

Detection of nano- and microplastics in water and wastewater samples: Challenges and perspectives

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Highlights:

- Three analytical methods for the identification and characterization of nano- and microplastics (NMPs) were tested and evaluated.
- Thermal-based methods are effective to determine plastic type, optics-based methods are effective to determine morphology.
- Samples from different sources were analyzed (wastewater and seawater).

Keywords: Microplastic; emerging contaminants; monitoring.

INTRODUCTION

Nano- and microplastics (NMPs) are persistent contaminants that have been found in many environmental settings - water, soil, air, sediments and even biota (Murugan et al., 2023). These plastics, ranging from fractions of a millimeter down to a few nanometers in size, come from many different sources, such as the degradation/weathering of larger plastic pieces, the direct release of microbeads used in commercial/industrial applications, and fibers from synthetic textiles (Hartmann et al., 2019).

Although there is convincing evidence of the negative environmental impacts brought by NMPs (Feng et al., 2023), it remains uncertain what the true risks are. To date, there are no significant regulations concerning exposure limits, permissible concentrations in water bodies, or monitoring measures for NMPs in the environment. This is due to some facts, including the current lack of standardized methods to analyze NMPs, which are crucial to establishing a scientific basis for these control measures. Therefore, addressing the challenges inherent to the analysis processes themselves is an important step to advance in this matter.

One of the primary challenges lies in the sampling and sample preparation prior to analysis. Collecting NMPs-contaminated samples in a representative manner can be challenging due to the low concentration of plastics observed in the environment, the risk of sample contamination during collection/preparation, and the difficulty in isolating NMPs from other sample components (e.g., organic, and inorganic matter). Furthermore, as the size of NMPs decreases, their detection becomes increasingly challenging, making it harder to observe and quantify them, therefore requiring more elaborate instrumentation and sample pre-processing steps (Shim et al., 2017).

This study proposes to review, evaluate, and adapt three emerging methods used for the analysis of MNPs in environmental samples. The specific instrumental techniques evaluated were Differential Scanning Calorimetry (DSC), Asymmetric Flow Field-Flow Fractionation coupled to Multi-Angle Light Scattering (AF4-MALS), and Pyrolysis followed by Gas Chromatography and Mass Spectrometry (Py-GC/MS). The applications, limitations and pre-treatment steps needed for each method were also assessed.

METHODOLOGY

Differential Scanning Calorimetry (DSC)

Samples were measured using a Metler Toledo DSC, under nitrogen (N₂) atmosphere using a two-stage, ramped heating, and cooling program to obtain the polymer melting temperatures. Calibration curves using increasing concentrations of pure plastics standards – Polyethylene (PE), Polypropylene (PP), Polyethylene terephthalate (PET), and Polyamide (PA) – were created to enable quantification of the polymer types in the samples (Figure 1).

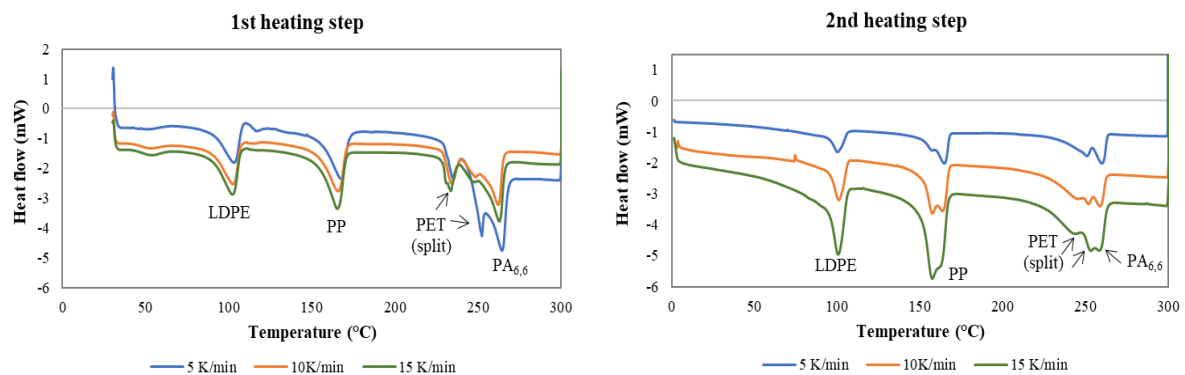


Figure 1: DSC Calibration Curve using pure plastics standards.

Two distinct sample types were analyzed: one being industrial wastewater originating from a plastics manufacturing facility; and the other being seawater samples collected from varying locations.

Asymmetric Flow Field Flow Fractionation (AF4)

Size fractionation of the aqueous samples was carried out using an Eclipse Neon (Wyatt technology), equipped with a short separation channel (dimensions 153 x 22 mm), with a fixed spacer height (250 µm). A Dawn Neon Multi-Angle Light Scattering device (Wyatt Technology) was coupled as a detector to the AF4. The samples came from a mechanical recycling facility of multilayer plastic bags, where the washing water used in the process was analyzed for the presence of nanoparticles.

Pyrolysis Gas Chromatography/Mass Spectrometry (Py-GC/MS)

The Py-GC/MS analysis was performed using a Gersel Thermal Desorption Unit (TDU 2) connected to a gas chromatograph and mass selective detector (Agilent Technologies 6890N / 5975). A protocol is currently under development, using microwave-assisted extraction to prepare samples for Py-GC/MS

analysis. Multiple solvents (dichloromethane, cyclohexane/ethyl acetate/dimethyl carbonate) are being evaluated and optimized for NMPs extraction. Calibration curves are being prepared for eight types of polymers (PP, PE, PET, PA, PMMA, PVC, PS, and PC) to quantify NMPs in real samples.

RESULTS AND CONCLUSIONS

DSC has proven to be a simple technique with relatively high analytical throughput. However, its low detection limits do not allow for the detection of NMPs in all environmental samples without a pre-concentration step. LDPE and PET were found in the analyzed wastewater samples (Figure 2a), but no plastics were detected in the seawater samples (Figure 2b).

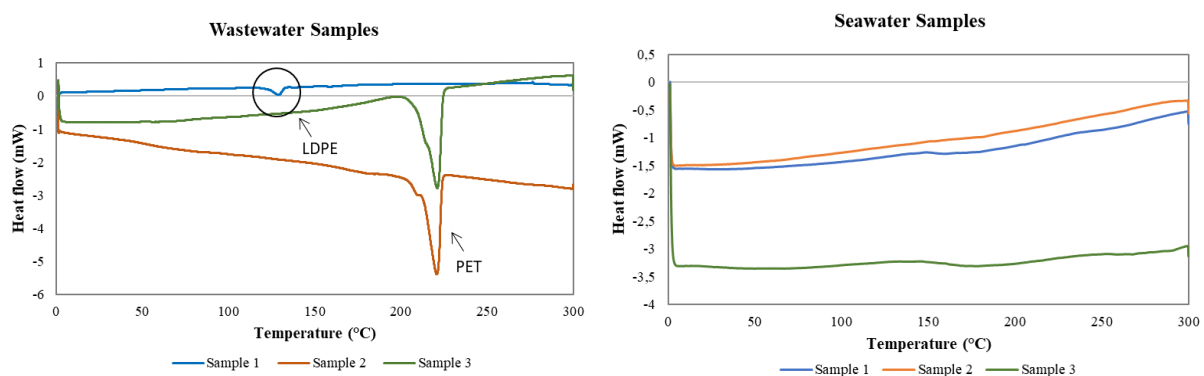


Figure 2: DSC results using wastewater and seawater samples.

AF4-MALS is a powerful tool for the separation and determination of nanoscale particle sizes. However, the technique requires careful optimization of operating parameters, is not robust regarding the types of matrices that can be analyzed and is unable to differentiate plastics from particles of other nature. In the analyzed samples, populations of nanoparticles of various sizes were found, ranging from 1.5 nm to over 200 nm.

Py-GC/MS is currently a widely used technique in literature and has great potential for both the identification and quantification of NMPs. However, applying Py-GC/MS in NMPs detection also has some challenges including using a representative sample and removing inferences from organic materials. Extraction tests are currently underway to evaluate the representativeness of the samples, but preliminary findings indicate that they are not visually homogeneous. Completing the calibration curve for Py-GC/MS is essential to accurately analyze the polymer extraction percentages and enable quantifying these compounds in real environmental samples. The challenges associated with developing the calibration curve stem from the amount of samples ingested into the pyrolysis tube, which leads to instrumental errors. Standards diluted in silica and calcium have been acquired to mitigate this issue, and the calibration curves are currently under development.

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