Polymer Analysis and Microplastics in the Environment

TED-GC-MS, a New and Fast Method

The abbreviation TED-GC-MS describes a two-step method for volatile diagnostics originating from polymers at high temperatures. First the entire sample is pyrolyzed and the polymer specific decomposition products are trapped on a solid-phase adsorbent (Thermal Extraction). In a subsequent step the decomposition products are thermally desorbed, chromatographically separated and then identified with mass spectrometry.

For the thermal extraction a thermo balance (TGA) is used, which can be heated up to 1100°C under controlled conditions. Due to its robust construction it is possible to use sample amounts of up to 100 mg, as well as selecting degradation processes to occur under inert or oxidizing atmospheres. The permanent flow of the purge gas (usually dry N₂) transports the decompositions products to the solid-phase adsorbent, which is positioned in a thermal desorption tube located in a customized coupling device downstream of the TGA. This coupling was developed by a joint venture between the Bundesanstalt für Materialforschung und –prüfung (BAM) and Gerstel and was further modified to work as part of a fully automatic sampling robot. This robot enables the loading of the coupling device with new thermal desorption tubes according to a preset program at identical temperatures and times. Therefore, fractionated measurements are possible, which increases the sensitivity of the method.

Microplastics

This new TED-GC-MS method was demonstrated to be very effective for the analysis of microplastics in environmental matrices. Most polymers start to decompose at about 350°C. It is therefore possible to eliminate the major part of the environmental matrix which starts to decompose at much lower temperatures. Always the same and reproducible part of the decomposition products (i.e. C5 –C30) is trapped on the solid-phase adsorbent. Pure PDMS was shown to be a well-suited adsorption material, especially for the analysis of polymer fragments. The PDMS adsorber has shown excellent reproducibility and it is commercially available in
different diameters and lengths.

Due to their low cost they are only used once and can be discarded after the measurement. This also prevents possible cross-contaminations and reduces the efforts of the overall method.

After the thermal extraction the loaded thermal desorption tubes are transported manually or automatically to the TDS-GC-MS [1-5]. An automatic process enables the thermal extraction and desorption without any manual transport of the thermal desorption tubes between the two devices. Therefore, the labor costs are reduced and the sample throughput as well as the sensitivity is significantly increased.

In the TDS the loaded solid-phase adsorbent is heated again. The earlier trapped decomposition products are thereby desorbed and transferred by an inert purge gas (Helium) into a cooled injection system (CIS). There they are deposited and concentrated at temperatures of 100°C. After this cryo-focusing the decomposition products are evaporated under controlled conditions and separated through a chromatographic column. Thereby, the separation depends on the compounds’ boiling points as well as the interaction with the separation phase. The identification and quantification of analytes with mass spectrometry is fast and very reliable. Pre-adjusted routines for examination enable a fast comparison of specific mass fragments of interest with actual mass fragments found in the sample. Only if several simultaneously occurring mass fragments representative of different decomposition products from one polymer are determined, the presence of this polymer will be confirmed and quantified. Due to the specificity of some mass fragments and their origin it is possible to determine several polymers simultaneously in one sample.

Due to the separation between the thermal extraction process with the TGA and the solid-phase adsorbent, and the thermal desorption process with the TDS-GC-MS system, maintenance requirements are also reduced. The solid-phase adsorber acts
as a filter for the sensitive GC-MS system. Only compounds which can be thermally desorbed at temperatures of 200 – 250°C can enter the sensitive GC-MS-System (upper limit on the order of Mw = 400). Therefore, the GC-MS system remains almost free of long chain polymer specific contaminants. The lower limitations of the overall method are usually molecules smaller than C5 species. Because of their higher vapor pressures they cannot be trapped on the solid-phase adsorbent.

**Complex Matrices**

The analytical approach described above was originally developed for pure polymer analysis. However, for example new thermal and thermo- oxidative degradation mechanism for Polyamide 66 could also be established in a cooperative project with BASF [2, 3]. In preliminary experiments as part of a collaborative project with the Umweltbundesamt (UBA) the new method turned out to be also well-suited for the analysis of microplastic particles in complex environmental matrices. In the focused project area “microplastic” the automatic sample transfer was developed in collaboration with Gerstel. Within the framework of the BMBF project “microplastics in the water cycle (MIWA)” the The TED-GC-MS will be used as routine method for the screening of microplastics in the anthropogenic environmental water cycle.

The underlying requirement for this methodology is that polymer specific decomposition products can be identified which must differ from decomposition products originating from the matrix. For instance, polyethylene (PE) yields three types of decomposition products: saturated aliphatic hydrocarbons as well as mono- and dienes. However, only the dienes serve as a specific signature for PE because the saturated hydrocarbons and the mono alkenes are also decomposition products of fatty acids and lipids often found in environmental samples [4]. In Fig. 2 (top) the TED-chromatogram of the fragment ion m/z = 55 for PE is presented. It is specific for many aliphatic compounds and shows high intensity in the mass fragment pattern. Groups of three peaks can be seen for which the first peaks belongs to a diene, followed by the mono alkene and the fully saturated aliphatic compound. These groups increase in retention time according to their number of carbon atoms. In Fig. 2 (bottom) pure PE is compared to three environmental matrices in which PE could be anticipated. Only the measured responses for the dienes (first peak of the triplet) are shown in detail. The diene is a unique signature originating from PE and can therefore be used for reliable detection [4].

In an expanded publication it was shown that a unique identification is possible for many of the major polymers, which are possible precursors for microplastics [5]. Fig. 3 for example shows the behavior of PE, Polypropylene (PP), Polystyrene (PS) and polyethylene terephthalate (PET), for which differing unique signatures serve
as unambiguous identification of the originating polymer. Additionally it was shown that in different environmental samples several microplastics could be identified in parallel.

**Conclusion**

With the TED-GC-MS a new methodology was developed for comprehensive polymer analysis through the identification and quantification of complex volatile hydrocarbons released at high temperatures. This method turned out to be especially suited for the analysis of microplastics in complex environmental samples. It relies on the combination of TGA with a TDS-GC-MS-System over a solid-phase adsorbent. A newly developed automation approach provides high reproducibility, and offers increased sensitivity as well as a high sample throughput. The solid-phase adsorbent acts as a filter for the sensitive GC-MS-system. Thus, no high molecular weight contamination products can reach the sensitive GC-MS system. Maintenance issues are thereby significantly reduced. Future efforts with the TED-GC-MS will focus on the optimization of the measurement parameters for different environmental samples and the development of quantification routines through external calibration as well as traditional addition of internal references.

**Authors:**
E. Duemichen¹, P. Eisentraut¹, M. Celina², U. Braun¹

**Affiliations:**
¹ Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
² Sandia National Laboratories, Albuquerque, USA

**Contact**
**Dr. Erik Dümichen**

German Federal Institute for Risk Assessment (BfR) Researcher FGr 75 - Product Research and Nanotechnology Department 7 Chemicals and Product Safety

erik.duemichen@bfr.bund.de

**References:**


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Contact

Bundesanstalt für Materialforschung und -prüfung (BAM)
Unter den Eichen 87
12205 Berlin
Deutschland