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

Introduction

In the production of semiconductor devices, the wafers are subjected to a so-called "Standard Clean 2" step, commonly referred to as an "SC2" step. The SC2 step is thought to desorb atomic and ionic contaminants from the wafers. In particular, the SC2 step is intended to remove metals deposited on the wafer surface. In a typical SC2 step, the wafers are submerged in a solution of $H_2O:HCl:H_2O_2$. Thus, it is important to analyze for the presence of metal contaminants in electronic-grade hydrochloric acid (HCl). SEMI Standard C27-0708 specifies the maximum concentration of metal contaminants by element and tier for hydrochloric acid.

Inductively coupled plasma mass spectrometry (ICP-MS) has been used for determination of ultra-trace impurity levels in various process chemicals. Nevertheless, under conventional plasma conditions, argon ions combine with matrix components to generate polyatomic interferences. Examples of chloride-based interferences observed during the analysis of HCl are listed in Table 1.

Table 1. **Chloride interferences observed during HCl analysis.**

Interference	Analyte
$^{37}Cl^{1}H_2$	^{39}K
$^{35}Cl^{16}O$	^{51}V
$^{35}C^{16}O^{1}H$	^{52}Cr
$^{37}Cl^{16}O$	^{53}Cr
$^{37}Cl^{16}O^{16}O$	^{69}Ga
$^{40}Ar^{35}Cl$	^{75}As
$^{40}Ar^{37}Cl$	^{77}Se

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Traditionally, two primary techniques have been used to overcome the interferences: double-focusing high resolution ICP-MS (HR-ICP-MS) and cool plasma. With HR-ICP-MS, the resolution of the mass analyzer is increased so that the analytes and interfering ions are separated. While cool plasma has been shown to be effective in reducing argon-based interferences, it is more prone to matrix suppression than hot plasma, especially for refractory elements or elements with high ionization potentials. In addition, some analyses cannot be accomplished successfully with HR-ICP-MS or cool plasma, such as the determination of the major vanadium (V) isotope and the only isotope of arsenic (As) in HCl because of the formation of ClO^+ and $ArCl^+$ at m/z 51 and 75, respectively. The theoretical resolutions required to separate V^+ from ClO^+ and As^+ from $ArCl^+$ will mean a drop in ion transmission to 18% and 2%, respectively. This makes low part per trillion (ppt) determination of V and As extremely difficult. The cool plasma not only cannot reduce the formation of ClO^+ and $ArCl^+$, it results in significant drop of As^+ and V^+ sensitivity: As^+ ion formation is reduced in cool plasma due to its high ionization potential, and V-oxide (formed in the plasma) cannot be effectively decomposed to form V^+.

Dynamic Reaction Cell™ (DRC) is an alternative technique to eliminate these kinds of interferences utilizing hot plasma. The DRC uses a quadrupole mass filter to create Dynamic Bandpass Tuning (DBT), where only ions of a specific mass range pass through the cell, thus allowing only controlled reactions to take place where undesirable by-product ions do not form within the cell, even when very reactive gases, such as NH_3 or O_2, are used.

The PerkinElmer NexION® 300 ICP-MS incorporates Universal Cell Technology™, which allows the use of Collision mode (with kinetic energy discrimination), Reaction mode (incorporating DBT), and Standard mode (where a cell gas is not used). The user can select whichever mode(s) are most appropriate for the application.

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

Experimental conditions

Normally, the concentration of HCl is around 35%. In this experiment, a direct analysis is carried out on 20% ultra pure HCl (Tamapure-AA 10, Tama Chemicals, Tokyo, Japan). 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). The operating conditions were determined using a 100 ppt standard solution in 1% HNO_3. Since a robust, high-temperature plasma was always used, optimization with matrix-matched standards was not required. Instrumental parameters and sample introduction components are shown in Table 2.

Results

HCl samples were quantitatively analyzed using additions calibrations; the calibration curves for As, Se, Cr, Fe, V and K are shown in Figures 1–6 and demonstrate good linearity, which is possible with all the polyatomic interferences removed by the reactive NH_3 gas in combination with the bandpass. In the case of As and Se, reactive O_2 is used to convert them into AsO^+ and SeO^+, moving them away from interferences at mass 75 and 80 arising from $^{40}Ar^{35}Cl$ and $^{40}Ar_2$.

Table 2. **Instrumental parameters and sample introduction components for the NexION 300S ICP-MS.**

Spray Chamber:	Quartz Cyclonic	Plasma Gas:	18 L/min
Torch:	Standard Quartz	Auxiliary Gas:	1.1 L/min
Torch Injector:	2-mm Quartz	Nebulizer Flow:	1.01 L/min
Sampler Cone:	Platinum	RF Power:	1500 W
Skimmer Cone:	Platinum	Integration Time:	1 sec/mass
Nebulizer:	Meinhard® Type A Concentric Quartz	Replicates:	3

The detection limits (DLs) and background equivalent concentrations (BECs) were both determined in 20% HCl, while accounting for the sensitivities in 20% HCl. DLs were calculated by multiplying the standard deviation of the blank by three, and BECs were determined by measuring the signal intensities. A spike recovery test was carried out based on SEMI guidelines. According to SEMI, the spike level must be 50% of the proposed specification level, and the recovery should be between 75% and 125% of the expected value. The specification level for Tier C grade is 100 ppt in 37% HCl; as such, 25 ppt spikes in 20% HCl were used in this experiment. Recoveries were determined from 25 ng/L spikes. The results are summarized in Table 3.
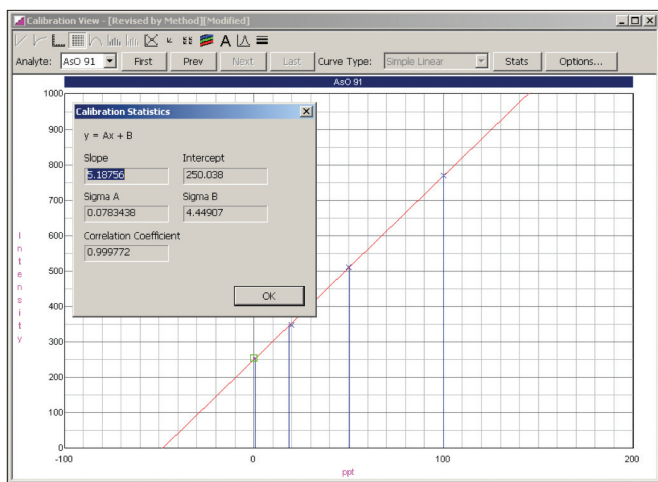

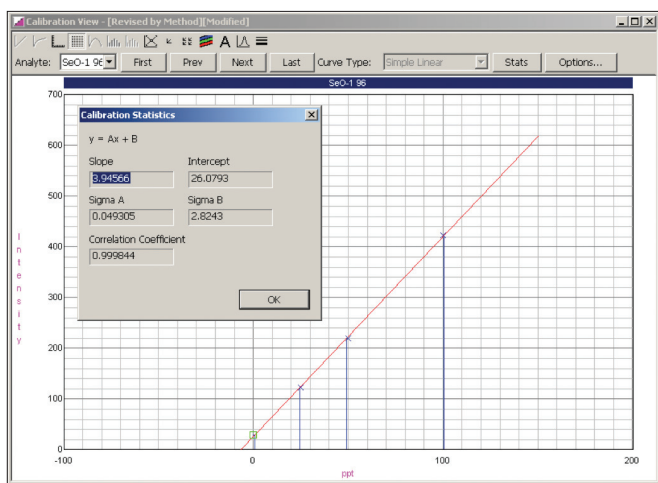Figure 1. As calibration, as AsO91, with O_2 cell gas flow of 0.5 mL/min.

Figure 2. $^{80}Se^+$ calibration, as $^{96}SeO^+$, with O_2 cell gas flow of 0.5 mL/min.

Table 3. Detection limits (DLs) and background equivalent concentrations (BECs) for all analytes in 20% HCl, spike recoveries at 25 ng/L level.

Analyte	Mass	Cell Gas Flow* (mL/min)	RPq	DL (ppt)	BEC (ppt)	25 ppt Recovery
Li	7	0	0.25	0.02	0.04	101%
Be	9	0	0.25	0.02	0.01	103%
B	11	0	0.25	2	10	92%
Na	23	0	0.25	0.3	< DL	101%
Mg	24	0	0.25	0.2	0.7	102%
Al	27	0.6	0.5	0.2	2	102%
K	39	1	0.65	1	30	105%
Ca	40	1	0.5	0.3	2.1	100%
Ti	48	0.3	0.75	0.5	1.3	97%
V	51	1	0.75	0.1	0.1	93%
Cr	52	0.6	0.7	1	7	96%
Mn	55	0.6	0.7	0.2	0.6	101%
Fe	56	0.6	0.5	1	10	90%
Co	59	0.3	0.5	0.4	< DL	103%
Ni	60	0.3	0.7	1	4	91%
Cu	63	0.3	0.7	0.3	4.7	105%
Zn	66	0.3	0.65	0.4	2	100%
Ga	71	0.6	0.65	0.1	0.4	101%
Ge	74	0.3	0.65	0.6	3	94%
As	91	0.5 (O_2)	0.5	5	50	94%
Sr	88	0	0.25	0.09	0.75	101%
Se	96	0.5 (O_2)	0.5	5	7	99%
Zr	90	0	0.25	0.7	3	101%
Nb	93	0	0.25	0.1	0.5	100%
Mo	98	0	0.25	0.3	0.6	98%
Ru	102	0	0.25	0.1	< DL	104%
Rh	103	0	0.25	0.1	< DL	101%
Pd	106	0	0.25	0.3	< DL	102%
Ag	107	0	0.25	0.1	0.2	99%
Cd	114	0	0.25	0.2	0.4	104%
In	115	0	0.25	0.1	0.5	102%
Sn	120	0	0.25	0.9	5.2	95%
Sb	121	0	0.25	0.8	2.7	103%
Ba	138	0	0.25	0.02	0.04	102%
Ta	181	0	0.25	0.02	0.01	101%
W	184	0	0.25	0.2	< DL	100%
Pt	195	0	0.25	0.3	< DL	99%
Au	197	0	0.25	0.1	0.3	102%
Tl	205	0	0.25	0.02	< DL	101%
Pb	208	0	0.25	0.06	0.15	101%
Bi	209	0	0.25	0.07	< DL	102%
U	238	0	0.25	< 0.02	< DL	102%

*Cell gas used is NH_3, unless otherwise noted

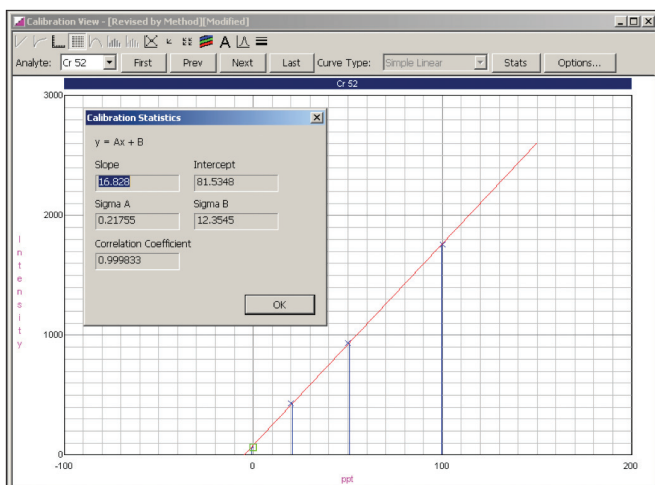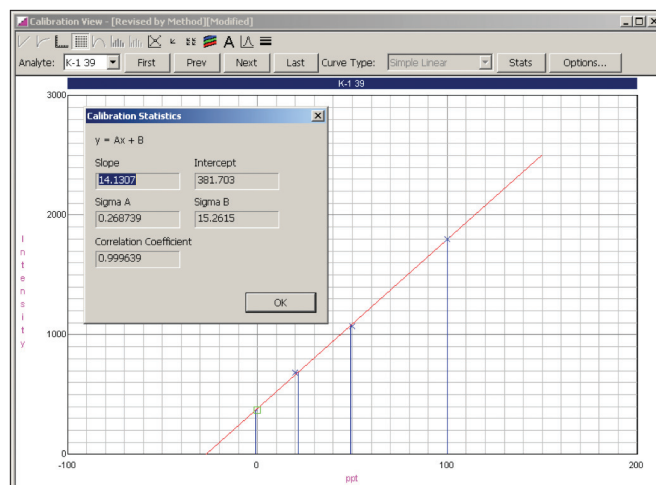*Figure 3.* Cr calibration, with NH$_3$ cell gas flow of 0.6 mL/min.

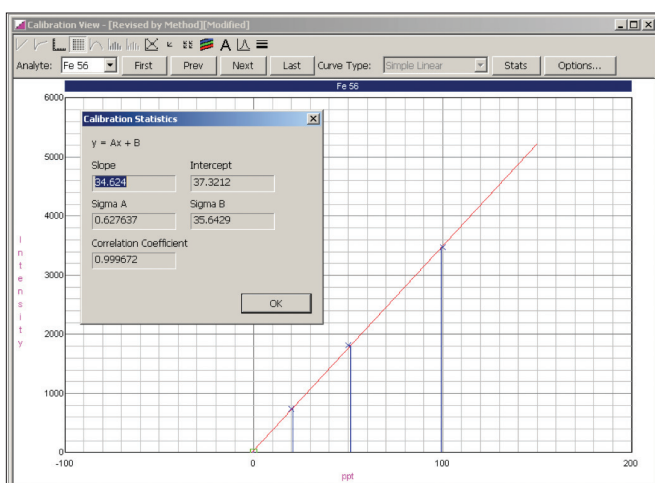*Figure 4.* Fe calibration, with NH$_3$ cell gas flow of 0.6 mL/min.

Figure 5. V calibration, with NH$_3$ cell gas flow of 1 mL/min.
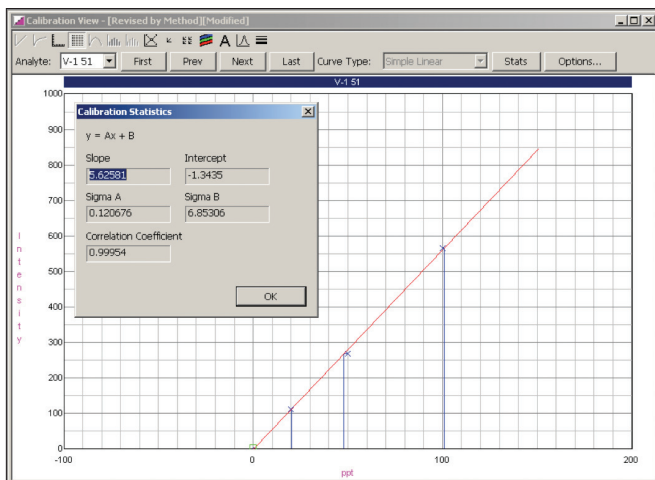

Figure 6. K calibration, with NH$_3$ cell gas flow of 1 mL/min.

Figures 7 and 8 show excellent stability, with RSDs of < 3% over 2 hours. The stability results, combined with the spike recovery data, highlight the ability of the NexION 300S ICP-MS for the determination of all SEMI-required elements in the HCl matrix.
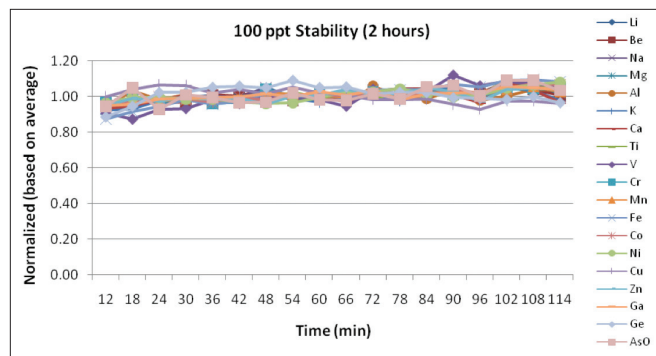
Conclusion

Figure 7. Two-hour stability (normalized intensity) for a 100 ng/L spike for first group of analytes.
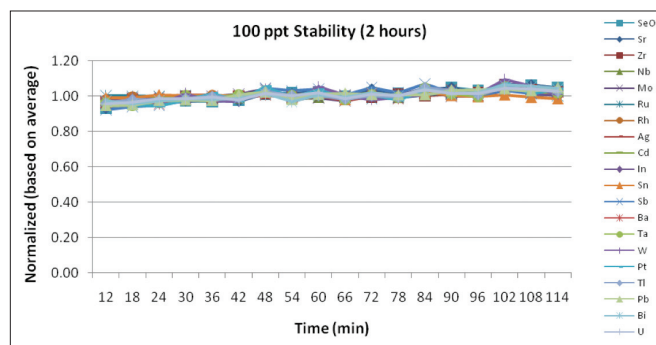

Figure 8. Two-hour stability (normalized intensity) for a 100 ng/L spike for second group of analytes.

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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 HCl. The data demonstrates the effectiveness of Reaction mode of the UCT for the elimination of chloride-derived interferences. By applying Reaction mode, 20% HCl can be analyzed directly for contaminants at SEMI Tier C levels, without the need for cumbersome sample pre-treatment. 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 C27-0708, SEMI Standards, http://www.semi.org/en/index.htm

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