Photo: Adobe Stock, G. Wahl

Raman Microspectroscopy

How to detect microplastics

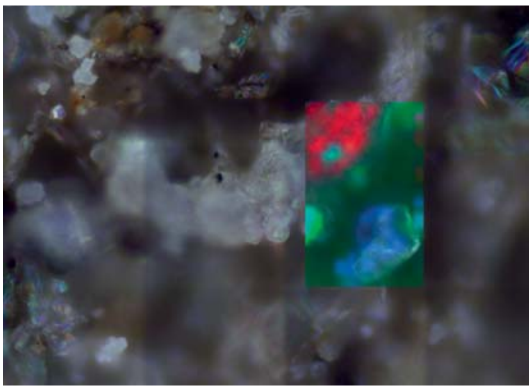
The contamination of aquatic environments with microplastics is of increasing scientific and public concern. Microplastics with sizes down to one micrometre can be identified and quantified by Raman microspectroscopy. Further development of automated analysis for smaller particles is needed.

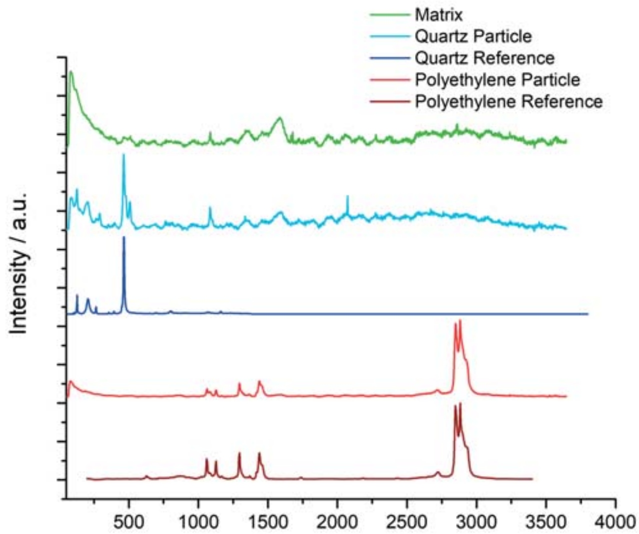
Synthetic polymer (or plastic) materials have become an inherent part of our everyday lives. Being lightweight, durable and corrosion-resistant, they offer remarkable technological and medical benefits. On the other hand, due to their high resistance to degradation, plastic materials accumulate in the environment. Plastic bottles, for instance, are expected to remain in the marine water for about 450 years. Therefore, it is not surprising that contamination with plastic materials and, especially, microplastics has been increasingly reported for marine, freshwater and terrestrial ecosystems.

Microplastics are defined as particles smaller than five millimetres, including both particles produced in this small size and those that result from fragmentation of larger plastic items.

What risks for environment and health?

Lethal consequences for aquatic organisms (seabirds, turtles, dolphins, etc.) which swallow, or are entangled in larger plastic debris, are well known. The potential harmful impact of microplastics on biota is also under discussion. The problem is the leaching of monomers and additives present in microplastics, since some of these substances have been proven to





Microscopic and 2D Raman images (left) as well as the corresponding Raman spectra of particles from river water. (images: N. P. Ivleva, sampling by A. S. Ruhl, analysis by P. M. Anger).

+++ Analytica Conference: Identification and quantification of microplastics, 11. April, 16.00, ICM, Saal 5 +++

be toxic, carcinogenic or endocrine-disrupting. Furthermore, microplastics can accumulate persistent organic pollutants or toxic metals from the aquatic environment, and can act as a vector for (pathogenic) microorganisms.

The small size of microplastics particles enables their ingestion by aquatic organisms from different trophic levels and with different feeding strategies. As a consequence, microplastics can enter the food chain and accumulate at higher trophic levels. Hence, there is a potential risk for humans consuming fish or mussels contaminated with microplastics. In this case, plastic litter will return to the original "culprits".

However, the actual impact of microplastic on the environment remains unclear despite an increasing number of studies for marine and freshwater biota. The reported results range from negative (including lethal) through no-effects up to detoxification (when the initial concentration of pollutants in organisms was higher than in ingested microplastics).

It is noteworthy that in most experiments very high concentrations of microplastics were used. Therefore, it is important to investigate the effects of microplastics under environmentally relevant conditions. However, the microplastics concentrations in the environment still remain uncertain. Depending on sampling, processing, and especially identification methods, the published values differ by several orders of magnitude. Although the concentrations of more than 10^5 microplastics particles per cubic metre were reported, most studies of water samples found fewer than one microplastics particle per cubic meter. Thus, reliable data on the degree of microplastics contamination for different samples will help enormously in the quest to assess the potential risks for the environment and human health.

Analytical methods for microplastics

The identification represents the crucial step in microplastics analysis. The commonly applied visual sorting can lead to a high level of false (positive and/or negative) results, especially for particles smaller than 500 micrometres. Quartz particles, for instance, are frequently mistaken for microplastics.

Detailed information on the polymer type of and additives found in microplastics can be achieved by thermoanalytical methods. For example, thermoextraction and desorption coupled with gas chromatography mass spectrometry (TED-GC/MS) can provide valuable data on the mass fraction of different polymer types in environmental samples. However, no information on the particle size distribution is available.

In contrast, spectroscopic methods – attenuated total reflection (ATR)-Fourier-transform infrared (FTIR) spectroscopy,

Umweltanalytik auf der Analytica

Mit dem 946 Portable VA Analyzer von **Metrohm (Halle A1, Stand 101)** wird die Schwermetallanalytik mobil. Herzstück der tragbaren All-in-one-Lösung ist ein Einwegsensor mit Plug-in-Design. Das Gerät misst Spurenkonzentrationen von Arsen, Quecksilber und Kupfer in wenigen Minuten.

A1-envirosciences (Halle A1, Stand 306) präsentiert mit dem Combustion-IC-System AQF-2100 einen Arbeitsplatz zur summarischen Bestimmung von per- und polyfluorierten Kohlenstoffverbindungen. Durch die Verwendung eines Keramikverbrennungsrohres und eines Fest-Flüssig-Autosamplers erlaubt das System die routinemäßige, automatische Bestimmung von extrahierbarem organisch gebundenem Fluor (EOF) und adsorbierbarem organisch gebundenem Fluor (AOF) in Anlehnung an die etablierten Halogen-Summenparameter AOX und EOX.

Der Spurengasanalysator PTR-TOF 6000 X2 von **Ionicon (Halle A2, Stand 441B)** besticht durch eine hohe Empfindlichkeit und niedrige Nachweisgrenzen. Das hochauflösende Flugzeitmassenspektrometer eignet sich auch für Flussmessungen biogener flüchtiger organischer Substanzen.

Die Gasanalysatoren der neoCLD-Produktserie von **Eco Physics (Halle A2 Stand 425)** zeigen sich in einem neuen äußeren und einem modularen internen Design. Die Chemilumineszenzdetektoren erfassen Stickoxide (NO, NO_2 und NO_X), aber auch weitere Gase wie Ammoniak, Sauerstoff, Ozon und Kohlenstoffdioxid. Ein interner Datenlogger erlaubt den Einsatz des Gasanalysators als autarke Messeinheit.

Echo (Halle A3, Stand 512) präsentiert ein tragbares Gerät für die simultane Messung von Kohlenstoffdioxid, Schwefelwasserstoff, Methan, Sauerstoff, Kohlenwasserstoffen und anderen Bodengasen. Verschiedene Sensoren messen die Gaskonzentration über einen dynamischen Bereich. Ein integriertes GPS-Modul bestimmt den genauen Standort der Messung. Über Bluetooth ist das System mit mobilen Endgeräten verbunden.

Für Umweltlabore hat **Milestone (Halle A1, Stand 429)** das Mikrowellenextraktionssystem Ethos X entwickelt. Kombiniert mit dem Rotor Fast EX-24 extrahiert das Gerät 24 Proben in 40 Minuten. Die Einwegvials fassen 30 Gramm Probe.

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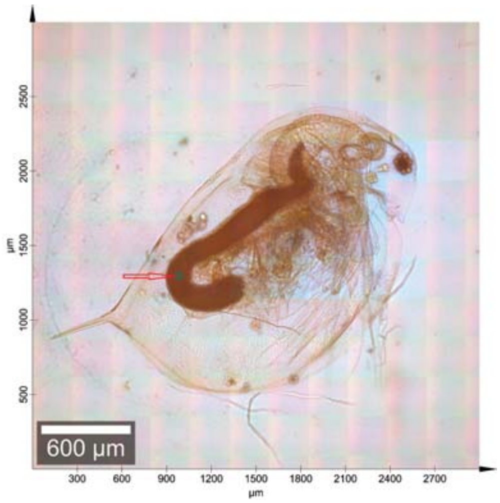

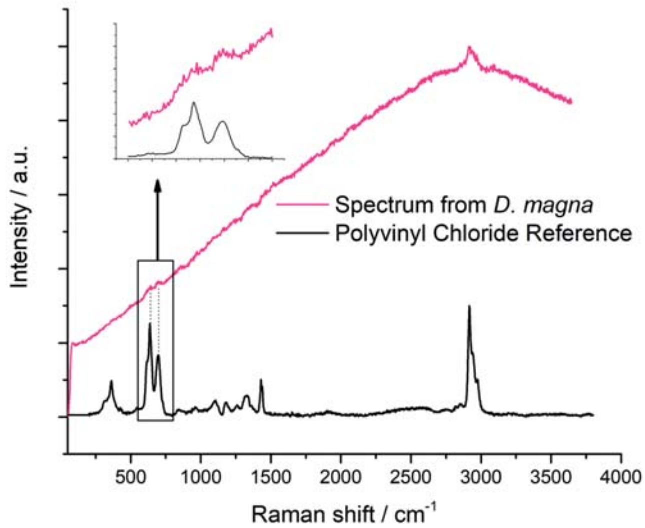

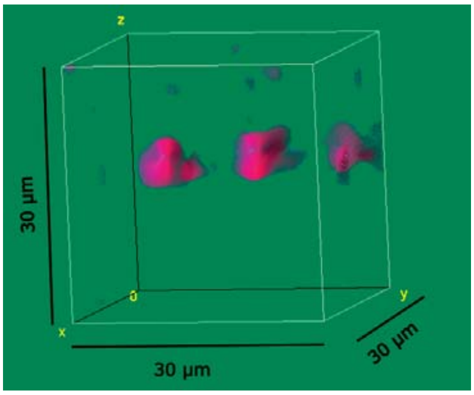

Microscopic image of Daphnia magna fed with polyvinyl chloride (top left) and 3D Raman image (left, red: polyvinyl chloride particles) of a detail as marked in the microscopic image as well as the corresponding Raman spectra (top right). (images: N. P. Ivleva, sample preparation by H. K. Imhof, analysis by P. M. Anger).

micro-FTIR spectroscopy and Raman microspectroscopy (RM) are appropriate for analyses of single particles. While ATR-IR is applied for the detection of particles larger than 500 micrometres, micro-FTIR enables an automated detection of particles down to ten to 20 micrometres. RM is suitable for the analysis of microplastics in the entire size range of one micrometer to five millimetres.

The comparison and harmonisation of different methods for microplastics analysis is the major topic of the joint project Miwa (Microplastic in water cycle) funded by the German Federal Ministry of Education and Research (BMBF). Here, the pool of appropriate analytical techniques will be defined.

Advantages of Raman analysis

RM is so far the only applicable method for the identification and quantification of environmental microparticles with the spatial resolution down to one micrometre. This nondestructive analytical technique is based on the effect of inelastic light scattering by molecules, providing vibrational fingerprint spectra. In contrast to IR spectroscopy, RM has no interference from water, but often suffers from strong fluorescence background caused by humic substances, clay minerals and other contaminations. This problem can be solved by sample processing and various technical measures (appropriate laser wavelength and power, confocal mode, photobleaching, etc.).

RM has been successfully applied in the analysis of marine and freshwater samples, providing reliable identification and quantification of (pigmented) microplastics and paint particles. Most polymers detected were polystyrene, polyethylene and polypropylene, but polyamide and polyvinyl chloride were also detected in fractions of particles smaller than 500 micrometres. The method is also suitable for the 3D visualization of microplastics ingested by biota.

The contamination of the environment and food with biopolymers remains unclear. This issue is studied in the joint project Mipaq (Microparticles in the aquatic environment and in food) funded by the Bavarian Research Foundation.

The identification and quantification of microplastics particles down to one micrometre is necessary for an adequate assessment of the environmental risks arising from microplastics, since small microplastics can be hazardous for biota. Furthermore, a negative impact of nanoplastic on the aquatic environment has been assumed. Therefore, in our new joint project SubµTrack (Tracking of (sub) microplastics of different identity) funded by BMBF, we focus on the development of methods (e.g. field flow fractionation in combination with RM) for analysis of plastic particles in the (sub)micrometre and nanometre range. Furthermore, optimisation and automation of RM measurements and spectral data evaluation will be an important step towards a reliable quantification of microplastics in environmental and food samples.

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Natalia P. Ivlevas's presentation at Analytica Conference will be in ICM, room 5 on April 11th at 4.00 pm.

+++ Analytica Conference: Programm auf www.gdch.de/analyticaconf2018 +++