Optimization of Single Nanoparticle ICP-MS Analysis for Controlling Nanoparticles in Process Chemicals and UPW used in Wet Surface Cleaning

Lisa M. Mey-Ami*, Jinjin Wang, and Fuhe Li

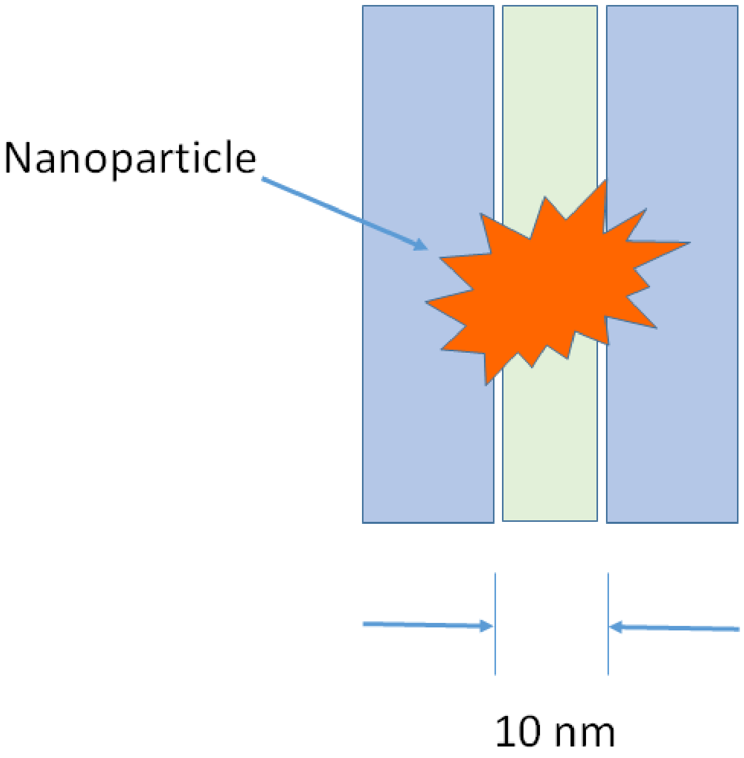
Air Liquide – Balazs NanoAnalysis
46409 Landing parkway, Fremont, CA
94538, USA

*Lisa.Mey-Ami@airliquide.com
(510) 624-4019

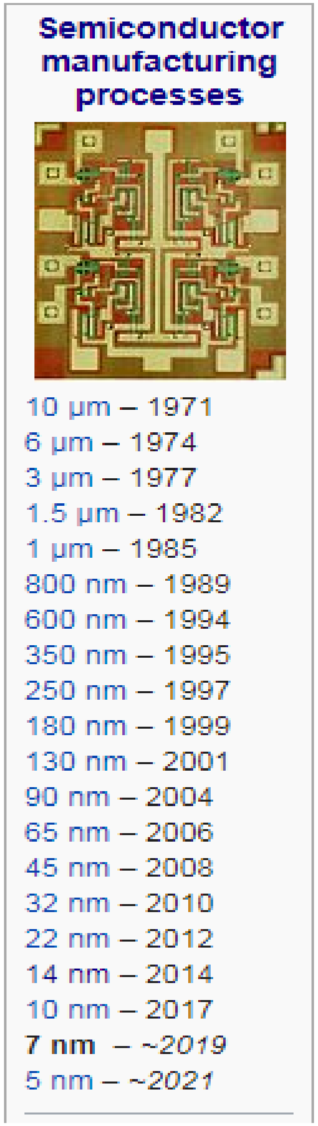
Introduction

- Nanoparticles are defined as particles with at least one dimension in the nano-scale (1-100 nm) range and they are either natural occurring or engineered.
- Natural occurring particles are often present as contaminants in all aspects of the chip fabrication process, including etching, lithography, chemical mechanical planarization (CMP), deposition, and implantation.
- Nanoparticle contaminants will have adverse impact on <10 nm device fabrication process and detrimental effect on production yield.
- Improvements in our SP-ICPMS methods since last year will be shown for UPW and process chemicals used in wet surface cleaning (e.g. sulfuric acid).
- Particle counts for aqueous surface extracts of various OEM parts (e.g. quartz ring, ceramic ring and Al coupon) will be presented

Why Nanoparticle Analysis is needed



10-100 nm particles are now critical. Monitoring & controlling single nm and near 1 nm particles will soon be required.



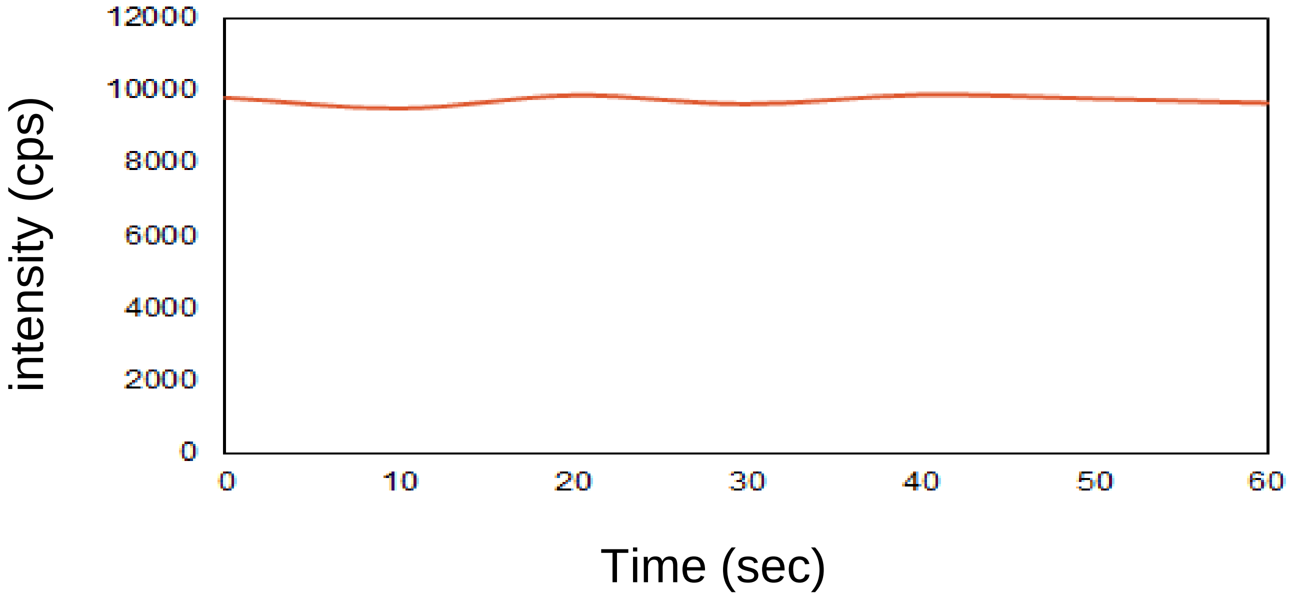
Semiconductor manufacturing processes

10 µm – 1971
6 µm – 1974
3 µm – 1977
1.5 µm – 1982
1 µm – 1985
800 nm – 1989
600 nm – 1994
350 nm – 1995
250 nm – 1997
180 nm – 1999
130 nm – 2001
90 nm – 2004
65 nm – 2006
45 nm – 2008
32 nm – 2010
22 nm – 2012
14 nm – 2014
10 nm – 2017
7 nm – *~2019*
5 nm – *~2021*

Nanoparticle Analysis Fundamentals

ICP-MS has been used regularly for the determination of trace metals in UPW, process chemicals and extraction solutions from OEM tool parts. The detection limits are often as low as sub parts per trillion (ppt). Since trace metals are completely dissolved and aspirated into the ICP plasma continuously, producing a constant signal intensity, only total elemental concentration is determined.

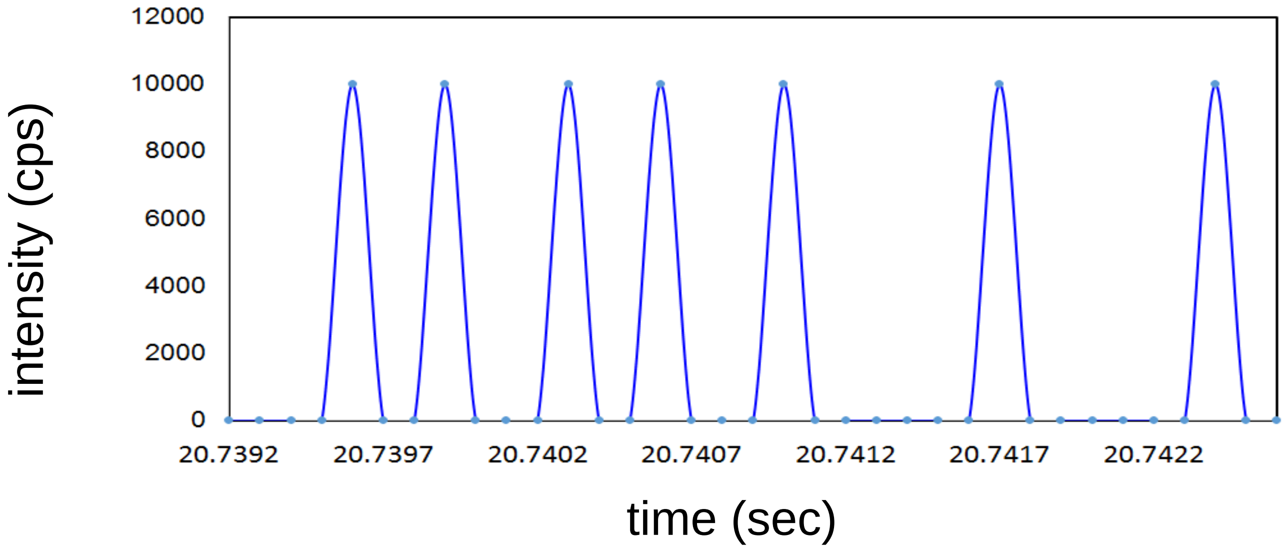
Continuous signal from dissolved ionic analyte



Nanoparticle Analysis Fundamentals

Using time resolved data acquisitions with short dwell times, the transient signal of each individual nanoparticle can be differentiated from the steady-state ICP-MS signal generated by dissolved ionic species. This unique feature coupled with fast electronics enables ICP-MS to characterize nanoparticles down to single nm sizes, producing results in the form of particle concentration, particle median size, and size distribution information.

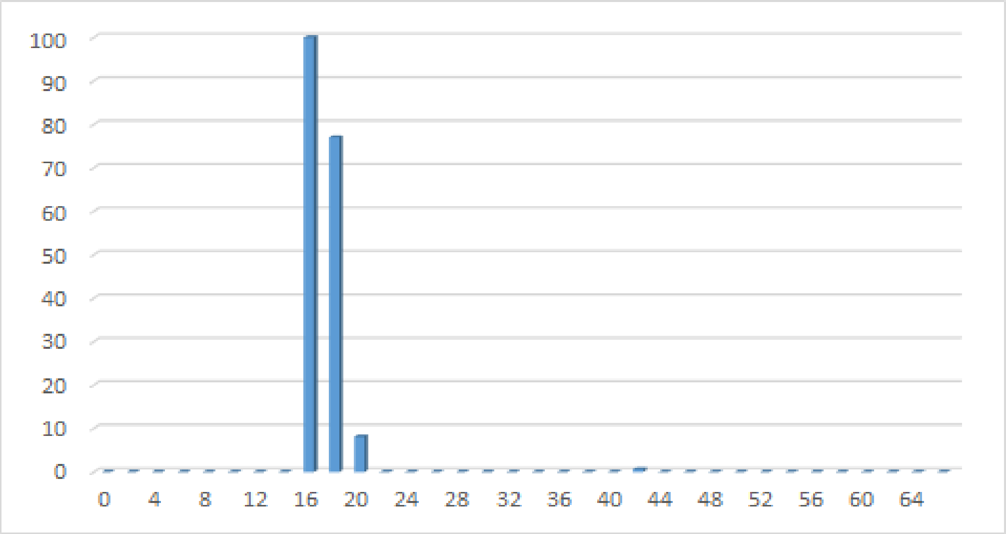
Each nanoparticle gives a transient signal, collected at point/0.1 ms



Particle Size Distribution: Fe vs. Si

(similar concentration of particles but different median particle size)

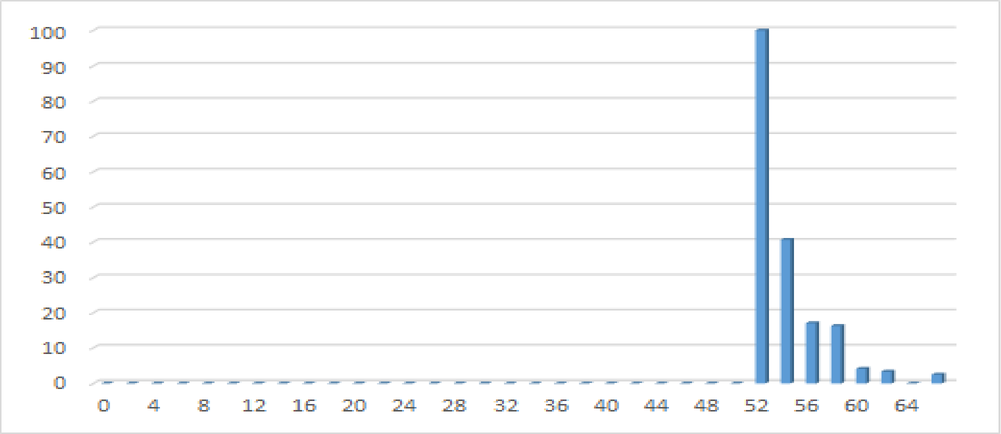
Normalized frequency



Fe

(75953 particles/mL)

Normalized frequency



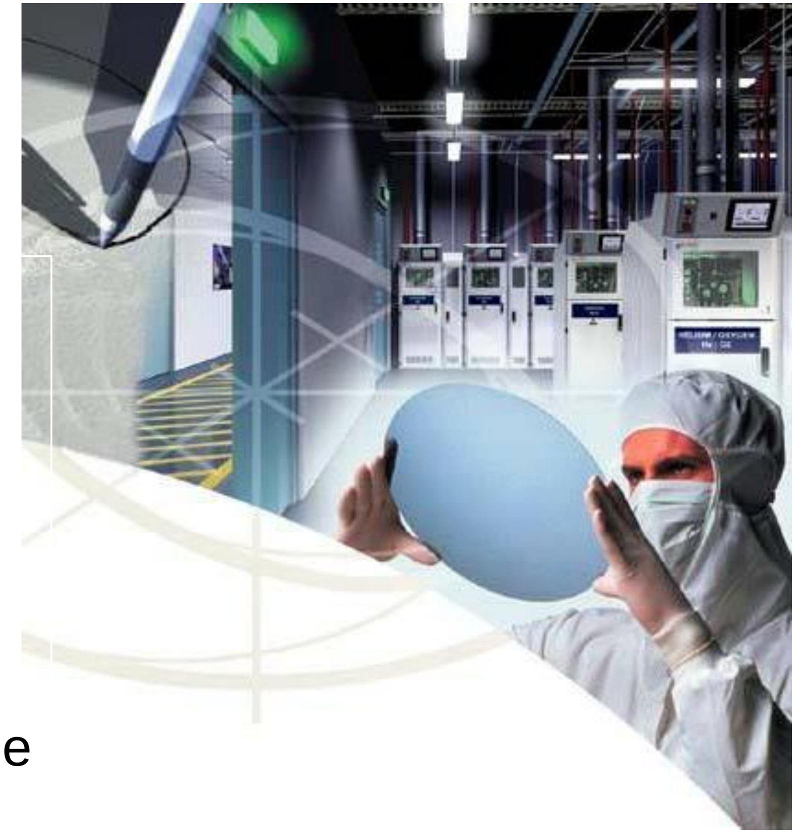
Si

(62420 particles/mL)

particle size (nm)

Typical Nanoparticle Analysis Figures of Merit

- Particle Concentration (number of particles/mL)
- Particle Size Distribution
- Median Particle Size; nm
- Elemental Composition of Particles
- BED (background equivalent particle diameter; nm)



Analysis of a UPW Sample Collected from a 10 nm Inline Filter (2018 vs 2019)

Element	**Particle Concentration (particles/mL) 2018**	**Particle Concentration (particles/mL) 2019**
Mg	4143	ND
Al	567,613	200
B	8286	200
Fe	75,953	ND
Si	62,420	5000
Zn	6629	ND
Cr	99,053	ND
V	268	ND
Ag	34,000	ND

Parameters contributing to the lowered particle concentrations

Some elements difficult to assess owing to background contribution and mass interferences…Consequently..

- ICP-MS conditions modified and optimized (e.g. reaction gas and different isotope selected)
  - ☐ Molecular and isobaric interferences avoided (e.g. ^{48}Ti vs $^{32}S^{16}O$ in sulfuric acid)
  - ☐ Signal/ background noise improved resulting in low BED (some single digit)

- Background contribution lowered (e.g. glassware modification)

- Cleaning/leaching methods of glassware improved

Analysis of a 96% Sulfuric Acid sample Using Modified SP ICP-MS method

Element	Particle Conc (particles/ mL)	BED (nm)	Median Size (nm)
Mg	390,000	12	22
Al	10,000,000	9	15
B	ND	19	—
Fe	640,000	6	13
Si	860,000	19	50
Ti	ND	12	—
Zn	22,000	11	31
Cr	21,000	5	15
V	ND	7	18
Ag	ND	4	12

Reproducibility of the Analysis of a 96% Sulfuric Acid Sample

Replicate	Aluminum (particles/mL)	Iron (particles/mL)	Magnesium (particles/mL)
1	1205612	2258615	504652
2	1508783	2558635	448637
3	1051614	2485782	541224
4	1287939	2347514	435879
5	995802	2159785	537894
6	1132575	2685763	495112
Average	1197054	2416016	493900
S.D.	185105	196516	44062
% RSD	15	8	9

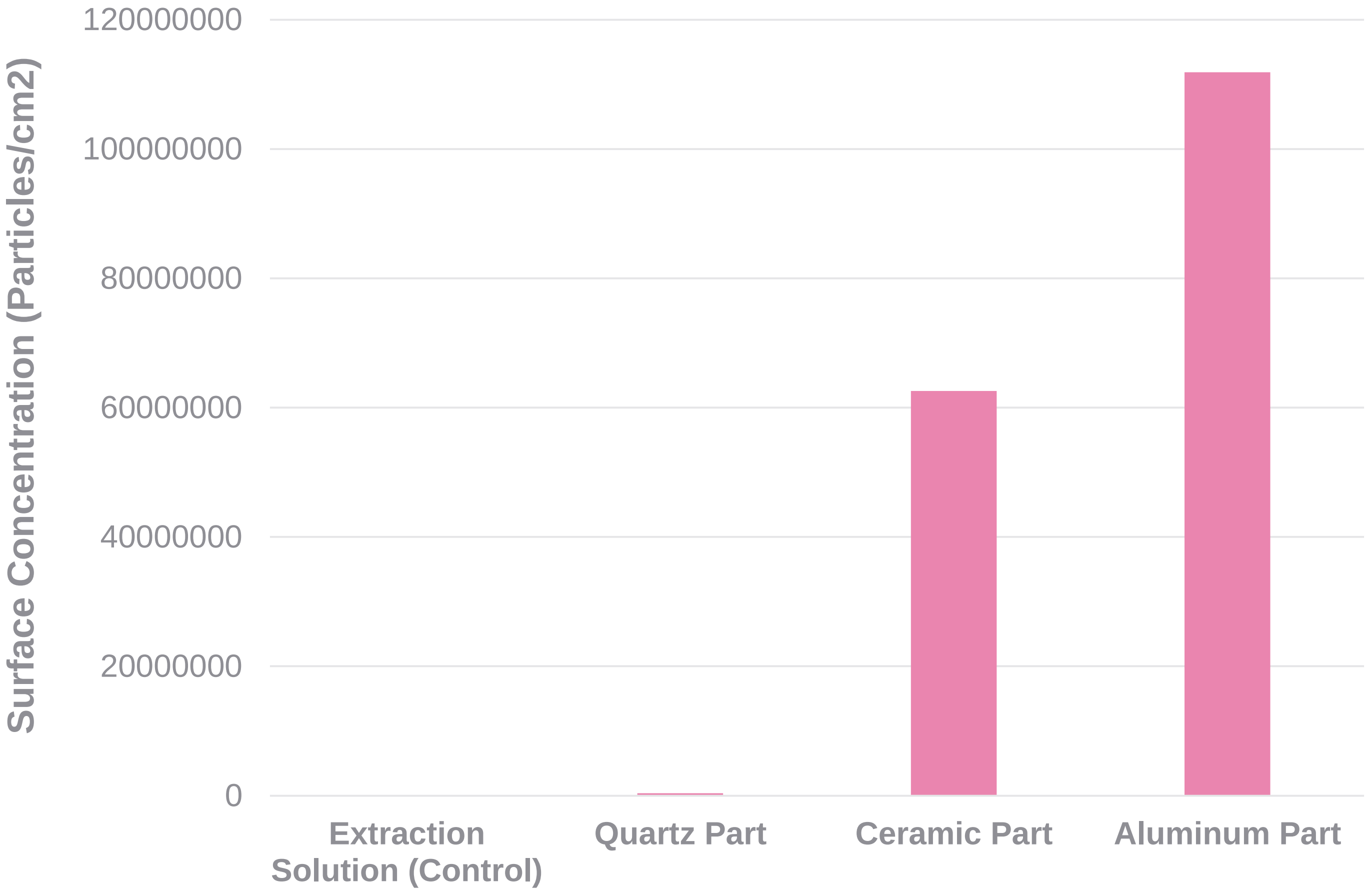
Laser Particle Counter (LPC) Results From Surface of OEM Parts: Only Total Particles Reported

Particles/cm^2	>0.1 –1 µM	>1 - 2 µM	>2 - 5 µM
Quartz Ring	100.9	159.8	50.2
Aluminum Coupon	70.1	11.5	1.4
Ceramic Ring	867.1	178.2	2.6

SP-ICPMS Results From the Surface of OEM Parts: Concentrations (particles/cm^2)

Element Tested	**Al**	**Mg**	**Mo**	**Ti**	**Zn**	**Ni**
Quartz ring	347,512	48,709	ND	296	3063	1778
Al coupon	111,867,151	79,921	ND	ND	57,699	2,465,754
Ceramic Ring	62,599,369	378,326	ND	89	876,918	2,619,337

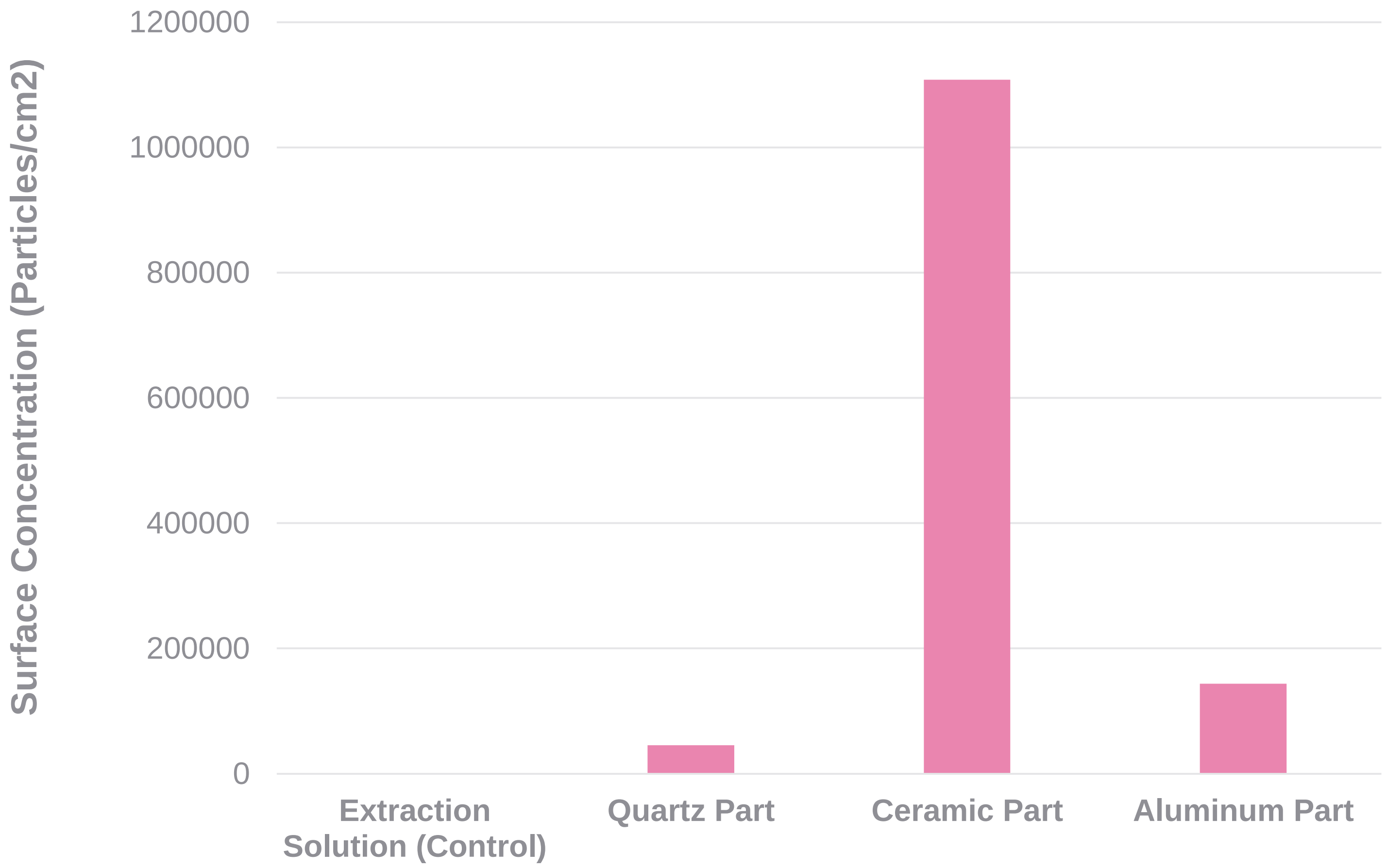
Aluminum (Al) Containing Nanoparticles Found From the Surface of Various OEM Parts



SP-ICPMS Results From the Surface of OEM Parts: Concentrations (particles/cm^2)

Element Tested	**Cu**	**Cr**	**Fe**	**Co**	**Si**
Quartz ring	2272	ND	45,547	1087	ND
Al coupon	154,283,928	198	143,458	ND	11,376
Ceramic Ring	5,550,154	1159	1,108,231	179	137,281

Iron (Fe) Containing Nanoparticles Found From the Surface of Various OEM Parts



Conclusion

- SP ICP-MS methods for determining nanoparticles in UPW and process chemicals have been improved
- SP ICP-MS background is low and consistent
- SP ICP-MS results are reproducible
- SP ICP-MS has successfully been used to measure nanoparticles extracted from surface of OEM parts used in etching and deposition chambers
- SP ICP-MS complements laser particle counter (LPC) technique by providing concentration and size distribution information of nanoparticles ranging from single nm to 100 nm.