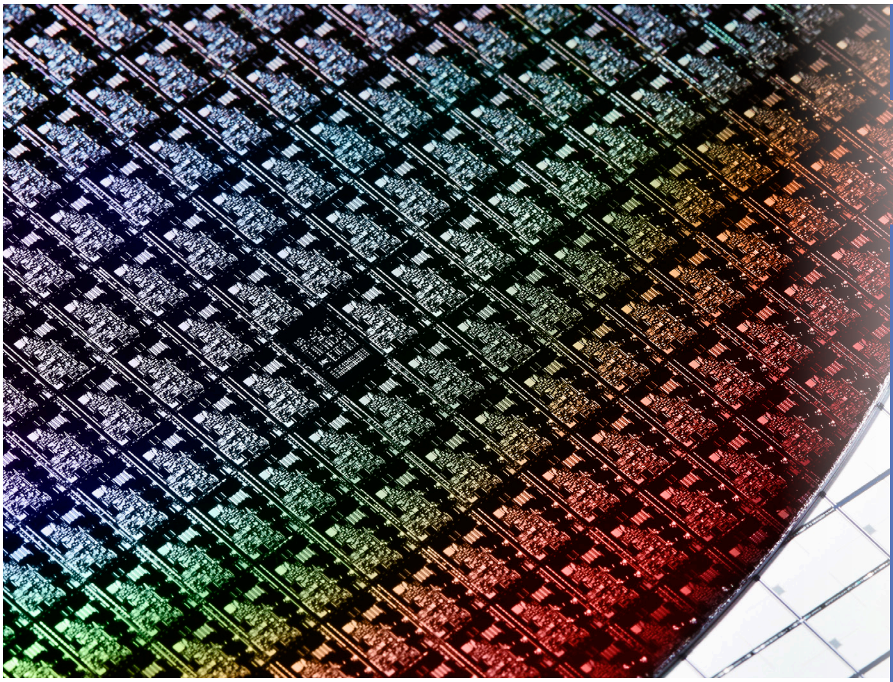

ICP - Mass Spectrometry

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Analysis of Impurities in Semiconductor-Grade Hydrochloric Acid with the NexION 2000 ICP-MS

Introduction

During the production of semiconductor devices, a series of acids are commonly used for a variety of processes. One of the more important chemicals is hydrochloric acid (HCl), whose primary use is to clean the surface of silicon wafers as part of a mixture with hydrogen peroxide and water. As semiconductor devices continue to shrink in size, the purity of the chemicals used in their production increases in importance, as even small levels of impurities can cause device failure. While international SEMI Standards exist for specifying the maximum concentrations of metal impurities (SEMI Standard C27-07081 is specific for HCl), semiconductor device manufacturers are pushing for ever-lower levels, placing the burden on the chemical suppliers. As a result, analytical instrumentation must also be capable of accurate measurements at ever-lower concentrations.

The best technique for measuring low metal concentrations is inductively coupled plasma mass spectrometry (ICP-MS) because of its ability to accurately measure ultra-trace concentrations: ng/L (part-per-trillion) or lower. Nevertheless, under conventional plasma conditions, argon, oxygen, and hydrogen ions combine with matrix elements which can produce polyatomic interferences on elements of interest.

PerkinElmer's NexION® 2000 ICP Mass Spectrometer offers several options for dealing with polyatomic interferences to allow for interference-free analyses, limited only by contamination. The Universal Cell with three gas channels allows for the ultimate flexibility when operated in Reaction mode. Because the Universal Cell is a quadrupole, the benefits of a quadrupole can be realized, including the ability to control the reaction chemistry through the implementation of the "q" parameter of the quadrupole. Controlling the chemistry allows the use of highly reactive gases in the cell, which greatly enhances the removal of interferences. With three gas channels available, three different gases can be used in the same method for ultimate flexibility in the ability to choose the best gas for a particular interference. In the analysis of HCl, the removal of chloride interferences is crucial and most effectively accomplished with 100% pure ammonia and 100% oxygen. Table 1 shows both chloride and non-chloride polyatomic interferences which form on analytes during the analysis of hydrochloric acid.

Table 1. Polyatomic Interferences Observed During Analysis of Hydrochloric Acid.

Analyte	m/z	Interferences
K	39	${}^{38}ArH$, ${}^{37}ClH_2$
Ca	40	${}^{40}Ar$
V	51	${}^{35}Cl^{16}O$
Cr	52, 53	${}^{35}Cl^{16}OH$, ${}^{37}Cl^{16}O$
Fe	56	${}^{40}Ar^{16}O$
Ga	69, 71	$Cl^{16}O_2H_2$
Ge	70, 72, 74	Cl_2
As	75	${}^{40}Ar^{35}Cl$
Se	77	${}^{40}Ar^{37}Cl$

Another option for dealing with polyatomic interferences available on the NexION 2000 ICP-MS is Cool Plasma mode, in which the power of the plasma is reduced, which limits ionization of argon (Ar) and the formation of polyatomic species. Although cool plasma has been used for many years, it has been limited by its ability to deal with heavy matrices, such as concentrated acids. As a result of the low power, ionization has been greatly suppressed in Cool Plasma mode. However, the NexION 2000's unique solid-state RF generator overcomes this limitation. The combination of Cool Plasma and Reaction modes provides the ultimate reduction of polyatomic interferences, allowing ultra-trace levels to be measured, limited only by contamination.

This work showcases the unique abilities of the NexION 2000 ICP-MS for the analysis of semiconductor-grade HCl, meeting or surpassing the SEMI standards.

Experimental

Samples and Sample Preparation

In semiconductor fabs, 35-38% HCl is most commonly used and is available from a number of suppliers. For analysis, it is generally diluted two times with ultrapure deionized water. Therefore, ultrapure 20% HCl (Tamapure-AA-10, Moses Lake Industries, Moses Lake, Washington, USA) was used in this work and analyzed without dilution. Calibration standards (10, 20, 40 ng/L) were made from the 10 mg/L multi-element stock solutions via serial dilution, with the final standards being prepared in 20% HCl.

Instrumental Conditions

All analyses were performed on the NexION 2000 S ICP-MS, using the SMARTintro™ High Purity sample introduction module. Table 2 shows the instrumental parameters used.

Table 2. Instrumental Parameters.

Component/Parameter	Type/Value
Nebulizer	PFA-ST with 0.5 mm id tubing
Sample Uptake Rate	0.4 mL/min
Spray Chamber	SiLQ quartz cyclonic in PC3
Spray Chamber Temperature	2 °C
Torch/Injector	SiLQ one piece, with 2.0 mm id
RF Power	1600 W (hot) 600 W (cool)
Cones	Pt
Integration Time	1 sec / isotope
Reaction Gases	Ammonia (100%) Oxygen (100%)

For most effective removal of polyatomic interferences, both Reaction mode and Cool Plasma were used. To maximize the effectiveness of Reaction mode, 100% ammonia and 100% oxygen were used in two different ways: while ammonia effectively removes interferences at the analytical mass, oxygen was used in mass-shift mode, which looks at the product ion of the analyte and oxygen. This was found to be most effective for arsenic (As). Syngistix™ for ICP-MS software allows all modes (i.e. Reaction, Standard, Hot Plasma, Cool Plasma) to be run in a single method using a single Conditions file, improving ease-of-use and analytical speed – no need to run samples multiple times under different conditions. Table 3 displays the method parameters used for this work.

Results and Discussion

Interference Reduction Strategies in Reaction Mode

Interferences were removed in Reaction mode in two different ways: removing the interference at the analytical mass and shifting the analyte to a new mass away from the interference.

An example of removing the interference at the analytical mass is the removal of the ClO^+ on V^+ at m/z 51. Although ammonia reacts rapidly with ClO^+ to remove it, the reaction is driven to completion by the ability to use 100% ammonia in the cell. In addition, because the Universal Cell is a quadrupole, the RPq parameter can be adjusted to control the chemistry and prevent the formation of new interferences, which is crucial when using highly reactive gases. This is particularly important in removing the ClO^+ interference since one of the intermediate products is Cl^+, which reacts with NH_3 to form $ClNH_2^+$ at m/z 51. However, because the RPq parameter serves as a low mass filter, it can be set to make Cl^+ unstable in the cell, which prevents the formation of $ClNH_2^+$ and allows V^+ to be measured interference-free.

Analytically, this functionality is demonstrated in Figure 1, which shows the optimization of the RPq parameter for 1 µg/L V in 10% HCl. As the RPq parameter increases, the background equivalent concentration (BEC) decreases sharply at RPq=0.7, which represents where Cl^+ is no longer stable in the Universal Cell. As a result, Cl^+ is ejected from the cell, meaning that the reaction to $ClNH_2^+$ can no longer occur, resulting in interference-free analysis of V^+ at m/z 51.

The second method of dealing with interferences is using Reaction mode in mass-shift mode, where the analyte reacts with the reaction gas moving it to a new analytical mass. An example of this is the analysis of arsenic (As), which reacts rapidly with oxygen to form AsO^+ at m/z 91, away from the $ArCl^+$ interference at m/z 75. Because $ArCl^+$ does not react with oxygen (O_2), AsO^+ is measured interference-free. Figure 2 shows the conversion of As^+ to AsO^+ as a function of oxygen flow: as the O_2 flow increases, the signal for $^{75}As^+$ decreases, while the signal for AsO^+ increases, demonstrating complete conversion.

Table 3. Method Parameters.

Analyte	Mass	Plasma Mode	Cell Mode	Cell Gas
Li	7	Cool	Standard	---
Be	9	Hot	Standard	---
B	11	Hot	Standard	---
Na	23	Cool	Standard	---
Mg	24	Cool	Standard	---
Al	27	Cool	Standard	---
K	39	Cool	Reaction	NH_3
Ca	40	Cool	Reaction	NH_3
Ti	48	Hot	Reaction	NH_3
V	51	Hot	Reaction	NH_3
Cr	52	Cool	Reaction	NH_3
Mn	55	Cool	Reaction	NH_3
Fe	56	Cool	Reaction	NH_3
Co	59	Cool	Reaction	NH_3
Ni	60	Cool	Standard	---
Cu	63	Cool	Reaction	NH_3
Zn	64	Hot	Reaction	NH_3
Ga	71	Cool	Reaction	NH_3
Ge	74	Hot	Reaction	NH_3
AsO	91	Hot	Reaction	O_2
SeO	98	Hot	Reaction	O_2
Sr	88	Hot	Reaction	NH_3
Zr	90	Hot	Standard	---
Nb	93	Hot	Standard	---
Mo	98	Hot	Reaction	NH_3
Ru	102	Hot	Standard	---
Rh	103	Cool	Standard	---
Pd	106	Hot	Standard	---
Ag	107	Hot	Standard	---
Cd	114	Hot	Standard	---
In	115	Hot	Reaction	NH_3
Sn	118	Hot	Standard	---
Sb	121	Hot	Standard	---
Ba	138	Hot	Standard	---
Ta	181	Hot	Standard	---
W	184	Hot	Standard	---
Pt	195	Hot	Standard	---
Au	197	Hot	Standard	---
Tl	205	Hot	Reaction	NH_3
Pb	208	Hot	Reaction	NH_3
Bi	209	Hot	Reaction	NH_3
U	238	Hot	Standard	---

One of the concerns of measuring AsO^+ at m/z 91 is that the presence of zirconium (Zr) in a sample can cause a false positive reading. However, because Zr^+ reacts rapidly with oxygen (rate constant ≈ 10^{-10}), it will move as AsO^+ forms, even if Zr is present at the same concentration as As, as shown in Figure 3. In this figure, m/z 91 is monitored as a function of oxygen flow for a 1 µg/L Zr standard (blue) and a mixed standard containing 1 µg/L Zr + 1 µg/L As.

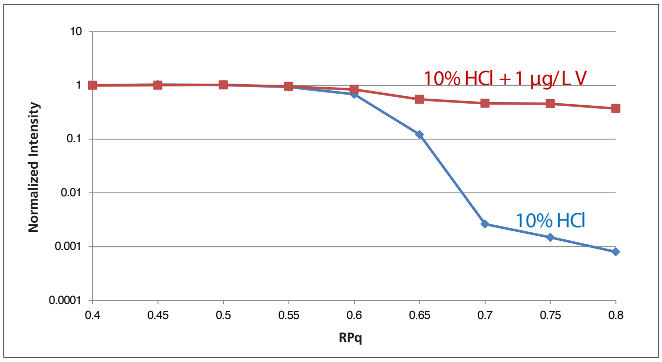

Figure 1. Signals at m/z 51 as a function of RPq for 10% HCl (blue) and 10% HCl + 1 µg/L V (red).

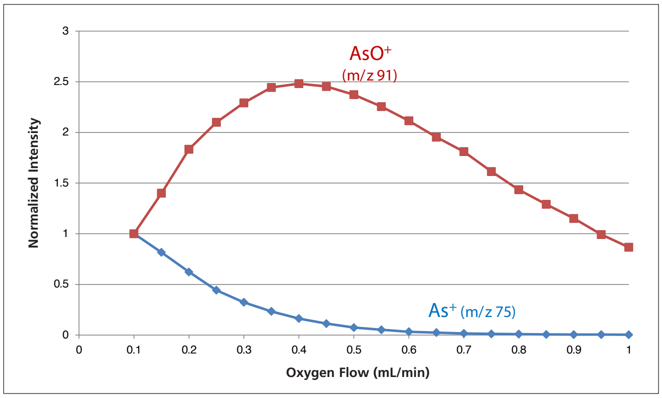

Figure 2. Conversion of As^+ to AsO^+ as a function of oxygen flow in 1% HNO_3.

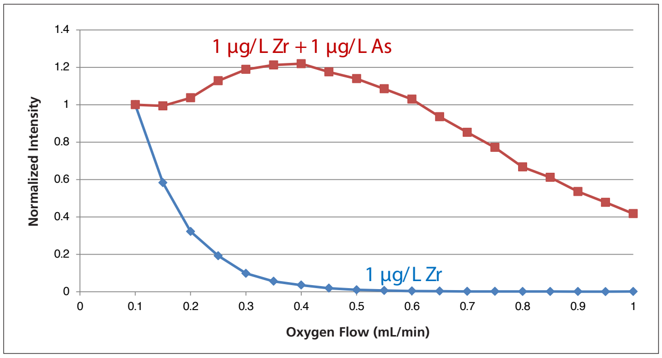

Figure 3. Signals at m/z 91 as a function of oxygen flow for 1 µg/L Zr (blue) and 1 µg/L Zr + 1 µg/L As (red).

Performance

In order to assess the effectiveness of interference removal, detection limits (DLs) and background equivalent concentrations (BECs) were determined in 20% HCl using one-second integration times. Table 4 shows both the DLs and BECs for all elements, with most being less than 1 ng/L, demonstrating the effectiveness of Reaction and Cool Plasma modes with the NexION 2000.

Table 4. Detection Limits, Background Equivalent Concentrations, and 10 ng/L Spike Recoveries in 20% HCl

Analyte	Mass	Detection Limits (ng/L)	BECs (ng/L)	10 ng/L Recoveries (%)
Li	7	0.01	0.01	99
Be	9	0.05	0.01	91
B	11	0.6	2.3	90
Na	23	0.09	0.4	99
Mg	24	0.03	0.08	99
Al	27	0.1	0.2	100
K	39	0.6	1.3	103
Ca	40	0.2	0.2	103
Ti	48	0.5	2.7	98
V	51	0.1	0.04	96
Cr	52	0.5	0.50	100
Mn	55	0.07	0.07	95
Fe	56	0.4	1.2	103
Co	59	0.1	0.02	94
Ni	60	0.2	0.3	100
Cu	63	1	2	101
Zn	64	0.7	3.3	102
Ga	71	0.09	0.06	97
Ge	74	2	0.50	92
AsO	91	1	54	99
SeO	96	1	7	103
Sr	88	0.06	0.46	92
Zr	90	1	3	108
Nb	93	0.3	1.1	95
Mo	98	0.5	1.3	92
Ru	102	0.3	0.4	90
Rh	103	0.04	0.007	95
Pd	106	0.3	0.6	91
Ag	107	0.3	0.4	91
Cd	114	0.4	0.9	95
In	115	0.3	1.6	96
Sn	118	0.9	5.5	91
Sb	121	0.6	1.3	92
Ba	138	0.1	0.5	92
Ta	181	0.04	0.02	91
W	184	0.2	0.1	90
Pt	195	1.0	15.0	97
Au	197	0.1	0.3	95
Tl	205	0.02	0.006	95
Pb	208	0.1	0.3	95
Bi	209	0.07	0.5	104
U	238	0.04	0.04	90

Calibration curves were established with 10, 20, and 40 ng/L standards. All curves had regressions > 0.999, demonstrating both the linearity of the analysis and the ability to accurately measure at low concentrations. Figure 4 shows three typical calibration curves, demonstrating the effectiveness of the interference reduction:

- Ca 40 and Fe 56 were acquired with ammonia and cool plasma, demonstrating the ability to remove significant plasma-based interferences ($^{40}Ar^+$, $^{40}Ar^{16}O^+$)
- V 51 was acquired with ammonia and hot plasma, demonstrating the ability to remove a significant chloride interference ($^{35}Cl^{16}O^+$)

The accuracy of low-level measurements was verified by measuring 10 ng/L spike recoveries in 20% HCl. As shown in Table 4, all spike recoveries are within 10% of the true value, demonstrating quantitative accuracy at 10 ng/L.

With the ability to remove interferences and quantitative accuracy established, the stability of the methodology was evaluated by measuring a 50 ng/L spike in 20% HCl over 10 hours of continuous aspiration. The results are shown in Figure 5 and demonstrate exceptional stability for all elements in all modes, with deviations of less than 10% from the initial reading. The RSDs over the 10 hours are less than 3% for all elements.

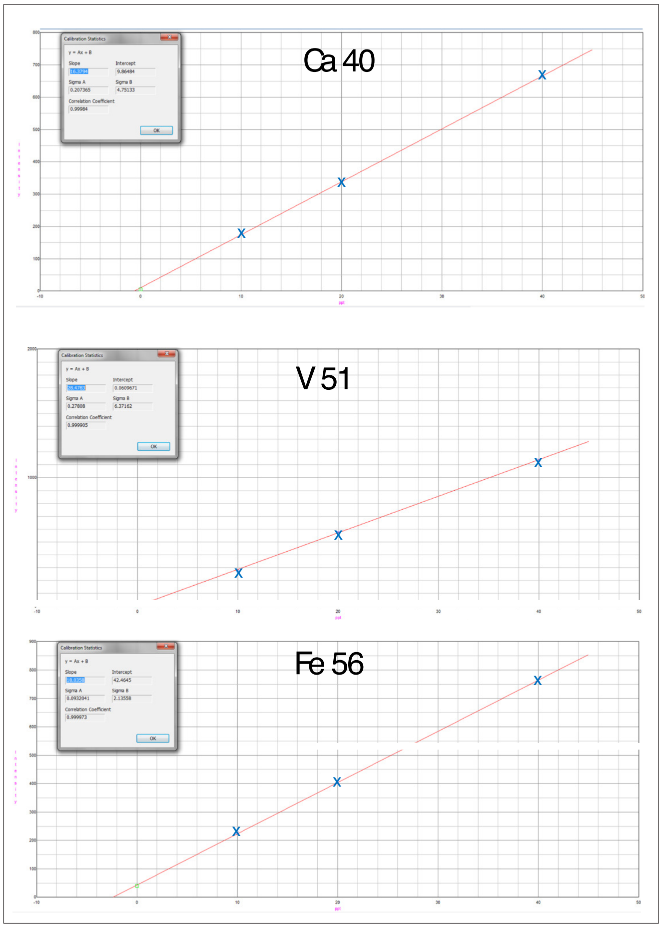

Figure 4. Calibration plots for 10, 20, 40 ng/L Ca, V, and Fe in 20% HCl.

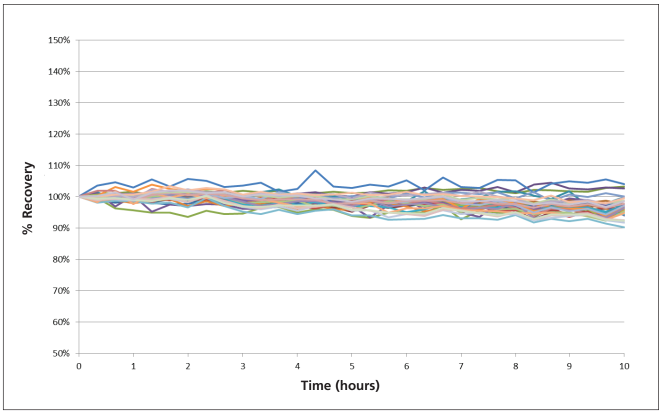

Figure 5. 10-hour stability of 50 ng/L analyte spike in 20% HCl, with continuous aspiration.

Conclusion

This work has demonstrated the ability of PerkinElmer's NexION 2000 ICP-MS to excel at the elemental analysis of 20% HCl at SEMI Tier C levels, without the need for sample pre-treatment. With the combination of Reaction mode using 100% ammonia and oxygen as well as a unique RF generator which overcomes traditional limitations of cool plasma, polyatomic interferences are eliminated, allowing for sub-ng/L detection limits and accurate quantitation at the 10 ng/L level, while providing exceptional long-term stability.

References

1. SEMI Standard C27-0708, Specifications and Guidelines for Hydrochloric Acid, http://www.semi.org/en/index.htm.

Consumables Used

Component	Description	Part Number
Spray Chamber Drain Tubing	Gray/gray (1.30 mm id), Santoprene, package of 12	N8152403
Multielement Solution 3	10 mg/L Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn	N9300233 (125 mL)
Multielement Solution 4	10 mg/L Au, Hf, Ir, Pd, Pt, Rh, Ru, Sb, Sn, Te	N9300234 (125 mL)
Multielement Solution 5	10 mg/L B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr	N9300235 (125 mL)

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