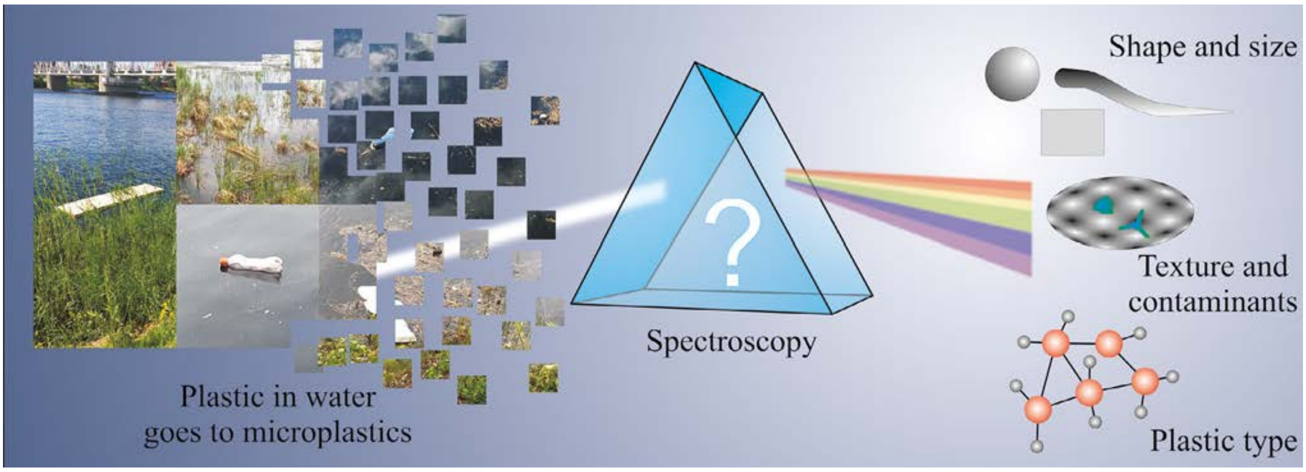
OPTICAL SPECTROSCOPY FOR THE DETECTION OF MICRO- AND NANOPLASTICS IN WATER

Matthieu ROUSSEY*, Benjamin O. ASAMOAH, and Kai-Erik PEIPONEN
Department of Physics and Mathematics, Institute of Photonics, University of Eastern Finland, P.O. Box 111, 80101 Joensuu, Finland
***matthieu.roussey@uef.fi**



Optical spectroscopy techniques offer an additional dimension to classical methods for the detection and identification of complex particles in complex environments. We present some of these techniques applied in the frame of the fight against the plague of Micro- and Nano-plastics.

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Plastic products have much importance for human beings in our everyday life. The resulting wastes from these products are usually sent for recycling especially in developed countries. Despite the contemporary regulations and suggestions to recycle plastics, this has not been the case in the past. Moreover, in less developed countries, the recycling of local wastes is still an issue. Consequently, lots of plastic litter have been buried in soil or ended up in the seas and lakes, where light plastics are floating, and heavier ones settle at different depths in these environments. The presence of plastics and their degradation into micro- and nanoplastics (MNPs, 100nm < MP < 5mm, NP < 100nm), due to UV-radiation and weathering, for example, pose a threat to the environment. There is scientific evidence that both MPs and NPs can accumulate in Flora and Fauna. Associated health-related issues, such as the toxicity of MPs and NPs, are currently under continuous investigation. Whatsoever, the detection of MPs and NPs is still in its infancy and, probably, our current knowledge of these particles is still limited.

Optical spectroscopy or spectrophotometry is a field of Photonics for the investigation of the interaction of light with matter. It yields information on the nature of matter through spectral response, *i.e.*, how different wavelengths are transmitted, reflected, absorbed, or re-emitted by an analyte under a particular illumination. Spectroscopy represents nowadays one of the most powerful techniques of analysis in domains of medicine, pharmacology, biology, chemistry, and environment. For decades, these methods have been improved and some of them are ready to be applied for the detection and identification of MNPs.

Plastics are man-made materials mainly based on polymers, *i.e.*, very large molecules that may be petroleum derivatives. Depending on the monomer molecule composing their long polymeric chain, plastics may have different physical and chemical properties that define their use. Ranging from containers, packaging, fabric to components used in industrial processes, plastics are everywhere for about 70 years. Since then, their production is in monotonic growth and so are the wastes. In one way or another, plastic particles end up in water, which is a perfect carrier of these particles to biological organisms. In addition to the complex nature of these particles, the host medium such as open water, wastewater, or tap water, can also be complex. Further to being small, various, and capable of hiding in the complex matrix, MNPs are preferential hosts for a multitude of organisms, such as bacteria or viruses, and other materials, such as heavy metals. Besides biological organisms, MNPs are also considered dangerous to human health. With all these complexities surrounding these particles and their hosts, spectroscopic techniques can reveal some relevant information about the particles elusive to other detection techniques.

There are some basic features of interest to characterize and identify MNPs. These include their size, abundance (especially in aquatic environments), and type. Although the problem is recent, there is already quite extensive literature reporting on the different detection and analysis methods for MPs [1]. For NPs, the situation is different since these particles are more difficult to detect; thus, identification and monitoring methods are still under development. A review focused on the different optical detection methods and the outlook of in-situ methods is presented in our recent paper [1]. While the size and shape of MNPs are typically obtained by imaging and microscopy, the identification of MNPs is principally based on optical spectroscopy. Thus, we deal with the current knowledge of MNPs detection by exploiting optical spectroscopy methods. Examples of optical spectra on transparent and translucent plastic particles, that are obtained from a municipal wastewater treatment plant, are presented.

OPTICAL SPECTROSCOPY FOR THE DETECTION OF MICROPLASTICS

Among the numerous variants of optical spectroscopy methods, we describe in this article only the most used ones in laboratories for the identification of MNPs. It is to be understood that most of these methods require sample preparation, which can be cumbersome for an inexperienced researcher or in-the-field measurements. This sample preparation usually starts by the collection of enormous amounts of water sediments and its filtering to isolate ultimately only a few particles. Then, samples are analyzed using the spectroscopy methods described in the following. Examples of methods (Raman microscopy, FT-IR, and transmission spectroscopy) are illustrated in Fig.1.

A very common technique is the Fourier transform infrared spectroscopy, FT-IR. This method is based on the measurement of the energy absorbed by molecules at the specific frequencies • • •

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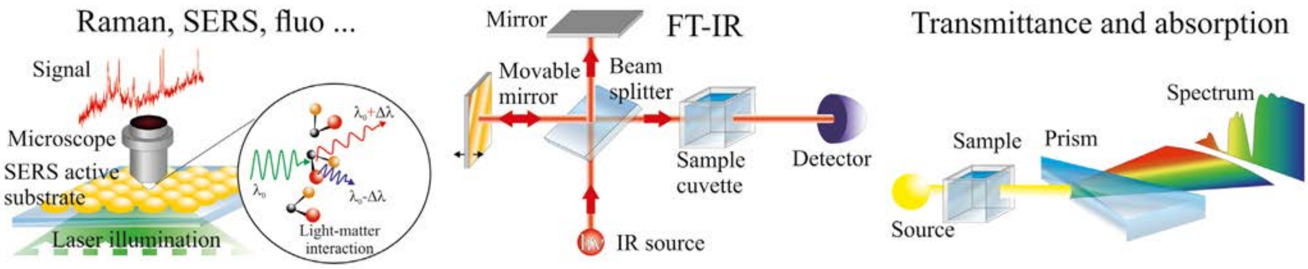


Figure 1. Illustration reproduced from [1] showing the principles of some optical spectroscopic techniques used in the detection and identification of micro- and nanoplastics.

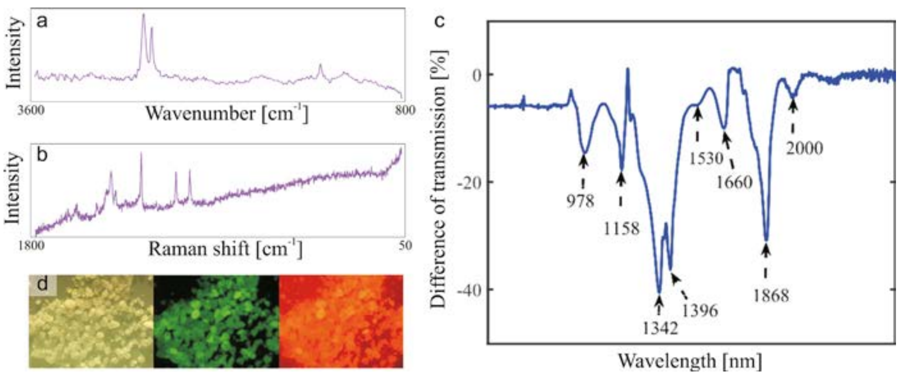
corresponding to the bonds linking atoms together. Very characteristic absorption peaks (Fig.2a) of plastics are certain in the infrared region of the electromagnetic spectrum, which makes FT-IR a suitable method for the identification of plastics. By measuring the position and shape of these peaks, one can identify, by comparison with a previously established database, the different types of MP particles. A limitation in size, however, exists, but by integrating a microscope with an FT-IR, the detection limit can be improved to detect particle sizes down to 10µm. Extensive details are given in the review article by Veerasingam *et al.* [2].

Another important technique used in the identification of the MNPs is the so-called Raman spectroscopy [3], which assigns a unique signature to a particular molecule, see Fig.2b. Based on the elastic scattering of photons by matter, a Raman spectrum gives the difference in energy between absorbed and re-emitted photons. This is quantified by the Raman shift, which depends on the vibrational state of each bond in a molecule. A Raman spectrometer can also be coupled to a microscope, which enables the detection of smaller particles (< 1µm). Raman spectroscopy is probably the most precise method for MP analysis since it provides reliable results over a relatively large (~ 50cm^{-1}) spectral range. However, the resulting weak Raman signal from this spectroscopic method and the difficulty in sample preparation reserves the method for experts only.

A third type of spectroscopy used in MPs identification is based on the study of the simple transmission spectra of samples [4,5]. Unlike FT-IR and Raman spectroscopy, the result of such a measurement does not provide a quantitative identification of the plastic types. Usually, peaks or dips of a transmission spectrum may overlap hiding some features important for the determination of the constituents. Typically, the spectral data is analyzed by combining the knowledge on the complex refractive indices of pristine plastics and that of the environment and performing advanced data processing of the spectral response of the analyte, such as investigating the difference of transmission, see Fig.2c. Once the protocol is set, transmission spectroscopy becomes a fast and easy-to-implement method to determine the composition of samples. No sorting is necessary, and a lower level of filtering is required.

One of the challenges in detecting MNPs in water environment is the low concentration of these particles. Therefore, it is typically needed to filter large quantities of liquid before obtaining a significant amount of MNPs to be characterized. For low concentration samples, fluorescence spectroscopy is very efficient especially at the counting phase of the sorting. This method is improved by using dyes, for instance, Nile Red, enabling easier observation as shown in Fig.2d. A technique recently applied in the detection and identification of MNPs involves the use of hyperspectral imaging allowing simultaneously the measurement of the shape (imaging) and the determination of the type (spectrum) of the particle. The data processing of the huge data files collected by such cameras is the key to providing relevant results. This

Figure 2. Examples of results obtained with different spectroscopic methods applied on microplastics identification. a) FT-IR [1], b) Raman microscopy [1], c) Transmission spectroscopy [1,5], d) Fluorescence microscopy [6].



processing is often based on machine learning including algorithms such as principal component analysis or other classification methods. The method is used for monitoring large geographical areas, *e.g.*, coastal monitoring [7]. This is a promising method for the detection of large microplastics (> 100µm).

In most of the methods described in this article, samples must be filtered, sorted, and then analyzed. It represents a huge work and therefore a need for fast and portable devices, which has emerged in the recent past years. Several techniques based on optical spectroscopy can be combined into handheld apparatus. However, the integration of laboratory-based techniques into smaller devices leads to a decrease in device resolution and sensitivity, unfortunately. However, in return, a large number of samples can be analyzed.

CONCLUSION

For all methods developed so far, the drawback comes from the matrix, *i.e.*, the environment surrounding the plastic particle. It may indeed contain all types of other particles that may perturb the identification of the MNPs. Typically, organic materials in wastewater or freshwater lead to fuzzy results, which makes filtering an important part of the analysis process.

Micro and nano-plastics are already everywhere, and their amount increases considerably at every moment. Many years of research and individual effort on limiting our usage of plastic are needed to achieve a significant change in this trend. Our duty as researchers is to now provide the tools to understand the problem deeply. Monitoring, detecting, and identifying MNPs is crucial as an initial step. However, the removal of these particles is even more important, and efforts are currently directed towards the development of techniques for such a task.

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REFERENCES

[1] B.O. Asamoah *et al.*, Polymers **13**, 730 (2021)

[2] S. Veerasingam *et al.*, Crit. Rev. Environ. Sci. Technol., 1-63 (2020)

[3] P.M. Anger *et al.*, TrAC Trends Anal. Chem. **109**, 214-226 (2018)

[4] K.E. Peiponen *et al.*, Chemosphere **214**, 424-429 (2019)

[5] B.O. Asamoah *et al.*, Polymers, **13**, 871 (2021)

[6] W.J. Shim *et al.*, Mar. Pollut. Bull. **113**, 469-476 (2016)

[7] S. Merlino *et al.*, Remote. Sens. **12**, 1260 (2020)