Determination of Micro Plastics in the Environment Using Total Flow Nebulization and Triple Quadrupole ICP-MS

Yan Cheung, Application Scientist, ICP-MS
Craig Jones, Application Scientist, ICP-MS
Emmett Soffey, Product Specialist, ICP-MS

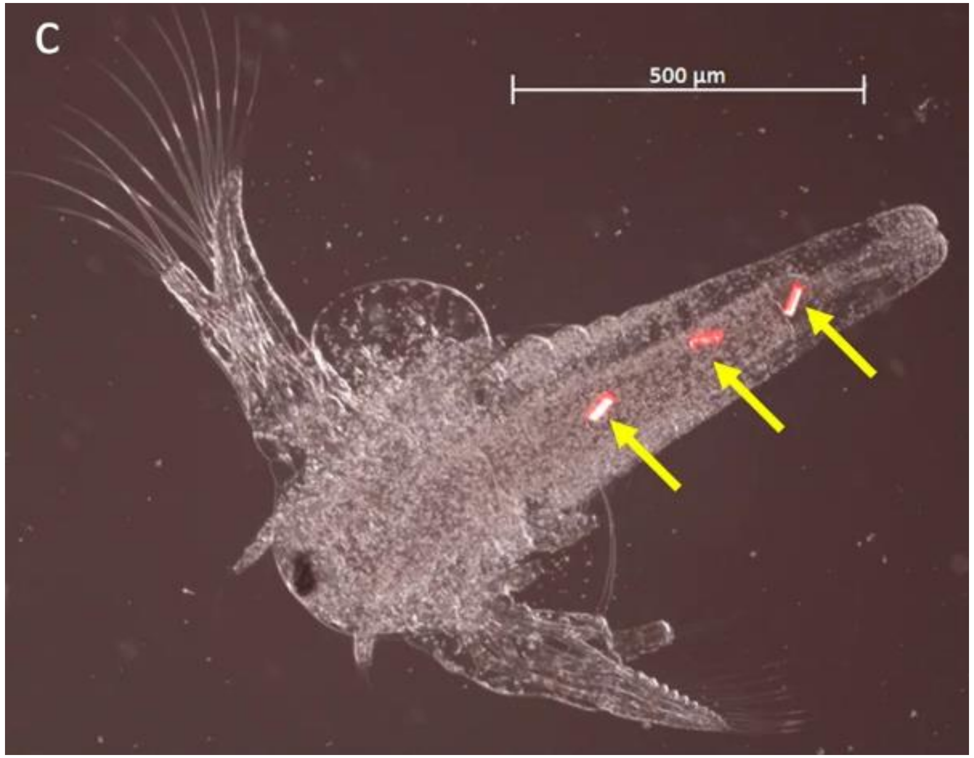
DE66835248

Characterizing Microplastics (MPs) by ICP-MS

In terms of size, number of particles, concentration, and elemental content

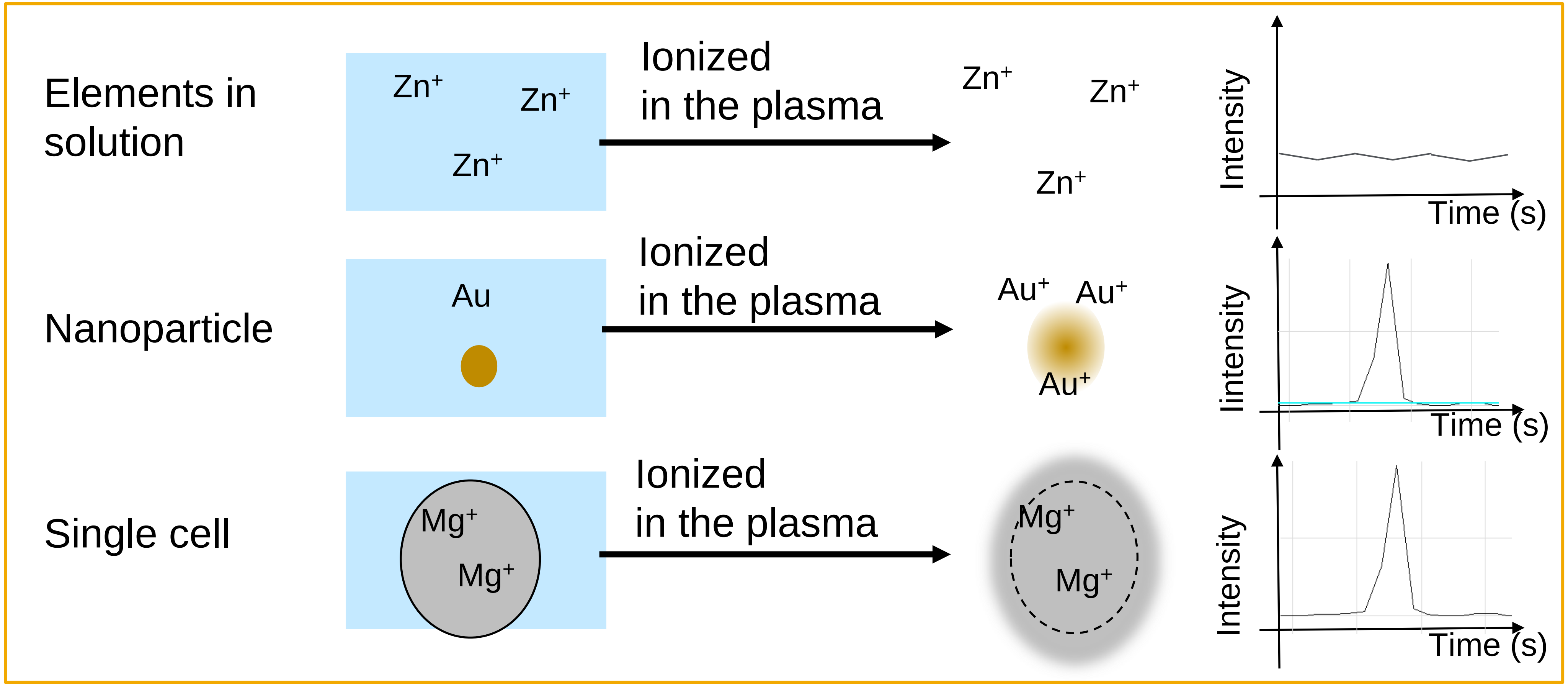
Challenges of elemental analysis of MPs:

- Compared to nanoparticles, the particle sizes of MPs are relatively large (in the order of µm to mm).
- The analysis of MPs by ICP-MS requires a non-standard sample introduction system to transport the relatively large particles to the plasma, in high efficiency.
- To identify Microplastic from other particles, ICP-MS will be measuring carbon (^{13}C) ion signal, which is less sensitive than other metals.
- Other studies had measured ^{12}C for microplastics with good results.



ICP-MS Modes of Analysis

Mechanism of ICP-MS detection of metallic ions in an ionic solution, in nanoparticles, and in single cells

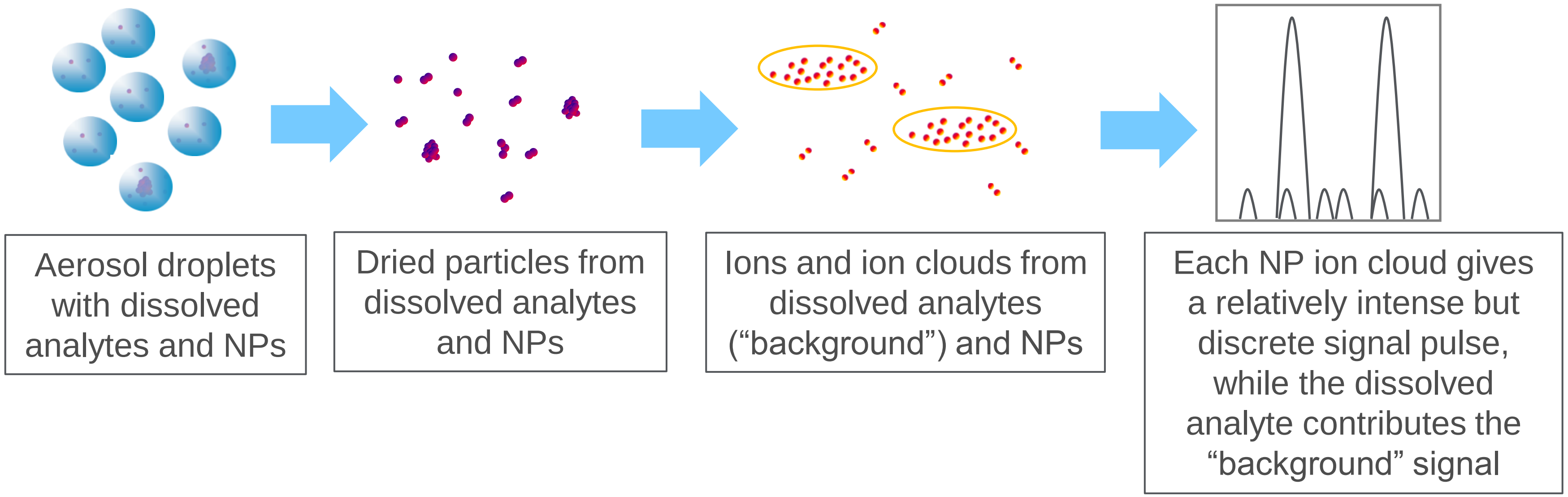


Single Particle ICP-MS (spICP-MS)

An established technique for the analysis of nanoparticles (NPs) and particles

Outline of spICP-MS technique:

- Suspension solutions containing particles are introduced directly into the ICP through a nebulizer where they are decomposed, atomized, and ionized.
- The ion plume is detected within 1 ms, which is much faster than the signal integration time used in conventional ICP-MS measurements (10–100 ms).
- To measure the signals from individual single particles, the fast TRA mode of Agilent single quadrupole ICP-MS or Agilent triple quadrupole ICP-MS (ICP-QQQ) uses an integration time of 0.1 ms.



High Efficiency Sample Introduction System

Benefits:

- Sample transport efficiency increases from ~10% in traditional setup to >50% (in some case 70% - 80%) transport efficiency
- Better transport for larger particles
- Greatly increase sensitivity

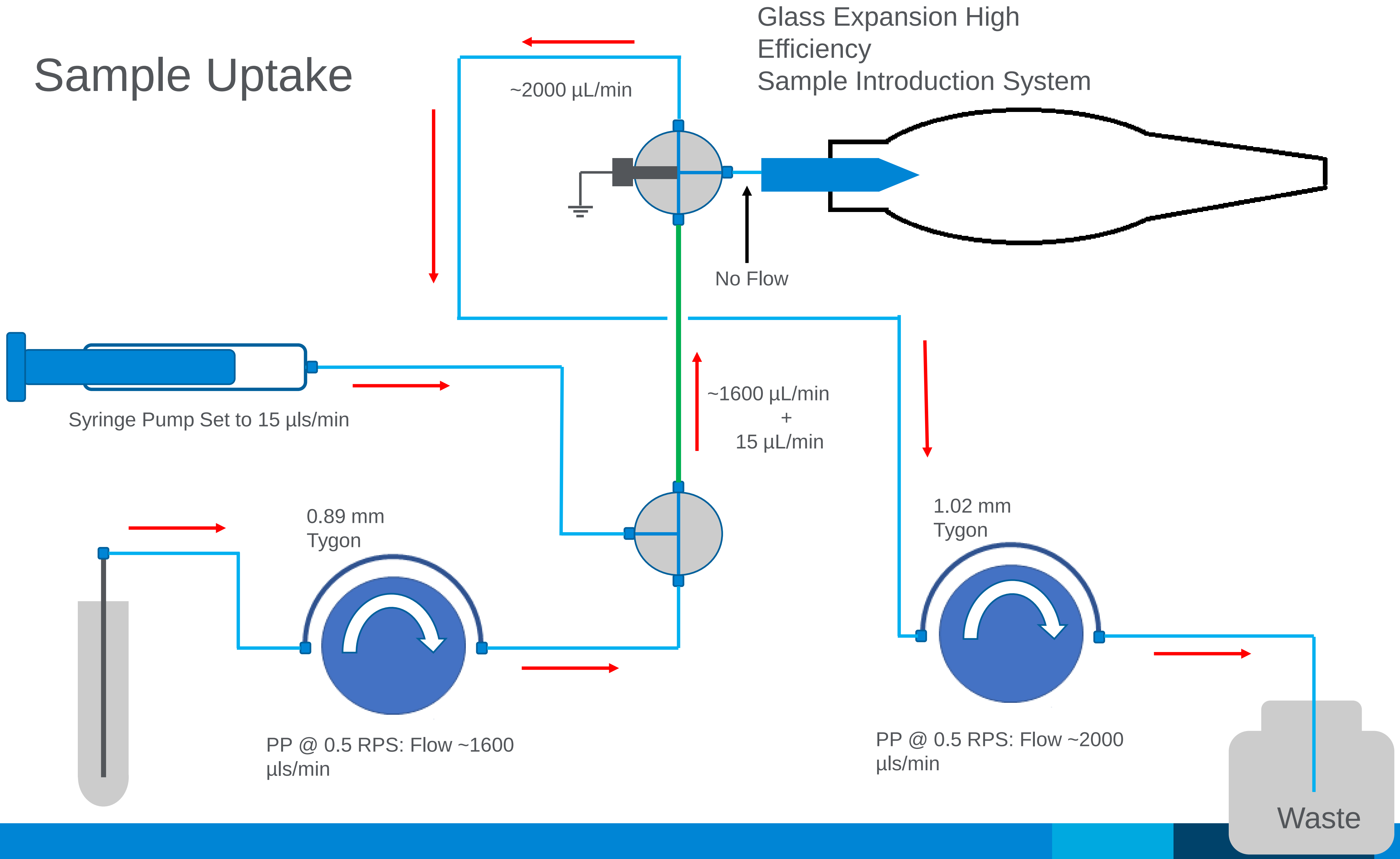
Limitations:

- Can only handle low sample flow (10-20 uL/min)
- Slow wash out
- Long analysis time

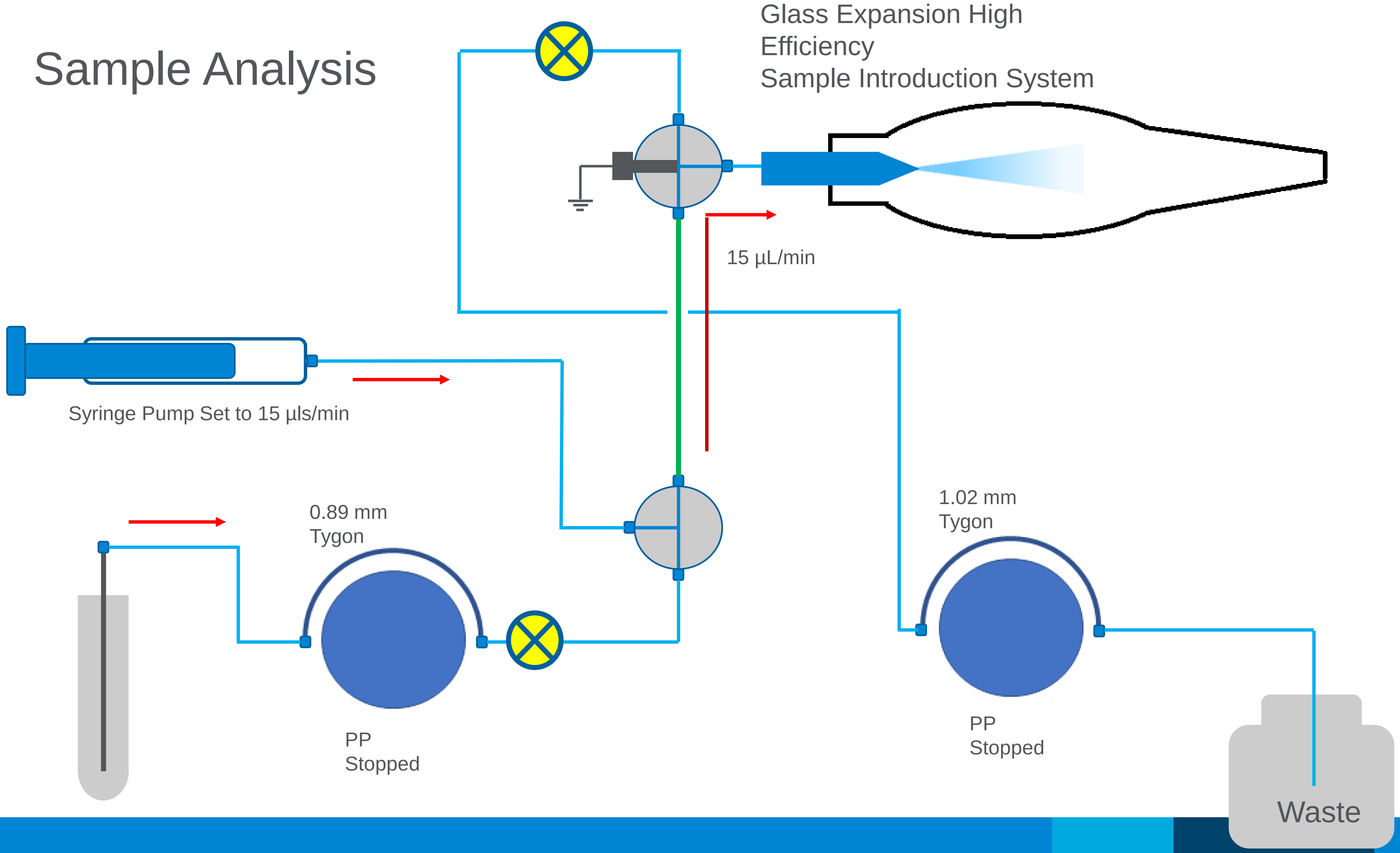
Remedies:

- **Syringe pump** to ensure smooth, slow, and accurate flow rate
- **Valves** to rinse during sample injection
- **Autosampler** available for sample batch

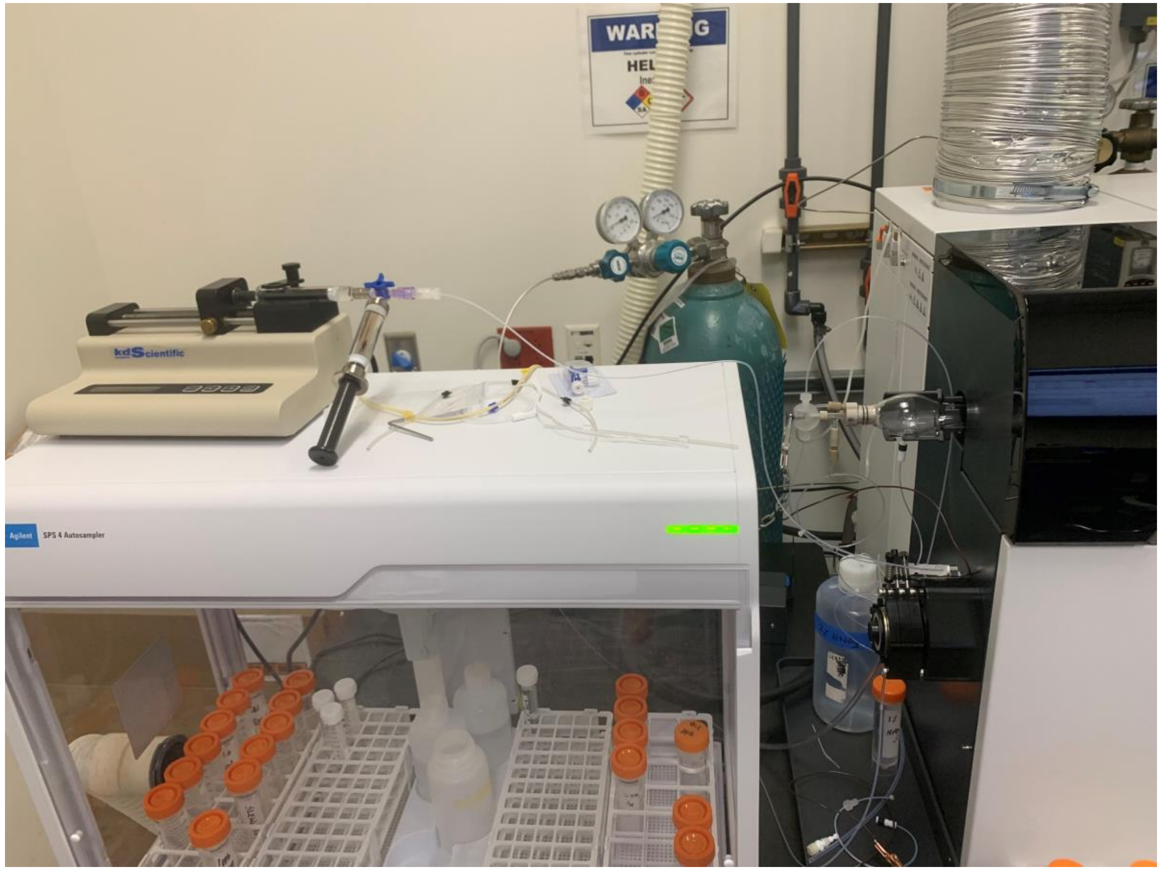
Sample Uptake

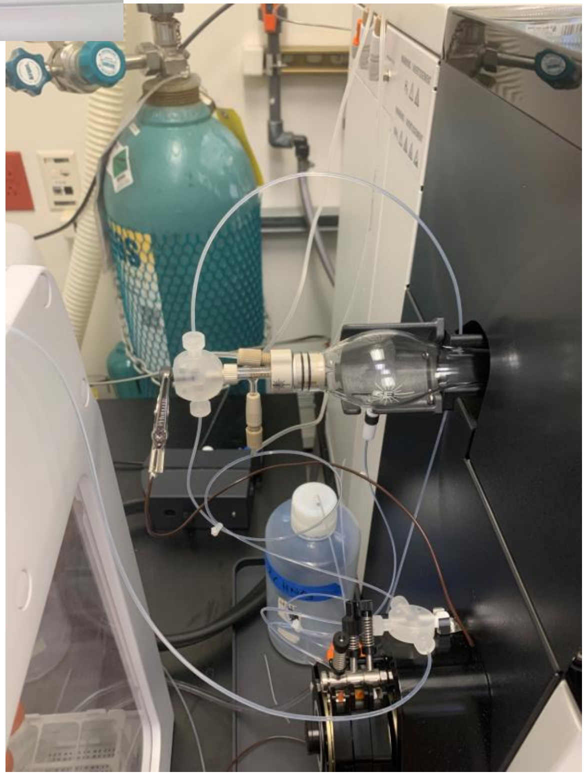


Sample Analysis



The Actual Setup in the Lab





ESI microFAST Single Cell (sc) Autosampler

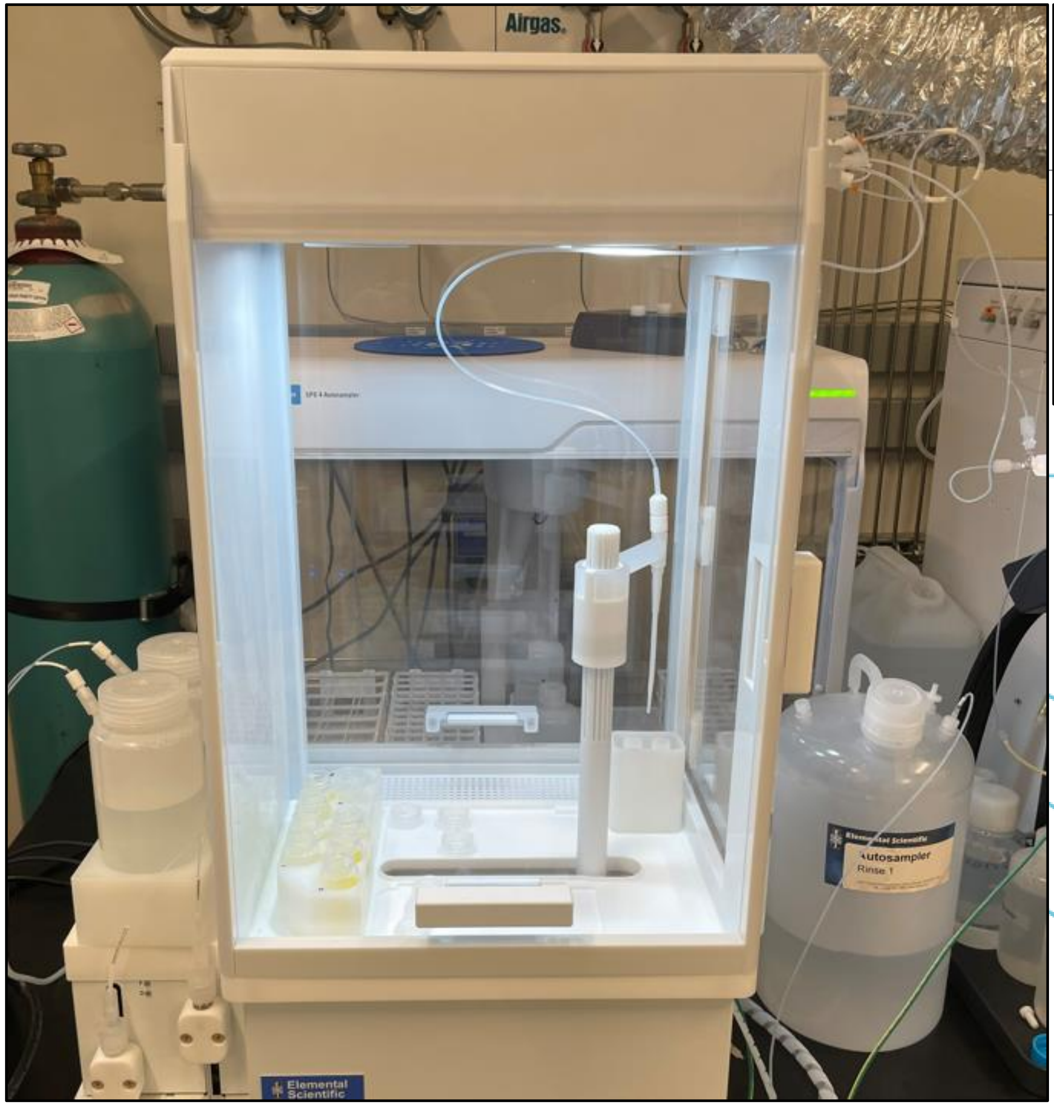
The ESI micro*FAST* comprises a complete system that includes:

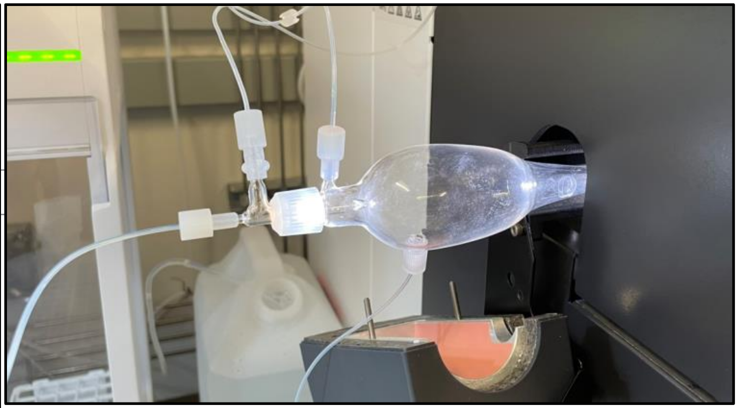
- Autosampler, CytoNeb nebulizer, CytoSpray spraychamber, and a one-piece torch.
- Spray Chamber: High transport efficiency of large particles to the ICP, the of the
- The ESI micro-sampling system is also compatible with the Agilent 7850 ICP-MS (with fast TRA) and the Agilent 7900 ICP-MS.

Elemental Scientific Inc., Omaha, NE, USA.

A fully automated, microflow technique for easy and efficient analysis of particles.

ESI microFAST Single Cell Sampler





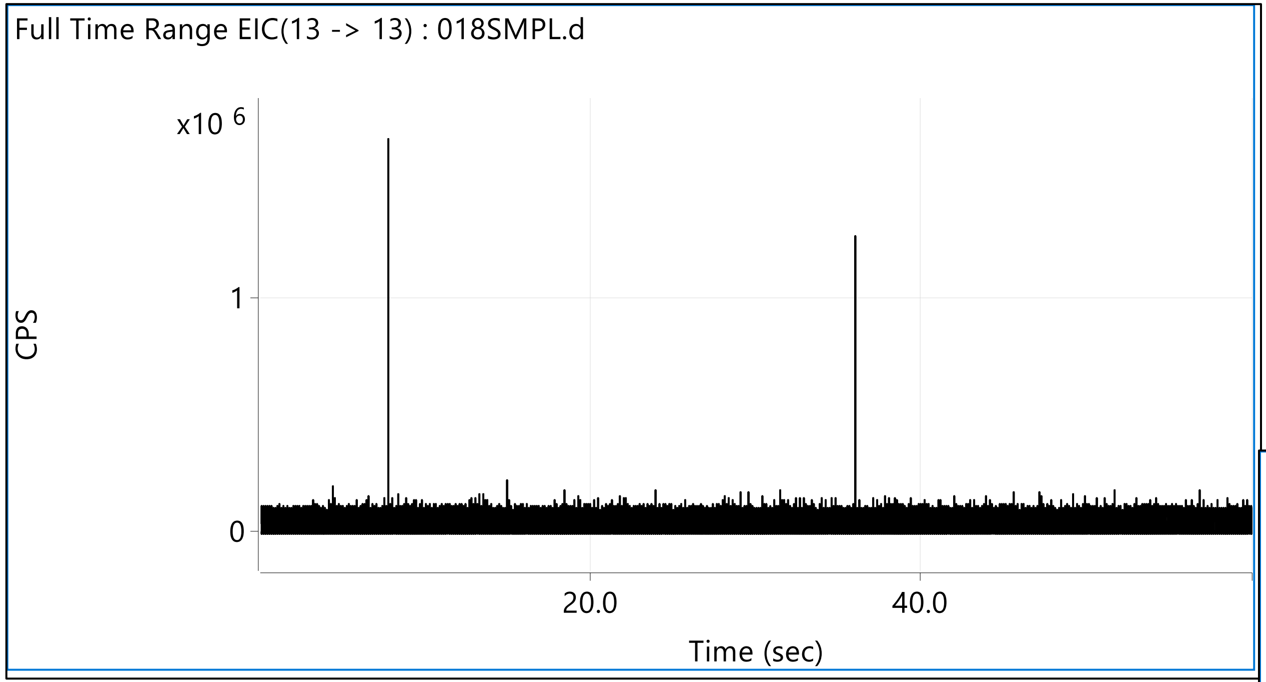
Optional Fluoronetic Z-rail
- True fluoropolymer mechanical action
- Magnetically coupled linear drive
- Chemically resistant and long-lived

Tapered Probe

Dual Rinse Station
- Low rinse consumption

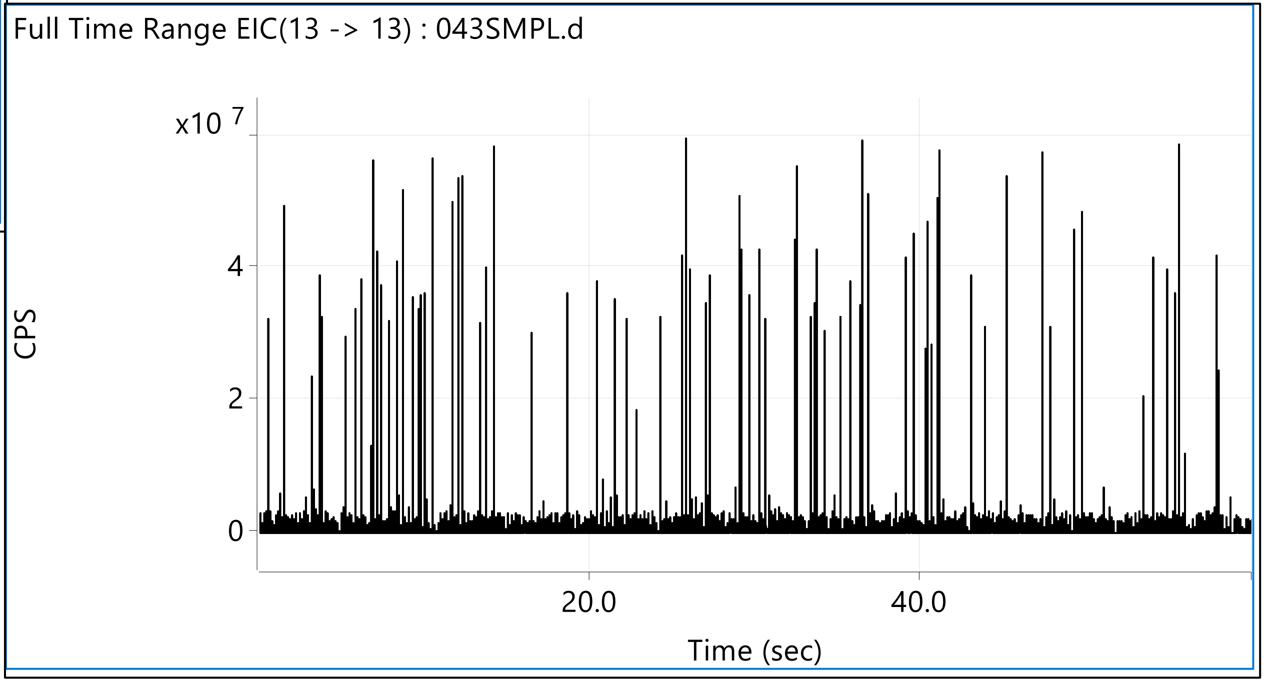
PTFE Autosampler Deck

Presence of Microplastics by Agilent MassHunter Software



Blank solution

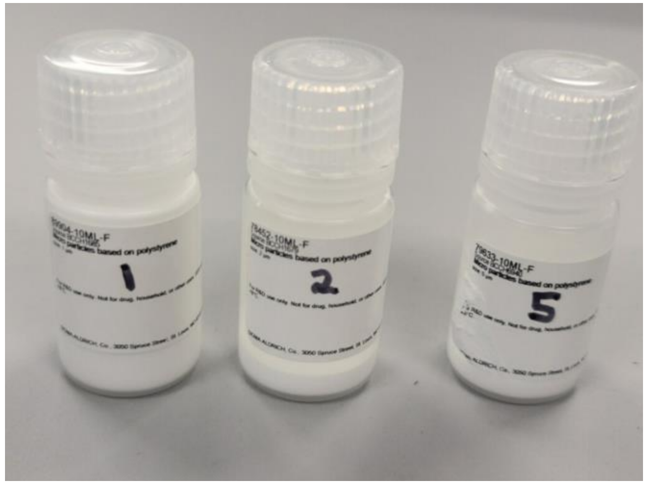
Microbeads solution



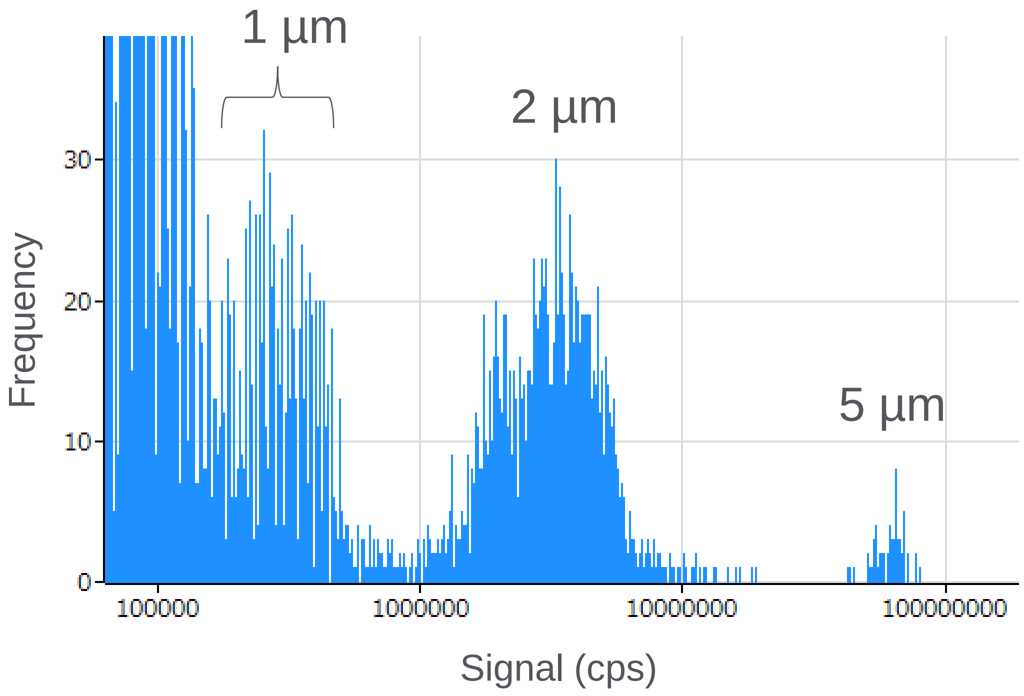
Characterization of Polystyrene Microbeads by spICP-MS

High sensitivity of the 8900 ICP-QQQ detects signals from 1, 2, and 5 µm PS microbeads

- Three PS suspensions of 1, 2, and 5 µm microbeads were obtained from Sigma Aldrich (St. Louis, MI, USA).
- A mixed solution containing 1, 2, and 5 µm PS microbeads was prepared in DI water.
- Size distribution plot of ^{13}C in the PS microbeads mixture.
- The data shows a clear separation between 1, 2, and 5 µm PS microbeads signals.
- A platinum (Pt) NP reference material (RM) containing 50 nm diameter NPs was used to calculate the nebulization efficiency of the method.



The results confirm the feasibility of the spICP-MS technique for the detection of the elemental content of MPs.



Showing 1, 2, and 5 µm microplastic signal distribution.

Analysis of Polystyrene Microbeads by Measuring ^{13}C

spICP-MS data for 1, 2, and 5 µm polystyrene microbeads

Solutions containing 1, 2, and 5 µm PS microbeads at 0.1, 1, and 10 ppm were prepared in triplicate by diluting the PS suspensions in DI water before analysis of ^{13}C using spICP-MS.

- There was good agreement of the measured particle concentration for each size of MP in the triplicate PS solutions, especially for the 2 and 5 µm PS microbead samples.
- Also, the measured median size results agreed with the nominal sizes of the PS microbeads.

The results demonstrate the effectiveness of the 8900 ICP-QQQ method coupled with the micro*FAST* autosampler for the detection of MPs down to 1 µm.

Polystyrene Sample	Number of Detected Particles	Particle Concentration (particles/L)	Median Size (µm)
1 µm 0.1 ppm - 1	2366	4.3×10^8	0.95
1 µm 0.1 ppm - 2	1616	2.9×10^8	1.04
1 µm 0.1 ppm - 3	2100	3.8×10^8	0.97
2 µm 1 ppm - 1	1733	3.1×10^8	1.9
2 µm 1 ppm - 2	1763	3.2×10^8	1.9
2 µm 1 ppm - 3	1947	3.5×10^8	1.9
5 µm 10 ppm – 1	197	3.5×10^7	5.2
5 µm 10 ppm – 2	181	3.3×10^7	5.1
5 µm 10 ppm - 3	211	3.8×10^7	5.2

Polystyrene Microbead Results

File | Home | View | Report | Tools

Open | Save | Import Samples | Batch

Process Batch | Process Order | Clear Results | Batch Option

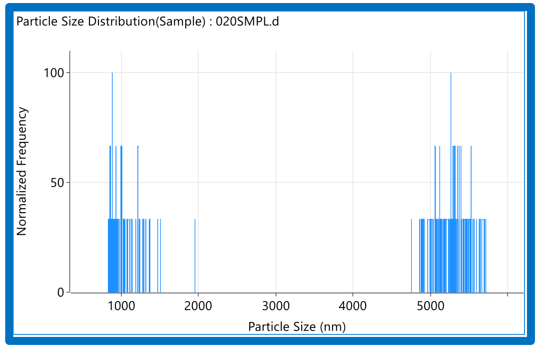
New | Import DA Method | Method

Batch Table : Single Particle

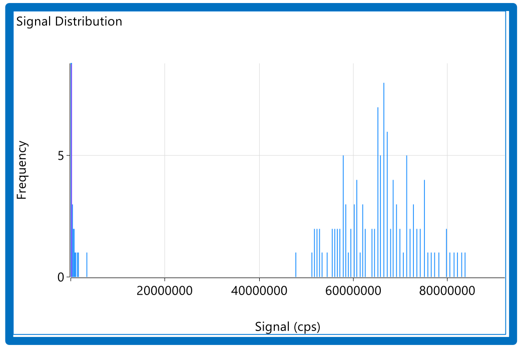
Sample: Sample Type: <All> Analyte: 197 Au

[1] [2] [3] [4] Reset

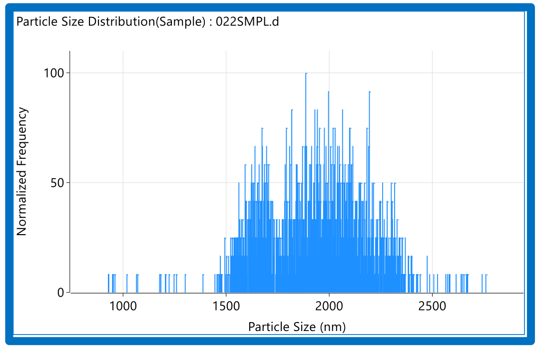
	Sample					13 -> 13 C				197 Au			
	Rjct	Data File	Acq. Date-Time	Type	Sample Name	# of Particles	Mean Size (nm)	Nebulization Efficiency	FullQuant Signal (cps)	# of Particles	Mean Size (nm)	Nebulization Efficiency	FullQuant Signal (cps)
5		005IONS.d	3/7/2023 3:40:17 PM	IonicStd (AN)	10ppm C 1ppb Au				114696.45				194817.67
6		006IONSRM.d	3/7/2023 3:47:09 PM	IonicStd (RM)	10ppm C 1ppb Au								190120.17
7		007SMPL.d	3/7/2023 3:52:22 PM	Sample	Blank	10			34800.13	2			1502.57
8		008_RM.d	3/7/2023 3:59:15 PM	RM	50nm 50ppt					199	49	0.551	9240.82
9		009SMPL.d	3/7/2023 4:04:28 PM	Sample	Blank	4	1469	0.551	35409.64	0		0.551	670.88
10		010SMPL.d	3/7/2023 4:11:20 PM	Sample	5µ 10 ppm	100	5192	0.551	47170.16	10	6	0.551	573.59
11		011SMPL.d	3/7/2023 4:18:13 PM	Sample	5µ 10 ppm	93	4841	0.551	45796.05	2	9	0.551	476.40
12		012SMPL.d	3/7/2023 4:25:06 PM	Sample	5µ 10 ppm	100	5101	0.551	46489.31	2	6	0.551	431.36
13		013SMPL.d	3/7/2023 4:31:59 PM	Sample	2µ 1 ppm	1928	1927	0.551	46030.01	5	10	0.551	394.16
14		014SMPL.d	3/7/2023 4:38:51 PM	Sample	2µ 1 ppm	1765	1934	0.551	46030.74	5	7	0.551	389.13
15		015SMPL.d	3/7/2023 4:45:44 PM	Sample	2µ 1 ppm	1856	1936	0.551	46783.03	6	8	0.551	463.08
16		016SMPL.d	3/7/2023 4:52:37 PM	Sample	1µ 0.1 ppm	1278	975	0.551	37510.70	7	9	0.551	402.88
17		017SMPL.d	3/7/2023 4:59:29 PM	Sample	1µ 0.1 ppm	1438	957	0.551	36699.41	4	6	0.551	394.96
18		018SMPL.d	3/7/2023 5:06:20 PM	Sample	1µ 0.1 ppm	1263	978	0.551	36405.01	0		0.551	349.92
19		019SMPL.d	3/7/2023 5:13:12 PM	Sample	50nm 50ppt	32	908	0.551	35991.59	211	48	0.551	9081.71



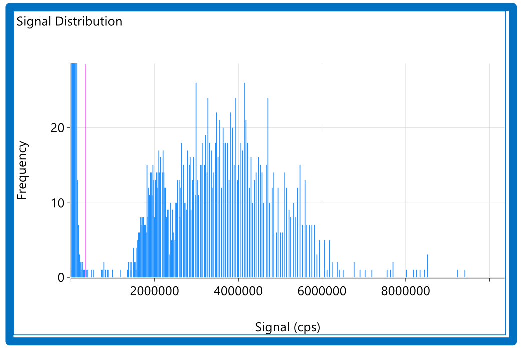
5µm size



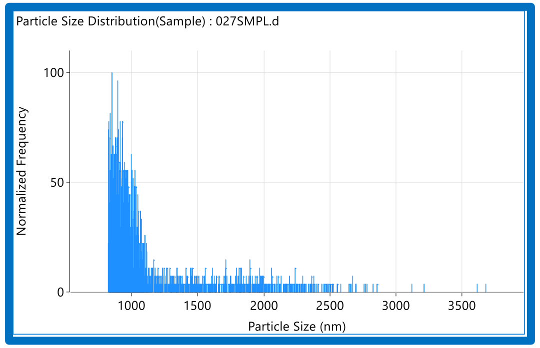
5µm signal



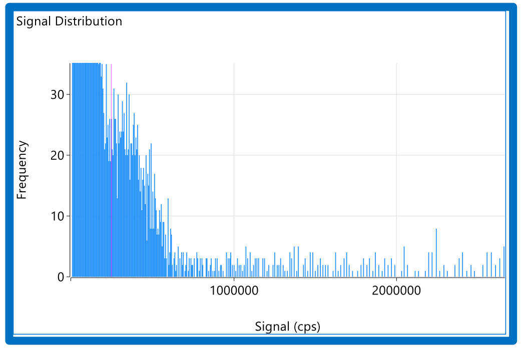
2µm size



2µm signal



1µm size



1µm signal

	13 -> 13 C				
Sample Name	Nebulization Efficiency	# of Particles	Particle Conc. (particles/L)	Median Size (nm)	N
5µm 20ppm	0.556	197	3.5E+7	5234	
5µm 10ppm	0.556	181	3.3E+7	5064	
5µm 10ppm	0.556	211	3.8E+7	5189	
2µm 1ppm	0.556	1733	3.1E+8	1942	
2µm 1ppm	0.556	1763	3.2E+8	1932	
2µm 1ppm	0.556	1947	3.5E+8	1925	
1µm 0.1ppm	0.556	2366	4.3E+8	945	
1µm 0.1ppm	0.556	1616	2.9E+8	1039	
1µm 0.1ppm	0.556	2100	3.8E+8	970	

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Detection of Polymer Particles in Ultrapure Water by Measuring ^{12}C

A related study in Agilent ICP-MS Journal 94

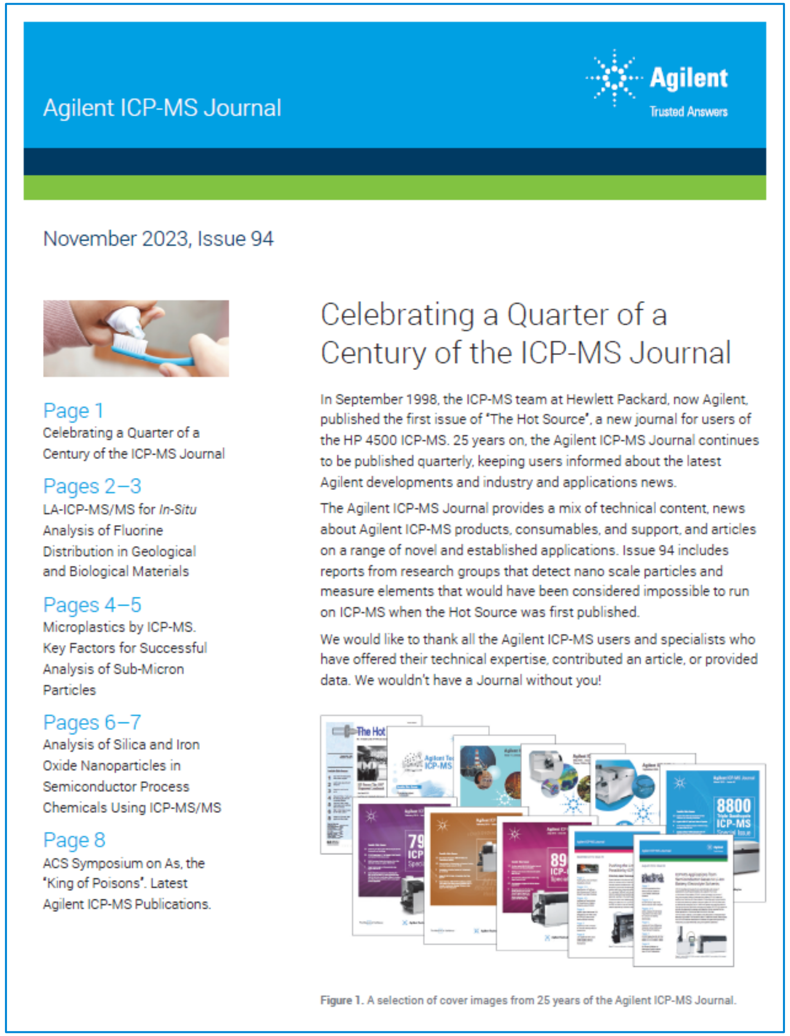
A separate study by Ching Heng Hsu (Jones), BASF Taiwan Ltd., Taiwan has shown that the 8900 ICP-QQQ can also be used to detect sub-micron polymer particles in ultrapure water by measuring ^{12}C.

However, careful control of the sample introduction system, plasma conditions, and carbon background is needed for the detection and characterization of such small particles at single ppb levels.

Article title: Microplastics by ICP-MS. Key Factors for Successful Analysis of Sub-Micron Particles in Ultrapure Water

Publication number: 5994-6725EN

Link: Agilent ICP-MS Journal, issue 94


Agilent ICP-MS Journal

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Celebrating a Quarter of a Century of the ICP-MS Journal

In September 1998, the ICP-MS team at Hewlett Packard, now Agilent, published the first issue of "The Hot Source", a new journal for users of the HP 4500 ICP-MS. 25 years on, the Agilent ICP-MS Journal continues to be published quarterly, keeping users informed about the latest Agilent developments and industry and applications news.

The Agilent ICP-MS Journal provides a mix of technical content, news about Agilent ICP-MS products, consumables, and support, and articles on a range of novel and established applications. Issue 94 includes reports from research groups that detect nano scale particles and measure elements that would have been considered impossible to run on ICP-MS when the Hot Source was first published.

We would like to thank all the Agilent ICP-MS users and specialists who have offered their technical expertise, contributed an article, or provided data. We wouldn't have a Journal without you!

Figure 1. A selection of cover images from 25 years of the Agilent ICP-MS Journal.

ICP-MS Application Note

5994-6951EN

Title

Automated Multielement Analysis of Single Cells and Microplastics by ICP-MS with Micro-Flow Sampling

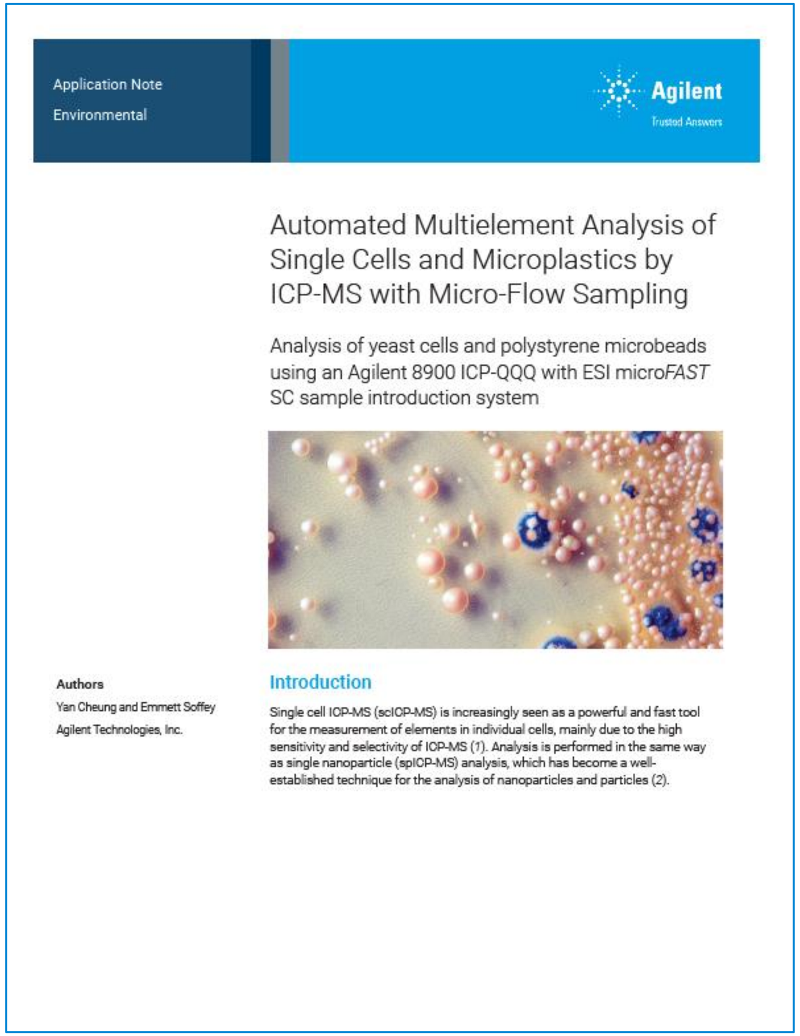
Authors

Yan Cheung and Emmett Soffey

Agilent Technologies, Inc.

Publication number: 5994-6951EN

Link: Automated Multielement Analysis of Single Cells and Microplastics by ICP-MS with Micro-Flow Sampling (agilent.com)


Application Note
Environmental

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Automated Multielement Analysis of Single Cells and Microplastics by ICP-MS with Micro-Flow Sampling

Analysis of yeast cells and polystyrene microbeads using an Agilent 8900 ICP-QQQ with ESI micro*FAST* SC sample introduction system

Authors
Yan Cheung and Emmett Soffey
Agilent Technologies, Inc.

Introduction

Single cell ICP-MS (scICP-MS) is increasingly seen as a powerful and fast tool for the measurement of elements in individual cells, mainly due to the high sensitivity and selectivity of ICP-MS (*1*). Analysis is performed in the same way as single nanoparticle (spICP-MS) analysis, which has become a well-established technique for the analysis of nanoparticles and particles (*2*).

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Yan.cheung@agilent.com