QUANTITATIVE TRACE ANALYSIS OF MICROPLASTICS IN ENVIRONMENTAL SAMPLES USING PYROLYSIS GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Microplastics in the environment are one of the key issues of current environmental sciences. Around 6.46 billion tons have been produced so far (calculated from PlasticsEurope, 2016), and conservative estimations predict that 10% of this will end up in the oceans (Thompson, 2007). Model estimations based on municipal (miss) management data of coastal zones worldwide calculate a terrestrial input of plastic waste between 5 and 13 Mio tons into the ocean for 2010 only (Jambeck et al., 2015). Due to their high persistence microplastics represent a quite potential biomarker for anthropogenic activity in recent times and likely future millennia as well.

The proportion of micro plastic (MP) in the environment is expected to increase steadily due to physical (fragmentation) and chemical (leaching) transformations. These particles interact variously with the bio- and chemosphere. Their bioavailability increases with decreasing particle size. Sources, distribution and accumulation behavior of small MP (< 1mm) is comparably poorly understood due to restricted availability of data (Cózar et al., 2014).

Identification and quantification of MP in the water column, sediment and biota is time-consuming and lacks of standardization. Exclusively microscopic recognition and counting forfeit reliability below 100 µm particle size. Combined microscopic and spectroscopic FTIR- and RAMAN-techniques are the most established approach in MP analysis (Löder and Gerdts, 2015).

Pyrolysis gas chromatography mass spectrometry (Py-GCMS) is frequently used for identification but rarely for quantification of single plastics in natural samples. Comparably fast, quantitative chemical and weight-related data complementary to number- and size-related records are generated.

Our study applies Py-GCMS combined with thermochemolysis for simultaneous analysis of nine majority plastics (PE, PP, PET, PS, PVC, PC, PA-6, PMMA, MDI-PUR). Selected fragment ions of specific pyrolysis products enable a sensitive polymer-specific identification and quantification on the µg trace level and even below. Prior to Py-GCMS environmental samples need a multistep enzymatic, oxidative treatment and occasionally density separation in order to reduce accompanying organic as well as inorganic matrix components and achieve a sufficient MP enrichment.

The potential of this method will be demonstrated for different environmental sample types (e.g. Fig. 1) concerning applicability, calibration range, recovery, reliability and possible interferences with common occasionally remaining natural organic polymers. In this context Curie-point and an improved oven pyrolysis will be compared regarding their sensitivity and linearity for trace quantification purposes. These aspects are of general relevance for the analysis of organic polymers in environmental samples.
Figure 1. Example for the method application on a Mediterranean raw salt sample. Total ion chromatogram of the organic fraction from the raw salt (after density separation) and indicator ion chromatograms of the respective polymers comparing sample, procedure blank and standard. PS, polystyrene; PE, polyethylene; PVC, polyvinylchloride; PET, polyethylene terephthalate; PC, polycarbonate.

References


