

ICP - Mass Spectrometry

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Determination of Impurities in Organic Solvents used in the Semiconductor Industry with the NexION 300S/350S ICP-MS

Introduction

Two of the most commonly used organic solvents in the semiconductor industry are isopropyl alcohol (IPA) and propylene glycol methyl ether acetate (PGMEA). While IPA is used frequently to clean silicon wafers, PGMEA is used as a thinner or stripper of photoresist. Both must be analyzed to check for trace metal contamination where the presence of contaminants would have detrimental effects on the reliability of memory devices. SEMI Standard C41-0705 specifies limits for high purity IPA Grade 4 with contamination limits of less than 100 ppt for each element.

With its ability to determine analytes rapidly at the ultratrace (ng/L or parts-per-trillion) level in various process chemicals, inductively coupled plasma mass spectrometry (ICP-MS) has become an indispensable analytical tool for quality control. However, it is extremely important to address certain potentially problematic areas when analyzing organic solvents directly, including: viscosity and volatility, compatibility of the sample introduction device, deposition of carbon on the interface cones, matrix-derived polyatomic interferences, as well as matrix suppression effects due to carbon content. A cooled spray chamber might help to reduce the vapor pressure with an optimized sample uptake rate for volatile organic solvents. Carbon deposited on the tip of the interface cones can be avoided by adding a small amount of oxygen into the injector gas flow between the spray chamber and the torch.

Although cool plasma has been shown to be effective in reducing argon-based interferences, it is even more prone to matrix suppression than hot plasma. Additionally, the low plasma energy may result in preferential formation of other polyatomic interferences, which are not seen under hot plasma conditions. Collision cells using multipoles and nonreactive gases have proven useful in reducing polyatomic interferences. However, kinetic energy discrimination results in the loss of sensitivity, which is an issue when analyzing ng/L levels. Reaction mode is another technique which uses a reactive gas, such as NH_3 , to selectively react with the polyatomic interference, and a quadrupole mass filter to create dynamic bandpass to prevent undesirable formation of by-product ions, thereby removing the polyatomic interference effectively without suppressing the analytes' signal.

The PerkinElmer NexION® 300 ICP-MS incorporates Universal Cell Technology™, which allows the use of Collision mode (with kinetic energy discrimination), Reaction mode (incorporating Dynamic Bandpass Tuning), and Standard mode (where a cell gas is not used). The user can select whichever mode(s) are most appropriate for the application and can switch from one to another within the same analytical method.

This application note demonstrates the ability of the NexION 300S ICP-MS to remove interferences so that trace levels of impurities in IPA and PGMEA can be easily measured using hot plasma conditions for all analytes in a single analysis. This was best accomplished using both Standard and Reaction modes in a single method.

Experimental conditions

The electronic-grade isopropyl alcohol and propylene glycol methyl ether acetate were provided by a semiconductor customer in Singapore. Samples were injected directly

without pre-treatment or dilution. Standard solutions were made from a 10 mg/L multi-element standard (PerkinElmer Pure, PerkinElmer, Shelton, CT USA). The instrument used for this experiment was a NexION 300S ICP-MS (PerkinElmer, Shelton, CT USA). Instrumental parameters and sample introduction components are shown in Table 1.

Results

IPA and PGMEA samples were quantitatively analyzed using the method of additions; the calibration curves in IPA for Mg, Al and Cr are shown in Figures 1–3 and demonstrate good linearity, which is possible with all the carbon-related polyatomic interferences removed by the reactive NH₃ gas in combination with the bandpass. The linearity of the B calibration curve (Figure 4) demonstrates good resolution of the instrument since the abundance of carbon present in the sample does not affect the calibration.

Table 1. Instrumental parameters and sample introduction components for the NexION 300S ICP-MS.

Spray Chamber	Quartz Cyclonic with PC ³	Plasma Gas	18 L/min
Torch	High Efficiency Quartz	Auxiliary Gas	1.0 L/min
Torch Injector	1-mm Quartz	Nebulizer Gas	0.8 L/min
Sampler Cone	Platinum	Oxygen Makeup Gas	0.1 L/min
Skimmer Cone	Platinum	RF Power	1600 W
Nebulizer	PFA-100 (100 µL/min)	Integration Time	1 sec/mass

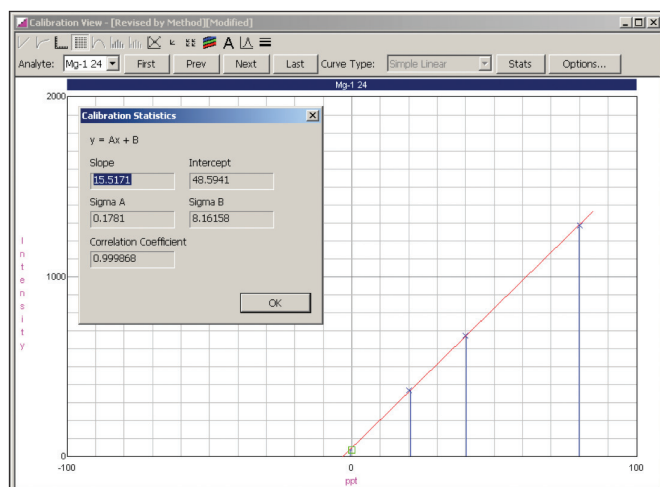


Figure 1. Mg calibration, with NH₃ cell gas flow of 0.3 mL/min.

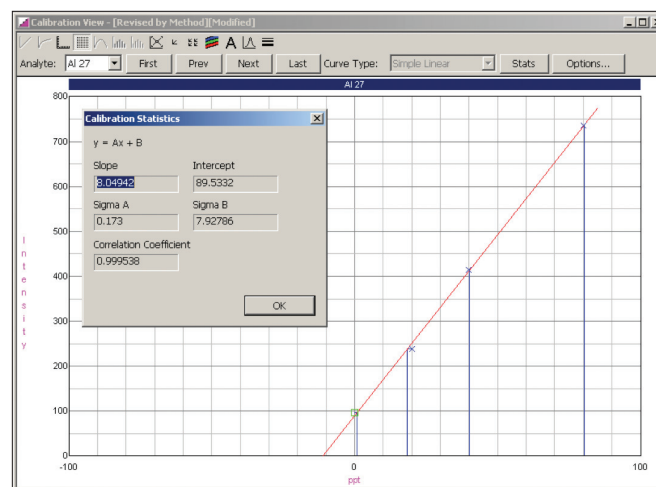


Figure 2. Al calibration, with NH₃ cell gas flow of 0.6 mL/min.

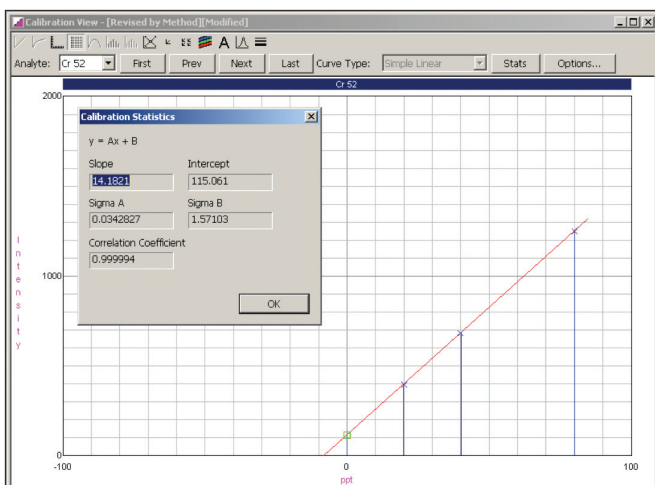


Figure 3. Cr calibration, with NH₃ cell gas flow of 0.6 mL/min.

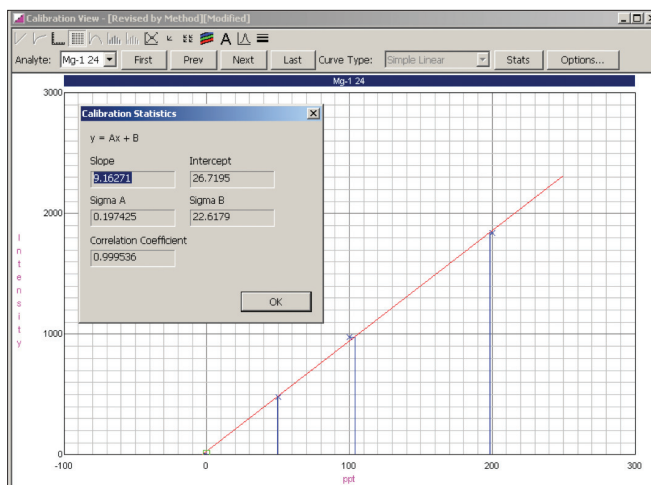


Figure 5. Mg calibration, with NH₃ cell gas flow of 0.3 mL/min.

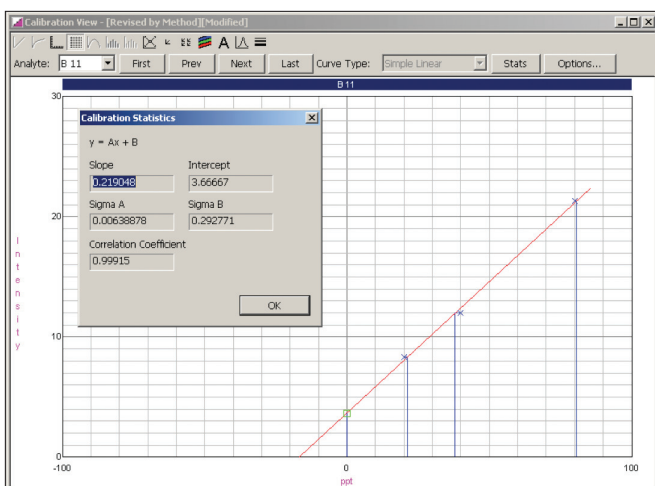


Figure 4. B calibration in Standard mode.

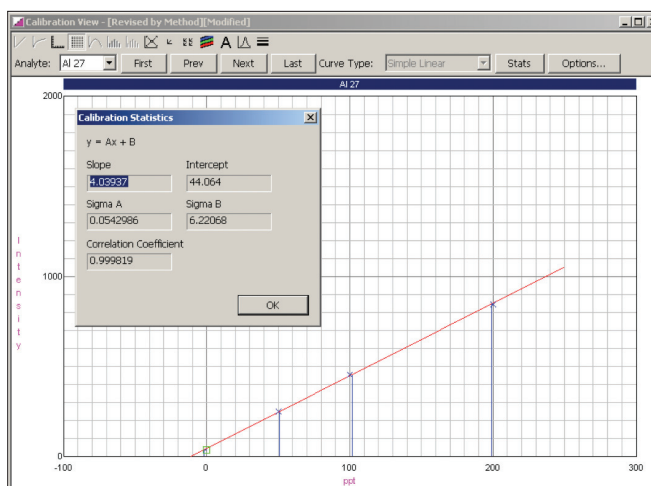


Figure 6. Al calibration, with NH₃ cell gas flow of 0.6 mL/min.

Similarly, the calibration curves in PGMEA for Mg and Al, shown in Figures 5 and 6, demonstrate good linearity. Higher level calibration standards were required in PGMEA than IPA due to the higher concentrations of elements present.

The results for IPA and PGMEA are summarized in Tables 2 and 3 (Page 4), respectively. The detection limits (DLs) and background equivalent concentrations (BECs) were both determined in IPA and PGMEA, while accounting for the sensitivities in IPA and PGMEA. DLs were calculated by multiplying the standard deviation by three, and BECs were determined by measuring the signal intensities. Recoveries were determined from 20 ng/L and 50 ng/L spikes for IPA and PGMEA, respectively.

Table 2. Detection limits (DLs), background equivalent concentrations (BECs), and 20 ng/L spike recoveries for all analytes in IPA (units in ng/L).

Analyte	Mass	Cell Gas Flow*		DL (ppt)	BEC (ppt)	20 ppt Recovery
		(mL/min)	RPq			
Li	7	0	0.25	0.02	< DL	95%
Be	9	0	0.25	0.1	< DL	99%
B	10	0	0.25	7	17	98%
Na	23	0	0.25	0.4	3.5	98%
Mg	24	0.3	0.5	0.4	< DL	104%
Al	27	0.6	0.5	1	5	95%
K	39	0.6	0.5	1	3	93%
Ca	40	1	0.5	0.8	< DL	97%
Ti	48	0.3	0.5	1	9	103%
V	51	0.6	0.5	0.6	< DL	103%
Cr	52	0.6	0.5	2	9	100%
Mn	55	0.6	0.7	1	11	110%
Fe	56	0.6	0.5	2	31	98%
Co	59	0.3	0.5	0.05	< DL	99%
Ni	60	0.3	0.7	1	< DL	106%
Cu	63	0.3	0.5	0.7	3.6	105%
Zn	64	0.3	0.65	0.8	2	102%
Ga	69	0.6	0.5	0.1	< DL	96%
Ge	74	0.3	0.65	0.3	< DL	100%
As	75	0	0.25	0.8	< DL	96%
Sr	88	0	0.25	0.01	< DL	100%
Zr	90	0	0.25	0.05	< DL	111%
Nb	93	0	0.25	0.1	0.3	112%
Mo	98	0	0.25	0.6	< DL	96%
Ru	102	0	0.25	0.06	< DL	96%
Rh	103	0	0.25	0.2	0.5	98%
Pd	106	0	0.25	0.08	< DL	98%
Ag	107	0	0.25	0.09	0.59	97%
Cd	114	0	0.25	0.1	0.4	93%
In	115	0	0.25	0.03	< DL	99%
Sn	120	0	0.25	0.6	7.9	101%
Sb	121	0	0.25	0.2	< DL	100%
Ba	138	0	0.25	0.01	< DL	97%
Ta	181	0	0.25	0.06	< DL	101%
W	184	0	0.25	0.7	< DL	111%
Pt	195	0	0.25	0.4	< DL	96%
Au	197	0	0.25	0.4	0.8	104%
Tl	205	0.6	0.5	0.006	< DL	99%
Pb	208	0.6	0.5	0.1	0.2	100%
Bi	209	0.6	0.5	0.04	< DL	100%
U	238	0	0.25	0.02	< DL	105%

*Cell gas used is NH₃.

Table 3. Detection limits (DLs), background equivalent concentrations (BECs), and 50 ng/L spike recoveries for all analytes in PGMEA (units in ng/L).

Analyte	Mass	Cell Gas Flow*		DL (ppt)	BEC (ppt)	50 ppt Recovery
		(mL/min)	RPq			
Li	7	0	0.25	0.06	< DL	99%
Be	9	0	0.25	0.1	< DL	95%
B	10	0	0.25	10	180	102%
Na	23	0	0.25	0.9	38.3	102%
Mg	24	0.3	0.5	0.9	1.4	98%
Al	27	0.6	0.5	2	9	102%
K	39	0.6	0.5	1	12	96%
Ca	40	1	0.5	3	< DL	94%
Ti	48	0.3	0.5	2	7	101%
V	51	0.6	0.5	1	2	111%
Cr	52	0.6	0.5	20	940	117%
Mn	55	0.6	0.7	2	7	99%
Fe	56	0.6	0.5	10	180	119%
Co	59	0.3	0.5	0.3	0.5	107%
Ni	60	0.3	0.7	6	150	103%
Cu	63	0.3	0.5	2	15	101%
Zn	64	0.3	0.65	3	10	90%
Ga	71	0.3	0.5	0.2	< DL	101%
Ge	74	0.3	0.65	2	< DL	91%
As	75	0	0.25	10	70	105%
Sr	88	0	0.25	0.03	< DL	100%
Zr	90	0	0.25	0.2	< DL	108%
Nb	93	0	0.25	0.2	0.4	104%
Mo	98	0	0.25	5	165	117%
Ru	102	0	0.25	0.06	< DL	106%
Rh	103	0	0.25	1	24	90%
Pd	106	0	0.25	0.1	< DL	99%
Ag	107	0	0.25	0.6	4.3	98%
Cd	114	0	0.25	2	13	101%
In	115	0	0.25	0.02	< DL	101%
Sn	120	0	0.25	0.9	12.2	102%
Sb	121	0	0.25	0.7	2.7	106%
Ba	138	0	0.25	0.04	< DL	100%
Ta	181	0	0.25	0.07	< DL	106%
W	184	0	0.25	20	130	89%
Pt	195	0	0.25	100	300	-26%
Au	197	0	0.25	0.1	< DL	99%
Tl	205	0.6	0.5	0.01	< DL	103%
Pb	208	0.6	0.5	0.1	0.3	100%
Bi	209	0.6	0.5	0.02	< DL	101%
U	238	0	0.25	0.05	< DL	112%

*Cell gas used is NH₃.

The higher than expected DL and BEC determined for Cr in PGMEA were due to the presence of Cr in the PGMEA. This was confirmed by looking at the mass spectrum of the Cr isotopes in PGMEA in Reaction mode, as shown in Figure 7. The peaks seen at m/z 50, 52, 53, and 54 correspond to the natural isotopic abundance of Cr, as indicated by the green lines in the figure, thus providing evidence of the presence of Cr.

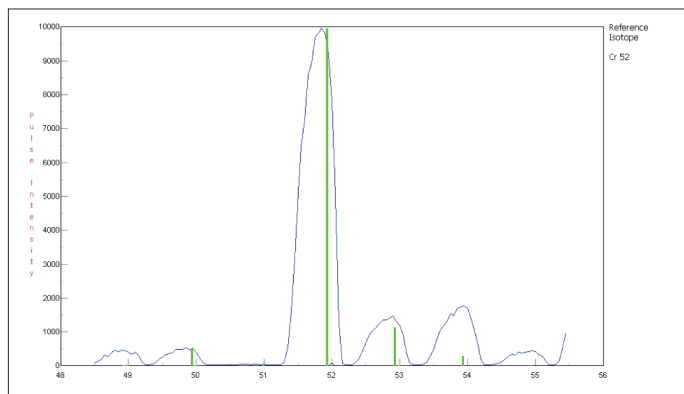


Figure 7. Mass scan of the Cr isotopes in PGMEA.

IPA is considerably more volatile than PGMEA, and as such, would have greater effect on the measurement stability by ICP-MS due to solvent loading and carbon formation on the cones. To demonstrate the stability of the NexION 300S ICP-MS in handling organic matrices with the parameters listed in Table 1, IPA spiked with 100 ng/L standard spikes (acidified with 1% HNO_3) was continuously introduced into the NexION 300S without rinse, for 14 hours. Figures 8 and 9 show excellent stability, with RSDs of < 3% over 14 hours. The stability results, combined with the spike recovery data, highlight the ability of the NexION 300S ICP-MS to successfully determine all of the SEMI-required elements in organic matrices.

Conclusion

It has been demonstrated that the NexION 300S ICP-MS operating under optimized sampling conditions can minimize the amount of undesirable carbon-based species entering the mass spectrometer when aspirating organic matrices. It also has been shown that by using the Reaction mode of the Universal Cell, the argon- and carbon-based polyatomic spectral interferences can be reduced significantly, allowing for the determination of many of the traditionally problematic elements with good spike recovery and precision. Using pure NH_3 as the reaction gas and one set of Reaction conditions, the full suite of semiconductor

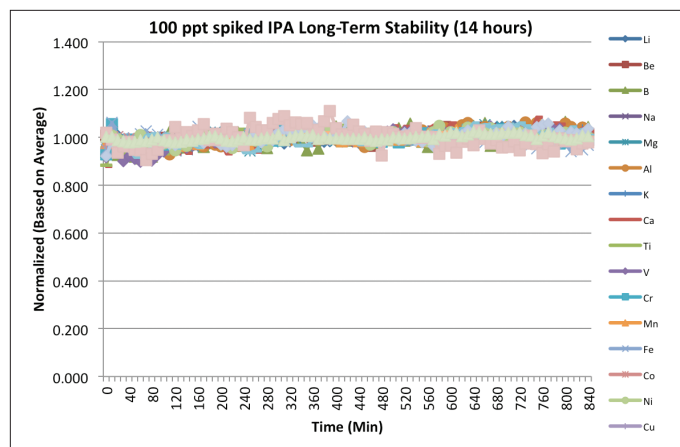


Figure 8. Fourteen-hour long-term stability (normalized intensity) for a 100 ng/L spike for first group of analytes.

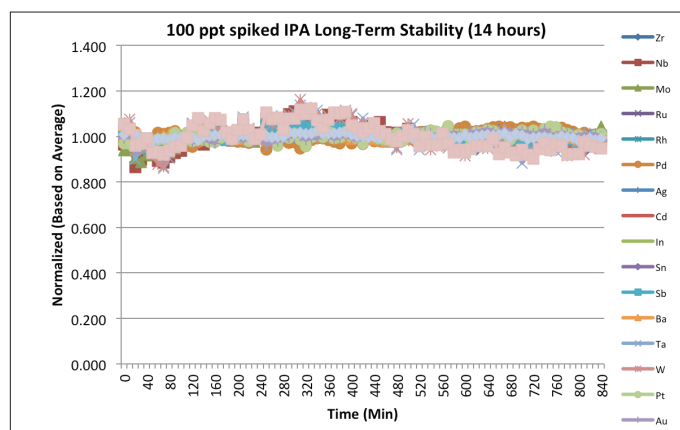


Figure 9. Fourteen-hour long-term stability (normalized intensity) for a 100 ng/L spike for second group of analytes.

elements can be determined in many of the organic compounds used in the industry, as demonstrated by the analysis of IPA and PGMEA. In addition, running with hot plasma conditions allows for the determination of elements with both high and low ionization potentials in a multielement run, with minimum matrix suppression, even for complex organic matrices. This work shows the robustness of the NexION 300S ICP-MS for the routine quantification of ultratrace impurities at the ng/L level in organic solvents important to semiconductor applications.

References

1. SEMI Standard C41-0705, Guideline for 2-Propanol, available from <http://www.semi.org/en/index.htm>