Characterization of Microplastics: Multi-Element Fingerprinting with Single Particle ICP-TOFMS

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Introduction

Building on previous work, where the icpTOF was successfully used to quantify commercially available polystyrene beads as proxies for microplastics [1-3], here we explore here the application of single-particle inductively coupled plasma time-of-flight mass spectrometry (sp-ICP-TOFMS) to analyze model microplastics derived from plastic waste [4].

Plastic samples were collected from the North Pacific Ocean. The large plastic items, which were environmentally weathered under natural conditions, were first fragmented into 1-2 cm pieces and further milled into micron-sized particles using a commercially available blender before analysis. After filtering and dilution into MilliQ water, the resulting suspension was analyzed using the icpTOF S2. The transient signals of these model microplastics were recorded, subsequently providing clear, distinguishable spikes of metals above the baseline which were associated with individual microplastics (Figure 1).

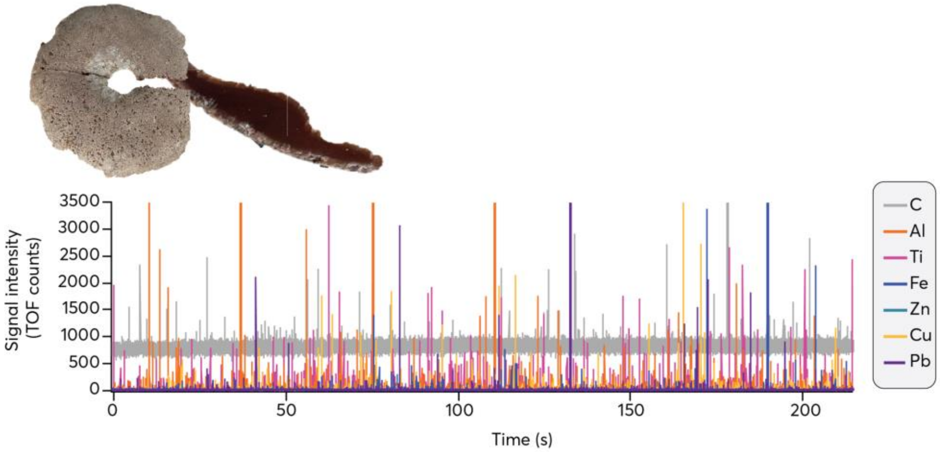

Figure 1. Transient signals of model microplastics derived from environmentally weathered plastic waste recorded using sp-ICP-TOFMS. This demonstrates clear, distinguishable spikes above the baseline, representing various metals associated with microplastics. Beside carbon, elements detected included among others, aluminum, titanium, iron, zinc, copper, and lead.

Characterization of Microplastics

Using TOFpilot and its dedicated single-particle workflow, which includes analyte selection, particle thresholding, split event correction, and background subtraction, the particle signals were extracted and evaluated. This data allowed for the identification of different elements associated with the microplastics based on the concurrence of different signals. Elements such as aluminum, titanium, iron, zinc, copper and lead— commonly used as colorants, stabilizers, and flame retardants in plastics manufacturing — were identified either individually or in combination with carbon. The analysis showed variations in the elemental fingerprint and concentration on a particle-by-particle basis, reflecting the heterogeneous nature of the metal distribution in the plastic itself. It is important to note that detecting all elements simultaneously requires not only a critical mass of the total material (i.e., particle mass) but also a sufficient metal loading in each individual microplastic. Without an adequate amount of material or metal loading, some elements may go undetected even if they are associated with microplastics.

The elemental fingerprints associated with each particle and their respective populations identified here depend heavily on the sensitivity and limits of detection (LODs) for each analyte. For instance, previous work on nanoparticle analysis revealed that the icpTOF achieved detection limits in terms of particle size in the tens of nanometers for various elements when the particle consisted solely of a single element [3]. However, detecting carbon is more challenging due to its high ionization potential and significant background interference. Consequently, the particle size LOD for carbon is approximately 1.5 micrometers [2,3]. This means that only micron-sized plastics will exhibit a carbon signature, whereas nano-sized plastics will predominantly show signatures of metal-based additives. Optimizing background levels and sensitivities is therefore critical to enhance detection capabilities, enabling the identification of smaller particles and more accurate characterization of microplastics, including their metal loading. Consequently, while icpTOF enables the determination of multi-element fingerprints, the populations detected here depend on the sensitivity and limits of detection (LODs) for each analyte as well as the heterogenous nature of the plastic being studied (Figure 2).

This analysis highlights the icpTOFs potential for accurate detection and characterization of microplastics in real-world environmental samples.

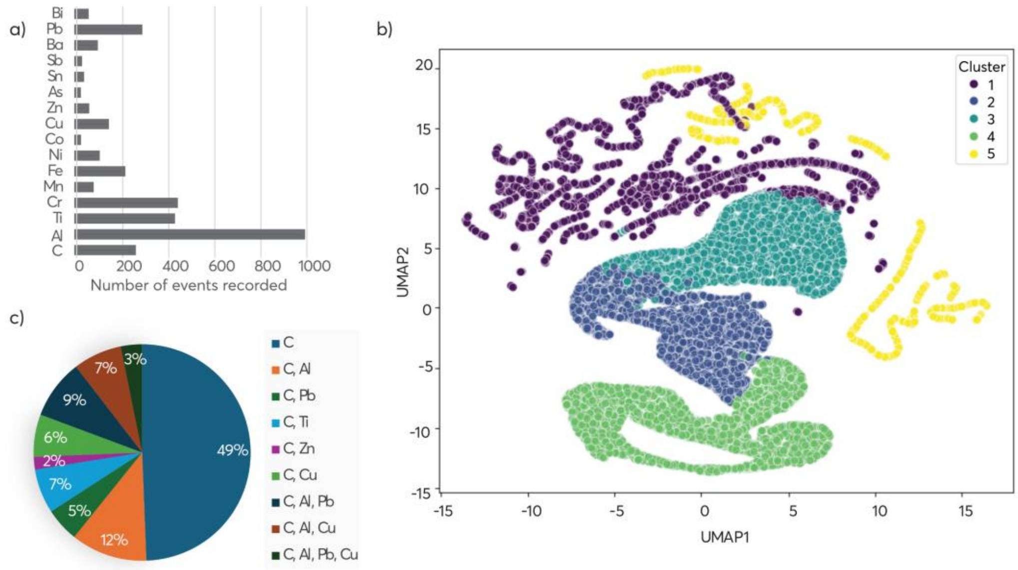

Figure 2. a) Event count recorded per analyte by sp-ICP-TOFMS. b) Visualization of the dataset using UMAP with 5 clusters identified, which correspond to different elemental fingerprints (i.e., combination of elements associated with microplastics). c) In postprocessing data analysis, after filtering the events to contain at least carbon, the pie chart illustrates the distribution of various elements and their combinations: C only, C with Al, Pb, Ti, Zn, Cu, as well as multi-element combinations such as C with Al and Pb, C with Al and Cu, and C with Al, Pb, and Cu.

Acknowledgements

We gratefully acknowledge The Ocean Cleanup for providing the oceanic plastic waste samples used in this study.

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