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Excellence in Science

Microplastics:
Rethinking Their Occurrence and Mitigation to Minimize Environmental Effects.

Ruth Marfil-Vega, PhD
Senior Market Manager - Environmental

Topics that will be covered today

1. Introduction
2. Infrared microscopy
3. Pyrolysis-GC/MS
4. MALDI

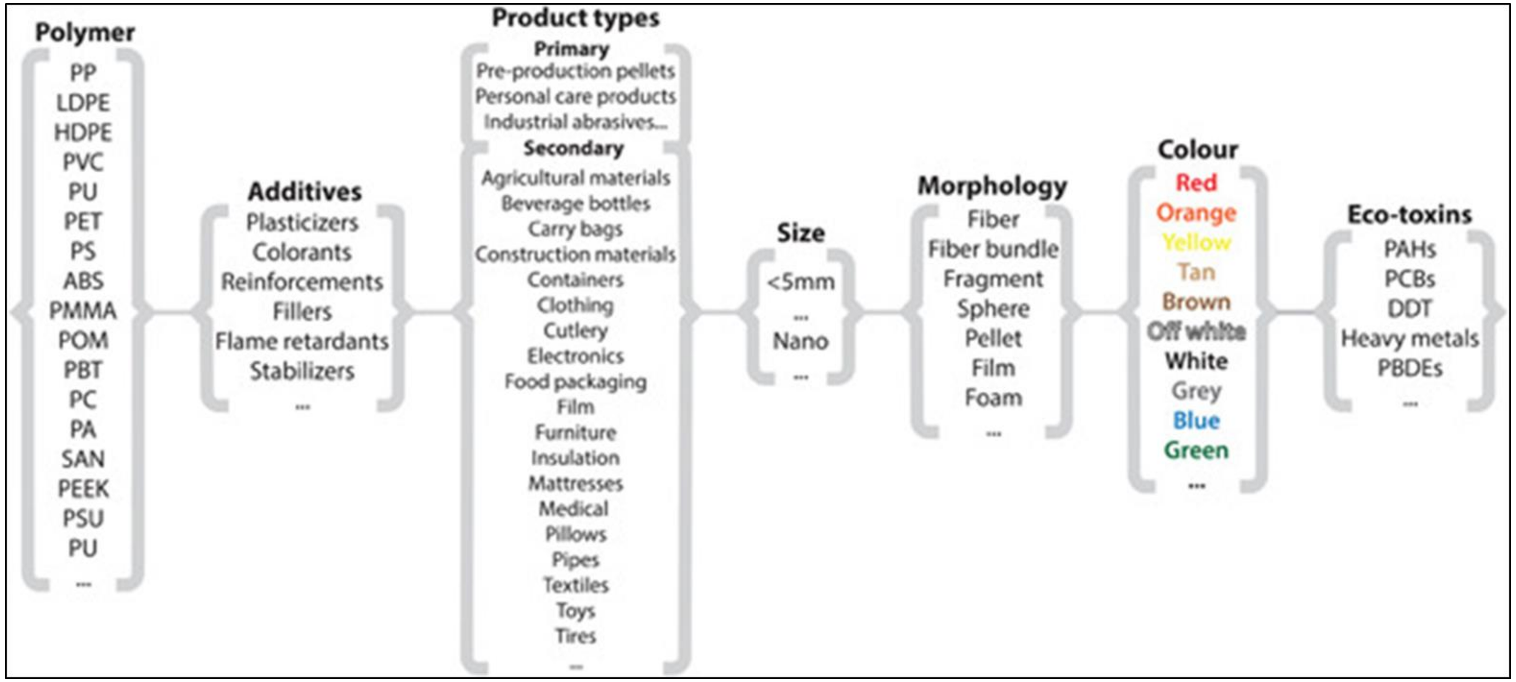
Microplastics

https://oceansasia.org/beach-mask-coronavirus/

The most pessimistic estimates suggest that the mass of microplastics in aquatic habitats will surpass that of the fish by 2050 (Pico and Barcelo, 2019).

Yolanda Picó and Damià Barceló. Analysis and Prevention of Microplastics Pollution in Water: Current Perspectives and Future Directions. ACS Omega 2019 4 (4), 6709-6719.

Why are microplastics different from other contaminants?



Rochman et al. Rethinking microplastics as a diverse contaminant suite. Environ Toxicol Chem, 2019 38: 703-711

How do we count, size and characterize microplastics?

Concentration Dimensions Composition

Why are microplastics different from other contaminants?

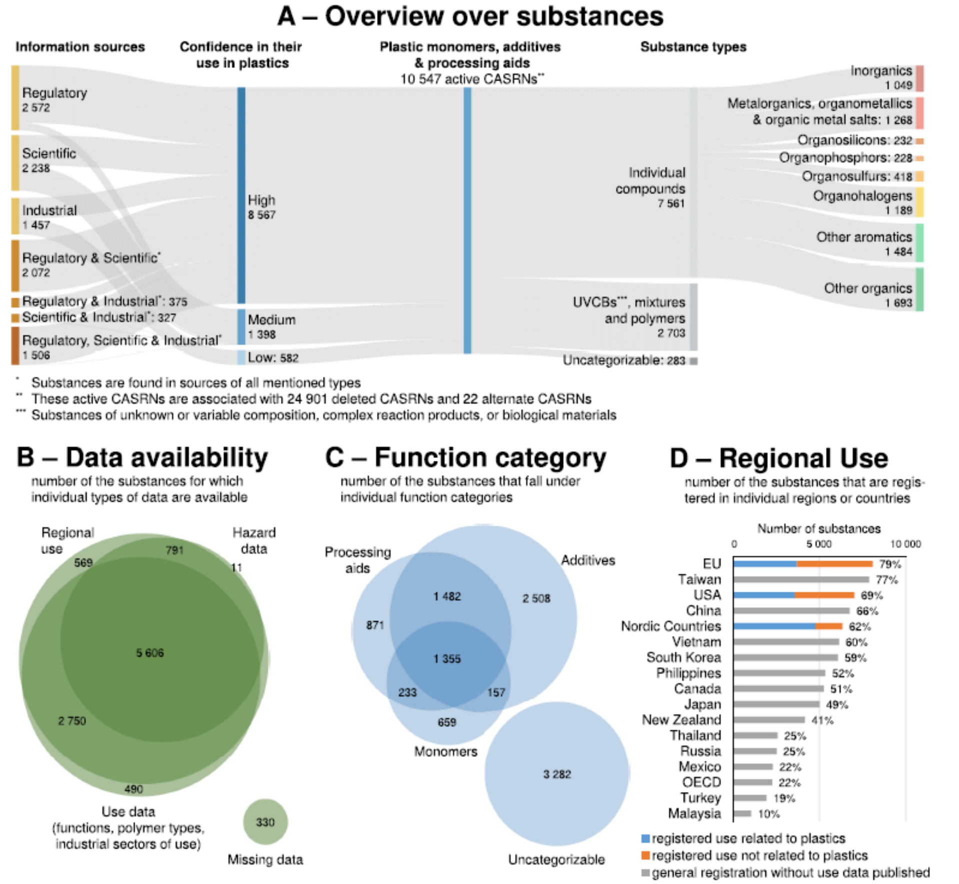


Figure 2. Overview of the substances that are (potentially) used as plastic monomers, additives, and/or processing aids. Part (A) illustrates the distribution of the substances identified in terms of information sources, assigned confidence scores of their use in plastics, and substance types. Part (B) shows examples of data availability in different areas. Part (C) depicts numbers of the substances falling under the broader function categories "monomers", "additives", "processing aids", and "uncategorizable". Part (D) exhibits numbers of the substances registered for production and/or use in different regions and countries; for those national or regional inventories with publicly accessible information on uses, the reported uses are analyzed whether they are linked to plastics (as defined in Sheet S1 in Supporting Information S1).

Wiesinger et al. Deep Dive into Plastic Monomers, Additives, and Processing Aids
Environmental Science & Technology Article ASAP

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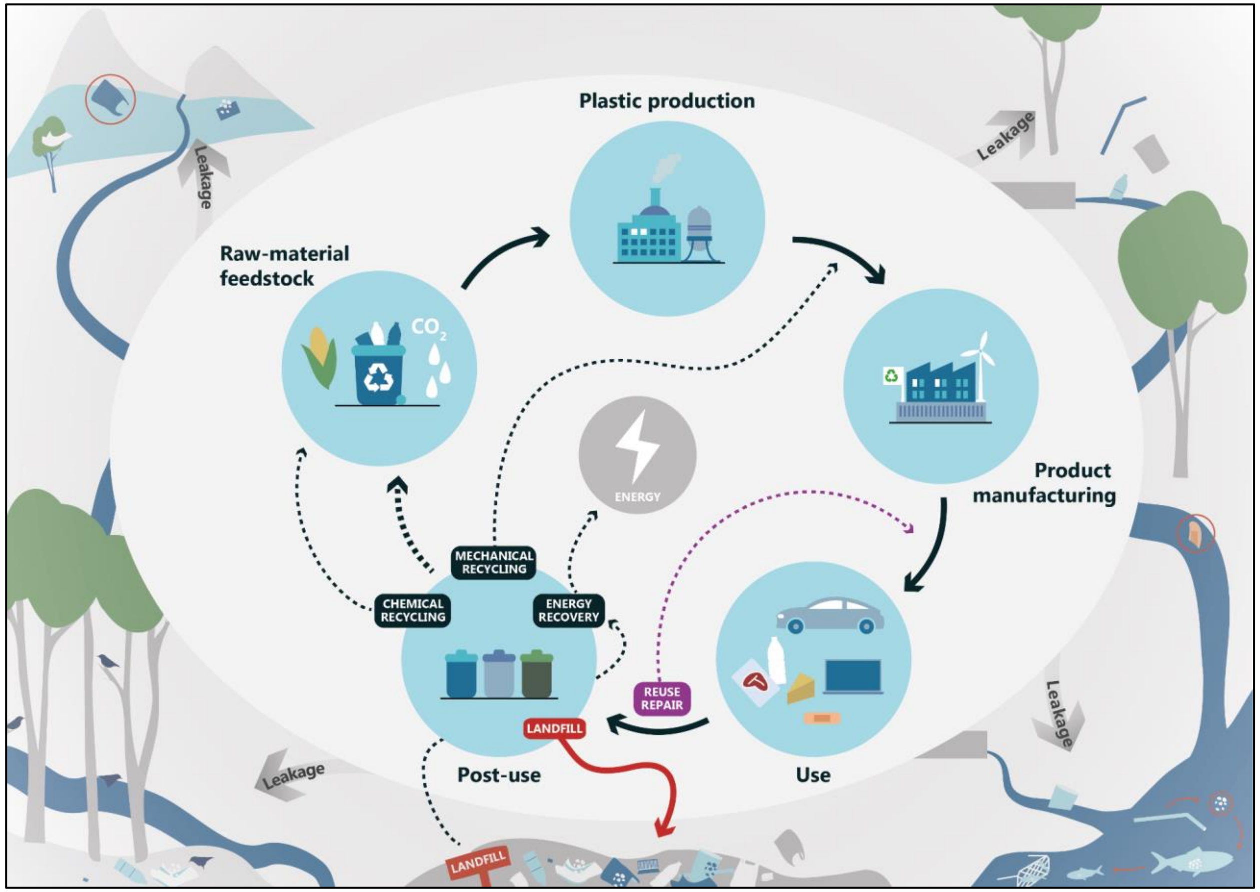
Life cycle of plastics



https://debrisfreeoceans.org/

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Life cycle of plastics

Table 1
Positive and negative consequences of COVID-19 pandemic and lockdown measures on the environment.

Positive impacts	Negative impacts
• Increased outdoor air quality [13-16] • Decreased pollution noise [17,18] • Decreased household food waste [19] • Decrease energy consumption and GHG emissions [20,21] • Global decrease on wildlife trade [22] • Decrease on deforestation [22] • Increase in surface water quality [23]	• Decreased indoor air quality [14,24] • Increased medical waste [25] • Decline in waste recycling with increase in incineration and landfilling [26] • Increased disinfection routines with hazardous chemical substances in household and outdoor environments [27,28] • Increased ecological risk to natural ecosystems due to the use of disinfectants [29]

Ana L. Patrício Silva, Joana C. Prata, Tony R. Walker, Armando C. Duarte, Wei Ouyang, Damià Barcelò, Teresa Rocha-Santos.
Increased plastic pollution due to COVID-19 pandemic: Challenges and recommendations.
Chemical Engineering Journal, Volume 405, 2021.

Pre COVID-19

Yolanda Picó and Damià Barceló. Analysis and Prevention of Microplastics Pollution in Water: Current Perspectives and Future Directions. ACS Omega 2019 4 (4), 6709-6719.

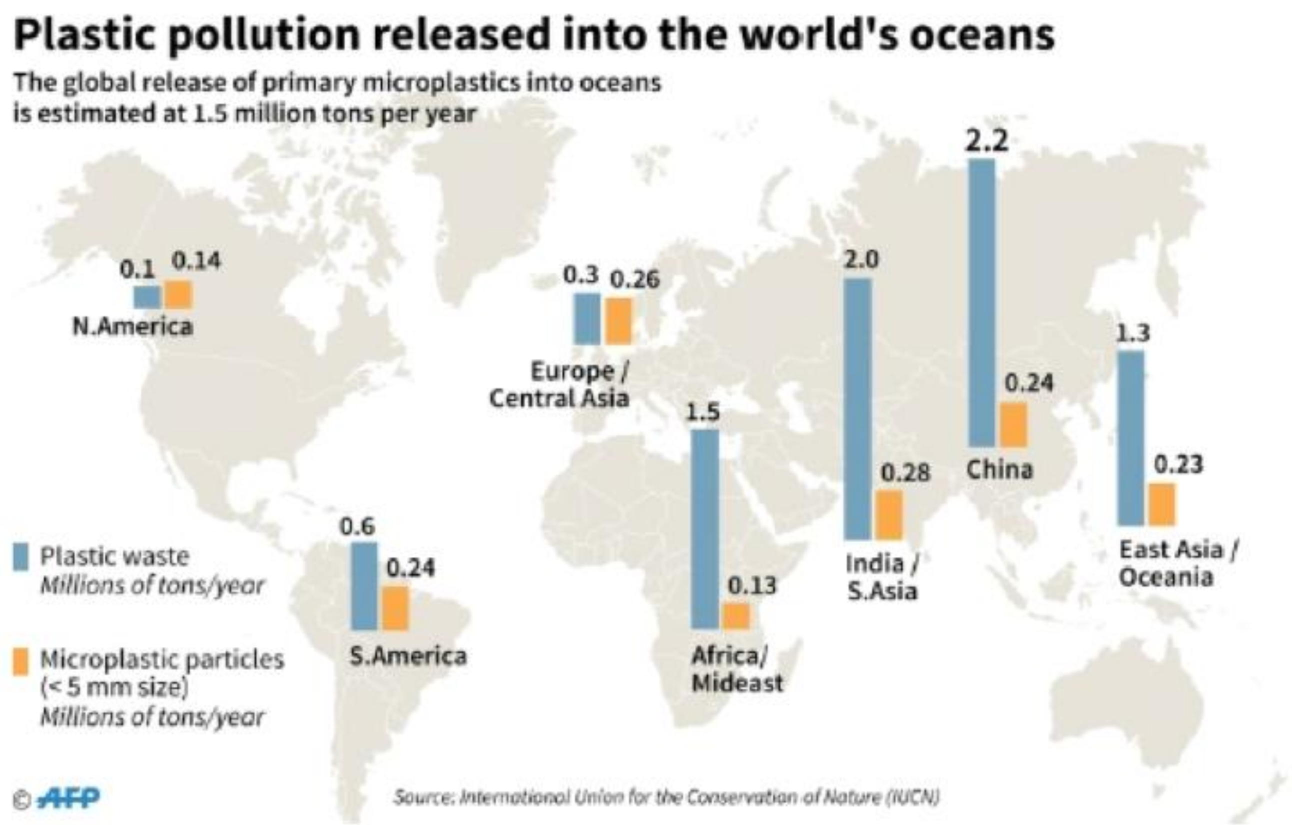


Figure 2. Global release of MPs to the world oceans. Comparison with plastics originated from mismanagement of wastes. Reprinted from ref 14 Copyright (2017) with permission from International Union for Conservation of Nature and Natural Resources (IUCN).

Post COVID-19

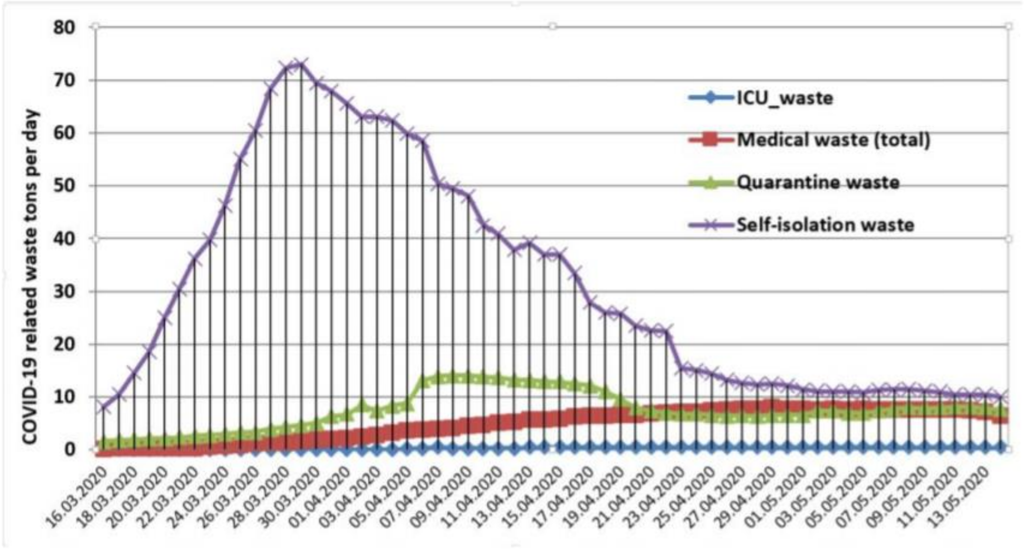


Figure 1. COVID-19 related waste flow in Romania during the emergency state.

Mihai, F.-C. Assessment of COVID-19 Waste Flows During the Emergency State in Romania and Related Public Health and Environmental Concerns. Int. J. Environ. Res. Public Health 2020, 17, 5439. https://doi.org/10.3390/ijerph17155439

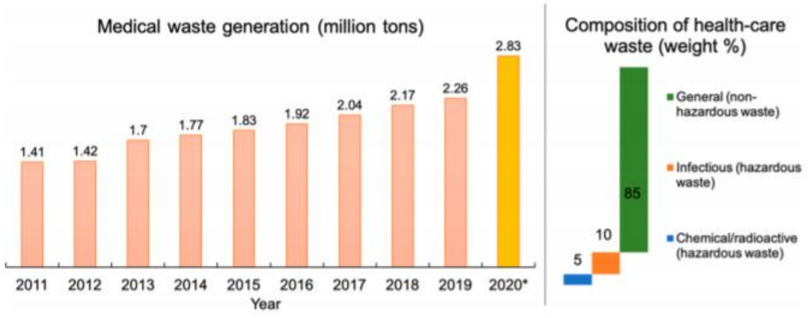


Figure 1. Medical waste generation and compositions in China. The quantity of waste is expected to increase by more than 25% in 2020.[7,11] In the U.S., there is no national database on medical waste generation because the Medical Waste Tracking Act (MWTA) of 1988 expired in 1991 and the U.S. Environmental Protection Agency has not had the authority, specifically for medical waste, since then.

Singh, N., Tang, Y., & Ogunseitan, O. A. (2020). Environmentally sustainable management of used personal protective equipment. Environmental science & technology, 54(14), 8500-8502.

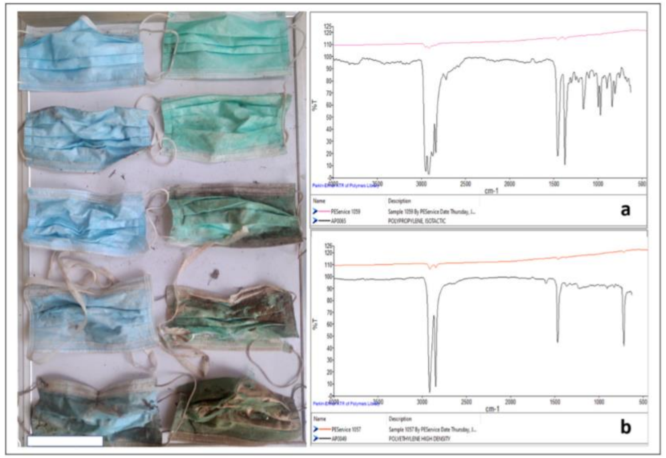
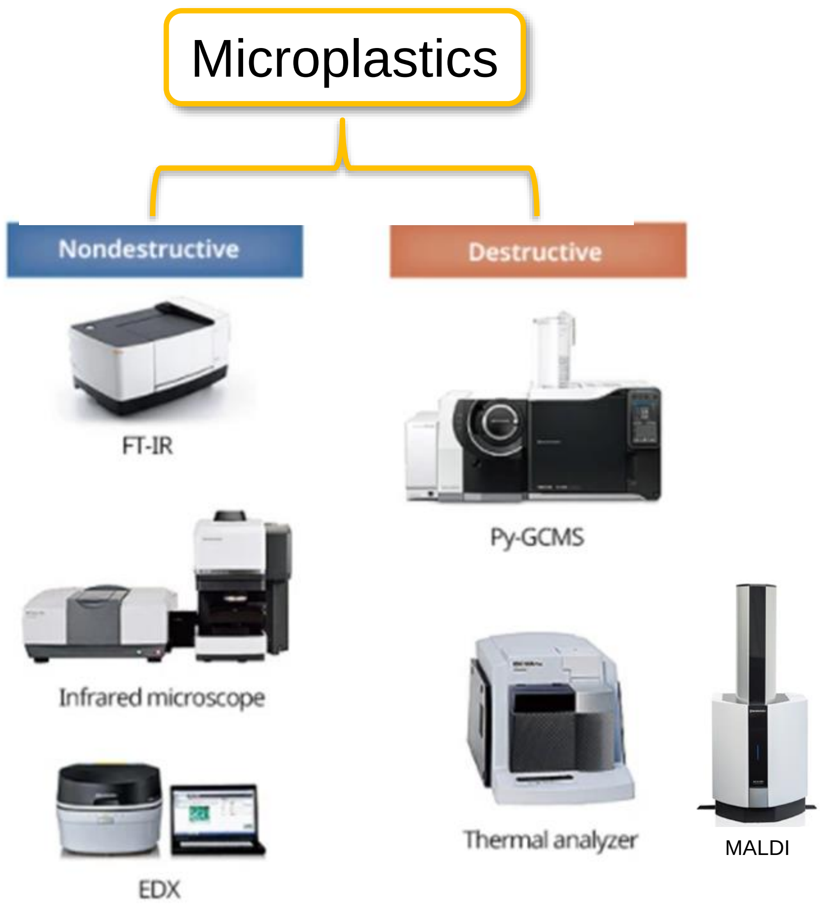
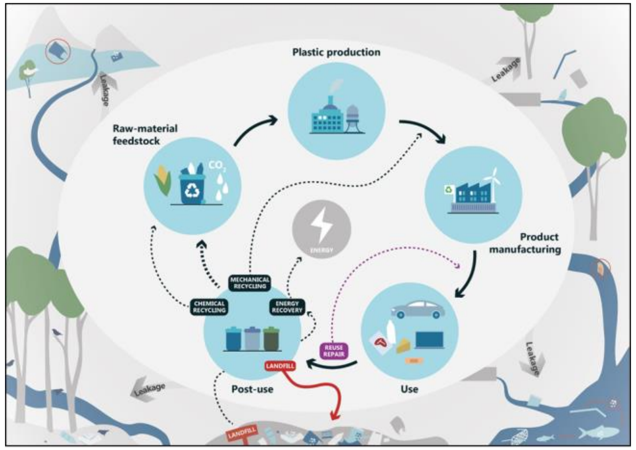


Fig. 3. Face masks at different stages of degradation in the environment and typical FT-IR spectra of the degrading fibers, outer layer (a) and inner layer (b). Photo Credit: Dr. Oluwatoyin Fadare.

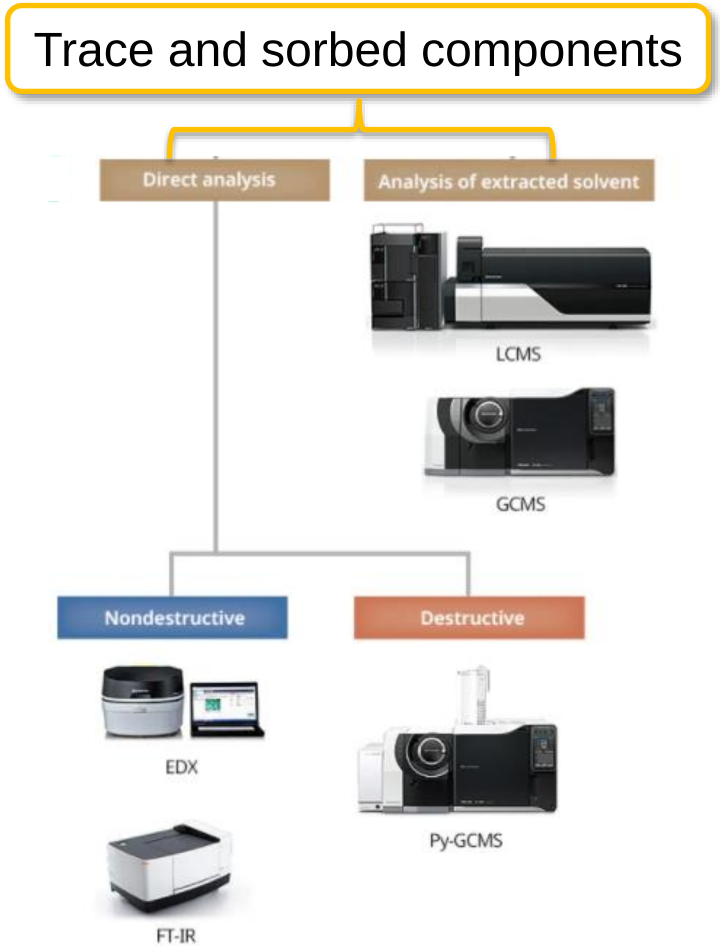
Fadare OO, Okoffo ED. Covid-19 face masks: A potential source of microplastic fibers in the environment. Sci Total Environ. 2020;737:140279. doi:10.1016/j.scitotenv.2020.140279

Comprehensive workflow



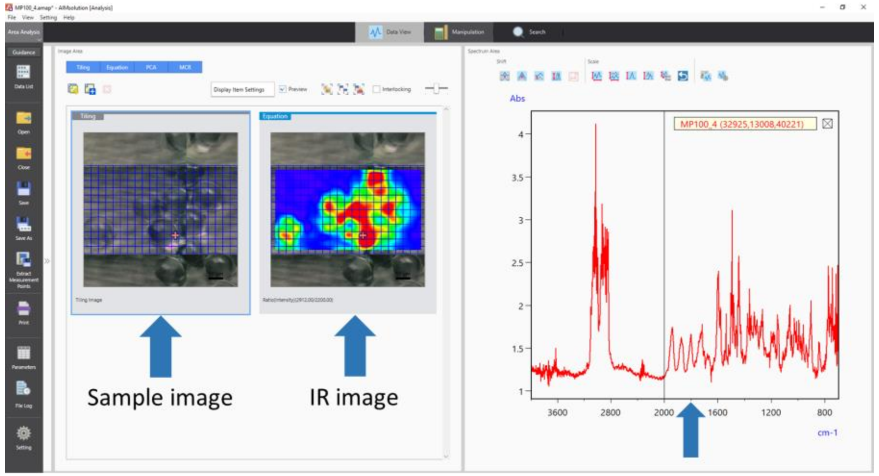


https://debrisfreeoceans.org/



Infrared microscopy: Concentration, size and composition

Infrared Microscope AIM-9000



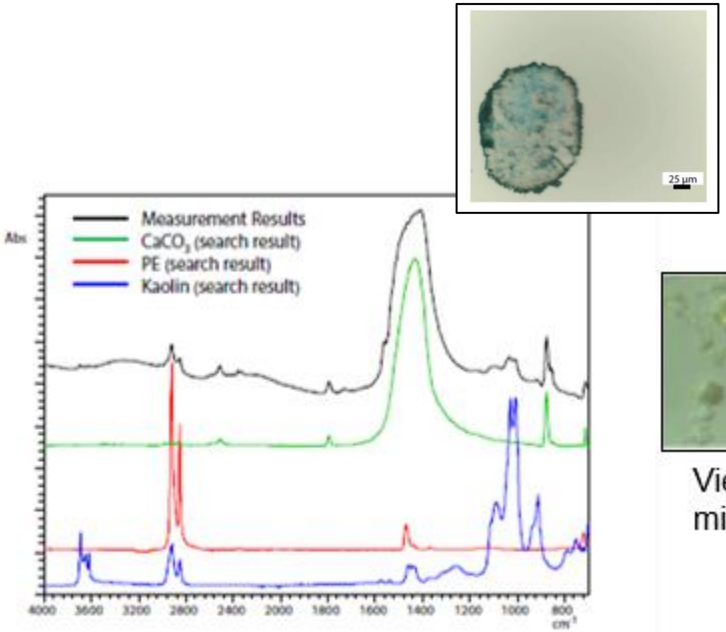
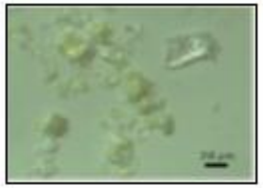
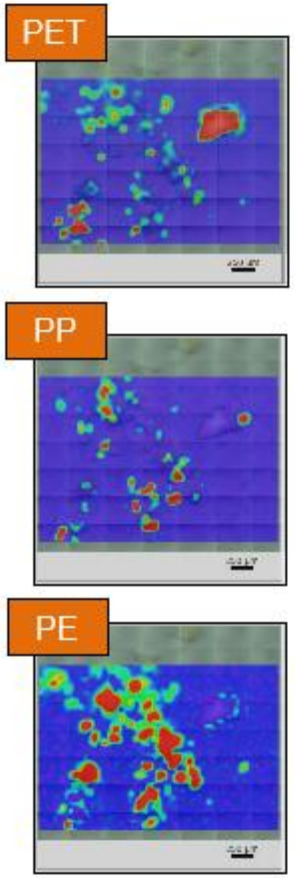


Fig. 6 Measurement Results for Microplastic Collected from Deepwater Shrimp



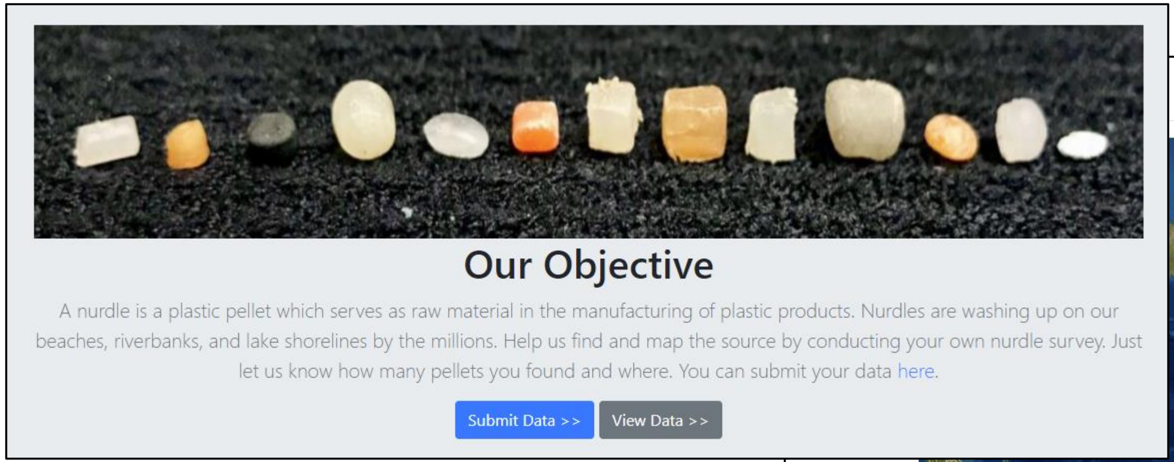
View under microscope

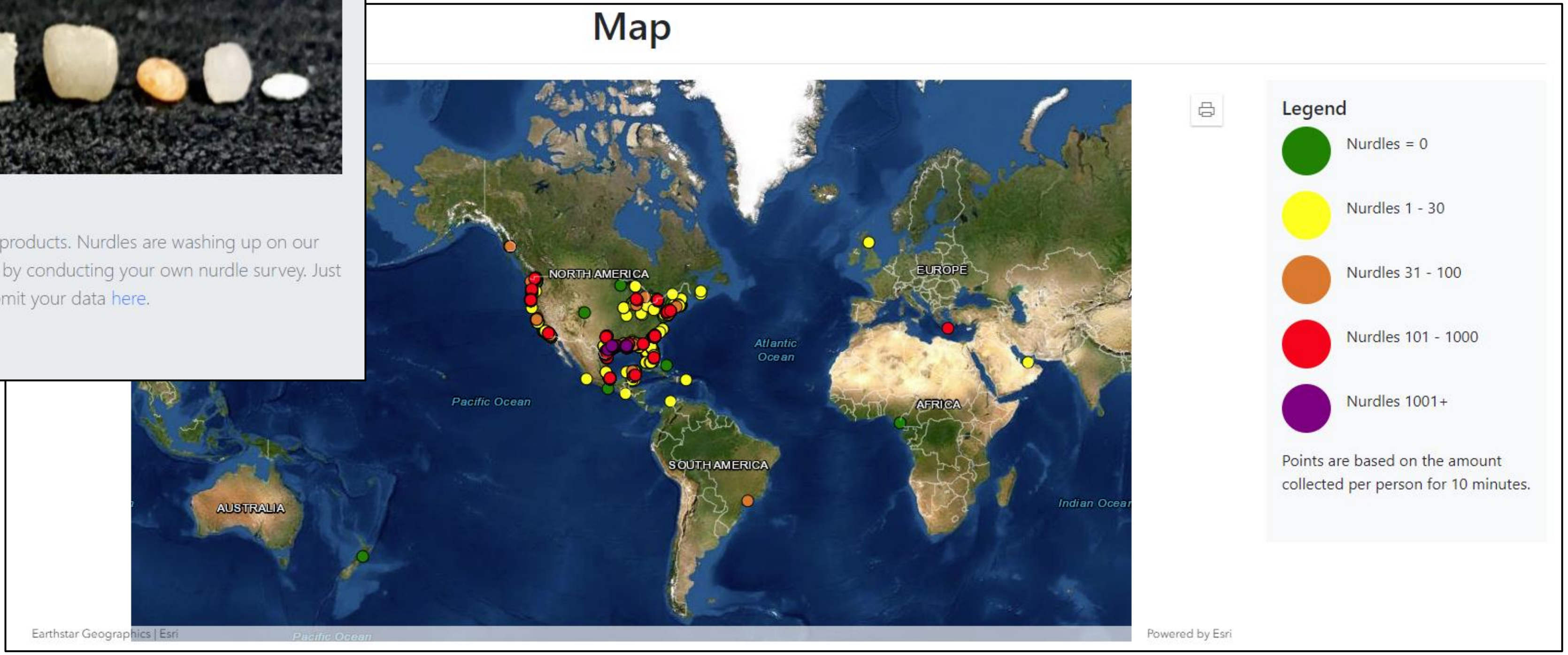


Chemically mapped images from Infrared microscope

Results from the field

Nurdlepatrol.org (University of Texas at Austin)





Xiangtao Jiang, Kaijun Lu, Jace W. Tunnell, Zhanfei Liu.
The impacts of weathering on concentration and bioaccessibility of organic pollutants associated with plastic pellets (nurdles) in coastal environments. Marine Pollution Bulletin, Volume 170, 2021.

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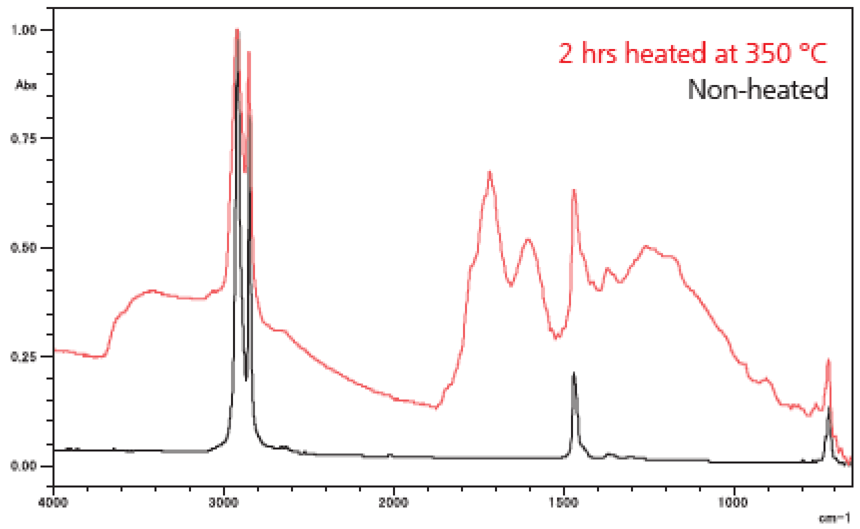
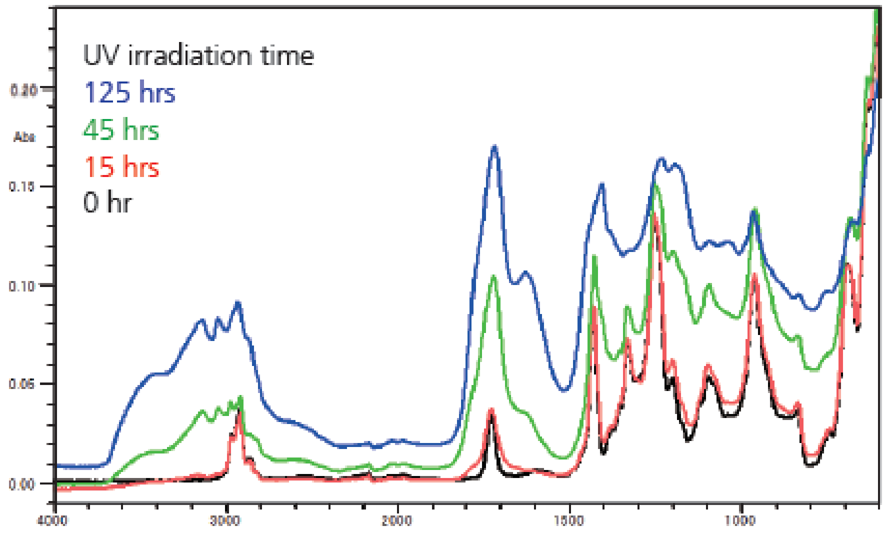
Weathered microplastics



Polyethylene Spectra Listed in the Thermal-damaged Plastics Library

Thermal weathering

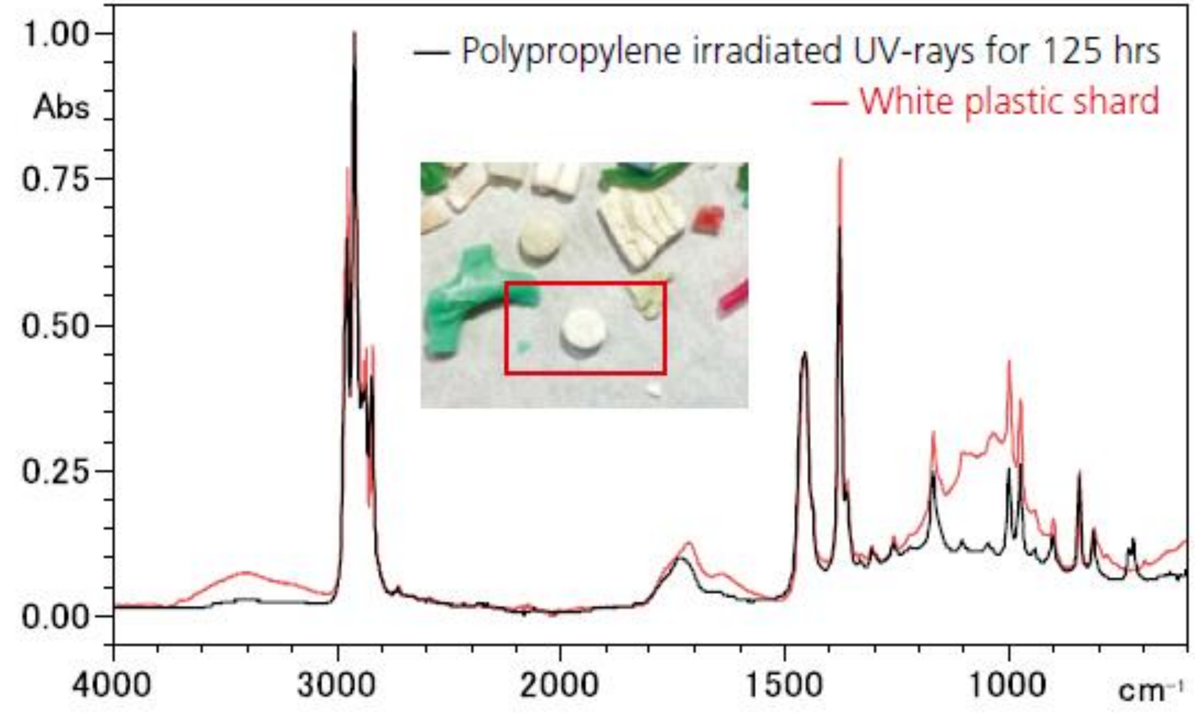


Hard PVC Spectra Listed in the UV-Damaged Plastics Library

UV weathering

Weathered microplastics

Fig. 2 Microplastics Collected at Sea Coast



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Results from the field

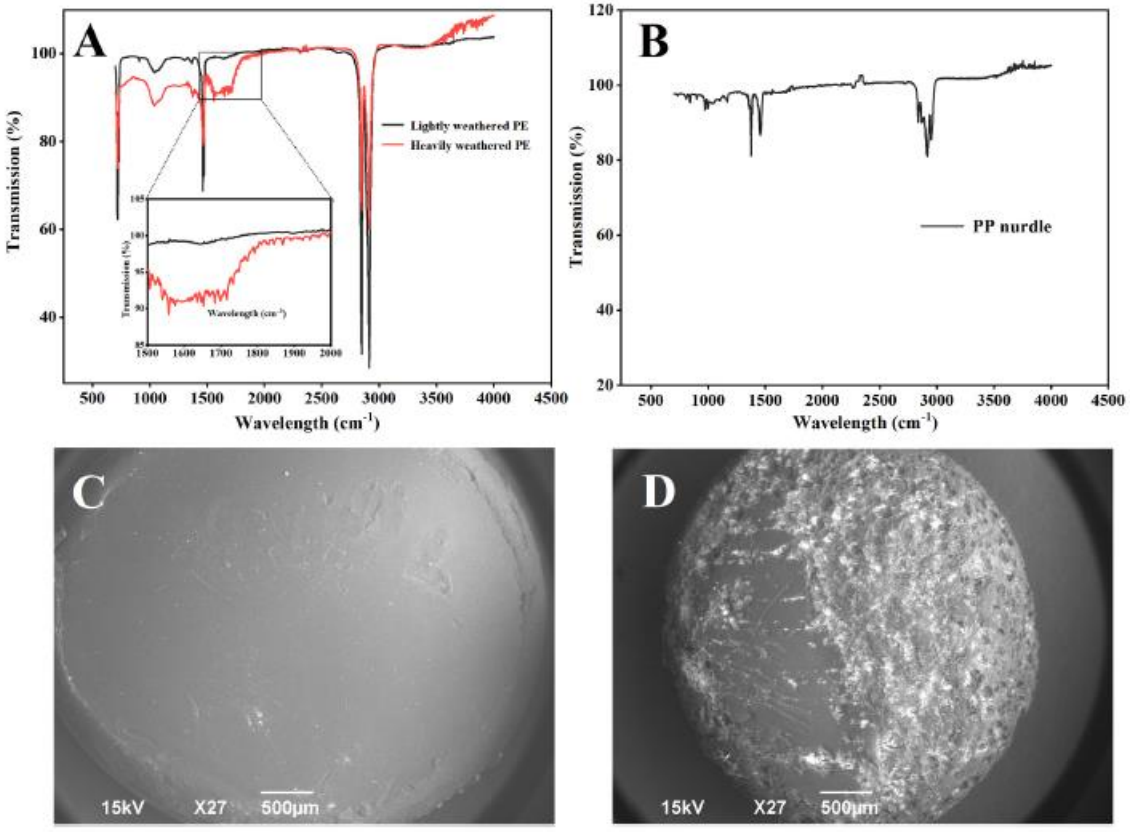

Fig. 2. FTIR spectra of PE-nurdles (A) and PP-nurdle (B) and SEM image of heavily weathered nurdle (C) and lightly weathered nurdle (D).

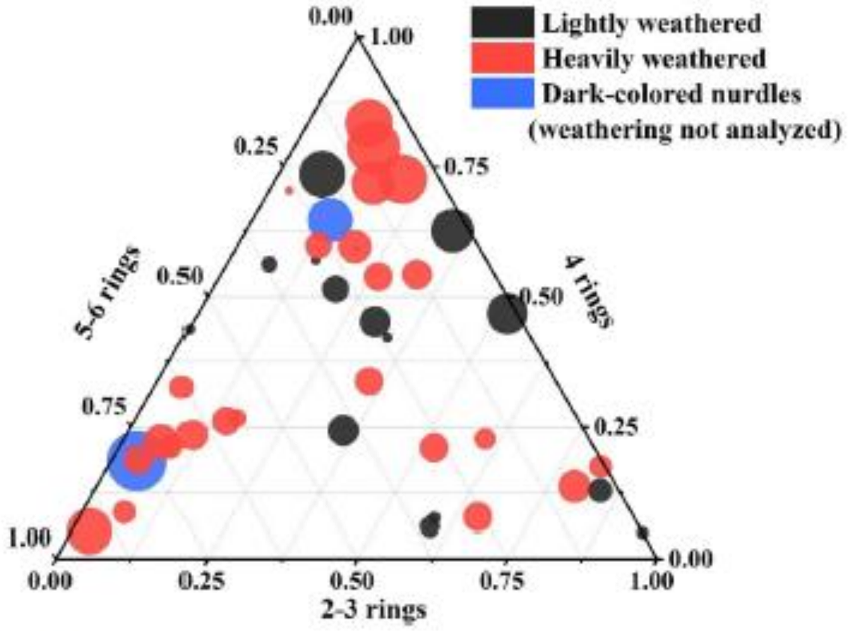

Fig. 4. Ternary plot of PAHs composition. Diameters of sample circles were normalized by the natural logarithm of total PAHs concentration at each site.

Xiangtao Jiang, Kaijun Lu, Jace W. Tunnell, Zhanfei Liu.
The impacts of weathering on concentration and bioaccessibility of organic pollutants associated with plastic pellets (nurdles) in coastal environments. Marine Pollution Bulletin, Volume 170, 2021.

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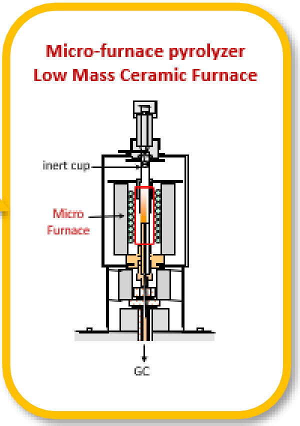
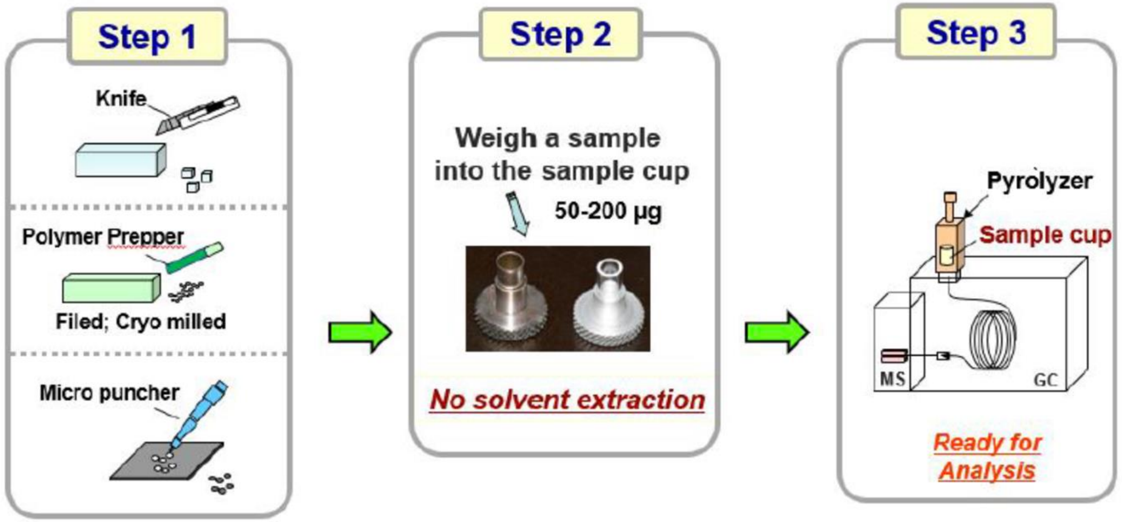
Pyrolysis – GC/MS: Concentration and composition

EGA/PY-3030D multi-shot pyrolyzer, AS-1020E auto-shot sampler (Frontier Laboratories Ltd.)

GCMS-QP™2020 NX





Pyrolysis, combined with GC/MS (or GC/MS/MS) can be used to identify breakdown temperatures and individual constituents of polymers, as well as compounds adsorbed on microplastics.

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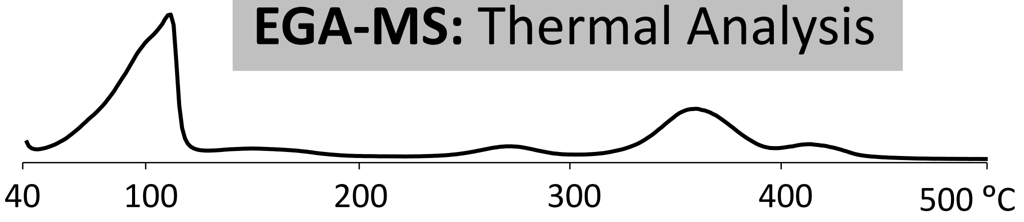
Pyrolysis – operation modes

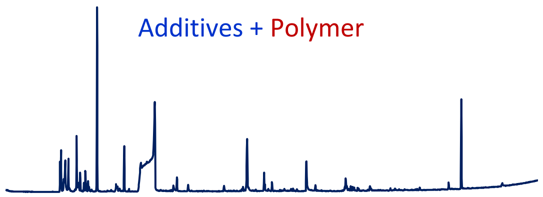
FRONTIER LAB

EGA-MS: Thermal Analysis

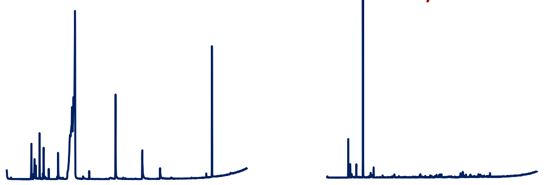


Separation Analyses

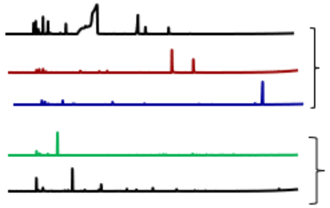
PY **Single-Shot GC/MS**
Flash Pyrolysis (Py)



DS **Double-Shot GC/MS**
TD Followed by Py



HC **Heart-Cut EGA-GC/MS**
Sequential Thermal Slicing of EGA



Identification of unknown peaks and samples:
Additives: F-Search (Additive Library), NIST Library
Polymers: F-Search (EGA, Polymer, Pyrolyzates Lib.)

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Results from the field

POLLUTION

Measuring microplastics in seafood

Analysis identifies the polymer types and concentrations found in seafood, including oysters, prawns, crabs, squid, and sardines

by **Lakshmi Supriya, special to C&EN**

AUGUST 7, 2020

ACS AUTHORCHOICE

Environmental Science & Technology

pubs.acs.org/est Article

Quantitative Analysis of Selected Plastics in High-Commercial-Value Australian Seafood by Pyrolysis Gas Chromatography Mass Spectrometry

Francisca Ribeiro,* Elvis D. Okoffo, Jake W. O'Brien, Sarah Fraissinet-Tachet, Stacey O'Brien, Michael Gallen, Saer Samanipour, Sarit Kaserzon, Jochen F. Mueller, Tamara Galloway, and Kevin V. Thomas

Cite This: *Environ. Sci. Technol.* 2020, 54, 9408–9417

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ELSEVIER

Identification and quantification of selected plastics in biosolids by pressurized liquid extraction combined with double-shot pyrolysis gas chromatography–mass spectrometry

Check for updates

Elvis D. Okoffo [a,*], Francisca Ribeiro [a,b], Jake W. O'Brien [a], Stacey O'Brien [a], Benjamin J. Tscharke [a], Michael Gallen [a], Saer Samanipour [c], Jochen F. Mueller [a], Kevin V. Thomas [a]

[a] Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, 20 Cornwall Street, Woolloongabba, QLD 4102, Australia
[b] College of Life and Environmental Sciences, University of Exeter, EX4 4QD Exeter, UK
[c] Norwegian Institute for Water Research (NIVA), 0349 Oslo, Norway

Results from the field


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Identification and quantification of selected plastics in biosolids by pressurized liquid extraction combined with double-shot pyrolysis gas chromatography–mass spectrometry

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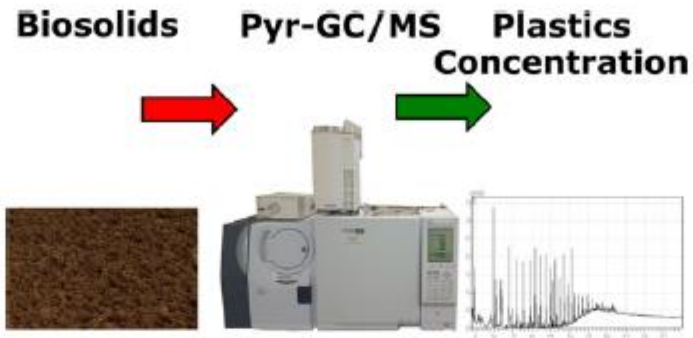
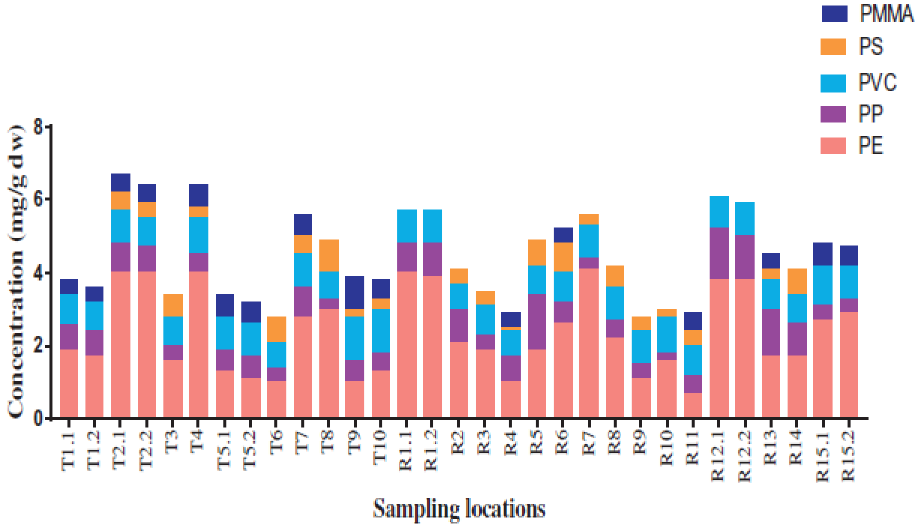
[a] Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, 20 Cornwall Street, Woolloongabba, QLD 4102, Australia
[b] College of Life and Environmental Sciences, University of Exeter, EX4 4QD Exeter, UK
[c] Norwegian Institute for Water Research (NIVA), 0349 Oslo, Norway

Table 3
Summary of method performance.

Plastic type	Recovery ($n = 5$)[a] (%)	RSD (%)	Recovery ($n = 5$)[b] (%)	RSD (%)	Indicator compound	Linear range (μg on column)[c]	LOQ (mg/g)[c]	Calibration function[c]	Linearity (r^2)[c]	Intraday[c] ($n = 5$) RSD (%)	Inter day[c] ($n = 5$) RSD (%)
PE	91 ± 8	8.4	83 ± 3	3.6	1-Decene	0.02–2	0.03	y = 49,370 x − 1242.1	0.939	12.0	6.1
PMMA	98 ± 3	3.4	91 ± 2	1.9	Methyl methacrylate	0.06–2	0.09	y = 20,000,000 x − 2,000,000	0.956	5.1	4.1
PS	98 ± 3	13.7	93 ± 3	2.9	5-Hexene-1,3,5-triyltribenzene (PS trimer)	0.01–2	0.01	y = 2,000,000 x − 30,212	0.995	4.6	3.6
PET	93 ± 9	9.4	85 ± 5	6.0	Vinyl benzoate	0.02–2	0.03	y = 152,301 x − 9309.1	0.961	7.0	4.4
PC	99 ± 8	8.3	95 ± 2	2.3	Bisphenol A	0.02–2	0.03	y = 59,126 x − 192,949	0.961	8.1	5.2
PP	94 ± 5	5.6	85 ± 4	4.5	2,4-Dimethyl-1-heptene	0.02–2	0.03	y = 26,265 x − 1241.8	0.997	9.8	3.1
PVC	87 ± 8	8.6	84 ± 3	3.1	Benzene	0.02–2	0.03	y = 17,360 x − 82,470	0.960	7.4	4.8

n = indicates number of analyzed samples. Polystyrene (PS), polycarbonate (PC), poly-(methyl methacrylate) (PMMA), polypropylene (PP), polyethylene terephthalate (PET), polyeth-





MALDI: composition

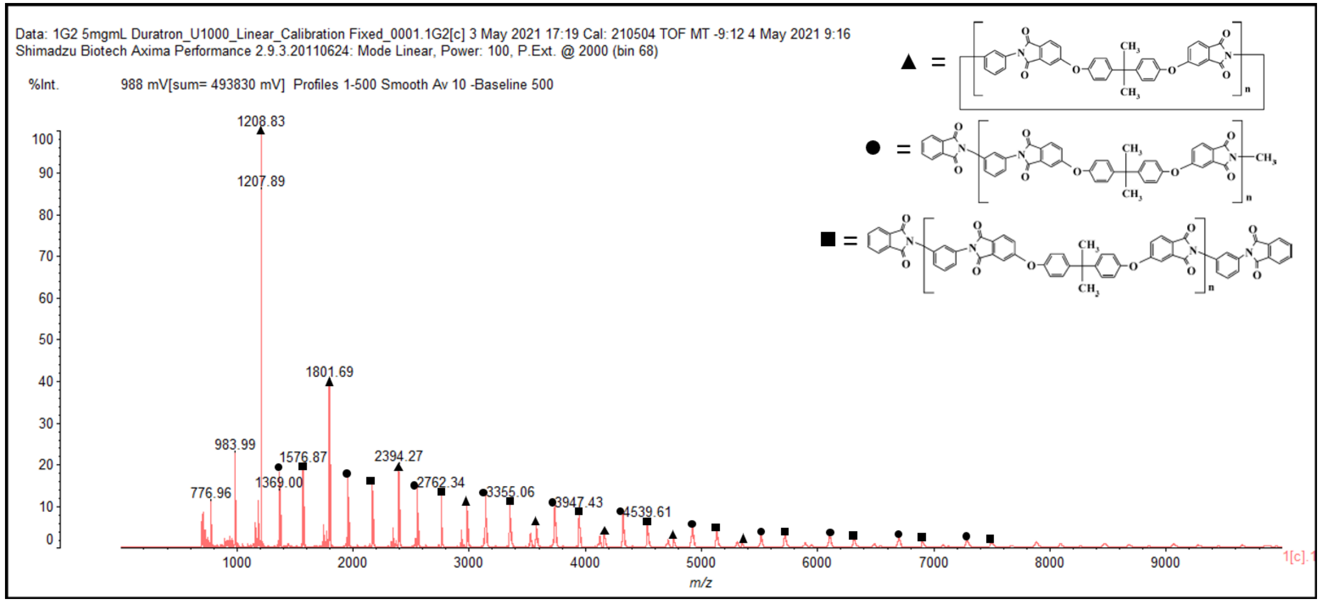
Assurance

Confidence

Performance

AXIMA Series

MALDI 8020



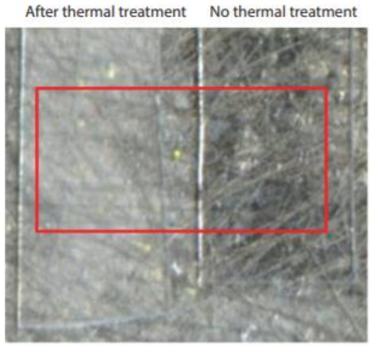


Fig. 2 Optical Microscopic Images of PET Film

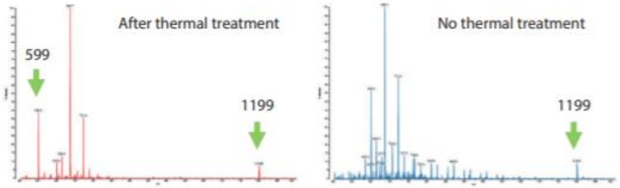


Fig. 3 Mass Spectrum of PET Film Surface

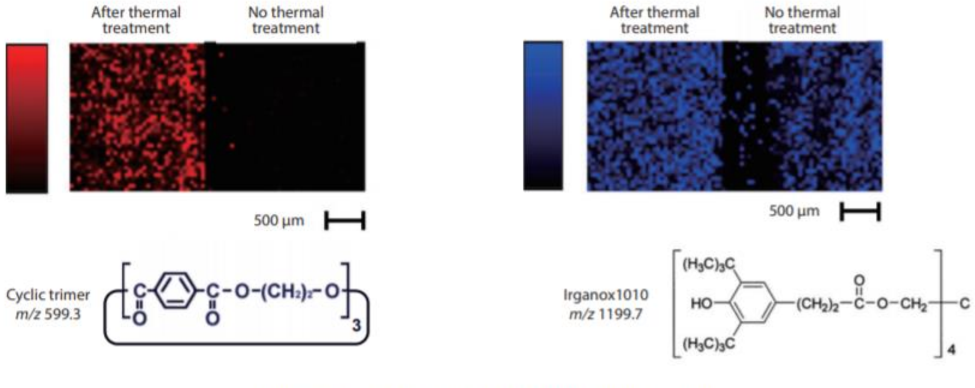
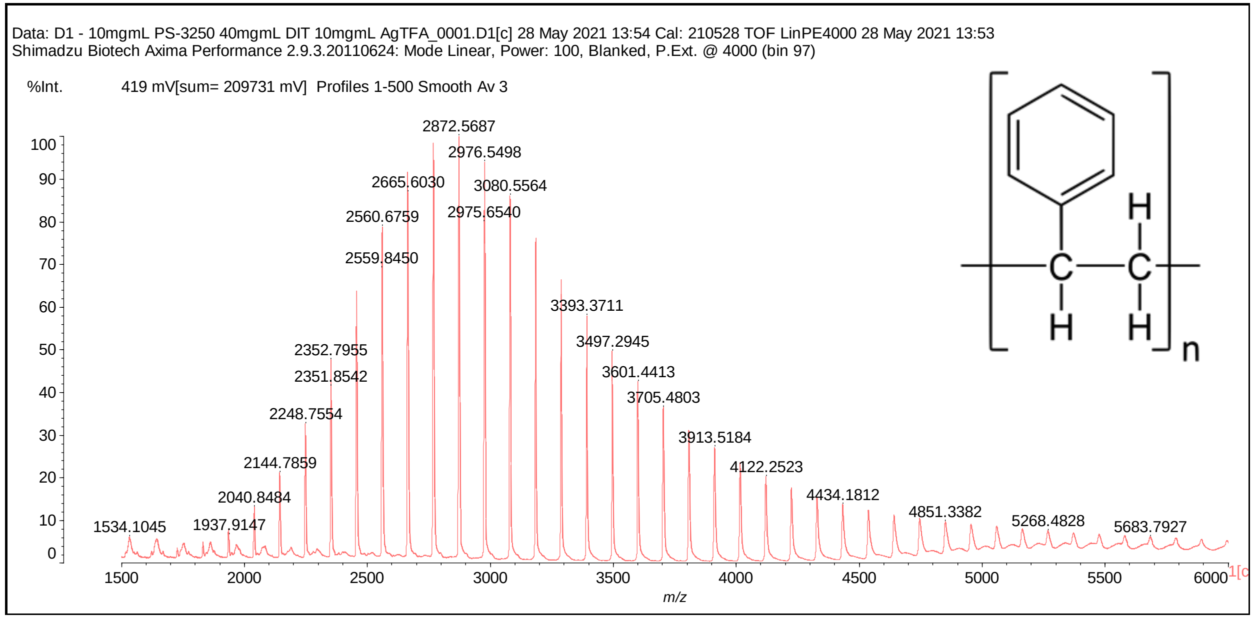


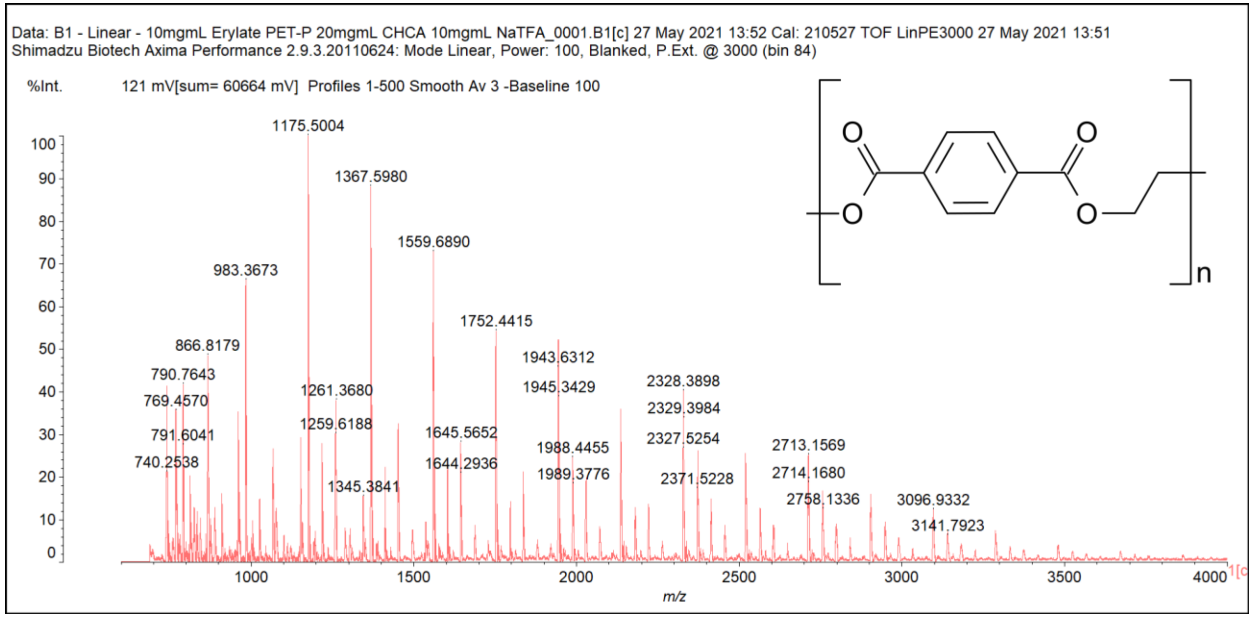
Fig. 4 Mapping Images of m/z 599 and 1199 (Fig. 2, in the red line)

Some results



- Repeating mass unit: 104
- Sample solution: PS in THF
  (M_n = 3250 Da)
- Matrix solution: 40 mg/mL dithranol and 10 mg/mL AgTFA in THF
- Matrix to sample ratio: 1/1 (v/v)
- 1µL matrix and sample mix deposited on plate

Some results



- Repeating mass unit: 192
- Sample solution: PET in TFA
- Matrix solution: 20 mg/mL CHCA and 10 mg/mL NaTFA in ACN/H_2O
- Matrix to sample ratio: 1/1 (v/v)
- 1µL matrix and sample mix deposited on plate

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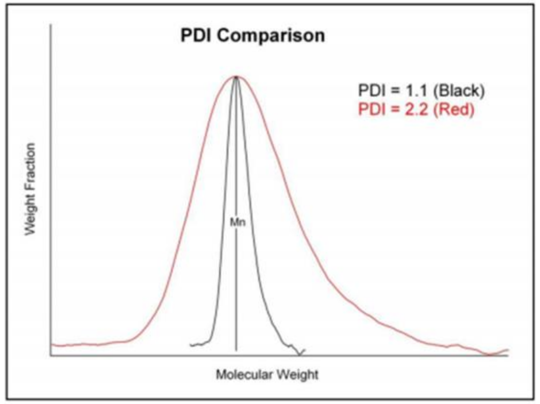
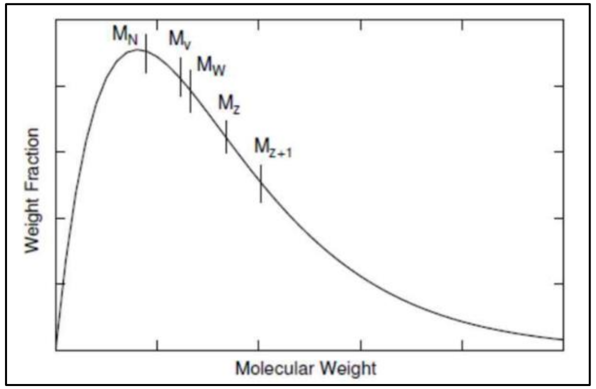
Results summary

Milaan Thirukumaran

Polymer	Sample solution	Matrix solution	Limit of Detection [mg/mL]
Polyetherimide (PEI)	Dichloromethane	Dichloromethane/ Tetrahydrofuran	0.005
Poly(methyl methacrylate) (PMMA)	Tetrahydrofuran	Tetrahydrofuran	0.01
Polystyrene (PS)	Tetrahydrofuran	Tetrahydrofuran	0.01
Polyethylene terephthalate (PET)	Trifluoroacetic acid	Acetonitrile/Water	0.1
Nylon 6	Formic acid	Dichloromethane/ Tetrahydrofuran	1

Advanced polymer characterization with Polymerix software





Conclusions

- ✓ Microplastics (and nanoplastics) are a byproduct from the life cycle of plastics.
- ✓ No individual analytical technique can fully characterize the occurrence of microplastics in environmental samples.
- ✓ Analysis is complex and there is limited method standardization, hence, occurrence and mitigation are not yet fully understood.

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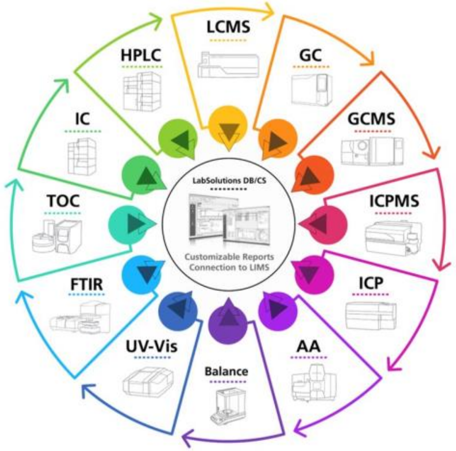

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