Application note

Analysis of microplastics in urban rains using Micro-FTIR-NIR

Authors

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Industry/Application

Microplastics analysis

Products Used

Thermo Scientific™ Nicolet™ RaptIR+™ FTIR Microscope

Goals

Demonstrate the advantages of a multirange FTIR microscope, working in the NIR region, for faster and more accurate analysis of microplastics, using filters that are not transparent in the mid-infrared region.

Key Terms

Microplastics, Particle analysis, NIR microscopy, Anodisc filters, libraries

Key Benefits

- Reduce time and error in microplastics analysis using a NIR microscope with filters that are not completely transparent in the mid-IR region.
- Increase cost benefits by using cheaper filters that are not completely transparent in the mid-IR region but are transparent in the NIR region.
- Take advantage of automation for mid-IR microscopy analysis using dedicated libraries for the NIR region.
- Make use of a complete integration solution for simplified analysis.

Introduction

Microplastics, or MPs, (defined as plastic particles ranging from 1 µm to 5 mm in size, according to ECHA 2019) have become a significant environmental concern due to their widespread presence in oceans, freshwater bodies, and even the air. Their persistence in the environment, especially for small (<100 µm) microplastics known as SMPs, poses a significant threat to biota and human health.

However, due to the lack of standardized procedures for their correct sampling, pretreatment, and analysis, some aspects of research on MPs and SMPs remain inconsistent and challenging. This variability can lead to discrepancies in data quality and reliability across different studies, making it difficult to compare results and draw conclusive insights. Hence, accurate chemical identification and quantification of MPs and SMPs are crucial for assessing their environmental impact and developing strategies to mitigate their presence.

Furthermore, pretreatment procedures (i.e., extraction and purification procedures) are essential to analyze these emerging contaminants in different environmental matrices. Effective pretreatment ensures accurate separation of analytes from other substances and interferences, allowing for precise identification and quantification while minimizing any degradation/denaturation of such polymers. Due to the lack of standardized guidelines, cross-validation of different analytical methods for assessing MPs, especially SMPs, is crucial to ensure consistent and reliable results.

In this application note, SMPs in different size ranges and polymer typologies were analyzed using two support typologies (BaF_2 support and an Anodisc filter) with micro-FTIR NIR spectroscopy. Additionally, a comparison with a real environmental sample—a wet deposition from the urban area of Mestre, Venice, Italy—filtered on an Anodisc support after an oleo extraction and purification procedure previously developed (Corami et al., 2021) demonstrates the effectiveness and accuracy of the applied methodologies. This comparison provides a practical benchmark for validating the analytical approach, ensuring that the results represent actual environmental conditions. Anodisc filters, while they cost less than other filters and are not made from polymer materials, are transparent in the mid-IR region only between 4,000 and 1,210 cm^{-1}; this limits their use for microplastics analysis in this range. However, they are fully transparent in the NIR region because aluminum oxide does not have peaks in this region.

FT-NIR spectroscopy

FT-NIR spectroscopy, or Fourier Transform near-infrared spectroscopy, is an analytical technique used to obtain the near-infrared absorption spectrum of a sample. This method involves measuring the frequences and amounts of near-infrared light (typically in the wavelength range of 780 to 2,500 nanometers) absorbed by a sample. When near-infrared light is directed at a sample, specific wavelengths are absorbed by the chemical bonds in the microplastics, producing a unique spectrum that serves as a fingerprint for the material, providing information about its molecular composition and structure.

An FT-NIR microscope allows the analysis of small samples and can also be employed for the analysis of microplastics, as along with FTIR and Raman microscopies. The obtained spectrum of a particle is compared with the spectra in reference libraries to identify plastic polymers in environmental samples. FT-NIR spectroscopy can analyze microplastics on Anodisc filters because these filters do not absorb in this spectroscopy region.

Reference polymers preparation

Three different reference polymers in known size and polymer typology were purchased (polyamide 6 (PA 6), maximum size 55 µm; low-density polyethylene (LDPE), maximum size 300 µm; and polyethylene terephthalate (PET), maximum size 300 µm; sourced from Goodfellow GmbH, Hamburg, Germany) and employed to create new spectra libraries.

Two supports were employed to identify each of these reference polymers and evaluate potential polymer spectra interferences:

- A **barium fluoride (BaF_2)** plate, since it does not absorb through the NIR range, allows for straightforward spectral acquisition without interference from the support material.
- **Anodisc filters** (aluminum oxide filters, 0.2 µm, 47 mm Anopore Inorganic Membrane, Whatman) purchased from Merck (Merck, Darmstadt, Germany) are commonly employed for MPs and SMPs analysis (Corami et al., 2021). This filter is designed such that it simulates environmental conditions more closely, providing a more realistic context for the real environmental samples analysis.

Wet deposition sampling, sample pretreatment, and filtration

Wet deposition samples were collected using a wet-dry automatic collector (Wet&Dry Sampler FAS005AB, 152 MTX, Padova, Italy), and then placed on the roof of the scientific campus of Ca' Foscari University of Venice in Mestre, Italy. The sampling collector was equipped with two stainless steel vessels, in which two decontaminated glass jars were placed, along with a rain sensor capable of changing the cover position over the two vessels. Hence, wet or dry depositions were collected, respectively, depending on the precipitation. Wet depositions were recovered in a decontaminated glass flask with ultrapure water and ethanol and stored at 4 °C. Then, the samples were pretreated and filtered using Anodisc filters, followed by a method optimized by Corami et al., 2020. The whole procedure, from sampling to pretreatment and filtration, with all the methodology details and the quality assurance and quality control (QA/QC) procedures, was submitted to a scientific journal and is under review (Rosso et al., 2024).

Analysis

The reference polymers and the samples were analyzed using a Thermo Scientific™ Nicolet™ RaptIR+™ FTIR Microscope with Thermo Scientific™ OMNIC™ Paradigm Software. The RaptIR microscope offers numerous advantages for advanced infrared microscopy applications. Its high spatial resolution, chemical imaging capabilities, non-destructive nature, versatility, enhanced sensitivity, and sophisticated data analysis tools make it a powerful instrument for a wide range of scientific and industrial applications.

The RaptIR microscope can use different types of detectors, including MCT detectors cooled with or without liquid nitrogen and InGaAs detectors. This versatility is useful for achieving flexibility and enhanced performance in IR and NIR microscopy.

Figure 1. Thermo Scientific Nicolet RaptIR+ FTIR Microscope.

Methodology

First, a visual mosaic was captured using the RaptIR microscope's 4x objective lens, providing a broad overview of the sample area. This was followed by a more detailed visual and infrared (IR) mosaic acquired with the 15x objective lens, which allowed for a closer examination and enhanced detection of microplastic particles. The combination of these imaging techniques ensured comprehensive coverage and detailed analysis, facilitating accurate identification and characterization of the microplastics within the sample. The resulting spectral resolution was 8 cm^{-1} with a 1-second acquisition time for each spectrum, and transmittance modes were employed. The particles on the surface were selected by employing OMNIC Paradigm software, where spectra and size were retrieved.

Results

Reference materials and NIR libraries

Visual mosaics from each support were captured using the 4x and 15x objective lens, and FT-NIR spectra were obtained from each particle analyzed. The combination of these mosaic images provided high-resolution visuals of the particles analyzed (Figure 2a, b). Then, the spectra from each reference polymer analyzed with FT-NIR Spectroscopy were retrieved using BaF_2 and Anodisc support, respectively (Figures 3 and 4). BaF_2 represents a material completely transparent in NIR and mid-IR region. Our purpose is to demonstrate that using Anodisc filters the spectra are the same. This is not true for the mid-IR region, where Anodisc has a total absorbtion under 1,210 cm^{-1}.

The results showed that both supports provided reliable FT-NIR spectra for the three MP polymer typologies, with no significant differences in the accuracy or clarity of the spectral data obtained from each substrate. Anodisc filters were confirmed to be a suitable support for MPs analysis in FT-NIR spectroscopy, opening possibilities for expanding the range of analytical techniques for the MPs and SMPs detection methodologies without compromising analytical reliability or data quality.

Anodisc filters are significantly preferred over silicon, gold-coated or silver-coated filters, in large part due Anodisc's much lower.

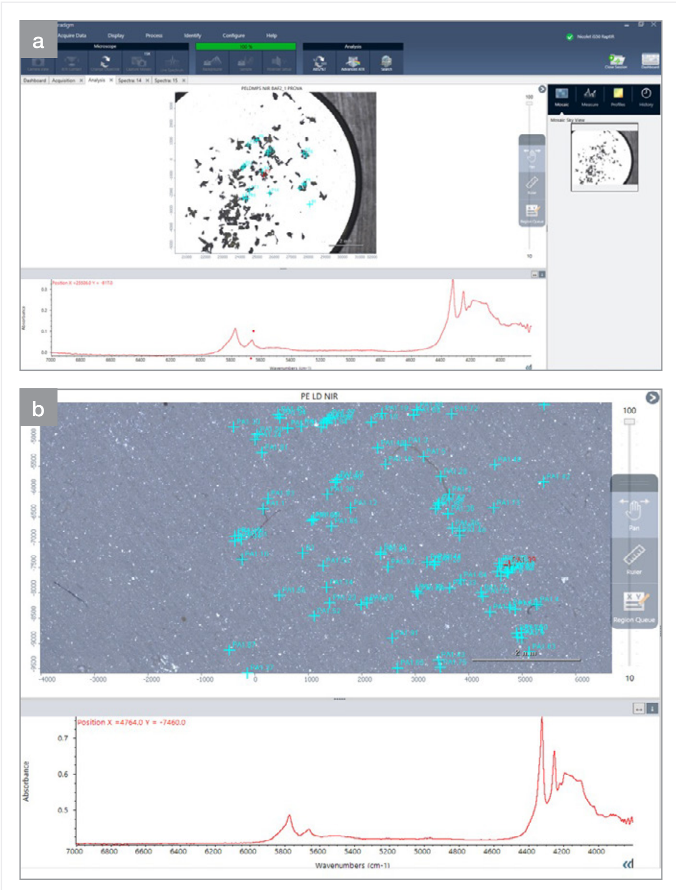

Figure 2. Visual mosaics with respective NIR spectra of a LDPE MP, obtained from (a) BaF_2 support and (b) ANODISC support.

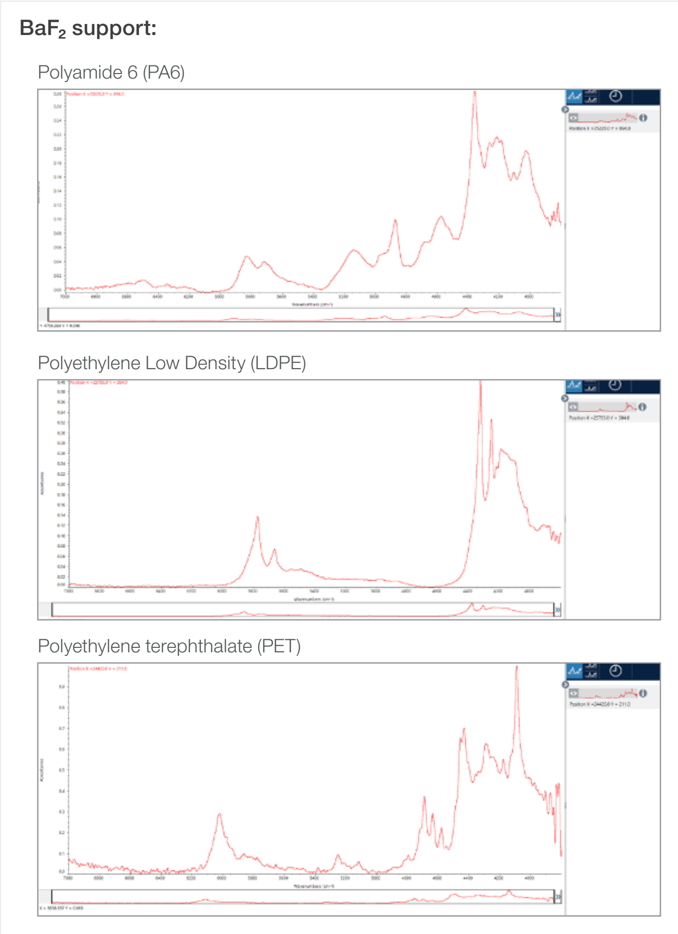

Figure 3. NIR spectra obtained from each polymer typology with BaF$_2$ support, used to create the library.

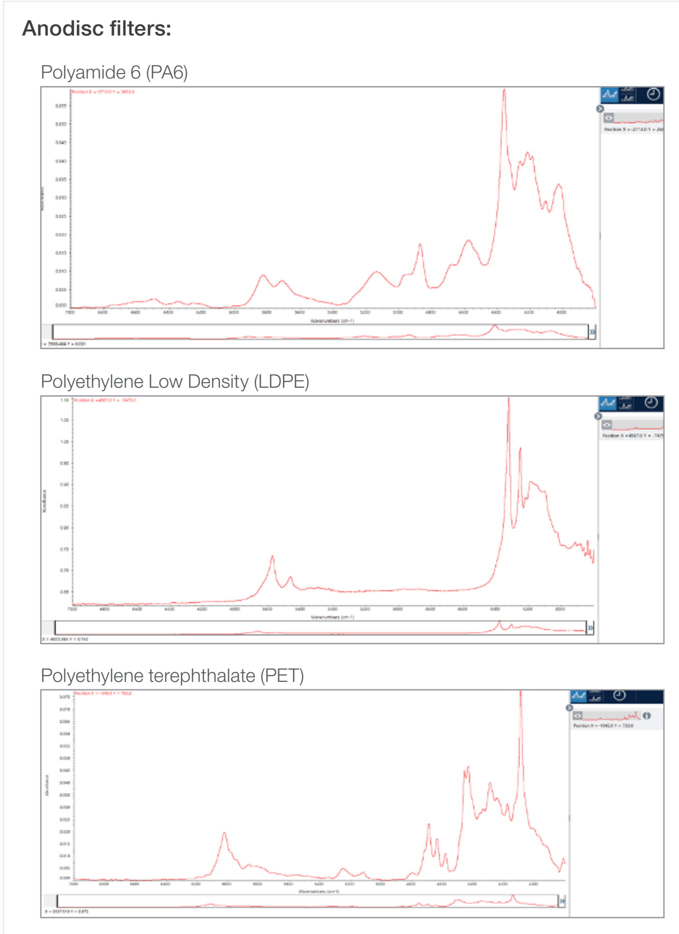

Figure 4. NIR spectra libraries obtained from each polymer typology with Anodisc support.

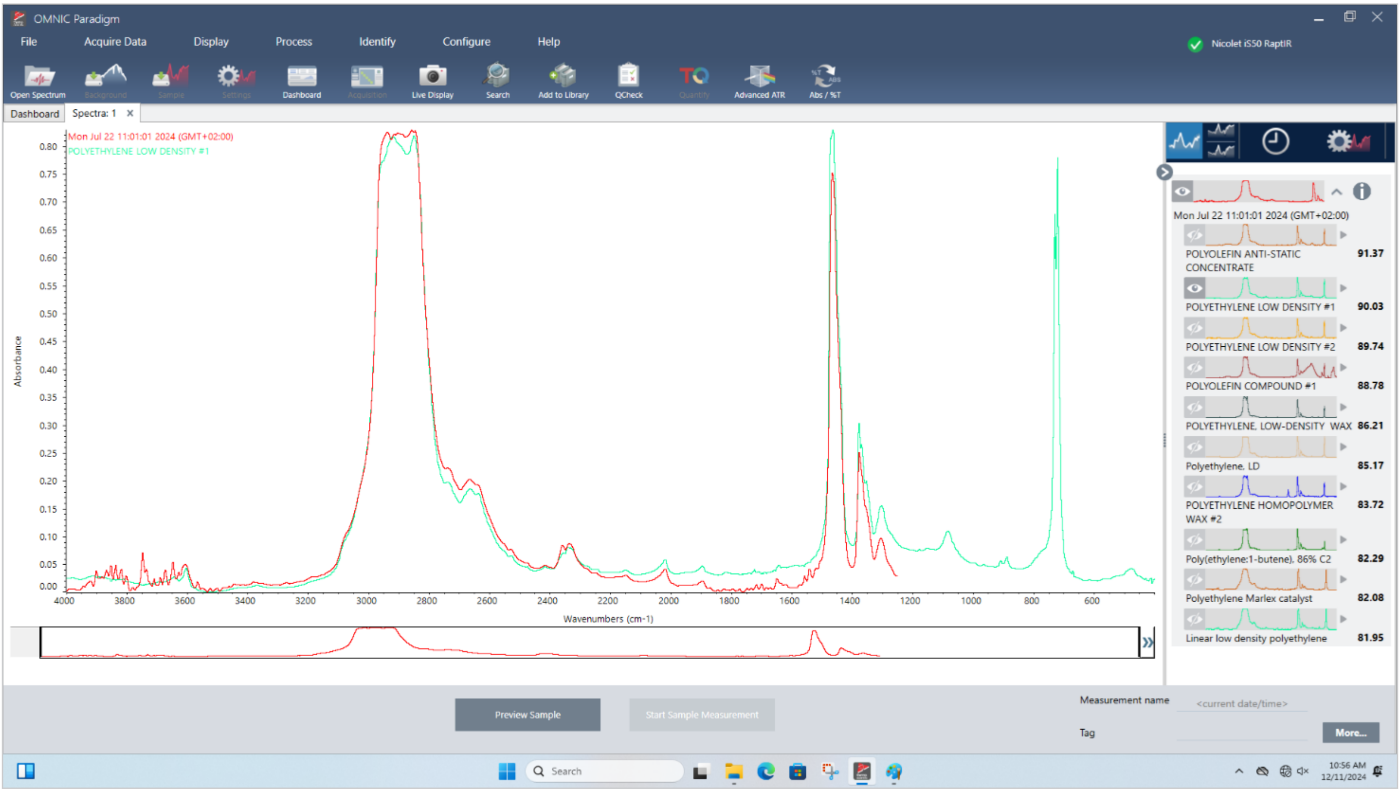

Figure 5. LDPE microplastic on Anodisc filter in mid-IR region. It's possible to identify the MP, but the spectral region is limited.

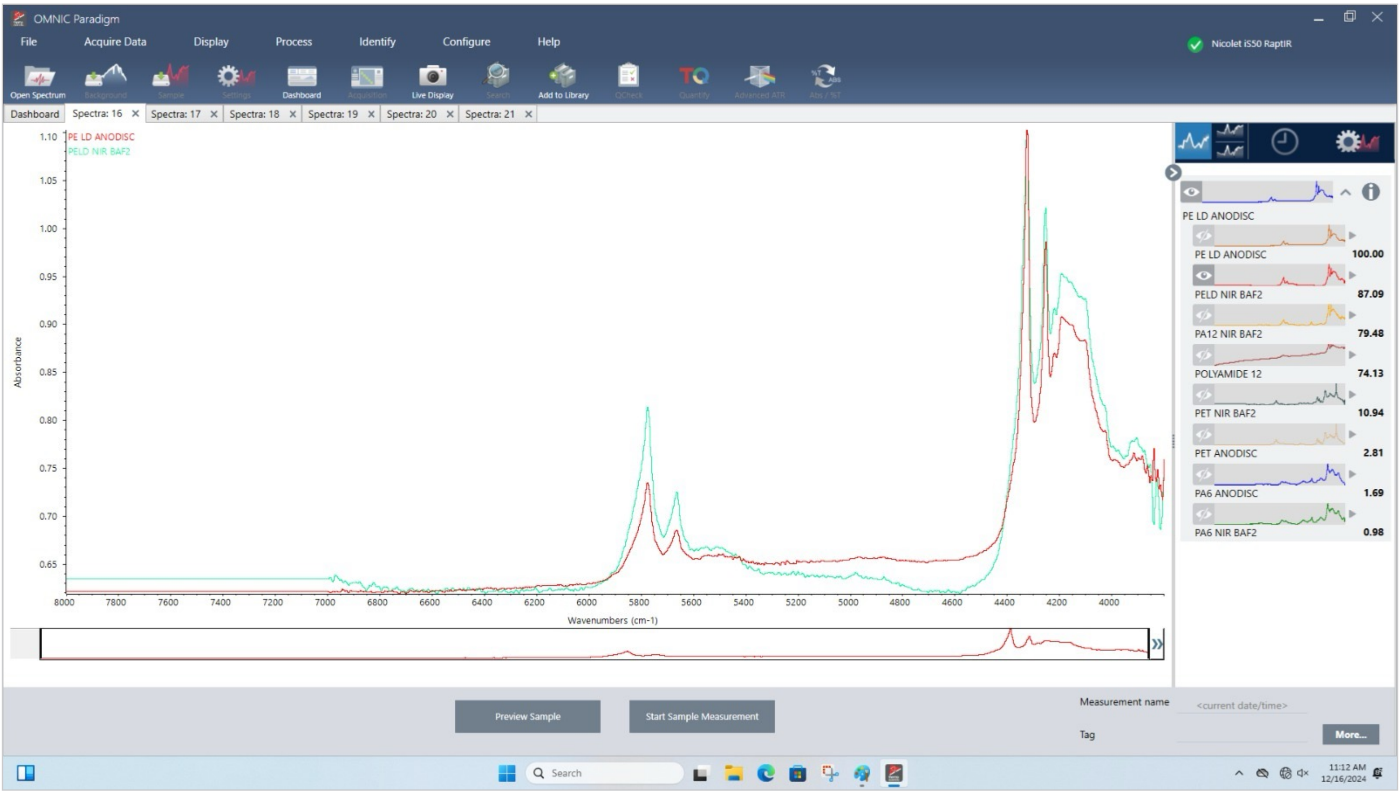

Figure 6. LDPE microplastic on Anodisc filter in NIR region. The spectral range is the same of the spectrum in the library.

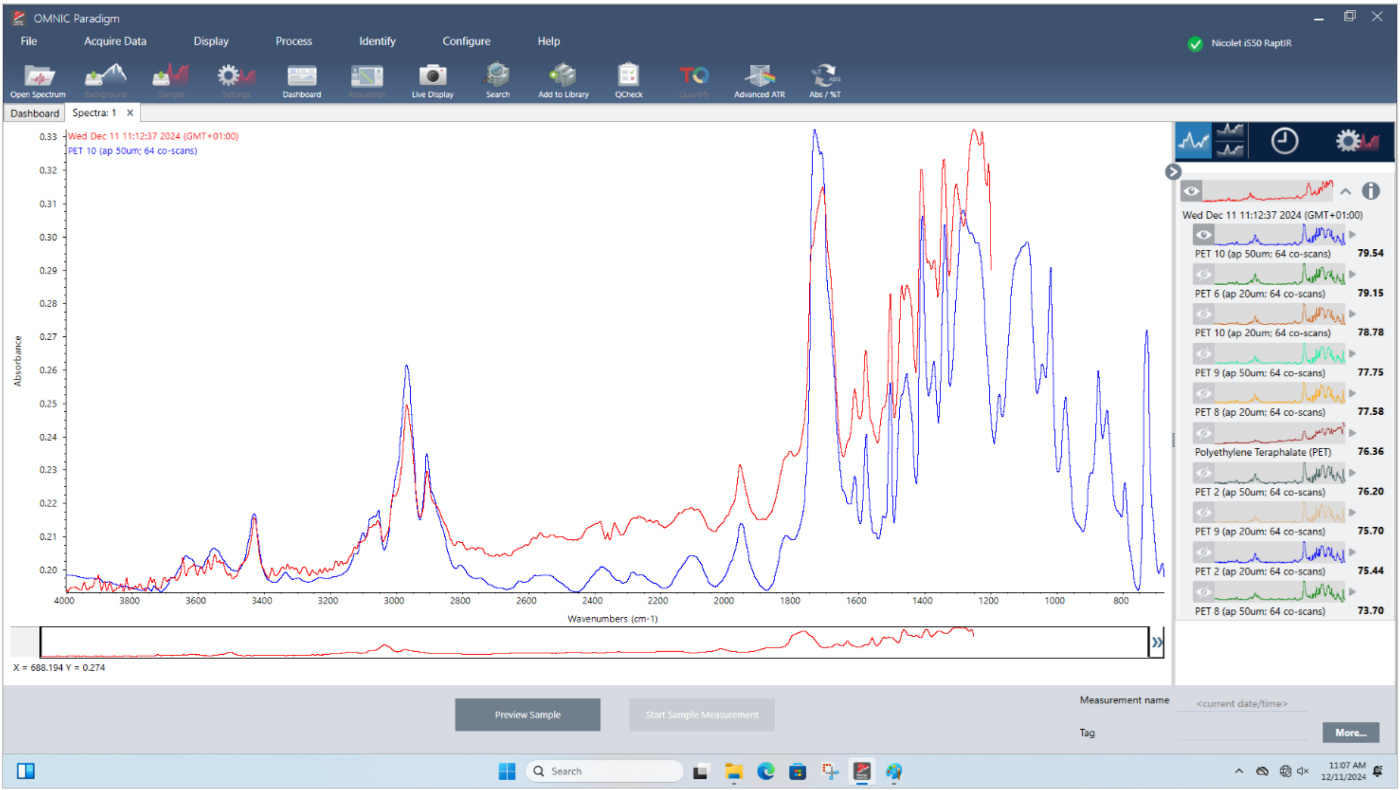

Figure 7. PET microplastic on Anodisc filter in mid-IR region. It is possible to identify the MP, but the spectral region is limited.

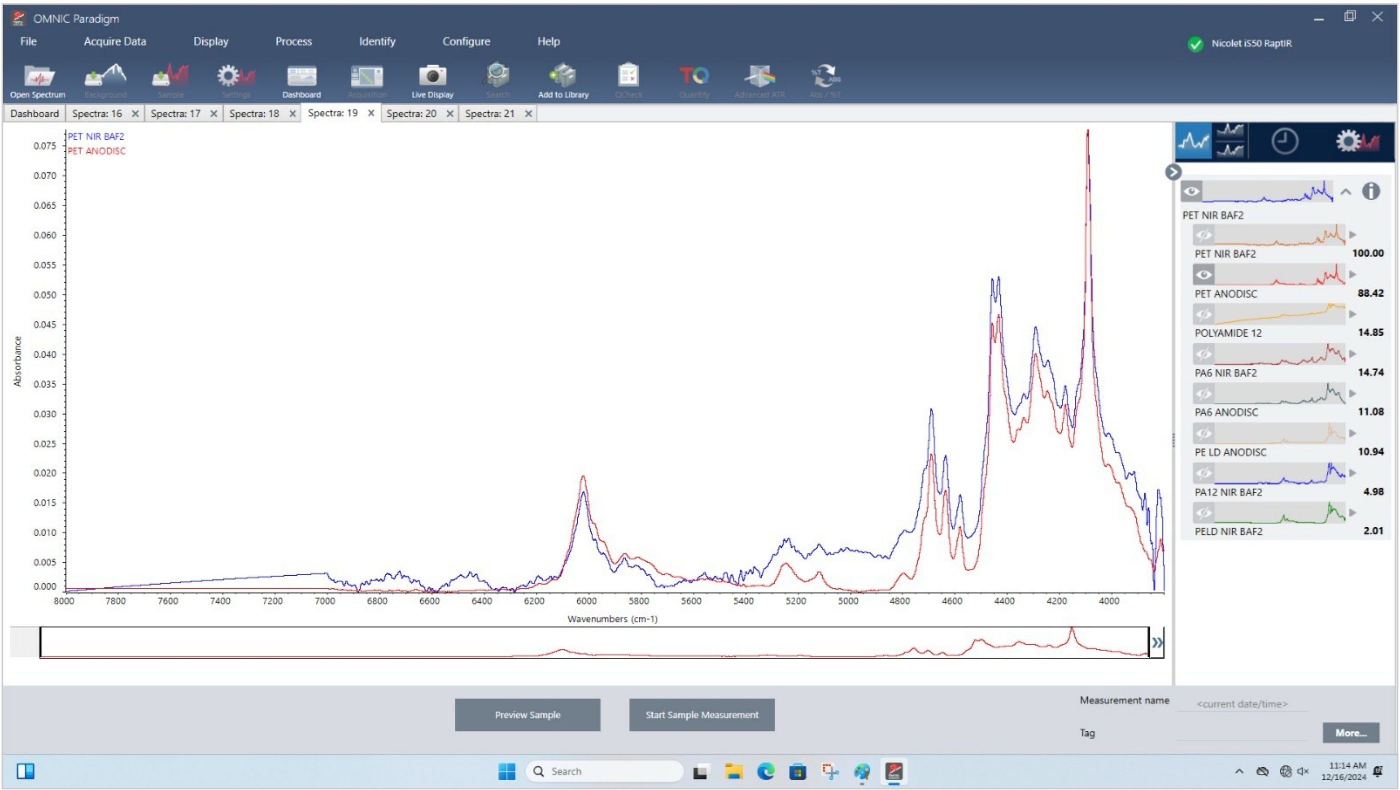

Figure 8. PET microplastic on Anodisc filter in NIR region. The spectral range is the same of the spectrum in the library.

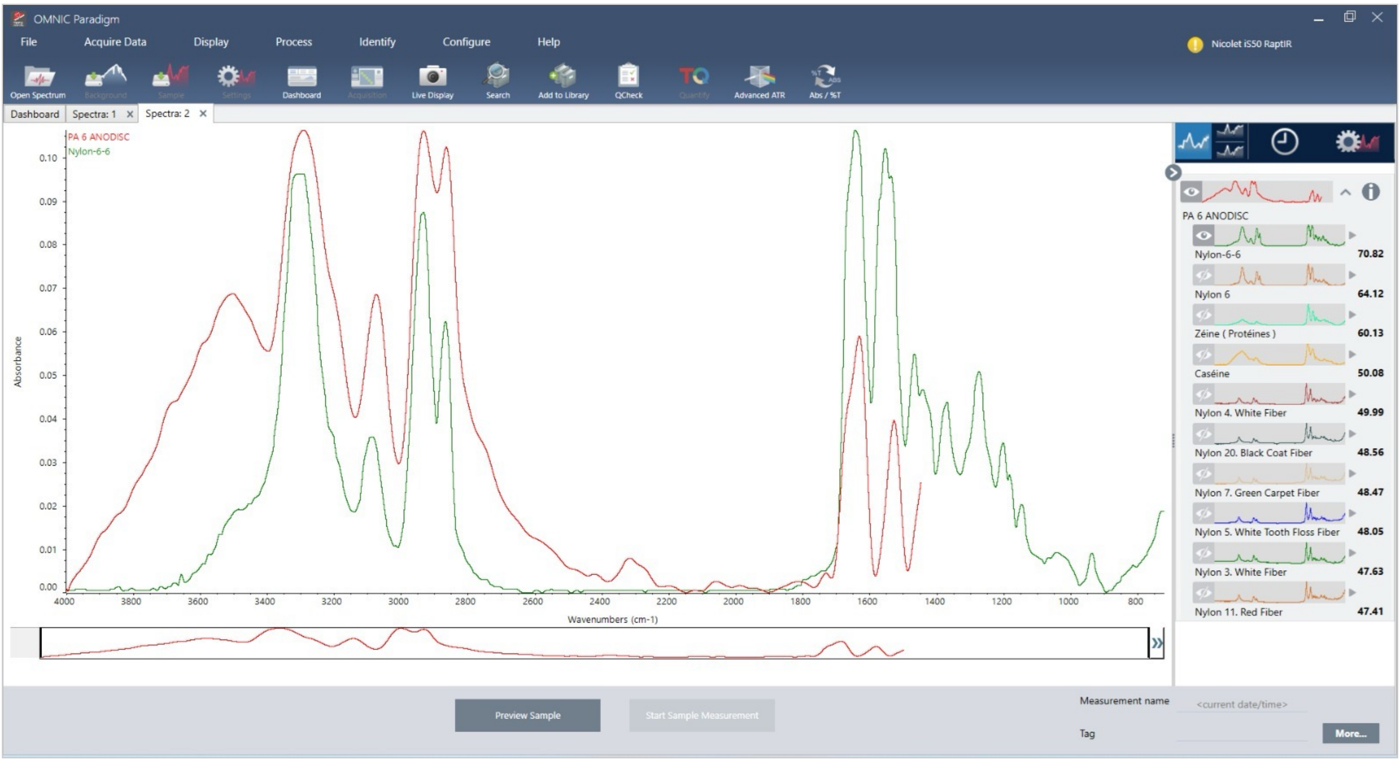

Figure 9. Polyamide 6 microplastic on Anodisc filter in mid-IR region. It is possible to identify the MP, but the spectral region is limited.

Figure 10. Polyamide 6 microplastic on Anodisc filter in NIR region. The spectral range is the same of the spectrum in the library.

MPs in wet deposition samples

Wet deposition samples were then analyzed employing the same FTI-NIR technique used for reference polymers. Visual mosaics were obtained (Figure 11a), and the particles were selected using the software (Figure 11b). Then, the particles were analyzed, spectra were obtained from each particle, and all were compared to the NIR libraries created before. From our first results, SMPs of LDPE were successfully identified with a match >85%, and their average size in length was 250 µm. For instance, a plastic particle with a length of 249 µm in length (Figure 11b) was successfully identified with a match at 93% agreement (Figure 11c).

Hence, the Anodisc filters were confirmed to be reliable for SMPs analysis in real environmental samples using FTIR-NIR spectroscopy.

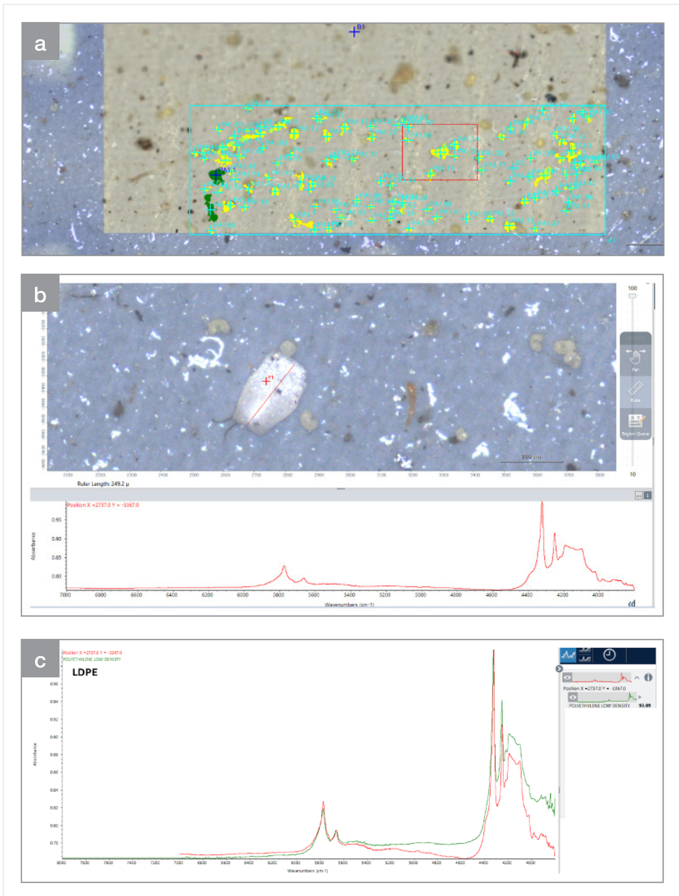

Figure 11. A visual mosaic obtained from wet deposition samples analyzed (a) on Anodisc filters; (b) a visual of an unknown sample and its spectrum; (c) library spectra of LDPE.

Conclusion

FT-NIR spectroscopy was confirmed to be a viable technique for the analysis of SMPs in environmental matrices. The technique offers fast analysis times and the potential for real-time monitoring. It can analyze a wide range of polymer types, from low to high densities, as well as sample matrices when an appropriate pretreatment methodology is followed. Further, it is a non-destructive technique since it allows for further analysis in the optics of SMPs' cross-validation methodology approach. This ensures consistent and reliable results in contrast to the lack of standardized MP procedures to date.

Further investigations are needed to increase the overall SMPs library with this technique.

Anodisc filters were confirmed to be the proper support for this analysis. They demonstrated the effectiveness and accuracy of the applied methodologies for SMPs' assessment in real environmental samples.

Further developments need to widen the environmental matrices to be analyzed to evaluate SMPs in different environmental conditions.

References

1. Corami, F., Rosso, B., Morabito, E., Rensi, V., Gambaro, A., & Barbante, C., 2021. Small microplastics (< 100 µm), plasticizers and additives in seawater and sediments: Oleo-extraction, purification, quantification, and polymer characterization using Micro-FTIR. Science of The Total Environment, 797, 148937. https://doi.org/10.1016/j.scitotenv.2021.148937
2. *"Quantification and chemical identification of small microplastics (SMPs <100 µm) in wet and dry deposition from an urban area", submitted to Environmental Pollution, under review (10/2024).*

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