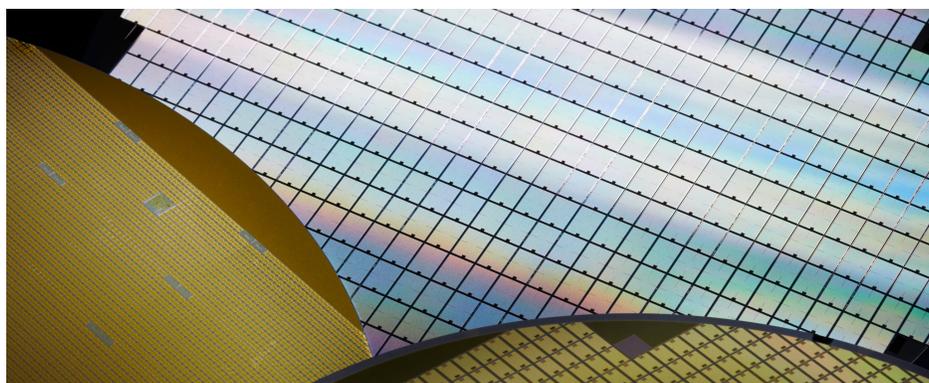


Analysis of Trace Metal Impurities in High Purity Hydrochloric Acid Using ICP-QQQ



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Introduction

Hydrochloric acid (HCl) is a component of the standard RCA cleaning process used to remove organic and metallic residues and impurities from the surface of silicon wafers used in semiconductor manufacturing. The cleaning steps are performed before high temperature processing steps such as oxidation and chemical vapor deposition (CVD). RCA Standard Clean 2 (SC-2) removes ionic contaminants from the wafer surface. SC-2 follows SC-1, which removes organic residues and particles. SC-2 consists of HCl combined with hydrogen peroxide (H_2O_2) and de-ionized water (DIW). Since the cleaning solutions are in direct contact with the silicon wafer surface, ultrahigh purity reagents are required for these solutions.

SEMI standard C27-0708 Tier-C protocol for HCl specifies a maximum contaminant level of 100 ppt for each element (HCl 37.0 - 38.0 %) [1]. The concentration of industrial grade HCl is usually 20 or 35%, depending on the method of production. The Cl matrix leads to the formation of several polyatomic ions, which cause significant spectral interferences on some key elements. For example, $H_2^{37}Cl^+$ on $^{39}K^+$, $^{35}Cl^{16}O^+$ on $^{51}V^+$, $^{35}Cl^{16}OH^+$ on $^{52}Cr^+$, $^{37}Cl^{16}O^+$ on $^{53}Cr^+$, $^{35}Cl^{37}Cl^+$ on $^{72}Ge^+$, $^{37}Cl_2^+$ on $^{74}Ge^+$, and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. As a result of these polyatomic interferences, it has been difficult to determine these elements at the required levels using conventional single quadrupole ICP-MS (ICP-QMS). Even ICP-QMS instruments fitted with a collision/reaction cell (CRC) or bandpass filter can only offer limited reduction of the spectral interferences arising from the Cl matrix. Consequently, some methods for the analysis of high purity HCl by ICP-QMS have recommended sample pretreatment steps to remove the chloride matrix, which can lead to analyte loss and/or sample contamination.

In this study, triple quadrupole ICP-MS (ICP-QQQ) was used to analyze 50 elements in HCl, using MS/MS mode to resolve the polyatomic interferences. All analytes, including the most problematic elements such as K, V, Cr, Ge, and As, could be determined directly in the undiluted HCl with single digit ppt detection limits.

Experimental

Instrumentation

An Agilent 8900 Semiconductor configuration ICP-QQQ was used in this study. The instrument was fitted with a PFA-100 nebulizer, Peltier-cooled quartz spray chamber, quartz torch, platinum-tipped sampling and skimmer cones and s-lens.

The nebulizer was operated in self-aspiration mode to minimize the potential for sample contamination from the peristaltic pump tubing. In advanced semiconductor applications, the key requirement is to deliver the absolute lowest possible detection limits (DLs) for each analyte. To achieve this goal, laboratories measuring ultratrace levels of contaminants can use a multi-tune method, where several tuning steps are applied sequentially during the measurement of each solution. This approach allows the tuning conditions to be optimized for the removal of different types of interferences, while maintaining maximum sensitivity for each analyte. In this work, several reaction cell gases (H_2 , O_2 , and NH_3) were used as appropriate for the large number of analytes being measured. He was used as a buffer gas in the NH_3 reaction gas modes. Tuning conditions are shown in Table 1 and other acquisition parameters are shown in Table 2.

Table 1. ICP-QQQ operating conditions.

	Cool	Cool-NH ₃	No gas	H ₂	O ₂	NH ₃	O ₂ -soft
Acquisition mode	MS/MS						
RF power (W)	600	1500					
Sampling depth (mm)	18.0	8.0					
Nebulizer gas (L/min)	0.70						
Makeup gas (L/min)	0.90	0.48					
Extract 1 (V)	-150.0	4.2	4.7	4.5	3.5		
Extract 2 (V)	-18.0	-17.0	-250.0			-120.0	
Omega bias (V)	-70.0	-140.0				-70.0	
Omega lens (V)	2.0	10.0	8.0	10.5	4.0		
Q1 entrance (V)	-15.0	-50.0					
He flow (mL/min)	-	1.0	-	-	-	1.0	-
H ₂ flow (mL/min)	-	-	-	7.0	-	-	-
NH ₃ flow (mL/min)	-	2.0 (20%)	-	-	-	2.0 (20%)	-
O ₂ flow (mL/min)	-	-	-	-	0.45 (30%)	-	0.45 (30%)
Axial acceleration (V)	0.0	1.5	0.0		1.0	0.2	1.0
Energy discrimination (V)	15.0	-5.0	5.0	0.0	-7.0		

Table 2. Acquisition parameters.

Parameter	Setting
Q2 peak pattern	1 point
Replicates	3 (spiked solution)
	10 (unspiked solution)
Sweeps/replicate	10
Integration time	2 s for all isotopes

Samples and standards

The samples of HCl used in this study included:

- Sample 1: 20% HCl (high purity grade).
- Sample 2: 36% HCl (non-high purity grade).
- Sample 3: 20% HCl (34% high purity grade diluted to 20% with DIW).

No further sample preparation was necessary as all samples were introduced directly into the ICP-QQQ. To run undiluted HCl routinely, it is recommended that the large (18 mm) insert Pt cone is fitted. Long-term corrosion of internal ICP-MS components can be minimized by fitting the dry pump option.

Calibration and quantification were done using the method of standard additions (MSA). Standard solutions were prepared by spiking a multi-element standard solution (SPEX CertiPrep,

NJ, US) into each HCl sample type to give spike levels of 10, 20, 30, and 40 ppt. The MSA calibrations were then automatically converted to external calibrations in the ICP-MS MassHunter data analysis table. This conversion allows other samples of the same type (HCl concentration) to be quantified without requiring separate MSA spike additions into each sample. All solutions were prepared just before analysis.

All preparation and analysis was performed in a Class 10,000 clean room.

Results and Discussion

DLs and BECs

In total, 50 elements including all SEMI specification analytes were measured using the 8900 ICP-QQQ operating in multiple tune modes. Data for each mode was combined automatically into a single report for each sample. Detection limits (DLs) and background equivalent concentrations (BECs) in 20% HCl are given in Table 3.

Table 3. DLs and BECs in high purity 20% HCl*.

Element	Cell gas mode	Q1 mass	Q2 mass	DL ng/L	BEC ng/L
Li	Cool-NH ₃	7	7	0.032	0.016
Be	No gas	9	9	0.022	0.021
B	No gas	11	11	0.55	4.1
Na	Cool-NH ₃	23	23	0.064	0.15
Mg	Cool-NH ₃	24	24	0.077	0.056
Al	Cool-NH ₃	27	27	0.20	0.19
P	O ₂ -soft	31	47	1.1	2.6
K	Cool-NH ₃	39	39	0.087	0.17
Ca	Cool-NH ₃	40	40	0.44	0.68
Sc	O ₂ -soft	45	61	0.014	0.012
Ti	O ₂ -soft	48	64	0.051	0.074
V	NH ₃	51	51	0.11	0.19
Cr	Cool-NH ₃	52	52	0.18	0.12
Mn	Cool-NH ₃	55	55	0.016	0.006
Fe	Cool-NH ₃	56	56	0.24	0.27
Co	Cool-NH ₃	59	59	0.10	0.038
Ni	Cool-NH ₃	60	60	0.66	0.26
Cu	Cool-NH ₃	63	63	0.10	0.12
Zn	NH ₃	66	66	0.14	0.097
Ga	NH ₃	71	71	0.015	0.026
Ge	NH ₃	74	107	0.90	3.0
Ge	NH ₃	74	107	0.32	0.77
As	O ₂	75	91	1.4	48
As	O ₂	75	91	0.73	6.2
Se	H ₂	78	78	0.44	0.52
Rb	Cool-NH ₃	85	85	0.041	0.013

Sr	NH ₃	88	88	0.003	0.001
Y	O ₂ -soft	90	106	0.010	0.006
Zr	O ₂ -soft	93	125	0.012	0.004
Nb	O ₂	93	125	0.004	0.005
Mo	He	98	98	0.13	0.57
Ru	He	101	101	0.016	0.003
Pd	He	105	105	0.010	0.001
Ag	He	107	107	0.032	0.014
Cd	He	114	114	0.090	0.10
In	He	115	115	0.035	0.021
Sn	He	118	118	0.57	3.3
Sb	He	121	121	0.66	1.5
Te	H ₂	125	125	0.37	0.31
Cs	NH ₃	133	133	0.008	0.019
Ba	NH ₃	138	138	0.005	0.005
Hf	No gas	178	178	0.005	0.004
Ta	He	181	181	0.013	0.010
W	No gas	182	182	0.039	0.062
Re	No gas	185	185	0.12	0.50
Ir	No gas	193	193	0.017	0.012
Au	He	197	197	0.027	0.022
Tl	No gas	205	205	0.007	0.004
Pb	H ₂	208	208	0.028	0.023
Bi	No gas	209	209	0.024	0.030
Th	No gas	232	232	0.017	0.021
U	No gas	238	238	0.009	0.005

* Shaded rows for Ge and As indicate results measured in Sample 3, due to suspected contamination for these elements in Sample 1.

Quantitative results

Table 4 shows quantitative data for all SEMI specification elements in high purity 20% HCl and non-high purity 36% HCl determined by MSA. The results show that the 8900 ICP-QQQ can measure contaminants in HCl at a much lower level than the 100 ppt maximum limit specified in the SEMI specifications. It is important to note that the concentration specified by SEMI is for 37–38% HCl while the data presented here is for 20 and 36% HCl. Even taking this difference into account, the 8900 ICP-QQQ is clearly able to measure contaminants at levels far lower than current industry requirements for high-purity HCl.

Table 4. Quantitative results for SEMI specification elements in high purity 20% HCl (Sample 1) and non-high purity 36% HCl (Sample 2).

Element	Cell gas mode	Q1	Q2	Sample 1 20% HCl, ng/L	Sample 2 36% HCl, ng/L	DL, ng/L
Li	Cool-NH ₃	7	7	<DL	<DL	0.032
B	No gas	11	11	4.1	15	0.55
Na	Cool-NH ₃	23	23	0.15	6.4	0.064
Mg	Cool-NH ₃	24	24	<DL	6.5	0.077
Al	Cool-NH ₃	27	27	<DL	23	0.20
K	Cool-NH ₃	39	39	0.17	1.5	0.087
Ca	Cool-NH ₃	40	40	0.68	13	0.44
Ti	O ₂ soft	48	64	0.074	1.4	0.051
V	NH ₃	51	51	0.19	4.6	0.11
Cr	Cool-NH ₃	52	52	<DL	0.55	0.18
Mn	Cool-NH ₃	55	55	<DL	0.071	0.016
Fe	Cool-NH ₃	56	56	0.27	7.6	0.24
Ni	Cool-NH ₃	60	60	<DL	<DL	0.66
Cu	Cool-NH ₃	63	63	0.12	0.57	0.10
Zn	NH ₃	66	66	<DL	1.1	0.14
As	O ₂	75	91	48	39	0.73*
Cd	He	114	114	0.10	0.34	0.090
Sn	He	118	118	3.3	2.3	0.57
Sb	He	121	121	1.5	0.95	0.66
Ba	NH ₃	138	138	0.005	<DL	0.005
Pb	H ₂	208	208	0.023	0.13	0.028

*DL for As measured in Sample 3, due to suspected contamination for this element in Sample 1.

Cr and K determination

Cool plasma is a proven technique used to remove plasma-based interferences. Although it has been largely superseded by CRC methodology, cool plasma remains the most effective analytical mode for some elements in certain matrices. Combining cool plasma with CRC technology has been shown to be a powerful mode for interference removal [2]. Because the major isotope of chromium (⁵²Cr⁺) suffers an interference from ³⁵Cl¹⁶OH⁺ in high purity HCl, Cr was determined using cool plasma with ammonia cell gas. The calibration curve for ⁵²Cr shows that ³⁵Cl¹⁶OH⁺ interference was removed successfully, allowing a BEC of 0.12 ng/L (ppt) to be achieved, with a detection limit of 0.18 ppt (Figure 1). The DL and BEC displayed in the ICP-MS MassHunter calibration plots are based on the 10 replicates of the unspiked high-purity 20% HCl sample.

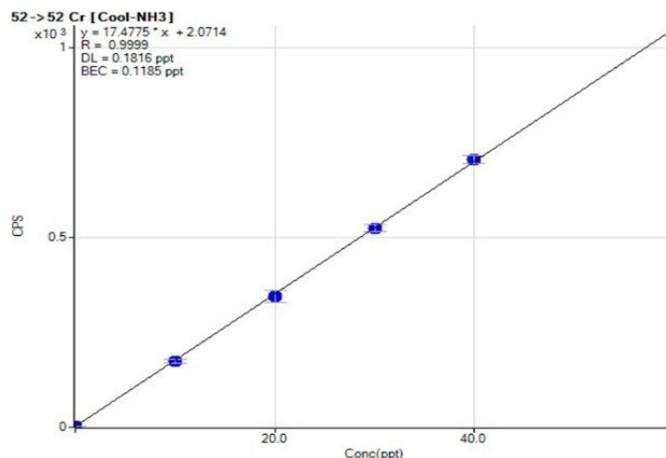


Figure 1. ⁵²Cr calibration curve obtained using cool plasma and NH₃ cell gas, showing low BEC and good linearity.

The same approach is effective for the determination of other interfered elements such as K. Figure 2 shows that the interference from H₂³⁷Cl⁺ on ³⁹K⁺ was suppressed using cool plasma and NH₃ cell gas, giving a BEC and DL for K of 0.17 ppt and 0.09 ppt, respectively.

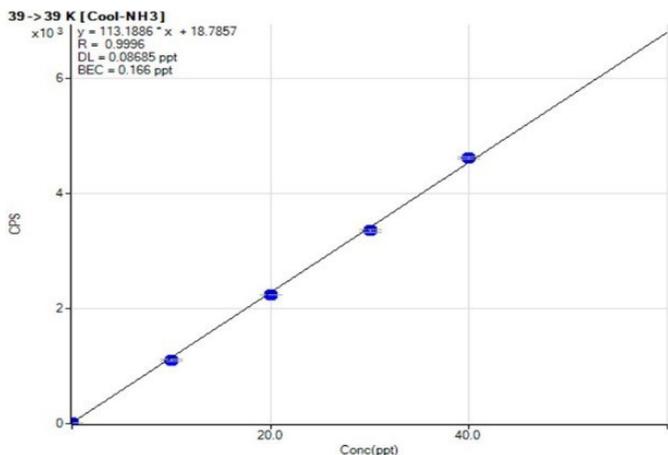


Figure 2. ^{39}K calibration curve obtained using cool plasma and NH_3 cell gas.

V and Ge determination

ICP-QMS fitted with a CRC operating in helium collision mode can successfully eliminate many polyatomic ions using He collision cell gas and kinetic energy discrimination (KED) [3]. However, ICP-QMS has some serious limitations when highly reactive cell gases, such as NH_3 , are used in the CRC.

ICP-QMS has no mass selection step before the cell, so all ions enter the CRC. It is likely, therefore, that new reaction product ions will form in the CRC that may overlap the target analyte mass of interest. Bandpass ICP-QMS instruments, where all ions within a certain mass range (usually about 10 u) of the target analyte can enter the cell and react, have similar limitations to traditional ICP-QMS in terms of controlling reaction chemistry with highly reactive cell gases.

ICP-QQQ with MS/MS removes this limitation, as the first quadrupole mass filter (Q1), which is located before the CRC, allows precise selection of the specific mass of ions that are allowed to enter the cell. This extra mass selection step ensures that reaction processes in the cell are controlled, which removes the potential for non-target product ion overlaps and dramatically improves the detectability of the analyte ions.

MS/MS acquisition mode using NH_3 as the reaction cell gas was used for the trace determination of V and Ge. The ClO^+ interference on ^{51}V was removed using NH_3 on-mass mode. Potentially, $^{14}\text{NH}_2^{35}\text{Cl}^+$ could form in the cell and interfere with V at m/z 51. However, the unit mass resolution of Q1 on the 8900 ICP-QQQ ensures that only ions at m/z 51 can enter the cell. All other matrix and analyte ions, e.g. $^{35}\text{Cl}^+$, are prevented from entering the cell and cannot, therefore, contribute to the signal at the analyte mass. This simple approach avoids the formation of any new product ion interferences on ^{51}V .

The ClCl^+ interference on ^{74}Ge was avoided by measuring a Ge-ammonia cluster ion, $^{74}\text{Ge}[\text{NH}_2(\text{NH}_3)]^+$, in mass-shift mode at mass 107. Q1 (set to m/z 74 to allow the $^{74}\text{Ge}^+$ precursor ions to enter the cell) rejects all non-target masses, including $^{107}\text{Ag}^+$, which would otherwise overlap the Ge- NH_3 product ion mass. Q1 (in contrast to a bandpass filter) also rejects all other nearby analyte ions, $^{70}\text{Zn}^+$, $^{71}\text{Ga}^+$, $^{73}\text{Ga}^+$, $^{75}\text{As}^+$, $^{78}\text{Se}^+$, etc., preventing them from forming potentially overlapping ammonia clusters at the target product ion mass.

Representative calibration curves for V and Ge are shown in Figure 3, again illustrating the low BEC (0.19 ppt for V and 0.77 ppt for Ge) and DL (0.11 ppt for V and 0.32 ppt for Ge) achieved with the 8900 with NH_3 cell gas in MS/MS mode.

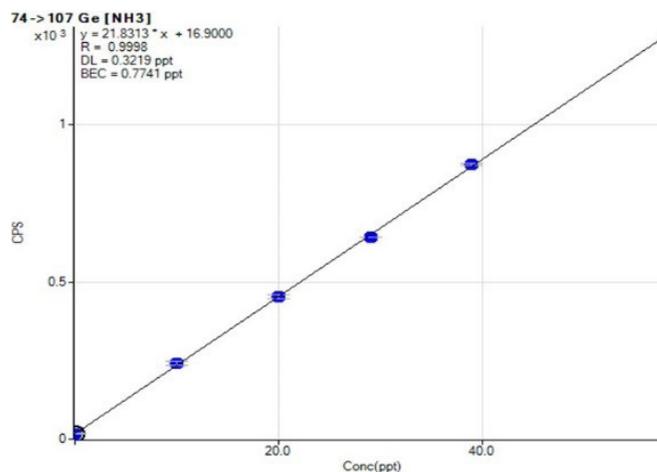
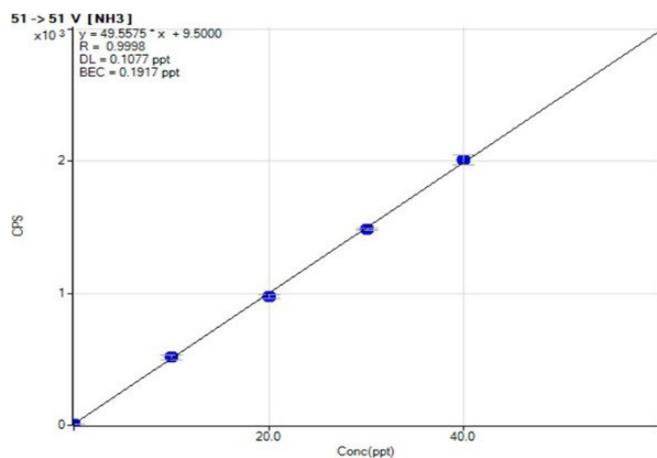


Figure 3. ^{51}V and ^{74}Ge calibration curve obtained using NH_3 cell gas.

Determination of As

Arsenic has a single isotope at m/z 75 that suffers an interference from the polyatomic ion $^{40}\text{Ar}^{35}\text{Cl}^+$. Since ArCl^+ readily forms in a chloride matrix, the polyatomic interference compromises the determination of As at ultratrace levels in

concentrated HCl using ICP-QMS. Oxygen can be used as the cell gas to avoid this overlap, with As being measured as the AsO^+ product ion at m/z 91. However, with ICP-QMS, the AsO^+ product ion at mass 91 suffers an interference from $^{91}\text{Zr}^+$. Helium collision mode in the Agilent ORS cell can reduce ArCl^+ effectively, allowing a BEC of less than 20 ppt to be achieved by ICP-QMS [3]. But, as semiconductor industry demands become more stringent, this sensitivity may not be sufficient for the lowest level of ultratrace analysis.

Using the 8900 ICP-QQQ with MS/MS, the $^{91}\text{Zr}^+$ ion is removed by Q1, which is set to the As^+ precursor ion mass of 75. MS/MS mode allows O_2 cell gas to be used successfully, with As being measured as the AsO^+ product ion at m/z 91 without overlap from $^{91}\text{Zr}^+$. A further benefit of O_2 cell gas is that measuring AsO^+ provides more sensitivity than direct measurement of As^+ in He mode.

A calibration curve for As in 20% HCl (Sample 3) is shown in Figure 4, demonstrating a BEC of 6.17 ppt and a DL of 0.73 ppt. While lower than the industry requirements for high-purity HCl, this BEC doesn't represent the best performance that can be achieved with the 8900 ICP-QQQ, so further investigation was done to identify the cause of the relatively high background.

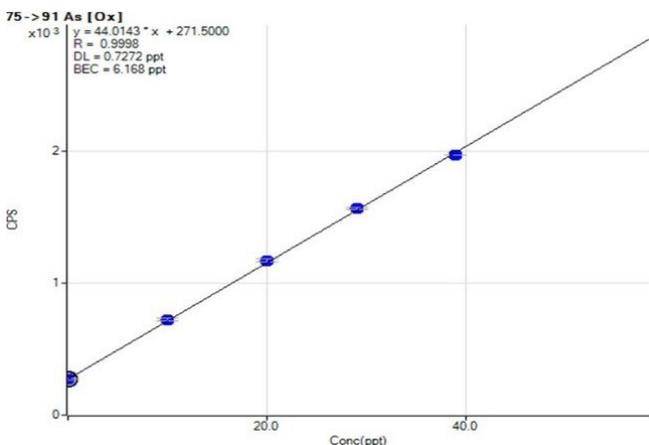


Figure 4. ^{75}As MSA calibration curve obtained in Sample 1 using O_2 cell gas.

Investigation of arsenic contamination

As the measured result for As was relatively high in high purity HCl Sample 1 (Table 4), the signal count at m/z 91 (mass of the product ion AsO^+) was investigated further. In a high Cl matrix, the polyatomic ion $^{40}\text{Ar}^{35}\text{Cl}^+$ forms in the plasma and during ion extraction. This polyatomic ion has the same nominal mass as the target $^{75}\text{As}^+$ precursor ion, so it passes through Q1 and enters the cell. While not thermodynamically favored, the ArCl^+ might react with the O_2 cell gas to form ArClO^+ , which would therefore remain as an interference on

AsO^+ at m/z 91. This possibility can be checked by comparing the isotopic signature of the Cl-based product ions observed in the mass spectrum. Since chlorine has two isotopes, 35 and 37, the ratio of the natural abundances of these isotopes (75.78%: 24.22%) can be used to confirm whether a product ion is Cl-based.

The signals of the mass-pairs 75/91 and 77/93, representing the potential Cl interferences $^{40}\text{Ar}^{35}\text{Cl}^{16}\text{O}^+$ and $^{40}\text{Ar}^{37}\text{Cl}^{16}\text{O}^+$ respectively, were measured by ICP-QQQ with MS/MS. A neutral gain scan spectrum (where Q1 and Q2 are scanned synchronously, with a fixed mass difference between them) was measured and the scan is presented in Figure 5. For this neutral gain scan, Q1 was scanned across the mass range from 74 to 78 u to pass any precursor ions to the CRC, and Q2 was scanned synchronously at $Q1 + 16$, monitoring any product ions formed by O-atom addition. The peak at mass-pair m/z 75/91 that caused the relatively high BEC for As in Sample 1 is clearly visible. However, if the signal at 75/91 was due to interference from $^{40}\text{Ar}^{35}\text{Cl}^{16}\text{O}^+$, there would also be a corresponding signal from $^{40}\text{Ar}^{37}\text{Cl}^{16}\text{O}^+$ at mass-pair 77/93. Since there was no signal observed at 77/93, we can conclude that the signal at m/z 75/91 is not due to any contribution from ArClO^+ , and the high reported concentration of As in Sample 1 is due to contamination.

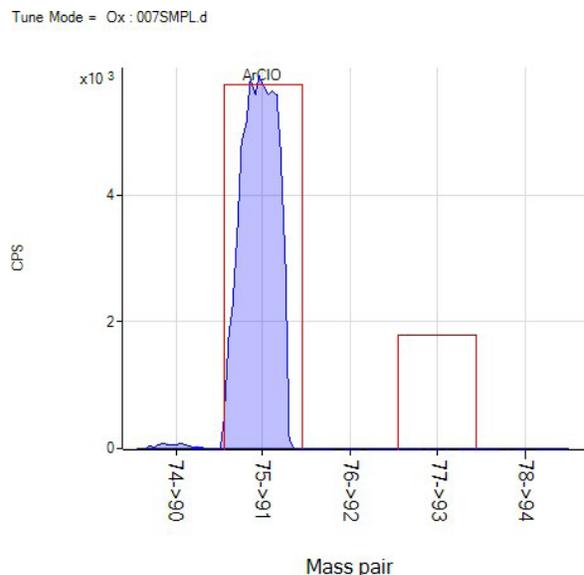


Figure 5. Neutral gain scan spectrum for 20% high purity HCl showing the theoretical isotope template for $^{40}\text{Ar}^{35}\text{Cl}^{16}\text{O}^+$ and $^{40}\text{Ar}^{37}\text{Cl}^{16}\text{O}^+$. Q1 was scanned from m/z 74 to 78, while Q2 was set to $Q1 + 16$.

Conclusions

The high performance of Agilent ICP-QQQ systems for the analysis of trace metallic impurities in concentrated HCl has been described previously [4]. Now, the Agilent 8900 Semiconductor configuration ICP-QQQ with flexible cell gas support, unique MS/MS capability, and unparalleled cool plasma performance, further improves the detection limits for the analysis of a wide range of trace metal contaminants in high purity acids. The advanced reaction cell methodology supported by the 8900 ICP-QQQ allows the SEMI elements, including those elements with potential matrix-based interferences such as K, V, Cr, Ge, and As, to be determined at lower concentrations in a chloride matrix than was previously possible.

References

1. SEMI C27-0708, Specifications and guidelines for hydrochloric acid (2008)
2. Junichi Takahashi and Katsuo Mizobuchi, Use of Collision Reaction Cell under Cool Plasma Conditions in ICP-MS, 2008 Asia Pacific Winter Conference on Plasma Spectroscopy
3. Junichi Takahashi, Direct analysis of trace metallic impurities in high purity hydrochloric acid by Agilent 7700s/7900 ICP-MS, Agilent publication, 2017, 5990-7354EN
4. Handbook of ICP-QQQ Applications using the Agilent 8800 and 8900, Agilent publication, 2017, pp 13-14, 5991-2802EN

More Information

When analyzing 20–36% HCl on a routine basis, it is recommended to use the following options:

- G3280-67056 Pt sampling cone (18 mm insert)
- G4915A Upgrade to dry pump
- G3666-67030 Interface valve kit - ball type valve

Since hydrochloric acid is corrosive, avoid placing open sample bottles near the instrument.

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