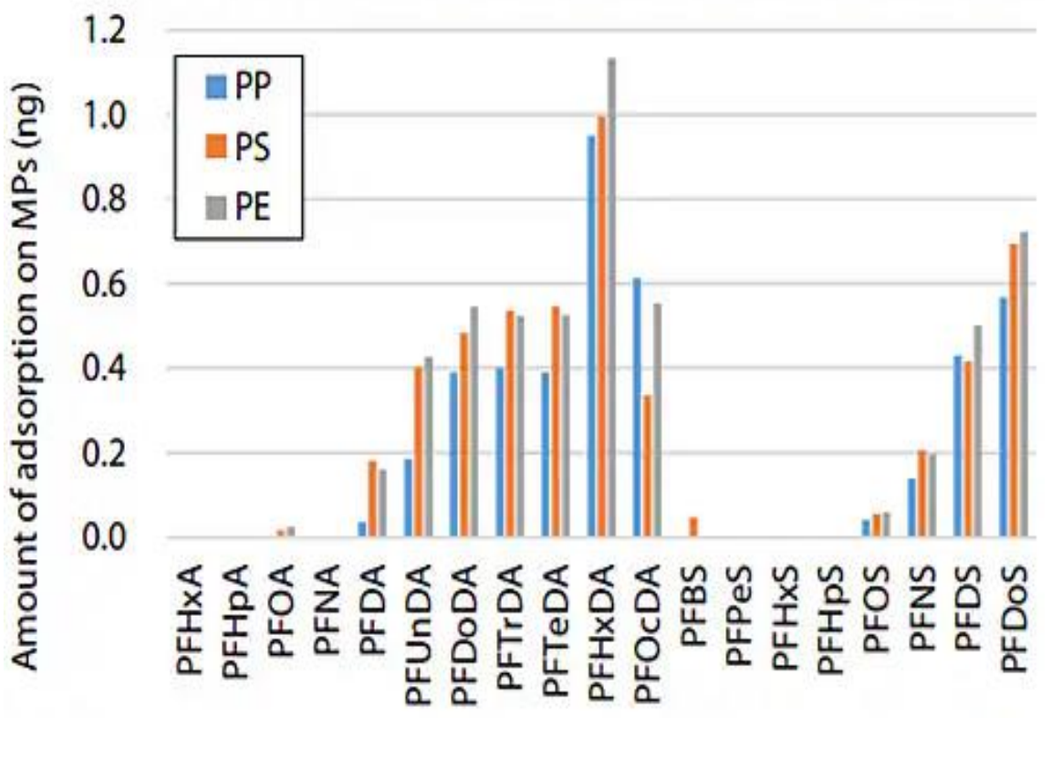
William Lipps

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NEMC 2023

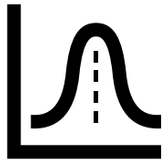
Why should we measure microplastics?





Chemical contaminants are trapped on the microplastics, then can be consumed and adsorbed into fish, animals, or humans

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



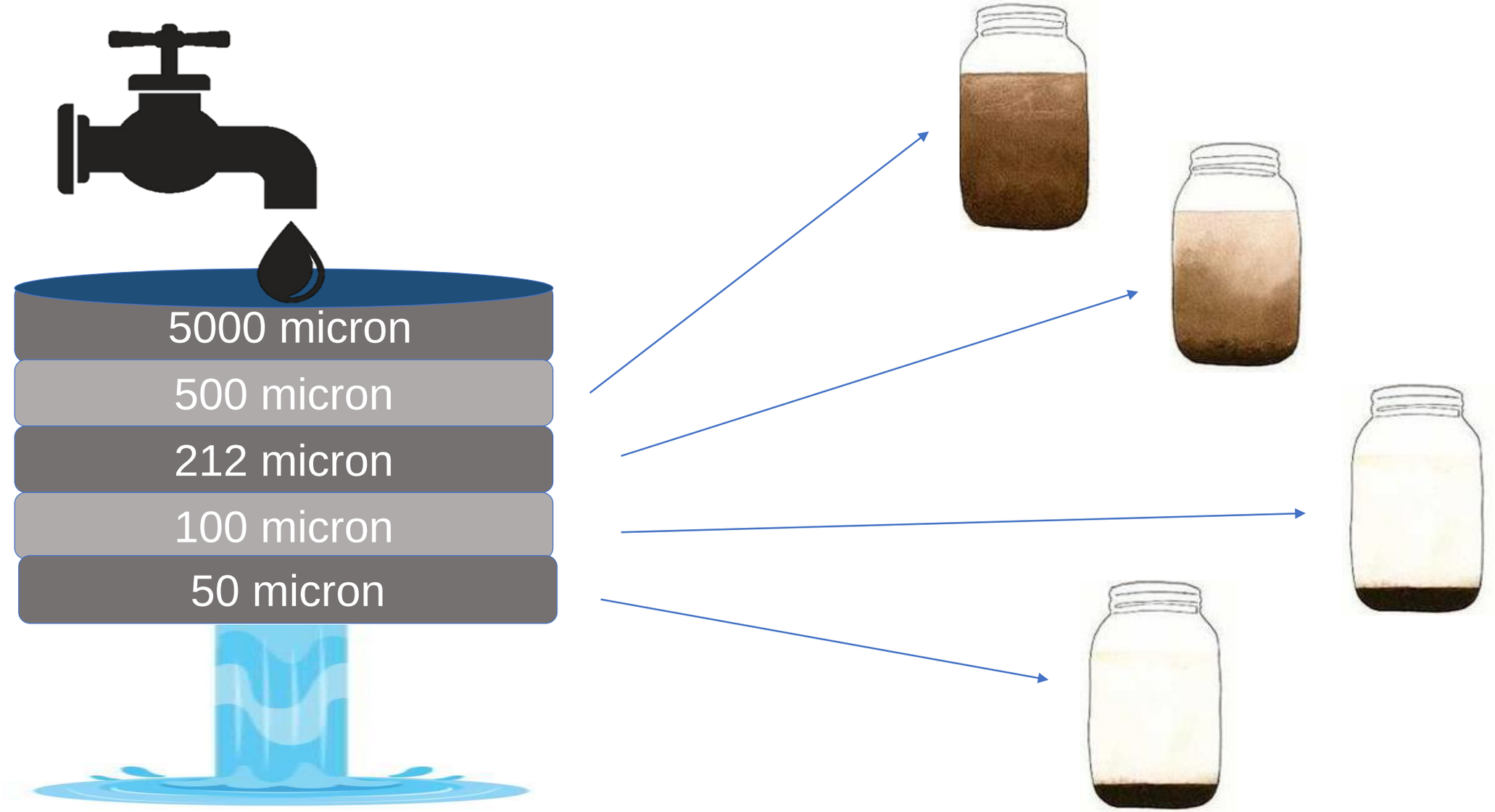
Analysis

DIA D8489

PY-GCMS WK67788

IR Microscopy WK67565

Sample collection by D8332



D8332 Sampling at a WWTP





The key is a large volume through sieves

Sample preparation by D8333

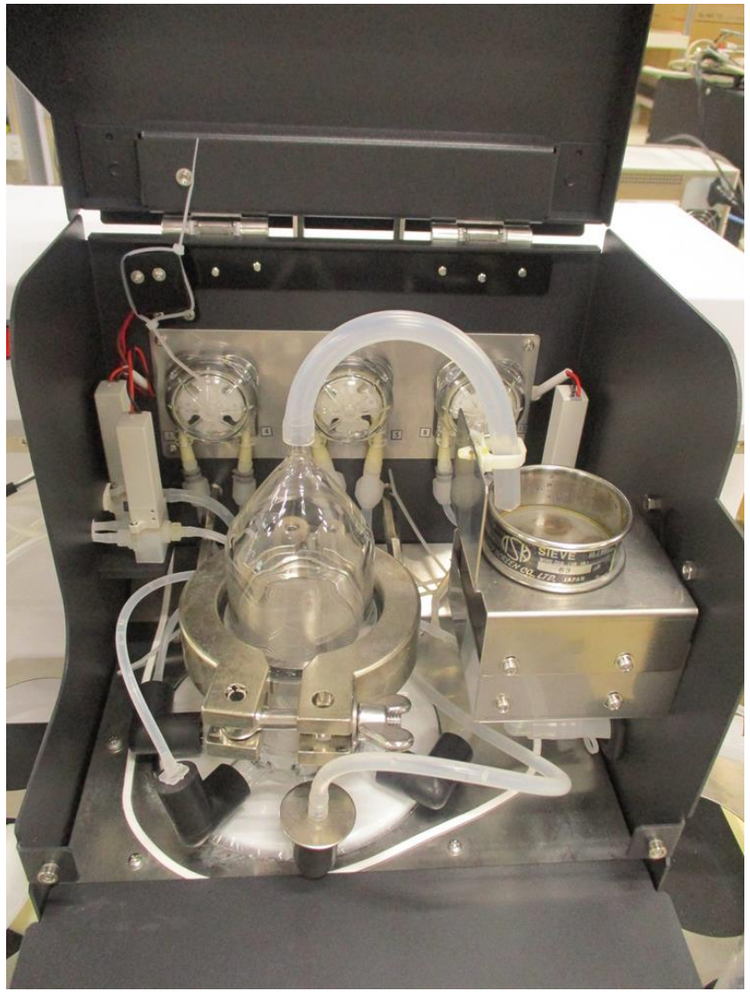


- H_2O_2
- Schweizer 5 minutes
- Ammonium Hydroxide 5 minutes
- Buffer
- Protease, buffer, lipase
- React 20 hours



Final sample = plastics suspended in methanol

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





Once the final sample is prepared it is ready for measurement



Pyrolysis GCMS

WK67788



Dynamic Imaging

D8489



WK67565

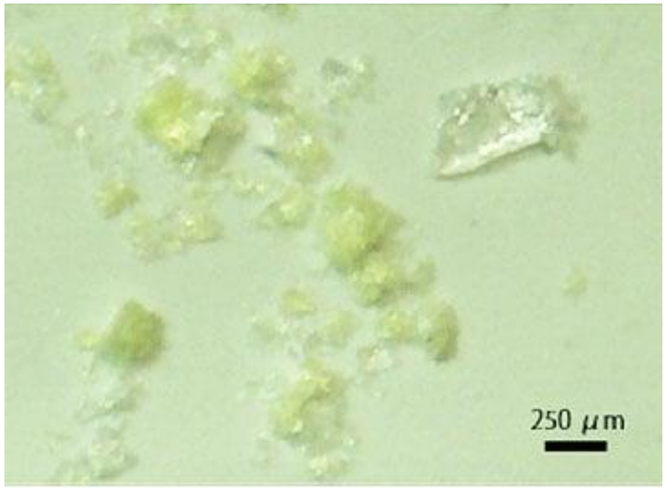


FTIR Microscopy

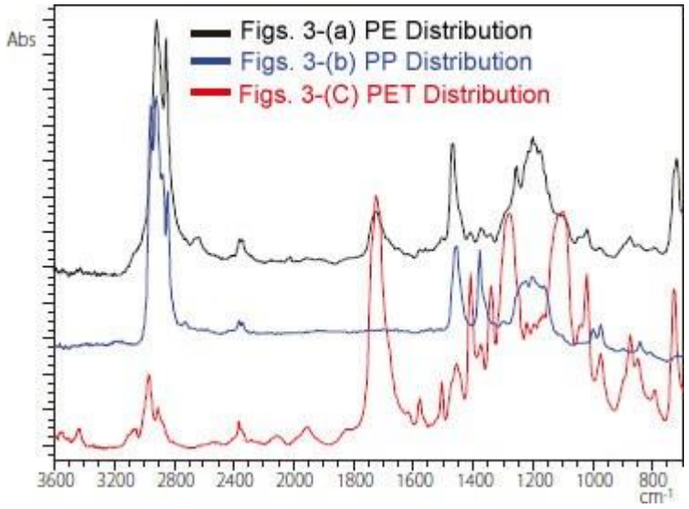


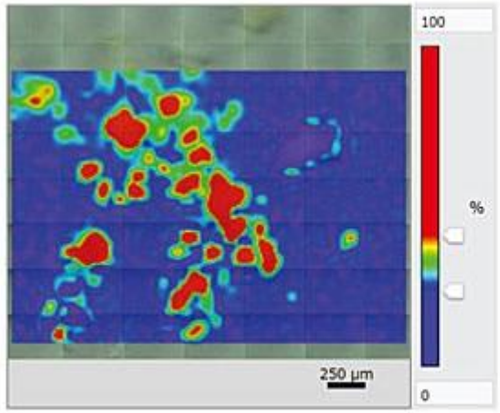
Manual IR Spectrometry

Smaller particles can be identified and counted using software and the IR Microscope

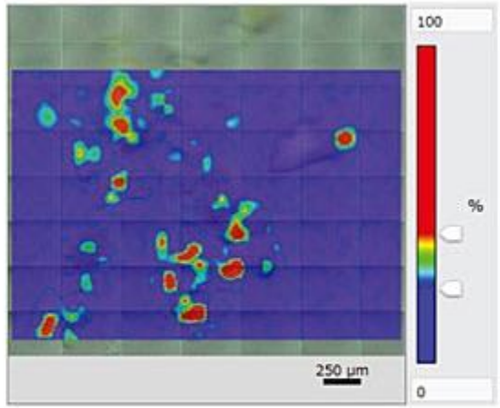


Microplastics on a filter

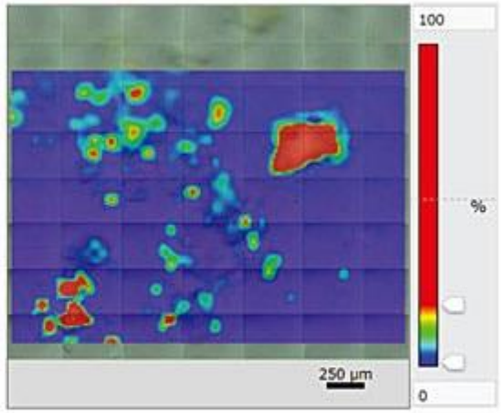




Figs. 3-(a) PE Distribution

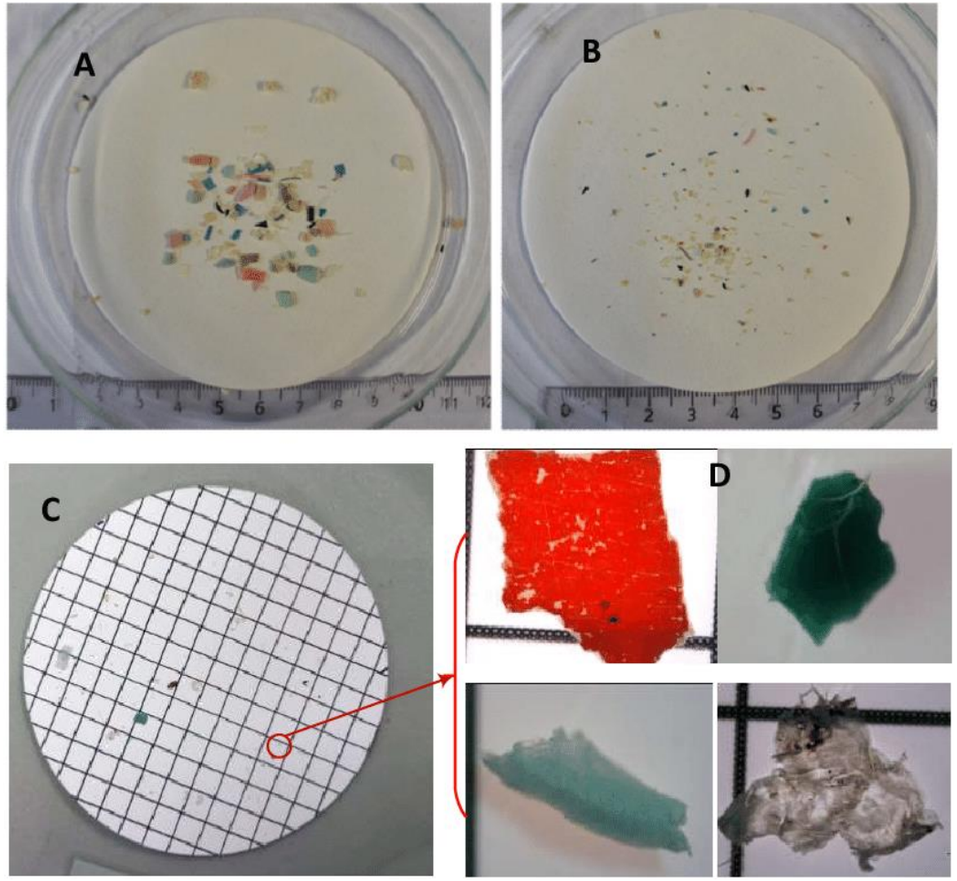


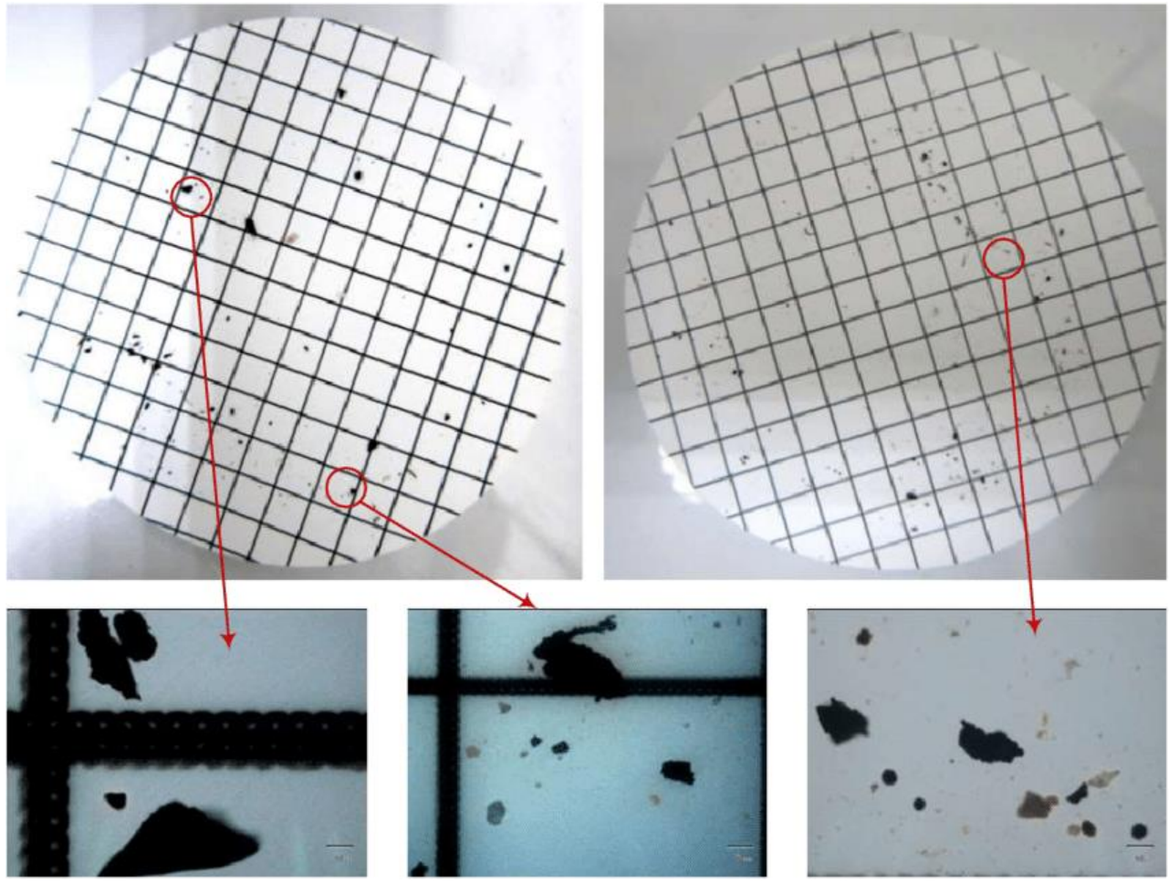
Figs. 3-(b) PP Distribution



Figs. 3-(C) PET Distribution

But what if you don’t have an IR Microscope?





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

Unlike the ISO TC147 workgroup on microplastics, ASTM WK67565 will include optical microscopy and manual IR

ASTM WK7565 is being written in collaboration with The Southern California Coastal Water Research Project (SCCWRP) to help ensure consistency with CA SOP, with special thanks to:

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Scott Coffin, Ph.D. State Water Resources Control Board 1001 I St. Sacramento, CA 95814 scott.coffin@waterboards.ca.gov

Scope:

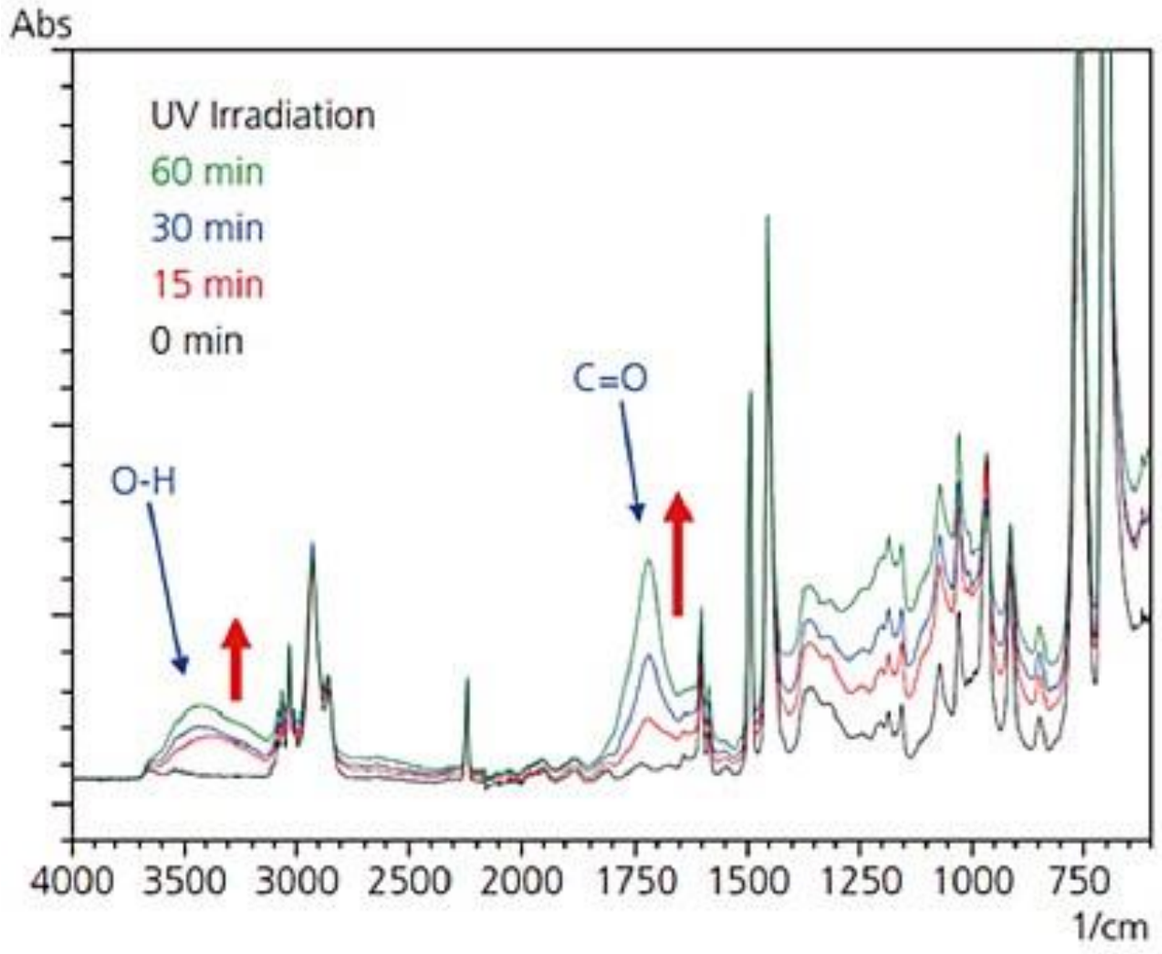
- identification and quantification of microplastic particles in
  - municipal wastewater influent,
  - treated effluent from a wastewater treatment plant,
  - ambient waters,
  - finished drinking water,
  - and bottled water.
- 20 µm-5 mm
- using visual microscopy for particle counts and infrared (IR) spectroscopy for chemical identification of counted particles.
  - Fourier transform IR (FTIR),
  - laser direct infrared (LDIR) imaging,
  - and other techniques capable of measuring IR spectra from particles in this size range.

Method Summary

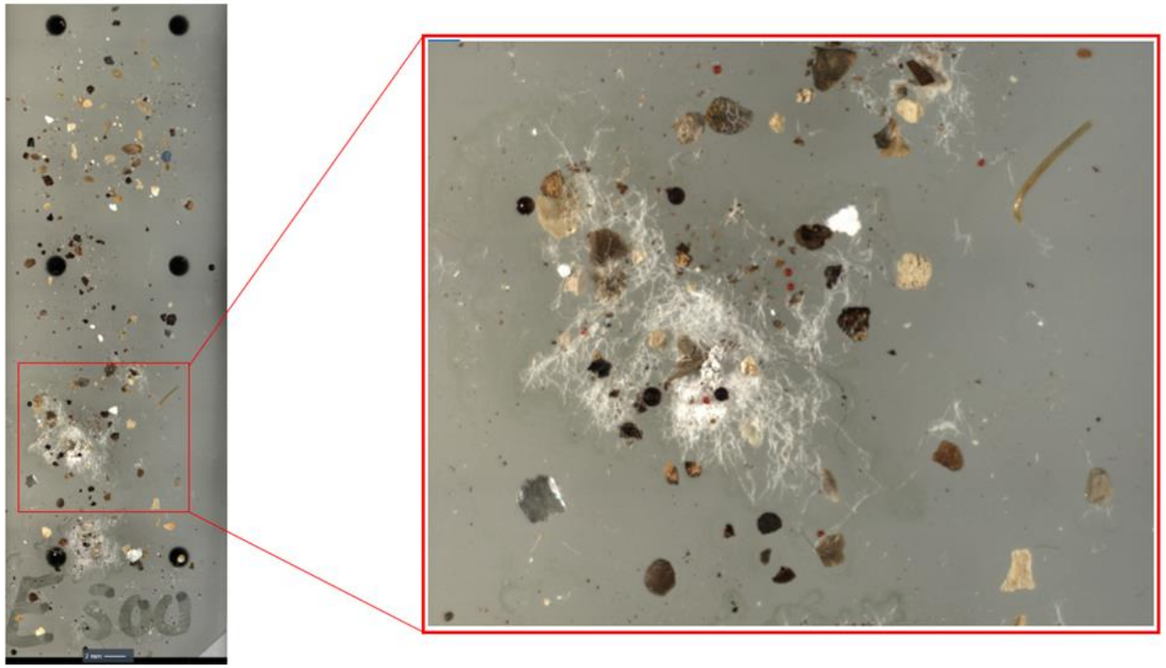
- samples collected using Practice D8332
- prepared for analysis using Practice D8333
- Samples are viewed using a stereomicroscope and microplastic particles are identified.
- A representative subsample of particles is selected and prepared for IR spectroscopy.
- Each subsampled particle is measured and optionally photographed
- identified individually using IR spectroscopy and spectral matching to a spectral reference library or standards of known composition.
- This method is applicable for the positive identification of common plastics including polyethylene (HDPE and LDPE), polypropylene (PP), polyvinyl chloride (PVC), polyurethane (PUR), polyethylene terephthalate (PET), and polystyrene (PS). (PVC may not be detectable if using a specific gravity separation process during sample preparation.)

Interferences

- Undigested organic matter and inorganics
- 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
- Other techniques, such as Pyrolysis GC-MS may be needed
- Visual microscopy limited to particles ≥ 106 µm



Stereo Microscope Counting and IR Analysis of Sieve Fractions <500 µm



- place a 20 µm filter onto the filter holder and secure the filtering funnel on top
- pour the prepared sieve fraction through the filtration system and rinse
- carefully remove the filter, avoiding sample loss, transfer into a clean petri dish
- Repeat for all sieve fractions

Use Visual Microscopy with appropriate magnification and illumination settings

- In each sieve fraction > 212 µm:
- Identify similar particles
- Count the similar particles
- Characterize by color and morphology
- Select a minimum of 30 each and transfer to the IR for reflectance or ATR

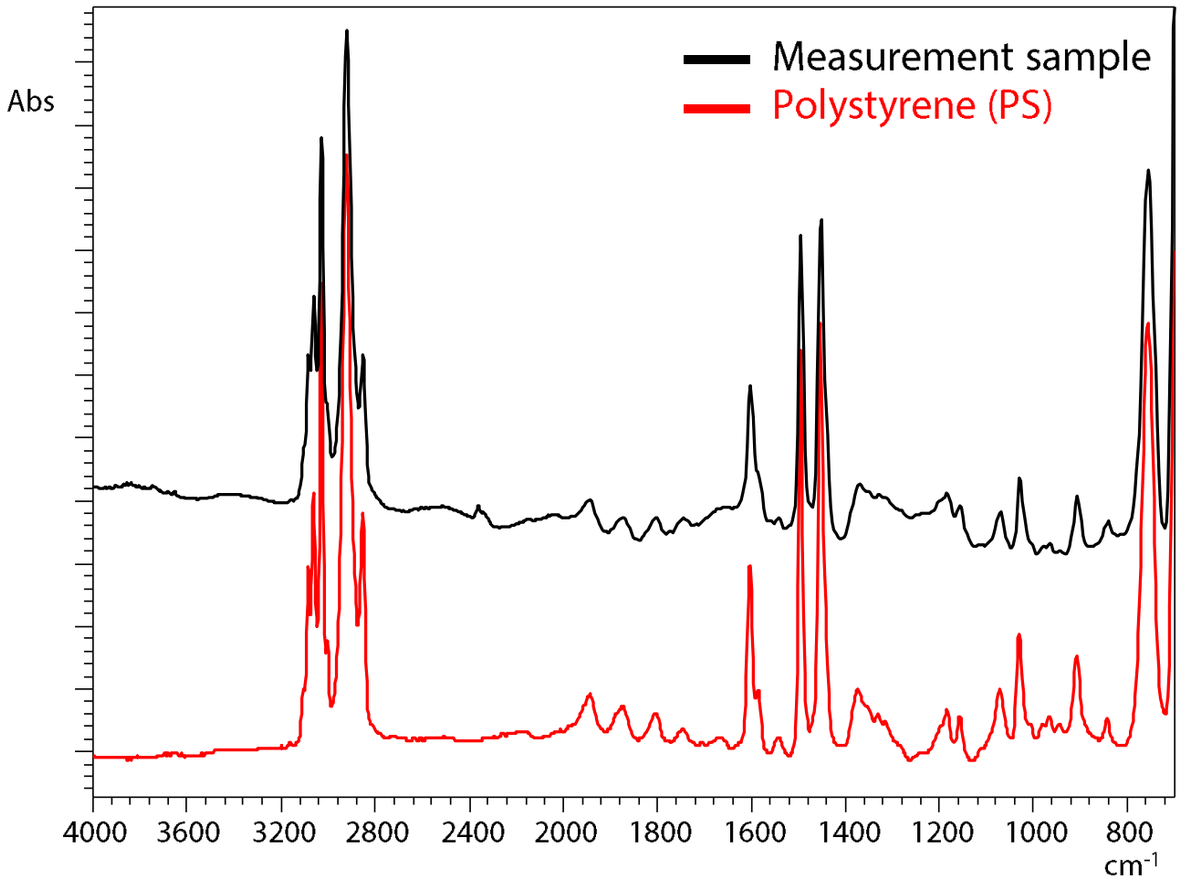


IR Microscopy Analysis of Samples on slides or filters < 212 µm

- For slides, transfer a representative sample aliquot from each prepared sieve fraction <212 µm to a mirrored microscope slide dropwise and evaporate to dryness.
- For filters, transfer each filter containing particulates from a prepared sieve fraction <212 µm to a glass petri dish, cover, and let dry.
- Dry each slide or filter completely before analysis and, if facilitated by heating, do not heat in excess of 50℃ to prevent possible degradation of the plastic material.
- Initiate optical image of the slide containing the sample for obtaining the location and size distribution of particles.



Identify the various plastics by comparing spectrum to a library



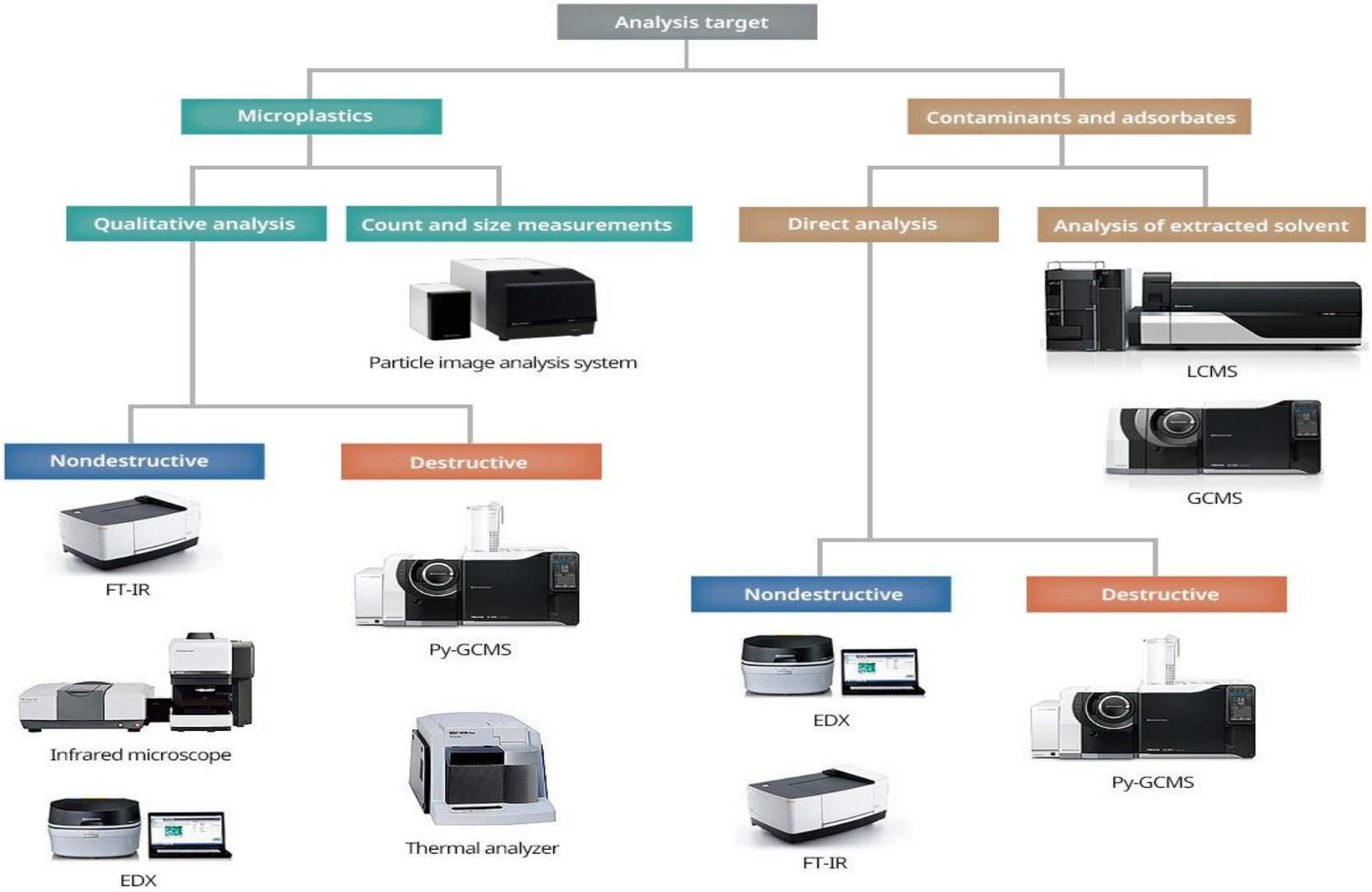
- Generate a spectrum of each of the above selected particles.
- Use a commercial or laboratory generated library to compare spectrum with reference spectrum. Positive identification is made with a ≥60 % match.
- Less than 60 % may mean interferences are present.
- An automated system may be used

What are the next steps

- Use D8402 to create reference materials
- Prepare a D8333 mix containing various plastics at different counts
- Analyze to obtain precision of counts and accuracy of ID

- Prepare samples for an Inter-lab study with a minimum of six labs

In addition, develop new techniques and methods that can be used to measure and ID microplastic pollution



Questions?

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