

ICP - Mass Spectrometry

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Ultra-Trace Elemental Analysis in High-Purity Sulfuric Acid

Introduction

The production of electronic devices is a complex process that requires the use of ultra-pure chemicals during the manufacturing steps.

High-purity-grade sulfuric acid (H_2SO_4) is generally used for cleaning components and etching all metal and organic impurities on silicon wafers.

One of the examples of sulfuric acid use is a solution called "piranha etch" or "caro acid", a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) used as a photoresist stripper.

Impurities in sulfuric acid, or any other chemicals used in semiconductor fabrication, can critically impact device quality and yield. For example, iron and copper can diffuse rapidly in silicon during thermal processing steps, which creates defects, and as a result, a degradation in device performance. Sodium impurities can spread rapidly through the wafer oxide and along the Si/SiO_2 interface, which can create voltage changes in the gate oxides and finally cause problems with respect to device operation.

As chips become more highly integrated and the requirement for smaller chips increases, there is more demand on the cleanliness of the chemicals used in semiconductor fabrication. The level of contaminants allowed in chemicals used in 10 nm fabs might not be sufficient for 5 nm technologies.

Even though the SEMI C44-0618 Specification and Guide for Sulfuric Acid¹ has impurity limits for Tier C elements at 100 ppt for several metal elements and 50 ppb or higher for many non-metals, these levels are already too high for many processes currently used in the industry.

In this application note, we describe the analysis of 52 elements in 10% H₂SO₄ using the NexION® 5000 Multi-Quadrupole ICP-MS in Multi Quad mode. The NexION 5000 ICP-MS² is designed to quantify contaminants in chemicals at extremely low levels (parts per quadrillion), which is essential to the semiconductor industry and its fine chemicals supply chain in the race for smaller and smaller nodes.

Experimental

Sample and Standard Preparation

In semiconductor fabs, 98% H₂SO₄ is most commonly used and available from several suppliers. For ICP-MS analysis, it is generally diluted 10 times with ultrapure deionized water. Therefore, diluted ultrapure H₂SO₄ (w/w) (BASF semi-grade acid, BASF, Taipei, Taiwan) was used in this work. Calibration standards were made from the 10 mg/L multielement stock solutions (PEPure, PerkinElmer, Shelton, Connecticut, USA) via serial dilutions, with the final standards being spiked in 10% H₂SO₄.

Instrumentation

PerkinElmer's NexION 5000 Multi-Quadrupole ICP-MS, described in detail in the NexION 5000 product note,² represents a truly significant advancement in ICP mass spectrometry and in the removal of spectral interferences in trace-elemental analyses.

The novel, second-generation Triple Cone Interface (TCI) with OmniRing™ technology³ and patented plasma generator with LumiCoil™ RF coil have been designed to enhance analytical performance and sensitivity of the instrument, as well as reliability. The balanced and free-running RF generator, specifically designed for ICP-MS applications, delivers improved robustness, high efficiency, a wide power range, and ensures fast power-switching between Cold and Hot Plasma modes. Multi-mode methods can now leverage these technologies in combination with Universal Cell Technology, and analysis using triple-quadrupole or multi-quadrupole technology yields superior polyatomic interference removal that can further improve detection limits (DLs) and background equivalent concentrations (BECs).

Unlike passive cells, such as octapoles and hexapoles, the Universal Cell is a quadrupole; therefore, it can control the reaction chemistry through the implementation of the rejection parameter "q". This parameter prevents by-products of the original reaction from forming new interferences with any water vapor residues or cell gas impurities which may have been introduced into the cell. In addition, controlling the chemistry allows the use of highly reactive, non-diluted gases in the cell, greatly enhancing the elimination of interferences and ensuring that reactions are predictable and repeatable. With four cell gas channels available, up to four distinct gases or mixture of these can be used in the same method, delivering ultimate flexibility in the removal of any specific interference.

Table 1. Instrumental Parameters.

Parameter	Description/Value
Sample Uptake Rate	~350 µL/min
Nebulizer	PFA ST with 0.3 mm ID Tubing (Self-aspirated)
Spray Chamber	SilQ™ Cyclonic with PC3 at 20 °C
Torch	SilQ Demountable
Injector	Pt 2 mm (for some experiments - SilQ 2 mm)
RF Power	1600 W (Hot) and 700 W (Cold)
Cones	Pt-tip Sampler, Skimmer and Hyper-skimmer
Integration Time	1 sec/isotope
Reaction Gases	Ammonia, oxygen, hydrogen (all 100%)
MS/MS and Mass Shift Modes	Q1 and Q3 operated at resolution 0.7 amu

Background equivalent concentrations (BECs) and detection limits (DLs) were measured in Hot Plasma mode using 1600 W RF power, and for a few elements that work well in Cold Plasma mode, 700 W RF power was used.

A combination of Focusing, Extraction and Cold Plasma modes³ with MS/MS or Mass Shift were used for the analysis.

A Reaction mode with either NH₃, O₂, H₂, or a mixture of gases is the most effective way of removing spectral interferences by changing them into atoms or ions of a different mass, or by creating a cluster ion with an analyte (Mass Shift). In MS/MS mode, Q1 and Q3 are set up at the same mass, while in Mass Shift mode, an analyte is measured as an ion product with a reaction gas at a higher mass. Some elements that do not have spectral interferences were measured in Standard mode without any gases entering the cell. All instrumental parameters are listed in Table 1.

Results and Discussion

Interference removal by chemical reactions and Mass Shift mode have been used for many years since the introduction of the Dynamic Reaction Cell (DRC) in 1999.⁴ Multi-quadrupole technology makes these modes even more effective since the first analyzer quadrupole (Q1) set at 0.7 amu resolution does not allow other species than those at the analyte mass to be transmitted further. This operation effectively cleans the ion beam and the background before it enters the cell. The Universal Cell, via gas reactions, handles spectral interferences, quickly eliminating reaction by-products and preventing side reactions from taking place. The second analyzer quadrupole (Q3), also set at 0.7 amu resolution, rejects products other than an analyte of interest and moves analytes to the detector.

Argon-based interferences are well known, but there are several additional spectral interferences observed while analyzing H₂SO₄ (Table 2).

Table 2. Potential Spectral Interferences in H₂SO₄.

Mass	Interference	Analyte
48	SO ⁺	Ti
51	SO ⁺ , SOH ⁺	V
52	SO ⁺ , SOH ⁺	Cr
64 - 68	S ₂ ⁺ , SO ₂ ⁺	Zn
70 - 74	ArS ⁺	Ge
98	H ₂ ³² S ¹⁶ O ₄	Mo

By using 100% pure ammonia and oxygen as cell gases with the MS/MS and Mass Shift modes, the reaction efficacy is superior to the use of diluted gas, delivering superior detection limits and background equivalent concentrations. Interferences are removed by either reacting with the gas, thus neutralized, or the reactive gas is reacting with the analyte and creating an analyte cluster at a higher mass.

The mechanism for removal of the spectral interference on Ti is shown in Figure 1.

The primary Ti isotope at mass 48 has 74.3% abundance. Ti^+ , SO^+ , POH^+ and other ions are formed in the plasma. SO^+ , POH^+ , and a low-abundance Ca^+ isotope create direct spectral interferences on Ti at mass 48. Ions that do not exist at mass 48 are rejected by the Q1. The Q1 allows only ions residing at

mass 48 to reach the Universal Cell, so only Ti^+ , SO^+ and POH^+ will enter the cell pressurized with NH_3 . Here, 100% NH_3 reacts rapidly with Ti^+ creating several clusters at higher masses. Thereafter, Q3 resolves $Ti(NH)_x^+$ from other masses, and the cluster ions reach the detector free from spectral interferences and can be measured at a desired mass.

The scan in Figure 2 shows Ti creating several clusters with NH_3 at masses 63, 80, 97, 114 and 131, where 131 was found to have the greatest sensitivity.

Vanadium is another element that suffers from SO^+ and SOH^+ interferences. It can be measured in MS/MS mode on mass 51 using NH_3 as a reaction gas to remove interferences, or also in Mass Shift mode as an NH_3 cluster on mass 117, 119 or 134 (Figure 3).

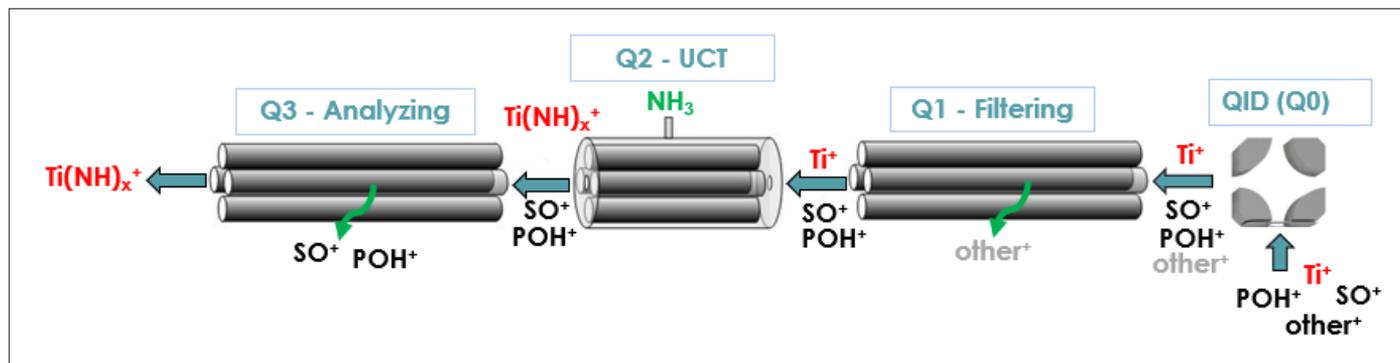


Figure 1. Mechanism of spectral interference removal on Ti in the presence of S and P.

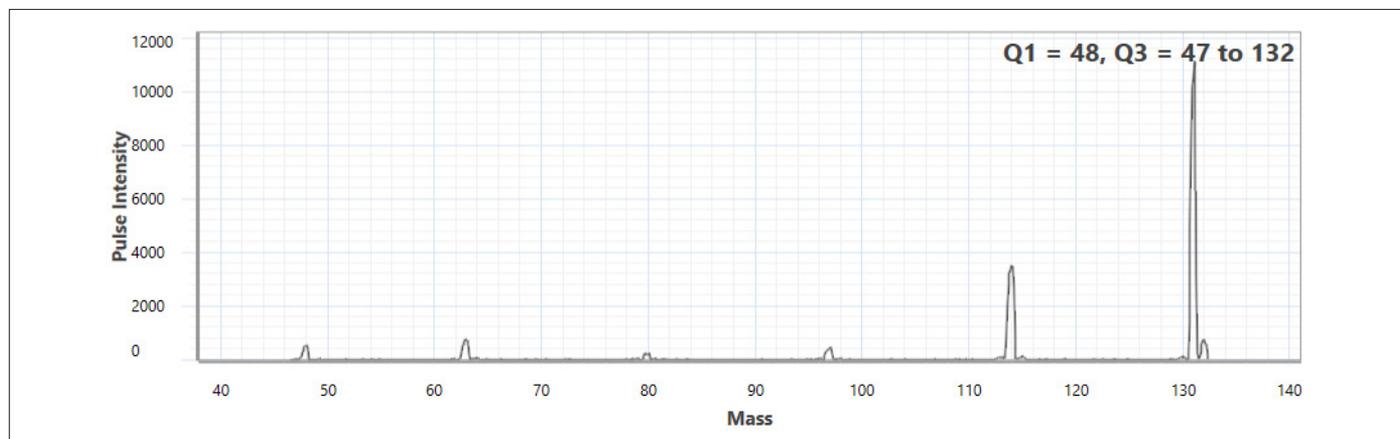


Figure 2. Scan of Ti clusters created with NH_3 in ultrapure water.

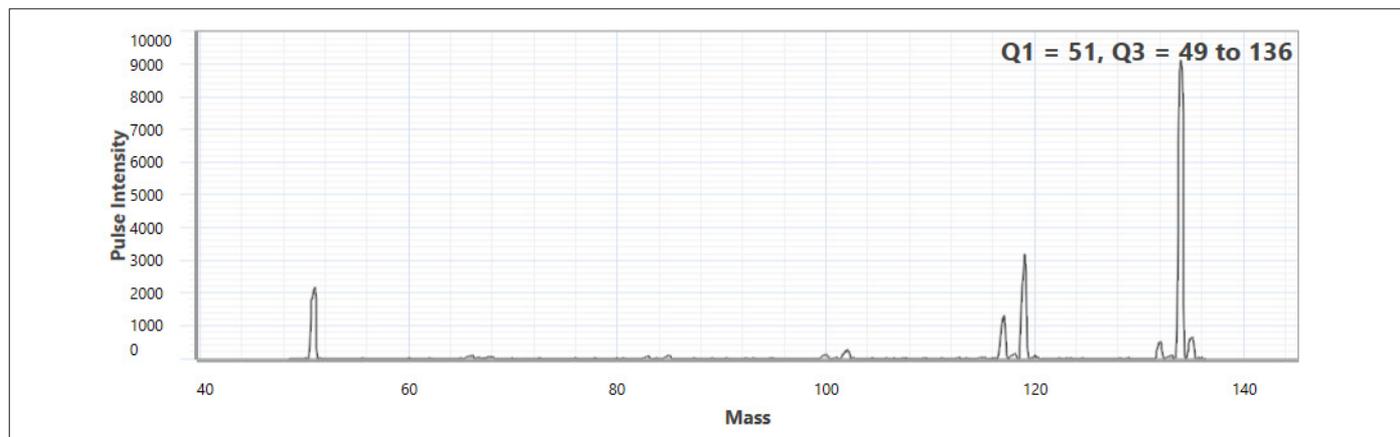


Figure 3. Scan of V clusters created with NH_3 in ultrapure water.

Sensitivity of each cluster depends on the NH₃ flow. In Figure 4, optimization of NH₃ flow is shown for Ti-NH₃ clusters at mass 114 and 131 and V-NH₃ clusters at mass 119 and 134. The Ti-NH₃ cluster at mass 114 optimizes at NH₃ flow of 0.5 mL/min, while the cluster at mass 131 optimizes at 0.8 mL/min with higher sensitivity. The V-NH₃ cluster at mass 119 optimizes at NH₃ flow of 1.5 mL/min, while the cluster at mass 134 optimizes at 1.2 mL/min with higher sensitivity.

Mass Shift mode is a very powerful technique for removing interferences applicable to those elements that can efficiently create clusters with reactive gases such as NH₃, O₂ and CH₄. In this application, Mass Shift mode was used for measuring Ti, V, Zn and Ge as clusters with NH₃ and P, Sc, As and Se as clusters with O₂.

Table 3. BECs and DLs in 10% H₂SO₄.

Element	Q1	Q3	Mode	DLs (ppt)	BECs (ppt)
Li	7	7	Standard Cold	0.0004	<DL
Be	9	9	Standard	0.039	<DL
B*	11	11	Standard	0.29	0.76
Na	23	23	Standard Cold	0.006	0.093
Mg	24	24	Ammonia Cold	0.010	0.055
Al	27	27	Ammonia Cold	0.025	0.14
Si*	28	28	Hydrogen+Ammonia	11.2	231
P*	31	47	Oxygen	0.39	1.03
K	39	39	Ammonia Cold	0.016	0.059
Ca	40	40	Ammonia Cold	0.020	0.203
Sc	45	61	Oxygen	0.028	0.057
Ti	48	131	Ammonia	0.062	0.077
V	51	134	Ammonia	0.082	<DL
Cr	52	52	Ammonia Cold	0.57	<DL
Mn	55	55	Ammonia Cold	0.012	0.023
Fe	56	56	Ammonia Cold	0.19	0.55
Co	59	59	Ammonia Cold	0.003	<DL
Ni	60	60	Ammonia Cold	0.020	0.020
Cu	63	63	Ammonia Cold	0.020	0.045
Zn	64	98	Ammonia	1.06	1.26
Ga	69	69	Ammonia	0.053	0.12
Ge	74	90	Ammonia	0.12	<DL
As	75	91	Oxygen	0.13	<DL
Se	78	94	Oxygen	0.89	<DL
Rb	85	85	Ammonia	0.013	0.017
Sr	88	88	Ammonia	0.017	<DL

* Obtained with SiQ injector due to contaminations in Pt

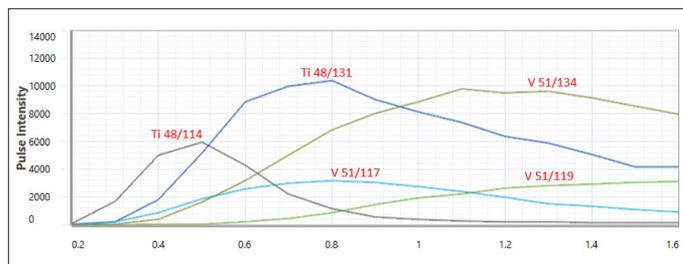


Figure 4. Ammonia flow optimization for Ti-NH₃ clusters. Concentration of Ti was 100 ppt.

In Table 3, background equivalent concentrations (BECs) and detection limits (DLs) in 10% H₂SO₄ for 52 elements, along with modes of operations, are shown. It is worth mentioning that BEC values reflect not only the performance of the instrument but also contamination levels in the analyzed acid.

Element	Q1	Q3	Mode	DLs (ppt)	BECs (ppt)
Zr	90	90	Ammonia	0.13	0.40
Nb	93	93	Standard	0.038	0.045
Mo	95	95	Ammonia	0.14	<DL
Ru	102	102	Standard	0.083	<DL
Rh	103	103	Standard	0.009	0.013
Pd	105	105	Standard	0.096	<DL
Ag	107	107	Ammonia	0.041	0.052
Cd	111	111	Oxygen	0.23	0.39
In	115	115	Ammonia	0.006	<DL
Sn	118	118	Ammonia	0.036	<DL
Sb	121	121	Ammonia	0.099	0.16
Te	128	128	Ammonia	0.064	<DL
Cs	133	133	Standard	0.021	<DL
Ba	138	138	Standard	0.014	0.02
Hf	178	178	Standard	0.076	<DL
Ta	181	181	Standard	0.035	0.052
W	184	184	Standard	0.11	<DL
Re	187	187	Standard	0.036	<DL
Ir	193	193	Standard	0.13	<DL
Pt**	194	194	Standard	1.3	4.2
Au	197	197	Ammonia	0.2	0.21
Hg	202	202	Oxygen	0.2	0.75
Tl	205	205	Standard	0.031	<DL
Pb	208	208	Standard	0.083	<DL
Bi	209	209	Standard	0.024	<DL
U	238	238	Standard	0.032	<DL

** Elevated due to Pt injector

For DL and BEC measurements, calibration curves for the elements listed in Table 3 were established with 1, 5, 10, 15 and 20 ppt standards using method of standard additions. Only the P and Si standards were 20 and 100 times higher, respectively. All curves had linear regressions values (r^2) > 0.999, demonstrating the linearity of the analysis and the ability to measure accurately at low concentrations. Figure 5 shows typical calibration curves obtained in different modes: Li in Standard Cold Plasma mode, K in Reaction (NH₃) Cold Plasma mode, Sc in Reaction (O₂) Mass Shift mode, and Ti in Reaction (NH₃) Mass Shift mode.

10% H₂SO₄ was spiked with 15 ppt spike (with the exception of Si and P that were spiked with 1500 ppt and 300 ppt respectively). The plot in Figure 6 shows excellent instrument accuracy with spike recovery within ± 10% for all elements.

Long-term stability is as equally important as DLs and BECs for the methodology to work well. The stability of the NexION 5000 ICP-MS was evaluated by measuring a QC sample (20 ppt spike of 48 elements, 400 ppt P and 2000 ppt Si in 10% H₂SO₄) for over nine hours. QCs were measured every four samples of 10% H₂SO₄. The plot (Figure 7) demonstrates exceptional stability for all elements in all modes. RSDs were less than 5% for all elements and the drift was within ±15% from the initial reading.

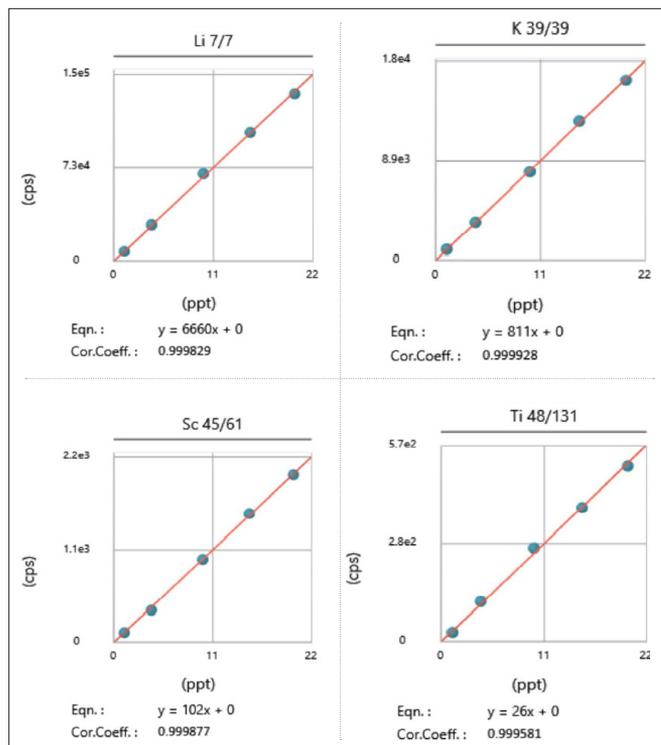


Figure 5. Examples for calibration curves in four different modes of analysis.

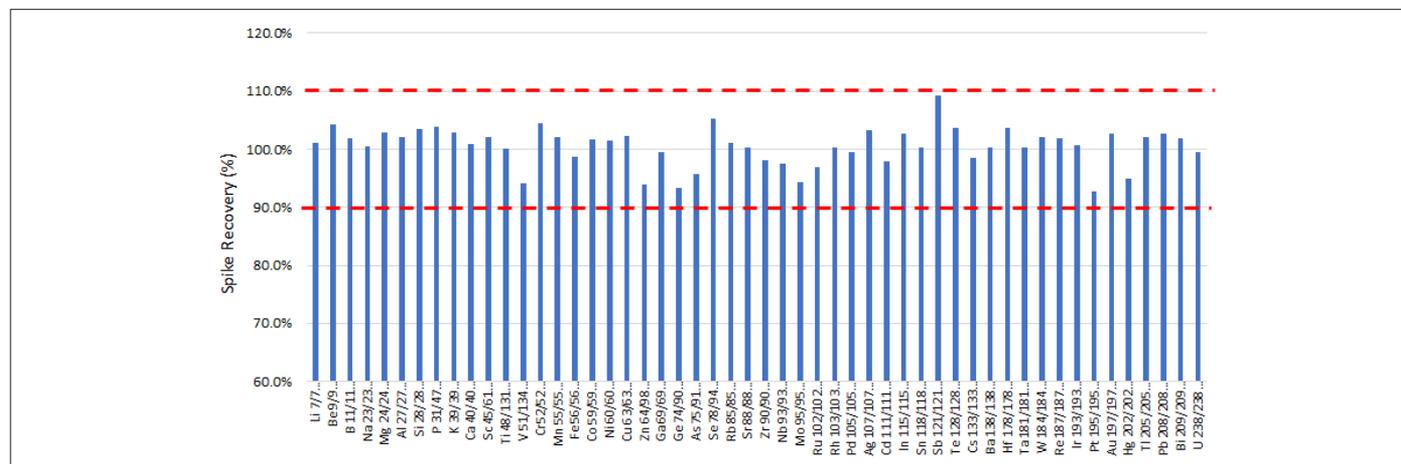


Figure 6. Spike recovery of 15 ppt in 10% H₂SO₄.

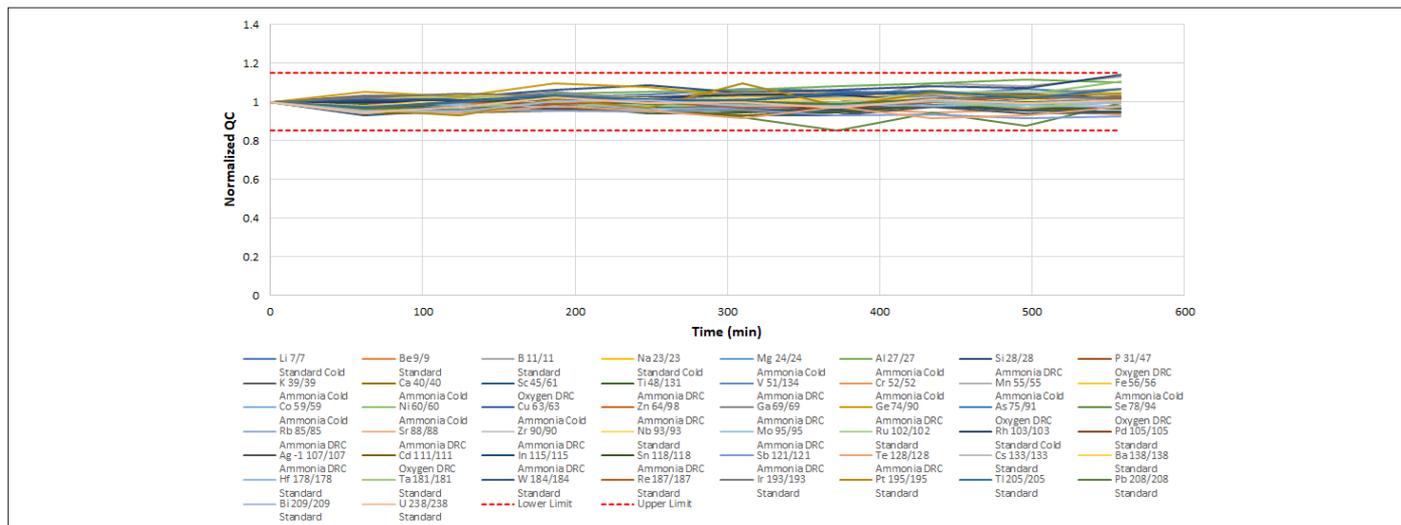


Figure 7. Long-term stability (nine hours) of a QC standard for 50 elements spiked into 10% H₂SO₄ at concentration of 20 ppt.

Conclusion

The results presented in this work demonstrate that the NexION 5000 ICP-MS with multi-quadrupole technology – in combination with the patented SMARTintro™ sample introduction system, the unique 34-MHz RF plasma generator with the LumiCoil RF load coil, and the quadrupole Universal Cell with up to four 100% pure reactive gases – provides the outstanding analytical performance needed for the semiconductor industry in a difficult matrix, such as 10% H₂SO₄.

References

1. SEMI C44-0618 "Specification and Guide for Sulfuric Acid".
2. "NexION 5000 Multi-Quadrupole ICP-MS" PerkinElmer Product Note, 2020.
3. Badiei H., "Advantages of a Novel Interface Design for NexION 5000 ICP-MS" PerkinElmer Technical Note, 2020.
4. Tanner S., "Theory, Design and Operation of a Dynamic Reaction Cell for ICP-MS", Atomic Spectroscopy, Vol. 20, March/April 1999.

Consumables Used

Component	Part Number
Sample Probe, 0.3 mm ID	N8152513
PFA ST3 Nebulizer	N8152378
SilQ Spray Chamber	N8152424
PC3 Peltier Cooler	N8152382
Demountable SilQ Torch	N8152448
Pt Injector	N8152429
Pt Cones	W1033614 and N8161041