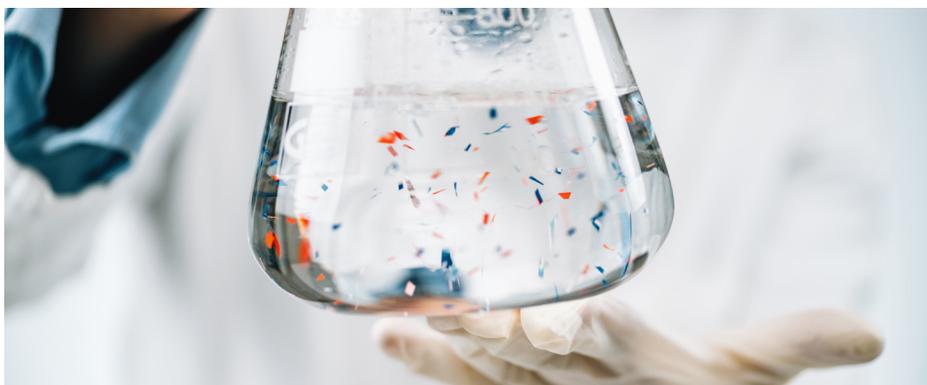


Particle Size Analysis of Polystyrene Microplastics by Single Particle (sp) ICP-MS

Investigation of plastic contamination during simulated UV-degradation by monitoring ^{13}C using the Agilent 8900 ICP-QQQ



Authors

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Introduction

Many everyday items such as packaging materials, storage and food containers, electronics, toys, and textiles contain plastic. From the 1950s onwards when plastics became a cost-effective material, huge amounts of plastics originating from consumer products, industry, agriculture, marine activities, recycling centers, and general waste have polluted the environment. Plastic contamination and plastic contaminating water are concerning issues since plastics never fully degrade but fragment, generating particles in the millimeter to nanometer diameter size range. Particles sized 5 mm to 1 μm are often called microplastics (MPs) and particles smaller than 1 μm are referred to as nanoplastics (NPs). The full extent of the risks posed by microplastics is still unknown, hence the need for reliable particle analysis and particle size analysis methods. Also, public awareness of the problem of plastic contamination of water, soil, air, and foods is increasing in all parts of the world (1). Given the scale of plastic pollution and gaps in knowledge about the behavior of plastic pollutants, more research is needed to understand the threat of plastic particles on ecosystems and human health.

To study the fate of MPs and NPs, various methods have been developed to sample and analyze the size, quantity, and material type of plastic particles. Most studies on MPs in complex environmental and biological media have focused on larger sized particles, while microplastic analysis methods for characterizing MPs smaller than 5 μm are rare (2).

Single particle (sp)ICP-MS is a feasible technique to quantitatively analyze MP and NP numbers and sizes, as it has been widely used to study metal-based nanoparticles (3). Researchers have used spICP-MS to quantify the size and number concentration of synthetic Au-coated MPs at the sub- μm size scale (4, 5). However, the method was based on indirect analysis of the Au coating, which required multistep sample pretreatment. Recent studies have shown that spICP-MS can quantify polystyrene MP particle sizes and number concentrations by monitoring ^{13}C (6–8). The method is a promising way to investigate MPs in a controlled research environment.

In this study, we further developed the spICP-MS method to quantify the particle number and size of polystyrene MPs during UV-degradation by monitoring the ^{13}C signal in a lab simulation environment.

Experimental

Materials and sample preparation

Polystyrene (PS) microbeads were used as MPs in this study. Two PS microbead suspensions (spherical shape, 10.0% wt/wt) with particle sizes of 800 nm (p/n: PL6008-4101; certified average diameter: 805 nm) and 1000 nm (p/n: PL6010-4101; certified average diameter: 1024 nm) were obtained from Agilent. Microbead powders containing three different sizes of PS (spherical shape, 1.8 μm , 3 μm , and 5 μm) were bought from Tesulang Inc. (Guangdong, China). The average diameters of the three PS microbead powders were measured by scanning electron microscopy (SEM, Hitachi SU8010, Japan). The diameters were $1.82 \pm 0.11 \mu\text{m}$, $2.97 \pm 0.19 \mu\text{m}$, and $4.96 \pm 0.14 \mu\text{m}$, as shown in Figure 1. All the MP suspension samples were prepared and/or diluted with de-ionized water (DIW) to a concentration range of 2–50 mg/L (depending on the MP particle size) before analysis.

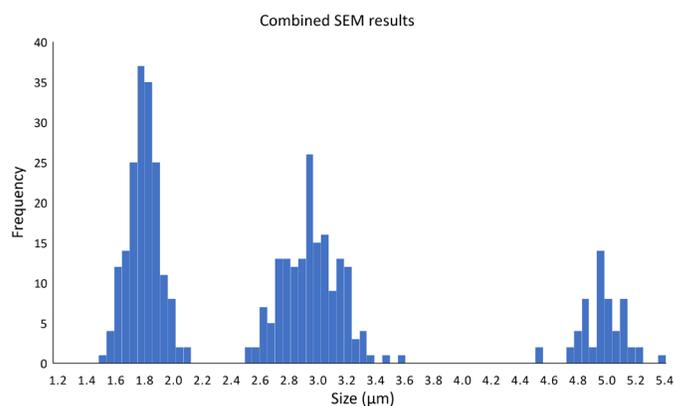


Figure 1. The combined SEM results of the three microbead powders used in this study. The sizes of PS measured in each powder were $1.82 \pm 0.11 \mu\text{m}$ ($n=175$), $2.97 \pm 0.19 \mu\text{m}$ ($n=168$), and $4.96 \pm 0.14 \mu\text{m}$ ($n=55$), respectively.

Instrumentation

An Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) was used for the spICP-MS method. The sample introduction system consisted of a quartz torch with 1.0 mm i.d. injector (p/n: G3280-80081), a standard quartz spray chamber, standard glass concentric nebulizer, and nickel-tipped interface cones. Samples were introduced into the ICP-MS by self-aspiration using 0.51 mm inner diameter PTFE tubing (p/n: 8003-0689). The 8900 includes two quadrupoles, Q1 and Q2, located either side of the ORS⁴ collision/reaction cell (CRC), enabling MS/MS mode of operation. In this study, ^{13}C was determined in no gas mode using MS/MS with Q1 and Q2 both set at $m/z = 13$. These operating conditions gave a better signal-to-noise (S/N) ratio and lower size detection limit, probably due to the elimination of the peak tailing overlap from ^{12}C in MS/MS mode. Typical instrument operating parameters are listed in Table 1. The single particle module within the Agilent ICP-MS MassHunter software version 5.1 was used for data collection, calibration, calculation of the particle number, concentration, and size distribution of particles in a sample.

Table 1. Typical Agilent 8900 ICP-QQQ operating parameters and acquisition settings for spICP-MS analysis of polystyrene microplastics.

Parameter	Setting
RF Power (W)	1600
Sampling Depth (mm)	6.0
Nebulizer Gas Flow Rate (L/min)	0.78
KED (V)	5
Sample Inlet Flow (mL/min)	0.08
Q1 → Q2 Masses (m/z)	13 → 13
Dwell Time (ms)	0.1
Acquisition Time (s)	60

UV-degradation treatment

To study the UV-degradation process of MPs, suspensions of the PS MPs (5 μm) were prepared in quartz beakers by multistep dilution using DIW to 10 mg/L. To ensure a homogenous dispersion of the MPs, the suspensions were mixed using glass stirrers, ultrasonicated, and vortexed. The UV-light degradation of MPs was carried out using a 36 W UV lamp (CNLIGHT, China), as illustrated in Figure 2. During the experiment, stirring ensured that the MPs were well-dispersed in the suspensions (there was no evidence that any MPs settled on the wall of the beakers). The UV-degraded MPs were collected by glass pipettes after 0, 12, 16, and 20 hours. The samples were then analyzed using the spICP-MS method.

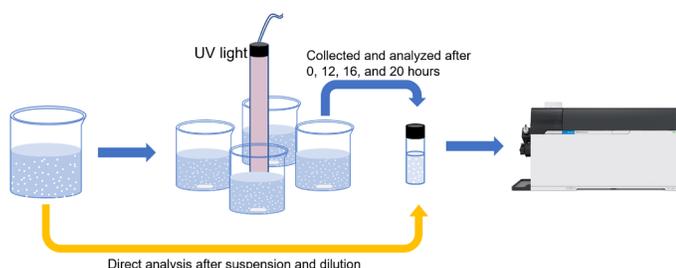


Figure 2. Illustration of the experimental workflow.

Results and discussion

The size and particle number concentration of the PS MPs in each suspension was determined using the 8900 ICP-QQQ operating in spICP-MS mode. The intensity of the ¹³C signal relates to the size of the PS MPs and the number of peak events within the acquisition time is used to determine the particle number concentration of MPs.

Determination of size and size distribution of PS MPs

The spICP-MS method was used to determine the size distributions of various PS MP suspensions (i.e., 0.8 μm, 1 μm, 1.8 μm, 3 μm, and 5 μm) by monitoring ¹³C. As shown in Figure 3, the mean intensity value (counts per second, CPS) of each PS MP suspension was plotted against the MP's volume (considered to be a solid sphere). A good linear relation ($R^2 = 0.9999$) was obtained for the five suspensions, showing that the instrument can analyze PS MPs with a wide dynamic range covering particle sizes from 0.8 to 5 μm.

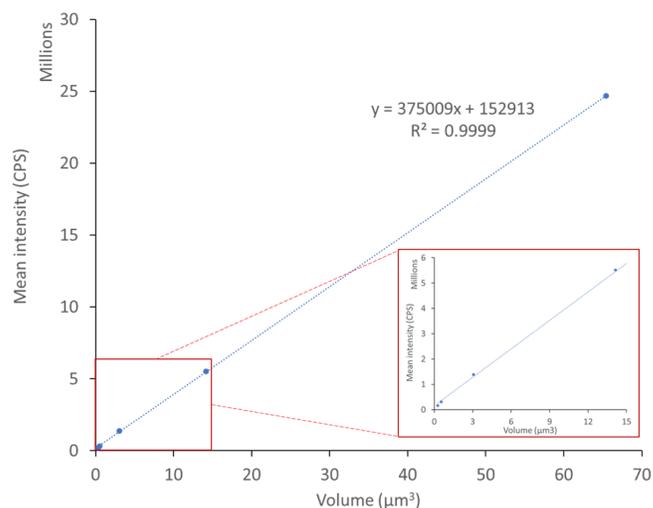


Figure 3. Calibration curve of PS MPs particle size determined by spICP-MS. The calibration was presented as mean intensity (CPS) versus particle volume (μm³). Data from Table 2.

The 1.8 μm, 3 μm, and 5 μm PS MPs were mixed with a mass ratio of 1 to 4.6 to 20.1 and analyzed by spICP-MS. The CPS results of each measured particle and calibration curve were used to calculate particle size data. As shown in Figure 4, the results were in good agreement with the statistical analysis of the size distribution obtained by SEM imaging across the tested size range.

The size distributions of the 0.8 and 1 μm PS MPs were also calculated based on the spICP-MS calibration curve shown in Figure 3. The average sizes were 0.86 ± 0.11 and 1.03 ± 0.18 μm, respectively, which is within the nominal value of the PS microbead suspensions. The results show that the spICP-MS method provides accurate size distribution data for PS MPs.

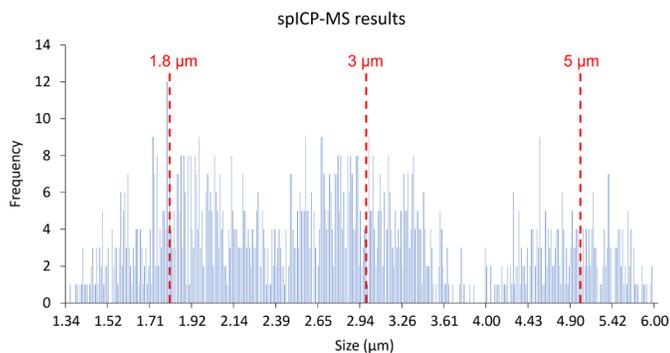


Figure 4. spICP-MS results of three different sizes of the mixed PS microbead powders.

Calculation of the nebulizer efficiency: The nebulizer efficiency (η_{neb}) is needed to calculate the number concentration of particles in an unknown sample. In this study, the η_{neb} of PS MPs was calculated based on equation 1.

$$\eta_{neb} = \frac{N_p}{C_{prepared} \times v \times T} \quad (\text{Eq 1})$$

Where N_p is the number of detected particles within the acquisition time. $C_{prepared}$ is the number concentration of particles (particles/L) prepared for spICP-MS analysis, v is sample inlet flow (L/s), and T is the total acquisition time (s).

The calculated results show that the nebulizer efficiency of the various PS MP suspensions ranged between 0.5 and 1.9%. Table 2 shows that the larger the particle, the smaller the η_{neb} value.

Calculation of particle number concentration detection limit: The particle number concentration detection limit (LOD, particles/L) was calculated based on equation 2.

$$LOD = 3 \times \frac{1}{\eta_{neb} \times v \times T} \quad (\text{Eq 2})$$

Where η_{neb} is the nebulization efficiency, v is sample inlet flow (L/s), and T is the total acquisition time (s).

Using equation 2, the spICP-MS method had a particle number LOD within the range of 2.0×10^6 to 6.9×10^6 particles/L, depending on the size of the MP.

The nebulization efficiency varies significantly with the MP particle size. So, when calculating the number concentration of MPs in unknown samples, the η_{neb} should be used according to different size-fractions (i.e., $>3 \mu\text{m}$, $1.8\text{--}3 \mu\text{m}$, and $0.8\text{--}1.8 \mu\text{m}$). This approach provides a better estimation of the number concentration of MPs.

Table 2. Typical nebulization efficiency and mean intensity of the spICP-MS method for analyzing five different-sized PS MPs.

Particle Size (μm)	Nebulization Efficiency (%)	Mean Intensity (CPS)
0.805	1.9	1.67E+05
1.011	1.5	3.07E+05
1.8	0.8	1.39E+06
3	0.8	5.51E+06
5	0.5	2.47E+07

PS MPs size changes during UV-degradation

The spICP-MS method developed to quantify the particle number and size of the $5 \mu\text{m}$ PS MPs was used to study the effects of UV-degradation in a lab simulation environment. In a preliminary study, samples were collected and analyzed by spICP-MS after 0, 12, 16, and 20 hours of UV exposure.

As shown in Figure 5, the spICP-MS measurements clearly show that the UV-degradation process generates secondary MPs with sizes at the submicrometer to micrometer scale within the 20 hours of the experiment. The measured particle size distribution shows that the dynamics of the MP degradation process can be tracked in detail. During the first 12 h of degradation, the average particle size decreased from 4.9 to 4.1 μm , and smaller sized ($<1.8 \mu\text{m}$) MPs were also detected. The changes in MP particle size distribution at 16 and 20 hours showed that the average size decreased to 3.3 and 2.2 μm , respectively, and large numbers of $<1.8 \mu\text{m}$ sized MPs were generated.

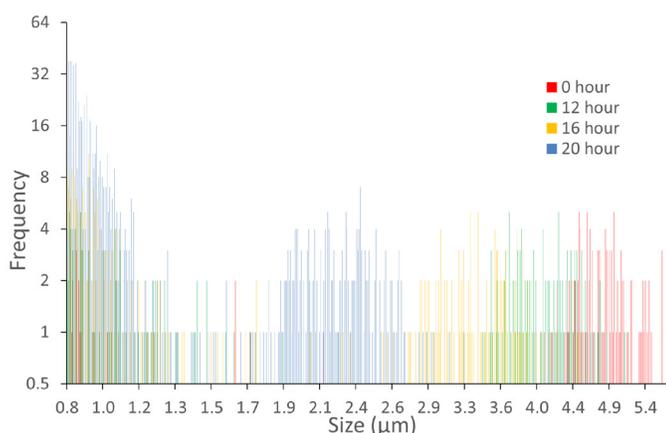


Figure 5. spICP-MS particle size distribution results of MPs after 0, 12, 16, and 20 hours of the UV-degradation experiment.

To understand the dynamics of particle number concentration changes of MPs during the UV-degradation process, size-fractionated particle number concentrations were obtained for the initially sized 5 µm particles by spICP-MS (Table 3). There was little variation in the size-fractionated particle number concentrations of MPs (>3 µm, 1.8–3 µm, and 0.8–1.8 µm) in the first 12 hours. After 16 and 20 hours, there was a significant increase in the particle number concentration of midsize (1.8–3 µm) MPs. This increase coincided with the larger-sized (>3 µm) MP particle number concentration declining to below the LOD of 4.6×10^6 particles/L after 20 hours. Also, after 12 to 20 hours UV exposure, there was a marked rise in the particle number concentration of the smaller MPs (0.8–1.8 µm) from approximately 4.14×10^7 to 3.58×10^8 particles/L. The increase in smaller-sized particles indicates the generation of secondary fragmented MPs during the UV degradation process.

Table 3. The mean particle concentration results after 0, 12, 16, and 20 hours of the UV-degradation experiment. The original size of the particles was 5 µm.

Time (Hours)	Particle Concentration (particles/L)			
	0.8–1.8 µm	1.8–3 µm	>3 µm	Total
0	7.53E+06	<LOD	1.78E+08	1.87E+08
12	4.14E+07	8.48E+06	1.63E+08	2.13E+08
16	6.08E+07	9.09E+07	1.49E+08	3.01E+08
20	3.58E+08	2.13E+08	<LOD	5.74E+08

Conclusion

A microplastic analysis method was developed using an Agilent 8900 ICP-QQQ to determine plastic particles by measuring ^{13}C . The single particle (sp)ICP-MS method provided accurate quantification of microplastic particle sizes and number concentrations over a wide size-range covering the submicrometer (0.8 µm) to micrometer (5 µm) scale. Taking into account the nebulizer efficiency of different sized particles, the number concentration detection limit ranged from 2.0×10^6 to 6.9×10^6 particles/L.

The UV-light accelerated degradation dynamics of polystyrene MPs were investigated using the spICP-MS method. The results showed clear fragmentation of polystyrene MPs over time, with the generation of large numbers of nano- and micro-sized particles over 20 hours of simulated exposure.

This research investigated and quantified the dynamics of degradation on particle size and number concentration of MPs. The data provided by the spICP-MS microplastic analysis method can be used to estimate and predict the long-term secondary MP generation process and the retention of MPs in the environment. These insights are essential for assessing the toxicological risks of micro- and nano-plastic contamination on ecosystems.

More information

For more information, please see Ziyi Liu, et al. Quantifying the Dynamics of Polystyrene Microplastics UV-Aging Process. *Environ. Sci. Technol. Lett.* **2022**, 9 (1), 50–56. <https://doi.org/10.1021/acs.estlett.1c00888>.

Consumables list

Polystyrene microbead suspension (spherical shape, 10.0% wt/wt) with particle sizes of 800 nm (p/n: [PL6008-4101](#))

Polystyrene microbead suspension (spherical shape, 10.0% wt/wt) with particle sizes of 1000 nm (p/n: [PL6010-4101](#))

Quartz torch with 1.0 mm i.d. injector (p/n: [G3280-80081](#))

0.51 mm inner diameter PTFE tubing (p/n: [8003-0689](#))

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