

# Microplastics: from Beach to Bench Characterization and Identification of Microplastics Using Mobile FTIR and FTIR Imaging Technologies

## Overview

Contamination in our waterways, soil, air, and food from microplastics (1  $\mu\text{m}$  to 5 mm in size) is gaining significant public interest due largely to its emergence as an environmental and potential human health threat.

Researchers across the world are now working towards standardized analytical solutions to best characterize these small particles in terms of chemical identity, size, shape, and total mass. Sample preparation, data measurement, and analysis protocols using mobile FTIR and FTIR imaging technologies are being developed. Rapid characterization and chemical identification of macroparticles (greater than 5 mm in size) can be measured at the point of collection using mobile FTIR, while microparticles down to approximately 10  $\mu\text{m}$  can be analyzed using laboratory-based FTIR imaging. Accurate, reliable measurements are necessary for addressing the microplastic pollution issue.

## Challenges in Quantifying Microplastics Pollution

Many consequences are associated with microplastic contamination of the environment. For example, small plastics can translocate to the tissues of organisms. In addition, microplastics may act as carriers for pollutants that are part of the plastics (e.g., plasticizers, flame retarders, metals, biocides, and vulcanization agents) or for external pollutants that have been adsorbed. Food contamination by microplastics has already been reported by several environmental research groups [1–3].

Until now, practical analytical techniques for very small particle analysis (<50  $\mu\text{m}$  and <10  $\mu\text{m}$ ) have not been available. This is a critical issue because it is these small particles that are most biologically and toxicologically relevant. The smaller the particle, the higher the risk.

Microplastics are now recognized as an emerging contaminant in the environment, yet sampling, extraction, purification, and identification approaches are not standardized. This makes it difficult, if not impossible, to compare the results of various microplastic studies. Thus, environmental scientists are working to develop generally accepted and consistent methods for quantifying microplastics.

Plastics are an extremely diverse group of materials with diverse chemical characteristics. There are many well known types of plastic such as those that are commonly recycled.

However, numerous other sources of plastic are just as common, but not as obvious. Rubber, for instance, comes in many forms and sources (e.g., road tyre wear), and paint formulations are based on polymeric binders such as resins, acrylate, silicone, alkyd, and epoxy. Copolymers and composites are also plentiful. Thus, the sources and types of microplastics are extremely varied.

Adding to the complexity of plastics pollution analysis is the variety of particle sizes and shapes. Macroplastic litter is easily visible to the naked eye, while microplastic litter ranges from 5 mm down to 1  $\mu\text{m}$ . It is assumed that nanoplastics also exist—those smaller than 1  $\mu\text{m}$  in size—however those have not yet been studied thoroughly. The shape of microplastic pollutants can vary as well, from spheres to fibers to odd-shaped fragments of larger plastics. Since spherical plastic beads from personal care products constitute only a small fraction of the total pollution, most microplastic pollution contains a variety of shapes and sizes that make them difficult to quantify.

Microplastics analyses are frequently reported only as the number of particles. However, this is a fundamentally flawed and inaccurate approach since plastics are brittle and they can easily break down into multiple smaller particles in the future. Thus, the sizes of particles should also be reported, and both the size and abundance should be considered for evaluating the toxicological impact of microplastics. It should be noted that the potential environmental and health impact of microplastics increases with decreasing size.

Size measurements typically report only the longest dimension of a particle and disregard the shape. As a result, long particles are considered to be the same as spherical or other shapes. For a more thorough understanding, plastic quantification should be thought of as a three-dimensional issue: Size x Shape x Material. In addition, the mass of microplastics would be beneficial to assess and compare sources as well as contamination levels.

Many challenges—plastic composition, size, shape, and matrix—must be addressed by environmental scientists who are working to standardize microplastic analyses. These factors are critical when determining the sampling approach, sample purification, microplastic extraction, analytical quantification method, and post-processing of the data.

## Analytical Methods

Figure 1 shows the typical size ranges covered by several analytical methods. Research groups around the world agree that FTIR-based techniques are the backbone of microplastic analyses. Small particles from 10  $\mu\text{m}$  to about 300  $\mu\text{m}$  are commonly analyzed using FTIR imaging, while ATR-FTIR is used for larger particles using mobile or more routine laboratory FTIR systems.

FTIR (Fourier Transform Infrared Spectroscopy) is a type of vibrational spectroscopy that relies on the absorbance, transmittance, or reflectance of infrared (IR) light interacting with a sample. As the chemical structure is unique for a given molecule, so too are the set of chemical bond vibrations of that molecule, which are then expressed as a unique FTIR spectrum. The result is a “fingerprint” of the materials being analyzed. This allows for the identification of a wide range of substances, both organic and inorganic.

As with any analytical technique, proper sample preparation is vital to the success of the measurement. Microplastic pollutants must be isolated from their matrix before they can be analyzed. Sampling and isolation techniques are dependent upon the matrix, such as air, water, soil, or food. Preparation protocols are based largely on the complexity of the matrix, the size of the particles, and which instrument will be used for the analysis. Figures 2 and 3 show the recommended steps for isolating and preparing samples of microplastic in wastewater and soil, respectively. The time it takes to collect, prepare, analyze, and interpret the data for these types of samples is typically 50 hours per sample. In contrast, microplastic preparation from simpler and cleaner matrices such as water (drinking water or samples from open waterways, such as seawater and freshwater) can be accomplished in about eight hours, due to the relative cleanliness of the samples, typically requiring only filtration. Microplastics in indoor air may simply be collected on filters. Care should be taken to avoid contamination of samples, and appropriate blanks that have undergone exactly the same treatment as the samples should be included in the workflow.

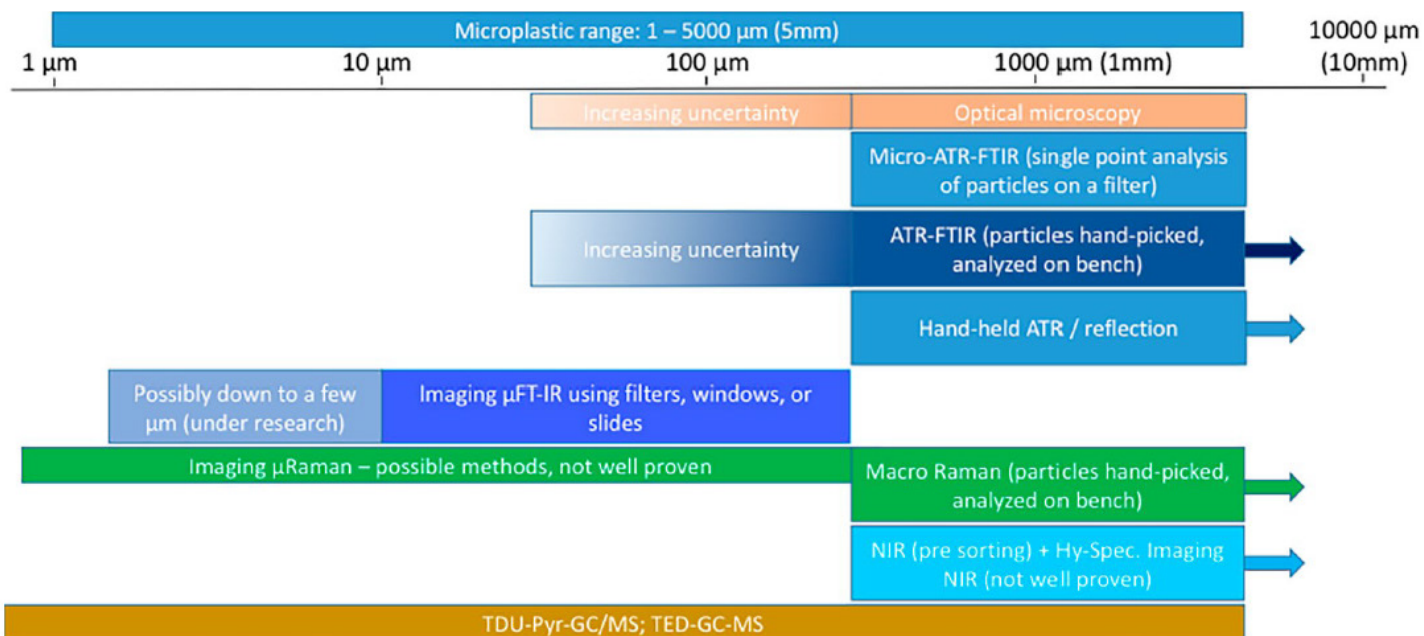


Figure 1. Size ranges versus analytical methods.

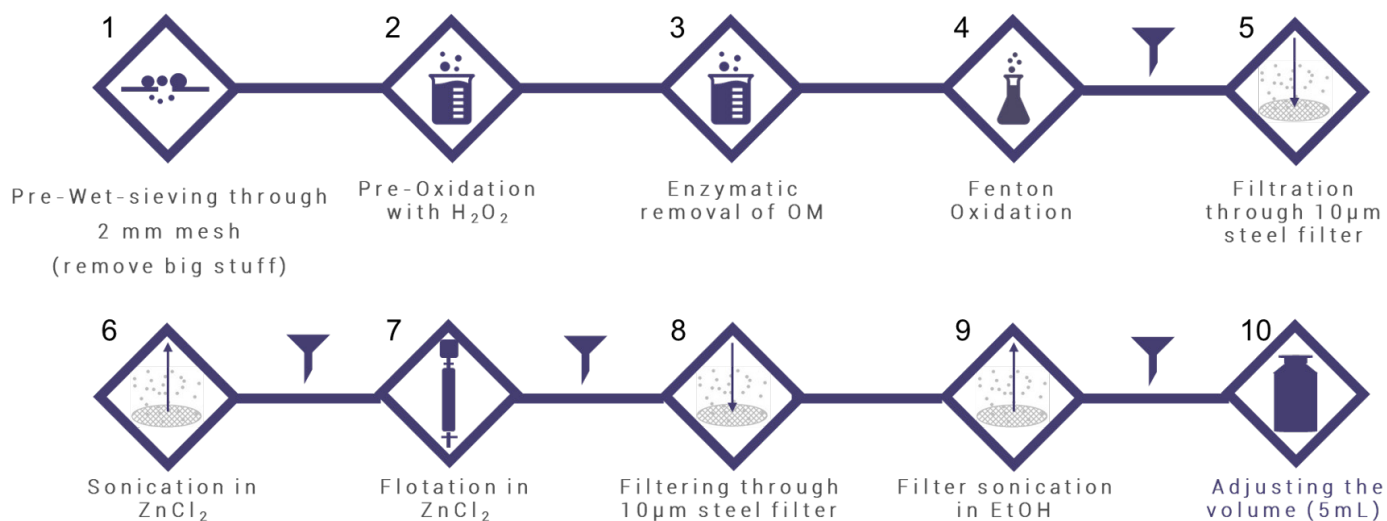
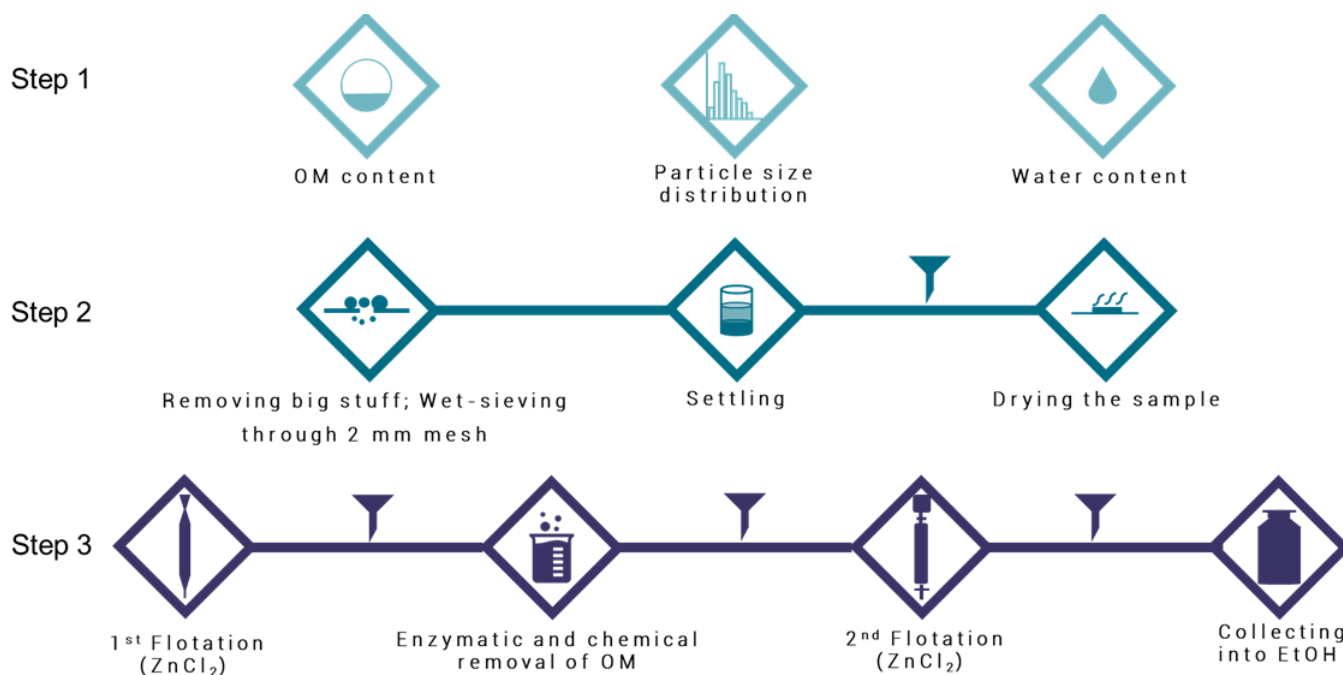


Figure 2. Processing 2 L of raw wastewater.



**Figure 3.** Processing 1 kg of soil or sediments.

After pretreatment, workflows for large particles (>300  $\mu\text{m}$ ) include sieving through 500- $\mu\text{m}$  mesh, cleaning with peroxide, visual inspection, and placing samples directly onto the attenuated total reflectance (ATR) sampling crystal of an FTIR spectrometer. Signal strength is typically good and the measurement rapid. The Agilent Cary 630 FTIR Spectrometer works well for this application. Its semi-portability makes it an excellent choice for studying urban plastic waste to understand littering behavior. Agilent offers two other, more portable, options for field use. The Agilent 4500 Series Portable ATR is about the size of a small toolbox, and the Agilent 4300 ATR is handheld. Both are recommended for in-situ sample triage and for particles that are easily visible to the naked eye.

For smaller microplastics (down to 10  $\mu\text{m}$ ), the preferred instrument is the Agilent Cary 670/620 FTIR micro imaging system. The instrument is equipped with a 14-megapixel visible image and a state-of-the-art 128x128 Focal Plane Array (FPA) infrared detector, which simultaneously generates 16,384 spatially resolved spectra (at each pixel) per measurement. Using three different objectives, the Agilent Cary 620/670 can achieve pixel resolution from 3.3 to 19  $\mu\text{m}$ , with software-controlled zoom optics can generate pixels as small as 0.66  $\mu\text{m}$ . Furthermore, its new Large-Area

ATR (LAATR) allows scanning of a mm areas with  $\sim 1\text{--}2$   $\mu\text{m}$  resolution. It also boasts comparatively rapid scanning speeds. For example, a 10x10 mm window at 5.5  $\mu\text{m}$  pixel resolution is scanned in four hours, creating 3.7 million spectra. For high-throughput labs, there is the potential for further reducing the time per scan by parameter optimization. The samples, once having completed the pretreatment steps, are collected in vials and then transferred to IR compatible slides or windows deposited onto a slide, window, or filter.

## Managing Large Datasets from Microplastic Analysis

Since FPAs collect thousands of IR spectra at a time, there is a need to manage the large datasets that are created when analyzing microplastics by  $\mu\text{FTIR}$  Imaging. A team of scientists from Jes Vollertsen's group at the Aalborg University have created a free software program called "MPhunter" that manages large microplastic datasets from  $\mu\text{FTIR}$  Imaging. It can correlate millions of IR spectra to reference spectra. In particular, the group has found that performing first and second derivatives on the spectra greatly minimizes sample shape and size related spectral scatter effects, leading to improved correlation to the references

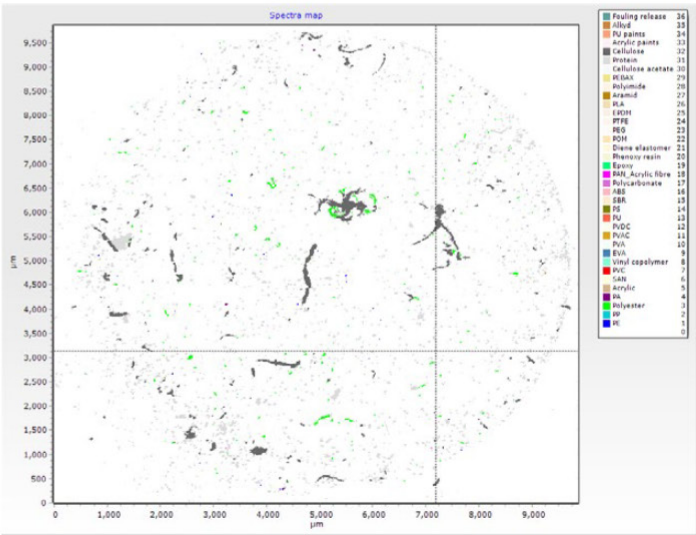
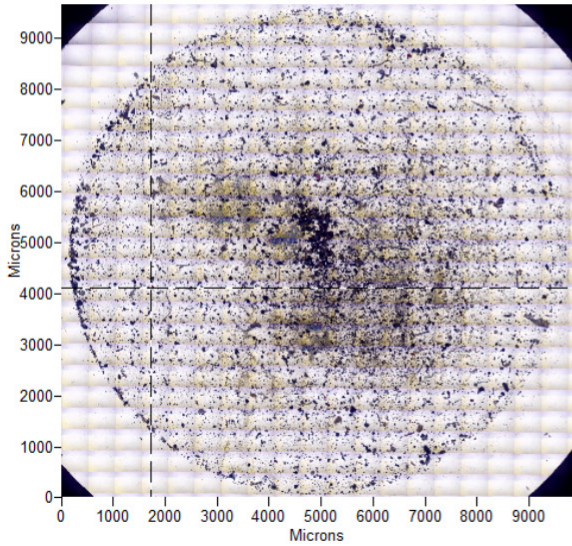


Figure 4. Data management and processing - MPHunter software.

spectra. The example in Figure 4 shows a visual image of microplastics on an infrared compatible window and a corresponding IR image. The algorithm allowed the IR image to show color-coded particles indicating the type of plastic of each particle. A demonstration of its utility identifies microplastics from the soil of a marina where small private boats have been renovated for many years. Some of the study results are presented in tabulated format in Figure 5, displaying microplastic identification, size, volume, and mass. Figure 6 indicates that the majority of microplastics in the soil analyzed in the study are related to marine paints. The software also facilitates searching for particular types of plastics in a sample. The software shortened the time spent on data interpretation from two to four weeks down to just a few hours.

MP identifier	Coordinates [pixels]	Coordinates [μm]	Polymer group	Area on map [μm <sup>2</sup> ]	Major dimension [μm]	Minor dimension [μm]	Volume [μm <sup>3</sup> ]	Mass [ng]
MP_1	[125;293]	[688;1612]	PE	424	38.5	14.0	2373	2.254
MP_2	[175;220]	[963;1210]	PE	908	49.1	23.5	8534	8.107
MP_3	[191;173]	[1051;952]	PE	4870	123.1	50.4	98157	93.249
MP_4	[284;343]	[1562;1887]	PE	2087	75.7	35.1	29303	27.838
MP_5	[303;347]	[1667;1909]	PE	4659	106.2	55.8	104058	98.855
MP_6	[172;348]	[946;1914]	PE	121	22.0	7.0	339	0.315
MP_7	[107;61]	[589;336]	PP	1785	64.9	35.0	23010	23.760
MP_8	[144;449]	[792;2470]	PP	787	35.1	28.5	8971	8.522
MP_9	[221;408]	[1216;2244]	PP	998	44.8	28.4	11335	10.768
MP_10	[222;382]	[1221;2101]	PP	363	25.3	18.2	2649	2.517
MP_11	[256;307]	[1408;1689]	PP	1603	56.2	36.3	23290	22.126
MP_12	[271;286]	[1491;1573]	PP	726	49.8	18.5	5386	5.116
MP_13	[339;240]	[1865;1320]	PP	5990	193.1	39.5	94613	89.883
MP_14	[397;111]	[2184;611]	PP	1694	72.2	29.9	20247	19.135
MP_15	[332;165]	[1826;908]	Polyester	2299	76.0	38.5	35403	48.855
MP_16	[71;38]	[391;209]	Polyester	3539	88.8	50.7	71803	98.370
MP_17	[221;195]	[1216;1073]	Polyester	2753	76.6	45.8	50400	69.048
MP_18	[296;232]	[1628;1276]	Polyester	121	17.8	8.7	419	0.574
MP_19	[335;251]	[1843;1381]	Polyester	1694	60.2	35.8	24268	33.247
MP_20	[138;62]	[759;341]	Polyester	303	22.9	16.8	2036	2.789
MP_21	[398;296]	[2189;1628]	Polyester	182	22.9	10.1	733	0.923
MP_22	[273;381]	[1502;2096]	PVC	1089	55.2	25.1	10951	14.784

Figure 5. Listing microplastic particles, their size and mass.

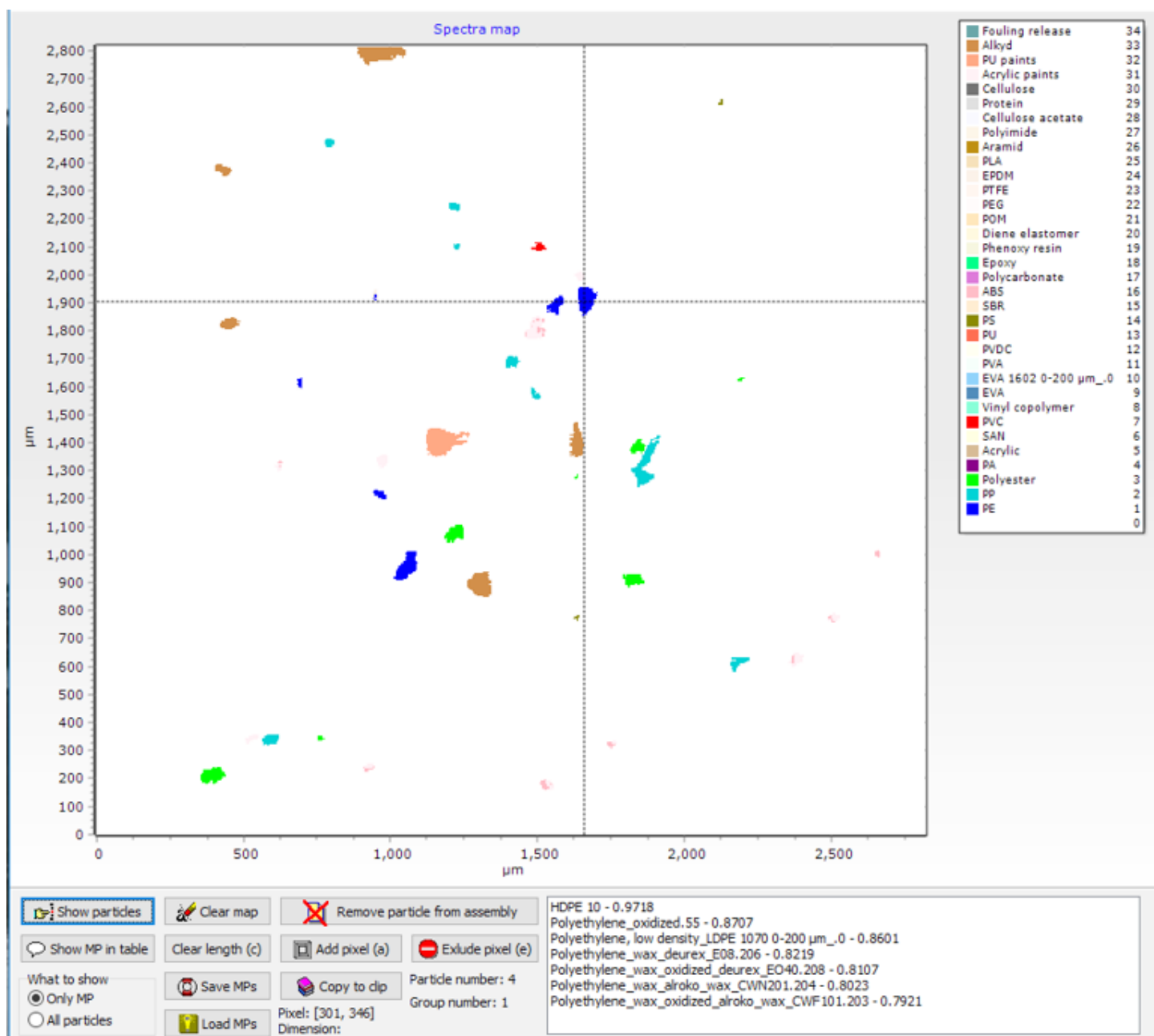


Figure 6. Detection using all spectra in the database. The correlations are ranked in the lower right hand side.

## Future Development

Although progress has been made, many more advances are required to achieve fast, reproducible microplastic quantification. With improvements in algorithms for interpreting data and in instrumentation, such as FPA-based FTIR imaging systems, data analysis has been accelerated and sample preparation has become the bottleneck in microplastic analysis, in particular for samples with a complex matrix (e.g., wastewater and soil). Faster

sample preparation is needed, with better recovery and less contamination. Better reference databases on both natural and plastic materials, as well as validation of mass estimates are essential. As smaller particles are more biologically and toxicologically relevant, the capability for quantifying particles smaller than 10  $\mu\text{m}$  has become a necessity. Additionally, researchers must continue to improve upon a fully automated, validated microplastic detection pipeline for data handling.

## Conclusion

As plastics continue to enter the environment, understanding their global impact is vital to addressing microplastic pollution. Since its emergence as an environmental and potential human health threat, researchers have strived to develop tools for accurately measuring microplastics in environmental and food matrices using FTIR-based techniques and automated data handling. Continued efforts aspire to a standardized analytical solution while the microplastics pollution issue gains global traction.

Note: This work was originally published in the May 2018 edition of Spectroscopy Magazine.

## References

1. L.V. Cauwenbergh et al., *Environ. Pollution*, **2014**, 193, 65-70,
2. A. Karamani et al., *Sci. Total Environ.* **2018**, 612, 1380-1386
3. G. Liebezeit et al., *Food Addit. Contamin.* **2014**, Part A, 31(9), 1574-1578

## More Information

Refer to the Agilent application note, "[Analysis of Microplastics using FTIR maging – Identifying and Quantifying Microplastics in Wastewater, Sediments and Fauna.](#)"



To hear Jes Vollersten speak about the work he and his team are doing to Analyze Microplastics and the impact on the Urban Environment Safety in the Lab, watch this [video](#).

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