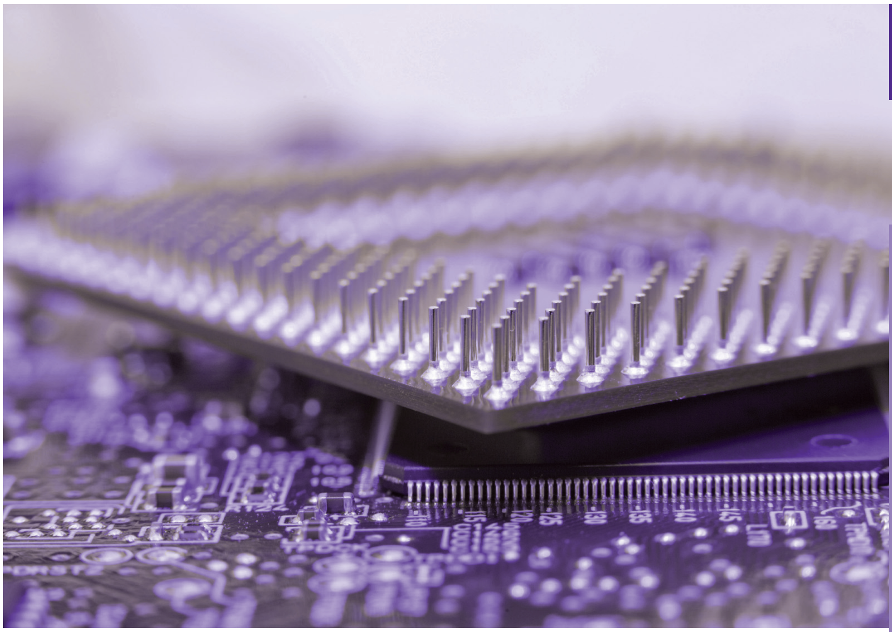

APPLICATION NOTE

ICP - Mass Spectrometry

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Determination of Impurities in Semiconductor-Grade Sulfuric Acid with the NexION 300S/ 350S ICP-MS

Introduction

The making of a semiconductor device comprises of forming a sacrificial layer on a substrate. Usually, a patterned resist layer forms the sacrificial layer so that ion implantation to the substrate can be performed, after which a wet etching solution is used to remove the patterned photoresist layer. Typically, an etching solution comprises of sulfuric acid (H_2SO_4) and peroxide (H_2O_2), known as piranha or ozonated sulfuric acid. As with other chemicals used, any metal impurities present would have detrimental effect on the reliability of an IC device and thus need to be of high purity and quality. SEMI Standard C44-0708 specifies the maximum concentration of metal contaminants by element and tier for sulfuric acid.

Inductively coupled plasma mass spectrometry (ICP-MS) is an indispensable analytical tool for quality control because of its superior capability to detect at the ultratrace (ng/L or parts-per-trillion) level. Nevertheless, under the conventional plasma conditions, argon ions combine with matrix components to generate polyatomic interferences. Some of the interferences in sulfuric acid are $^{32}S^{15}N^+$ on $^{47}Ti^+$, $^{32}S^{16}O_2^+$ on $^{64}Zn^+$, ArS^+ on $^{70\text{-}74}Ge^+$, $^{38}Ar^1H^+$ on $^{39}K^+$, $^{40}Ar^+$ on $^{40}Ca^+$, $^{40}Ar^{16}O^+$ on $^{56}Fe^+$.

The Dynamic Reaction Cell (DRC™), which uses a quadrupole mass filter to create Dynamic Bandpass Tuning (DBT), is a powerful correction technique to remove interferences on analytes of interest. Collision cells, using nonreactive gases, have proven to be another simple method in reducing specific polyatomic interferences. Both of these techniques are available in PerkinElmer's NexION® 300 ICP-MS through its unique Universal Cell Technology™, which allows the use of all three modes (Standard, Collision and Reaction) within one analytical method.

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This application note demonstrates the ability of the NexION 300 ICP-MS to remove interferences so that trace levels of impurities in H_2SO_4 can be measured under a single set of hot plasma conditions for all analytes in one analysis.

Experimental conditions

Normally, the concentration of H_2SO_4 is around 98%. In this experiment, a ten-fold dilution is carried out on 98% semiconductor-grade H_2SO_4 from our customer. Standard solutions were made from a 10 mg/L multi-element standard (PerkinElmer Pure, PerkinElmer, Shelton, CT USA). The instrumentation used for this experiment was the NexION 300S ICP-MS (PerkinElmer, Shelton, CT USA). Instrumental parameters and sample introduction components are shown in Table 1.

Results

H_2SO_4 samples were quantitatively analyzed using additions calibrations; the calibration curves for Zn, K, Ca, Fe and Ni are shown in Figures 1–3, indicating good linearity. This is possible with all the polyatomic interferences removed by the reactive NH_3 gas in combination with the bandpass.

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

Spray Chamber:	PFA-Scott	Plasma Gas:	18 L/min
Torch:	High Efficiency Quartz	Auxiliary Gas:	1 L/min
Torch Injector:	PFA-Platinum	Nebulizer Flow:	0.96 L/min
Sampler Cone:	Platinum	RF Power:	1500 W
Skimmer Cone:	Platinum	Integration Time:	1 sec/mass
Nebulizer:	PFA-100 (100 µL/min)	Replicates:	3

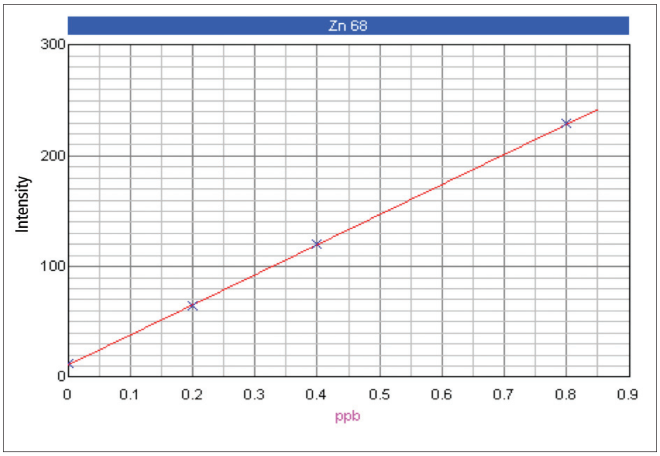

Figure 1. Zn calibration, with He cell gas flow of 3 mL/min.

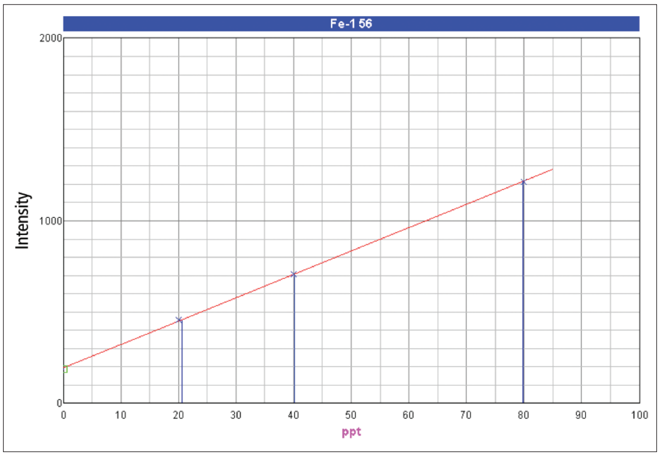

Figure 2. Fe calibration, with NH_3 cell gas flow of 0.6 mL/min.

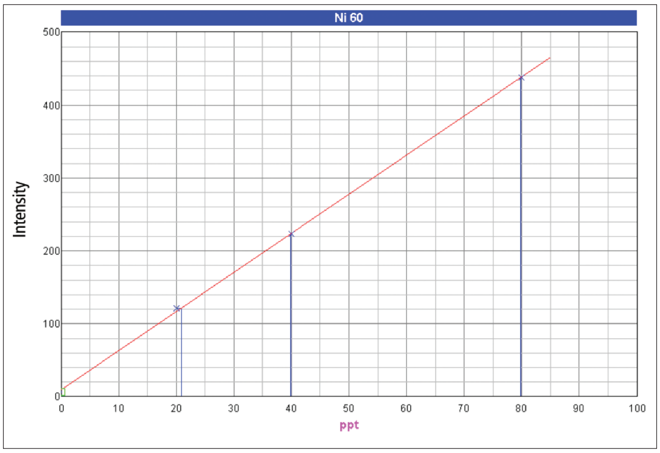

Figure 3. Ni calibration, with NH_3 cell gas flow of 0.3 mL/min.

The detection limits (DLs) and background equivalent concentrations (BECs) were both determined in 10% H_2SO_4, while accounting for the sensitivities in 10% H_2SO_4. 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 spikes. The results are summarized in Table 2.

Stability was determined by continuous introduction into the NexION 300S of 10 ng/L spikes in 10% H_2SO_4 (without rinse) for 10 hours. Figures 4 and 5 show excellent stability, with RSDs of < 3% over 10 hours. The stability results, combined with the spike recovery data, highlight the ability of the NexION 300S ICP-MS to determine all SEMI-required elements in the H_2SO_4 matrix.

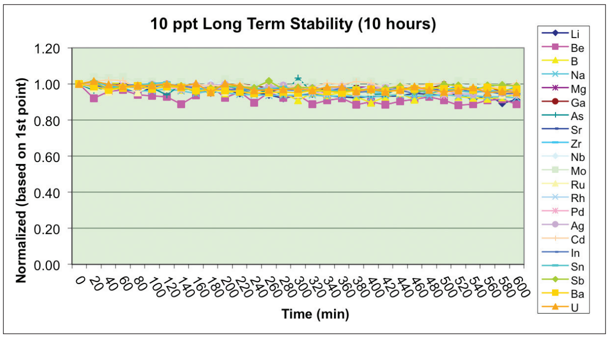

Figure 4. Ten-hour long-term stability results at 10 ng/L level for first group of analytes.

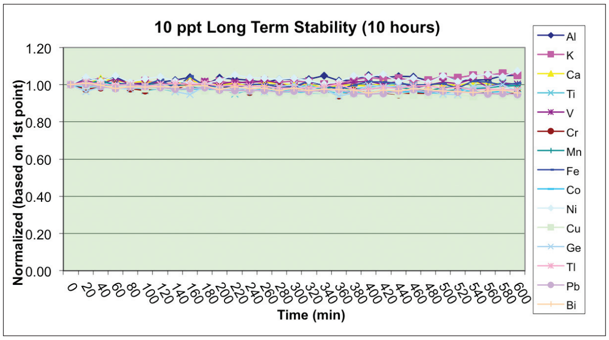

Figure 5. Ten-hour long-term stability results at 10 ng/L level for second group of analytes.

***Table 2.* Detection limits (DLs), background equivalent concentrations (BECs), and 20 ng/L spike recoveries for all analytes in 10% H_2SO_4.**

Analyte	Mass	Cell Gas Flow* (mL/min)	RPq	DL (ppt)	BEC (ppt)	20 ppt Recovery	% RSD
Li	7	0	0.25	0.04	0.04	102%	2.7
Be	9	0	0.25	0.2	0.03	103%	3.3
B	11	0	0.25	0.9	11	100%	3.2
Na	23	0	0.25	0.7	3.3	103%	2.1
Mg	24	0	0.25	0.2	0.4	102%	1.3
Al	27	0.6	0.5	0.7	1.0	96%	1.5
K	39	0.6	0.7	2	7	113%	1.7
Ca	40	1	0.5	1	3.2	97%	1.1
V	51	0.6	0.5	0.9	ND	103%	1.3
Cr	52	0.3	0.5	5	155	102%	1.8
Mn	55	0.6	0.7	0.4	2.2	98%	1.3
Fe	56	0.6	0.7	2	22	113%	1.5
Co	59	0.3	0.65	0.1	0.3	106%	1.4
Ni	60	0.3	0.7	1	2	99%	1.8
Cu	63	0.3	0.75	1	2	103%	1.9
Zn	68	3(He)	0.25	10	40	103%	2.9
Ga	69	0.6	0.7	0.2	0.3	103%	1.1
Ge	74	0.3	0.65	1	2	105%	1.8
As	75	0	0.25	0.4	0.9	100%	2.1
Sr	88	0	0.25	0.1	ND	106%	1.4
Zr	90	0	0.25	0.5	1.9	102%	1.4
Nb	93	0	0.25	0.1	ND	100%	1.2
Mo	98	0.3	0.5	0.9	ND	98%	1.8
Ru	102	0	0.25	0.3	0.19	96%	1.5
Rh	103	0	0.25	0.03	0.4	104%	1.2
Pd	106	0	0.25	0.4	ND	102%	1.8
Ag	107	0	0.25	0.4	0.5	102%	1.7
Cd	114	0	0.25	0.3	0.6	101%	1.5
In	115	0	0.25	0.07	0.1	102%	1.6
Sn	120	0	0.25	1	8	99%	1.7
Sb	121	0	0.25	0.2	ND	103%	1.6
Ba	138	0	0.25	0.07	ND	101%	1.3
Ta	181	0	0.25	0.2	ND	103%	2.0
W	184	0	0.25	0.3	ND	100%	1.8
Pt	195	0	0.25	0.5	ND	105%	1.9
Au	197	0	0.25	1	ND	93%	-
Tl	205	0.6	0.5	0.02	ND	104%	1.2
Pb	208	0.6	0.5	0.1	ND	102%	1.5
Bi	209	0.6	0.5	0.02	ND	103%	1.8
U	238	0	0.25	0.06	ND	102%	1.9

*Cell gas used is NH_3.

Conclusion

The NexION 300S ICP-MS is shown to be robust and suitable for the routine quantification of ultratrace impurities at the ng/L level in H_2SO_4. By means of computer-controlled switching between Standard mode and Reaction mode in the Universal Cell, interference-free analysis using hot plasma conditions for all analytes is possible during a single sample run.

References

1. SEMI Standard C44-0708, SEMI Standards, http://www.semi.org/en/index.htm

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