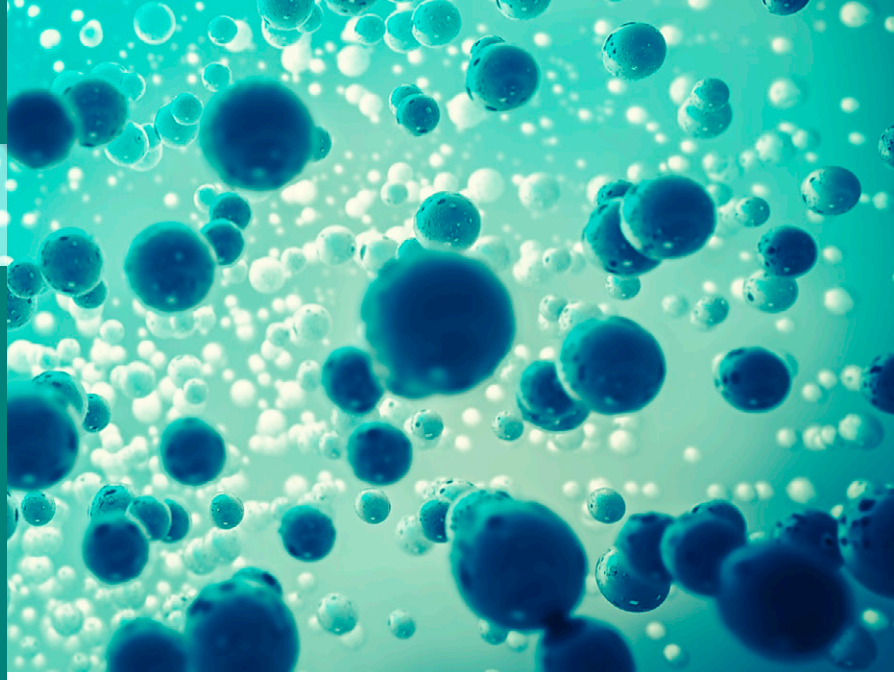
TECHNICAL NOTE

ICP - Mass Spectrometry



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Unlocking Carbon-13 with Single Particle ICP-MS: Feasibility Study for Microplastic Detection

Introduction

Carbon is difficult to measure with ICP-MS because of its high ionization potential (11.3 eV) and its presence in both the argon used to generate the plasma (primarily in the form of CO_2, as an impurity) and in reagents, including acids and water. As a result, extremely high backgrounds exist at both of the naturally occurring isotopes of carbon: C12 (99.9% abundance) and C13 (1.1% abundance). With no easy way to remove these sources of carbon, limits of detection with either isotope are severely affected.

One way to greatly reduce backgrounds is by shortening the measurement times using dwell times in the range of microseconds, as is typically done with single particle ICP-MS (SP-ICP-MS)[1,2]. Working at these short dwell times in SP-ICP-MS mode, the background signal is reduced whereas the overall signal from the particles remains unaffected, allowing particles to be detected and measured at levels that were previously unattainable[3].

By using SP-ICP-MS, the C13 background is reduced significantly, permitting carbon-containing particles to be detected, counted, and measured. As a result, SP-ICP-MS may be used as a screening tool for the detection of microplastics, as discussed in detail by Laborda *et al.*[4]. This work summarizes the principles involved in the detection of microplastics with SP-ICP-MS, and also shows examples.

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Reduction of Carbon Background

All measurements were made on a NexION® ICP-MS due to its ability to use microsecond dwell times, leveraging the Syngistix™ for ICP-MS Nano Application software module, which combines real-time single particle acquisition with fast data processing for routine analytical use. However, in this work, dwell times between 100-200 µs were found to give the best limits of detection for microplastic particles because of the relatively large size of these particles. Although the backgrounds for both C12 and C13 are greatly reduced, C13 was selected for this work since it had a lower background. As shown in Figure 1, the average C13 background acquired with a dwell time of 200 µs is less than 50 counts, which allows for the detection of typical microplastic particles. While acquiring multiple data points per particle provides the highest accuracy [1], it also decreases the height of the particle signals, and hence their detectability. Since the particles detected in this study were in the micron range [4], a dwell time of 200 µs was found to provide the best compromise between accuracy and detection limits.

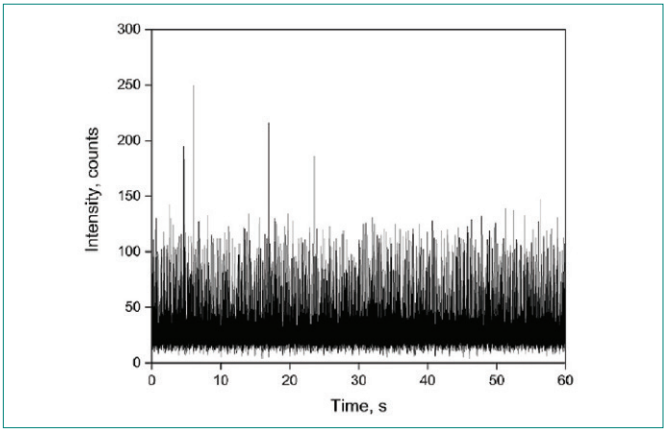

Figure 1: C13 background in SP-ICP-MS acquired with a dwell time of 200 µs.

Sample Transport of Microplastic Particles to the Plasma

With the carbon background reduced, but before the detection of microplastic particles can be evaluated, the transport of microplastic particles from solution to the plasma must be optimized. Transport efficiencies of conventional sample introduction systems (i.e., concentric pneumatic nebulizer with a cyclonic spray chamber) are ≈2% for liquids, where the spray chamber is designed to prevent droplets of about 4 µm and larger from reaching the plasma. Most SP-ICP-MS work has focused on nanometer-size particles (generally smaller than 100 nm), which have transport efficiencies to the plasma of ≈10% with conventional sample introduction systems: the smaller particles pass more efficiently through the spray chamber than larger droplets. However, typical microplastic particles are in the micron-size range, where conventional spray chambers limit them from reaching the plasma.

This issue has been addressed with the development of the Asperon™ spray chamber [5] for single cell ICP-MS (SC-ICP-MS) where cells up to 50 µm must be transported to the plasma. Asperon is a unique linear-pass spray chamber where a sheath flow tangential to the spray chamber wall reduces the number of impacts of cells with the wall, and the laminar flow within the spray chamber carries more cells to the plasma. As a result, the transport efficiency of the Asperon spray chamber is typically ≈30% for micron-sized particles and cells [6,7], making it ideal for the analysis of micron-sized microplastic particles. Therefore, the Asperon spray chamber was used in these studies of microplastic particles.

Detection of Polystyrene Microparticle Standards

For these studies, seven commercially available polystyrene microparticle suspensions with nominal diameters ranging from 1-5 µm were evaluated. The transport efficiencies of the various spheres were evaluated and found to vary from 26-28% for both the 2.2 and 4.8 µm spheres, which corresponds to the transport efficiency measured for cells [6,7]. With the transport of polystyrene spheres to the plasma confirmed, the next step was detection and measurement.

Figure 2 shows a typical particle event distribution and the corresponding size distribution for 2.2 µm polystyrene spheres. The particle event distribution clearly shows that 2.2 µm particles can be detected, with the size distribution being centered on the nominal size, demonstrating accuracy.

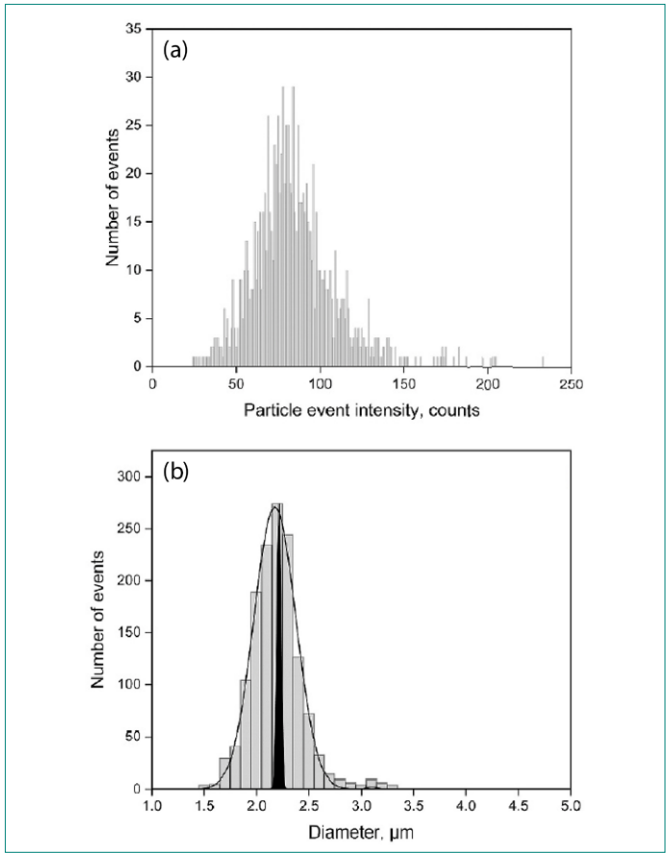

Figure 2: (a) Particle event intensity and (b) corresponding size distribution histogram of 2.2 µm polystyrene spheres.

To determine the accuracy at different sizes, the seven polystyrene microparticle standards were analyzed, with the results shown in Table 1. These results show accurate size measurements for particles from 2-5 µm, while the 1 µm particles (close to the size detection limits) are overestimated, suggesting that SP-ICP-MS can accurately size microplastic particles down to 2 µm.

Table 1: Particle Size Measurements for Seven Different Polystyrene Microparticle Standards.

Particle Standard	Certified Diameter (µm)	Measured Mean Diameter (µm)	% Bias
1	1.04 + 0.03	1.69 + 0.07	140
2	1.98 + 0.01	1.83 + 0.01	93
3	2.02 + 0.02	1.93 + 0.01	96
4	2.22 + 0.01	2.10 + 0.02	94
5	3.03 + 0.09	2.74 + 0.01	91
6	4.00 + 0.04	3.56 + 0.06	91
7	5.00 + 0.04	4.55 + 0.05	92

Detection of Polystyrene Microparticles in Consumer Products

Plastic microparticles are added to exfoliants as abrasives. Three different exfoliants were prepared by mixing with water, sonicating, and filtering through 10 µm filters prior to analysis. As shown in Figure 3, the size distributions differ between the products, as do the particle number concentrations, with the middle exfoliant containing significantly more particles than the other two samples (numerical results in Table 2). This emphasizes the importance of particle concentration: when unknown samples are analyzed, the sample preparation should be adjusted so that the particle concentration is less than ≈250,000 particles/mL, as higher concentrations may result in multiple particles being ionized at the same time, leading to inaccurate results. Therefore, the appropriate sample dilution is a bit of trial and error.

Table 2: Carbon-Containing Particle Results from Exfoliants.

Sample	Mean Diameter (µm)	Particle Concentration (g^{-1})
Blank	---	---
Exfoliant 1	2.89	3.6×10^{7}
Exfoliant 2	3.08	3.1×10^{11}
Exfoliant 3	2.11	4.4×10^{10}

Next, three different plastic tea bags were examined by first removing the contents, washing and drying, and then heating for 5 minutes at 100 °C in ultrapure water to replicate the process of making tea. Figure 4 shows that incidental carbon-containing particles were found in all samples, with all having roughly the same number and size of microparticles, as shown in Table 3. While the particle size is similar to that of the the exfoliants, the particle concentrations are significantly lower in the tea bags: in the exfoliants, microparticles are added to aid in scrubbing, while in tea bags, they most likely originate from leaching or from the breakdown of the tea bags themselves.

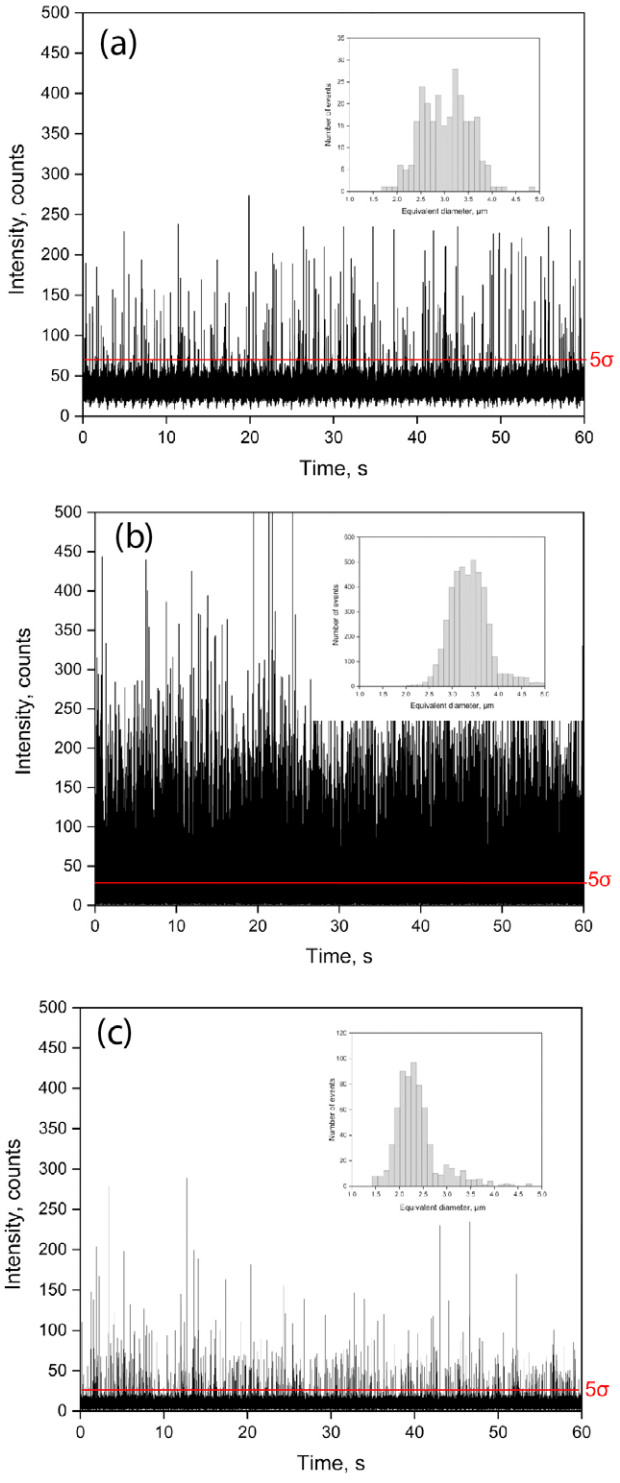

Figure 3: Time scans and size distributions of carbon-containing particles in three different exfoliants, where: (a) Exfoliant 1 has the broadest size distribution; (b) Exfoliant 2 contains the most particles; and (c) Exfoliant 3 has the smallest particle sizes.

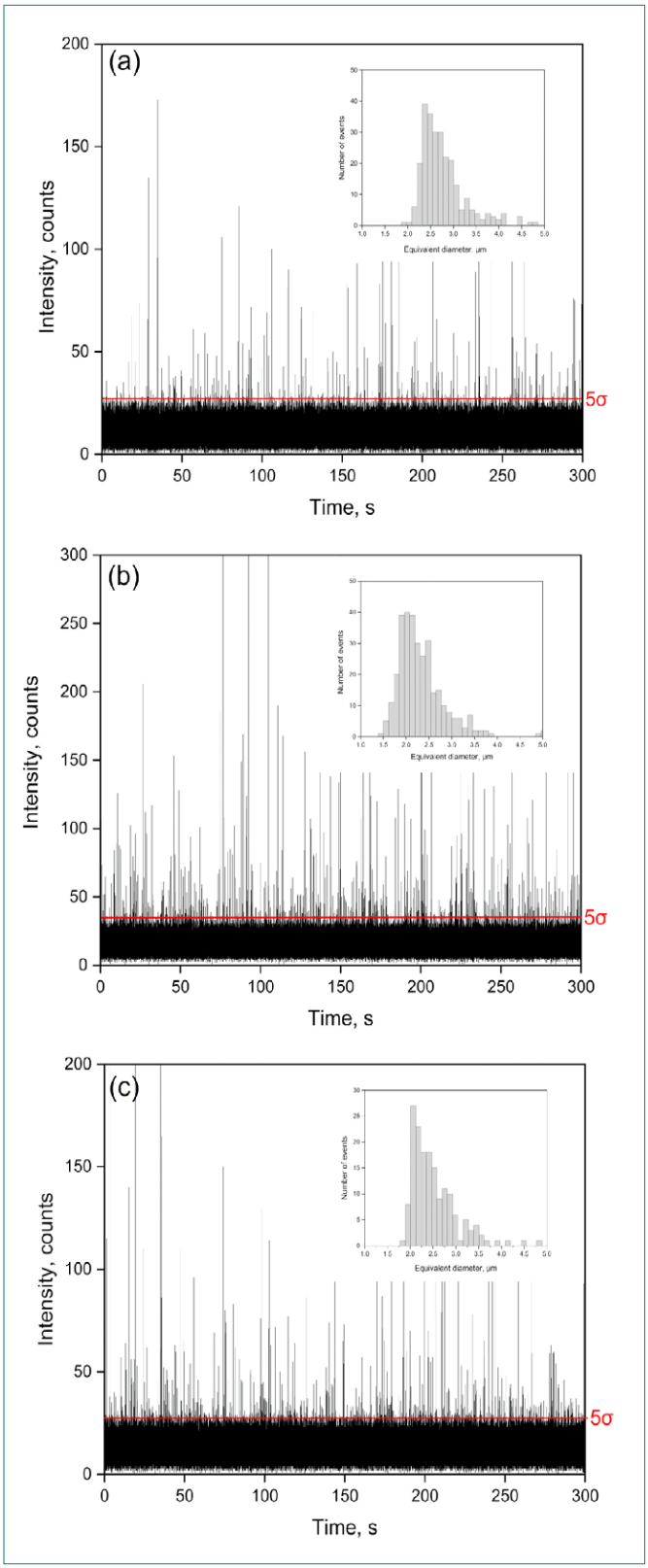

Figure 4: Time scans and size distributions of carbon-containing particles in three different plastic tea bags, each containing similar numbers and sizes of microparticles.

Table 3: Carbon-Containing Particle Results from Plastic Tea Bags.

Sample	Mean Diameter (µm)	Particle Concentration (g^{-1})
Blank	---	---
Tea Bag 1	2.70	2.2 x 1^{04}
Tea Bag 2	2.18	5.5 x 10^4
Tea Bag 3	2.26	1.9 x 10^4

Conclusions: SP-ICP-MS as a Screening Technique for Microplastics

Since any carbon-containing microparticles will produce carbon signals, the signals achieved using SP-ICP-MS in the determination of microplastic particles cannot be unambiguously linked to microplastics. As such, SP-ICP-MS is regarded as a complementary technique for the characterization of microplastics. To determine if the microparticles are plastic, additional techniques are required. In this work [4], both microscopy and ATR-FT-IR (PerkinElmer Spectrum 100) were used to confirm the presence and identity of the microparticles as plastics (polystyrene, polylactic acid, polyethylene terephthalate).

In order to obtain accurate particle size and number results for carbon in microplastics, the mass fraction of the carbon in the particles must be known. However, since the mass fraction can vary depending on the composition of the plastic, the carbon mass fraction can only be estimated (i.e., use the carbon mass fraction for polystyrene, which is 0.9231). However, because of its analysis speed, SP-ICP-MS can sample many more particles in much shorter times than conventional analytical techniques, providing more information about particle size distribution and particle concentration within a short space of time. Consequently, SP-ICP-MS is an ideal technique to be used in screening for microplastics.

In summary, SP-ICP-MS using the NexION system can be successfully used as either a screening tool or complementary technique for microplastic determination by monitoring the signal of C13. By taking advantage of analysis speed, the background from C13 is greatly reduced, allowing microplastic particles as small as 2 µm to be accurately sized and measured. By combining SP-ICP-MS with techniques which can identify the composition of microplastics, such as ATR-FT-IR, more thorough information about microplastics can be attained.

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