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Cross-Cutting Topic 1: Analytics and Reference Materials: Comparative test

Results

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1 Background and test design

- The aim of this comparative study was to classify different analytical methods for the identification and quantification of microplastics (MP) with regard to their informative value and to work out the strengths and limitations of the respective methods. The comparative test was intended to provide the prerequisites for comparing the analytical results of the individual projects within a given framework. No evaluation of the different analytical methods is intended.
- The test was not a classical interlaboratory test, but a comparative test. The main distinction from a full interlaboratory test is the fact that the homogeneity and stability of the reference samples could only be determined with regard to the microplastic mass. However, no information was available on the homogeneity of the reference samples with regard to the particle size class distribution and particle number. This inhomogeneity of reference materials is currently the greatest challenge in performing MP comparison tests. In addition, the comparison test was designed for both thermoanalytical and spectroscopic analysis methods, which is why the following points had to be taken into account:
  - Thermoanalytical measurements (Py-GC/MS, TED-GC/MS) provide information on the mass content of the different polymers, while spectroscopic measurements (µ-FTIR, µ-Raman) provide information on the particle number and size/size distribution of the different polymers. The results of the two approaches are not interchangeable.
  - Integral, thermoanalytical methods require a certain minimum amount of analyte to be able to detect it (limit of detection, limit of quantification). Imaging, spectroscopic methods can identify and quantify individual particles. The lateral resolution depends on the method applied – FTIR or Raman – and on the measurement parameters used.
  - Consequently, the joint comparative test for both methods presents a compromise and a first attempt to obtain technical information about the two different detection concepts.
- The reference material used consisted of tablets of compressed potassium bromide (KBr) as a water-soluble salt, to which a polymer, either aged polyethylene (PE) or non-aged polyethylene terephthalate (PET), was added. In addition, samples of pure KBr were provided for blank control.
- The reference material used was subjected to a homogeneity control prior to the comparative test with regard to the mass content (thermo-gravimetric analysis) in the individual sample containers (one-shot) and showed variations of 17 % for PE (0.596±0.107µg) and 60 % for PET (5.96±3.58µg). A homogeneity control with respect to the number of particles and their size distribution was not performed. Consequently, neither a target value nor

information on the homogeneity of the reference samples was available for spectroscopic methods.

» For each analysis method, the participants received three tablets with the respective polymer type and two additional blank samples. The samples were prepared by dissolution and filtration by the participants. This sample preparation and its associated effects (e.g. agglomeration of microplastic particles, aliquoting, loss of particles due to adhesion to surfaces) influenced the results.

2 Results

» With one exception, all laboratories involved in microplastic analysis as part of the German research focus "Plastics in the Environment" participated in the comparative test (cf. Table 1).

Table 1: Participating laboratories and analysis methods

Analysis method	Participating laboratories
Py-GC/MS	» German Federal Institute of Hydrology (*Bundesanstalt für Gewässerkunde*, BfG) » Institut für Energie- und Umwelttechnik e.V. (IUTA) » University of Oldenburg, Institute for Chemistry and Biology of the Marine Environment (*Universität Oldenburg, Institut für Chemie und Biologie des Meeres*, ICBM)
TED-GC/MS	» Federal Institute for Materials and Testing (*Bundesanstalt für Materialforschung und -prüfung*, BAM) » Institut für Energie- und Umwelttechnik e.V. (IUTA)
µ-FTIR	» Alfred Wegener institute (*Alfred*-Wegener-Institut, AWI) » Fraunhofer Center for Silicon Photovoltaics (*Fraunhofer-Center für Silizium-Photovoltaik*, CSP) » Bavarian Environment Agency (*Bayerisches Landesamt für Umwelt*, LfU) » University of Bayreuth (*Universität Bayreuth*, UBT)
µ-Raman	» Fraunhofer Center for Silicon Photovoltaics (*Fraunhofer-Center für Silizium-Photovoltaik*, CSP) » RheinMain University (*Hochschule RheinMain*, HSRM) » Leibniz Institute of Polymer Research (*Leibniz-Institut für Polymerforschung Dresden*, IPF) » Technical University of Munich (TUM), Institute of Hydrochemistry (IWC) » German Water Centre (*TZW: DVGW-Technologiezentrum Wasser*, TZW) » Wessling GmbH

Source: own illustration

» The polymer types PE and PET contained in the reference samples were correctly identified by all laboratories.

Contamination of the reference materials with polystyrene (PS) was identified and quantified by the spectroscopic methods. Using the thermoanalytical methods, the concentrations of PS contamination were mostly below the limit of detection or quantification, which is why they could not be quantified.

3 Thermoanalytical methods

» The results were evaluated by normalization to the target value (DIN ISO 5725-2). To do so, the measured value is divided by the target value and expressed as a percentage. Due to the small number of participants, the results of the TED-GC/MS and Py-GC/MS were evaluated jointly. No meaningful tendencies for the application of the individual methods can be derived from the available results.

» For PE, the average recovery across all laboratories was 83.3±28.1% (0.496±0.167mg).

» For PET, the average recovery over all laboratories was much lower at 66.6±17.5% (3.868±1.044mg). The reason for this could be the optimization of the measuring devices for non-polar polymers, which disadvantages the detection of polar polymers such as PET.

» The mass fraction/aliquot of the measured sample appears to be a relevant factor for the accuracy of the measurement results.

4 Spectroscopic methods

» The results were evaluated using the z-value (according to DIN 38405). Here, the difference between the measured value of each individual laboratory (the mean value of the measurement results within a laboratory – arithmetic mean) and the expected value (mean value over all measured values) is determined and set in relation to the standard deviation over all measured values. Consequently, a z-value of 0 corresponds to a maximum agreement between the measured value and the expected value, taking into account the standard deviation. In interlaboratory comparisons, a z-value of |2.00| is generally considered a solid result and indicates a satisfactory measurement accuracy of the participating laboratories. In the evaluation of the z-value presented here, no distinction was made between µ-Raman and µ-FTIR analysis due to the small number of participants.

- The determined z-values of all spectroscopic laboratories ranged from -0.94 to +1.45 for PE and from -1.09 to +1.31 for PET.
- Numerically, more smaller particles than large particles were detected. Within the scope of the comparative test, only the particle counts for particle diameters ≥10 µm were considered. In the present comparative test, µ-Raman detects more particles than µ-FTIR. Due to the small number of participants, however, no valid statement can be made about this observed trend.
- The inhomogeneity of the samples (variations in mass content of up to 17 % for PE and up to 60 % for PET) could have lead to considerable differences in the particle counts in the reference samples. Especially for small particles (<50 µm), a slight mass difference can cause a particle number difference of several orders of magnitude.

5 Conclusions:

- In general, the comparative test can be considered successful. It was demonstrated that the different analytical methods for the identification and quantification of microplastics within the two approaches (thermoanalytical / spectroscopic) provide comparable results.
- All four analytical methods (Py-GC/-MS, TED-GC/MS, µ-Raman, µ-FTIR) were able to identify the two polymers, PE and PET.
- For the thermoanalytical methods, all determined values for the mass contents fall within the range of the target value. Recovery was better for PE than for PET, probably due to the properties of the marker compound.
- Regarding the spectroscopic methods, all results are within a z-value of |2.00|.
- In the spectroscopic measurement of small microplastic particles, even a slight difference in mass (e.g. inhomogeneity of the reference material, contamination) in the samples and agglomeration of these small particles can lead to particle number differences of several orders of magnitude.
- Recommendations for future interlaboratory comparisons in the field of microplastics analysis:
  - The reference material should be stable, homogeneous and well suspendable in a suitable matrix.
  - The production of realistic and homogeneous microplastic reference materials is a major challenge when conducting comparative micro-plastic studies and interlaboratory tests.
  - The reference materials should have suitable concentration ranges (mass or particle numbers) for the respective analytical procedure. The

data of the homogeneity control must be taken into account in the presentation of results.

» The use of reference materials in which microplastic particles are embedded in water-soluble salt allows detection of the particles without interference from a matrix. However, sample preparation is a major challenge.