

## Supporting Information for Characterization of a High-Sensitivity ICP-TOFMS Instrument for Microdroplet, Nanoparticle, and Microplastic Analyses

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#### *Polystyrene Bead Sizing with Scanning Electron Microscopy (SEM) Procedure*

10  $\mu$ L of a polystyrene bead suspension in ultrapure water (18.2 M $\Omega$ PURELAB flex, Elga LabWater, United Kingdom) was pipetted directly onto the center of a double-sided adhesive carbon tab, 12 mm in diameter (PELCO™, TedPella, CA) attached to an aluminum flat end pin mount (Zeiss specimen mount). The pin was left uncovered in a hood for a few hours to dry. After drying, the pin was directly analyzed via SEM. A JEOL JSM-IT200 (Peabody, MA) SEM-EDS was used with a secondary electron detector to image particles, and an X-ray detector for EDS analysis. Acceleration voltage used was 15 kV, with magnifications of 650x – 3700x and a working distance of ~9.1 mm. ImageJ (NIH, Bethesda, MD, USA) was used with scale bars provided in microscope images to size the bead.

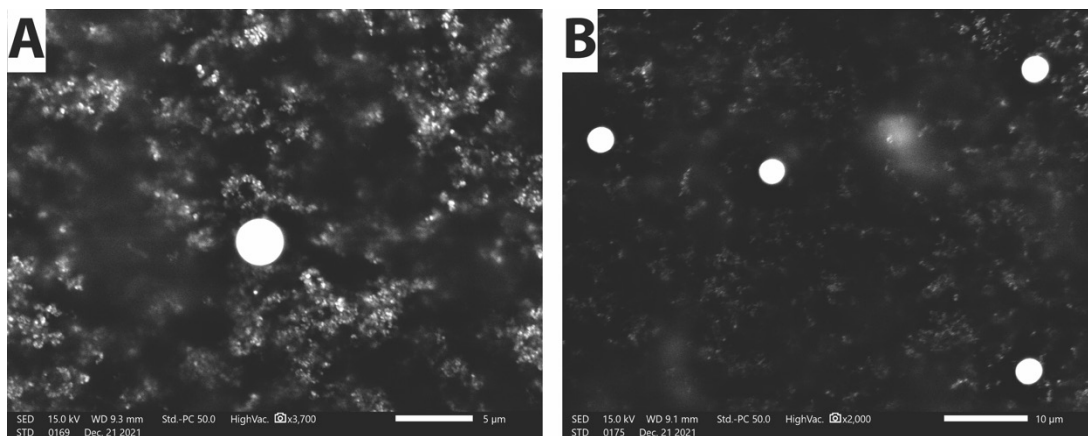


Figure S1. SEM images of Fluidigm polystyrene beads at 6000X magnification (A) and 2000x magnification (B).

Table S1. Sizing results from SEM measurements of 11 polystyrene beads in the horizontal and vertical direction.

Size (vertical)	1	Size (horizontal)	2	Magnification
3.14		3.06		3700x
3.05		3.20		2000x
2.95		3.05		2000x
3.16		3.25		2000x
3.06		3.25		2000x
3.10		3.05		2000x
3.10		3.25		2000x
3.00		3.01		2000x
3.39		3.23		650x
3.23		3.09		650x
<b>Average</b>		<b>3.13±0.11</b>		

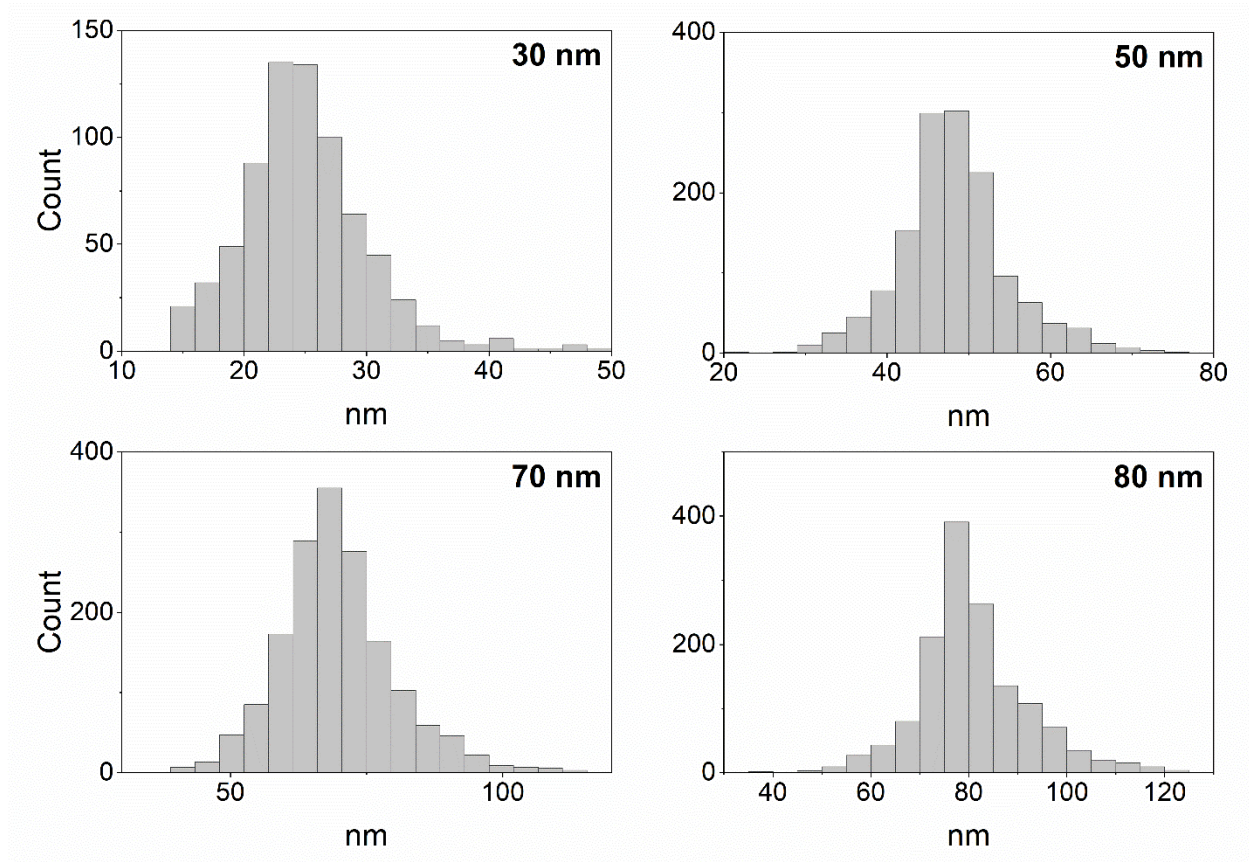


Fig. S2. Nominally 30, 50, 70, and 80 nm Ag NPs sized by spICP-TOFMS with online microdroplet calibration. Median measured diameters: 24.4 nm, 47.9 nm, 68.6 nm, 79.14 nm, respectively.

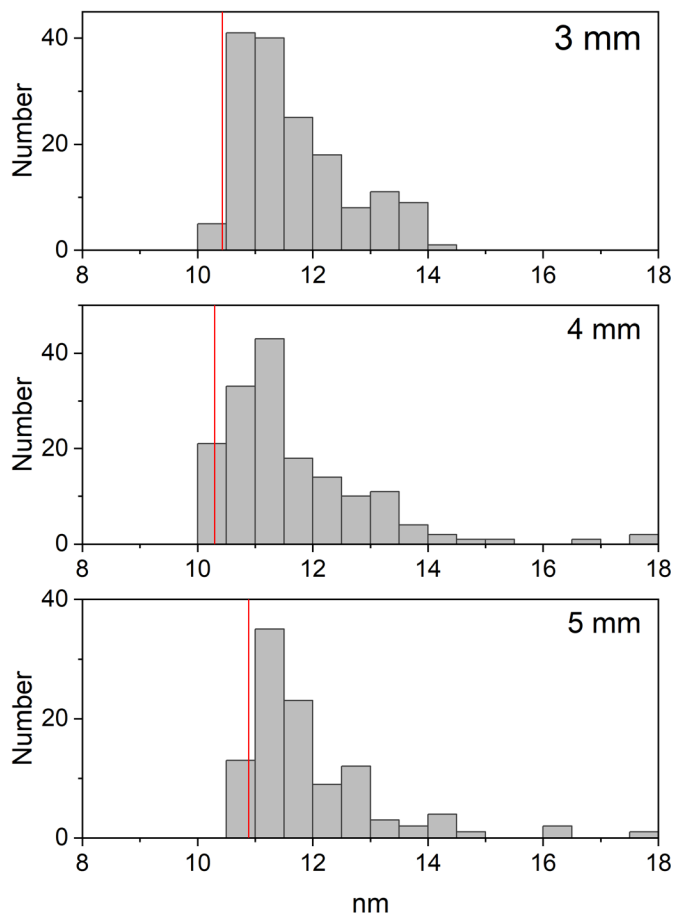


Fig. S3. Nominally 10 nm Au-NPs measured by spICP-TOFMS with plasma sampling depths of 3 mm, 4 mm, and 5 mm. Median diameters (top to bottom): 11.3 nm, 11.3 nm, 11.6 nm. The red lines indicate the critical diameter.

Table S2. Average signals and standard deviations for all measured nuclides in the polystyrene microbeads.

**Microdroplets (67  $\mu\text{m}$  diameter)**

	Average Bkgd Signal			RSD (%)	Bkgd-Subtracted Average Signal (Cts)			Poisson-Predicted RSD (%)	Predicted RSD (with bkgd subtraction)	Measured / Predicted RSD
	Average	Stdev	Bkgd	RSD (%)	Average	Stdev	RSD (%)	Poisson-Predicted RSD (%)	Predicted RSD (with bkgd subtraction)	Measured / Predicted RSD
$^{12}\text{C}$	76.1	$\pm$ 10.6		14%	409.6	$\pm$ 81.6	20%	4.9%	5.6%	3.6
$^{140}\text{Ce}$	0.041	$\pm$ 0.19		458%	1484.7	$\pm$ 104.2	7%	2.6%	2.6%	2.7
$^{151}\text{Eu}$	0.022	$\pm$ 0.14		648%	1025.9	$\pm$ 61.9	6%	3.1%	3.1%	1.9
$^{165}\text{Ho}$	0.019	$\pm$ 0.13		664%	1925.7	$\pm$ 96.2	5%	2.3%	2.3%	2.2
$^{175}\text{Lu}$	0.027	$\pm$ 0.16		577%	1768.6	$\pm$ 100.0	6%	2.4%	2.4%	2.4

**PS Microbeads**

	Average Bkgd Signal			RSD (%)	Bkgd-Subtracted Average Signal (Cts)			Poisson-Predicted RSD (%)	Predicted RSD (with bkgd subtraction)	Measured / Predicted RSD
	Average	Stdev	Bkgd	RSD (%)	Average	Stdev	RSD (%)	Poisson-Predicted RSD (%)	Predicted RSD (with bkgd subtraction)	Measured / Predicted RSD
$^{12}\text{C}$	76.1	$\pm$ 10.6		14%	304.4	$\pm$ 119.7	39%	5.7%	6.7%	5.9
$^{140}\text{Ce}$	0.041	$\pm$ 0.19		458%	491.0	$\pm$ 78.2	16%	4.5%	4.5%	3.5
$^{151}\text{Eu}$	0.022	$\pm$ 0.14		648%	395.7	$\pm$ 59.0	15%	5.0%	5.0%	3.0
$^{165}\text{Ho}$	0.019	$\pm$ 0.13		664%	246.3	$\pm$ 38.1	15%	6.4%	6.4%	2.4
$^{175}\text{Lu}$	0.027	$\pm$ 0.16		577%	322.5	$\pm$ 50.5	16%	5.6%	5.6%	2.8