Particle Analysis of Two High Purity Grades of N-Methyl-2-Pyrrolidone (NMP) using Single Particle (sp)ICP-MS/MS Method

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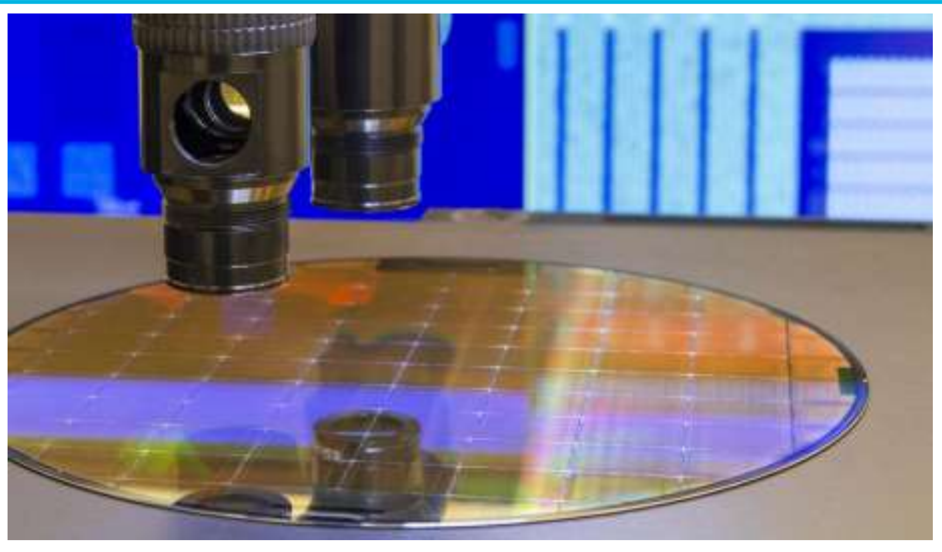
Introduction

Advanced quality control of semiconductor chemicals

Contamination control is vital to the quality, reliability, and yield of semiconductors, especially chips with linewidths at the nanometer scale. Some FABs are now monitoring metallic nanoparticles (NPs) in bulk chemicals, and wafer processing and cleaning baths, as well as dissolved metals.



Single particle (sp) ICP-MS

ICP-MS can measure the number, size, and composition of NPs using a technique called single particle (sp-)ICP-MS.

The key requirements for ICP-MS for NP analysis include:

- **Very high sensitivity** (high signal-to-noise, S/N) is essential to allow the counts from individual NPs to be distinguished above the background.
- **Fast acquisition speed** that enables multiple measurements to be collected during the short-lived signal pulse that is generated as each individual NP is decomposed as it passes through the plasma.
- **Dedicated spICP-MS software** that enables fast, accurate multi-element NP analysis and reduces sample carryover and risk of contamination (Figure 1).

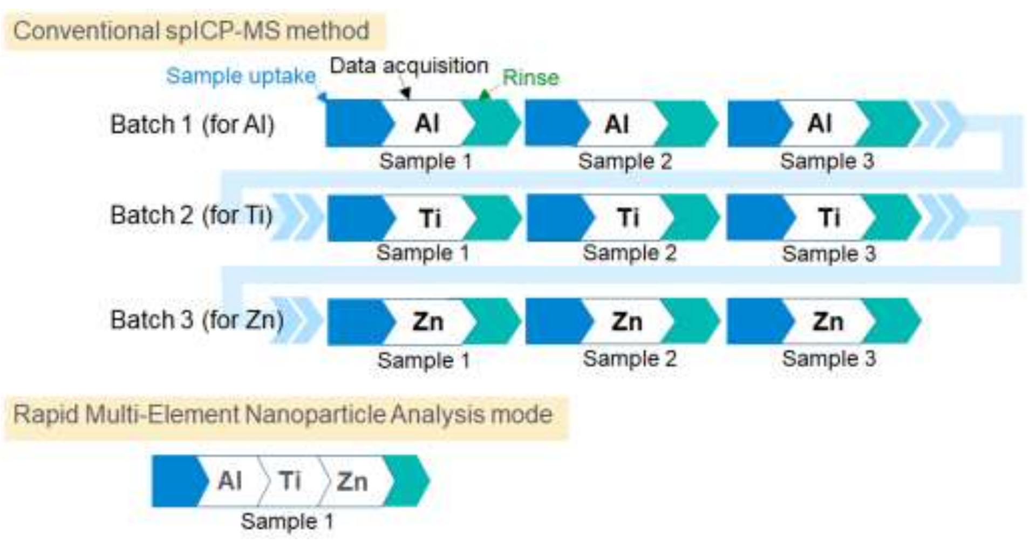
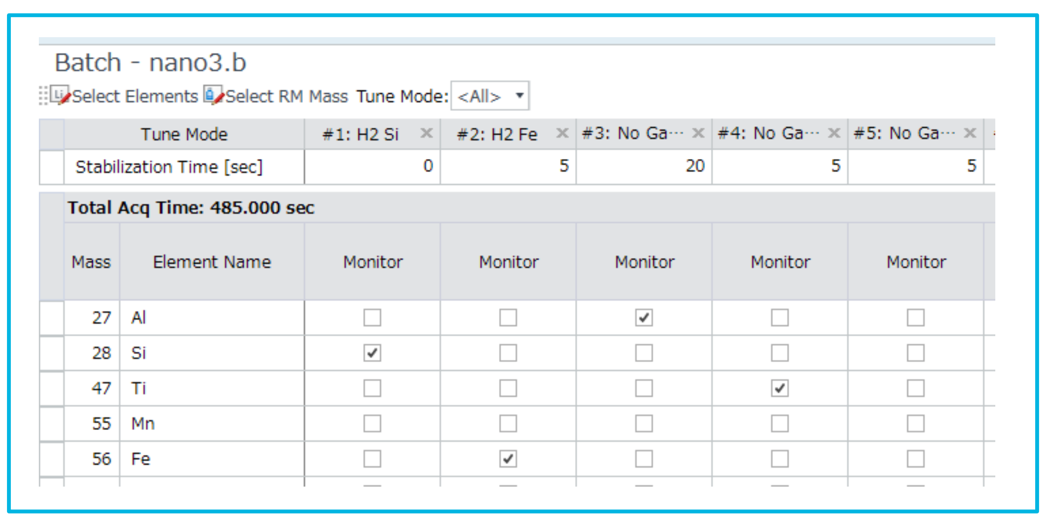


Figure 1. Time saving with multi-element spICP-MS method compared to conventional spICP-MS method.

- Using Agilent ICP-MS MassHunter software revision 5.2 onwards, analysts can now set up spICP-MS methods to monitor a virtually unlimited number of analytes in NPs in each sample, as shown in Figure 2.
- Different NP elements are measured sequentially, each under optimum conditions.



Batch - nano3.b

Tune Mode	#1: H2 Si	#2: H2 Fe	#3: No Ga···	#4: No Ga···	#5: No Ga···
Stabilization Time [sec]	0	5	20	5	5

Total Acq Time: 485.000 sec

Mass	Element Name	Monitor	Monitor	Monitor	Monitor	Monitor
27	Al	☐	☐	☑	☐	☐
28	Si	☑	☐	☐	☐	☐
47	Ti	☐	☐	☐	☑	☐
55	Mn	☐	☐	☐	☐	☐
56	Fe	☐	☑	☐	☐	☐

Figure 2. ICP-MS MassHunter 5.2 setup of single particle acquisition in the Rapid Multi-Element Nanoparticle Analysis software module.

Experimental

Instrumentation

The 8900 semiconductor configuration ICP-QQQ (Fig. 3) and Agilent I-AS autosampler were used to measure NPs in EL (for Electronics industry) and SP (supreme pure) Grade NMP samples provided FUJIFILM Wako Pure Chemical Corporation.[1, 2]

Fast and automated method

To control spectral interferences on some important SEMI elements such as Mg, Al, and Cr (Table 1), optimized ICP-MS/MS acquisition conditions were used for different elements, as shown in Table 2.

Isotope	Polyatomic Ion Interference
^{24}Mg	$^{12}C^{2+}$
^{27}Al	$^{12}C^{15}N^+$, $^{13}C^{14}N^+$, $^{12}C^{14}NH^+$, $^{12}C^{12}CHHH^+$
^{52}Cr	$^{40}Ar^{12}C^+$

Table 1. Examples of potential spectral interferences on some SEMI elements in an organic solvent such as NMP.

- For sp-ICP-MS, once measurement conditions that provide good S/N for each element are set, measurements are performed automatically and continuously as shown in Figure 1.
- During data acquisition, the ORS[4] cell gases and measurement modes are switched automatically, giving a fast and automated analysis using the best mode for each analyte.
- Several reaction cell gases (NH_3, H_2, He, and O_2) were used as appropriate for the number of analytes being measured (Table 2).

NP Analysis	Mg	Al	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ti	W	Pb	Si
RF Power (W)	1400														
Sampling Depth (mm)	22.0											18.0			
Nebulizer Gas (L/min)	0.70														
Option Gas (L/min)	0.30														
Spray Chamber Temp (℃)	2.0														
Makeup Gas (L/min)	0.45										0.35	0.31			
Extraction Lens 1 (V)	−150														
Extraction Lens 2 (V)	−10														
Octopole Bias (V)	−10.0											−3.0	−18.0		
Axial Acceleration (V)	2.0											1.5	1.0		
Energy Discriminaton (V)	−10.0											−7.0	2.0		
He Flow (mL/min)	1.0											-	2.0		-
H_2 Flow (mL/min)	-														5.0
NH_3 Flow (mL/min)	2.5 (25%)										2.0 (20%)	-	-		
O_2 Flow (mL/min)	-											0.45 (30%)	-		

Table 2. Agilent 8900 ICP-QQQ operating conditions for characterization of multi-element NPs in NMP using spICP-MS.

Experimental

Figure. 3. Agilent 8900 ICP-QQQ uses tandem mass spectrometry (MS/MS) operation for control of reaction chemistry in the ORS[4] collision reaction cell (CRC).

Determination of nanoparticles in NMP

Nebulization efficiency

The nebulization efficiency was calculated by measuring the particle concentration of the SiO_2 NP reference material. The Single Nanoparticle software automatically calculated the nebulization efficiency as 0.196 (19.6%).

spICP-MS method validation

- A 25 nm Fe_3O_4 NP standard was measured using the 8900 ICP-QQQ.
- The size distribution graph (Figure 4) for the NP standard measured using ICP-QQQ agreed with the expected result of 25 nm.
- The 25 nm Fe_3O_4 particles have a theoretical mass of 42 attograms (ag) per particle.
- ICP-MS MassHunter automatically calculated the particle mass from the spICP-MS measurement as 40 ag, which was in good agreement with the theoretical value.

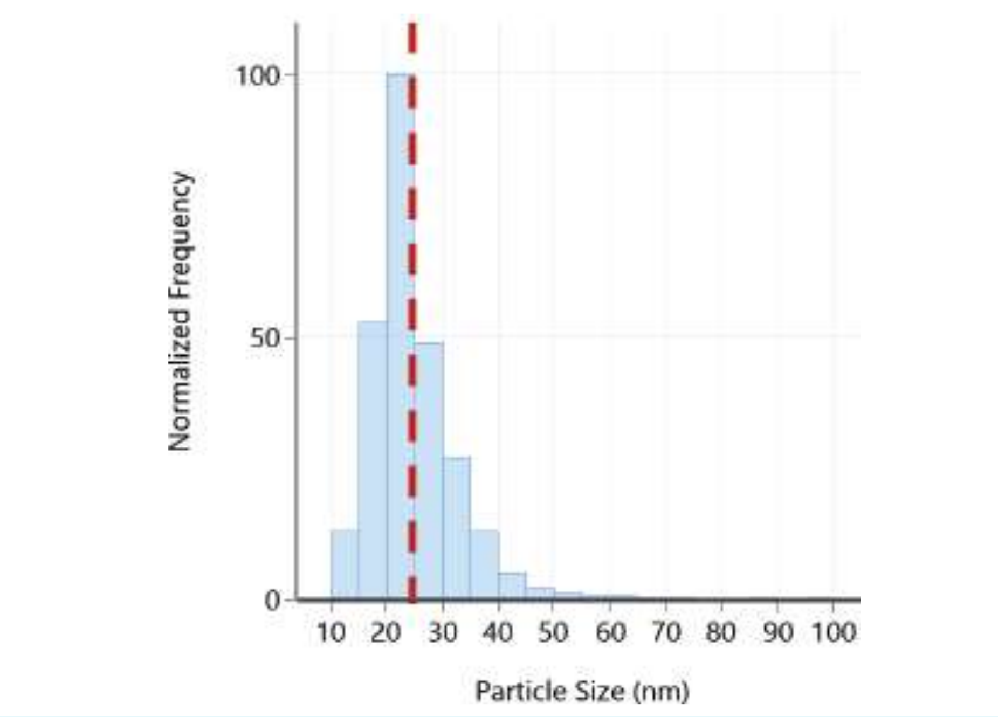


Figure. 4. spICP-MS size distribution graph for 25 nm Fe_3O_4 standard.

Fast Time Resolved Analysis for particle contaminants

- The 8900 ICP-QQQ was operated in spICP-MS mode using a continuous fast TRA acquisition with an integration time of 0.1 ms to check for the presence of 14 elements in the NPs in the two grades of NMP.
- The 14 elements were selected after a preliminary screening step to check which elements were present above background levels in particles in the samples.
- The raw NP signal data in the TRA data display indicated clear differences in the NP content for several elements in the EL and SP grades of NMP.
- TRA time plots for Fe in the two grades of NMP are shown in Figure 5.

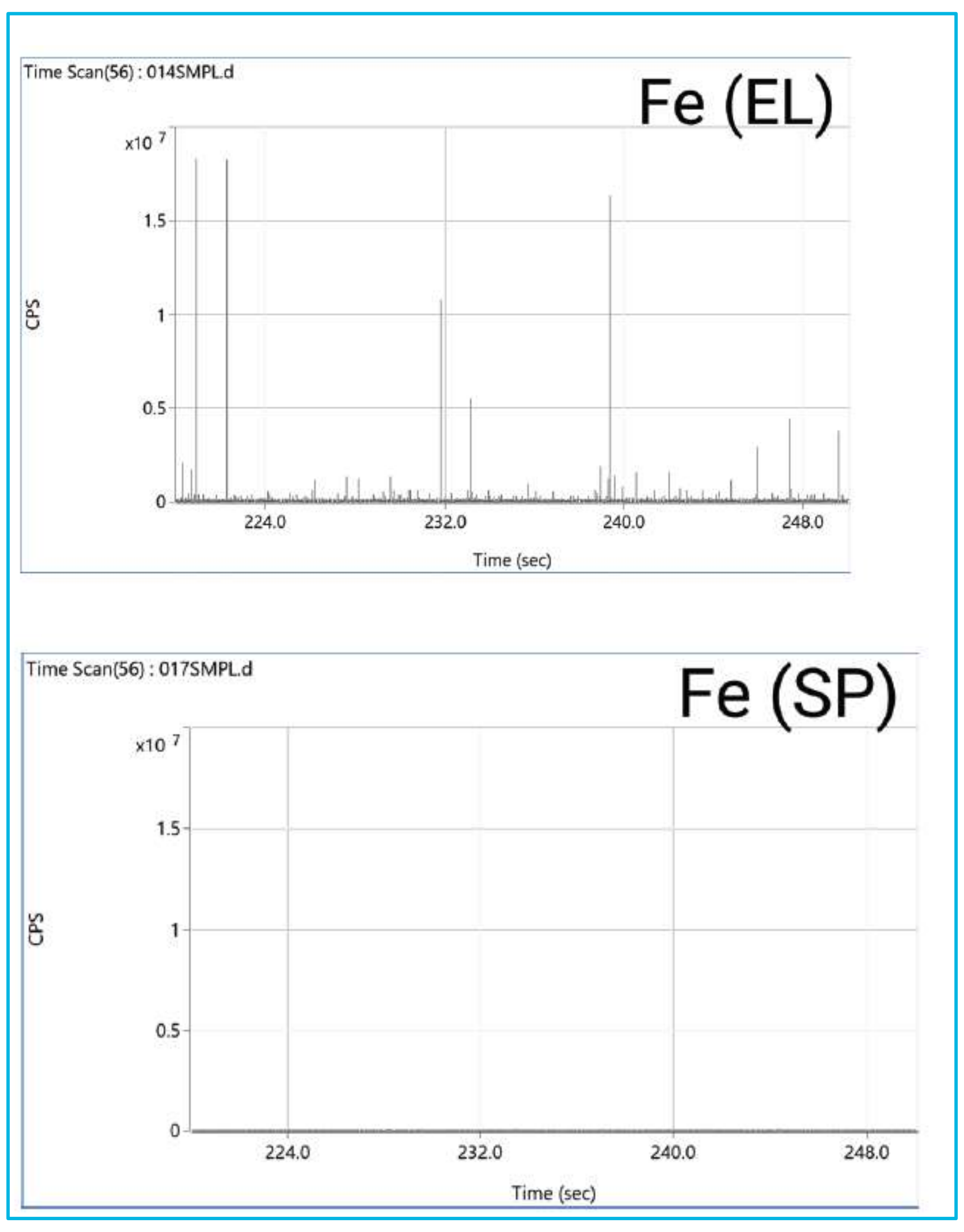


Figure. 5. Time Resolved Acquisition signals for Fe NP acquisitions in EL (top) and SP (bottom) grades of NMP.

Results and Discussion

Particle size distribution by element

The measured NP size and size distribution data obtained for multiple NPs in the two grades of NMP using the 8900 in spICP-MS mode are shown in Figure 6.

The data confirms that the high purity SP grade of NMP (Figure 6, bottom) had far fewer particles that contained the elements Mg, Al, Ca, Mn, Fe, and Cu.

The SP grade also contained mainly smaller-sized particles compared to the EL grade sample (Figure 6, top).

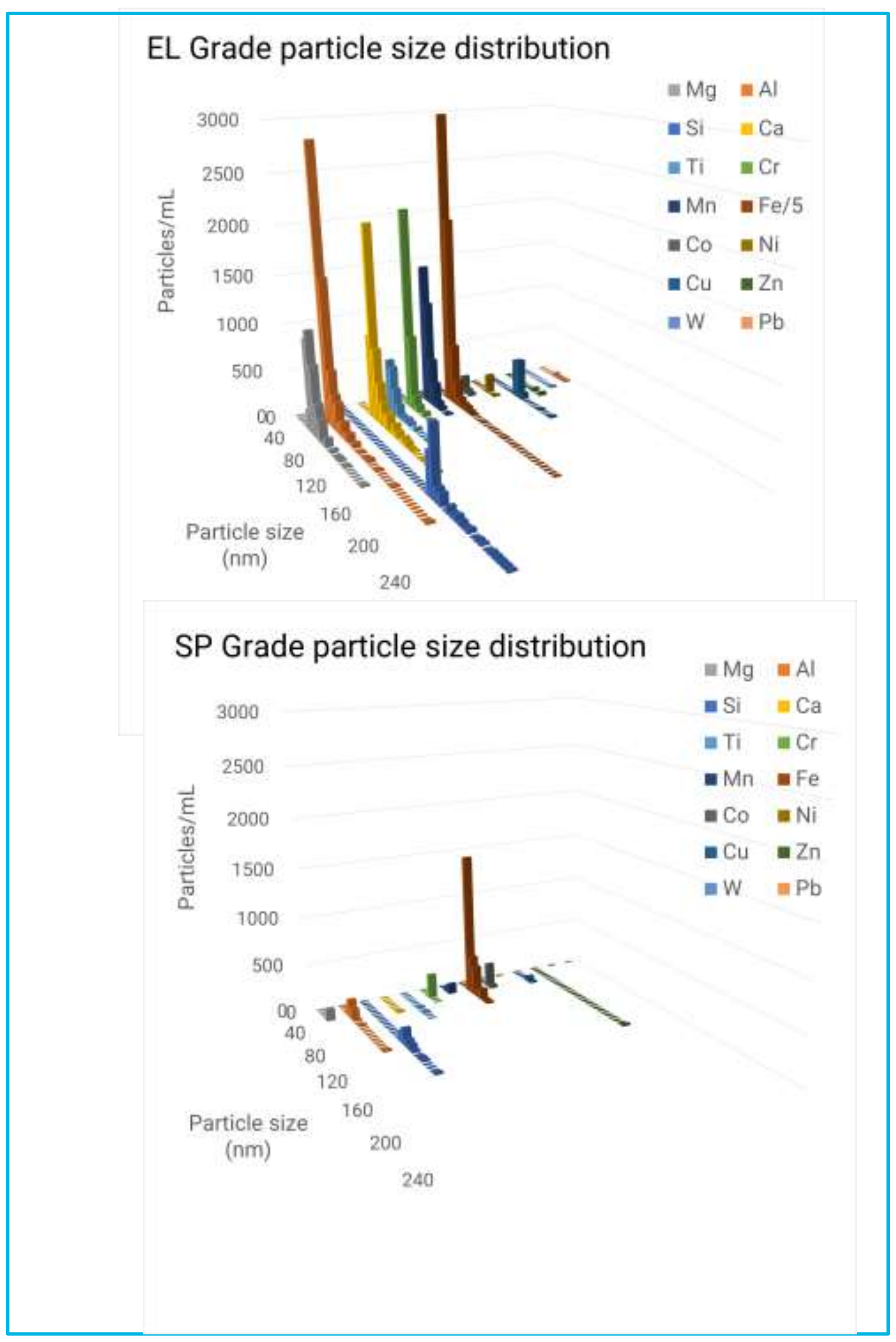
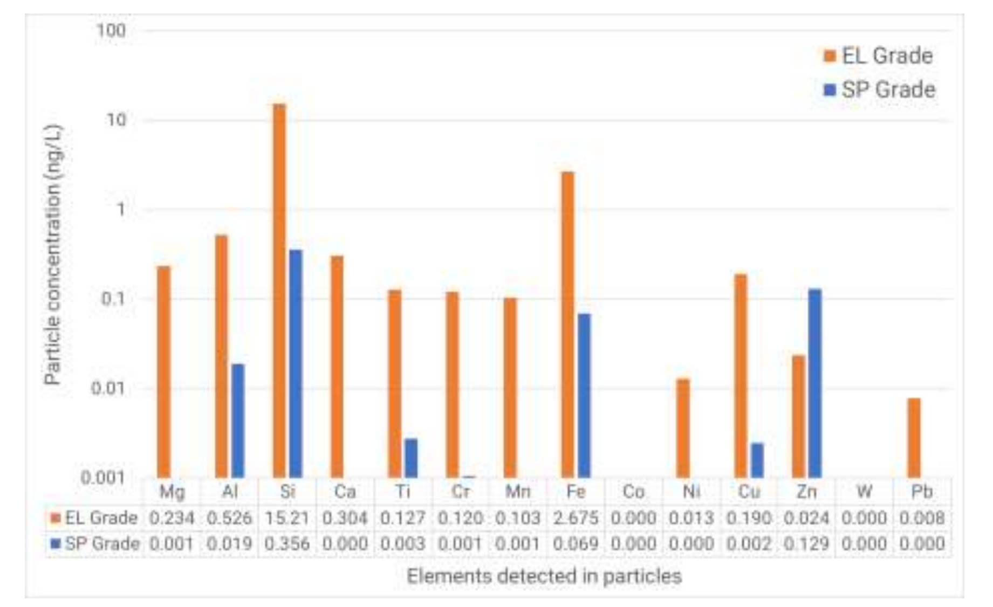


Figure. 6. Metallic particle size distribution for 14 elements in two grades of NMP: EL (for Electronics industry) and SP (supreme pure) grade.

Note the number of Fe particles measured in EL grade NMP has been divided by five to fit on the same scale as the other elements.

Particle concentration by element

The concentration of the NPs was lower in the higher purity SP grade NMP than in the EL grade sample (Figure 7). The data provides valuable information. For example, the SP grade was relatively free of Fe particles, with only 69 picograms (pg)/L (ppq), while the EL grade was found to contain 2.7 ng/L (ppt) of Fe particles, mostly sized between 20 to 30 nm (Fig. 6).



	Mg	Al	Si	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	W	Pb
EL Grade	0.234	0.526	15.21	0.304	0.127	0.120	0.103	2.675	0.000	0.013	0.190	0.024	0.000	0.008
SP Grade	0.001	0.019	0.356	0.000	0.003	0.001	0.001	0.069	0.000	0.000	0.002	0.129	0.000	0.000

Figure. 7. Comparison of particle concentration results measured in EL and SP grades of NMP using the 8900 ICP-QQQ in spICP-MS mode.

Conclusions

Agilent ICP-MS systems provide fast, sensitive NP analysis as well as dissolved element quantification, giving a total analysis solution for semiconductor labs.

- New software developments have extended the multielement NP analysis capability of the Agilent 8900 ICP-QQQ for routine monitoring of particle contamination in process chemicals.
- The 8900 ICP-QQQ offers a unique combination of extremely high sensitivity, ultralow background, fast time resolved data acquisition, and exceptional control of spectral interferences.
- The multi-element spICP-MS method provided information on the identity, size distribution, and concentration of element NPs of interest to semiconductor integrated circuit FABs.
- The elemental species of the particles detected by spICP-MS provide clues to the likely source of contamination. For example, the measured NPs included Fe, Cr, and Ni that may be derived from stainless steel processing equipment or storage and distribution systems.
- Differences were found in the presence or absence of particles in the two grades of NMP, as well as in the size distribution and concentration of the particles.
- Lower concentrations of NPs were determined in the SP NMP product than in the EL sample.

References

1. High-purity Solvent and Acid, FujiFilm Wako Pure Chemical Corporation, EL grade NMP: https://labchem-wako.fujifilm.com/us/category/00282.html
2. High-purity Solvent and Acid, FujiFilm Wako Pure Chemical Corporation, SP grade NMP: https://biz.fujifilm.com/ffwkLP_SP-NMP_contact.html
3. Elemental and Particle Analysis of N-Methyl-2- Pyrrolidone (NMP) by ICP-QQQ, Agilent publication 5994-5365EN