

Advancing Nanomaterial Measurement Science with Single Particle Inductively Coupled Plasma Mass Spectrometry

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Introduction

- Analytical methods for reliable characterization of nanomaterials in environmental, nanomedicine, and industrial applications can address current gaps in knowledge.
- Single particle inductively coupled plasma-mass spectrometry (spICP-MS) is an emerging technique that enables measurements of size distributions and number concentrations of nanomaterials suspended in liquids.
- Special characteristics of spICP-MS that make it attractive for the analysis of nanomaterials include extremely good particle detection capability (down to truly environmentally relevant levels) and extremely rapid analysis.
- Although spICP-MS has been applied for the characterization of nanomaterials in different fields, metrological challenges and limitations remain in obtaining accurate size and particle number concentration measurements, particularly with respect to the lack of reference materials and standardization of spICP-MS methodologies.

Goals

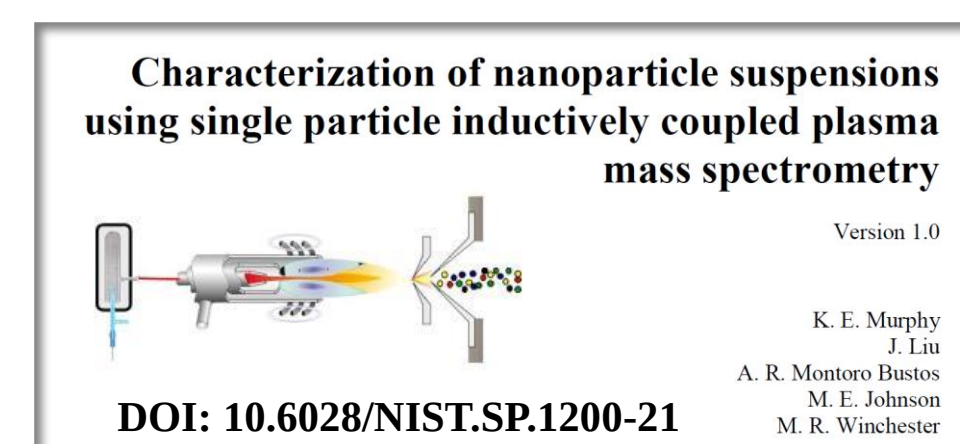
- This poster highlights a few examples of the work that has been done within the NIST Inorganic Chemical Metrology Group toward the metrological advancement of spICP-MS as a mature technique.
- This work has provided a foundation for developing the standards and reference materials that are necessary to enable the characterization of nanomaterials.
- In the past decade, our group has engaged in several activities to build a robust nanomaterial spICP-MS measurement infrastructure, leading to the validation and establishment of its metrological quality, including:
 - validation of spICP-MS for routine characterization of gold nanoparticles of different sizes, coatings, and surface charge at environmentally relevant concentrations in water,
 - analysis of silver and titanium dioxide nanoparticles (NPs) in water,
 - characterization of silicon dioxide food additive materials in water,
 - characterization of the uptake of gold NPs in *Caenorhabditis elegans*, and
 - potential application of spICP-MS for the characterization of microplastics suspended in water, and for the determination of inorganic NPs in food.

- Certain commercial products or equipment are described in this paper in order to specify adequately the experimental procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

Conclusions and Future Directions

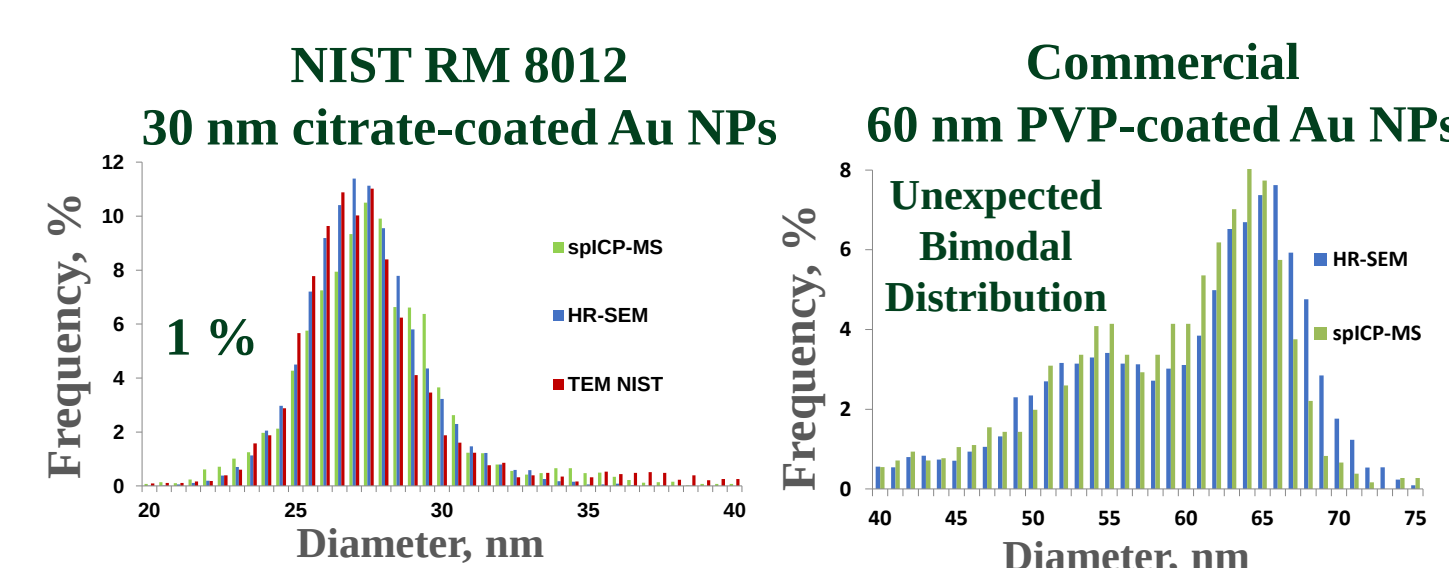
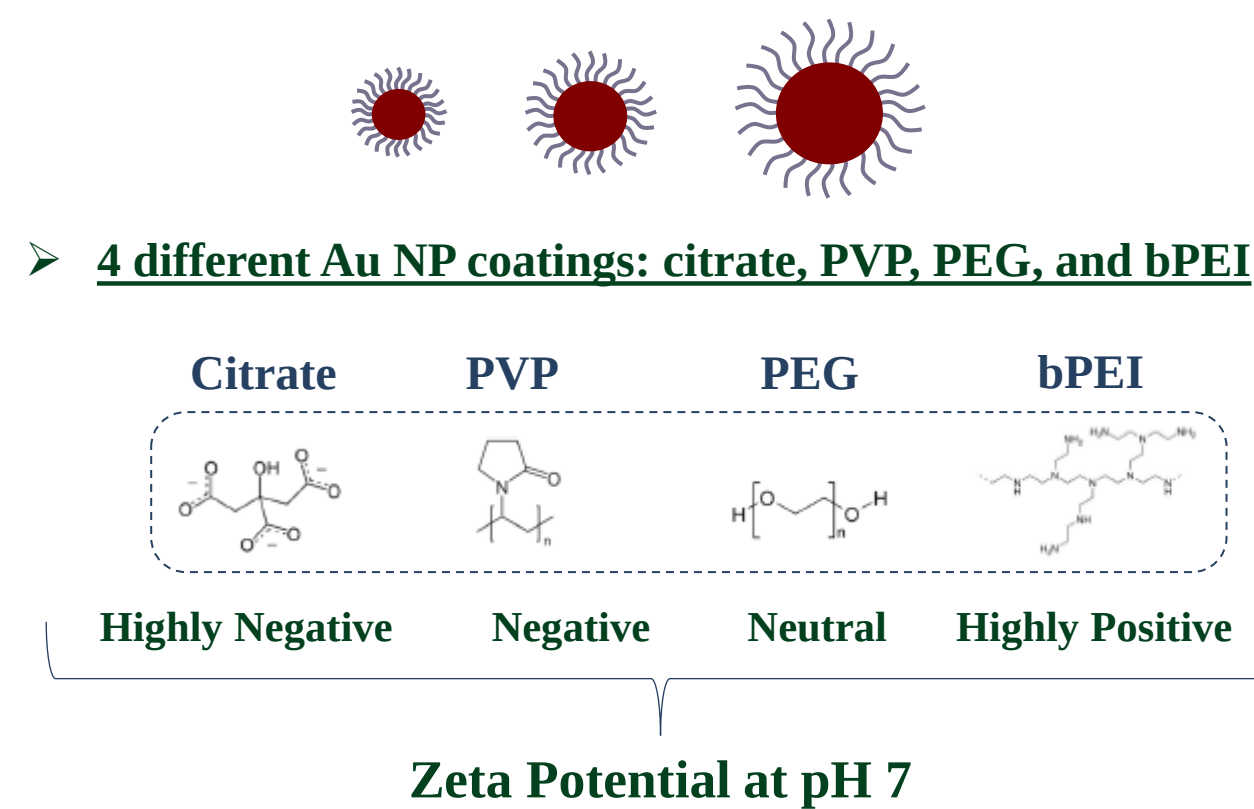
- As shown in this poster, with the spICP-MS technique at our disposal, our group is positioned to tackle the challenges of analyzing metallic NPs of different sizes and surface coatings in environmental matrices, capable of providing measurements of mean NP size and particle number concentration. In principle, spICP-MS is applicable to many NPs containing elements that can be detected using ICP-MS. As such, we have utilized the technique to successfully measure challenging samples like silver NPs (prone to dissolution over time), titanium and silicon dioxide NPs (challenging elements for ICP-MS), and gold NPs in biological tissues.
- Additional efforts to build a robust spICP-MS measurement infrastructure that will enable reliable characterization of microplastics suspended in water reveal that a high sensitivity single-cell sample introduction system operated at 20 % lower nebulizer gas flow rate is necessary to achieve a quantitative analysis of larger Polystyrene Latex Microspheres (5 µm) when using ¹³C detection, extending the dynamic linear range of spICP-MS for the quantification of microplastics over an order of magnitude.
- Future research directions will include exploring the feasibility of detecting elements in the plastic matrix as an alternative approach to measuring microplastics by spICP-MS, as well as assessing the release of microplastics from 3D printed toys, revisit aerosol transport phenomena in spICP-MS, production of reference materials, standard measurement protocols, data automation, and the evaluation of a selection of existing food reference materials by spICP-MS.

NIST Special Publication 1200-21



spICP-MS analysis of Au NPs

➤ 3 different Au NP sizes: 30, 60, and 100 nm



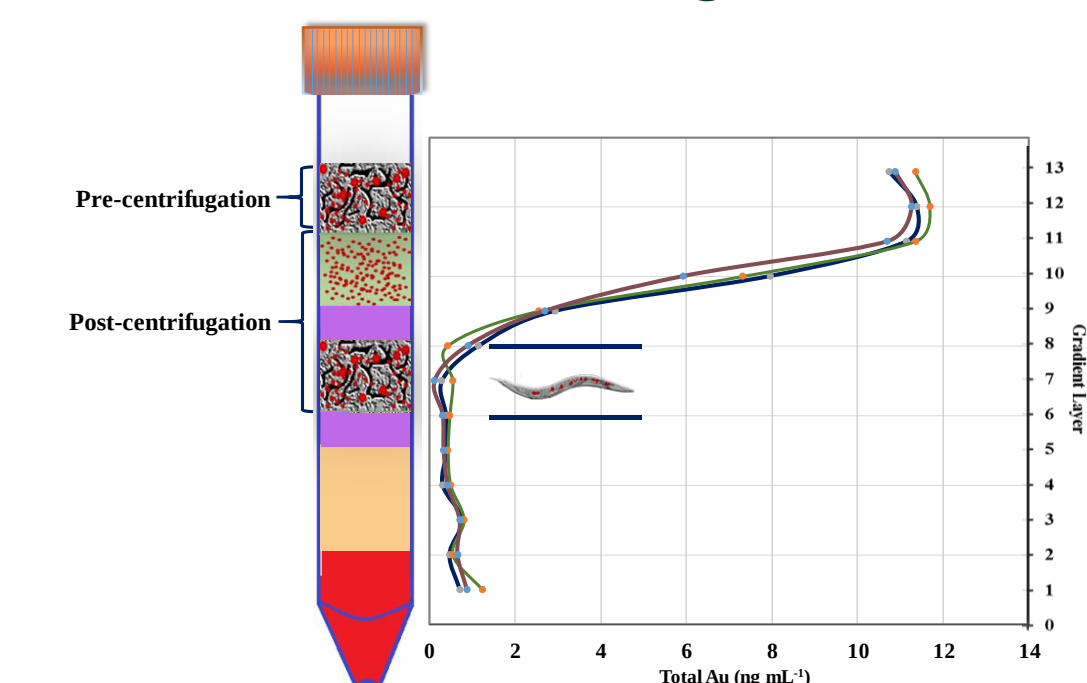
A.R. Montoro Bustos, et al.; Anal. Chem., 2018, 90, 14376-14386

Number Concentration (PNC)

Au NPs	PNC _{direct}	PNC
	spICP-MS	Recovery (%)
30 nm PVP	2.19 ± 0.20 × 10 ¹⁴	97.0 ± 1.0 (15.3)
30 nm bPEI	2.03 ± 0.36 × 10 ¹⁴	98.3 ± 6.4 (19.7)
30 nm PEG	2.16 ± 0.30 × 10 ¹⁴	108.9 ± 6.0 (17.6)
60 nm PVP	2.69 ± 0.24 × 10 ¹³	91.7 ± 1.1 (14.9)
60 nm bPEI	2.46 ± 0.28 × 10 ¹³	90.8 ± 3.5 (21.7)
60 nm PEG	2.99 ± 0.41 × 10 ¹³	96.3 ± 0.5 (13.8)
100 nm Citrate	5.75 ± 0.73 × 10 ¹²	91.4 ± 5.2 (16.0)
100 nm PVP	4.68 ± 0.74 × 10 ¹²	93.0 ± 5.2 (19.1)
100 nm bPEI	4.93 ± 0.59 × 10 ¹²	100.0 ± 3.4 (16.9)
100 nm PEG	6.33 ± 0.59 × 10 ¹²	104.3 ± 1.3 (15.6)

A.R. Montoro Bustos, et al.; Anal. Chem., 2022, 94, 3091-3102

Sucrose density gradient centrifugal separation of *Caenorhabditis elegans* and Au NPs



M.E. Johnson, et al.; ACS Nano, 2017, 526-540

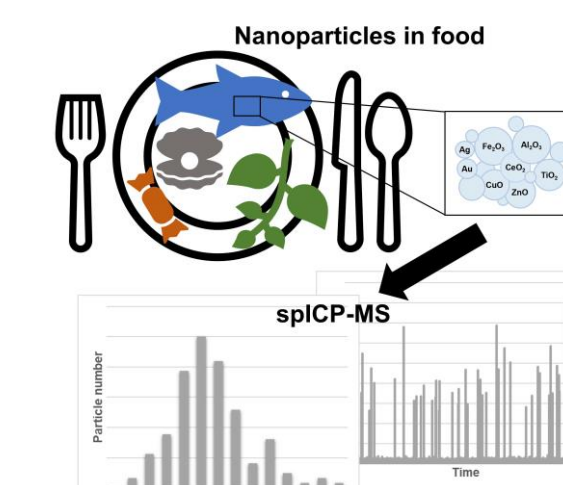
M.E. Johnson, et al.; Anal. Bioanal. Chem., 2016, 408, 7629-7640

spICP-MS analysis of TiO₂ NPs in sunscreens

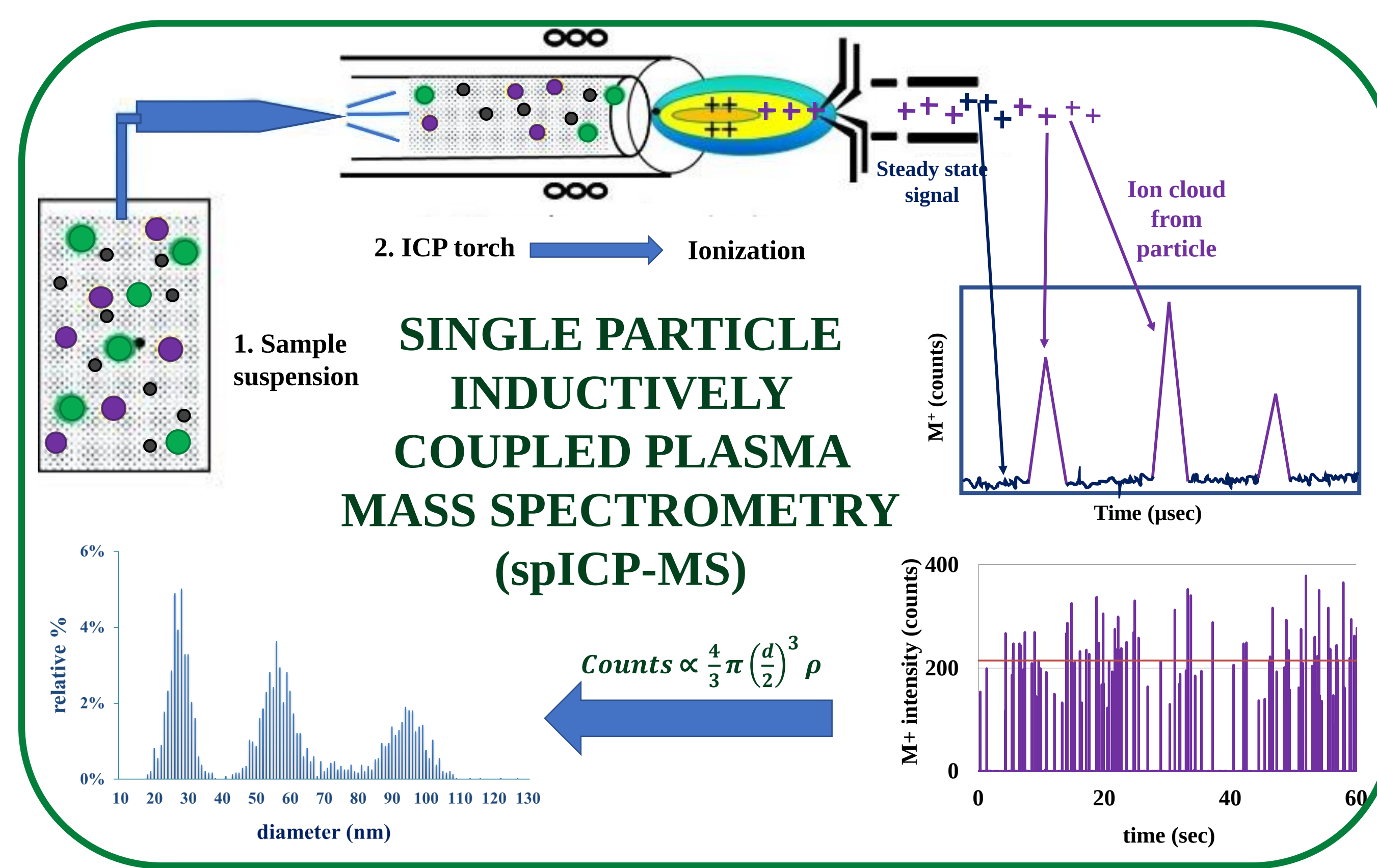


➤ The EU FP7 NanoDefine Project

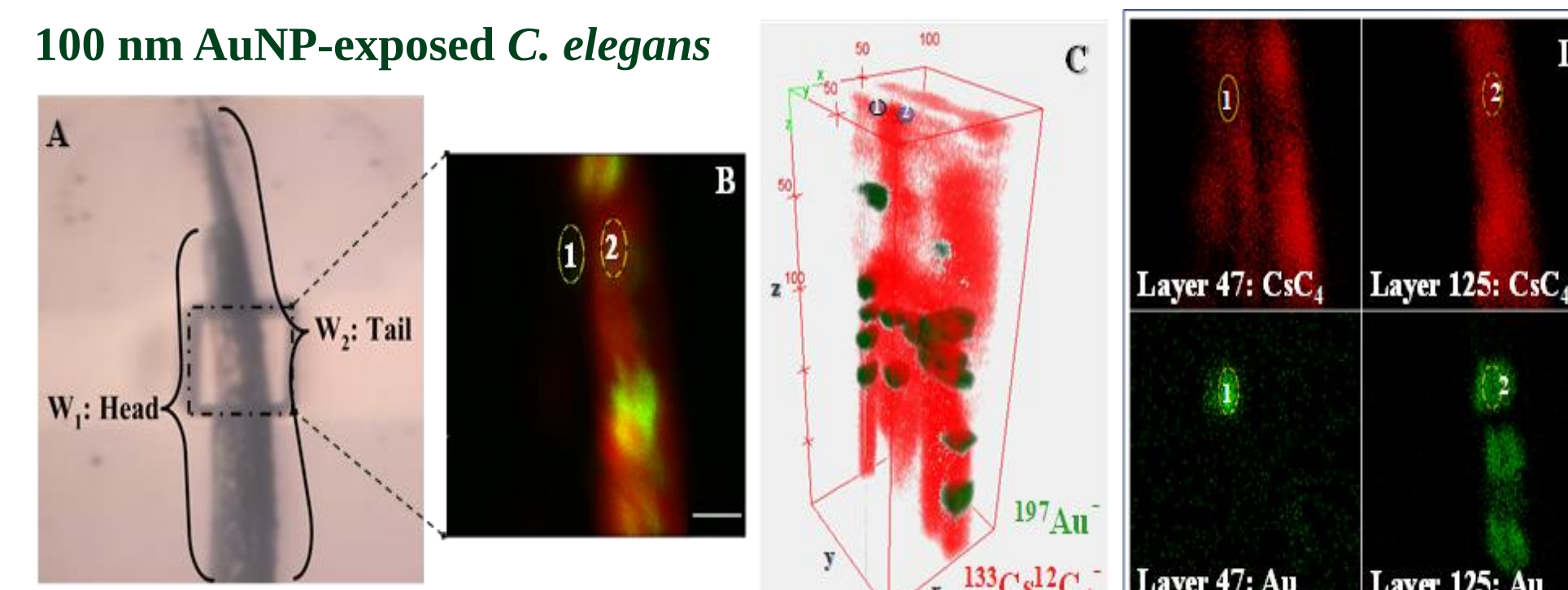
Application of spICP-MS for Determination of NPs in Food



K Loeschner, et al.; Nanomaterials, 2023, 13, 2547



Au NP uptake in *Caenorhabditis elegans* via Secondary Ion Mass Spectrometry analysis



M.E. Johnson, et al.; Anal. Chim. Acta, 2021, 1175, 338671

spICP-MS analysis of Polystyrene Microspheres: ¹³C detection at 20% lower neb gas

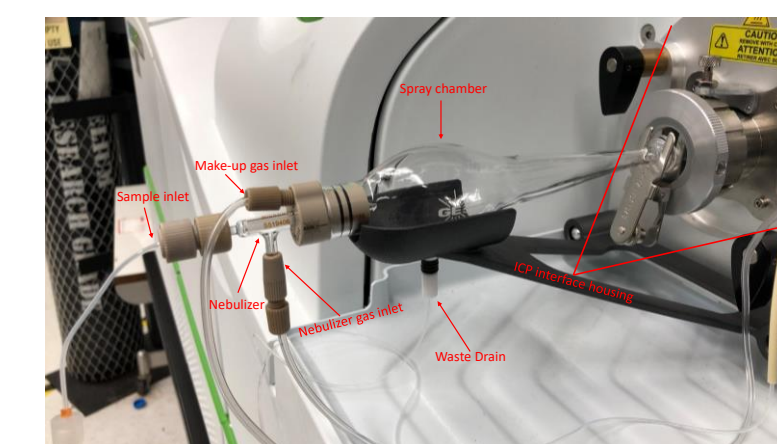
High sensitivity single-cell sample introduction system for ICP-MS (Glass Expansion)



- Designed for larger droplets (> 5 µm) entering plasma
- High transport efficiency at low sample uptake rates

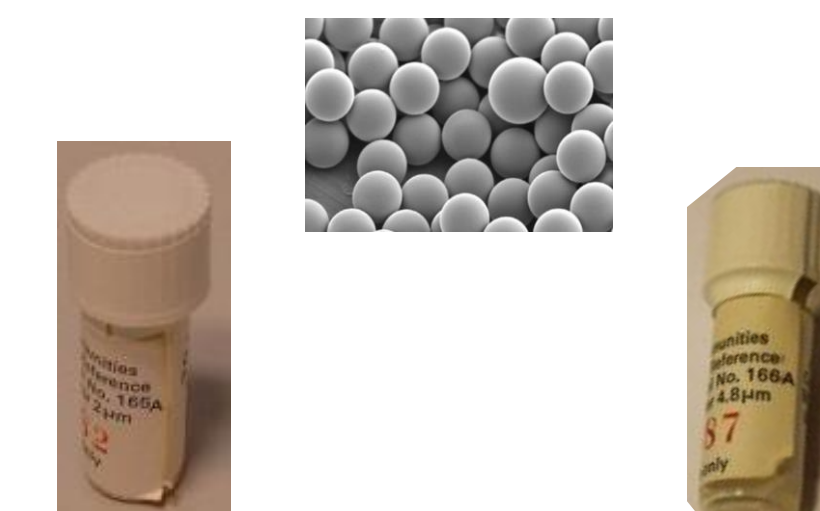
- Nebulizer gas flow rate: 0.25 to 0.35 L/min
- Make-up gas required
- Torch injector diameter 1.5 mm i.d.
- Optimum sample flow rate: 10 µL/min to 40 µL/min

NexION 350D Quadrupole (PerkinElmer)

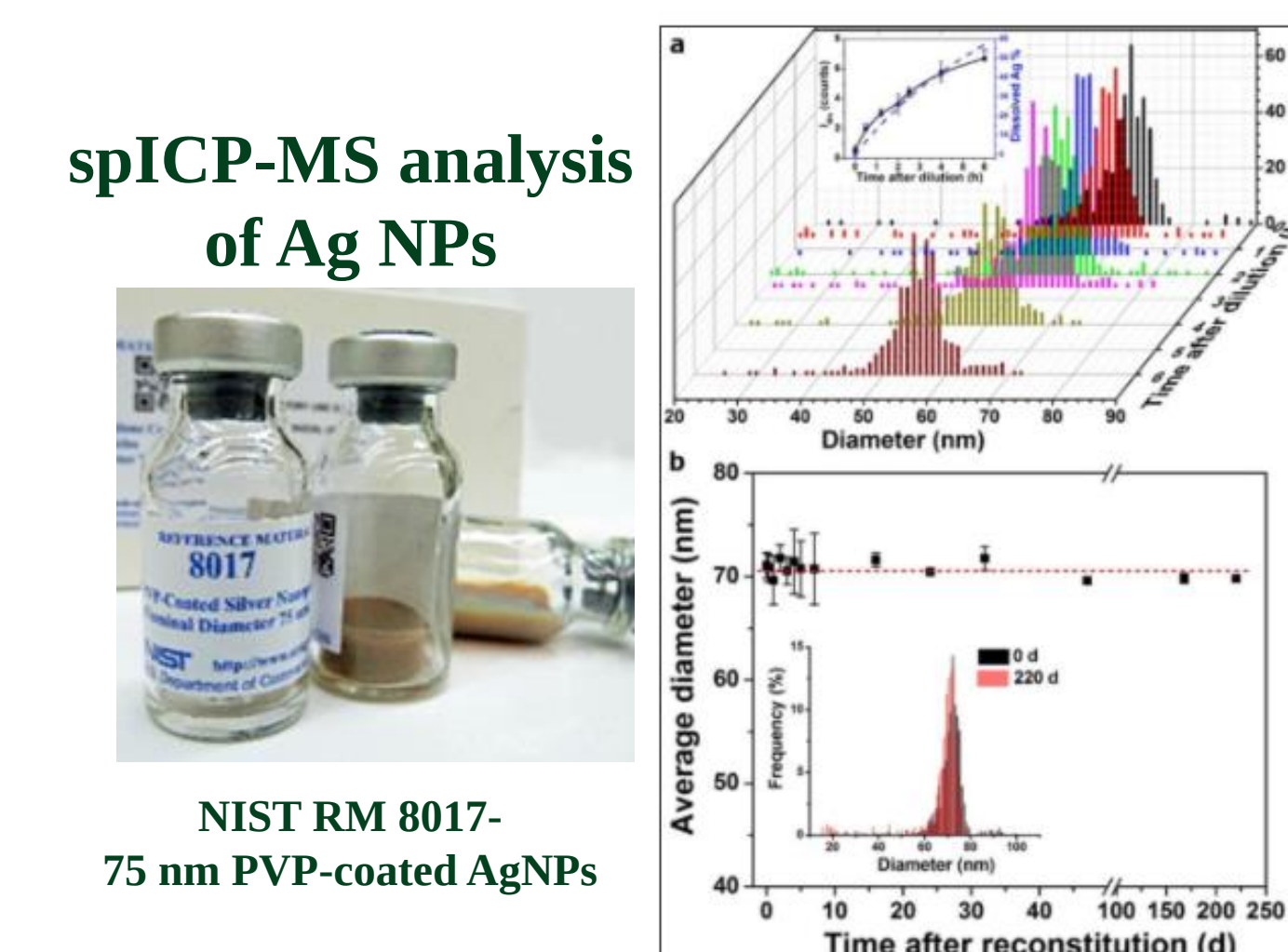


- RF Power: 1400 W; Dwell time: 100 µs
- Nebulizer gas flow rate: 0.29 L/min
- Make-up gas flow rate: 0.69 L/min
- Sample flow rate: 14 µL/min
- Transport Efficiency: 40 % to 50 %

Monodispersed Latex Microspheres Certified Reference Materials



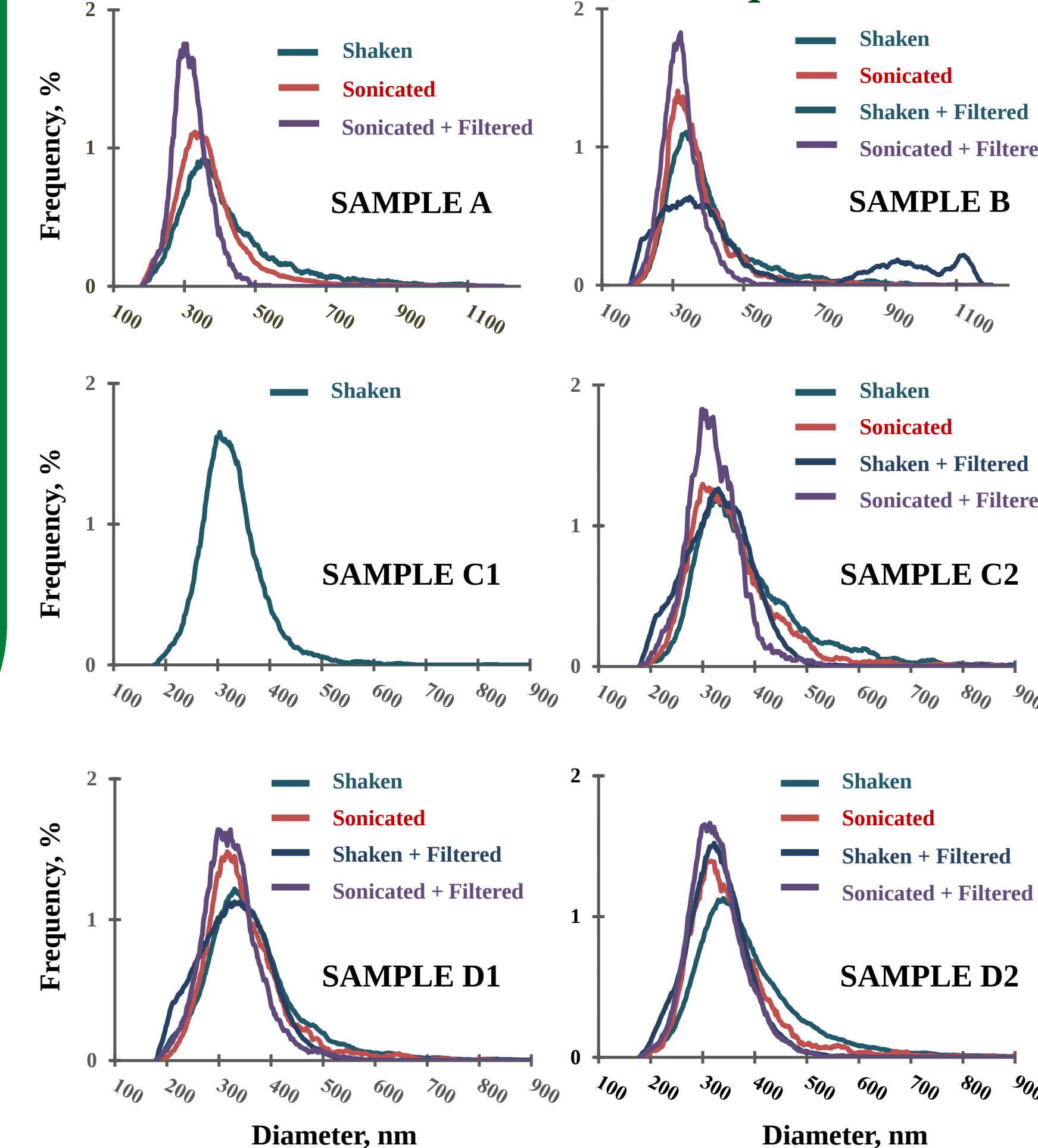
- BCR® - 165 - 2.2 µm
- BCR® - 166 - 4.8 µm



NIST RM 8017-75 nm PVP-coated AgNPs

J. Liu, et al.; Anal. Bioanal. Chem., 2017, 409, 6027-6039

spICP-MS of Silicon Dioxide Food Additive Materials in Aqueous Media



All six silicon dioxide food additive powders were in the 300 nm to 400 nm size range regardless of the sample dispersion method.

S. Afrin Khan, et al.; Food Additives & Contaminants: Part A, 41(1), 9-21

