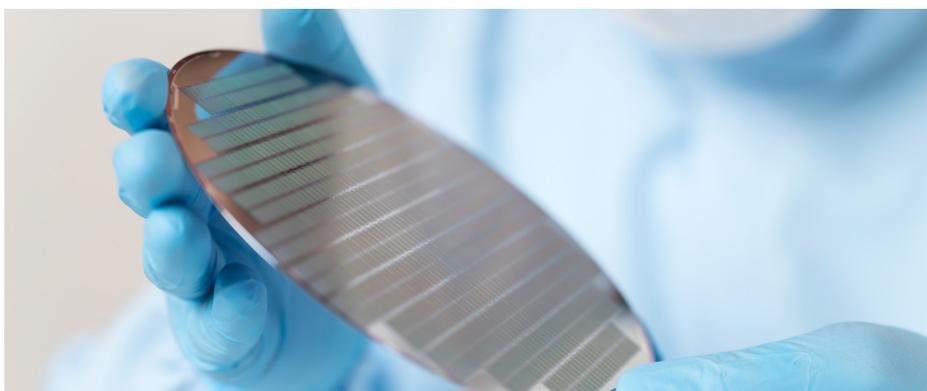


Elemental and Particle Analysis of N-Methyl-2-Pyrrolidone (NMP) by ICP-MS/MS

Analysis of dissolved and particulate inorganic impurities in two grades of NMP using the Agilent 8900 ICP-QQQ



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Introduction

Ideally, analytical quality control (QC) testing procedures should keep pace with the technologies they support. This has long been the case in semiconductor fabrication plants (FABs) where industry requirements have driven many of the developments in ICP-MS (1). The development of triple quadrupole ICP-MS (ICP-QQQ) in 2012 expanded the capabilities of the technique to include the measurement of nonmetals such as sulfur, phosphorus, and chlorine at lower levels, including in organic matrices (2). More recently, device manufacturers and chemical suppliers have started to monitor metallic nanoparticles (NPs) in bulk chemicals, and wafer processing and cleaning baths (3). This trend shows that control of all types of inorganic impurities during semiconductor manufacturing processes is important to the development of integrated circuits (ICs) with progressively narrower line widths.

Industry requirements for process chemicals

To control the concentration of elemental impurities in reagents used in the semiconductor industry, SEMI publishes specifications and testing procedures to support the specifications. The current specifications for the highest purity grade of N-methyl-2-pyrrolidone (NMP), grade 3, are shown in Table 3. The specifications were last updated in 2013 (4), so many users and chemical suppliers analyze elements below the levels specified in the standard.

SEMI is continually developing standards to support industry requirements for advanced IC manufacturing, including particle control of ultrapure water (5) and reagents. Also, some large FABS are already routinely monitoring levels of particles using techniques such as laser particle counters. These techniques can measure the number of particles in a sample but cannot identify the metal species of the NPs. Contamination from metal NPs such as iron, chromium, and nickel are of particular concern because these elements are used in IC processing equipment. Therefore, the determination of multiple element NPs in process chemicals and baths is fast becoming a priority for the industry. A multi-elemental technique such as ICP-MS operating in single particle (sp-)ICP-MS mode is needed to fully assess the identity, number, size, and concentration of multiple elemental NPs in a sample.

The high sensitivity, low background, and interference removal power of Agilent ICP-QQQ instruments enable individual NPs to be detected and characterized in spICP-MS mode. For applications where multiple elements are of interest, the Rapid Multi-Element Nanoparticle Analysis function within ICP-MS MassHunter software supports the acquisition of multi-element NP data from one visit to the sample. From ICP-MS MassHunter version 5.2, there is no limit to the number of elements that can be acquired. The software also provides the method setup, analysis, and data interpretation tools to simplify single NP analysis.

This note describes the performance of the Agilent 8900 Triple Quadrupole ICP-MS for the quantitative measurement of 54 dissolved elements in NMP per SEMI C33-0213 (4) and monitoring of 14 elemental NPs in NMP. The NMP grades analyzed comprised an electronic industry (EL grade) sample and a new, supreme pure (SP grade) sample.

Experimental

Reagents and sample preparation

Electronic (EL grade, maximum concentration of elements from 1 to 50 ppb) NMP and a new, higher purity (SP grade, maximum concentration of 32 elements < 20 ppt) NMP samples were provided by FUJIFILM Wako Pure Chemical Corporation (Tokyo, Japan) (6). The 32 elements with maximum contamination levels listed in SP grade NMP include Li, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Sr, Zr, Mo, Pd, Ag, Cd, Sn, Sb, Ba, Ta, W, Os, Au, and Pb.

For quantitative analysis of dissolved elements in NMP, the samples were analyzed directly (without acidification or dilution) for 54 elements using the method of standard addition (MSA). Standard solutions were prepared from a mixture of XSTC-331, XSTC-7, XSTC-8 (SPEX CertiPrep, USA) and single element standards for In (Agilent p/n 5190-8467), Os, and Hg (Kanto Chemical Co., Inc., Japan).

For NP analysis of NMP, the samples were analyzed directly (without acidification or dilution) for 14 elements using multi-element spICP-MS mode. A 200 nm silica (SiO_2) NP (nanoComposix, p/n SISI200) reference material (RM) was used to measure the nebulization efficiency (calculated by particle concentration method by the ICP-MS MassHunter software). The nebulization efficiency value is required for the calculation of particle size.

A solution containing 25 nm iron oxide (Fe_3O_4) NPs (Sigma Aldrich, p/n 747408) was used as the NP standard. Both the SiO_2 NP RM and Fe_3O_4 NP standard were prepared in solution using the SP grade NMP as the dilution solvent.

Instrumentation

An 8900 semiconductor configuration ICP-QQQ and Agilent I-AS autosampler were used throughout. The 8900 was equipped with the standard MFN-100 nebulizer, standard quartz spray chamber, and standard copper-based platinum (Cu/Pt) sampling and skimmer cones. To reduce plasma loading by the organic matrix, a 1.5 mm injector quartz torch (p/n G3280-80080) was used. An option gas flow of 20% O_2 in Ar was added to the carrier gas to prevent the carbon in the NMP from building up on the interface cones.

To achieve the lowest BEC for each analyte in the two grades of NMP, optimized ICP-QQQ acquisition conditions were used for different elements. Using ICP-MS MassHunter software, many elements can be analyzed using a single multitune method that includes multiple optimized cell gas modes. During data acquisition, the ORS⁴ 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 (NH₃, H₂, He, and O₂) were used as appropriate for the large number of analytes being measured. Details of the configuration and principles of ICP-QQQ and MS/MS are explained elsewhere (7, 8).

Data was acquired for all cell gas modes during one visit to the sample vial, and three replicate measurements were acquired for each sample (10 measurements of the blank). The He mode conditions used Single Quad (SQ) mode (Q1 operated as an ion guide, rather than as a true mass filter). No gas mode and the NH₃, H₂, and O₂ cell gas conditions used MS/MS mode (both Q1 and Q2 operated as true mass filters) with either on-mass measurement of the analyte ion, or mass-shift measurement where an analyte reaction product ion is measured. The plasma, cell, and tuning parameters were optimized for best performance for the application, as shown in Table 1.

Table 1. Agilent 8900 ICP-QQQ operating conditions for the analysis of NMP.

	Warm NH ₃	NH ₃	No Gas	H ₂	He	O ₂
Scan	MS/MS			Single	MS/MS	
RF Power (W)	800	1400				
Sampling Depth (mm)	18.0					
Nebulizer Gas (L/min)	0.70					
Option Gas* (L/min)	0.40	0.30				
Spray Chamber Temp (°C)	2					
Makeup Gas (L/min)	0.2	0.25	0.15	0.30	0.32	
Extraction Lens 1 (V)	-10	-125				
Extraction Lens 2 (V)	-180	-2.5				
Octopole Bias (V)	-10.0	-3.0	-8.0	-18.0	-3.0	
Axial Acceleration (V)	2.0	1.5	0	2.0	1.0	1.5
Energy Discrimination (V)	-10.0	-7.0	5.0	3.0		-7.0
He Flow (mL/min)	1.0		-	-	5.0	-
H ₂ Flow (mL/min)	-		-	5.0	-	-
NH ₃ Flow** (mL/min)	3.0 (30%)		-	-	-	-
O ₂ Flow (mL/min)	-		-	-	-	0.45 (30%)

* 20% O₂ balanced with 80% Ar. ** 10% NH₃ balanced with 90% He.

Notes: P can be measured as PO in oxygen mode. However, to obtain the best data, PH₄ measurement is recommended. To promote the formation of PH₄⁺ ions in the cell, the following parameters were optimized: H₂ flow rate (10 mL/min), OctP bias (-30 V), axial acceleration (+0.1 V), and energy discrimination (-20 V).

Results and discussion

Some important SEMI elements such as Mg, Al, P, and Cr suffer matrix-based polyatomic interference overlaps in NMP, as shown in Table 2.

Table 2. Examples of potential spectral interferences on some SEMI elements in an organic solvent such as NMP.

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 ⁺
³¹ P	¹⁵ N ¹⁶ O ⁺ , ¹⁴ N ¹⁷ O ⁺ , ¹⁴ N ¹⁶ OH ⁺ , ¹³ C ¹⁸ O ⁺ , ¹² C ¹⁶ OH ₃ ⁺
⁵² Cr	⁴⁰ Ar ¹² C ⁺

The low background equivalent concentrations (BECs) and linearity of the MSA calibration plots in Figure 1 show that the carbon-based interferences listed in Table 2 were successfully removed using the 8900 ICP-QQQ multitune method.

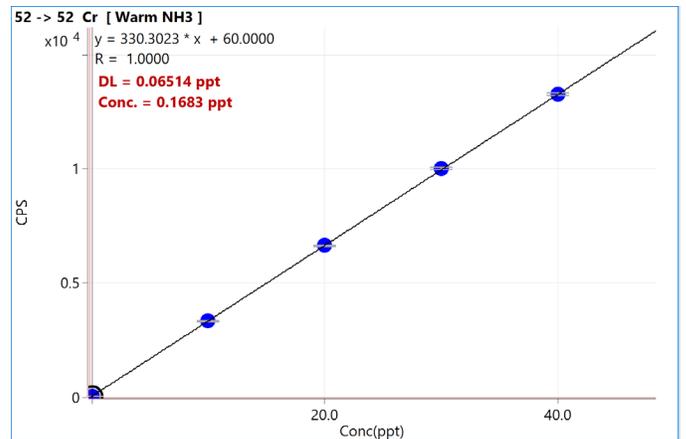
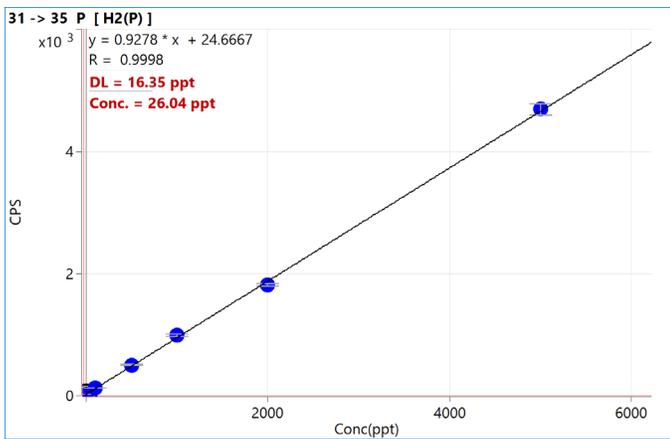
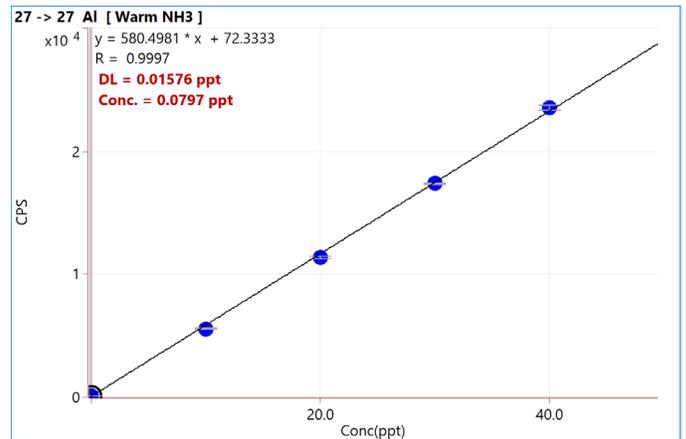
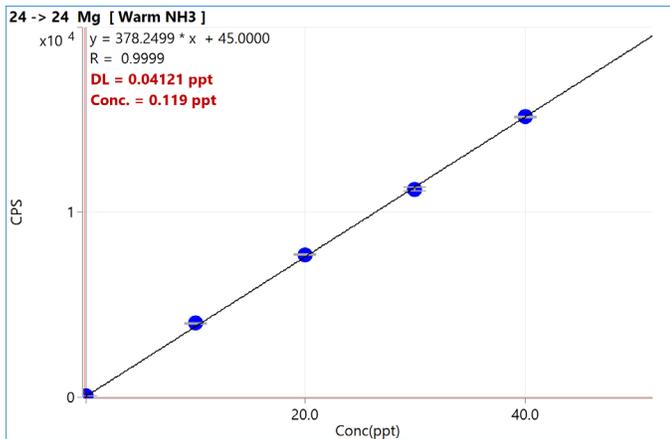


Figure 1. MSA calibration plots for Mg, Al, P, and Cr in SP grade NMP. The low concentration levels determined in the unspiked NMP sample show the low contaminant levels and successful removal of carbon-based interferences.

The detection limits (DLs) and unspiked sample concentrations (BECs) that were calculated automatically by the ICP-MS MassHunter software for the two grades of NMP are shown in Table 3. When using MSA, the BEC is equivalent to the measured concentration in the unspiked sample. No background subtraction or blank correction was performed. The measured concentrations of most of the elements were significantly lower in the SP grade NMP sample than the EL grade sample, confirming the higher purity of the new grade of reagent. All DLs (ppt) were well below the maximum concentration specifications provided in SEMI C33-0213 for the highest (grade 3) purity of NMP.

Table 3. Comparison of Agilent 8900 ICP-QQQ DLs and measured concentrations (BECs) of 54 elements in two grades of NMP. The SEMI C33-0213 specifications for the highest purity (grade 3) of NMP are also shown. SEMI elements in bold text.

Analyte	Q1	Q2	Tune	EL Grade		SP Grade		SEMI C33-0213 Grade 3
				DL (ppt)	Conc (ppt)	DL (ppt)	Conc (ppt)	Maximum Conc (ppt)
Li	7	7	Warm NH ₃	0.018	< DL	0.018	< DL	20000*
Be	9	9	No gas	0.035	0.065	0.018	0.048	
B	11	11	No gas	0.95	9.3	0.37	3.3	10000
Na	23	23	Warm NH ₃	0.20	1.1	0.20	1.1	10000
Mg	24	24	NH₃	0.20	1.8	0.041	0.12	5000
Al	27	27	NH₃	0.12	2.3	0.016	0.080	5000
Si	28	28	H ₂	131	3982	17	885	
P	31	35	H ₂	20	38	16	26	250000**
S	34	50	O ₂	212	1475	304	5233	250000**
K	39	39	Warm NH ₃	0.97	7.6	0.028	0.50	5000
Ca	40	40	NH ₃	0.95	6.0	0.017	0.043	5000
Ti	48	64	O ₂	0.40	0.48	0.011	0.014	5000
V	51	67	O ₂	0.042	0.050	0.006	0.007	20000*
Cr	52	52	NH ₃	0.49	6.8	0.065	0.17	10000
Mn	55	55	NH ₃	0.34	3.0	0.014	0.044	5000
Fe	56	56	NH ₃	3.9	47	0.072	0.48	10000
Co	59	59	NH ₃	0.14	< DL	0.018	< DL	
Ni	60	60	NH ₃	0.95	7.7	0.11	< DL	5000
Cu	63	63	NH ₃	4.4	289	0.040	0.33	5000
Zn	66	66	NH ₃	1.4	1.7	0.24	0.64	10000
Ga	71	71	NH ₃	0.019	< DL	0.013	0.022	
Ge	74	74	O ₂	0.15	< DL	0.11	< DL	
As	75	91	O₂	0.18	< DL	0.077	< DL	10000
Se	78	78	H ₂	1.6	3.2	2.4	3.3	
Rb	85	85	NH ₃	0.028	0.082	0.010	0.088	
Sr	88	88	NH ₃	0.021	< DL	0.002	< DL	
Zr	90	106	O ₂	0.10	< DL	0.009	< DL	
Nb	93	93	No gas	0.021	0.042	0.012	0.026	
Mo	95	127	O ₂	0.98	1.6	0.043	< DL	
Ru	101	101	No gas	0.16	< DL	0.082	< DL	
Rh	103	103	NH ₃	0.025	0.026	0.012	< DL	
Pd	105	105	O ₂	0.061	< DL	0.028	0.043	
Ag	107	107	NH ₃	0.064	0.30	0.037	< DL	
Cd	111	111	O₂	0.30	< DL	0.15	< DL	20000
In	115	115	NH ₃	0.005	< DL	0.006	< DL	
Sn	118	118	NH₃	0.26	0.48	0.20	< DL	5000
Sb	121	121	O₂	0.18	< DL	0.043	0.13	10000
Te	128	128	O ₂	1.6	2.6	0.52	2.2	
Cs	133	133	NH ₃	0.011	0.027	0.011	0.029	

Table 3 continues on next page

Table 3 continued...

Analyte	Q1	Q2	Tune	EL Grade		SP Grade		SEMI C33-0213 Grade 3
				DL (ppt)	Conc (ppt)	DL (ppt)	Conc (ppt)	Maximum Conc (ppt)
Ba	138	138	NH ₃	0.010	0.085	0.006	< DL	
Hf	178	194	O ₂	0.13	< DL	0.051	0.097	
Ta	-	181	He	0.073	< DL	0.006	< DL	
W	-	182	He	0.26	< DL	0.022	0.047	
Re	-	185	He	0.17	< DL	0.042	0.081	
Os	-	197	He	0.19	0.30	0.071	< DL	
Ir	193	193	O ₂	0.069	0.29	0.069	< DL	
Pt	195	195	O ₂	0.10	0.22	0.10	0.20	
Au	-	197	He	0.058	0.078	0.026	< DL	
Hg	-	202	He	1.2	< DL	0.53	0.71	
Tl	-	205	He	0.018	0.049	0.032	< DL	
Pb	-	208	He	0.27	0.41	0.033	0.081	5000
Bi	-	209	He	0.085	< DL	0.029	0.044	
Th	-	232	He	0.055	0.20	0.055	< DL	
U	-	238	He	0.054	0.086	0.020	0.027	

* Grade 2 specifications, as no values are defined for Grade 3. ** Concentration specified for PO₄ and SO₄

Determination of nanoparticles in NMP

The principles of multiple element nanoparticle analysis using spICP-MS mode are outlined elsewhere (3, 9). First the nebulization efficiency was calculated by measuring the particle concentration of the SiO₂ NP RM. The Single Nanoparticle software automatically calculated the nebulization efficiency as 0.196 (19.6%).

To validate the spICP-MS method, the 25 nm Fe₃O₄ NP standard was measured using the 8900 ICP-QQQ. The size distribution graph (Figure 2) for the NP standard measured using the 8900 ICP-QQQ agreed with the expected result of 25 nm. Also, the 25 nm Fe₃O₄ 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. The results show that the particle size and particle mass were measured correctly, confirming the accuracy of the spICP-MS method.

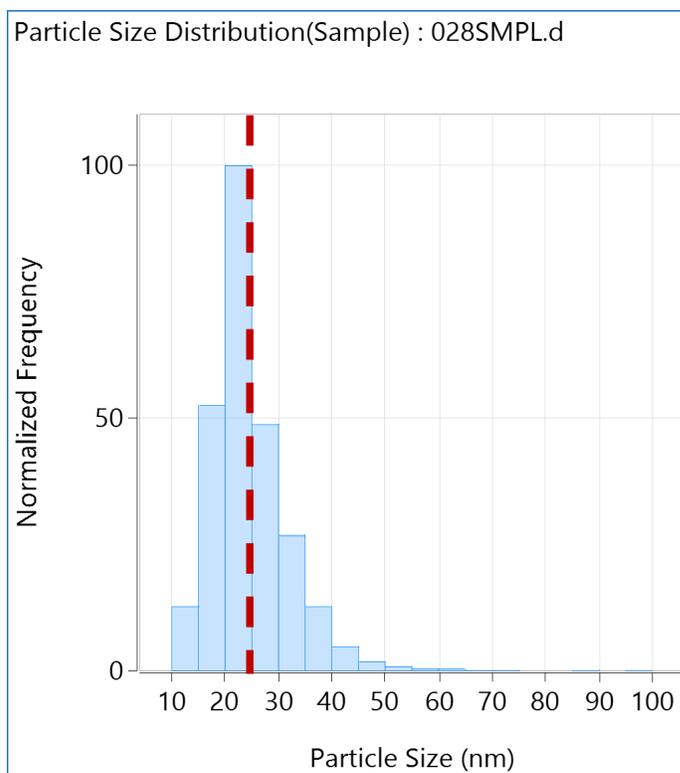


Figure 2. spICP-MS size distribution graph for 25 nm Fe₃O₄ standard.

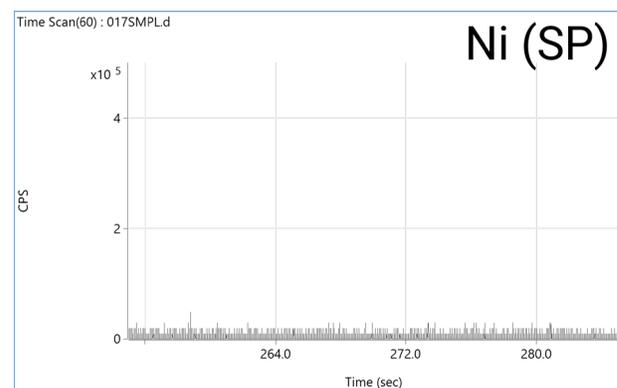
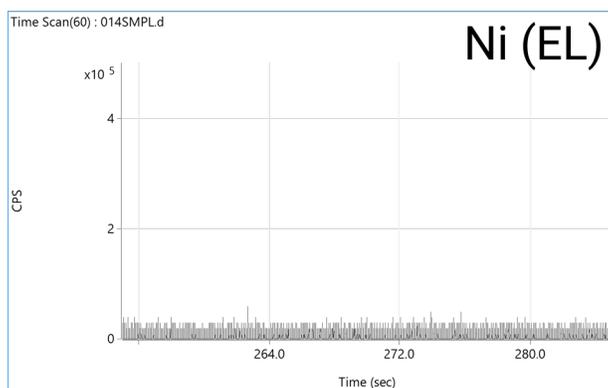
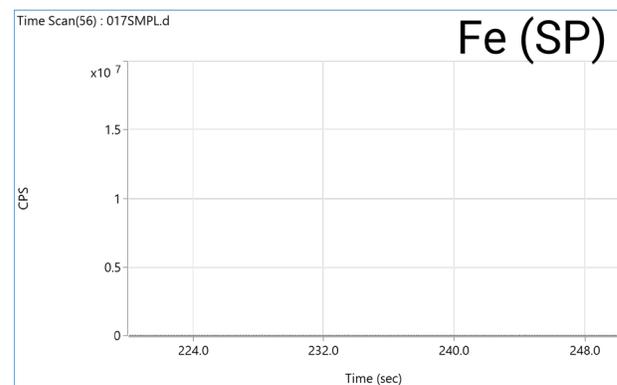
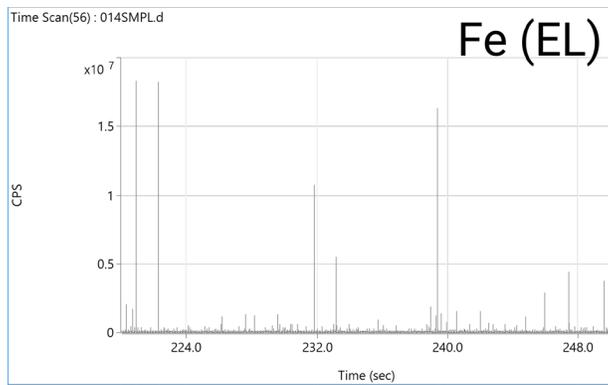
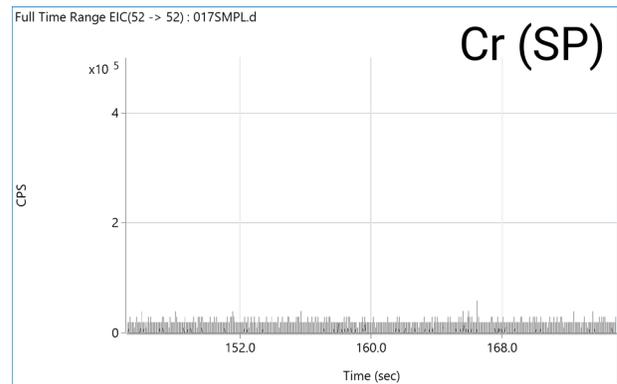
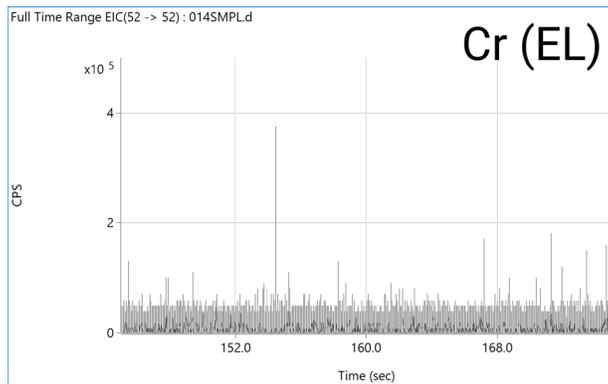
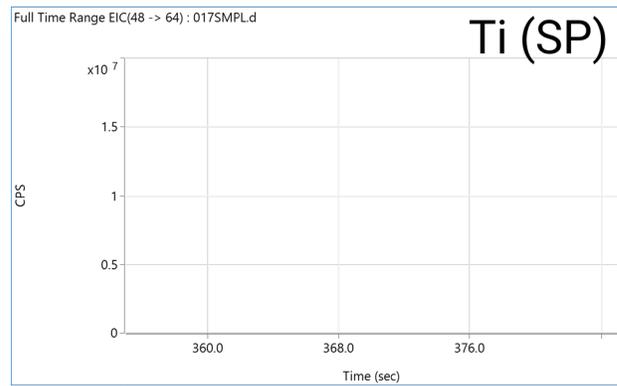
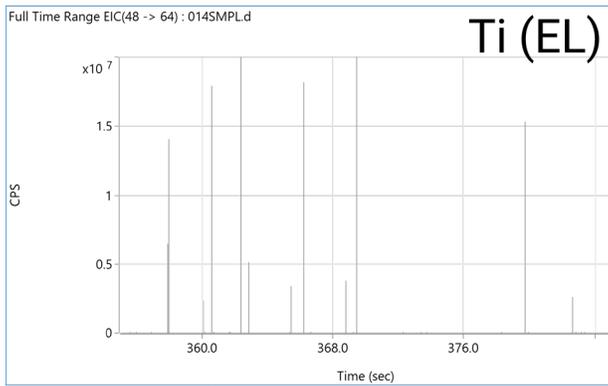


Figure 3. Representative Time Resolved Acquisition signals for multi-element NP acquisitions in EL (left) and SP (right) grades of NMP.

Fast Time Resolved Analysis for particle contaminants

In this study, 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

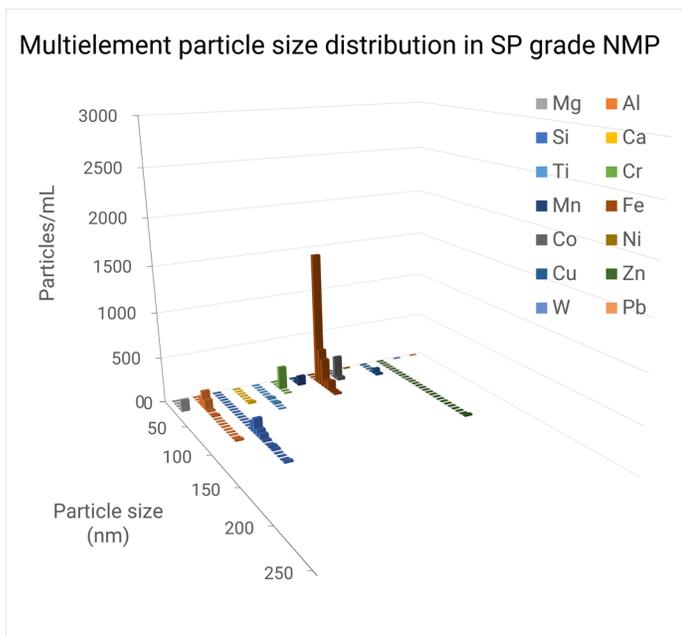
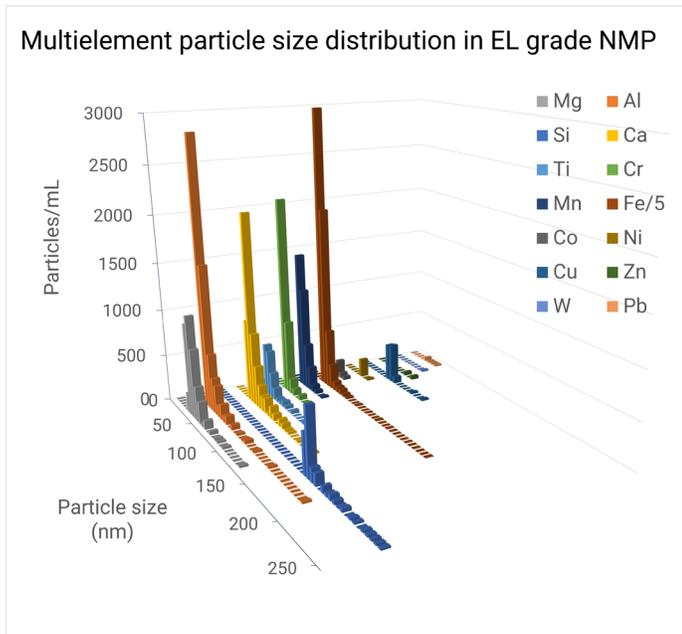


Figure 4. Particle number and size distribution for elements detected in EL grade (top) and SP grade (bottom) NMP. Note the actual number of Fe particles measured in EL grade NMP has been divided by five to fit on the same scale as the other elements.

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 Ti, Cr, Fe, and Ni in the two grades of NMP are shown in Figure 3. The spICP-MS method can be used to identify particle contamination that may be derived from raw materials or processing equipment such as stainless steel.

Particle size distribution per 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 4. The data confirms that the high purity SP grade of NMP (Figure 4, 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 4, top).

Figure 5 shows that the concentration of the NPs measured was also much lower in the higher purity SP grade sample than in the EL grade sample. 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 iron particles, mostly sized between 20 to 30 nm.

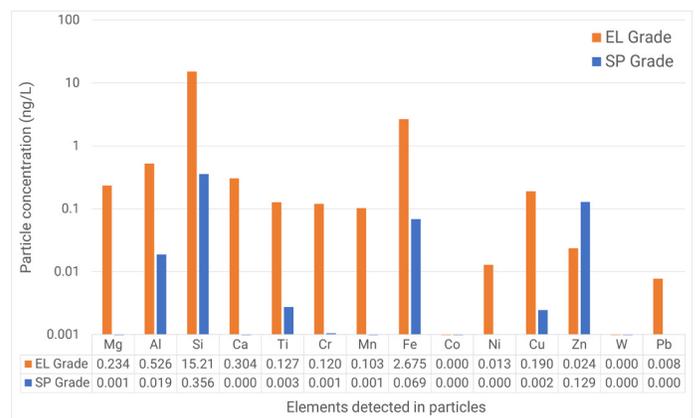


Figure 5. Comparison of particle concentration results measured in EL and SP grades of NMP using the Agilent 8900 ICP-QQQ in spICP-MS mode.

Conclusion

An advanced quality control analysis of dissolved and particulate inorganic impurities in two semiconductor grades of the organic solvent NMP was performed using an Agilent 8900 ICP-QQQ. Concentrations of 54 dissolved elements were quantified in the two grades of NMP, using the method of standard additions. The quantitative data obtained for the electronics (EL) and high purity (SP) grade NMP samples showed that both products easily met the specifications provided in SEMI C33-0213. Most of the measured element concentrations were significantly lower in the SP grade NMP than in the EL grade sample, confirming its higher purity.

In addition, the nanoparticle (NP) content of the samples was characterized by measuring particles containing 14 insoluble elements using the 8900 ICP-QQQ in single particle (sp) ICP-MS mode. The Rapid Multi-Element Nanoparticle Analysis module for ICP-MS MassHunter software (version 5.2 onwards) supports the acquisition of single NP data for an unlimited number of elements in a single run. The multi-element spICP-MS method provided information on the identity, size distribution, and concentration of element NPs of interest to semiconductor IC FABs. 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 types of metallic particles in the EL and SP grades of NMP, while the size distribution and concentration of the particles also differed significantly. While both grades of NMP were high purity, the study showed that the overall level of impurities –dissolved elements and NPs –were lower in the SP grade sample than the EL grade product.

The quantitative and spICP-MS methods outlined in this study demonstrate the flexibility and capability of the 8900 ICP-QQQ in supporting the semiconductor industry to address QC and contamination control challenges. Both the dissolved elemental and insoluble nanoparticle content of the latest high purity chemicals, reagents, and solutions used throughout the IC manufacturing process can now be monitored using a single ICP-QQQ technique.

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