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RESEARCH

Development and evaluation of a pretreatment procedure for single particle ICP-MS quantitative analysis of microplastics in inorganic-carbon-rich water samples

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Abstract This study evaluates the applicability of single particle inductively coupled plasma mass spectrometry (spICP-MS) for the quantitative detection of small microplastics (MPs) through monitoring of the carbon signal in tap water. To overcome high background signal originating from dissolved inorganic carbon typically present in tap water at elevated levels, a sample pretreatment procedure was developed to remove inorganic dissolved carbon while preserving the physicochemical properties of MPs. The optimized protocol involved mild acidification with 0.05% HNO_3 followed by ultrasonication for 60 min. This treatment effectively reduced the concentration of dissolved inorganic carbon by up to 97%, achieving background carbon levels comparable to those of ultrapure water, and enabling the detection of MPs smaller than 2 µm. The impact of the pretreatment on MPs was evaluated using polystyrene (PS) MPs in the 1 – 4.5 µm size range. In addition, systematic optimization of spICP-MS instrumental parameters was conducted across four configurations differing in sample introduction system and torch injector inner diameter. Among the tested setups, the combination of a conventional concentric nebulizer and a 2.5 mm torch injector provided the most reliable performance for detecting MPs. Under optimized conditions, the spICP-MS method was used for MPs spiked to tap water, followed by the proposed pretreatment, which showed the procedure had negligible effects on particle concentration, size distribution, morphology, and surface characteristics. This was also confirmed by field-emission scanning electron microscopy (FE-SEM). The proposed pretreatment strategy, coupled with optimized spICP-MS conditions, shows potential for the first assessment of the contamination of tap water with MPs.

Keywords Microplastics · Tap water · Single particle ICP-MS · Sample pretreatment · Inorganic carbon

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Introduction

Excessive plastic production and poor waste management have led to widespread microplastic pollution, as larger plastics break down under environmental conditions into microplastics (MPs, 1 µm – 5 mm)

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and nanoplastics (NPs, < 1 µm) [1, 2]. These particles vary in composition and can carry other environmental contaminants, cross biological barriers, and accumulate in organisms, posing risks to the environment and human health [3]. Detecting MNPs remains challenging due to their low environmental concentrations, the complexity of environmental samples, and the lack of standardized analytical methods [4]. To accurately assess their presence, impacts, and environmental fate, more sensitive, selective, and non-destructive techniques are required, especially for the smallest particles.

The most common analytical techniques typically used for the determination of MPs particle size, concentration, and/or composition are microscopy, spectroscopy, mass spectrometry, and light scattering [4–6]. One potential technique for detecting MPs is inductively coupled plasma-mass spectrometry in single-particle mode (spICP-MS), which has been widely used to study inorganic nanoparticles in different complex samples [7]. Recently, it has been proposed as a suitable technique for the size characterization and quantification of MPs in the lower µm size range when monitoring ^{13}C isotope [8–13] or ^{12}C isotope [14, 15]. So far, the spICP-MS has demonstrated the ability to detect polystyrene (PS) MPs in the 1–5 µm size range in ultrapure water [11–13], seawater [15, 16], river waters [8], personal care products [12], and MPs released from plastic teabags [9, 12] and after UV degradation [10, 14]. Moreover, the spICP-time-of-flight(TOF)-MS technique, which is capable of simultaneous measurement of the entire elemental spectrum in individual particles, has recently been demonstrated as a promising approach for distinguishing MPs from algae cells and dissolved organic matter based on the elemental fingerprint of particles [17]. Various sample introduction systems have been used for spICP-MS analysis of MPs, including total consumption nebulizers (also called high-efficiency nebulizers), which were specifically designed for efficient transport of larger particles like cells [8, 12, 13, 16] and are particularly advantageous when low MP number concentrations are expected or when sample amounts are limited. Conventional concentric nebulizers have also been used [9–11, 14, 15, 17], as well as online microdroplet calibration systems to minimize matrix effects [16].

Despite the demonstrated potential of spICP-MS for the detection of MPs in the lower µm size range by monitoring the carbon signal, the technique still suffers from some limitations that are related to the low ionization efficiency of carbon in the plasma (between 1 and 5%), its high first ionization potential (11.26 eV), and its low transmission in the ICP-MS interface due to space charge effects. This results in poor ICP-MS sensitivity for carbon and, combined with a high carbon background, leads to relatively high detection limits for MPs. To date, the lowest size detection limit for MPs achieved by Gonzalez de Vega et al. [15] is 0.62 µm. Elevated carbon background that hinders the signal of small MPs can originate from either inorganic forms of carbon (e.g., carbon dioxide present in air and/or dissolved in water, (hydrogen)carbonates in waters) or organic carbon (e.g., dissolved organic matter) that can be naturally present in samples [18]. Moreover, spICP-MS cannot distinguish between particulate carbon originating from MPs and other sources, such as bacteria and algae. Sample pretreatment approaches commonly used in the analysis of MPs (e.g., sample digestion using strong acids, bases, hydrogen peroxide or Fenton reagents, density separation using saturated saline solutions, etc.) [19] cannot be for this purpose, as they may lead to the degradation of small MPs and contamination of the ICP-MS instrumentation. Instead, Trujillo et al. [8] suggested pretreating river water samples with 10% nitric acid for 24 h to reduce dissolved carbon and digest microorganisms prior to spICP-MS analysis. This treatment showed no significant effect on the size of 2 µm and 3 µm PS particles, while yielding recoveries of 83% and 60% for their respective particle number concentrations. Another approach combining optical tweezers with Raman spectroscopy and spICP-TOF–MS has been proposed to remove interfering matrix constituents prior to spICP-MS analysis of MPs [20]; however, this strategy requires specialized instrumentation that is often not readily available.

Tap water can represent an important source of MPs of varying sizes, polymer compositions, shapes, and concentrations [21] that originates from several stages along the water supply chain, including the contamination of source water, treatment processes that may employ polymer-based filtration membranes, and distribution infrastructure made of polymer materials. Although the presence of MNPs in drinking water is currently not regulated by specific maximum concentration limits, they are subject

to monitoring and risk assessment. In the EU, the Drinking Water Directive (EU) 2020/2184 identifies MPs as an emerging contaminant of concern, enabling the European Commission to place MPs on a "watch list" of substances requiring monitoring and risk assessment [22]. It also mandates the development of harmonized analytical methods for measuring MPs in drinking water, which is supported by Commission Delegated Decision (EU) 2024/1441 establishing a standardized methodology based on vibrational spectroscopy for the measurement of MPs in the size range from 20 µm up to 5 mm [23]. In this context, extending the detectable size range towards the lower µm fraction using spICP-MS could provide complementary information on the presence of MNPs in tap water, without the need for cascade filtration of the tap water typically required for vibrational spectroscopy techniques.

To detect MPs smaller than 20 µm in drinking water, which are considered more toxic than their larger counterparts [24], the main objective of this study was to evaluate the suitability of spICP-MS for the quantitative analysis of MPs smaller than 10 µm via carbon detection in tap water. To support this, we developed a sample pretreatment procedure aimed at eliminating inorganic dissolved carbon that is typically present in high concentrations in tap water. For this purpose, mild pretreatment with low acid concentration and short duration was applied to effectively reduce the carbon background while preserving the original properties of polystyrene (PS) MPs in the size range from 1 to 5 µm. The efficiency of the optimized sample pretreatment procedure was then assessed using the spICP-MS method with the most suitable instrument configuration (selected after testing different sample introduction systems and torch injectors), along with operating parameters systematically optimized for our ICP-MS system.

Materials and methods

Standards and chemicals

Four monodisperse Polybead® polystyrene (PS) microsphere standards with nominal diameters of 1 µm (1.06 ± 0.01 µm; hereinafter referred to as 1 µm PS MP), 2 µm (2.07 ± 0.04 µm; 2 µm PS MP), 3 µm (3.00 ± 0.06 µm; 3 µm PS MP), and 4.8 µm (4.78 ± 0.24 µm; 4.8 µm PS MP) were purchased from Polysciences, Inc. (Warrington, PA, USA). For method validation, another batch of 3 µm PS MPs standard with a nominal diameter of 3.10 ± 0.06 µm was used. The stock PS MPs standards were supplied as aqueous suspensions with around 2.6% solids (w/v). Ionic carbon stock standard solution containing 1000 mg/L of C in H_2O (Assurance Grade, SPEX CertiPrep™, NY, USA) was used for the preparation of the ionic calibration standards. A BCR-165A reference material of latex sphere suspension with a certified average particle diameter of 2.223 ± 0.013 µm, provided at a mass concentration of about 0.2 g/L by the Joint Research Centre (JRC, Geel, Belgium), was used for the determination of the transport efficiency (TE). Superpure nitric acid (HNO_3) (67–69%) used for acidification of water samples and for rinsing of the ICP-MS system between each sample was purchased from Carlo Erba Reagents GmbH, Germany. Ultrapure water (resistivity of 18.2 MΩcm) was obtained from a Millipore Element apparatus (Millipore, Bedford, MA, USA) and used throughout the work for sample preparations and dilutions.

Single particle ICP-MS analysis

An Agilent 7900 ICP-MS instrument from Agilent Technologies (Santa Clara, CA, USA) was used for spICP-MS analysis. The spICP-MS analysis of MPs was performed by measuring the ^{13}C isotope (with the abundance of 1.16%) in time-resolved analysis mode. The instrument was operated at 0.1 ms dwell time, and data were collected for a total measurement time of 60 s (equivalent to 600,000 data points).

Two different sample introduction systems in combination with two injectors with different inner diameters (1.0 and 2.5 mm) were tested. The sample introduction system consisted either of the MicroMist glass concentric nebulizer (Glass Expansion, Australia) with a quartz Scott double pass spray chamber cooled to 2 °C (in this study referred to as conventional sample introduction system), or the DS-5 Microflow concentric nebulizer equipped with single pass low-volume (8 mL) spray chamber (both purchased from Teledyne CETAC, Omaha, NE, USA) (in this study referred to as high-efficiency microflow sample introduction system). The latter system is designed for very low-flow (3–10 µL/min) applications, as no liquid waste accumulates in the spray

chamber at such low flows. The following instrument set-ups were studied: conventional sample introduction system and torch with 2.5 mm injector (instrument set-up 1), conventional sample introduction system and a torch with 1.0 mm injector (instrument set-up 2), high-efficiency microflow sample introduction system and a torch with 2.5 mm injector (instrument set-up 3), and high-efficiency microflow sample introduction system and a torch with 1.0 mm injector (instrument set-up 4). For each instrument set-up, different ICP-MS settings, including the nebulizer gas flow rate with or without make-up or dilution gas, sample uptake flow rate, sampling depth, and radiofrequency (RF) plasma power, were first optimized in several steps, as shown in Table S1, using PS MPs standard solutions of different sizes.

The quantification and sizing of MPs were based on a calibration curve constructed from blank (ultrapure water) and ionic carbon standards prepared at four concentration levels (1, 10, 50, and 100 mg/L) in ultrapure water. The TE was determined according to the ′particle size′ method, as described by Pace et al. [25], using the BCR-165A MPs standard diluted to a concentration of 2 mg/L, and ionic carbon standards prepared in ultrapure water. Argon of 99.999% purity was used, containing ≤ 0.05 ppmV of C_nH_m. Prior to spICP-MS analysis, the stock PS MPs standards were sonicated for 10 min using an ultrasonic bath (Nickel-Electro Ltd. Clifton SW3H, Switzerland) and immediately diluted with ultrapure water in several successive steps to a final particle concentration of around 10^8 particles/L. Between each dilution step, the suspensions were mixed on a vortex mixer (Vibromix 10, Domel, Slovenia) for 10 s.

Data were processed with the use of the Single Nanoparticle Application Module of Agilent MassHunter 5.2 Workstation software. Particle mass was converted into particle diameter by considering spherical particles consisting of polystyrene (C mass fraction 0.923 with a density of 1.04 g/cm^3). The particle detection threshold for discriminating between the particle signals and the background (i.e., instrumental noise/dissolved C) was manually set to the lowest value for which no additional peak would appear on the lower size of the particle size distribution histogram. The experimental size LOD was established by identifying the particle size obtained at the designated particle detection threshold, which corresponds to the minimum detectable particle diameter. In addition, the theoretical limits of detection (LODs) for particle size and number concentrations were calculated using the equations reported by Laborda et al.[26] (Equation S1 and Equation S2).

Optimization of tap water sample pretreatment

To demonstrate the applicability of the spICP-MS method for the detection of MPs in tap water, tap water samples were spiked with 1, 2, 3, and 4.8 µm PS MPs standards at concentrations of 0.26, 1.73, 10.8, and 108 mg/L, respectively, corresponding to particle number concentrations of 4.01×10^8 particles/L, 3.58×10^8 particles/L, 7.34×10^8 particles/L and 1.82×10^9 particles/L, respectively. These concentrations were selected to obtain an optimal number of particles detected during a 1 min spICP-MS acquisition. Only results with a minimum of 100 and a maximum of 2000 particles detected in a single acquisition were considered (to keep the relative standard deviation of the Poisson distribution and relative bias due to multiple particle events below 10% and 3%, respectively) [27].

Tap water was collected at Jožef Stefan Institute, Ljubljana, and stored in a glass bottle at 4 °C. The properties of the tap water used for spiking are shown in Table S9. Different pretreatment procedures were tested, including mild acidification with the use of different HNO_3 concentrations (ranging from 0.05 to 0.1%) or 0.1% phosphoric acid (H_3PO_4), followed by purging either with nitrogen or ultrasonication (using Elmasonic P 30 H sonication bath, Elma Schmidbauer GmbH, Germany). Parameters, including ultrasonication time and temperature, as well as the type of vial material (using either 10 mL polypropylene vials obtained from Simport Scientific Inc., Québec, Canada, or 40 mL vials made of clear borosilicate glass obtained from Macherey–Nagel, Düren, Germany) in which the samples were treated, were also investigated. The performance of the developed sample pretreatment procedure was evaluated by determining the recoveries of particle number and mass concentrations (Equation S3) as well as particle size. This was achieved by comparing the values obtained for PS MPs spiked into tap water after pretreatment with the expected values measured for PS MPs prepared in ultrapure water. In addition, the efficiency of inorganic carbon removal from the tap water matrix was assessed by calculating the carbon removal

efficiency (Equation S4). Together, these parameters were used to verify both the effectiveness of the pretreatment in reducing background carbon and its ability to preserve the concentration and size characteristics of the microplastic particles. To evaluate the method's performance, six independent samples were prepared using the optimized pretreatment procedure and analyzed by spICP-MS.

The optimal sample pretreatment procedure was as follows: An aliquot of 4 mL of tap water spiked with PS MPs standard was acidified with 0.05% (v/v) HNO_3 and ultrasonicated for 60 min at 80 kHz and 100 W in the degas program. The sample was treated in an open plastic vial to remove CO_2 generated during treatment. After treatment and prior to spICP-MS analysis, the samples were manually shaken and vortexed for 10 s to ensure uniform dispersion of PS MPs. Upon acidification with nitric acid, carbonate species are converted to carbon dioxide gas, which is subsequently removed from the sample by ultrasonication. An example of the corresponding reaction is shown below:

$$HNO_3\,(aq) + HCO_{3^-}(aq) \rightarrow CO_2\,(g) + NO_{3^-}(aq) + H_2O(aq)$$

Scanning electron microscopy analysis

A field emission scanning electron microscopy (FE-SEM) analysis of PS MPs standards before and after the sample pretreatment was performed using Helios NanoLab NL650, FEI. Prior to the FE-SEM analysis, the PS MPs samples were ultrasonicated for 10 min, applied to the sample holder, air-dried, and coated with gold (SCD 005 Sputter Coater, BAL-TEC). FE-SEM images were processed with the ImageJ program (Image processing and analysis in Java) to determine the MPs particle diameter from the measured surface area. Based on the measurement of 20 particles, the average value and standard deviation of particle diameter were calculated. However, owing to the limited number of analyzed particles, the statistical robustness of the quantitative size analysis was limited. Therefore, the SEM measurements were primarily used to independently confirm the approximate dimensions of the investigated standards rather than to provide a comprehensive characterization of the full particle size distribution.

Results and discussion

Optimization and evaluation of the spICP-MS analysis of MPs

Conventional and high-efficiency microflowl sample introduction systems in combination with two different torch injectors were first tested to identify the optimal configuration for the detection of MPs using spICP-MS. The optimization of spICP-MS parameters for each instrument set-up was carried out in several steps (Table S1). The most suitable spICP-MS instrumental parameters were selected based on two criteria: (1) the highest signal-to-background (S/B) ratio achieved for MPs suspension in ultrapure water, calculated as a ratio between the particle event intensity and baseline intensity, and (2) the highest number of particles detected in one spICP-MS run. An example of this optimization for the configuration using a conventional sample introduction system and torch with a 2.5 mm injector (instrument set-up 1), commonly used in spICP-MS analysis of inorganic nanoparticles, is shown in Fig. 1. Detailed optimization procedures for all instrument set-ups are provided in the Supplementary Information (Fig. S2–S12), while the final optimized spICP-MS parameters for all instrument set-ups studied are summarized in Table S2.

Briefly, for instrument set-up 1, consisting of a conventional sample introduction system and a 2.5 mm torch injector, a nebulizer gas flow rate of 1.1 L/min, yielding the highest number of nebulized particles (Fig. 1a), was selected for further optimization. Since particle transport and residence time in the plasma can be affected not only by the total nebulizer gas flow but also by the addition of a make-up or dilution gas [28, 29], the influence of a make-up gas (Fig. 1b) and dilution gas (Fig. 1c) on the spICP-MS performance was also investigated. The addition of make-up gas significantly increased both particle counts and S/B ratios. The optimal combination chosen was 0.7 L/min make-up gas with 0.4 L/min nebulizer flow (Fig. 1b). Dilution gas, despite raising S/B ratios through baseline reduction, was excluded due to its negative impact on particle counts (Fig. 1c). Lower sample uptake flow rates produced fewer detected particles but higher S/B ratios (Fig. 1d). To maintain the lowest possible baseline suitable for detecting smaller PS MPs, a flow rate of 30 µL/min

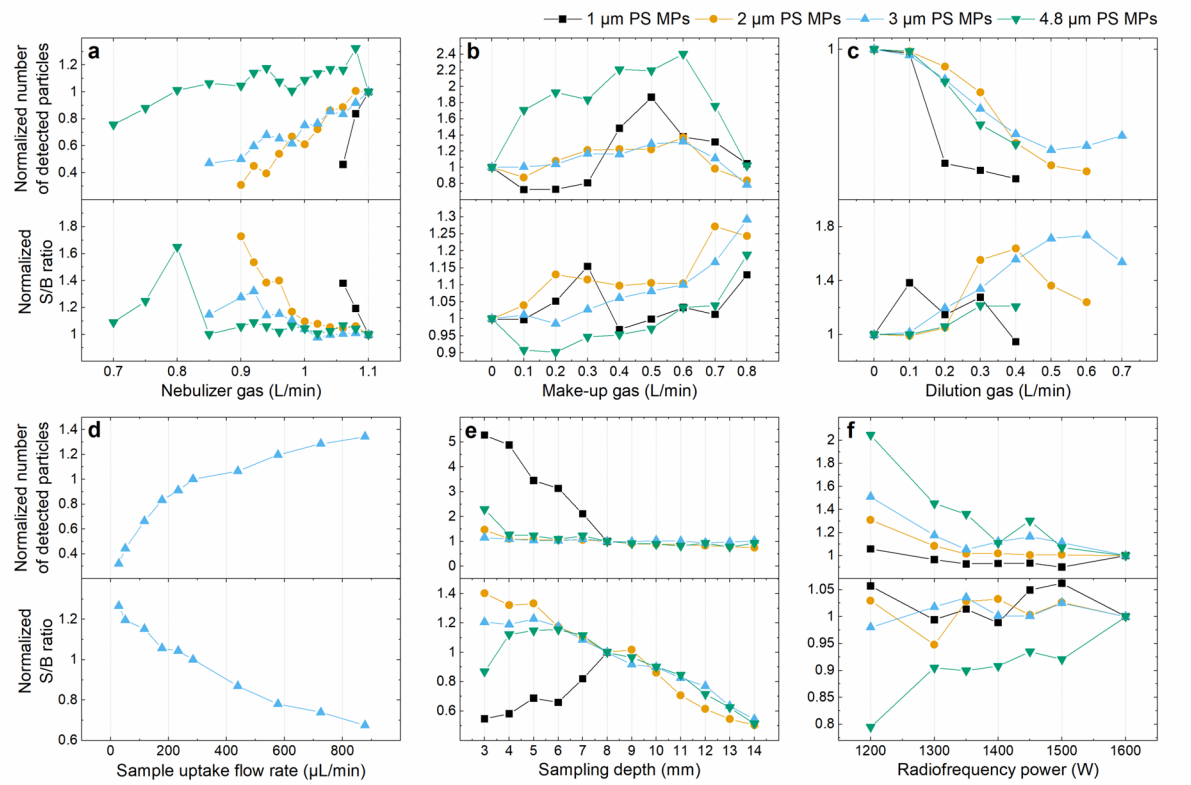

Fig. 1 Normalized number of detected particles and S/B ratio determined for PS MPs standards of four different sizes for instrument set-up 1 at varying **a**) nebulizer gas flow rates, **b**) make-up gas flow rates, **c**) dilution gas flow rates, **d**) sample uptake flow rates, **e**) sampling depths, and **f**) RF powers. In each optimization step, the values were normalized to the corresponding values of the starting spICP-MS parameters. The optimal operating parameters for set-up 1 were determined as follows: make-up gas flow rate of 0.7 L/min, nebulizer gas flow rate of 0.4 L/min, sample uptake rate of 30 µL/min, sampling depth of 4.0 mm, and RF power of 1600 W

was chosen. Reducing the sampling depth slightly improved particle detection and S/B ratios, with 4 mm identified as optimal (Fig. 1e). RF power had little effect on smaller particles and greater impact on the largest 4.8 µm PS MPs standard, with higher RF power increasing the ionization of larger particles, making 1600 W the most suitable RF setting (Fig. 1f).

Figures of merit The performance of the four optimized instrument set-ups was evaluated and compared based on TE, S/B ratios, particle number and mass concentration, particle size (Table S4) and their repeatability (Table S5), as well as particle size distribution using PS MPs standards with sizes ranging from 1 µm to 4.8 µm. Briefly, among all instrument configurations tested, instrument set-up 1 proved the most suitable for spICP-MS analysis of MPs, offering the highest particle number and mass concentration recoveries, satisfactory S/B ratios, accurate size determination across different MPs standards, and acceptable size and particle number concentration LODs. The TE of 8.4% was obtained for set-up 1 using the 'particle size' method with the 2.223 µm BCR PS MPs standard (Table S3) and was higher than those reported by Gonzalez de Vega et al. [15] (5–6%, particle size method) for the same type of conventional sample introduction system. The particle size-based TE values, determined using 1–4.8 µm PS MPs standards (Fig. S13), were consistent with those obtained with the BCR 165 A standard and showed no dependence on particle size. This indicates that carbon from PS MPs is ionized with the same efficiency as dissolved carbon and that PS MPs were completely vaporized, atomized, and ionized in the

plasma regardless of their size. This is further supported by the linear relationship between mean particle intensity and particle diameter [12] (Fig. S14). Good linearity of calibration curve ($R^2 = 1$) and close agreement of the slope to the theoretical value of 3 indicate that the PS MPs in the size range from 1 µm to 4.8 µm were completely vaporized, atomized, and ionized in the plasma.

Particle number and mass concentration recoveries, calculated by comparing the measured values with those reported by the manufacturer, ranged from 84 to 112% for 1–3 µm PS MPs and 29% for 4.8 µm PS MPs standard, with repeatability better than 15% (Table 1). The lower recoveries observed for larger particles can be related to their poorer TE in the ICP-MS system, and/or particle loss during sample preparation due to particle agglomeration and sedimentation. Laborda et al. [12] also reported the potential underestimation of particle number concentration for MPs with sizes over 3 µm. Caceres et al. [11] observed similarly reduced recoveries for larger MPs, but were able to improve them by using even lower nebulizer flow rates. In contrast, Liu et al. [10] reported particle number concentration recoveries of 99.0–102.5% for 0.8—5 µm PS MPs when using a concentric nebulizer and 1.0 mm torch injector. Data processed using the ICP-MS vendor software with manual particle threshold selection was also compared to results obtained using the open-source, Python-based software "SPCal" (Version 1.4.9) [30], which applies an iterative thresholding approach based on Gaussian statistics ($\sigma = 5$). Particle number concentration, particle mass concentration, and particle size were comparable between the two processing approaches, with differences remaining within the expected range of analytical uncertainty (Table S6), suggesting that the ICP-MS software can be considered reliable for processing spICP-MS data for MPs analysis.

Good agreement was obtained between the average particle diameters determined by spICP-MS and the manufacturer-reported values for all particle sizes, with repeatability better than 2%. Average particle diameters determined by spICP-MS were also comparable to the particle diameters determined by FE-SEM (Table S7). The broadening of the particle size distribution observed for instrument setup 1 equipped with a 2.5 mm torch injector, compared to setups employing a 1.0 mm injector diameter (Fig. S15), can be attributed to the well-established effect of injector inner diameter on signal dispersion, as described by Olesik et al. [31]. A larger injector inner diameter allows a broader radial distribution of the aerosol entering the plasma, increasing the probability of off-axis particle introduction, reducing the reproducibility of ion cloud sampling, ultimately resulting in broader and more variable detected signals. In contrast, narrower injector inner diameters improve aerosol focusing along the plasma axis, resulting in more uniform vaporization conditions, more efficient ion extraction, and narrower apparent particle size distributions [32]. Consistent with these observations, Laborda et al. [12] reported similar broadening effects in spICP-MS analysis of MPs when wider torch injectors were used. The theoretical size LOD of 624 nm was achieved with set-up 1, whereas the experimental size LOD, equivalent to the minimum detectable particle size, was slightly higher (806 nm) (Table S8). These values are comparable to, or better than, those previously reported (620 nm [15], 800 nm [10], 1.26 µm [8], 1.4 µm [11], and 1.56 µm [17]). The LOD for particle number concentration (1.06×10^6 particles/L obtained with set-up 1) was slightly higher (5×10^5/L

Table 1 Recoveries for particle number and mass concentrations, and average particle diameters determined for PS MPs standards of different sizes, using instrument set-up 1. Results present an average value ± standard deviation of six replicates. Relative standard deviations (RDS, %) are presented in parentheses

PS MPs	Recovery (%)		Particle diameter (µm)
	Particle number concentration	Particle mass concentration	
1.06 ± 0.01 µm	99 ± 15 (15%)	112 ± 16 (15%)	1.04 ± 0.02 (2.1%)
2.07 ± 0.04 µm	104 ± 5 (4%)	91 ± 5 (5%)	1.92 ± 0.01 (0.5%)
3.1 ± 0.06 µm	102 ± 5 (5%)	84 ± 4 (4%)	2.84 ± 0.01 (0.2%)
4.78 ± 0.24 µm	29 ± 1 (4%)	29 ± 1 (5%)	4.73 ± 0.02 (0.4%)

[12]) or lower (7.1×10^6/L [10]) than the LOD values reported elsewhere. Importantly, the particle number concentration LODs obtained in this study fall within the environmentally relevant concentrations of MPs (10^5–10^{11}/L) expected across different water samples and water types [33].

In this study, microsecond dwell time was prioritized due to its improved temporal resolution of particle transients, reduced probability of coincidence events, and, most importantly for carbon-based MP detection, the substantially reduced contribution of the continuous carbon background signal. Because the background is integrated over the dwell time, reducing the dwell time proportionally decreases the number of background ions recorded per dwell. This improves signal-to-background discrimination and is therefore particularly advantageous for the analysis of small MPs. However, this advantage is accompanied by a redistribution of the ion cloud from individual particles across multiple acquisition bins, resulting in fewer counts per bin and increased relative background noise and particle signal variability. This can hinder the discrimination of low-intensity particle events from background fluctuations, particularly near the detection limit, where only a limited number of ions are generated per particle. In contrast, longer (millisecond) dwell times integrate a larger fraction of the particle ion cloud within a single data point, increasing counts per event and potentially improving detectability of small particle signals. This advantage is offset by proportionally higher background accumulation, which can degrade signal-to-background ratios and obscure small particle signals.

Pretreatment of tap water for the measurements of MPs by spICP-MS

The applicability of the spICP-MS method for the detection of MPs in water samples with elevated dissolved inorganic carbon was tested by analyzing the tap water with a total inorganic carbon content of 53.9 mg/L (Table S9), which was spiked with PS MPs standards. The high concentration of dissolved carbon in environmental samples often masks the signals of small-sized MPs, making it difficult to distinguish them from background noise. To remove dissolved inorganic carbon present in tap water, either as a bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), or carbon dioxide (including both dissolved CO_2 and carbonic acid, H_2CO_3), mild acidification of the sample followed by sample purging was applied. For purging, an evaporation system using nitrogen gas was first tested (Fig. S16). However, due to non-reproducible results and the risk of sample contamination between consecutive treatments when using this system, ultrasonication treatment was chosen instead. The concentration of HNO_3 acid (ranging from 0.05 to 1%) and time of ultrasonication (15, 30, and 60 min) were optimized next (Fig. S17). Particle number recovery was the highest and closest to 100% when the spiked tap water was acidified with the lowest HNO_3 concentration (0.05%). At higher acid concentrations, a loss in particle number concentration occurred (up to 40% loss in particle number after 30 and 60 min ultrasonication, see Fig. S17a). It can be reasonably assumed that the addition of HNO_3 may induce PS MPs aggregation, leading to their subsequent sedimentation, and a decrease in their particle number concentration. A 40% decrease in particle number concentration following treatment with 0.2% HNO_3 and heating the sample for 5 min at 100 °C was also reported by Trujillo et al. [8]. They reported an even greater loss of 73% of particles using 50% HNO_3. As can be further seen from Fig. S17b, no observable effect of ultrasonication time or acid concentration on carbon removal efficiency can be identified. A reduction in baseline with increasing HNO_3 concentration or ultrasonication time resulted in an increase in the S/B ratio (Fig. S17c), while the concentration of HNO_3 and ultrasonication time did not have any effect on the particle size (results not shown), as aggregates do not remain suspended in the sample and are therefore not detected during spICP-MS analysis. Extending ultrasonication time from 60 to 120 min did not improve the particle number recovery and carbon removal efficiency (Fig. S18). Therefore, a 60 min ultrasonication time in combination with 0.05% HNO_3 acidification was chosen as the most suitable sample pretreatment procedure. Moreover, a higher temperature (80 °C) applied during ultrasonication had no observable effect on carbon removal efficiency, but resulted in a 26% loss in particle number concentration (Fig. S19), which was also observed by Trujillo et al. [8]. Using H_3PO_4, which is commonly applied in the spectrophotometric determination of carbon, instead of HNO_3, also did not improve the recovered particle

number concentration or S/B values for the treated tap water spiked with PS MPs standard (Fig. S20). When analyzing MPs, it is advisable to avoid using plastic materials to prevent sample contamination. However, in our study, the use of glass instead of plastic vials in the pretreatment procedure resulted in a 30% loss of particles, 8% lower carbon removal efficiency, and 50% lower S/B ratios achieved compared to the plastic vials (Fig. S21). The loss of particles in the glass vials may be attributed to changes in glass surface charge resulting from acid addition (transition from negatively to positively charged) [34], which can cause increased adsorption of the negatively charged MPs onto the positively charged glass surface. Therefore, plastic vials were used in this study to treat PS MPs in the tap water samples.

Figures of merit The optimized sample pretreatment procedure involved acidification with 0.05% HNO_3, followed by ultrasonication for 60 min, during which a temperature below 45 °C was maintained. This was applied to both tap water samples and tap water samples spiked with PS MPs standards of different sizes and analyzed by spICP-MS using instrument set-up 1 with optimized instrumental parameters. From the time scans of untreated and treated tap water shown in Fig. 2a, it can be observed that the baseline intensity in the treated tap water (7.1 counts) was significantly lower than in untreated

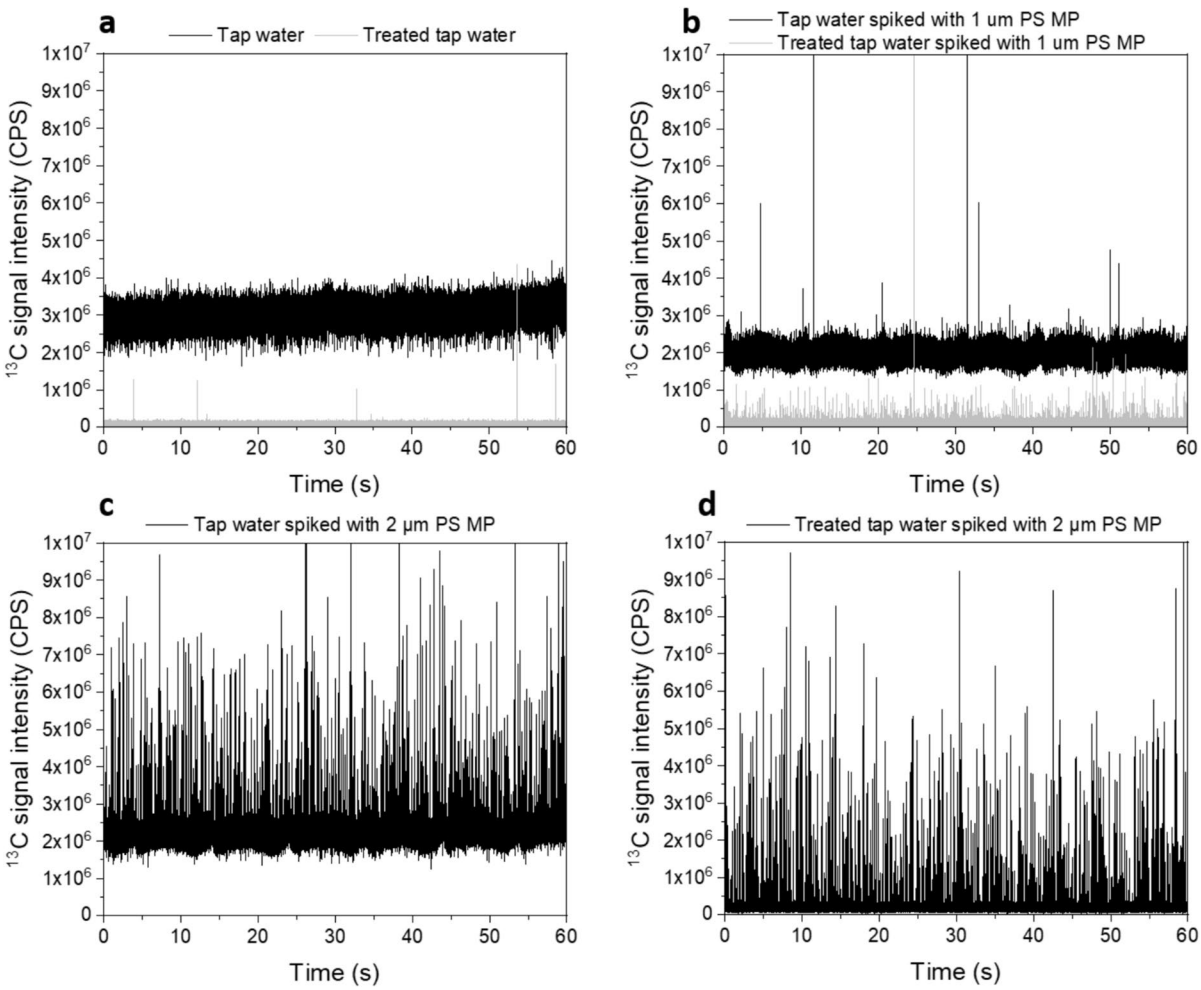

Fig. 2 Time scans of **a**) untreated and treated unspiked tap water, **b**) untreated and treated tap water spiked with 1 µm PS MPs, **c**) untreated tap water spiked with 2 µm PS MPs, and **d**) treated tap water spiked with 2 µm PS MPs

Table 2 Carbon removal efficiency, recovery for particle number and mass concentration, and average particle diameter determined in the treated tap water samples spiked with 1, 2, 3 µm, and 4.8 µm PS MPs standards. Results present an average value ± SD of six replicates

Spiked tap water	Carbon removal efficiency (%)	Recovery (%)		Particle diameter (µm)
		Particle number concentration	Particle mass concentration	
1 µm	95 ± 0	68 ± 9	68 ± 8	1.10 ± 0.02
2 µm	94 ± 1	74 ± 5	73 ± 6	2.01 ± 0.01
3 µm	95 ± 1	81 ± 6	80 ± 6	2.95 ± 0.01
4.8 µm	88 ± 3	95 ± 3	104 ± 4	4.93 ± 0.02

tap water (300.6 counts), and was comparable to the particle baseline of the ultrapure water (5.9 counts). This shows that the developed sample pretreatment procedure was very effective in reducing dissolved inorganic carbon from the tap water. Moreover, analysis of untreated tap water spiked with 1 µm PS microplastics resulted in an elevated continuous background signal, hindering the detection of particle signals (Fig. 2b), which means that detection of 1 µm MPs in tap water without any treatment is not feasible by spICP-MS. Following mild acid treatment, distinct particle signals became detectable and clearly

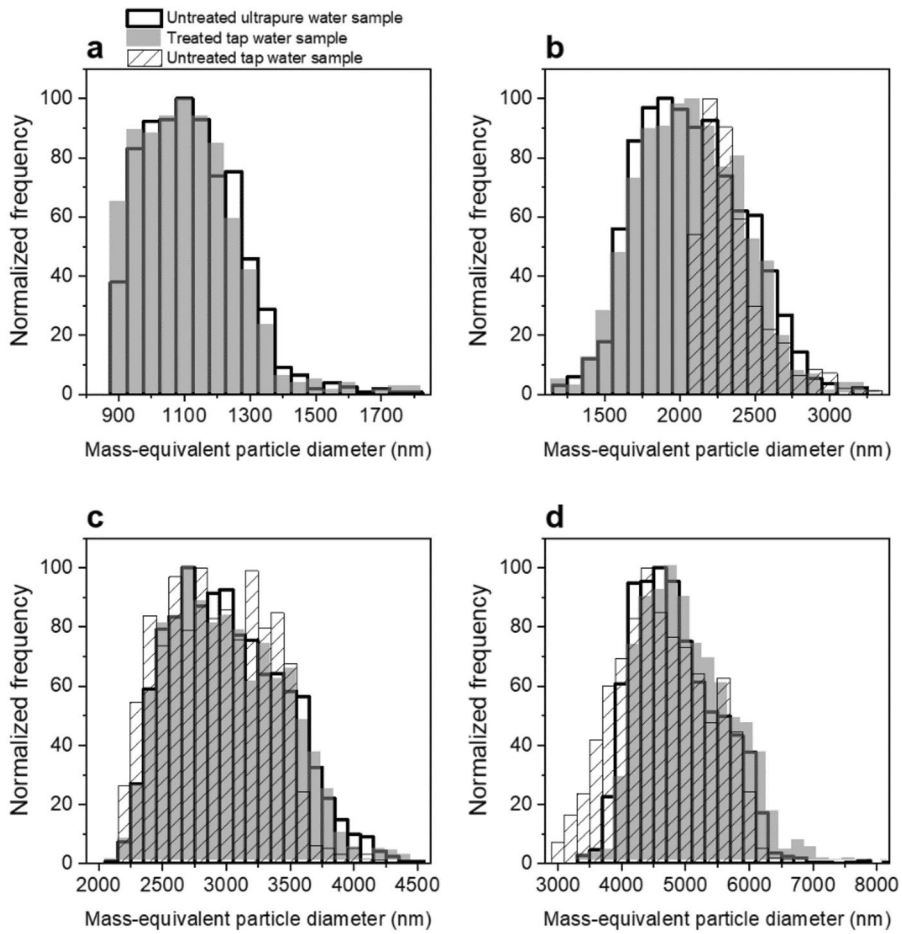

Fig. 3 Particle size distributions of PS MPs standards of different sizes **a**) 1 µm, **b**) 2 µm, **c**) 3 µm, and **d**) 4.8 µm in untreated ultrapure water (control), treated tap water samples, and untreated tap water samples, determined by spICP-MS

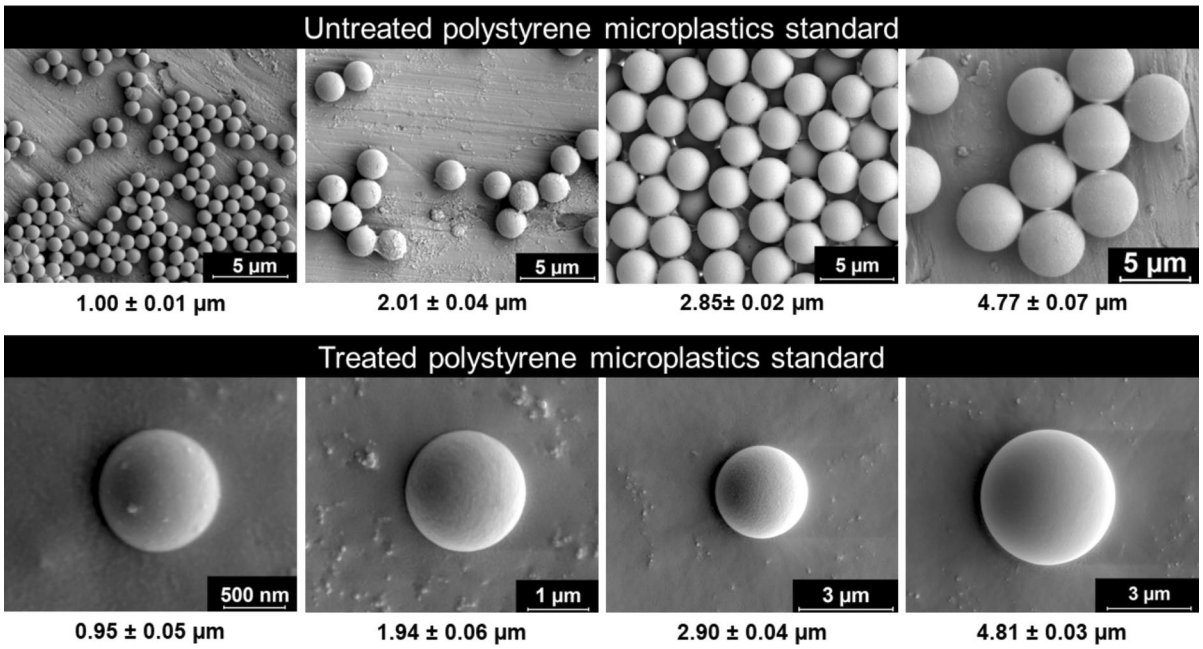

Fig. 4 FE-SEM analysis of untreated (top row) and treated (bottom row) 1 µm, 2 µm, 3 µm, and 4.8 µm PS MPs standards. Particle diameters of PS MPs are presented as an average value ± SD of FE-SEM analysis of 20 particles (untreated sample) or 7 particles (treated sample)

resolved from the background, providing direct evidence of improved detection limits. In contrast, larger 2 µm particles spiked into untreated tap water were still observable as peaks superimposed on the elevated background (Fig. 2c), which was reduced to levels comparable to ultrapure water after treatment (Fig. 2d).

The efficiency of inorganic carbon removal ranged between 88 and 95% with good repeatability achieved (RSD ≤ 3.6%, $N = 6$) (Table 2). The carbon content in the treated tap water determined by spectrophotometry (Fig. S22) further confirmed that the applied sample pretreatment procedure was effective in removing inorganic carbon from tap water, and was comparable to the carbon values in the ultrapure water (Table S10). Particle number and mass concentration recoveries for MPs in untreated tap water were 74% and 113% for 2 µm MPs, 78% and 77% for 3 µm MPs, and 118% and 109% for 4.8 µm MPs, respectively, while 1 µm MPs were not detected, as shown in Fig. 2a. The recoveries determined in the treated tap water spiked with PS MPs standards were in the range of 68% − 95% (RSD ≤ 12.5%, $N = 6$) for particle number concentration and 68% − 104% (RSD ≤ 11.6%, $N = 6$) for particle mass concentration (Table 2). The recoveries increased as the size of the PS MPs increased, suggesting that smaller MPs may be more susceptible to acid treatment than larger ones. The average particle diameter of PS MPs standards did not change after applying the sample pretreatment procedure, resulting in mass-equivalent particle diameter recoveries in the range of 98% − 101% (RSD ≤ 1.8%, $N = 6$).

Moreover, particle size distributions of PS MPs standards in treated tap water were comparable to those obtained in ultrapure water (Fig. 3). In contrast, untreated tap water yielded only a partial size distribution for 2 µm MPs, while distributions for 3 and 4.5 µm MPs were comparable to those observed in both ultrapure and treated tap water. The minimum detectable particle diameter in untreated tap water was 2050 nm, which decreased to 894 nm in treated tap water, but remained higher than that in ultrapure water (experimental size LOD of 806 nm

obtained with instrument set-up 1, Table S8). This difference is attributed to the slightly elevated baseline signal intensity still present in treated tap water compared to ultrapure water. The shape, surface, and size of PS MPs before and after the treatment were also investigated with FE-SEM analysis. From the obtained FE-SEM images of the treated PS MPs (Fig. 4), it is evident that there was no change in particle shape or surface when exposed to the conditions of the developed sample pretreatment procedure. Moreover, the average particle diameters of treated PS MPs obtained by FE-SEM were in good agreement with the untreated PS MPs standards in ultrapure water.

Conclusions

The presence of MPs in drinking water has become an important environmental and public health concern, particularly for particles in the lower micrometer size range due to their higher mobility and potential bioavailability. In this study, the applicability of spICP-MS for the detection of small MPs via carbon monitoring in tap water was investigated. A key limitation of this approach is the elevated concentration of dissolved inorganic carbon in tap water, which increases the carbon baseline and interferes with the detection of MPs smaller than 2 µm. To overcome this challenge, a sample pretreatment procedure based on mild acidification followed by ultrasonication was developed. The procedure effectively reduced the inorganic carbon background to levels comparable to ultrapure water while preserving the concentration and size characteristics of PS MPs. FE-SEM analysis confirmed that the treatment did not alter particle morphology, surface properties, or size. Additional experiments demonstrated that higher acid concentrations, elevated temperatures, or the use of glass vials may lead to particle losses, highlighting the importance of carefully optimized pretreatment conditions.

The study also showed that instrumental configuration plays a critical role in the performance of the spICP-MS method. Differences in sample introduction systems and instrumental parameters significantly affected particle transport and processes occurring in the plasma, such as vaporization, atomization, and ionization. A conventional introduction system consisting of a concentric nebulizer, spray chamber and a 2.5 mm torch injector provided the most reliable performance for the quantitative analysis of MPs in the size range from 0.8 µm (minimum detectable particle diameter achieved with selected parameters) to 4.5 µm.

Nevertheless, complementary analytical techniques remain necessary for polymer identification and detailed characterization of the size and shape of MPs. Further development of sample pretreatment procedures will also be required for more complex environmental water samples, particularly those containing high levels of particulate or organic carbon and very low concentrations of MPs, where additional purification and preconcentration steps may be necessary.

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Data availability The data supporting this article have been included in the manuscript and are part of Supplementary Information.

Declarations

Competing interests The authors declare no competing interests.

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References

1. Frias JPGL, Nash R (2019) Microplastics: finding a consensus on the definition. Mar Pollut Bull 138:145–147. https://doi.org/10.1016/j.marpolbul.2018.11.022
2. Gigault J, ter Halle A, Baudrimont M, Pascal PY, Gauffre F, Phi TL, El Hadri H, Grassl B, Reynaud S (2018) Current opinion: what is a nanoplastic? Environ Pollut 235:1030–1034. https://doi.org/10.1016/J.ENVPOL.2018.01.024
3. Prata JC, da Costa JP, Lopes I, Duarte AC, Rocha-Santos T (2020) Environmental exposure to microplastics: an overview on possible human health effects. Sci Total Environ 702:134455. https://doi.org/10.1016/j.scitotenv.2019.134455
4. Ivleva NP (2021) Chemical analysis of microplastics and nanoplastics: challenges, advanced methods, and perspectives. Chem Rev 121:11886–11936. https://doi.org/10.1021/acs.chemrev.1c00178
5. Schwaferts C, Niessner R, Elsner M, Ivleva NP (2019) Methods for the analysis of submicrometer- and nanoplastic particles in the environment. TrAC Trends Anal Chem 112:52–65. https://doi.org/10.1016/j.trac.2018.12.014
6. Mintenig SM, Bäuerlein PS, Koelmans AA, Dekker SC, Van Wezel AP (2018) Closing the gap between small and smaller: towards a framework to analyse nano- and microplastics in aqueous environmental samples. Environ Sci Nano 5:1640–1649. https://doi.org/10.1039/c8en00186c
7. Vidmar J (2021) Detection and characterization of metal-based nanoparticles in environmental, biological and food samples by single particle inductively coupled plasma mass spectrometry. Anal Charact Metal-Based Nanomat, Comprehensive Anal Chem, Elsevier 93:345–380. https://doi.org/10.1016/bs.coac.2021.02.008
8. Trujillo C, Pérez-Arantegui J, Lobinski R, Laborda F (2023) Improving the detectability of microplastics in river waters by single particle inductively coupled plasma mass spectrometry. Nanomaterials (Basel) 13:1–16. https://doi.org/10.3390/nano13101582
9. Sakanupongkul A, Sirisinha K, Saenmuangchin R, Siripinyanond A (2024) Analysis of microplastic particles by using single particle inductively coupled plasma mass spectrometry. Microchem J 199:110016. https://doi.org/10.1016/J.MICROC.2024.110016
10. Liu Z, Zhu Y, Lv S, Shi Y, Dong S, Yan D, Zhu X, Peng R, Keller AA, Huang Y (2022) Quantifying the dynamics of polystyrene microplastics UV-aging process. Environ Sci Technol Lett 9:50–56. https://doi.org/10.1021/acs.estlett.1c00888
11. Caceres GC, Johnson ME, Molloy JL, Lee SB, Montoro Bustos AR (2025) Extending the linear dynamic range of single particle ICP-MS for the quantification of microplastics. Anal Chem 97:19818–19828. https://doi.org/10.1021/acs.analchem.5c03552
12. Laborda F, Trujillo C, Lobinski R (2021) Analysis of microplastics in consumer products by single particle-inductively coupled plasma mass spectrometry using the carbon-13 isotope. Talanta 221:121486. https://doi.org/10.1016/J.TALANTA.2020.121486
13. Bolea-Fernandez E, Rua-Ibarz A, Velimirovic M, Tirez K, Vanhaecke F (2020) Detection of microplastics using inductively coupled plasma-mass spectrometry (ICP-MS) operated in single-event mode. J Anal At Spectrom 35:417–634. https://doi.org/10.1039/c9ja00379g
14. Gonzalez de Vega R, Moro TT, Grüner B, de Andra Maranhão T, Huber MJ, Ivleva NP, Skrzypek E, Feldmann J, Clases D (2024) Studying the degradation of bulk PTFE into microparticles via SP ICP-MS: a systematically developed method for the detection of F-containing particles. J Anal At Spectrom 39:2030–2037. https://doi.org/10.1039/d4ja00101j
15. Gonzalez de Vega R, Goyen S, Lockwood TE, Doble PA, Camp EF, Clases D (2021) Characterisation of microplastics and unicellular algae in seawater by targeting carbon via single particle and single cell ICP-MS. Anal Chim Acta 1174:338737. https://doi.org/10.1016/J.ACA.2021.338737
16. Harycki S, Gundlach-Graham A (2023) Single-particle ICP-TOFMS with online microdroplet calibration: a versatile approach for accurate quantification of nanoparticles, submicron particles, and microplastics in seawater. Anal Chem. https://doi.org/10.1021/acs.analchem.3c02785
17. Hendriks L, Mitrano DM (2023) Direct measurement of microplastics by carbon detection via single particle ICP-TOFMS in complex aqueous suspensions. Environ Sci Technol 57:7263–7272. https://doi.org/10.1021/acs.est.3c01192
18. Nischwitz V, Gottselig N, Missong A, Meyn T, Klumpp E (2016) Field flow fractionation online with ICP-MS as novel approach for the quantification of fine particulate carbon in stream water samples and soil extracts. J Anal At Spectrom 31:1858–1868. https://doi.org/10.1039/c6ja00027d
19. Rist S, Hartmann NB, Welden NAC (2021) How fast, how far: diversification and adoption of novel methods in aquatic microplastic monitoring. Environ Pollut. https://doi.org/10.1016/j.envpol.2021.118174
20. Neuper C, Šimić M, Lockwood TE, Gonzalez de Vega R, Hohenester U, Fitzek H, Schlatt L, Hill C, Clases D (2024) Optofluidic force induction meets raman spectroscopy and inductively coupled plasma-mass spectrometry: a new hyphenated technique for comprehensive and complementary characterizations of single particles. Anal Chem 96:8291–8299. https://doi.org/10.1021/acs.analchem.3c04657
21. Bhowmik A, Saha G (2025) Microplastics in our waters: insights from a configurative systematic review of water bodies and drinking water sources. Microplastics. https://doi.org/10.3390/microplastics4020024
22. European Parliament, Council of the European Union (2020) Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast). Official Journal of the European Union L 435:1–62. https://eur-lex.europa.eu/eli/dir/2020/2184/oj
23. European Commission (2024) Commission Delegated Decision (EU) 2024/1441 of 11 March 2024 supplementing Directive (EU) 2020/2184 of the European Parliament

and of the Council by laying down a methodology to measure microplastics in water intended for human consumption. Official Journal of the European Union L, 2024/1441. https://eur-lex.europa.eu/eli/dec_del/2024/1441/oj
24. Sharma VK, Ma X, Lichtfouse E, Robert D (2023) Nanoplastics are potentially more dangerous than microplastics. Environ Chem Lett 21:1933–1936. https://doi.org/10.1007/s10311-022-01539-1
25. Pace HE, Rogers NJ, Jarolimek C, Coleman VA, Higgins CP, Ranville JF (2011) Determining transport efficiency for the purpose of counting and sizing nanoparticles via single particle inductively coupled plasma mass spectrometry. Anal. Chem 83:9361–9369. https://doi.org/10.1021/ac201952t/p
26. F. Laborda, A.C. Gimenez-Ingalaturre, E. Bolea, J.R. Castillo, About detectability and limits of detection in single particle inductively coupled plasma mass spectrometry, Spectrochim. Acta Part B At. Spectrosc. 169 (2020). https://doi.org/10.1016/j.sab.2020.105883.
27. Abad-Álvaro I, Peña-Vázquez E, Bolea E, Bermejo-Barrera P, Castillo JR, Laborda F (2016) Evaluation of number concentration quantification by single-particle inductively coupled plasma mass spectrometry: microsecond vs. millisecond dwell times. Anal Bioanal Chem 408:5089–5097. https://doi.org/10.1007/s00216-016-9515-y
28. Kinnunen V, Perämäki S, Matilainen R (2021) Optimization of instrumental parameters for improving sensitivity of single particle inductively-coupled plasma mass spectrometry analysis of gold, Spectrochim. Acta Part B At Spectrosc. 177. https://doi.org/10.1016/j.sab.2021.106104.
29. Kálomista I, Kéri A, Ungor D, Csapó E, Dékány I, Prohaska T, Galbács G (2017) Dimensional characterization of gold nanorods by combining millisecond and microsecond temporal resolution single particle ICP-MS measurements. J Anal At Spectrom 32:2455–2462. https://doi.org/10.1039/c7ja00306d
30. Lockwood TE, Gonzalez De Vega R, Clases D (2021) An interactive Python-based data processing platform for single particle and single cell ICP-MS. J Anal At Spectrom 36:2536–2544. https://doi.org/10.1039/D1JA00297J
31. Olesik JW, Gray PJ (2012) Considerations for measurement of individual nanoparticles or microparticles by ICP-MS: determination of the number of particles and the analyte mass in each particle. J Anal At Spectrom 27:1143–1155. https://doi.org/10.1039/C2JA30073G
32. Aghaei M, Bogaerts A (2016) Particle transport through an inductively coupled plasma torch: elemental droplet evaporation. J Anal At Spectrom 31:631–641. https://doi.org/10.1039/c5ja00162e
33. Koelmans AA, Mohamed Nor NH, Hermsen E, Kooi M, Mintenig SM, De France J (2019) Microplastics in freshwaters and drinking water: critical review and assessment of data quality. Water Res 155:410–422. https://doi.org/10.1016/j.watres.2019.02.054
34. Amadu M, Miadonye A (2017) Determination of the point of zero charge pH of borosilicate glass surface using capillary imbibition method. Int J Chem 9:67. https://doi.org/10.5539/ijc.v9n3p67

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