



Application Note AN M144

Analysis of Microplastics using FTIR and Raman-Microscopy

The omnipresent occurrence of microplastics and the expected consequences are subject of modern research and the topic receives more and more public awareness. Due to the fact that plastic waste is degrading only very slowly the amount of microplastics in the environment is steadily increasing. In particular, the contamination of the world's oceans is a problem. Currently, an annual entry of microplastics into the world's oceans of about 210 g per person or a total of approximately 1.5 megatons is estimated.^[1] The uptake by marine organisms and fish results in a contamination of the human food-chain through microplastics including substances such as plasticizers or adsorbed pollutants.

According to definition, polymer particles with a diameter of less than 5 mm are referred to as microplastics particles (MPP). Depending on their origin, they are further subdivided into primary and secondary particles. Primary particles are those which are specifically produced industrially like for instance peeling particles in cosmetic products. Secondary microparticles are formed by physical, biological and chemical degradation of macroscopic plastic parts and are the main source of all released microparticles. They are mainly formed by the degradation of improperly disposed plastic waste, tire abrasion and washing of synthetic textiles.

Keywords	Instrumentation and Software
Microplastics	HYPERION FTIR Microscope
Particle analysis	SENTERRA II Raman Microscope
Polymers	OPUS Spectroscopy Software

A careful analysis of the MPP allows drawing conclusions about both origin and formation and to determine the degree of contamination. It is in many respects demanding, since generally the concentrations are relatively low, and particles of biological or inorganic origin such as chitin, cotton fibers or sand grains are also typically detected during sampling. Therefore, a complex sample preparation with the aid of sieves, density separation methods and oxidative or enzymatic steps for the removal of interfering organic components is necessary first.

After separation, various methods for chemical identification are used. A simple procedure determines the density and the C:H:N-ratio from microplastics particles in order to get a coarse classification.^[2] However, a clear determination of the polymer type is not possible with this method, the sample throughput is low and smaller particles cannot be analyzed this way.

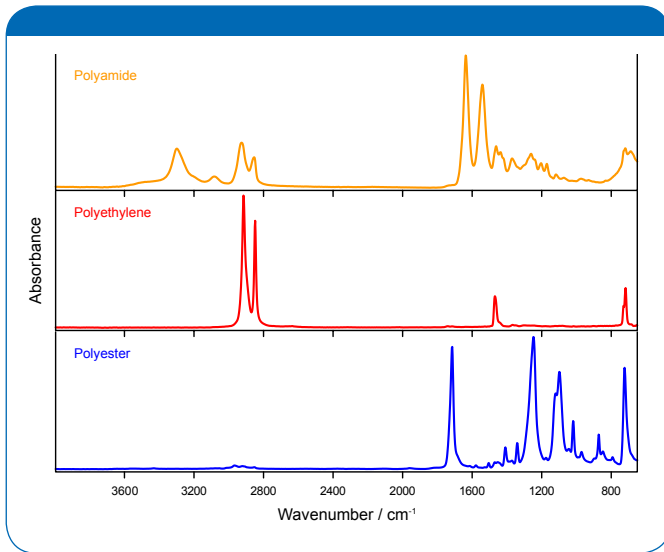


Figure 1: IR-spectra of different polymer types.

Another method is the pyrolysis-gaschromatography in combination with mass spectrometry.^[3] This method allows a reliable determination of the polymer type. However, the particles have to be manually placed into the pyrolysis tube thereby significantly reducing the sample throughput.

A high sample throughput combined with reliable identification of even the smallest particles is possible with microspectroscopic FTIR and Raman spectroscopy. Both methods are universally applicable and permit the selective analysis of individual particles with a size of a few micrometers. The rapid analysis of larger accumulations of microplastics particles is also possible by means of automated grid measurements.

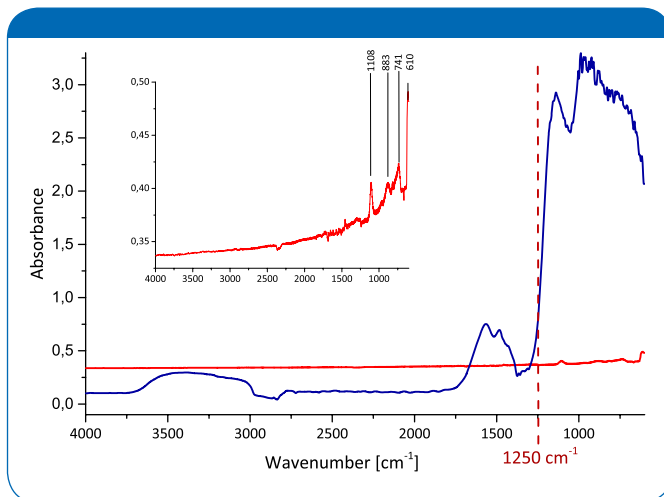


Figure 2: Comparison spectrum of a silicon- (red) and alumina-filter (blue).^[6]

FTIR analysis of microplastics

Fourier transform infrared (FTIR) spectroscopy is a proven method for the identification of all types of polymers. It allows a reliable differentiation between substances of natural and synthetic origin and allows determining the polymer type (see figure 1). Typically, the identification is carried out by means of an automated comparison against extensive spectral libraries.

With conventional FTIR spectrometers, it is already possible to easily examine larger microparticles. In comparison, FTIR microscopy allows the analysis of single particles with a size of only a few micrometers. Depending on the size of the particle, it is even possible to record several spectra at different points on a single particle.

The most frequently used measurement geometry for MPP analysis is transmission. Here, the particles have to be prepared on an IR-transparent material and must not exceed a maximum layer thickness, since otherwise saturation significantly reduces the spectral quality. Aluminum oxide filters which have a usable spectral range between 3800 and 1250 cm^{-1} are often used as the carrier material and allow the MPP to be measured directly on the filter substrate.^[4,5] A relatively new and promising filter material is silicon that can be produced with 10 μm -sized pores by means of a photolithographic etching process and has virtually no restrictions with respect to the spectral range. Figure 2 shows the transmission spectrum of such a Si filter (red) compared to a conventional alumina filter (blue).^[6]

The measurement itself can be performed in two ways, either discrete points on the sample are defined and measured manually or automatically, or one uses a detector-array which is able to measure thousands of spectra in parallel. These so-called focal planar array (FPA) detectors consist of a matrix of typically 64x64 detector elements and can thus capture 4096 infrared spectra in one operation. This is by far the most frequently used method, since it allows even larger surfaces to be measured in a relatively short time.

The Bruker HYPERION 3000 microscope (see Figure3) is equipped with an FPA detector which can have up to 128x128 detector elements. Its lateral resolution is only limited by the diffraction of light. Being very flexible, the HYPERION allows the use of different objectives and measurement techniques such as ATR, transmission, reflection and GIR. By combining the FPA detector with a motorized sample stage, even larger areas can be analyzed in a short time.



Figure 3: HYPERION 3000 FTIR imaging microscope coupled to an INVENIO spectrometer.

Literature example: Detection of false positive MPP

Gerds et al. were able to show, that even after a density separation with $ZnCl_2$ -solution ($\rho = 1.5 \text{ g/cm}^3$) the majority of the particles still can consist of inorganic material resulting in false positive results and the determination of a too high microplastics content.^[7] As the FPA-based analysis with a HYPERION 3000 microscope revealed, only 1.4 % of the particles analyzed were actually MPPs. The predominant rest of the particles consisted of quartz (see Figure 4) that, with a density of about 2.65 g/cm^3 , in principle should have been separated. This shows how important a careful spectroscopic analysis is, since this allows to safely identify such false positive particles.

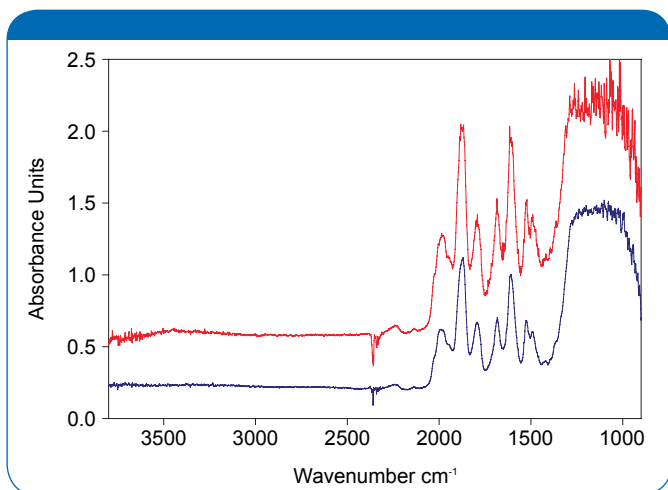


Figure 4: FPA-comparison spectra of a quartz-reference (blue, Merck p.a.) and a typical particle (red).^[7]

Literature example: Automated analysis of filters

An example for the analysis of large surfaces is shown by Gerds and co-workers.^[5] They analyzed a sediment-sample from the German Bight. The MPP were separated with a $ZnCl_2$ -solution. After filtration and enzymatic purification and a further density separation process, the sample was filtered through an alumina filter. By means of FPA-based measurements, a complete 25 mm diameter alumina filter was analyzed and subsequently automatically evaluated. With dedicated software it was possible to evaluate files with up to one million spectra and to graphically display the results. Figure 5 shows such an image that displays size and polymer type of the analyzed particles.

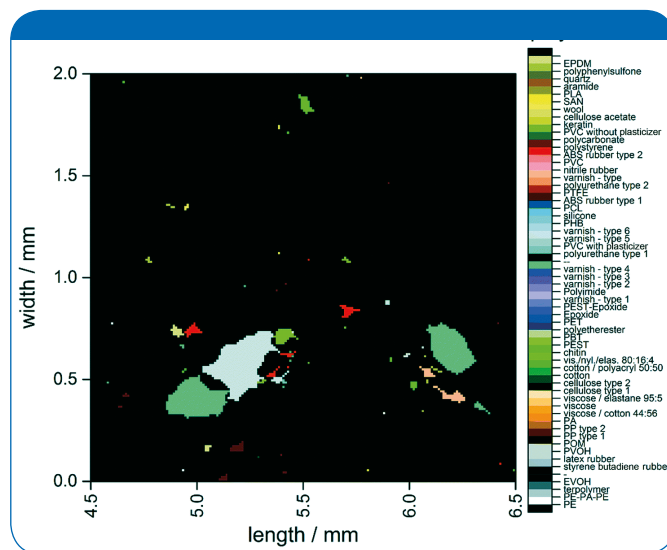


Figure 5: Color coded analysis of the polymer types on an alumina filter. ^[5]

Literature example: Differentiation of viscose and cellulose

The synthetically produced viscose and the natural cellulose are from the chemical side practically indistinguishable since both consist of β -1,4 linked β -D-glucose units. If one compares the spectra of both materials there are certain characteristic differences that can be used for differentiation. Figure 6 shows an example spectrum of both cellulose (blue) and viscose (red). According to the research of Lendl and co-workers the differentiation of rayon/viscose and natural cellulose fibers is possible based on IR-spectra that were measured using the ATR-technique.^[8] Differentiation was possible with ATR crystal materials. Also, the different moisture content of the fibers was not an obstacle for the identification. The natural cellulose has bands which do not appear in the synthetic cellulose or are only weakly expressed (1425 , 1105 and 1051 cm^{-1}). Differentiation of spectra measured in transmission was less reliable due to spectral artifacts related to fringing and sample thickness.

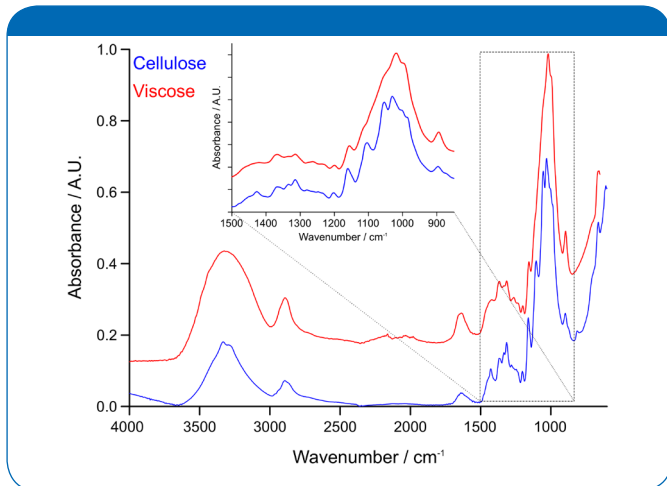


Figure 6: ATR-Spectra of natural cellulose (blue) in comparison to synthetic viscose (red).

Raman-analysis of microplastics

As a complementary method, Raman microscopy is used for the analysis of MPP enabling a contactless sample measurement. In doing so, the inelastically scattered light of a laser beam is analyzed. Typically, a CCD sensor is used as a detector with laser wavelengths of 532 and 785 nm. When compared to the IR-microscopy, the lateral resolution of the Raman microscope is higher and particles with a size in the lower micron range can be identified. In the case of inorganic samples, the Raman technique also offers a better differentiation. A disadvantage of the technique, however, is that many samples show fluorescence. The typically broad and intense fluorescence signal can even completely cover the signal of the sample. This can be circumvented very often by the choice of a larger laser wavelength.

Bruker's SENTERRA II microscope allows the use of up to four excitation lasers including a near-infrared laser with a wavelength of 1064 nm. Accordingly, the optimal sample wavelength can be selected for any sample.

A literature study on the use of Raman microscopy shows the analysis of MPP in deep sea sediments by Janssen and co-workers.^[9] Up to one MPP per 25 cm² was detected and identified with a SENTERRA Raman-microscope.

In another recent study, the prevalence of microplastics in the northwestern pacific ocean was investigated by the SENTERRA II and the mainly contributing micro plastic pollutants identified as polyethylene (57.8%), followed by polypropylene (36.0%) and nylon (3.4%).^[10]

Summary

FT-IR microscopy has established itself as the standard method for the analysis of MPP; it can be applied universally and enables a secure identification of all polymer types. Mapping measurements or FPA imaging allows determining thousands of MPPs in a fully automated manner. Raman microscopy is a complementary method with which even the smallest particles can still be measured. However, due to the fluorescence of some samples, these are often difficult to measure.

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