



Fast identification of microplastics in complex environmental samples by a thermal degradation method



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HIGHLIGHTS

- Determination of polymer specific degradation products.
- Fast measurements without a time consuming sample preparation.
- Identification of microplastic in real environmental samples.

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ABSTRACT

In order to determine the relevance of microplastic particles in various environmental media, comprehensive investigations are needed. However, no analytical method exists for fast identification and quantification. At present, optical spectroscopy methods like IR and RAMAN imaging are used. Due to their time consuming procedures and uncertain extrapolation, reliable monitoring is difficult. For analyzing polymers Py-GC-MS is a standard method. However, due to a limited sample amount of about 0.5 mg it is not suited for analysis of complex sample mixtures like environmental samples. Therefore, we developed a new thermoanalytical method as a first step for identifying microplastics in environmental samples. A sample amount of about 20 mg, which assures the homogeneity of the sample, is subjected to complete thermal decomposition. The specific degradation products of the respective polymer are adsorbed on a solid-phase adsorber and subsequently analyzed by thermal desorption gas chromatography mass spectrometry. For certain identification, the specific degradation products for the respective polymer were selected first. Afterwards real environmental samples from the aquatic (three different rivers) and the terrestrial (bio gas plant) systems were screened for microplastics. Mainly polypropylene (PP), polyethylene (PE) and polystyrene (PS) were identified for the samples from the bio gas plant and PE and PS from the rivers. However, this was only the first step and quantification measurements will follow.

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1. Introduction

Due to the high amount of plastics produced in all areas of material sectors (packing, construction and transport), the contamination of the environment with plastics and plastic particles is becoming increasingly apparent. In 2014 global polymer production reached 311 million tons, and it is projected to rise

further (PlasticsEurope, 2015). About 39.5% are used for packaging materials. Due to improper waste disposal, most of these packaging materials end up in the environment. Although there are many types of polymers, only a few are used as packaging materials. Thus, these types of polymers are preferentially reported in microplastic (MP) investigations (Hidalgo-Ruz et al., 2012): low- and high-density polyethylene (LD/HD-PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET). In addition, traces of polyamide (PA) fibers, which are used as fishing nets and in textile production, were sometimes found as well (Duis and Coors, 2016; Lozoya et al., 2016).

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Plastic is practically ubiquitous in the environment. Plastic findings have been reported in the ocean (Moore, 2008; Lusher et al., 2014), in lakes (Imhof et al., 2013; Free et al., 2014) in rivers (McCormick et al., 2014) and even in aquatic and terrestrial animals due to ingestion (Wegner et al., 2012; Ugolini et al., 2013; Wright et al., 2013; Ivar do Sul and Costa, 2014). When plastics, or more accurately polymers, are exposed to environmental impacts like sunlight, oxidizing atmosphere and mechanical stress (e.g. abrasion) polymer degradation occurs, yielding small polymer particles. If the polymer particles are smaller than 5 mm they are called microplastics, which are currently the objects of many investigations (Ivar do Sul and Costa, 2014; Van Cauwenberghe et al., 2015).

Due to the possible harmful impact on the environment, qualitative and quantitative monitoring of MP is necessary (Hidalgo-Ruz et al., 2012). For analysis, nondestructive imaging techniques like FTIR (Tagg et al., 2015) and RAMAN (Fischer et al., 2015; Ivleva and Nießner, 2015; Wiesheu et al., 2016) imaging are preferred. These techniques are able to identify certain polymer types at a resolution from about 10 μm (IR) (Löder et al., 2015) to 0.5 μm (RAMAN, 532-nm laser and a $\times 100$ objective) (Käppler et al., 2015). Major disadvantages of these methods are the time consuming scanning procedure, their representativeness, their robustness and the required sample preparation; therefore, these methods are obviously difficult to implement as routine analysis. Another well-established method for analyzing polymers as well as microplastics is Py-GC-MS (Fabbri et al., 2000; Fries et al., 2013). There, single polymer particles are pyrolyzed under inert conditions. The thermal degradation products are first cryo trapped, then separated using a chromatographic column and subsequently identified with mass spectrometry. This method works very well for single particles and can be applied for sample weights of 0.1–0.5 mg. Therefore, a time consuming preselection of single particles is necessary. In addition, this method is prone to contaminations or even blockades (Wampler, 2007). Especially during the pyrolysis of polymers degradation products with high molecular weights (over 400 g mol^{-1}) are produced which can condensate in the small transfer capillary (from pyrolysis compartment to GC-MS, diameter of about 1 mm), which is commonly heated to maximum Temperature of 350–400 °C. Thus, the maintenance is very high.

In a first work we demonstrated that MP particles of PE can be identified and quantified in environmental samples by a combination of thermal extraction with thermogravimetric analysis (TGA) on solid-phase adsorbers and subsequent analysis of these adsorbers with thermal desorption gas chromatography mass spectrometry (TDS-GC-MS). This combination (TGA-solid-phase extraction, TDS-GC-MS) is called TED-GC-MS (Dümichen et al., 2014, 2015). The complete sample is pyrolyzed in the TGA at temperatures of up to 600 °C. The polymer-specific characteristic degradation products, which have to be different from the degradation products of the environmental matrix, are trapped on the solid-phase adsorbers. Analysis with a GC-MS system makes identification and even quantification possible (Dümichen et al., 2015). Although in this method the information about size distribution is lost, as the polymeric particles melt before degradation, the method can provide fast measurements.

For pyrolysis, a TGA is used, which can be heated up at controlled temperatures up to 1000 °C under different atmospheres and enables relatively large samples (up to 100 mg). The TGA is a robust method and was constructed to even measure samples which release a high amount of compounds with a high molecular mass. The use of GC-MS analysis enables the identification of simple, but specific organic decomposition products (especially of PE and PP), even at low concentrations. With the solid-phase adsorber a reproducible mixture of the relevant thermal

decomposition products of environmental samples which were weight out in milligram scale is extracted and reduced for the following trace analysis with GC-MS. Through the separation of the thermal extraction process from the thermal desorption with the TDS-GC-MS there is no contamination of a transfer capillary like at Py-GC-MS. Thus, the GC-MS system stays clean and the maintenance is very low.

One of the most challenging problems presented by analyzing MP in environmental samples is the representativeness of the sample. Real environmental samples consist of a complex mixture of organic matter, like plant and animal residues as well as cells and tissues of organisms, with a high content of inorganic matter. Sampling MP in a water column is normally done using filtering or sedimentation techniques that restrict the particle size distribution to a lower limit, and also by applying different filter steps up to an upper limit. For the present work we investigated samples taken with a centrifuge in constant operation. The resulting filtrates were dried, yielding a homogeneous sample that allowed subsequent measurement with TED-GC-MS without further preparation.

The sampling of soil or other solid materials such as composts yields samples with a high particle size distribution, because no filtering is performed beforehand. One possibility is sieving, and subsequent analysis of the different particle size fractions, which would result in a number of measurements. For our task the complete homogenization of the sample is sufficient, because determination of the particle size is not relevant for TED-GC-MS analysis. In our case the samples were homogenized by various cutting and milling steps.

In this work we document the progress of TED-GC-MS as a fast tool for MP analysis in environmental samples. In a first step, unique polymer specific degradation products of major types of polymers have to be identified and selected for unambiguous identification in complex environmental samples. Subsequently real samples were screened for MP, taken from three different rivers, from a soil, a bio gas plant and a waste water treatment plant.

2. Experimental/materials

2.1. TED-GC-MS

The thermal extractions were carried out with a horizontal single-arm thermo balance TGA/SDTA 851 equipped with an auto sampler (Mettler/Toledo, Gießen, Germany). About 2 mg of the pure polymer and about 20 mg of the environmental samples were weighed out in a 150 μL aluminum oxide crucible and heated up under nitrogen atmosphere (90 ml min^{-1}) to 600 °C at a heating rate of 10 °C min^{-1} . To collect the thermal degradation products, a thermal desorption glass tube (outer diameter 6 mm, inner diameter 4.5 mm, length 178 mm) was placed into the outlet of the TGA with an interface devised in-house. In the glass tube a Sorb-Star[®] (IMT Innovative Messtechnik GmbH, Vohenstrauß, Germany) was affixed with two stainless steel sieves. A Sorb-Star is a defined piece of polydimethylsiloxane (PDMS) with a length of 20 mm and a diameter of 2 mm, especially designed for the ultratrace analysis. When thermal extraction was complete, the thermal desorption glass tube including the Sorb-Star[®] was placed in the TDS-GC-MS. The thermodesorber was a TDS A2 (Gerstel, Mülheim, Germany) mounted on a cooling injection system (CIS 4, Gerstel) cooled with liquid nitrogen. The thermodesorption temperature was set to 200 °C and held for 5 min in splitless mode. For cryo-focusing the CIS was cooled to –100 °C and heated afterwards to 270 °C. The GC (6890, Agilent Technologies, Palo Alto, CA, USA) was equipped with a HP1-MS column (30 m \times 0.25 mm i.d. \times 0.25 μm film thickness) suited for the separation of predominately nonpolar species. A

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