



A Microsampling Solution for Identification of Microplastics in the Environment

Introduction

One of the main constituents of marine pollution, microplastics have been documented in our watersheds as far back as the 1970's [1]. Microplastics are differentiated from other plastic particles as determined by sizes less than 5 mm. Degradation of larger pieces and direct waste run off are noted as likely sources of most microplastics. Not only do plastic materials themselves cause harm to fish and invertebrates in our waters, but microplastics have been noted as a means of concentrating toxic, hydrophobic chemicals commonly found in our waters. Studies into the various effects of plastics on the marine ecosystem are ongoing and constantly shedding light on the widespread effects of these pollutants.

Fortunately, microplastics are primarily comprised of organic polymers that are easily characterized using infrared (IR) spectroscopy. In the case of sub 5 mm microplastics, IR microscopes play a crucial role in not only visualizing, but also identifying the plastic particles. The study of small particles with a microscope that interfaces to a Fourier transform infrared (FTIR) spectrometer is commonly referred to as IR microspectroscopy.

Instrumentation

The SurveyIR microspectroscopy accessory seen in Fig. 1 was used to image and analyze all samples. When coupled with modern, compact and portable FTIR spectrometers, SurveyIR provides a transportable, integrated solution for field measurements.

IR spectra were recorded at 8 cm^{-1} resolution using a room temperature L-alanine doped, deuterated triglyceride sulfate (DLATGS) detector with a potassium bromide (KBr) window and KBr beamsplitter. The SurveyIR's all-reflecting optics allowed for data collection from 4000 to 400 cm^{-1} . Data collection times were a minute or less for all spectra. Samples run in reflection/absorption were collected with an aperture mask corresponding to 60 μm at the sample. An aperture mask corresponding to 250 μm at the sample was used to collect spectra in attenuated total reflection (ATR) mode.



Figure 1: SurveyIR microsampling accessory mounted in a FTIR spectrometer sample compartment.

Materials and Methods

Samples were collected from waters near New York City. The first two samples were from water filtered from the Hudson River, downstream from the Newtown Creek wastewater treatment facility. The filter was then allowed to dry and mounted to a standard 1" X 3" microscope slide.

The second set of samples were taken from oysters purchased at a local seafood market. The samples were collected through a series of separation techniques and the remnants filtered and mounted in the same fashion as the first set.

A diamond internal reflection element (IRE) was used in the ATR attachment. The ATR method was used to screen larger particles without any subsequent sample preparation, for all filtered samples. For ATR analysis a 1" X 3" low-E glass microscope slide was placed underneath the standard microscope slide for added support. Smaller samples were transferred to low-E glass microscope slides and flattened using a roller knife before being analyzed.





Results and Discussion

The white, jagged plastic particle seen in Fig. 2 was first analyzed directly on the filter. Due to particles and fibers overlapping the suspected microplastic, it was transferred to a clean low-e glass microscope slide for further analysis.



Figure 2: White plastic particle viewed under oblique illumination through the diamond ATR.

The irregular nature of the transferred particle suggests it was sheared or broken off a larger piece rather than a small microbead or similar micro-plastic. Looking at the IR spectrum in Fig. 3, a good library match (Fig. 3, magenta) is noted for oxidized polyethylene, a very common plastic material.

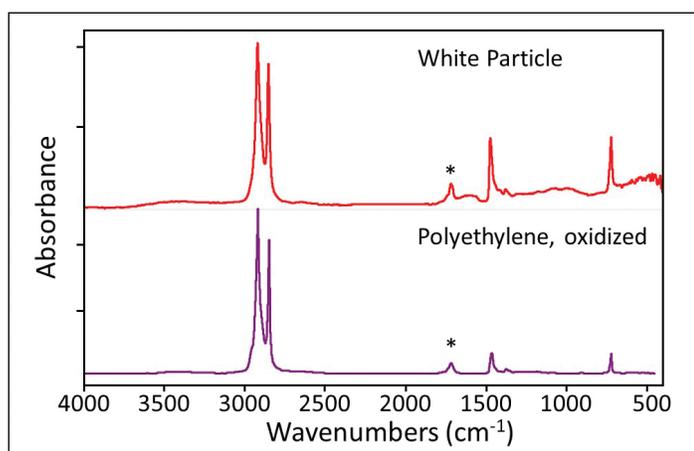


Figure 3: IR spectra of the white particle from Fig. 1 (top, red) and the best library match (bottom, magenta).

The appearance of the band at 1718 cm^{-1} (*) is due to oxidation of polyethylene. The observation of oxidation in the polyethylene spectrum further suggests this particle was broken off a larger piece of plastic as environmental elements degraded the plastic material. Due to the varied and numerous applications of polyethylene and the fact that no further components were identified within the plastic, it is challenging to determine the probable source of this particular contaminant. Other types of plastic have more unique uses that can aid to determine the originating source, as seen in the next example.

The red tinted particle in Fig. 4 was originally a small, $20\text{ }\mu\text{m}$ in length, red fibrous material.



Figure 4: Flattened red fiber (approx. $60\text{ }\mu\text{m}$ in diameter) viewed in transmitted illumination using the SurveyIR microscope.

The IR spectra in Fig.5 shows that the major component of the red fiber (top, red) is in good agreement with the library match, polypropylene copolymer (bottom, purple). Additional bonds are observed, consistent with a minor component.

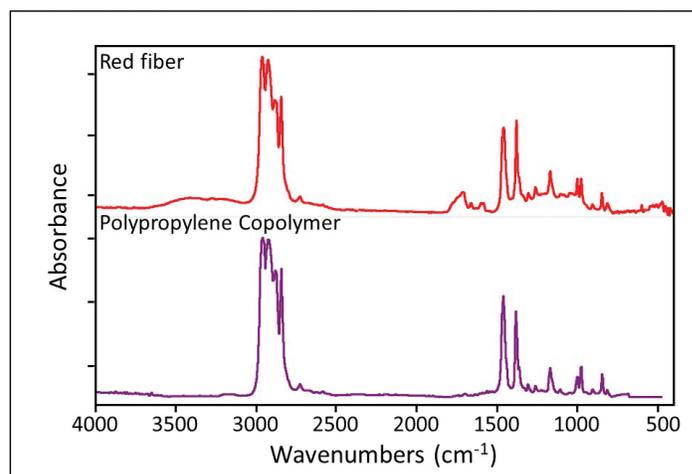


Figure 5: IR spectra of the flattened red fiber (top, red) and the top library match (bottom, purple).





Polypropylene copolymers are commonly used in carpet manufacturing and carpet could very well have been the source for the red fiber contaminant. Altogether, several plastic particles were found in the collected water samples with the majority size of those particles ranging from 20-250 μm .

After investigating microplastics in the Hudson River, the team began to study how microplastic pollution migrates into the marine ecosystem. By examining mollusk remains, the team hoped to identify microplastics in the environment that humans could ingest. In Fig. 6 a small pink particle is observed. The sample was flattened on a low-E glass substrate.

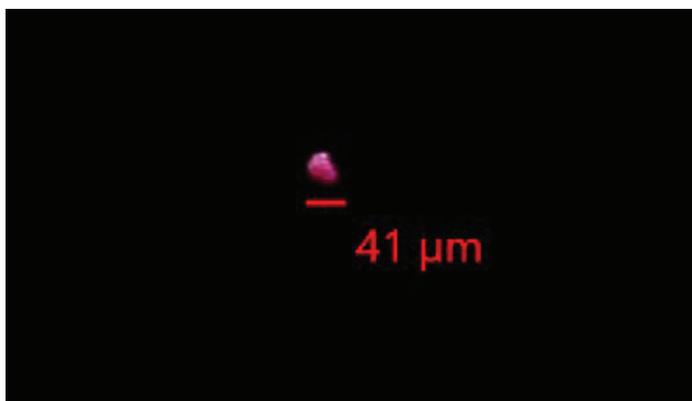


Figure 6: Small pink particle imaged with oblique illumination using the SurveyIR microscope on a low-E glass microscope slide.

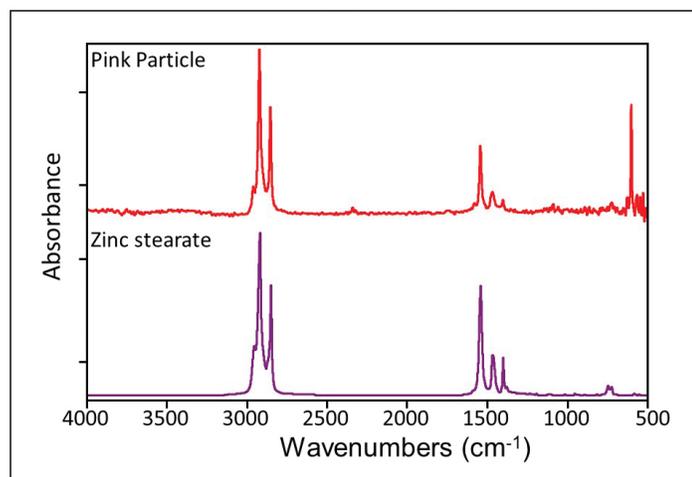


Figure 7: IR spectra of the pink particle (top, red) and the best library match, Zinc Stearate (bottom, magenta).

The color of the plastic material is due to a dye used in the separation process to aid in visual identification of potential microplastics. IR interrogation of the small pink particle, revealed a simple IR spectrum (top, red) with a good library match to Zinc Stearate (bottom, magenta), seen in Fig. 7.

Zinc Stearate is commonly used as a release agent in the polymer and rubber industry, as well as, in the cosmetic industry as a lubricant and thickening agent [2]. Zinc Stearate was the second most common particulate found in the oyster samples next to cellulosic fibers.

Similar to the Hudson River filtered water samples, mollusk samples contained an abundance of fibers. The composition of the fibers mainly consisted of cellulosic materials, most probably cotton, in various colors. However, the image in Fig. 8 shows another common man-made material found inside an oyster.



Figure 8: Flattened blue fiber imaged with transmitted illumination on a low-E glass microscope slide.

The appearance of the single blue fiber was smooth and rigid, contrasted to woven natural cotton fibers. The IR spectrum of the blue fiber in Fig. 9 (top, red) resulted in a good library match with a well-known plastic material, polyethylene terephthalate (PET) (bottom, magenta).



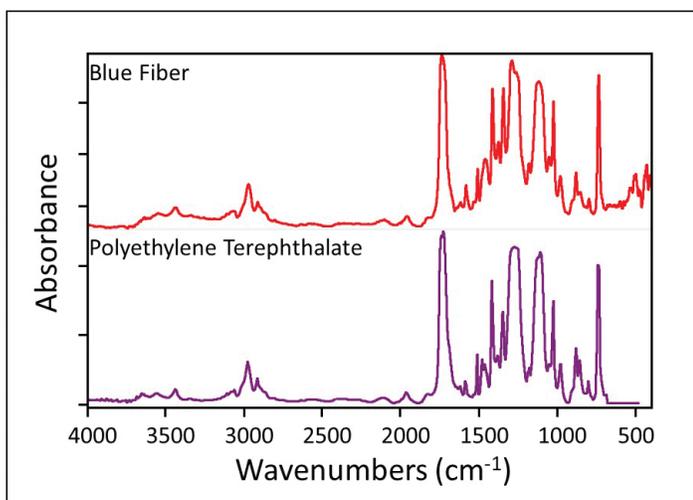


Figure 9: IR spectra of the flattened blue fiber (Top, Red) and the best library match, polyethylene terephthalate (Bottom, magenta).

PET is a very common plastic material used in everything from everyday water bottles to polyester clothing. For instance Dacron® fibers are composed of PET. The most likely source of the blue fiber is from an article of clothing. Microfibers have been noted by Verschoor, et al. and numerous others to shed during washing [3]. These fibers can be very small and pass through filtration systems, ultimately making their way into marine ecosystems.

Conclusion

As research identifies the far-reaching effects of manmade pollution on various ecosystems, microplastics have become an especially high priority research topic over the past few years. For instance, starting in July, 2018, the US will ban all microplastics in cosmetics. As shown in this application note, clothing, larger plastic debris and possibly cosmetic products were the sources of the microplastics found in both the mollusk and Hudson river water samples. To aid researchers studying various avenues of microplastic pollution, FTIR microspectroscopy can provide the necessary composition information to identify microplastics. The added flexibility of the SurveyIR microsampling accessory enhances microplastic research. As plastic production continues to thrive it's imperative we understand the effects microplastics have on our environment.

References:

1. Carpenter, E.J., Anderson, S.J., Harvey, G.R., Miklas, H.P., & Peck, B.B. Polystyrene spherules in coastal waters. *Science*, 17(4062):749-750 (1972).
2. David J. Anneken, Sabine Both, Ralf Christoph, Georg Fieg, Udo Steinberner, Alfred Westfechtel "Fatty Acids" in *Ullmann's Encyclopedia of Industrial Chemistry 2006*, Wiley-VCH, Weinheim. doi:10.1002/14356007.a10_245.pub2
3. Verschoor AJ, de Porter L, Roex, E (2014) Quick Scan and Prioritization of Microplastic Sources and Emissions, RIVM Advisory Letter 250012001, National Institute for Public Health and Environment, Bilthoven, The Netherlands. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5099352/>

Acknowledgment: Czitek acknowledges the Lamont Doherty Earth observatory, Columbia University, for providing the samples used in this study.

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