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Determination of Impurities in Electronic-Grade Hydrochloric Acid with the NexION 5000 ICP-MS

Introduction

During the production of semiconductor devices, it is crucial to ensure that the silicon wafers are free of contaminants and impurities. Wafers are subjected to a wet clean process before high-temperature operations. The most commonly used technique is called RCA Clean, developed by Werner Kern from Radio Corporation of America in 1965.[1] In the four-step procedure of cleaning, organic films, some metals and particles are first removed, followed by hydrous oxide stripping. The final step uses the so-called RCA-2 solution to remove the remaining traces of metallic ion contamination and create a thin inert layer that protects the surface from further contamination. The RCA-2, commonly referred to as SC-2 (Standard Clean 2) or HPM (Hydrogen Peroxide Mixture), is a mixture of $H_2O:HCl:H_2O_2$ (6:1:1 by volume).

The use of high-purity chemicals during the cleaning process is critical to the semiconductor product's overall quality and performance. Therefore, it is essential to analyze electronic-grade hydrochloric acid (HCl) and hydrogen peroxide[2] for the presence of trace metal contaminants. The SEMI Standard C27-0918[3] specifies the maximum concentration of metal contaminants by element and tier for hydrochloric acid. With more and more elements added into the list of critical analytes by the semiconductor manufacturers, the determination of ultra-trace impurity levels is now commonly carried out using inductively coupled plasma mass spectrometry (ICP-MS).

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In an ICP-MS analysis, in addition to spectral interferences from Ar, O_2, N_2 and H_2, the HCl matrix could generate some further 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
$^{37}Cl^1H_2$	^{39}K
$^{35}Cl^{16}O$	^{51}V
$^{35}C^{16}O^1H$, $^{37}C^{16}O^1$	^{52}Cr, ^{53}Cr
$^{37}Cl^{16}O^{16}O$, $^{37}Cl^{16}O^{16}O^1H_2$	^{69}Ga, ^{71}Ga
$^{35}Cl^{35}Cl$, $^{35}Cl^{37}Cl$, $^{37}Cl^{37}Cl$	^{70}Ge, ^{72}Ge, ^{74}Ge
$^{40}Ar^{35}Cl$	^{75}As
$^{40}Ar^{37}Cl$	^{77}Se

This application note demonstrates the extreme power of PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS to remove interferences in order to achieve low BECs (background equivalent concentrations) in HCl for all analytes.

Experimental

Sample and Standard Preparation

A direct analysis was carried out on undiluted 20% ultra-pure HCl (Tamapure-AA 10, Tama Chemicals, Tokyo, Japan) using a method of standard addition (MSA). Standard solutions were prepared from 10 mg/L multi-element standards (PE Pure, PerkinElmer, Shelton, Connecticut USA) via serial dilutions, with the final standards being spiked directly into 20% HCl.

Instrumentation

The instrument used for the described experiments was a NexION 5000 Multi-Quadrupole ICP-MS[4] (PerkinElmer). The NexION 5000's Universal Cell Technology (UCT) function, while operating in Reaction (DRC) mode, is an extremely effective technique to eliminate atomic and polyatomic interferences even in hot plasma conditions. The UCT uses a quadrupole mass filter to create dynamic bandpass tuning, wherein only ions of a specific mass range pass through the cell, thus allowing only controlled reactions to take place, preventing undesirable by-product ions from forming within the cell even when very reactive gases, such as 100% NH_3 and O_2, are used. The NexION 5000 ICP-MS – running on a patented 34-MHz solid-state RF generator (patent no. 9,420,679), especially created for ICP-MS operation, together with the LumiCoil™ RF coil and the second-generation Triple Cone Interface (TCI) with OmniRing™ technology – provides superior analytical performance with great sensitivity and stability.

Fast power-switching between Cold and Hot Plasma modes is made possible by the balanced and free-running RF generator, allowing multi-mode methods to leverage these technologies in combination with a cell-based Reaction mode (in the Universal Cell) and multi-quadrupole technology. As a result, superior polyatomic interference removal is achieved that further improves detection limits (DLs) and background equivalent concentrations (BECs).

Instrumental Conditions

All preparation and analysis steps were performed under a Class 100 performance clean booth within a controlled laboratory room.

In this work, three reaction gases (NH_3, H_2, and O_2) were used to remove all spectral interferences on measured analytes. To analyze P, Ti, As, and Se most effectively, O_2 is recommended as a reaction gas in Mass Shift mode to create oxide ions with analytes and measure them at higher masses away from interferences existing on their original masses. NH_3 is applicable for 18 elements analyzed mostly in MS/MS mode.

While this work demonstrates Cold Plasma conditions being applied for few elements to provide the lowest background equivalent concentrations (BECs), the NexION 5000 ICP-MS can achieve ppt levels of BECs in this matrix even in Hot Plasma mode.

The operating conditions were determined using a 200-ppt standard solution in 1% HNO_3. Instrumental parameters and sample introduction components are shown in Table 2.

Table 2. NexION 5000 ICP-MS Instrumental Conditions.

Parameter	Value
Sample Uptake	~500 µL/min
Nebulizer	PFA ST3
Spray Chamber	SilQ™ Cyclonic (Standard)
Torch	SilQ One Piece with 2-mm Injector
RF Power	1500 W (Hot), 700 W (Cold)
Reaction Gases	NH_3, O_2 and H_2

Results and Discussion

20% HCl was quantitatively analyzed using the method of standard addition (MSA). The calibration curves for K, V, Cr, Ge, As, and Se are shown in Figure 1. Even though they were obtained using different modes (MS/MS and Mass Shift), reaction gases (NH_3 and O_2) and plasma conditions (Hot and Cold), they demonstrate good linearity and low BECs, which is only possible when all the polyatomic interferences are removed by reactions with pure, undiluted NH_3 and O_2 combined with the Universal Cell's dynamic bandpass tuning.
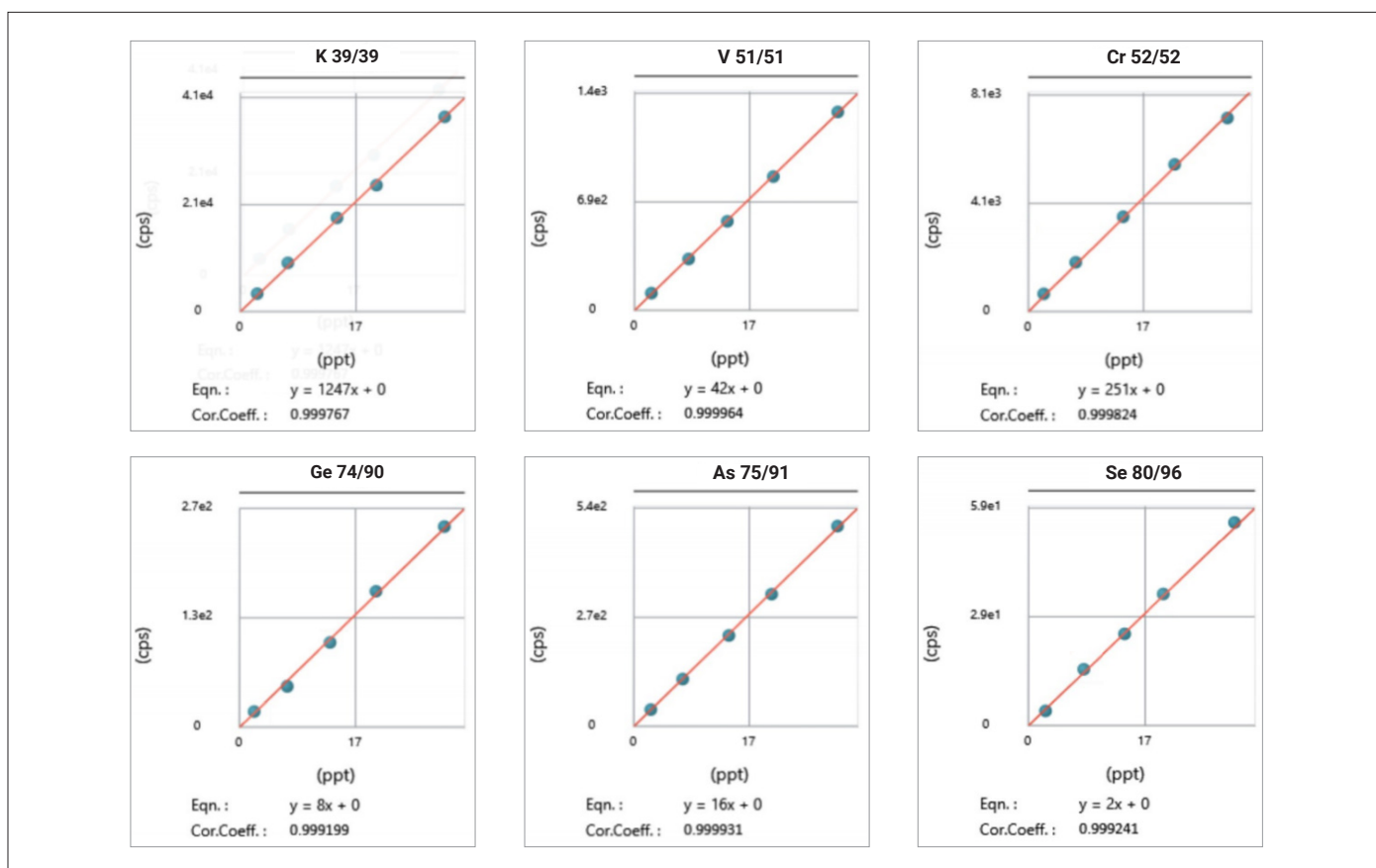
Figure 1. Calibration curves for K, V, and Cr in MS/MS mode with NH$_3$, Ge in Mass Shift mode with NH$_3$, and As and Se in Mass Shift mode with O$_2$.

One very interesting case is the analysis of Ge because its major isotope at mass 74 suffers serious interference from the dimer of $^{37}Cl_2$. While NH$_3$ can remove the dimer of $^{37}Cl_2$ via a charge transfer reaction, Ge itself is quite reactive to NH$_3$, resulting in lower intensity at mass 74. Taking advantage of Ge's reactivity and the Mass Shift capability of NexION 5000 ICP-MS, Ge can be measured as a GeNH$_2$$^+$ cluster at mass 90, or as Ge(NH$_3$)NH$_2$$^+$ cluster at mass 107, moving it away from the $^{37}Cl_2$ interference at mass 74. The cluster formation can be demonstrated by a product ion scan for ^{74}Ge with Q1 set at mass 74 and Q3 scanning from mass 62 to 120 (Figure 2). Sensitivity of each cluster depends on the NH$_3$ flows.

Another example of the power of the NexION 5000 system is the $^{35}Cl^{16}O^+$ and $^{35}Cl^{16}OH^+$ interference removal on ^{51}V and ^{52}Cr. V$^+$ and Cr$^+$ ions have a low reactivity rate with NH$_3$, while $^{35}Cl^{16}O^+$ and $^{35}Cl^{16}OH^+$ react spontaneously. This spontaneous reaction, nevertheless, will also create by-products such as $^{35}ClNH_2$$^+$ and (NH$_3$)$_2$NH$_4$$^+$ interfering with V$^+$ and Cr$^+$ in the absence of bandpass within the reaction cell, as is the case of an octupole cell or a quadrupole cell when the bandpass is open with a low RPq value setting.
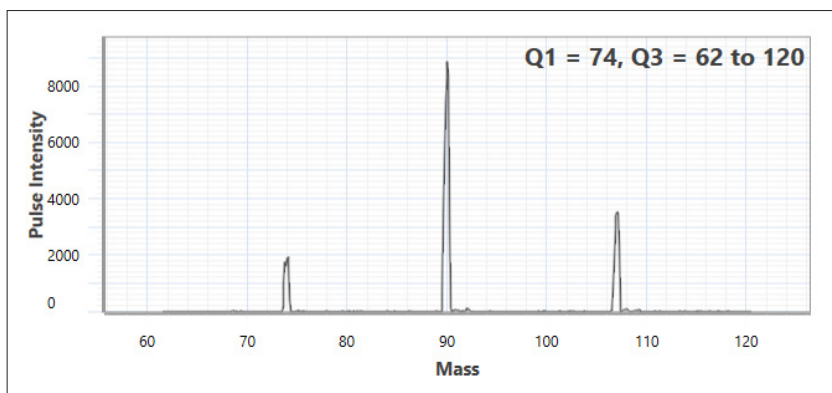

Figure 2. ^{74}Ge Product ion scan showing two Ge clusters with NH$_3$ at mass 90 and 107.

The importance of bandpass can be demonstrated through a spectral scan of a clean HCl sample with a minimal presence of V, when Q1 is set at mass 51 (51V and $^{35}Cl^{16}O^+$), and Q3 is scanning masses from 34 to 53. With RPq set to a low value of 0.25, equivalent to the operation of an octupole, quite substantial counts can be observed at mass 35 and some at masses 51 and 52 (Figure 3). It was concluded that the ions observed at mass 35 are NH$_3$NH$_4$$^+$, at mass 51 are $^{35}ClNH_2$, and at mass 52 are (NH$_3$)$_2$NH$_4$$^+$.

When RPq is increased to a higher value, the side reactions that produce the by-product interferences at masses 51 and 52 are stopped, allowing very low BEC detection of V and Cr in HCl, as shown in Figure 4. More information on the advantage of Reaction Cell with dynamic bandpass tuning can be found in "Multi-Quadrupole ICP-MS: Pushing limits of detection to the next decimal".[5]
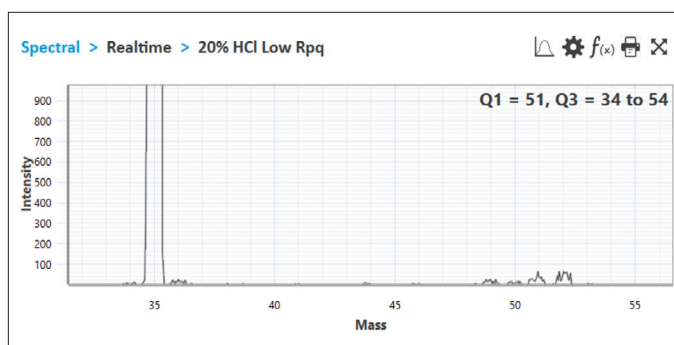
Figure 3. Product ion scan of a 20% HCl with Q2 bandpass open acting as ion guide (low RPq).

Figure 4. Product ion scan of a 20% HCl with Q2 bandpass for mass-dependent cut off (high RPq).

The detection limits (DLs) and background equivalent concentrations (BECs) were determined in 20% HCl. DLs were calculated by multiplying the standard deviation of seven measurements of the blank by three. These values are greatly affected by the impurity level in samples.

A spike recovery test was carried out based on SEMI guidelines. According to SEMI, the spike level must be at least 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. However, 10 ppt spikes in 20% HCl were used in this experiment, much lower than required. The results are summarized in Table 3.

Table 3. BECs, DLs and Spike Recoveries in 20% HCl.

Element	Isotope Selection (Q1/Q3)	Scan Type	Cell Mode	BEC (ppt)[*1]	DL (ppt)[*1]	10 ppt Recovery (%)[*2]
Li	7/7	MS/MS	Cold Standard	0.007	0.002	102
Be	9/9	MS/MS	Standard	<DL	0.07	101
B	11/11	MS/MS	Standard	1.4	0.3	97.5
Na	23/23	MS/MS	Cold Standard	0.04	0.01	101
Mg	24/24	MS/MS	Cold Standard	0.07	0.02	98.9
Al	27/27	MS/MS	Cold Ammonia DRC	0.15	0.05	99.0
Si	28/28	MS/MS	Hydrogen DRC	14.5	0.3	101
P	31/47	Mass Shift	Oxygen DRC	0.009	0.006	87.7
S	32/48	Mass Shift	Oxygen DRC	0.77	0.04	102
K	39/39	MS/MS	Cold Ammonia DRC	0.05	0.02	103
Ca	40/40	MS/MS	Cold Ammonia DRC	0.08	0.03	99.1
Ti	48/64	Mass Shift	Oxygen DRC	0.1	0.1	106
V	51/51	MS/MS	Ammonia DRC	<DL	0.08	105
Cr	52/52	MS/MS	Cold Ammonia DRC	<DL	0.04	104
Mn	55/55	MS/MS	Cold Ammonia DRC	<DL	0.009	103
Fe	56/56	MS/MS	Cold Ammonia DRC	0.44	0.06	99.2
Co	59/59	MS/MS	Ammonia DRC	0.021	0.006	97.9
Ni	60/60	MS/MS	Cold Ammonia DRC	0.06	0.05	104
Cu	63/63	MS/MS	Cold Ammonia DRC	1.4	0.2	97.7
Zn	66/66	MS/MS	Ammonia DRC	<DL	0.6	105
Ga	69/69	MS/MS	Cold Ammonia DRC	<DL	0.003	99.4
Ge	74/90	Mass Shift	Ammonia DRC	0.8	0.3	106
As	75/91	Mass Shift	Oxygen DRC	13	4	102
Se	80/96	Mass Shift	Oxygen DRC	<DL	1	123
Sr	88/88	MS/MS	Ammonia DRC	<DL	0.005	103
Zr	90/106	Mass Shift	Oxygen DRC	<DL	0.02	93.2

Table 3. BECs, DLs and Spike Recoveries in 20% HCl continued...

Element	Isotope Selection (Q1/Q3)	Scan Type	Cell Mode	BEC (ppt)[*1]	DL (ppt)[*1]	10 ppt Recovery (%)[*2]
Nb	93/93	MS/MS	Standard	0.9	0.3	102
Mo	98/98	MS/MS	Ammonia DRC	<DL	0.1	99.2
Ru	102/102	MS/MS	Standard	<DL	0.2	99.1
Rh	103/103	MS/MS	Cold Standard	0.025	0.009	99.1
Pd	106/106	MS/MS	Standard	<DL	0.2	99.1
Ag	107/107	MS/MS	Standard	0.7	0.1	97.2
Cd	111/111	MS/MS	Standard	<DL	0.6	101
In	115/115	MS/MS	Standard	0.2	0.1	107
Sn	118/118	MS/MS	Standard	8	2	96.5
Sb	121/121	MS/MS	Ammonia DRC	0.2	0.1	107
Ba	138/138	MS/MS	Standard	1.0	0.5	93.2
Hf	180/180	MS/MS	Standard	<DL	0.2	95.7
Ta	181/181	MS/MS	Standard	<DL	0.06	95.7
W	184/184	MS/MS	Standard	<DL	0.06	100
Pt	195/195	MS/MS	Cold Standard	<DL	0.2	97.7
Au	197/197	MS/MS	Standard	<DL	0.3	92.2
Tl	205/205	MS/MS	Ammonia DRC	<DL	0.01	97.1
Pb	208/208	MS/MS	Ammonia DRC	<DL	0.07	97.2
Bi	209/209	MS/MS	Standard	<DL	0.06	94.0
U	238/238	MS/MS	Standard	<DL	0.06	99.9

*1: Si, P, S values are shown in ppb
*2: Spikes for P were 1 ppb and spikes for S, Si were 10 ppb

Another important attribute of good analysis, besides low BECs and excellent DLs, is the long-term stability of an ICP-MS system to handle corrosive matrices, such as concentrated hydrochloric acid. Figure 5 shows excellent stability of 50-ppt multi-element spikes into 20% HCl with RSDs of < 3% and variation <15% over five hours. This stability is brought about through the novel design of the second-generation Triple Cone Interface with OmniRing, developed specifically for the NexION 5000 ICP-MS. More information on this can be found in the technical note "Advantages of a Novel Interface Design for NexION 5000 ICP-MS".[6]

Figure 5. Signal stability for a multi-mode analysis of 50 ppt spiked in undiluted (20%) HCl.

Conclusion

The NexION 5000 Multi-Quadrupole ICP-MS is shown to be robust and suitable for the routine quantification of ultra-trace impurities at the ng/L level in concentrated HCl. The data demonstrates the effectiveness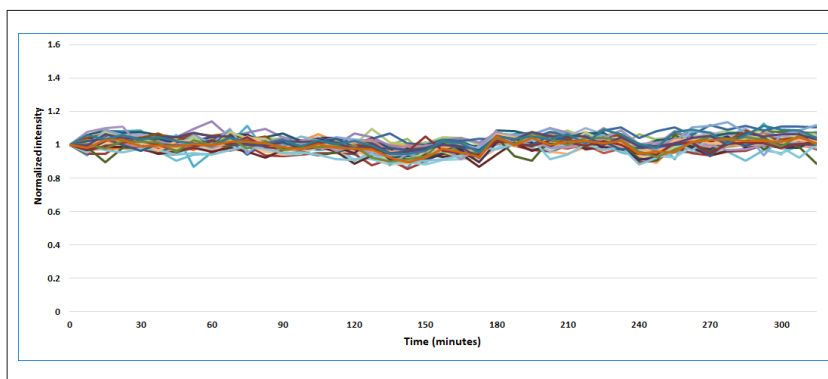 of Reaction mode in the Universal Cell coupled with multi-quadrupole operation to eliminate chloride-derived interferences. By applying the most effective Reaction mode, 20% HCl can be analyzed directly for contaminants at SEMI Tier C levels, without the need for cumbersome sample pre-treatment or dilution. Employing computer-controlled switching between Hot and Cold Plasma as well as Standard and Reaction modes in the Universal Cell, interference-free analysis for all elements crucial to semiconductor manufacturing is possible in a single sample run.

References

1. Wolf S. et al., "Silicon Processing for the VLSI Era," Vol. 1, Lattice Press, Sunset Beach, CA, 2000.

2. Ong K. et al., "Analysis of Semiconductor-Grade Hydrogen Peroxide Using the NexION 5000 ICP-MS", PerkinElmer Application Note, 2020.

3. SEMI Standard C27-0918, Specification and Guide for Hydrochloric Acid.

4. "NexION 5000 Multi-Quadrupole ICP-MS", PerkinElmer Product Note, 2020.

5. Kroukamp E. et al. "Multi-Quadrupole ICP-MS: Pushing limits of detection to the next decimal", Spectroscopy 35 (9) 19, 2020.

6. Badiei H. et al., "Advantages of a Novel Interface Design for NexION 5000 ICP-MS", PerkinElmer Technical Note, 2020.

Consumables Used

Component	Part Number
Sample Probe, 0.3 mm ID	N8152513
PFA ST3 Nebulizer	N8152378
SilQ Spray Chamber	N8152539

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