**Multivariate classification of Raman spectra from synthetic polymeres ­­– an approach for the improved detection of microplastics**

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The increasing pollution of terrestrial and aquatic ecosystems with plastic debris, which leads to the accumulation of microscopic plastic particles of still unknown fate, is an upcoming problem of our time. In order to monitor the degree of contamination and to understand the underlying processes of degradation and internalization of plastic debris, analytical methods are urgently needed, which help to identify and quantify micro plastic are urgently needed. Currently, expensive collected and purified materials enriched on filters are investigated by (micro) infrared spectroscopy (FTIR, [1]). Few studies using micro-Raman spectroscopy have been published as well [2]. In contrast to FTIR, Raman spectroscopy can handle wet samples, but it suffers from interference of fluorescent materials. Both micro-FTIR- and micro-Raman, always include time consuming scanning and mapping procedures followed by the manual inspection and measurement of selected particles.

Here we tested an alternative approach based on the application of a Raman process-spectrometer with fiber optical probes in combination with multivariate data analysis (MDA) for plastics classifcation.

At first, a library of Raman spectra including samples from more than 14 common plastics was established. Raman scattering was recorded in the spectral range 100–1850 cm-1 using 785 nm laser excitation (200 mW). To provide a huge range of variation and to test for the best registration parameters, materials were investigated by three different types of optical probes, by variation of registration conditions and different intensity correction modes.

For MDA several mathematical pre-treatments of the spectra were tested. Raman spectra were classified by principal component analysis (PCA), by hierarchical cluster analysis (HCA), and by support vector machine classification (SVM). In a next step, partial least squares discriminance analysis (PLS-DA) was performed and models were established for each polymer. A hierarchical approach is favored starting with a SVM classification followed by inspection of non-identified spectra by PLS-DA models for selected plastics.

In test runs with typical contaminants of environmental samples such as sand, wood, organic litter, dried leaves, and glass, no false-positive detection occurred. 95% of our test samples of “unknown” materials, on a macroscopic level, were correctly identified. In a next step, the model was applied on systematically aged materials from polypropylene (PP) [3], which could clearly be identified, independend on the aging status. Tests with mixtures of polystyrol (PS), PP, polyethylene (PE) and polyethylene­terephthalat (PET) particles (diamter < 1mm), with sand, earth or peaces of dried seawood sealed under glas demonstrated a higher classification power for PS and PET than for PP and PE.

Our results show the high potential of process Raman spectroscopy in combination with MDA for the identification of microplastics in environmental samples, however, further research is necessary to improve the prediction power of this approach, which might be a time-efficient and robust alternative to micro-FTIR- and micro-Raman spectroscopy.

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[2] H.K. Imhof, J. Schmid, R. Niessner, N. Ivleva, C. Laforsch, A novel, highly efficient method for the separation and quantification of plastic particles in sediments of aquatic environments, Limnol. Oceanogr. Methods, 10 (2012) 524-537.

[3] [Bajer, K](http://apps.webofknowledge.com/OneClickSearch.do?product=UA&search_mode=OneClickSearch&excludeEventConfig=ExcludeIfFromFullRecPage&SID=V2e7eVTKCYPo4GHu1OP&field=AU&value=Bajer,%20K); [Braun, U](http://apps.webofknowledge.com/OneClickSearch.do?product=UA&search_mode=OneClickSearch&excludeEventConfig=ExcludeIfFromFullRecPage&SID=V2e7eVTKCYPo4GHu1OP&field=AU&value=Braun,%20U), Different aspects of the accelerated oxidation of polypropylene at increased pressure in an autoclave with regard to temperature, pretreatment and exposure media. Polym Test, 37 (2014) 102-11.