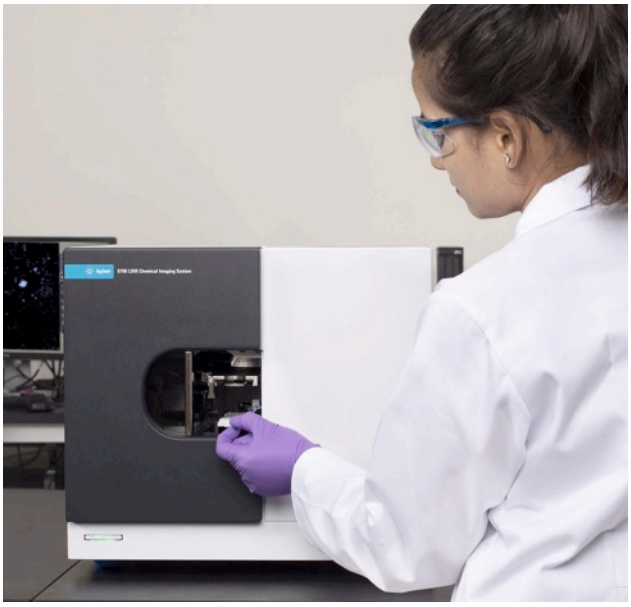
MORPHOLOGY AND MASS QUANTIFICATION COMBINED APPROACH FOR MICROPLASTICS CHARACTERIZATION WITH AGILENT LDIR AND FRONTIER LAB PYROLIZER

Federico Saccoa, Paolo Scardinab
[a]*SRA Instruments SpA* *sacco@srainstruments.com*
[b]*Agilent Technologies* *paolo.scardina@agilent.com*

Introduction

Many analytical laboratories and scientists around the world are seeking new technologies and developments that can analyse 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 represents a key information. Besides morphology, quantifying the polymer mass is important too since let to assess the amount related to litre of water, kg of sediment or biota. Agilent LDIR 8700 (laser direct infrared) represent a new leading technique based on quantum cascade lasers able to perform an automatic morphology analysis, including polymer identification, in about one hour. Frontier Lab Pyrolizer mounted on GCMS let to close the loop performing quadrupole mass detection with excellent LOD for MPs and additives.

AGILENT LDIR – MORPHOLOGY APPROACH



The LDIR QCL Technology

The LDIR 8700 is a new powerful infrared chemical imaging system that eliminates much of the problems associated with other system. By coupling the bright quantum cascade laser (QCL) with rapidly scanning optics and using a thermoelectrically cooled MCT detector, LDIR provides a **new approach to chemical imaging and spectral analysis** at an unprecedented **speed** without coherence artifacts. Because of the use of tunable laser, LDIR can rapidly acquire an image over a large area with diffraction limited spatial resolution by simply using some diagnostics wavelengths that are necessary for analysis. LDIR 8700 let to measure the **size, shape**, and **chemical identity** of every plastic particle.

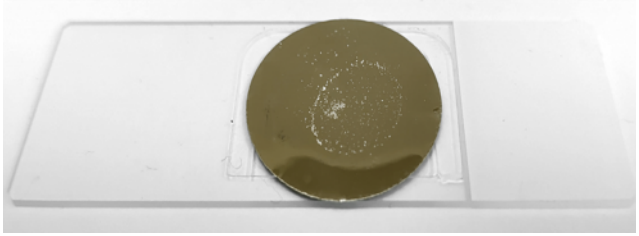
Rapid, large-area, on-filter analysis of microplastics from plastic bottles using laser direct infrared imaging[1].

In this recent study, microplastics derived from polyethylene terephthalate (PET) bottles were analysed on gold-coated membrane filters using the Agilent 8700 LDIR chemical imaging system. The direct on-filter analysis of particles is suitable for the routine testing of microplastics in environmental samples.

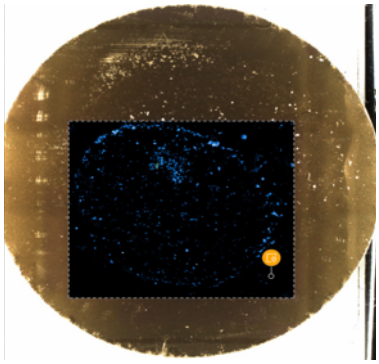
Sample preparation: part of a PET bottle was ground into a fine powder using a diamond-coated metallic tool. The particles were collected into a vial containing ethanol, shaken vigorously, and left overnight. Small-volume aliquots of the solution were pipetted into de-ionized (DI) water to create working microplastic solutions. The microplastic solutions were then filtered as described in the next section.

Vacuum filtration apparatus: due to the delicate, flexible nature of the gold-coated membrane filters, a small-pore glass frit vacuum filtration filter base was used as the supporting structure for the filters. The vacuum filtration glassware was attached to a gentle vacuum system capable of 70 mbar maximum vacuum. Gold-coated polycarbonate membrane filters from SPI Supplies Inc (West Chester, PA, USA), 25 mm diameter, 0.8 µm pore size were used to extract particles from solution.

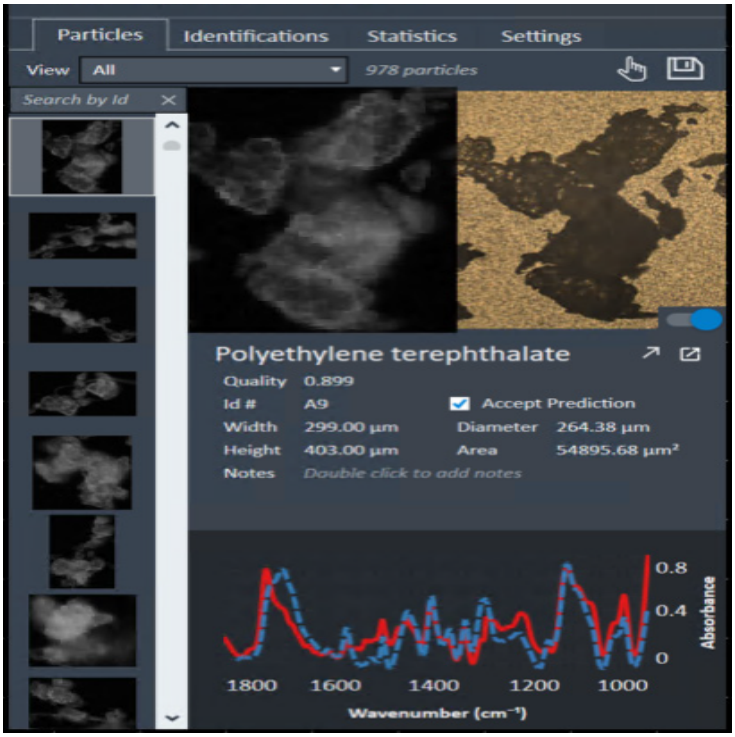
Filter processing: the filters were premoistened with solvent (DI water) before filtration. Due to the delicate nature of the membrane filters, a gentle vacuum pressure of 600 mbar was applied to filter each particle solution. This setting translated to approximately 15 mL filtration in 90 seconds. The filters were left to rest for at least 30 minutes to allow any temporary deformation during vacuum filtration to relax and regain a flat profile. The goal for 8700 LDIR is to prepare samples with a surface of no more than 10 µm difference in surface topography. However, it is common to see up to 50 µm difference across the surface when working with filters and still

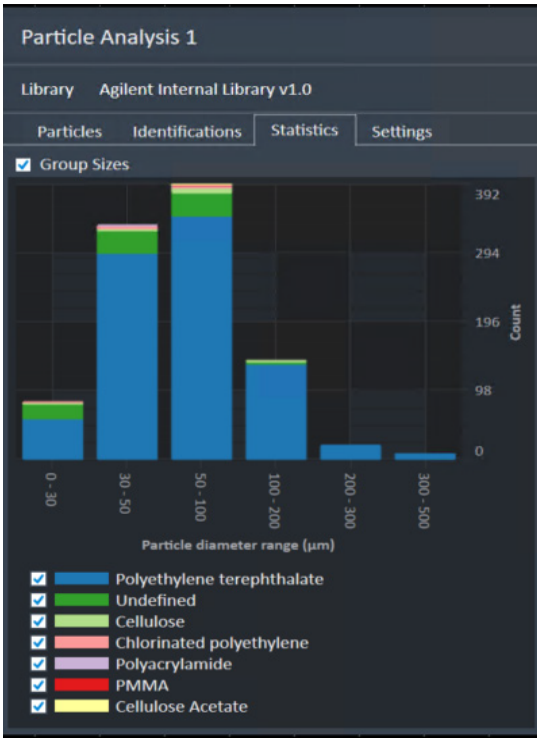


On-filter analysis of particles: the Particle Analysis workflow automatically identifies all particles within a user-defined area of the sample, draws boundaries around each particle, photographs, and identifies each one. The software performs a library search to confirm each particle's identity based on its IR spectrum.



Results and discussion: the **number of particles detected** by the 8700 LDIR on the filter totalled **978**, spanning a size **range of 20 to 478 µm in diameter**. Out of the detected particles, 88% (863) were correctly identified as PET, 9% (89) were undefined, and 1% (14) were identified as cellulose; there was an insignificant number of other trace contaminants (poly-methyl-methacrylate, polyacrylamide, and a few others). The speed and simplicity of the 8700 LDIR helps microplastic research activities, which involve high numbers of samples and fast sample throughput. Due to a high degree of automation and intuitive software, the 8700 requires no training in microscopy or IR spectroscopy to use successfully. User can benefit from the large area analysis, automated particle detection, identification and classification, ability to reprocess results with new libraries, and visible and IR images of all detected particles.





FRONTIER LAB 3030D PYROLIZER WITH AGILENT GCMS – MASS QUATIFICATION APPROCH

Thermal analysis and analytical pyrolysis methods are based on the thermal degradation of polymers or polymer mixtures which follows the characterization of molecules produces (pyrolysates). These approaches are recognized crucial and powerful tools for polymeric materials like microplastics. Pyrolysis can be considered as a sample preparation/introduction step which is followed by gas chromatography and mass spectrometry. When Py-GC–MS is used, quantitative information is obtained in mass, with very low instrumental limits of detection and quantification.

Frontier Lab Multi-Shot pyrolizer (EGA / PY-3030D) is the most capable model in the Multi-functional Pyrolizer series which let to perform pyrolysis measurements together with thermal desorption. Its furnace could heat sample from room temperature +10°C to 1050 °C (1 °C increment) / within ± 0.1 °C

Pyrolysis-gas chromatography-mass spectrometry to detect micro- and nanoplastics in marine sponges[4]

Marine sponges are sessile and active filter-feeding invertebrates, ubiquitous in all marine habitats; sponges are capable of processing large quantities of water (24 L/hour per gram of sponge), accumulating consistent amounts of particles, which makes them susceptible to water pollution.

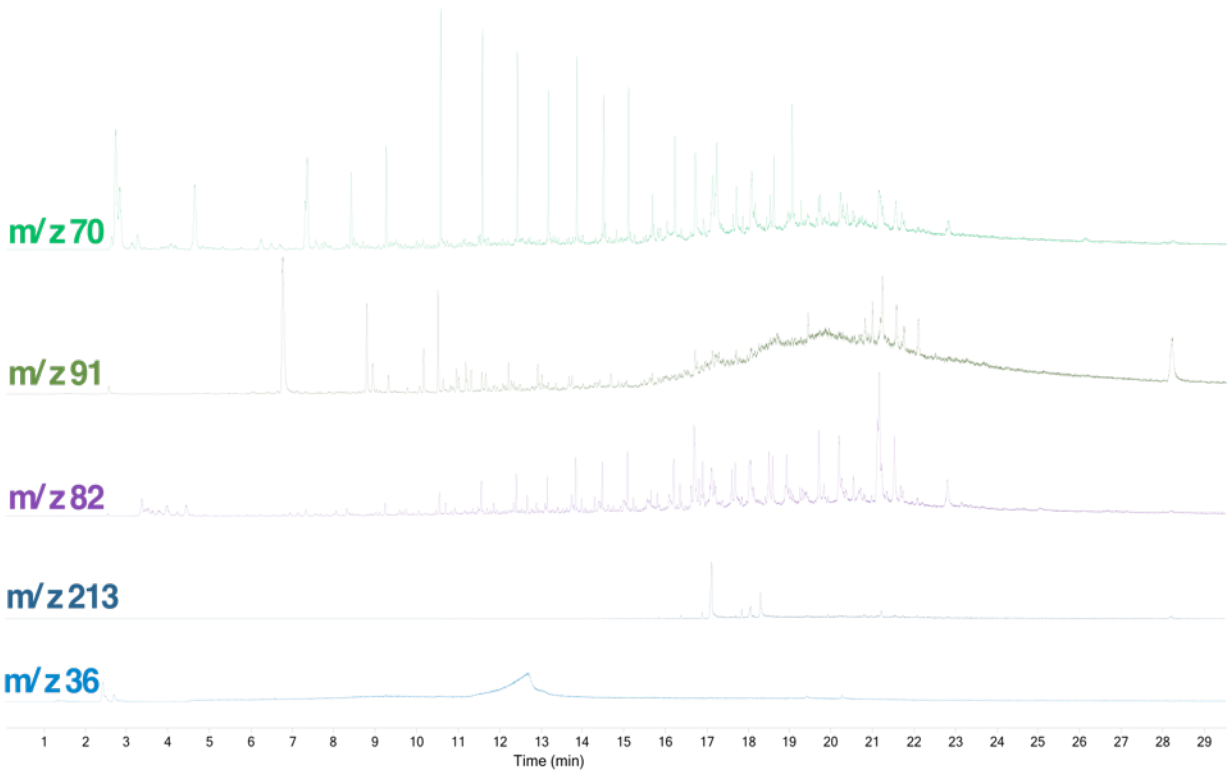
Sampling and sample treatment: marine sponges cf. Haliclona (Haplosclerida) were collected in the water surrounding two Maldivian islands. Sampled sponges were subjected to different sample treatments in order to degrade all organic matter and separate any other particle other than microplastics. The followed protocol consists in alkaline digestion with KOH (60°C, 24h), density separation with $ZnCl_2$, neutralization and pressurized solvent extraction (PSE) on filters. The obtained processed filter was later cut in pieces and places in a pyrolysis cup.

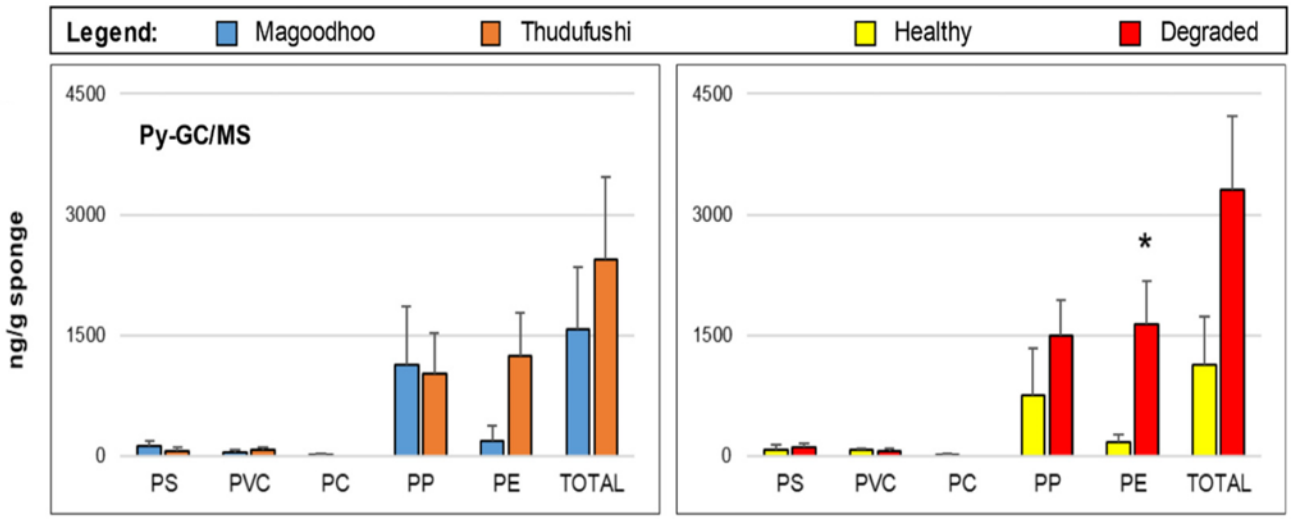
Results: Before analysing samples a method validation parameter for the Py-GC-MS quantitative analysis was held identifying m/z typical profile for each polymer. After that, calibration curve for quantitative analysis were built for PS, PVC, PC, PP and PE.

Polymers	Selected Py products	m/z signals	LOD* (ng/g)	LOQ* (ng/g)	r^2
PS	2,4-diphenyl-1-butene (dimer)	91, 208	6.6	9.3	0.9905
PVC	HCl	36, 38	4.8	9.4	0.9915
PC	bisphenol	213	3.0	6.6	0.9866
PP	2,4-dimethyl-1-heptene	70, 126	9.8	13.8	0.9994
PE	α,ω-alkenes C15-C25 (average of the areas**)	82	25.1	30.2	0.9972

**In column; **11 peaks were integrated for quantifying PE (average of the areas).*

70% of the analyzed samples showed the presence of plastic particles with an average contamination of 1.2 particles/g tissue (25-150 µm size range) and an average of 2.0 µg/g for the 0.2-25 µm size range; PP and PE were the most represented polymers in both the size ranges. The proposed analytical workflow allowed to compare the plastic contamination levels between the sites surveyed and demonsstrated the suitability of marine sponges to monitor plastic pollution in marine environments.





[1]. F. Saliu, G. Biale, C. Raguso, J. La Nasa, I. Degano, D. Seveso, P. Galli, M. Lasagni, F. Modugno, Science of The Total Environment, 2022. 819: p. 152965
[2]. J. La Nasa, G. Biale, D. Fabbri, F. Modugno, Journal of Analytical and Applied Pyrolysis, 2020. 149: p. 104841
[3]. D. Robey, D. Troiani, Agilent Application Note 5994-4873EN. 2022
[4]. G. Biale, F. Saliu, C. Raguso, J. La Nasa, I. Degano, D. Seveso, P. Galli, M. Lasagni, F. Modugno, "Pyrolysis-gas chromatography-mass spectrometry and microspectroscopy to detect micro- and nanoplastics in marine sponges", PYRO2022 23rd edition of the International Conference on Analytical and Applied Pyrolysis, 15-20 May 2022, Ghent

SRA INSTRUMENTS ANALYTICAL SOLUTIONS

SRA Instruments S.p.A
20063 Cernusco S/N (MI)
Tel +39 02 9214 3258
www.srainstruments.com
info@srainstruments.com

SRA Instruments SAS
69280 Marcy l'Etoile Lyon
Tel +33 04 7844 2947
www.srainstruments.com
info@sra-instruments.com

Agilent Premier Solutions Partner