Investigation of Microplastic Size and Number Changes During Simulated UV-Degradation Using Single Particle ICP-MS/MS

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Introduction

Over the decades, increased plastic contamination has become more prevalent and visible. Since the early 1990s, the rate of single-use plastic production has grown many fold, contributing to contamination of the environment. Despite a network of plastic recycling facilities, only a minor share of plastic waste is successfully recycled. Many unrecycled plastic waste ends up in landfill, rivers, and oceans. Most plastic never fully degrades; it simply disintegrates into smaller and smaller pieces. So, unrecycled plastic waste can potentially remain in the environment as microplastics (MPs) for centuries irrespective of where it resides – whether on land or in water. MPs (1 μm to 5 mm in size) could enter the food chain and onto our dinner tables. The full extent of the risks posed by MPs is still unknown, hence the need for reliable particle analysis and particle size analysis methods.

Current methods for identifying MPs mostly include using stereomicroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), hyperspectral imaging (HSI), Raman microspectroscopy (RM), Fourier transform infrared spectroscopy (FTIR), and pyrolysis GC-MS.[1] However, most of the methods encounter difficulties when analyzing MPs smaller than 5 μm. Recent studies have shown that spICP-MS (Figure 1) can quantify polystyrene (PS) MP particle sizes and number concentrations by monitoring ^{13}C. The method could analyze PS MPs as small as 1 μm.[2]

The spICP-MS method has been further developed to analysis sub-micrometer MPs and applied to the quantification of the particle number and size of PS MPs during UV-degradation in a lab simulation environment.
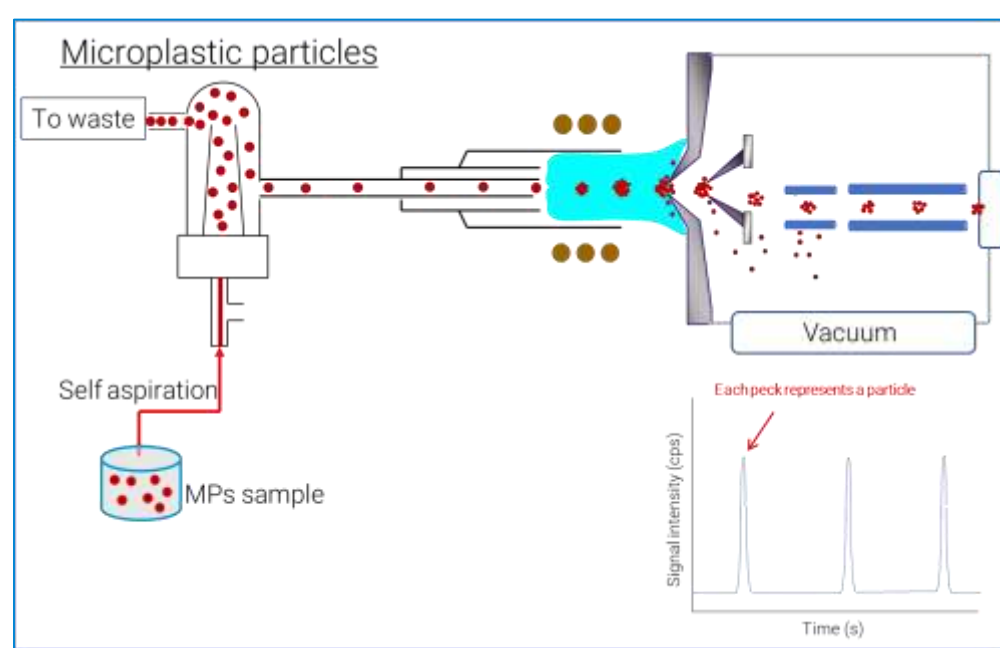

Figure 1. Illustration of the spICP-MS method for detection of MPs.

Experimental

Samples and regents

- Two PS MP suspensions (800 nm, P/N: PL6008-4101; 1000 nm, P/N: PL6010-4101) were obtained from Agilent. Three different sizes of PS MPs powders (1.8, 3, 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 ± 0.11, 2.97 ± 0.19, and 4.96 ± 0.14 μm, respectively.

- All MP suspension sample dilutions were to a concentration range of 2–50 mg/L (depending on the MP particle size) before analysis using 18.2 MΩ·cm deionized water (DIW. Millipore, USA).

Instrument settings

- An Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) was equipped with a MicroMist glass concentric nebulizer, quartz spray chamber, quartz torch with 1.0 mm i.d. injector (p/n: G3280-80081), and nickel 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 ICP-MS was optimized using autotuning functions within the Agilent ICP-MS MassHunter software. The ^{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.

- The single particle module within the ICP-MS MassHunter software version 5.1 was used for data collection, calibration, and calculation of the particle number and concentration.

- The typical instrument operating parameters used in this study are shown in Table 1.

Table 1. Typical Agilent 8900 ICP-MS/MS operating conditions used in this study.

Parameter	Value	Parameter	Value
RF Power (W)	1600	KED (V)	5
Sampling Depth (mm)	6	Q1 (m/z)	13
Nebulizer Gas (L/min)	0.78	Q2 (m/z)	13
Sample Inlet Flow (mL/min)	0.08	Gas Mode	No Gas
Deflect (V)	12.8	Dwell Time (ms)	0.1
OctP Bias (V)	-9.0	Acq Time (s)	60

Experimental

UV-degradation treatment

- To study the UV-degradation process (using a 36 W UV lamp) 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.

- 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.
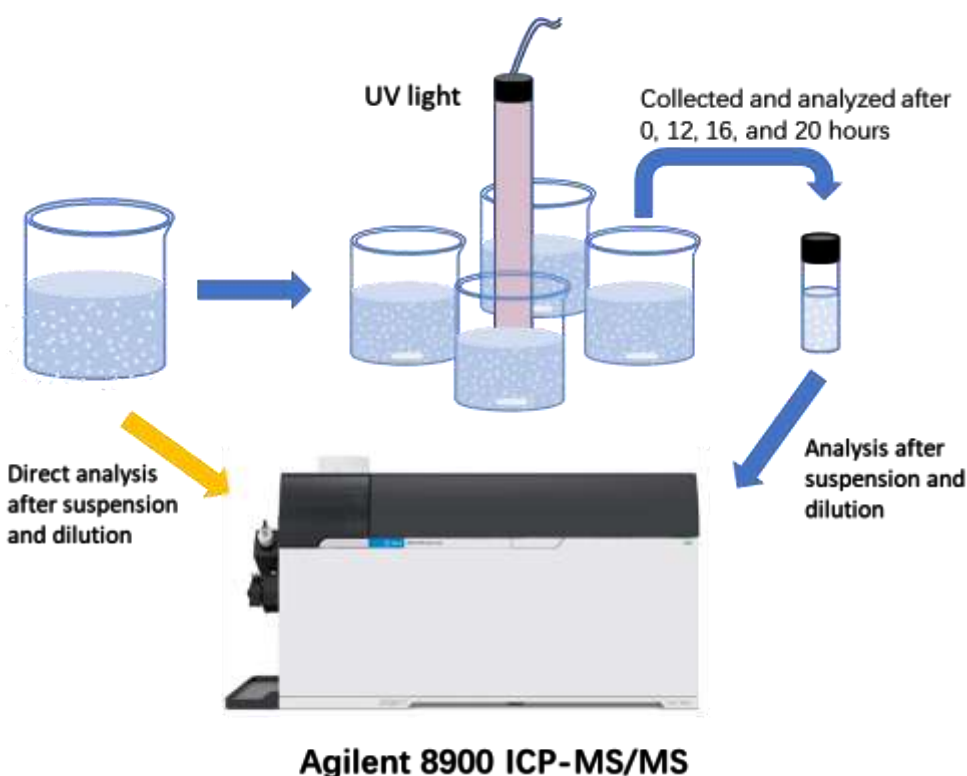

Figure 2. Illustration of the UV-degradation experimental workflow.

Results and Discussion

Size and size distribution of PS MPs

- The 0.8, 1.0, 1.8, 3, and 5 μm PS MPs were prepared to contain similar particle concentration when diluted with DIW.

- The mean intensity value (counts per second, CPS) of each PS MP suspension was plotted against the MPs' volume (considered to be a solid sphere). A good linear relation (R^2 = 0.9999) was obtained for the five suspensions, showing that the 8900 ICP-QQQ can analyze PS MPs with a wide dynamic range covering particle sizes from 0.8 to 5 μm (Figure 3).

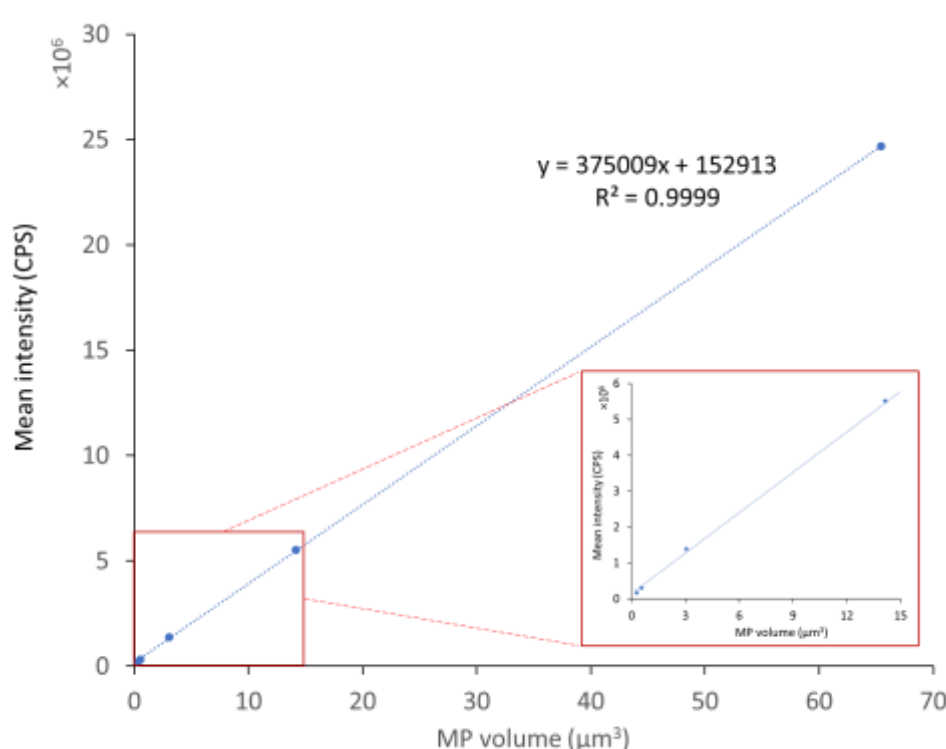- The background ^{13}C signal significantly affect the size detection limit of MPs.

Figure 3. Calibration curve of PS MPs particle size determined by spICP-MS. The calibration was presented as mean intensity of ^{13}C (CPS) versus particle volume (μm³).

- By mixing the 1.8, 3, and 5 μm PS MPs at a mass ratio of 1 to 4.6 to 20.1 and analyzing by spICP-MS, it could be demonstrated that clear separation of different size MPs could be achieved (Figure 4).

- The CPS results of each measured particle and calibration curve were used to calculate particle size data.

- The results were in good agreement with the statistical analysis of the size distribution obtained by SEM imaging across the tested size range.
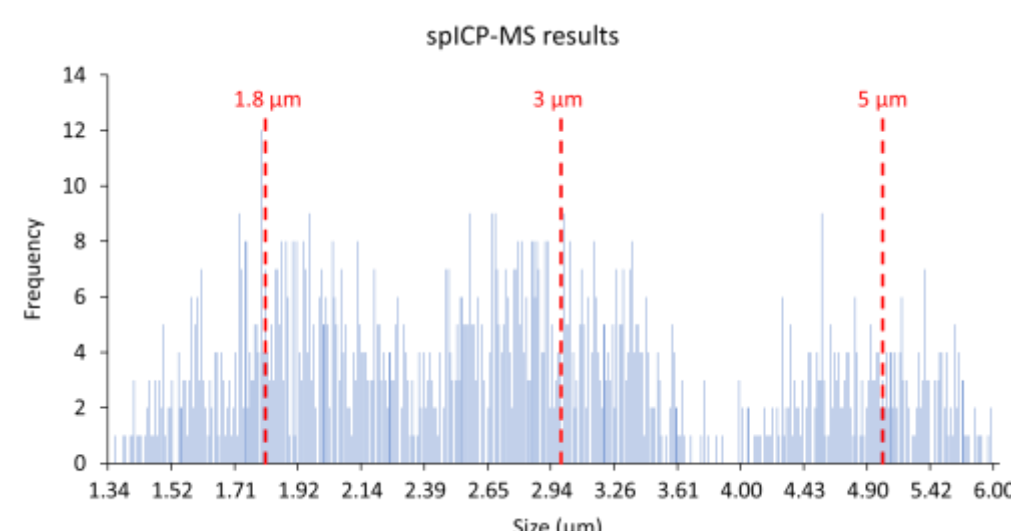

Figure 4. spICP-MS results of three different sizes of the mixed PS microbead powders.

Nebulizer efficiency and particle number LOD

- The nebulizer efficiency (η_{neb}) is needed to calculate the number concentration of particles in an unknown sample.

$$\eta_{neb} = \frac{N_p}{C_{prepared} \times v \times T}$$

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).

Results and Discussion

Nebulizer efficiency and particle number LOD

- The particle number concentration detection limit (LOD, particles/L) was calculated based on the following equation:

$$LOD = 3 \times \frac{1}{\eta_{neb} \times v \times T}$$

Where η_{neb} is the nebulization efficiency, 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%, leading to 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 MPs.

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

Particle Size	Nebulization Efficiency	Mean Intensity
(μm)	(%)	(CPS)
0.8	1.9	1.67E+05
1.0	1.5	3.07E+05
1.8	0.8	1.39E+06
3.0	0.8	5.51E+06
5.0	0.5	2.47E+07

- When calculating the number concentration of MPs in unknown samples, the η_{neb} should be used according to different size-fractions (i.e., >3 μm, 1.8–3 μm, and 0.8–1.8 μm). This approach provides a better estimation of the number concentration of MPs.

PS MPs size changes during UV-degradation

- The analysis clearly shows that the UV-degradation process generates secondary MPs with sizes at the sub-micrometer 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 (Figure 5).
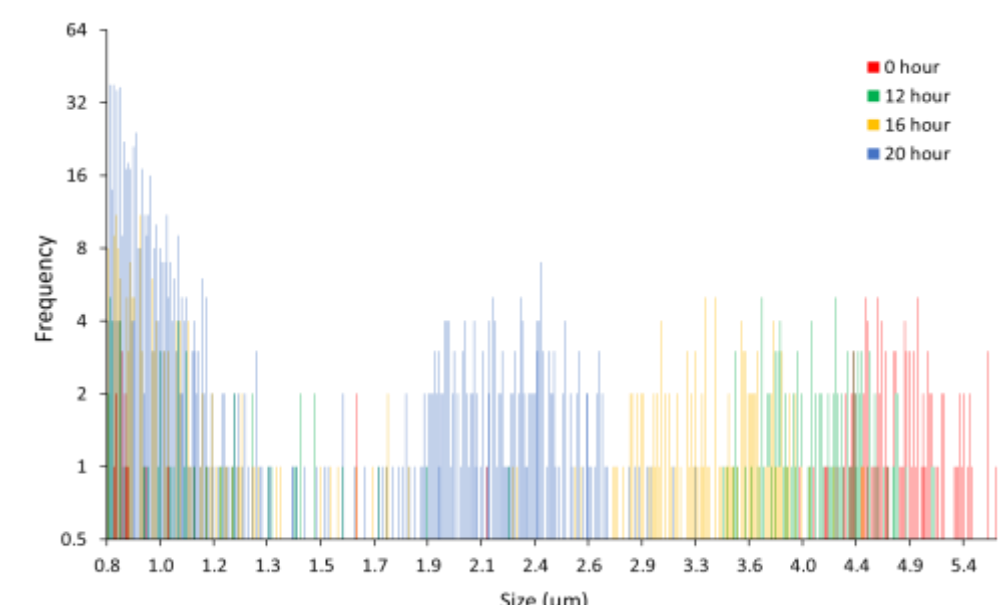

Figure 5. spICP-MS particle size distribution results of MPs after 0, 12, 16, and 20 hours of the UV-degradation experiment.

- 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. The increase in smaller-sized particles after 12 hours indicates the generation of secondary fragmented MPs during the UV degradation process, leading to a significant increase in MP particle concentration.

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

Conclusions

- Using an Agilent 8900 ICP-MS/MS to determine plastic particles by measuring ^{13}C in spICP-MS mode provided accurate quantification of microplastic particle sizes and number concentrations over a wide size-range covering the sub-micrometer (0.8 μm) to micrometer (5 μm) scale.

- Considering 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 degradation dynamics of PS MPs 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.

- 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.

References

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2. E. Bolea-Fernandez et. al., J. Anal. At. Spectrom. 35 (2020) 455-460
3. Ziyi Liu, et al. Environ. Sci. Technol. Lett. 2022, 9 (1), 50–56