BALAZS™ nanoanalysis

Single Nanoparticle ICP-MS Analysis of Process Chemicals and UPW Used in Surface Cleaning and Preparation

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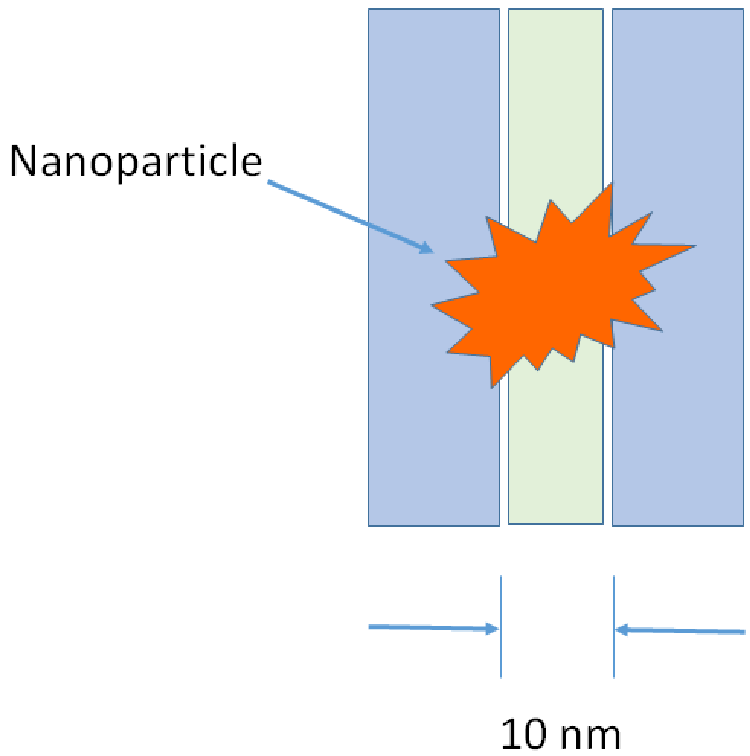
Introduction

Nanoparticles are ultrafine particles having size ranges from 1 to 100 nm. Nanoparticles are often present in the cleaning chemicals and UPW used in surface cleaning and preparation. Nanoparticles are very difficult to be removed and they can cause random device defects and lower the manufacturing yield, especially of current and next generation semiconductor devices.

As the leading chip makers have already begun the 10 nm processes in 2017, the control of the process/cleaning chemicals and UPW for nanoparticles is becoming crucial to the success and profitability of the semiconductor manufacturing. However, monitoring nanoparticles is a rather challenging task.

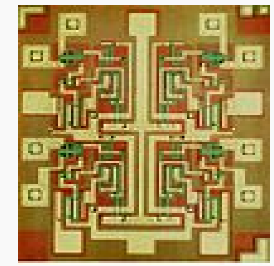
This paper introduces a non-traditional ICP-MS analysis for nanoparticles. Nanoparticle results obtained from UPW and the chemicals commonly used in the surface cleaning and preparation will be presented.

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.

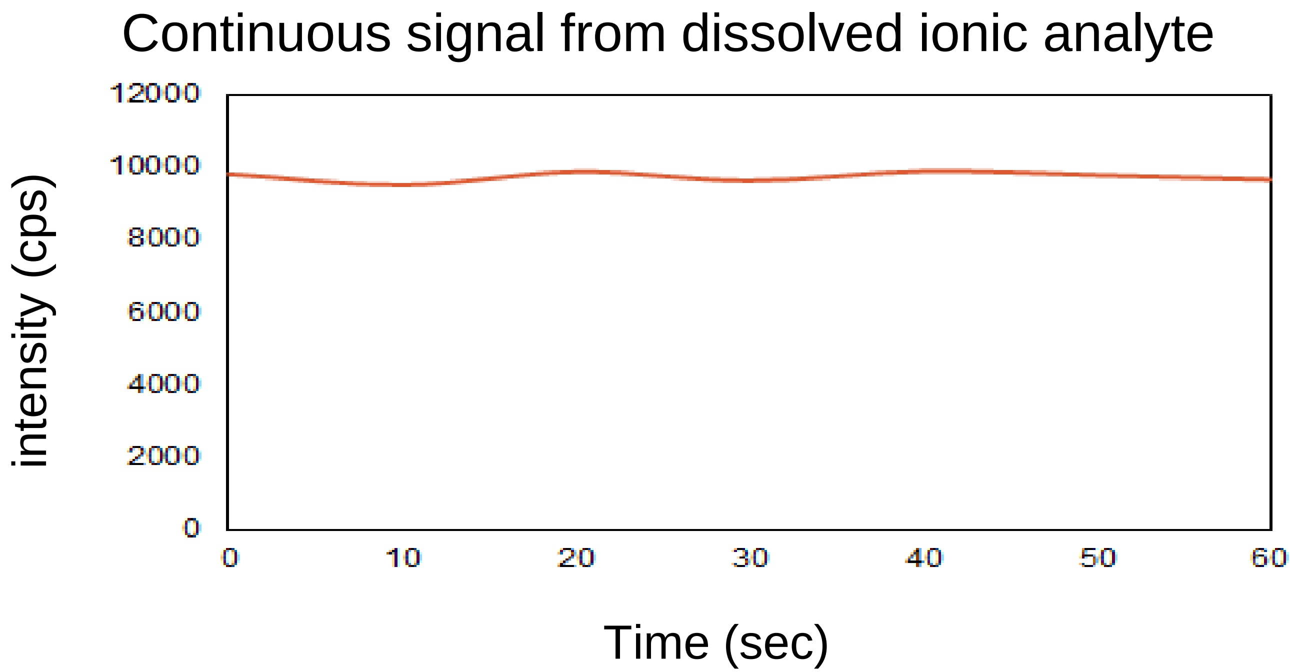
Semiconductor manufacturing processes



- 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

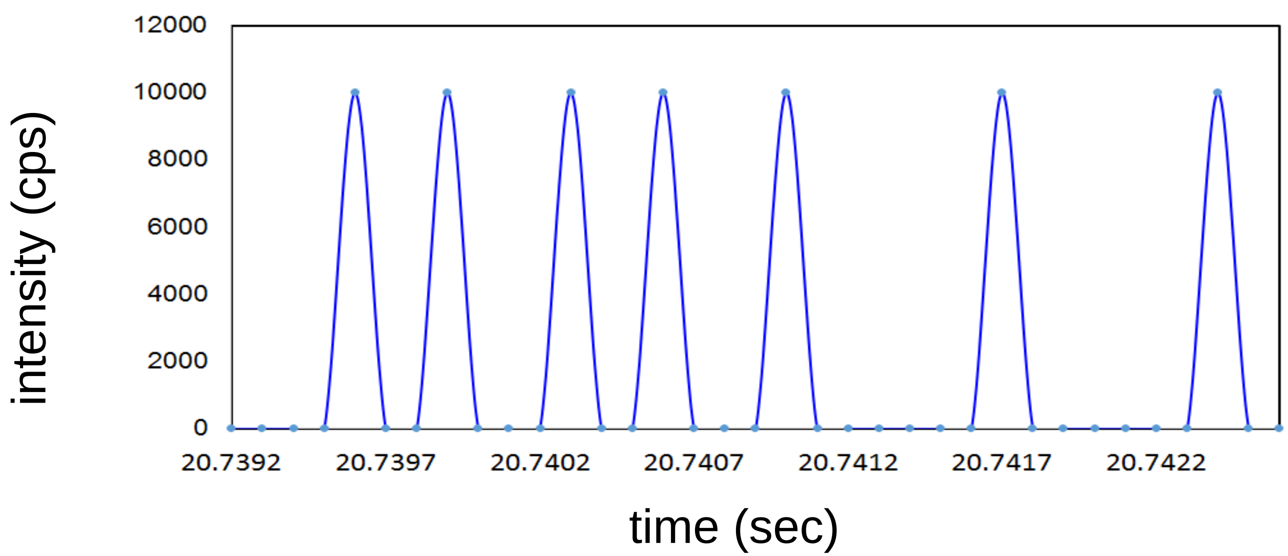
ICP-MS has been used regularly for the determination of trace metals in UPW, process chemicals and extraction solutions from OEM tool parts. The detection limits are often as low as sub parts per trillion (ppt). Since trace metals are completely dissolved and aspirated into the ICP plasma continuously,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



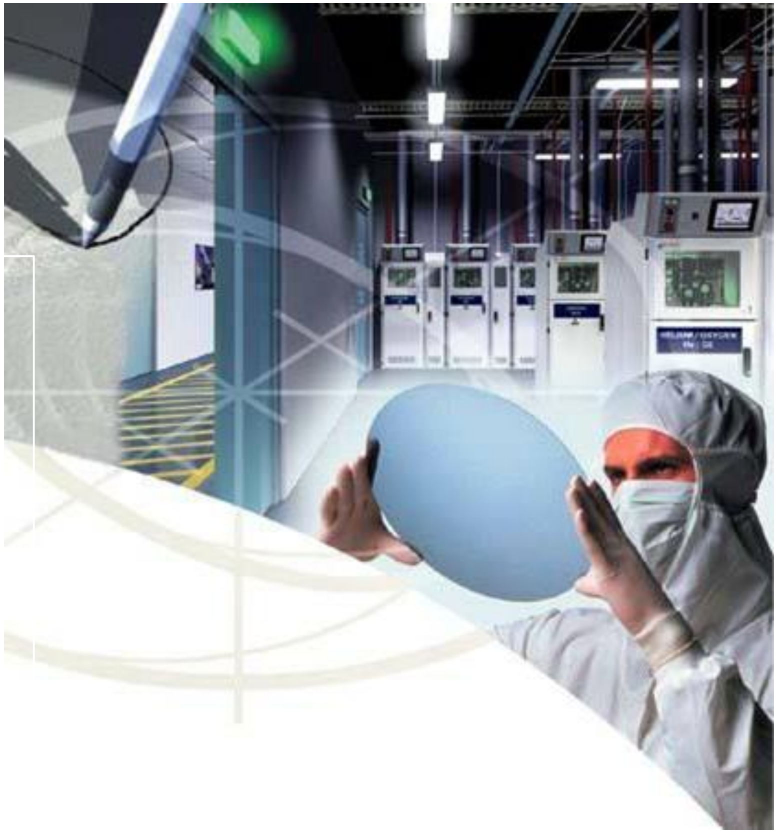
Nanoparticle Analysis Fundamentals

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



Typical Nanoparticle Analysis Figures of Merit



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

Analysis of a UPW Sample

Element	Particle conc (particles/mL)	Ionic conc (ppb or ng/mL)	BED (nm)	Median Size (nm)
Li	34175	0.008	21	40
Mg	4143	<0.001	8	21
Sn	668	<0.001	5	21
Al	567613	<0.001	10	18
Na	4679	<0.001	24	59
K	45950	<0.001	20	35
Fe	75953	0.021	9	16
Pb	0	<0.001	4	NA
Ni	501	0.005	10	33
Mn	52413	0.014	9	16

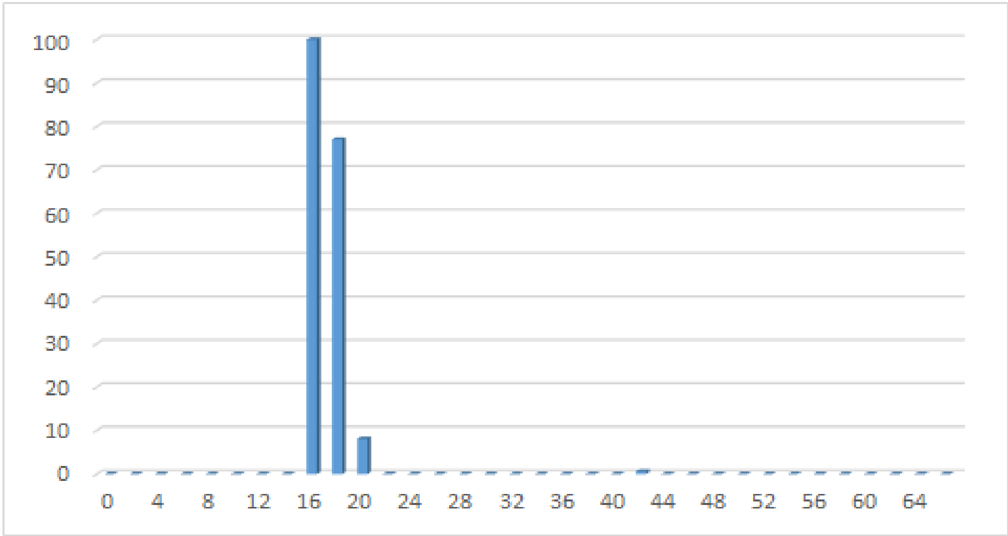
Analysis of a UPW Sample - continued

Element	Particle conc (particles/mL)	Ionic conc (ppb or ng/mL)	BED (nm)	Median Size (nm)
Ca	1865164	0.004	15	32
B	8286	<0.001	12	29
Cr	99053	<0.001	8	15
V	268	0.003	4	15
Zn	6629	0.007	12	29
Ti	0	<0.001	11	NA
Cu	63801	0.004	6	12
Sb	0	<0.001	4	0
Si	62420	0.110	28	52
Ba	0	<0.001	3	NA

Particle Size Distribution: Fe vs. Si

(similar concentration of particles but different median particle size)

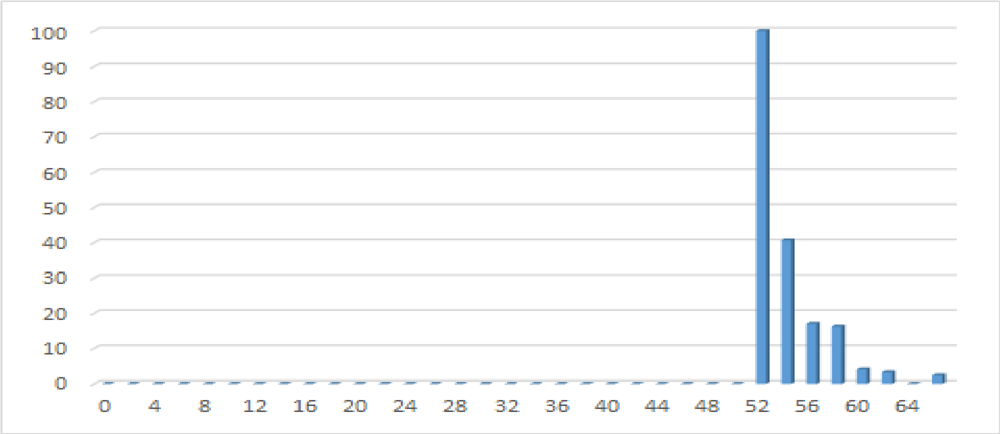
Normalized frequency



Fe

(75953 particles/mL)

Normalized frequency



Si

(62420 particles/mL)

particle size (nm)

Analysis of a 35% H_2O_2 Sample

Element	Particle conc (particles/mL)	Ionic conc (ppb or ng/mL)	BED (nm)	Median Size (nm)
Li	18546	<0.001	17	36
Mg	6048	<0.001	9	23
Sn	0	<0.001	5	NA
Al	73080	0.007	11	21
Na	2714	0.012	22	59
K	54695	<0.001	20	36
Fe	12683	<0.001	11	18
Pb	0	<0.001	4	NA
Ca	1053523	<0.001	15	30
B	7308	0.016	13	31

Analysis of a 35% H_2O_2 Sample - continued

Element	Particle conc (particles/mL)	Ionic conc (ppb or ng/mL)	BED (nm)	Median Size (nm)
V	3276	0.012	6	19
Cr	73332	0.019	9	17
Zn	1454	<0.001	9	27
Ti	0	<0.001	11	NA
Cu	29573	<0.001	5	11
Sb	0	<0.001	4	NA
Ba	0	<0.001	4	NA
Ni	0	<0.001	10	NA
Si	68655	2.2	44	84
Mn	22632	<0.001	8	16

Analysis of a 25% HF Sample

Element	Particle conc (particles/mL)	Ionic conc (ppb or ng/mL)	BED (nm)	Median Size (nm)
Li	55705	<0.001	21	38
Mg	20430	0.004	10	21
Sn	3400	0.057	8	22
Al	35753	<0.001	15	30
Na	232106	<0.001	22	72
K	70792	<0.001	17	33
Fe	6218	<0.001	9	21
Pb	0	<0.001	3	NA
Ca	36673	<0.001	15	30
B	673	<0.001	10	30

Analysis of a 25% HF Sample - continued

Element	Particle conc (particles/mL)	Ionic conc (ppb or ng/mL)	BED (nm)	Median Size (nm)
Cr	34604	<0.001	15	30
V	26648	0.034	9	18
As	0	<0.001	8	NA
Zn	448	<0.001	9	29
Ti	897	<0.001	17	52
Cu	7859	0.001	5	13
Sb	0	<0.001	5	NA
Ba	680	<0.001	6	20
Ni	227	<0.001	8	27
Mn	696	<0.001	6	16

Two 35% HNO_3 Samples: Grade A vs. Grade B

Element	Nitric Acid Grade	Particle conc (particles/mL)	Ionic conc (ppb or ng/mL)	Median Size (nm)
Mg	A	722	<0.001	29
Mg	B	1254522	0.212	45
Sn	A	947	<0.001	20
Sn	B	1284869	1.012	43
Al	A	23453	<0.001	27
Al	B	36180	22.676	118
Na	A	0	<0.001	NA
Na	B	1715238	1.632	96
K	A	31712	<0.001	33
K	B	1025138	0.133	62

Two 35% HNO3 Samples: Grade A vs. Grade B - continued

Element	Nitric Acid Grade	Particle conc (particles/mL)	Ionic conc (ppb or ng/mL)	Median Size (nm)
Fe	A	12508	<0.001	39
Fe	B	1710222	0.362	42
Ca	A	42067	<0.001	30
Ca	B	107447	5.992	102
Ti	A	3486	<0.001	82
Ti	B	25842	1.521	65
Pb	A	0	0	NA
Pb	B	34923	0.036	15
Ni	A	0	<0.001	NA
Ni	B	3459	0.176	34

Conclusion

The single nanoparticle ICP-MS enables direct measurement of liquid-borne nanoparticles in UPW and cleaning chemicals, providing not only nanoparticle concentration but also particle median size and size distribution information. In addition, elemental composition of nanoparticles can also be identified.

ICP-MS' ability to distinguish between ionic and nanoparticle concentration results gives more comprehensive understanding of elemental impurities in a sample solution. There were many examples in which the ionic concentrations were low for a particular element but particle concentrations high for that same element.

The nanoparticle results have been utilized to assist engineers with their process optimization. The databases and the trending charts built using the nanoparticle results can also be used to control the quality of UPW and cleaning chemicals used in various surface preparation and cleaning steps, e.g. final rinsing.