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

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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**. 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 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 GC/MS Agilent 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 infrared chemical imaging system that eliminates much of the problems associated with classical FTIR instruments. 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. LDIR 8700 let to measure the **size**, **shape**, and **chemical identity** of every plastic particle.

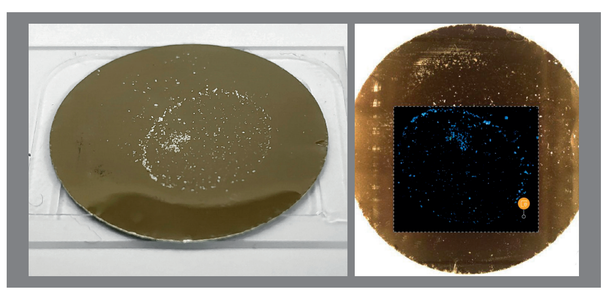
Rapid, large-area, on-filter analysis of microplastics from plastic bottles using laser direct infrared imaging

In this recent study, microplastics derived from 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. 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 by vacuum.

Filter processing: due to the delicate nature of the membrane filters, a gentle vacuum pressure of 600 mbar was applied to filter each particle solution. 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 produce acceptable results.

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.

PY-GC/MS-MASS QUANTIFICATION

Frontier Lab 3030D Pyrolizer with Agilent GC/MS

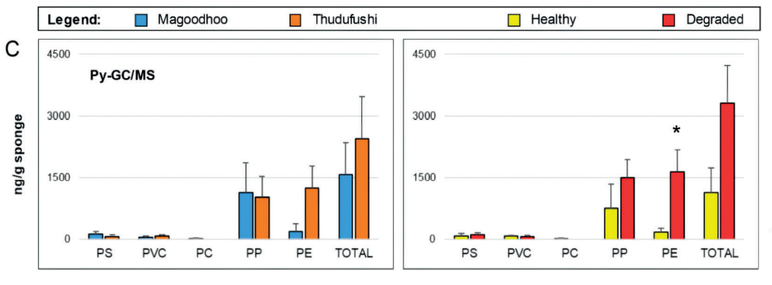
Thermal analysis and analytical pyrolysis methods are based on the thermal degradation of polymers or polymer mixtures which follows the characterization of molecules produces (pyrolysates). These approaches are recognized crucial and powerful tools for polymeric materials like microplastics.

Frontier Lab Multi-Shot pyrolizer (EGA/PY-3030D) is the model to perform pyrolysis measurements together with thermal desorption.

Pyrolysis-gaschromatography-mass spectrometry and microspectroscopy to detect micro and nanoplastics in marine sponges

Marine sponges are filter-feeding invertebrates, 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.

Sample treatment: sampled sponges were subjected to 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, density separation with $ZnCl_2$, neutralization and pressurized solvent extraction 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.

Spectroscopic data, out of scope, are not going to be mentioned.

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