

Distinguishing Between Polyamide Microplastics and Natural Polyamide

Using an Agilent 8700 LDIR chemical imaging system to successfully discriminate between natural and synthetic polymers



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Introduction

Accurately distinguishing between polyamide (PA) and natural polyamide (nPA) can be a challenge in the analysis of microplastics by spectroscopic techniques. There are often only marginal differences in spectra that can be difficult to detect. It is, however, vital as samples may well contain both natural polyamides from biological sources in addition to synthetic polyamides such as Nylon that are considered a microplastic. This study describes a workflow to meet this challenge using an Agilent 8700 Laser Direct Infrared (LDIR) Chemical Imaging System (Figure 1).



Figure 1. The Agilent 8700 LDIR Chemical Imaging System allows the high-speed routine analysis of microplastics. Plastics can be identified and quantified in terms of their size, shape number, and chemical ID.

To identify and quantify polyamide and natural polyamide in the samples, the Agilent 8700 LDIR Chemical Imaging System was used. The LDIR, utilizes a Quantum Cascade Laser (QCL) as the source. The QCL is a semi-conductor-based laser in which electrons tunnel through a series of quantum wells and emit light, allowing it to be rapidly tuned through the wavenumber (λ^{-1}) range. When combined with a single-point mercury cadmium telluride (MCT) detector (thermometrically cooled) and rapid scanning optics, two useful modes of action arise. In the first mode, the LDIR selects a single wavelength and scans through the rapidly moving microscope objective as it moves over the sample at a high speed. In the second mode, the microscope objective is parked at a single point. The QCL then scans through the wavelength range, obtaining a full spectrum of that point in less than one second.

The instrument operating software, Clarity, is used for all instrument operation, data analysis and reporting. The automated microplastics analysis workflow within Clarity utilized both modes of the LDIR. The scanning mode was first used to rapidly scan the sample area at a single wavenumber. The resulting IR image was used to both locate particles in the sample and describe their size and shape. Once each particle was located, the LDIR then rapidly and automatically moved to each and acquired a full spectrum. Once acquired from a particle, it was immediately, and in real-time, compared to a microplastics spectral library. The best fit match for the spectrum was determined and reported for each particle. The library was derived from well-established sources and included a range of spectra relevant to the analysis of microplastics in marine water derived samples.

The instrument utilized a large field of view camera to obtain an entire view of the sample and a microscope-grade objective to capture high magnification visual images as needed. Fully automated analysis of 800 particles and comparison of the generated spectra to the database took about 1 hour to complete.

Experimental

Two commercially available polyamide samples were obtained for the study and examples of each particle type are shown here.

– Nylon 6 (Sigma Aldrich)



– Pollen in dry powder form



These reference samples were regularly shaped and sized which made them easily distinguished from each other and other contaminants, using the high-magnification visual camera in the LDIR.

In preparation for analysis, all samples were suspended in ethanol (50%) and deposited on infrared reflective glass slides (7.5 x 2.5 cm, MirrIR, Kevley Technologies). The ethanol was allowed to evaporate at room temperature before analysis.

The LDIR operates in the so-called fingerprint region of the mid-infrared, covering the range of 1800 cm^{-1} to 975 cm^{-1} . The automated particle analysis workflow contained within the Clarity software was used for all samples. This workflow sets all the necessary instrument settings automatically, including scan speed, sweep speed, and attenuation and these cannot be altered. An analyst can adjust several options, including the sensitivity of the particle detection system, set to the maximum for this analysis. The analyst may also set their own hit quality index ranges. Hit quality describes how closely the spectrum of the sample matches that in the reference library. For this experiment, classification ranges (i.e. the characterization of spectral match quality by “high”, “medium” and “low”) were set to:

- low confidence 0.65 to 0.75
- medium confidence 0.75 to 0.85, and
- high confidence 0.85 to 0.99.

Any particles falling outside this range, i.e. <0.65 , were classified as “undefined”.

The minimum particle size was set to 10 μm (20 μm is the default), while the default maximum particle size of 500 μm was retained. The instrument collects spectral data at 0.5 cm^{-1} steps by default. However, for this workflow, the spectral resolution was adjusted to 8 cm^{-1} , in line with industry practice in order to match available libraries.

A starter library of around 420 spectra and 25 polymer types (provided with the LDIR) was used to do the analysis. While the library does contain spectra of both PA and nPA, more spectra were added to improve performance as described, following.

Results

To determine the ability of the LDIR to distinguish PA from nPA, the samples of pollen and nylon 6 were assessed first separately and then together.

Pollen

The first step was to assess the spectra obtained for each pollen (nPA) sample against the spectral library provided with the Clarity software. In a scanned area containing a total of 106 particles, 65 (60%) particles were identified as nPA. It is notable that no particles were classified as PA and there were no undefined particles (Figure 2). There was however a significant amount of other material present (Figure 3). It should be noted that this study was not conducted in a laminar flow environment so contamination could have been present. However, as the nPA particles were easily identifiable in the visual images, contamination was not considered a concern. As the results of this step were acceptable, no spectra from the pollen (nPA) samples were added to the library.

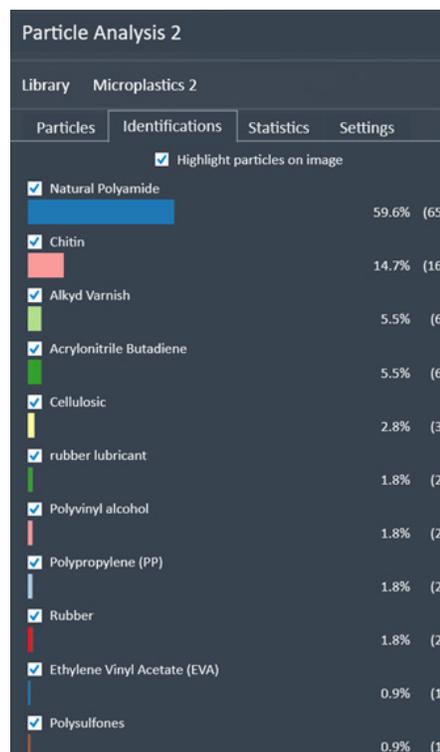


Figure 2. Pollen samples analyzed with modified library containing more nylon 6 spectra.

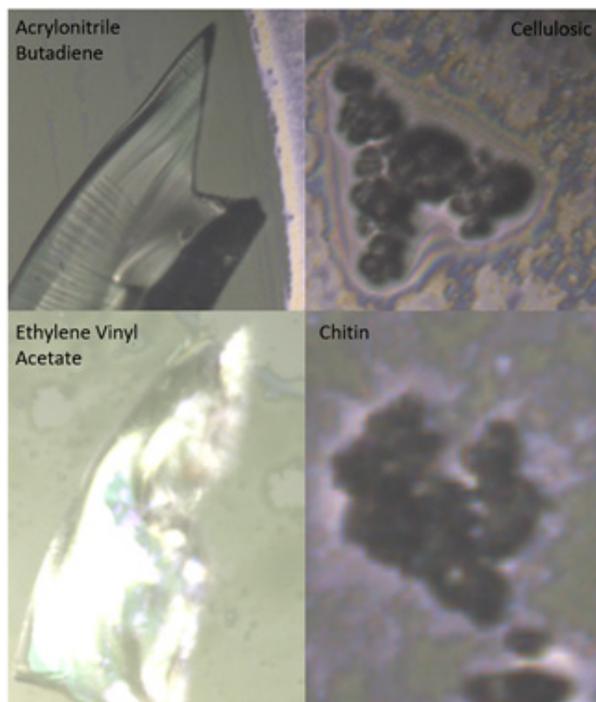


Figure 3. Other materials found in the samples in addition to PA and nPA were identified as defined by the Clarity software.

Nylon 6

The next step was to repeat this process and assess the nylon 6 (PA) sample against the spectral library provided with the Clarity software. Of the 2482 particles found in the sample, a total of 1886 were identified as a polyamide (Figure 4). Notably however, 729 (39%) were incorrectly identified as nPA as confirmed by visual assessment of the particles. Notably, many of the particles incorrectly assigned had low hit quality scores. Hit quality describes how close the match is between the spectrum obtained from a particle matches that in the reference library. The hit quality ranges used in this study are described in the Experimental section. The particle in Figure 5 has a hit quality of 0.699 and would this be considered as a low quality match.

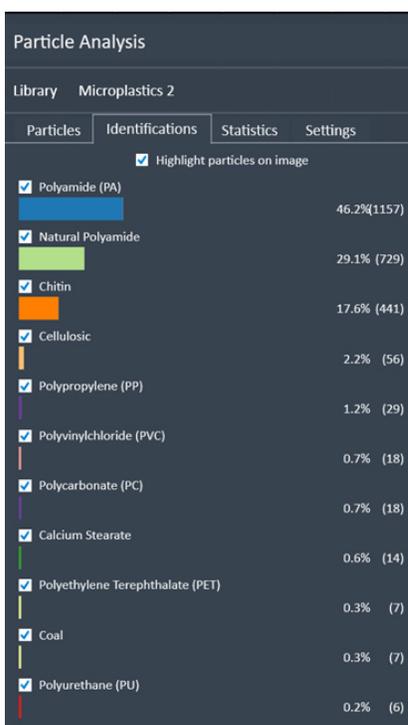


Figure 4. Results of the Nylon 6 sample.

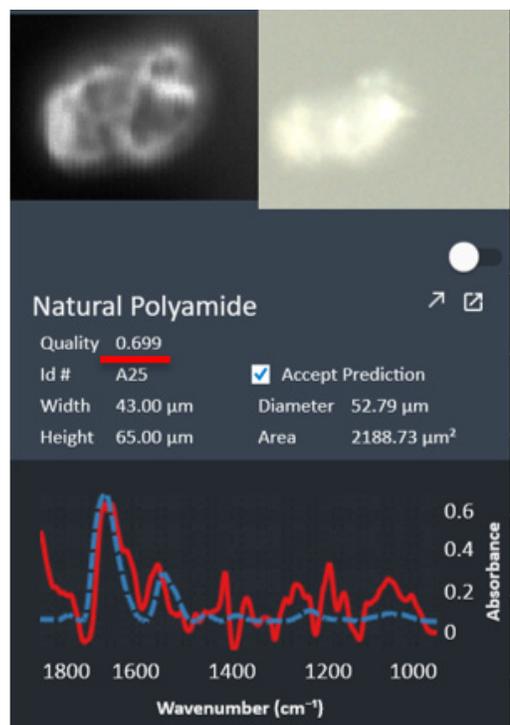


Figure 5. While showing a hit quality above 0.66, this particle has most likely been incorrectly classified.

To improve the identification results, 30 spectra of particles incorrectly classified as nPA but visually confirmed to be nylon 6 (PA) were added to the spectral library. The added spectra were labelled as polyamide (PA). In addition, the minimum hit quality score was raised from 0.66 to 0.72. Particles with a best match hit quality of <0.72 would now be classified as "undefined" in the results.

Following these changes, another, smaller area was scanned. Of the 102 particles found in this area, 87 (95.6%) were now correctly classified as nylon 6 (PA) and there were no misclassifications as nPA. Six particles were classified as undefined (Figure 6).

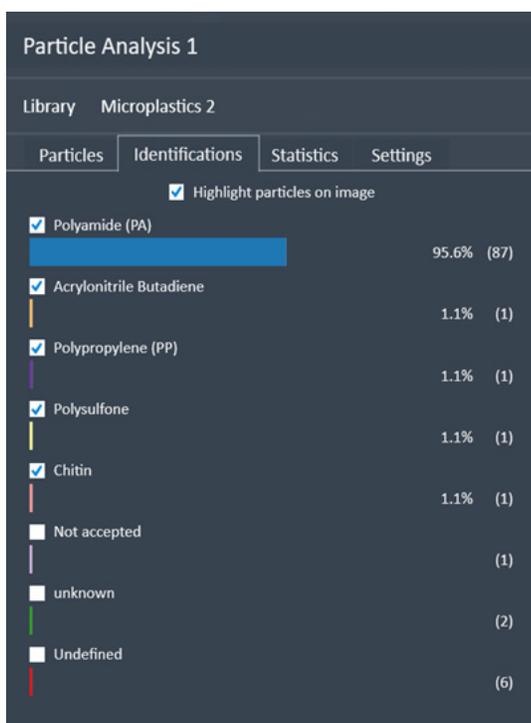


Figure 6. Analysis after nylon 6 (PA) spectra were added to the spectral library.

Mixed sample

The final step in the process was to assess a sample of mixed pollen and nylon 6. Each type was easily distinguished visually using the in-built high-magnification camera, which allowed system-generated results to be verified (Figure 7).

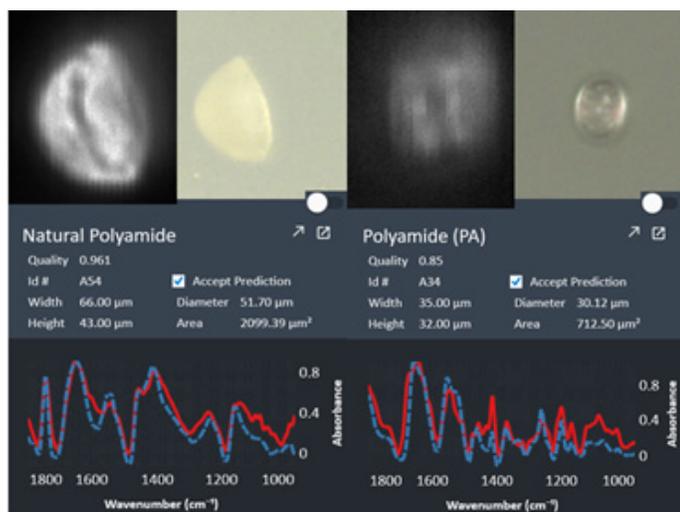


Figure 7. Samples of Pollen and Nylon 6 are easily distinguished visually using the on-board high-magnification camera.

A small area of this sample was scanned in which 60 particles were detected. Of these particles, 28 (53%) were classified as PA and 23 (43%) as nPA (Figure 8). Following visual confirmation, it was noted that:

1. All Nylon 6 and pollen particles were correctly classified and
2. There were no particles of either Nylon 6 or pollen visually identified that had not been classified correctly, i.e. there were no false negatives.

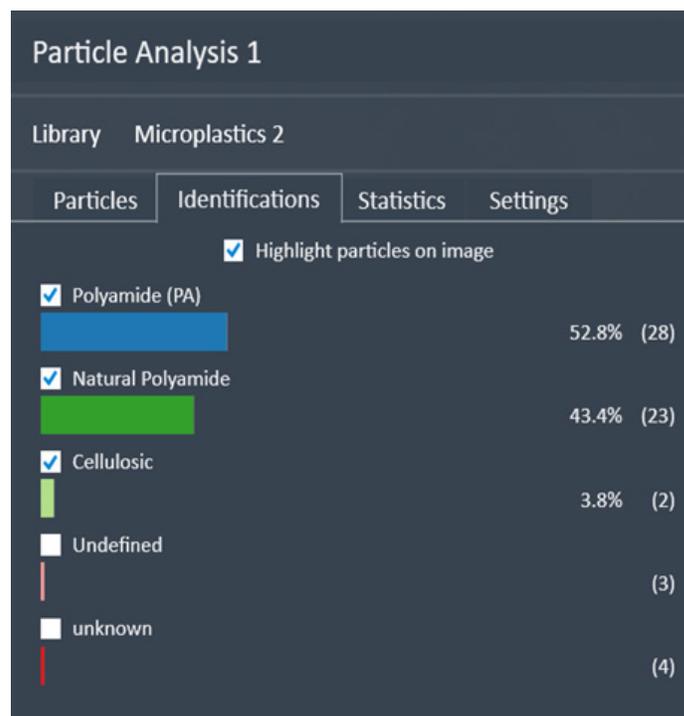


Figure 8. All polyamides were correctly classified.

A larger area of the same sample was also scanned (>500 particles). While it was not practical to inspect every particle, a random selection were visually confirmed as correctly identified as PA or nPA. (Figure 9)

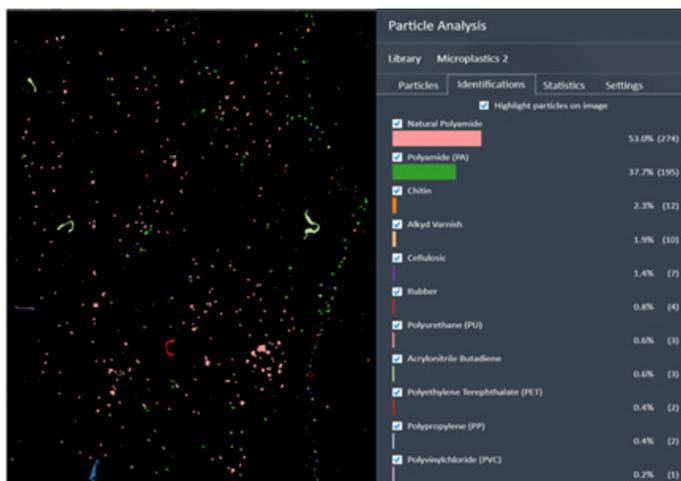


Figure 9. All polyamides were correctly classified.

Conclusion

The Agilent 8700 LDIR could successfully classify and differentiate polyamides from natural polyamides in a mixed sample of both. There are two points that need to be considered:

- Spectra of PA needed to be added to the spectral library that was supplied with the instrument software.
- Increasing the cut-off hit quality score was required to eliminate poor matches. This change did not result in an increase in the number of undefined particles.

Agilent recognizes the need for an increased standard library and is continuously adding components and improving the library. Customers can also add their own spectra to existing libraries or create their own, a task the Clarity software makes quick and simple to achieve.

Lastly, this study again showed that the 8700 LDIR, with its routine workflow and its fast automated process (less than 45 min analysis time for each sample), can obtain reproducible and robust results.

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