SRA INSTRUMENTS
ANALYTICAL SOLUTIONS

Microplastics Analysis- Analysis by shape (LDIR) and by mass (Py-GC/MS)

Introduction - Measurement Challenge

Many analytical laboratories and scientists around the world are seeking new technologies and developments that can analyze microplastics (MPs) qualitatively and quantitatively.
For properly evaluate these particles, their evaluation must include two aspects: **morphology characterization and mass quantification**.
Since MPs pollution is strongly related to particle diffusion, a morphology study of particle sizes represent a key information.
Besides morphology, quantifying the polymer mass is important too since let to assess the amount related to liter of water, kg of sediment or biota.
Agilent LDIR 8700 (laser direct infrared) represent a new leading tecnique based on quantum cascade lasers able to perform an automatic morphology analysis, including polymer identification, in about one hour.
FrontierLab Pyrolizer mounted on Agilent GC/MS let to close the loop performing quadrupole mass detection with excellent LOD for MPs and additives.

Shape
LDIR spectroscopy

- Particle size
- Morphological distribution
- Shape (fibers, spherical, cylindrical, ...)
- UOM: n° of particles/kg or L of sample.

Mass
Pyrolisis-GC/MS

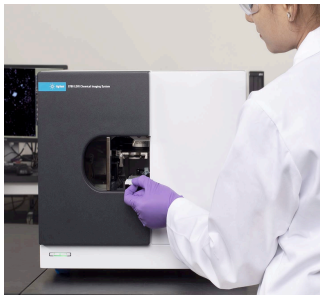
- "How much mass of microplastics do I have"
- Quantitative analysis (MP and additives, internal or external std)
- UOM: ug/kg or L of sample.

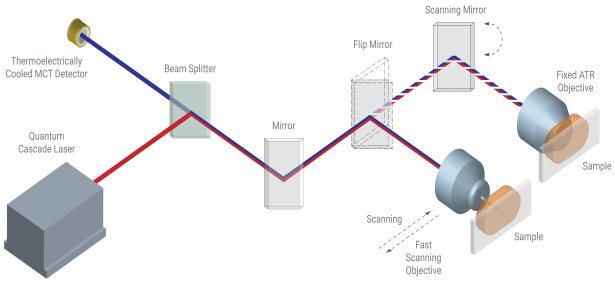
Analytical technique	Shape info	Chemical ID	MP_{Num}	MP_{Mass}
Optocal microscopy; Fluorescence microscopy	🟢 🟢	🔴 🔴	🟢 🟢	🔴 🔴
ATR-FTIR uFT-IR-Imaging	N/A 🟢	🟢 🟢	N/A 🟢	🟢* 🟡
LDIR	🟢	🟢	🟢	🔴
uRaman	🟢	🟢	🟢	🔴
Py-GC/MS TED-GC/MS	🔴 🔴	🟢 🟢	🔴 🔴	🟢 🟢

* Using a balance to weight particles

Agilent 8700 Laser Direct Infrared (LDIR)

Agilent's innovative design uses quantum cascade laser (QCL) light, high spatial imaging, and intuitive Agilent Clarity software to create detailed chemical images so the LDIR is NOT an FTIR.

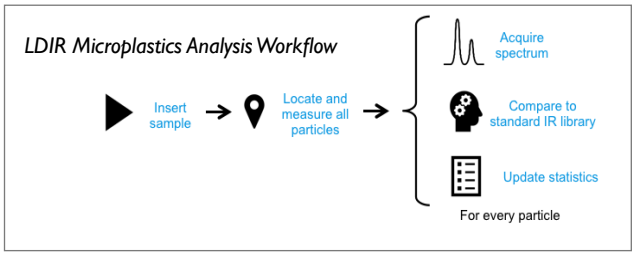




The laser wavelength is selected using a monochromator. Unlike other QCL imaging systems that use 2D focal plane array (FPA) detectors, the 8700 LDIR employs a single-element electrically cooled detector to eliminate laser coherence artifacts from images and spectra. This produces the sharpest images and most reliable spectral data.

Modes of Analysis

The 8700 LDIR works in either reflectance or attenuated total reflectance (ATR) mode, automatically switching between these two modes by directing the incident beam to the appropriate objective. The movement of the sample relative to the beam is fully automated, this process yields a high-quality two-dimensional molecular image in a remarkably short time period. The 8700 LDIR has two visible channels: a large field of view camera to obtain an entire view of the sample and a microscope grade objective to capture high magnification detail.



Fast, Automated Microplastics Analysis Using Laser Direct Chemical Imaging

Purified samples (< 300 µm) were suspended in ethanol (50%) and deposited on infrared reflective glass slides; then analyzed in transflection by Agilent automated LDIR (QCL) Imaging within the Agilent Clarity software.

Sensitivity was set to the maximum and the spectral resolution to 8 cm-1. Particles in the size range 20 - 5000 µm were analyzed, but can be extended down to approximately 10 µm.

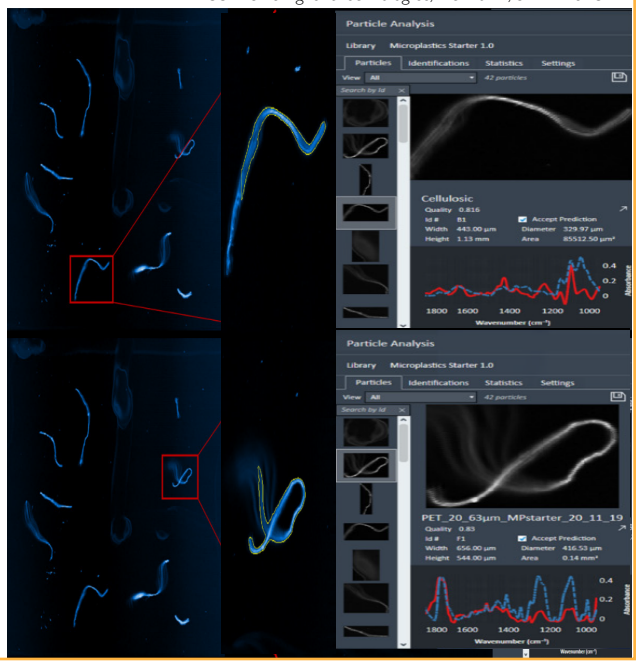
The automated workflow within the Agilent Clarity software acquires IR spectra from each particle and, in real-time, conducts the spectral database comparison (> 420 reference spectra) and data processing. The statistics as well as the thresholds for a positive assignment were adapted according to the analysis.

After running the automated workflow, the results were manually checked in transflection mode and partially by means of the LDIR's µ-ATR function.

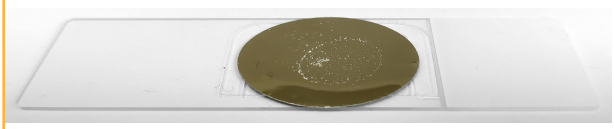
Potential microplastics particles and fibers with d >300 µm were analyzed by ATR-FTIR spectroscopy (on a diamond or germanium crystal) and also by the LDIR using both transflection mode and its µ-ATR unit. The ATR-FTIR spectra were compared to the siMPle database.

The results of the automated workflow were thoroughly rechecked by visual inspection, at least 5 manual transflection IR measurements, and partially by µ-ATR IR analysis. For the fraction >300 µm, good agreement was achieved between LDIR imaging, using a well-established microplastics spectral database, and conventional ATR-FTIR analysis. Extension of the database with typical matrix spectra helped to further increase the accuracy of the workflow. Due to its time-efficiency and high degree of automation, the technique has a great potential to become the micro-spectroscopic method of choice, e.g. during large scale microplastics studies or for monitoring activities, which require fast data provision.

DE.73311518 Agilent Technologies, Inc. 2022, 5994-4873EN



Rapid, Large-Area, **On-Filter** Analysis of Microplastics from Plastic Bottles Using Laser Direct Infrared Imaging



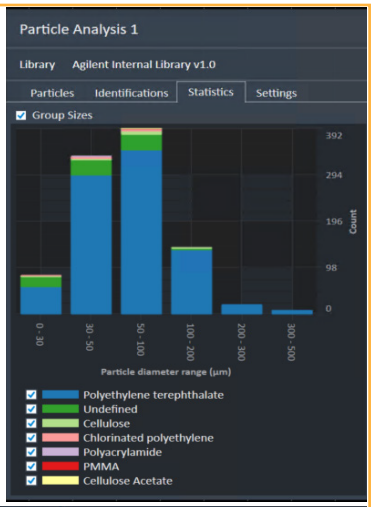
In this study, microplastics derived from polyethylene terephthalate (PET) bottles were analyzed on gold-coated membrane filters using the Agilent 8700 laser direct infrared (LDIR) chemical imaging system. The direct on-filter analysis of particles by the 8700 LDIR is suitable for the routine testing of microplastics in environmental samples. Using a simple experimental design, the LDIR method provided high identification accuracy, significant time savings compared to other techniques, and easy implementation by nonexpert operators.

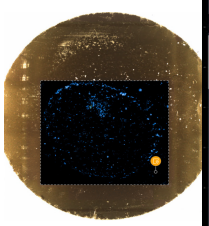
On-filter analysis of particles

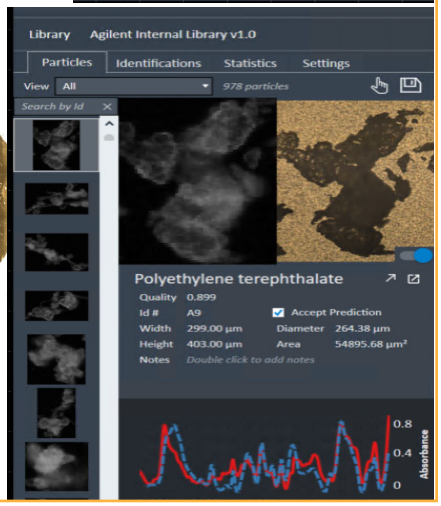
The automated Particle Analysis workflow in the Clarity software was used to analyze the filter samples using the 8700 LDIR. Once the preloaded microplastics analysis method has been selected, the Particle Analysis workflow automatically identifies all particles within a user-defined area of the sample, draws boundaries around each particle, photographs, and identifies each one. The software performs a library search to confirm each particle's identity based on its IR spectrum.

The highly IR-reflective coating of the gold-coated polycarbonate filters provided excellent spectral response and contrast, as well as sharp IR and visible images of particles.

Although attention is required at some points during sample prep, the benefits of direct on-filter analysis outweigh the laborious, multistep process of transferring particles from filter to slide. The direct method significantly reduces the potential contamination as it requires less sample handling and fewer preparation steps.







DE.60839 12037 Agilent Technologies, Inc. 2020, 5994-2421EN

FRONTIERLAB PY-GC/MS SOLUTION for analyzing microplastics:

Pyrolysis (Py)-GC/MS enables direct analysis of solids and liquids to determine the formulation and chemical structures of the samples. This technique can be applied to samples that are insoluble due to the large molecule and/or cross-linked structure. This technique **requires minimal sample preparation and only a small amount of sample for analysis.** It even generates unique information about each polymer, therefore, Py-GC/MS is a critical technique for plastics analysis.

Frontierlab has developed a **Micro-Furnace Py-GC/MS system** optimized for the analysis of microplastics in environmental samples.

System configuration:

Multi-Shot Pyrolyzer (EGA/PY-3030D)

A vertical micro-furnace pyrolyzer based on a ceramic heater. Sample heated in the furnace forms gaseous pyrolyzates which are directly introduced into the GC.

Auto-Shot Sampler (AS-1020E)

The Auto-Shot sampler automates a continuous series of analyses of up to 48 samples. This feature saves labor and improves reliability.

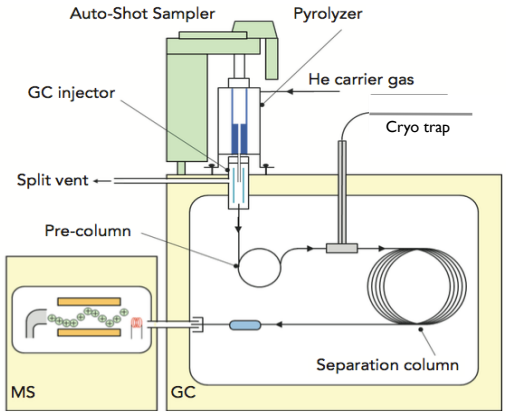
F-Search MPs 2.0 (JPN patent 6683335)

The unique search algorithm allows users with little experience in polymer analysis to obtain reliable microplastic identification and quantification results.

MicroJet Cryo-Trap (optional)

The device guarantees: high trapping efficiency of low-boiling-point compounds, rapid cooling with low energy consumption and controllable cooling temperature.

GC/MSD 8890/5977 Agilent is a routine and reliable workhorse for routine, robust, and reliable quantification of microplastics.



Workflow for Microplastics Analysis with Micro-Furnace Py-GC/MS System

1. Sampling and pretreatment

Microplastics are extracted from environmental samples by appropriate pretreatment dependig from origin. The sample is then placed in a sample cup and weighed using a semi- micro balance.

2. Set of the sample cup on the Auto-Shot Sampler

The sample cups are placed onto the Auto-Shot Sampler. Up to 48 cups can be loaded each time.

3. Pyrolysis of the sample

The sample is introduced into the Micro-Furnace pyrolyzer by the Auto-Shot Sampler and is pyrolyzed. The plastics become pyrolysis products (pyrolyzates) and are introduced into the GC directly. On the other hand, the inorganics in the sample remain in the sample cup as residues.

4. GC/MS analysis

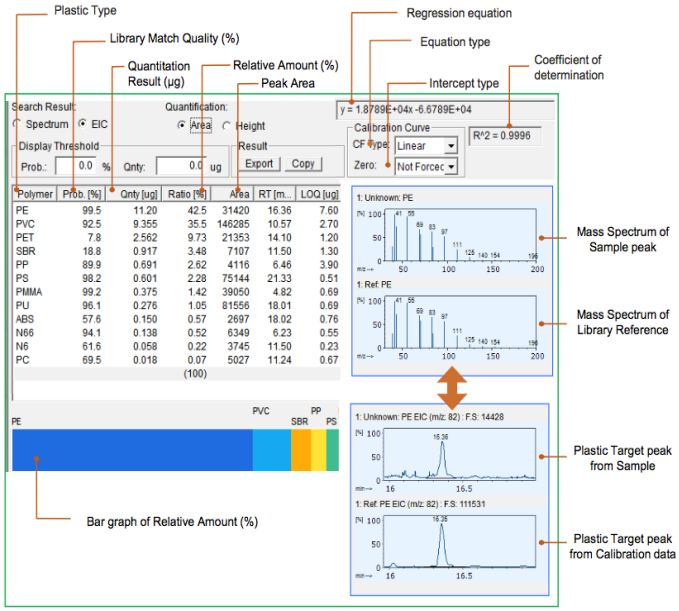
Pyrolyzates are separated on a GC column and detected by a single Quad mass spectrometer. The resulting pyrogram generally includes a peak for each pyrolyzate. The mass spectrum from each peak reflects the chemical structure of each pyrolyzate. Each polymer generates a unique set of pyrolyzates.

5. Data analysis

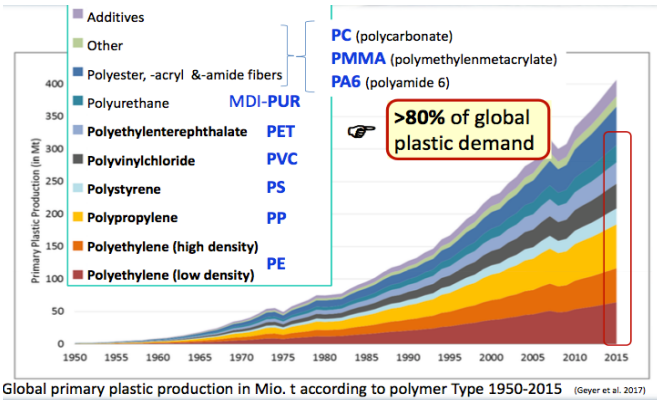
Reliable and quick data analysis can be done using F-Search MPs 2.0. Calibration curves are created automatically based on the analytical results from the reference polymer mixture. Then F-Search MPs 2.0 performs quantitative calculation automatically and results are reported for each sample.

Identification/Quantitation Analysis of Microplastics with F-Search MPs 2.0

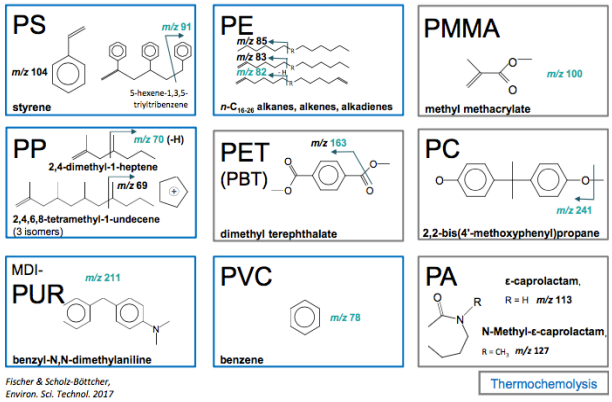
The F-Search software results screen shown below identifies the detected plastic types, displays the match quality for the library search, and lists quantitation interpretation. All information can be seen at a glance. The Mass Chromatogram and Mass Spectrum of a sample are shown side by side on the screen in comparison with the Mass Chromatogram and Mass Spectrum of the library reference.



Py-GC/MS Indicator ions of 9 polymers



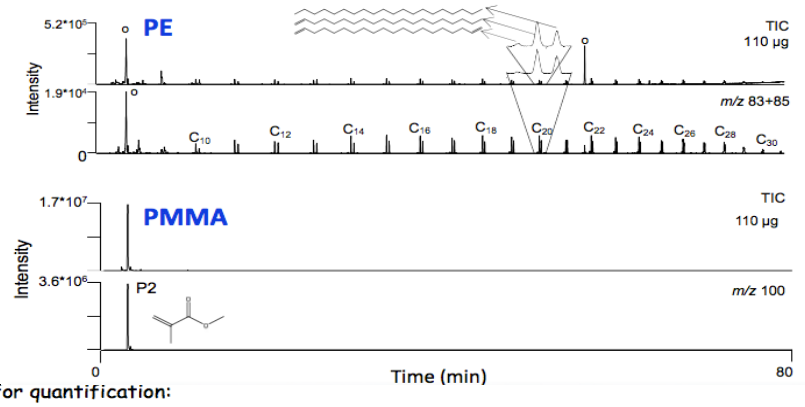
Global primary plastic production in Mio. t according to polymer Type 1950-2015 (Geyer et al. 2017)



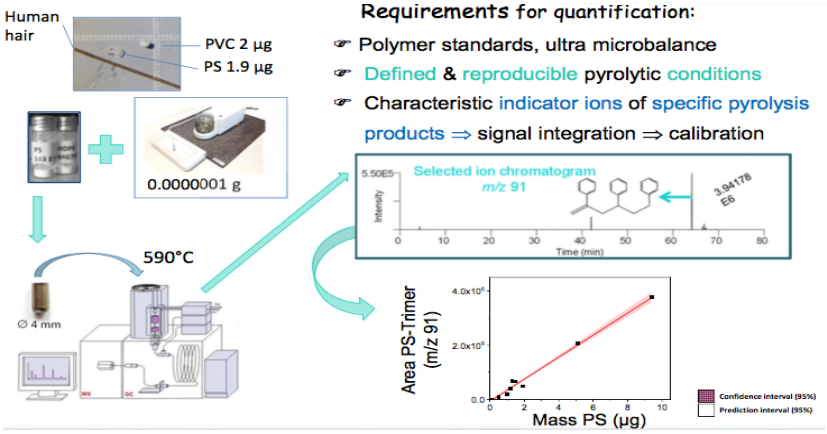
Fischer & Scholz-Böttcher, Environ. Sci. Technol. 2017

Thermochemolysis

Different pyrolytic behavior of polymers

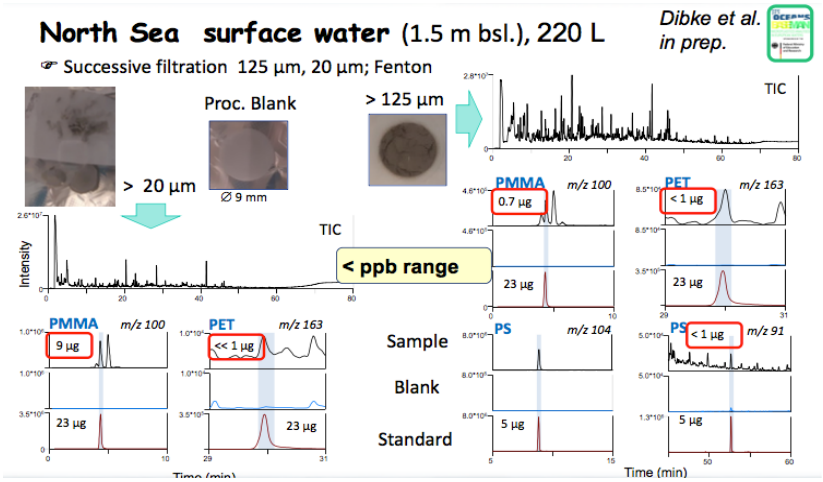


Py-GC/MS MP quantification



Scholz-Böttcher et al. Webinar on the Analysis of microplastics using Py-GCMS, 04-2019

Py-GC/MS – Environmental samples



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