High sensitivity quantification and mass distribution analysis of microplastics in water using single particle ICP-MS

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ABSTRACT

Purpose: To demonstrate how ICP-MS can be used to assess the microplastic mass distribution with the environmental water samples.

Methods: A single quadrupole Thermo Scientific™ iCAP™ RQ ICP-MS system, in conjunction with the scQuant single cell analysis plug-in for Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution software was used for all measurements.

Results: The analytical method was rigorously tested for performance, and the determination of microplastic mass distribution using polystyrene beads in environmental water samples was clearly demonstrated.

INTRODUCTION

Microplastics are of growing concern due to their abundance, potential for bioaccumulation, and potential for negative health effects. Raman spectroscopy and PY-GC-MS are common analytical methods for characterization of microplastics in environmental samples. However, these techniques may require large sample volumes and pre-concentration prior to analysis.
ICP-MS has been used for the analysis of nanoparticles, providing data on their size, quantity, and composition. Since there are few trace metals present in microplastics, direct ICP-MS analysis was not historically feasible, as analysis of carbon by ICP-MS is difficult due to the low ionization yield and elevated backgrounds levels. However, the use of ICP-MS operated in time-resolved mode for carbon measurement presents an alternative for studying the rate of plastic degradation.[1]

MATERIALS AND METHODS

Sample Preparation

All blanks and calibration standards used for the determination of the detection sensitivity were prepared from ultrapure water using IPA (Sigma-Aldrich, semiconductor grade) as a carbon source.
The transport efficiency standard solutions containing microplastic particles were prepared using commercially available polystyrene beads with 2 and 5 µm nominal diameter (Sigma-Aldrich) to assess transport of actual microplastic particles in the system. These solutions were further diluted using ultrapure water.

Potable and surface water samples were collected in Bremen, Germany for analysis as real sample matrices. The surface water sample originated from a pond and contained partially undissolved matter. For purification prior to analysis, 5 mL HNO_3 and 2 mL H_2O_2 were added into 50 mL of pond water and left to react for one week. After this period, the sample was centrifuged and diluted 20x with ultrapure water. All samples were vortexed during preparation and again prior to analysis to resuspend potentially settled particles.

Test Method(s)

A Thermo Scientific™ iCAP™ RQ ICP-MS was used for all measurements. The instrument was equipped with a specialized nebulizer and spray chamber to allow the introduction of single cells with high transport efficiency (CytoNeb and CytoSpray, Elemental Scientific, Inc., Omaha, NE, USA). To achieve this, the sample flow rate had to be reduced significantly, such that sample delivery was accomplished using a syringe pump (Chemyx, Stafford, Texas, USA) instead of the conventional peristaltic pump commonly used.

Data Analysis

The scQuant plug-in was used for method creation and data evaluation. The Qtegra ISDS Software also contains a dedicated plug-in to integrate the operation of the syringe pump into the overall workflow for the microplastic analysis such as example rinsing, priming the system, and starting the sample delivery for data acquisition. The scQuant plug-in is capable of automatically determining key evaluation parameters, calculating accurate mass content of analyte in each cell, and displaying mass distribution, box plots, and summary data for each sample analysis in one place.

Table 1. Typical instrument parameters used in this study.

Parameter	Value
Spray chamber	CytoSpray spray chamber
Torch	One-piece quartz torch with 2.0 mm i.d., injector
Nebulizer	CytoNeb
Syringe pump speed	Syringe pump @ 20 µL·min^{-1}
Interface	Pt sampler and Pt tipped skimmer cone with high sensitivity skimmer cone insert
Plasma power	1550 W
Nebulizer gas	0.4 L·min^{-1}
Additional gas	0.5 L·min^{-1}
QCell setting	O_2 CCTS
Qcell gas flow	100% O_2, 0.3 mL·min^{-1}
Scan settings	0.001 - 0.01 sec dwell time
Quadrupole	High resolution (0.3 amu)
Scan analyte	$^{12}C^+$
Sample analysis duration	30 - 120 s analysis + sample/uptake 100 s

RESULTS

Detection of carbon in microplastics

Using optimized O_2 CCTS settings, a calibration curve for carbon was generated by running the respective standard solutions over a range of 31 to 60 mg·L^{-1}. The calibration curve (fig. 1) showed excellent linearity with a coefficient of determination (R^2) value of better than 0.99995, a background equivalent concentration (BEC) of 2 mg·L^{-1} for carbon, and an instrumental detection limit (IDL) of 0.4 mg·L^{-1}.

Figure 1: Calibration curve for $^{12}C^+$

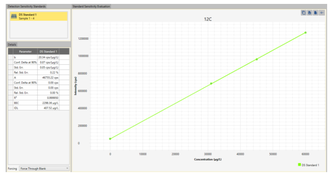

Figure 2: Raw signal intensity data for 2 µm polystyrene (200,000-fold dilution) using scQuant plug-in.

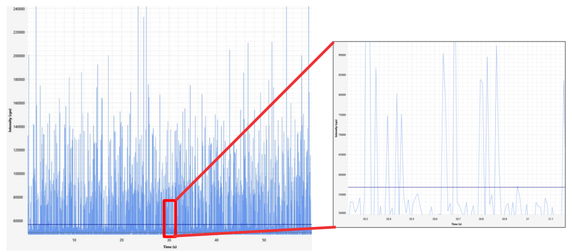

Table 2: Particle number concentration results with different dilution factors

Sample	Dilution Factor	Particles number expected [n·mL^{-1}]	Particles number concentration [n·mL^{-1}]	Particle transport efficiency [%]
Polystyrene beads, 5µm	5,000	291,026	18,968	4.19
	10,000	145,513	10,108	
Polystyrene beads, 2µm	100,000	227,364	20,717	30.08
	200,000	113,682	10,658	

Analysis of polystyrene standards as a surrogate for microplastics

2 and 5 µm polystyrene beads were diluted and analyzed (2 µm raw data is in fig. 2). In both cases, the overall number of signals increases with decreasing dilution as more particles enter the plasma and become ionized. The quantitative assessment of the particle number concentration correlates well with the dilution factor, as can be seen in Table 2. The transport efficiency for different polystyrene beads was estimated to be around 4.19% for 5 µm sized particles and 30.08% for 2 µm sized particles.

Both particle sizes investigated in this study were calculated and compared. Assuming a spherical shape of the particles, the approximate number of atoms per particle should change following the nominal size relation. The absolute signal intensity should change as per the following calculation:

Volume 5 µm / Volume 2 µm =
(3/4π(2.5)^3) / (3/4π(1.0)^3) =
15.625/1 =
15.625

Table 3 shows the intensity of ten selected signals from the measurement of polystyrene microplastics monitoring $^{12}C^+$ and observed very close to the theoretical result determined.

Table 3. Intensity ratio results with 2 and 5 µm microplastics monitoring $^{12}C^+$

	Diameter of microplastics	
	2.0 µm	5.0 µm
1	59,441	916,027
2	59,240	923,348
3	59,140	910,275
4	59,843	905,046
5	59,541	923,348
6	59,642	911,844
7	59,541	916,550
8	59,039	929,101
9	59,843	925,963
10	59,742	918,642
Average	59,501	918,014
SD	285	7,569
Experimental ratio	15.4 ± 0.17	
Theoretical ratio	15.63	

Analysis of unknown environmental samples

Two different environmental water samples (potable water and pond surface water) were screened for the presence of microplastics. A challenge in the analysis of real water samples, compared to standard solutions prepared in ultrapure water, is the higher amount of dissolved carbon dioxide (CO_2), causing an increase of the background signal observed in the measurement, and potentially overlaying the microplastic particles present (fig. 3).

Figure 3. Mass distribution result of potable water with and without dilution, showing reduction of signals resulting from background CO_2

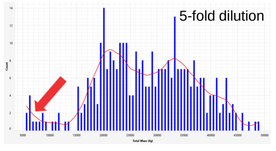

Table 4 shows the analysis results for the 5 µm polystyrene beads spike recovery test in both natural waters. A 5 µm spike recovery result for five-fold diluted potable water of 84.9% was obtained, while approximately 50% for pond water was achieved. Diluting the sample improves the accuracy of the particle number analysis, which is one of the key steps required to ensure accurate analysis of microplastics.

Table 4. Spike recovery results for two environmental water samples

Parameter	5-fold dilution		20-fold dilution		5 µm in ultra pure water (reference value)
	Potable water	Spiked potable water	Pond water	Spiked pond water	
Durations (s)	120	120	60	60	30
Mean (fg)	60,225 ± 7,538	57822 ± 8,920	60,865 ± 12,280	59,576 ± 10,676	62,146 ± 10,995
Number (particle)	3	153	5	46	48
Number per volume (particle·mL^{-1})	149	13726	415	7652	15973
Spiked particle recovery (%)	84.9%		45.30%		-

CONCLUSIONS

A highly sensitive method for microplastics analysis using the iCAP RQ ICP-MS equipped with scQuant software was developed and applied to the analysis of two environmental water samples. The analytical method was rigorously tested for performance, and the results obtained clearly demonstrated the following analytical advantages:

- Interference-free analysis was achieved using high-performance collision / reaction cell operation with high mass resolution (0.3 amu). By minimizing the carbon background during sampling, a carbon BEC of 2 mg·L^{-1} can achieved, allowing the use of $^{12}C^+$ for the direct ICP-MS analysis of microplastics in environmental samples.
- Polystyrene beads could be detected via single particle events and, from the data, the mass distribution for 2 and 5 µm particle sizes could be determined.
- The scQuant evaluation tool offers automatic calculation of the particle transport efficiency, mass, and signal distribution enabling effective analysis of microplastic particles in the samples studied.

REFERENCES

1. González-Pleiter M, Tamayo-Belda M, Pulido-Reyes G, Amariei G, Leganés F, Rosal R, Fernández-Piñas F (2019) Secondary nanoplastics released from a biodegradable microplastic severely impact freshwater environments. *Env Sci Nano*, 6, 1382.

TRADEMARKS/LICENSING

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