

Determination of challenging elements in ultrapure semiconductor grade sulfuric acid by Triple Quadrupole ICP-MS

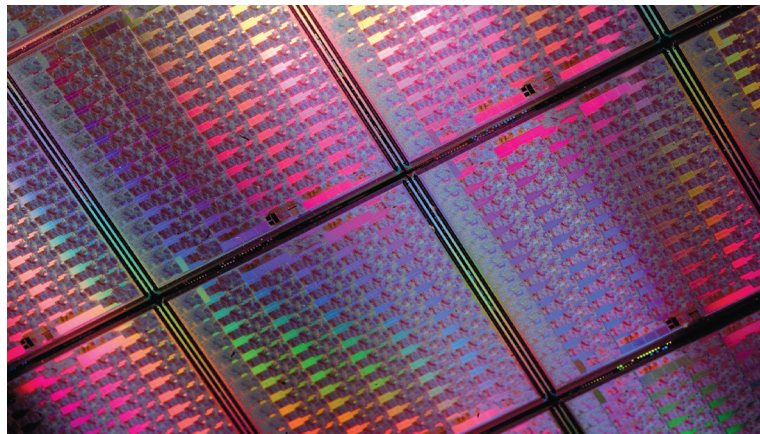
Application note

Semiconductor

Authors

Junichi Takahashi

Agilent Technologies, Japan



Introduction

The relatively recent technology of collision/reaction cell (CRC) has become widely used with quadrupole ICP-MS (ICP-QMS) to remove polyatomic ions, which can cause problematic spectral interferences on analytes in complex matrices. By utilizing CRC, background equivalent concentrations (BECs) can be reduced to the ppt or sub-ppt level for almost all elements in semiconductor grade chemicals. In certain sample matrices, however, some polyatomic species which are either very stable, or were originally present at high levels, may not be completely removed by the cell and can therefore still cause residual spectral interferences. For example, a sulfur matrix gives rise to SO^+ and SN^+ ions in the ICP, both of which can interfere with the determination of titanium. The first ionization potentials (IP) of the polyatomic species SO and SN are 10.2 eV and 8.9 eV respectively and so both are more readily ionized in the ICP than S (IP 10.36 eV). In addition, SO^+ has a dissociation energy of 5.44 eV, so it is not easily dissociated



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when the CRC is used in collision mode with an inert cell gas. Titanium has 5 isotopes: ^{46}Ti (8%), ^{47}Ti (7.3%), ^{48}Ti (73.8%), ^{49}Ti (5.5%) and ^{50}Ti (5.4%). The two most abundant isotopes of Ti (^{48}Ti and ^{46}Ti) are also the ones that suffer the most intense interferences, from $^{32}\text{S}^{14}\text{N}^+$ at m/z 46 and $^{32}\text{S}^{16}\text{O}^+$ at m/z 48, so the minor isotope ^{47}Ti is usually chosen for the analysis of Ti in high purity H_2SO_4 . The BEC of Ti in 10x diluted H_2SO_4 measured with ICP-QMS in CRC mode is approximately 50 ppt [1]. Semiconductor process chemical manufacturers need a lower BEC in order to be able to determine metal contaminants at the required levels in the 10x dilute acid. A similar issue occurs with phosphoric acid analysis. In this case, in order to avoid spectral interferences from $^{31}\text{P}^{16}\text{O}^+$ and $^{31}\text{P}^{16}\text{OH}^+$, a different minor titanium isotope, ^{46}Ti , is used. In the worst case, a mixed chemical containing both sulfuric and phosphoric acids would leave no Ti isotope available free from polyatomic interferences. The newly developed technology of triple quadrupole ICP-MS (ICP-QQQ) offers a better solution for this issue. In this application note, ICP-QQQ was used for the successful analysis of Ti and other elements which have historically been very difficult to determine at trace levels in sulfuric acid.

Experimental

The Agilent 8800 Triple Quadrupole ICP-MS differs from conventional ICP-QMS, in that it features an additional quadrupole mass filter (Q1) positioned in front of the Octopole Reaction System (ORS³) cell and the analyzer quadrupole mass filter (now called Q2). This enables the 8800 ICP-QQQ to be operated in MS/MS mode, which is unique to tandem mass spectrometer configurations such as the ICP-QQQ. Q1 operates as a mass filter, selecting the ions that enter the cell, and therefore controlling the ions that can take part in reactions in the cell. Because plasma ions are eliminated from the cell by Q1, ion transmission through the cell is greatly increased [2]. When using reaction gas methods, reaction efficiency is also greatly enhanced, enabling the use of lower reaction gas flow rates which also increases ion transmission and therefore sensitivity.

Furthermore, the 8800 ICP-QQQ's four stage vacuum system results in a higher final vacuum than the three stage systems used in ICP-QMS, which also gives the 8800 ICP-QQQ increased sensitivity compared to ICP-QMS.

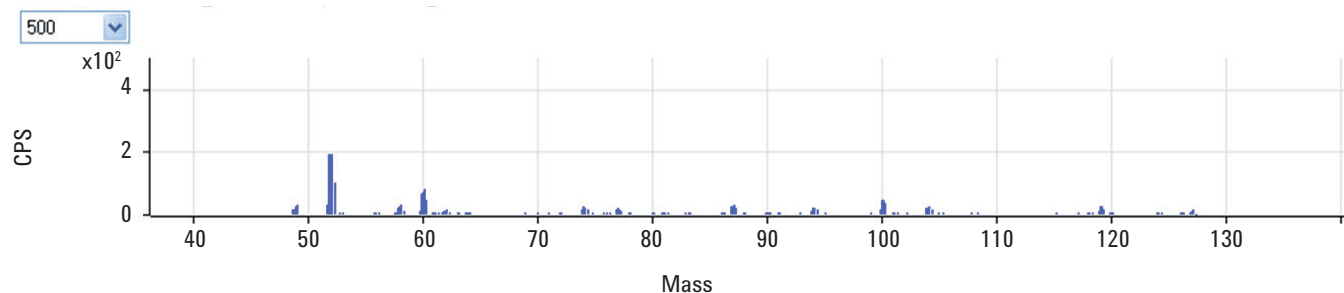
However, the greatest benefit of MS/MS mode is that it allows the full potential of reaction cell mode to be exploited. MS/MS mode can be used with either on-mass or mass-shift measurements. In MS/MS on-mass mode (used when the analyte ion is less reactive than the interfering ions), Q1 and Q2 are both set to the mass of the analyte ion. The reaction gas reacts with the interference, neutralizing it or combining with it to form a new product ion at a different mass, thereby allowing measurement of the analyte at its original mass. Alternatively, in MS/MS mass-shift mode (used when the analyte is more reactive than the interfering ions), the analyte is reacted with an appropriate reaction gas, and measured as a new product ion at a new mass — away from the interference. In both cases, the key role of Q1 is to allow only ions at the mass of the analyte precursor ion to enter the cell, excluding all potential interfering ions that would also react with the reaction gas. This application uses a combination of both on-mass mode and mass-shift mode, depending on the analyte being measured.

Prior to the actual multi-element analysis, reaction product ions were investigated. The 8800 ICP-QQQ supports several unique MS/MS acquisition modes including product ion scan, which is a very useful approach to method development for reaction gas methods. In a product ion scan, Q1 is fixed at the analyte (precursor) ion mass, and Q2 is scanned across a selected mass range, giving a spectrum showing all potential product ions that can be formed from reactions between the precursor ions and the cell gas. This can be used to confirm expected reaction pathways and identify useful analyte product ions, but it also gives an indication of potential unwanted product ions that may affect the measurement of other analytes in ICP-QMS or

in ICP-QQQ when operated in Single Quad mode. In this case, the product ion scan was performed for a matrix of 10x diluted high purity H_2SO_4 (98% sulfuric acid, Tama Chemicals, Japan), and NH_3 reaction gas was used in the cell. Q1 was set at the mass of the precursor ion of interest (m/z 48 for $^{48}\text{Ti}^+$) and Q2 was scanned between m/z 45 and 130. The same product ion scan was then performed for a second aliquot of H_2SO_4 spiked with 100 ppt of Ti. Figure 1 shows the product ion scan spectra obtained for the two samples with Q1 set to m/z 48 (major isotope of Ti). The upper spectrum is the blank H_2SO_4 while the lower spectrum shows the new product ion peaks observed from the 100 ppt Ti spike solution. Since Q1 was fixed at m/z 48, the resulting peaks are all species formed due to the reaction of $^{48}\text{Ti}^+$ with NH_3 . Thus we can select a suitable product ion peak to use as a surrogate for Ti measurement.

The following useful analytical species were identified in the spiked spectrum: $^{48}\text{TiNH}^+(m/z\ 63)$, $^{48}\text{TiNH}_2^+(m/z\ 64)$, $^{48}\text{Ti}(\text{NH})(\text{NH}_3)^+$ or $^{48}\text{Ti}(\text{NH}_2)_2^+(m/z\ 80)$, $^{48}\text{Ti}(\text{NH}_3)_2\text{NH}^+(m/z\ 97)$, $^{48}\text{Ti}(\text{NH}_3)_3\text{NH}^+(m/z\ 114)$, $^{48}\text{Ti}(\text{NH}_3)_3\text{NH}_2^+(m/z\ 115)$ and $^{48}\text{Ti}(\text{NH}_3)_4^+(m/z\ 116)$. It is worthwhile to note that most of these product ions can give unreliable data when NH_3 cell gas is used for Ti analysis on quadrupole ICP-MS. This is because there may be native ions, such as $^{63}\text{Cu}^+$, $^{64}\text{Zn}^+$, $^{114}\text{Cd}^+$ and $^{115}\text{In}^+$, present at the same mass as the $^{48}\text{Ti}^+$ product ions. With ICP-QMS, these co-existing ions cannot be excluded from the cell and so remain as overlaps on the $^{48}\text{Ti}^+$ product ions used for quantification. The performance obtained using the product ions at m/z 64, m/z 114 and m/z 115 was similar, but the BEC at m/z 114 (product ion $^{48}\text{Ti}(\text{NH}_3)_3\text{NH}^+$) was slightly better, so this ion was chosen for the measurement of Ti. Unidentified peaks were also found in the blank spectrum. Those were assumed to be $^{32}\text{S}^{16}\text{O}\text{N}_x\text{H}_y^+$, formed from the other ions such as $^{32}\text{S}^{16}\text{O}^+$ that would enter the cell when Q1 is set to m/z 48.

Tune step 1 : 12B23NH3_TiH2SO4 blk spectra 49-127_Data.D



Tune step 1 : 12B23NH3_TiH2SO4 100ppt spectra 49-127_Data.D

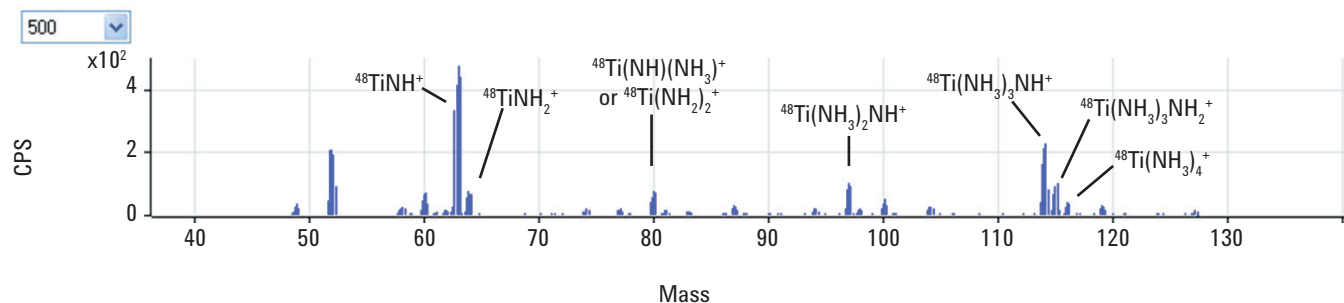


Figure 1. Product ion spectra of $^{48}\text{Ti}^+$ in 9.8% H_2SO_4 (NH_3 cell gas, Q1 48, Q2 45-130). Upper spectrum blank H_2SO_4 , lower spectrum with 100 ppt Ti spike added.

Operating parameters

Operating parameters used for the analysis are shown in Table 1. Sample solution was introduced by free aspiration using a C-Flow PFA micro-concentric nebulizer (Agilent part # G3285-80000) with an uptake rate of 200 $\mu\text{L}/\text{min}$, together with the 8800 ICP-QQQ's standard quartz torch and quartz spray chamber. A Pt sampling cone (Agilent part # G3280-67036 or 67056) and Pt skimmer cone (Agilent part # G3280-67064 or 67065) are also necessary for H_2SO_4 analysis.

Calibration

Calibration standards were prepared by spiking mixed standard solutions into the 10x diluted high purity H_2SO_4 . The calibration plots for Ti and Cr are shown in Figures 2 and 3. Good linearity down to 10 ppt for both elements was observed, with sub-ppt detection limits. With conventional ICP-QMS with CRC, both these elements are heavily interfered by sulfur-based polyatomic ions, and cannot be determined at low ppt level in this matrix.

Table 1. Operating parameters

	O_2 MS/MS	NH_3 MS/MS
RF power, W	1600	
Sampling depth, mm	8	
Carrier gas, L/min	0.8	
Makeup gas, L/min	0.41	
Extract 1, V	6.6	5.7
Extract 2, V	-50	-160
Octopole bias V	-20	
Q2 bias V	-40	
He mL/min	3	1
O_2 mL/min ¹⁾	0.4	N/A
NH_3 mL/min ²⁾	N/A	3

1) 100% O_2

2) 10% NH_3 balanced with 90% He

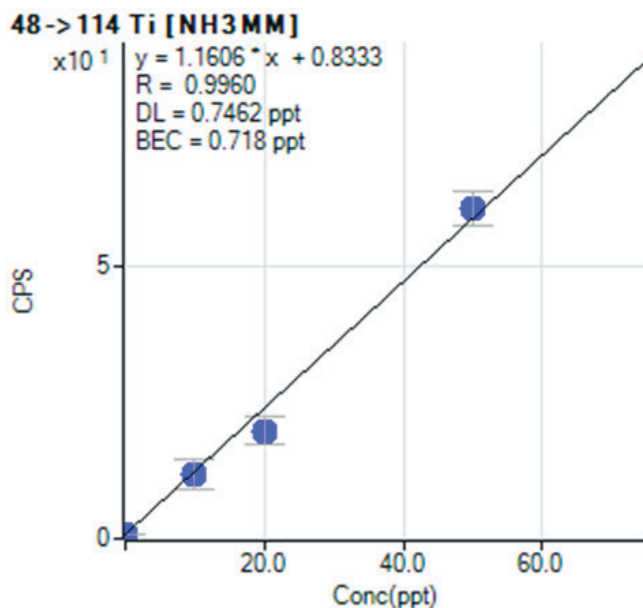


Figure 2. Calibration curve of Ti using MS/MS mass-shift mode with NH_3 cell gas

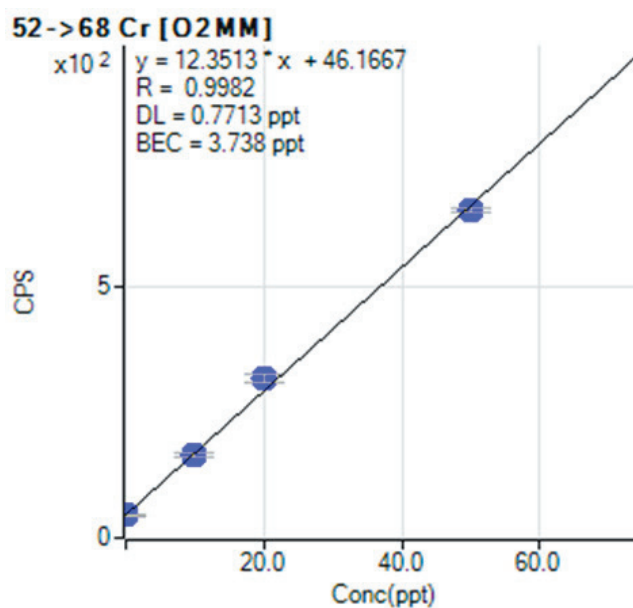


Figure 3. Calibration curve of Cr using MS/MS mass-shift mode with O_2 cell gas

Results and discussion

The analytical data for a number of difficult elements in high purity H_2SO_4 is shown in Table 2. Q1 and Q2 settings and reaction gas used are shown for each element. Mass-shift mode was used for all elements except V. All analytes measured using O_2 cell gas were measured as their MO^+ product ions, so Q2 was set 16 amu higher than Q1. Ti was measured as $Ti(NH_3)_3NH^+$ at m/z 114, as discussed earlier, while V, which is unreactive with both O_2 and NH_3 , was measured at its original mass 51 using NH_3 cell gas. NH_3 reaction mode was used because the overlap on $^{51}V^+$ from $^{34}S^{16}OH^+$ cannot be completely removed using helium collision mode. The BEC of V obtained using NH_3 is two orders of magnitude better than the BEC obtained using He. The concentrations of all the analytes measured in a 10x diluted H_2SO_4 sample were calculated by MSA (method of standard addition) and converted to concentration values in the original (undiluted) sulfuric acid. Results are shown in Table 2; except for Si and P, the sulfuric acid can be certified as 10 ppt impurity level grade.

Table 2. Results of impurity analysis of a commercial 98% high purity sulfuric acid

	Q1 m/z	Q2 m/z	Cell gas	Conc. (ng/kg)
Si	28	44	O_2	6800
P	31	47	O_2	800
Ti	48	114	NH_3	7.2
V	51	51	NH_3	1.6
Cr	52	68	O_2	37
Ge	74	90	O_2	4.5
As	75	91	O_2	2.7
Se	78	94	O_2	2.0

Conclusions

The Agilent 8800 Triple Quadrupole ICP-MS, operated in MS/MS mode, eliminates problematic spectral interferences that cannot be removed with CRC-ICP-QMS. The great benefit of MS/MS mode is that the mass selection performed by the first quadrupole (Q1), positioned in front of the cell, allows the cell to operate much more efficiently and selectively, opening up the true potential of reaction cell chemistry in a way not possible with conventional ICP-QMS. The 8800 ICP-QQQ now enables the routine analysis and certification of some key analytes in high purity process chemicals such as sulfuric acid.

References

1. Junichi Takahashi, Kouichi Youno, Analysis of Impurities in Semiconductor Grade Sulfuric Acid using the Agilent 7500cs ICP-MS, Agilent ICP-MS application note, publication number 5988-9190EN, 2003.
2. Agilent ICP-MS Journal Issue 49, publication number 5990-9942EN, 2012.

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