

ICP - Mass Spectrometry

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Analysis of Semiconductor-Grade Hydrogen Peroxide Using the NexION 5000 ICP-MS

Introduction

Contaminants, such as particles, trace metals, and non-metals in chemicals used during manufacturing processes have

a direct impact on product yield and the reliability of semiconductor devices. Within the whole process of integrated circuit (IC) manufacturing, wafers are sent for repeated cleaning before each critical process – such as diffusion, implant or deposition – and after photolithography steps to remove organic photoresist solvents from the wafer surface. In all these cleaning processes, a common chemical is used: hydrogen peroxide. For example, chemicals such as ammonia peroxide mixture (APM) and hydrochloric peroxide mixture (HPM) (also known as SC-1 and SC-2 respectively) are mixtures of ammonia solution (NH_4OH) and hydrochloric acid (HCl) with hydrogen peroxide (H_2O_2) and are effective in the removal of particulate and metal contamination. The sulfuric peroxide mixture (SPM) (piranha etch or caro acid) is a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide and is used in the removal of organic photoresist residues. Hydrogen peroxide is also employed in vapor phase deposition (VPD) etching with mixture of hydrofluoric acid (HF) to convert the surface of wafers into a hydrophobic layer for metal contamination studies.

Semiconductor Equipment and Materials International (SEMI) standard for H₂O₂, SEMI C30-1110 – Specifications for Hydrogen Peroxide SEMI Grade 51, specifies maximum contamination levels of 10 ppt for most trace elements. While a conventional quadrupole ICP-MS (ICP-QMS) technique could be used to monitor trace-element contaminants at ppt levels, the detection capability for silica (Si), phosphorus (P) and sulfur (S) is limited to ppb levels. With semiconductor devices getting down to N5 nodes, it is becoming imperative to be able to analyze Si, P and S at much lower levels.

In this application note, we describe the analysis of 46 elements in 35% H₂O₂ using PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS. The NexION 5000 ICP-MS offers flexibility for the determination of non-metallic elements down to ppt levels together with other trace metals down to sub-ppt levels within a single analysis. This capability is critical in the analysis of trace contaminants in H₂O₂, which is used in multiple stages of the wafer fabrication process.

Instrumentation

The NexION 5000 ICP-MS is a four-quadrupole system that offers capabilities beyond conventional triple-quadrupole technology in the elimination of spectral interferences, providing excellent sensitivity and the lowest background for each analyte.

The analytical performance, sensitivity and stability of the instrument is elevated through the novel Triple Cone Interface (TCI) with OmniRing™ technology² and the patented plasma generator with the LumiCoil™ RF coil. The balanced and free-running RF generator design delivers improved robustness, high efficiency, 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 a cell-based Reaction mode (in the Quadrupole Universal Cell) and multi-quadrupole technology, yielding superior polyatomic interference removal that can further improve detection limits (DLs) and lower background equivalent concentrations (BECs).

The NexION 5000's Universal Cell is a true quadrupole reaction cell that allows the control of reaction chemistry within the cell, not achievable with an ion-guide (passive) cell, such as hexapole or octopole. This is achieved through the application of bandpass within the cell, preventing by-products of the original reaction from forming new interferences with the cell gas or cell gas impurities which may have been introduced into the cell. The bandpass of the reaction cell allows predictable and reproducible interference removal using either 100% pure or a mixture of highly reactive gases in the cell. Plus, the NexION 5000 ICP-MS provides four gas channels, which allows on-the-fly gas mixing of reaction and/or collision gases within the same analytical method, delivering ultimate flexibility in the removal of interferences.

Experimental

Reagents and Samples

TAMAPURE-AA-10 hydrogen peroxide (35%, Tama Chemicals, Kawasaki City, Japan) was used as a sample and TAMAPURE-AA-10 nitric acid (68%, Tama Chemicals) was used for acidification of the samples.

A 1000-ppt multi-element standard solution was prepared by diluting a set of 10-ppm multi-element standard solutions (PE Pure, PerkinElmer, Shelton, Connecticut, USA) with 1% HNO₃. This final 1000-ppt solution was then used for matrix matching calibration standards (method of standard addition – MSA) and spike recovery tests for metallic elements. Some non-metallic elements were calibrated at higher levels than other elements.

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 (NH₃, H₂ and O₂) were used to remove all spectral interferences on measured analytes. 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. Instrumental conditions are shown in Table 1.

Table 1. NexION 5000 ICP-MS Instrumental Conditions.

Parameter	Value
Nebulizer	PFA ST3 Self-aspirating
Sample Uptake	~500 µL/min
Nebulizer Flow	1.0 L/min
Torch	SilQ One Piece with 2 mm ID Injector
RF Power	1500W Hot Plasma, 700W Cold Plasma
Measuring Time/Isotope	1 second
Cell Modes	Standard and Reaction
Cell Gases	NH ₃ , H ₂ and O ₂

Although there are various modes being used in this work, the optimization procedure can be easily achieved on the intuitive Syngistix™ for ICP-MS software, through the SmartTune wizard. Most parameters that are linked or inter-related do not require individual tuning in each mode of operation. This simplified optimization procedure aids in achieving the most optimized conditions for interference removal while maintaining maximum sensitivity for the analytes.

Results and Discussion

The most abundant spectral interferences in H_2O_2 analysis are argon, nitrogen and oxygen-related polyatomic species. Examples of potential interferences are listed in Table 2.

Table 2. Analytes and Their Potential Interference in H_2O_2 .

Analyte	Interference
^{28}Si	$^{12}\text{C}^{16}\text{O}$, $^{14}\text{N}^{14}\text{N}$
^{31}P	$^{15}\text{N}^{16}\text{O}$, $^{14}\text{N}^{16}\text{O}^1\text{H}$
^{32}S	$^{16}\text{O}^{16}\text{O}$
^{35}Cl	$^{16}\text{O}^{19}\text{F}$
^{39}K	$^{38}\text{Ar}^1\text{H}$
^{40}Ca	^{40}Ar
^{48}Ti	$^{36}\text{Ar}^{12}\text{C}$, $^{32}\text{S}^{16}\text{O}$
^{52}Cr	$^{40}\text{Ar}^{12}\text{C}$
^{56}Fe	$^{40}\text{Ar}^{16}\text{O}$
^{75}As	$^{40}\text{Ar}^{35}\text{Cl}$
^{78}Se	$^{40}\text{Ar}^{38}\text{Ar}$

A combination of MS/MS, Q3 and Mass Shift in Standard, Reaction- NH_3 , Reaction- O_2 , and Reaction- H_2 modes was used in the analysis. Also, some elements were analyzed under cold plasma conditions in Standard Cold and Reaction Cold- NH_3 modes.

The Mass Shift mode is a very powerful technique for removing spectral interferences on those elements that can efficiently create clusters with reactive gases, such as NH_3 , O_2 , CH_4 and others. Mass Shift allows to move an element of interest as a cluster to a higher mass where no other ions exist and measure it virtually interference-free. In this application, Mass Shift mode was used for measuring phosphorus (P), sulfur (S), titanium (Ti), arsenic (As), and selenium (Se) as clusters with O_2 .

For example, Ti at mass 48 (the most abundant isotope) is one of the challenging analytes due to the presence of many spectral interferences at its mass. However, Ti reacts readily with O_2 and NH_3 , creating clusters at higher masses. In this application, using O_2 as a reaction gas, Ti^+ was measured as TiO^+ at mass 64. Any ions residing on mass 64 were eliminated by the first transmission analyzer quadrupole (Q1); therefore, Ti can be analyzed at ultra-low concentrations without any spectral interferences.

Figure 1 shows a scan of 100-ppt Ti in H_2O_2 solution without the addition of oxygen to the cell (Standard mode). Here, the Ti stays at mass 48.

In Figure 2, Ti^+ at mass 48 is shifted and measured at mass 64 as TiO^+ after the reaction with O_2 in the Universal Cell.

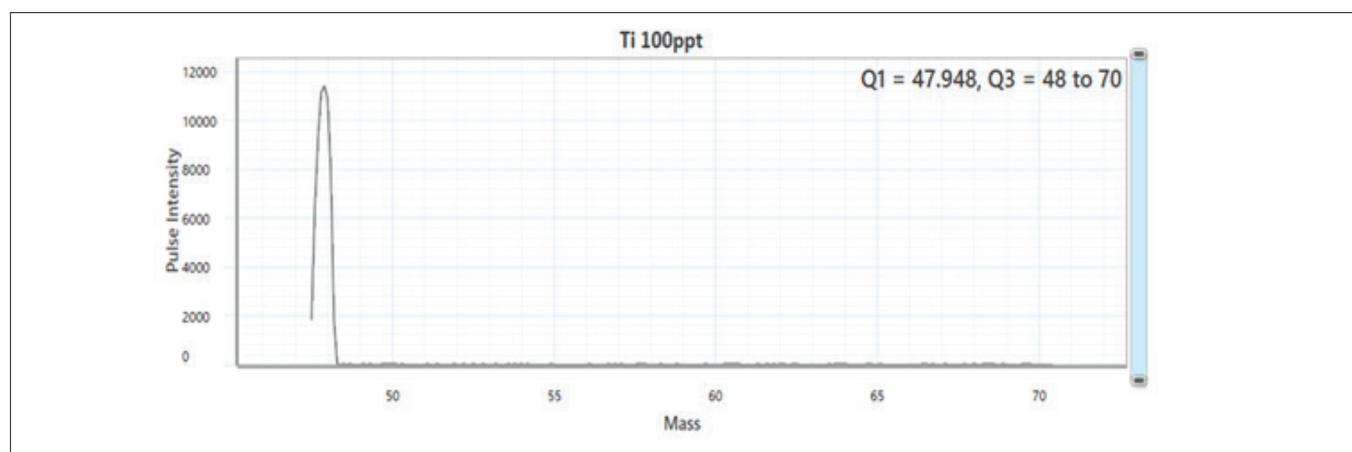


Figure 1. Product Ion scan of 100-ppt Ti in 35% H_2O_2 in Standard mode. Q1 transmits only mass 48 and Q3 scans from mass 48 to 70.

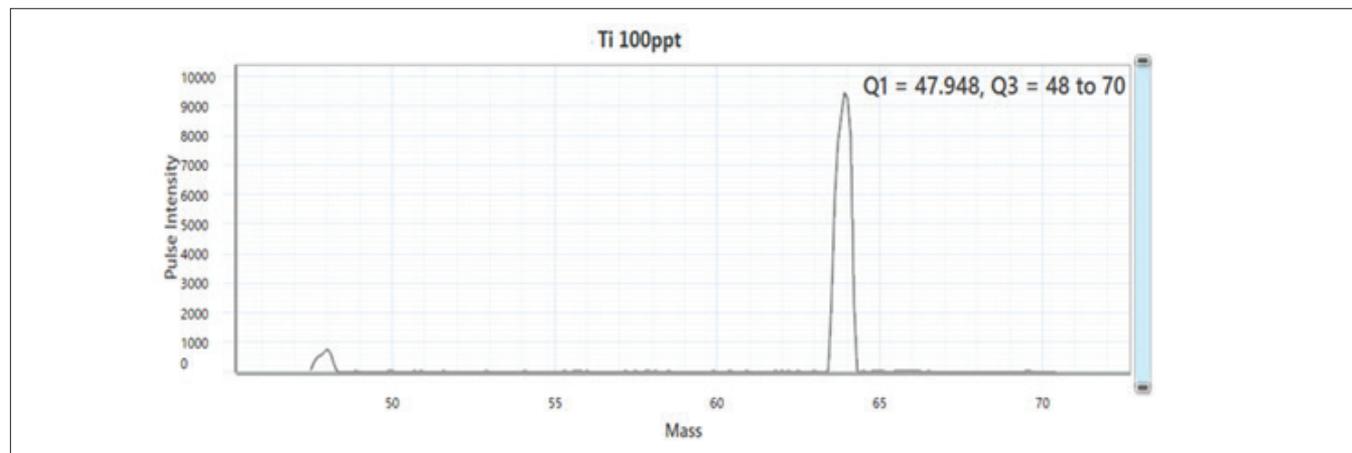


Figure 2. Product Ion scan of 100-ppt Ti in 35% H_2O_2 in the Reaction- O_2 mode. Q1 transmits only mass 48 and Q3 scans from mass 48 to 70.

The calibration curves for metallic impurities were obtained using the method of standard additions (MSA) with spikes of 5, 10, 20 and 50 ppt into 35% H₂O₂. The calibration curves for non-metallic elements (Si, S and P) were based on higher spike concentrations of 1, 2 and 4 ppb. All curves had linear regressions values (r^2) > 0.999,

demonstrating the superb linearity and the ability of the instrument to measure accurately at low concentrations. Figure 3 shows typical calibration curves obtained in four different modes: Na in Standard Cold Plasma mode, Ti in Reaction (O₂) Mass Shift mode, Fe in Reaction (NH₃) Cold Plasma mode and Si in Reaction (H₂) mode.

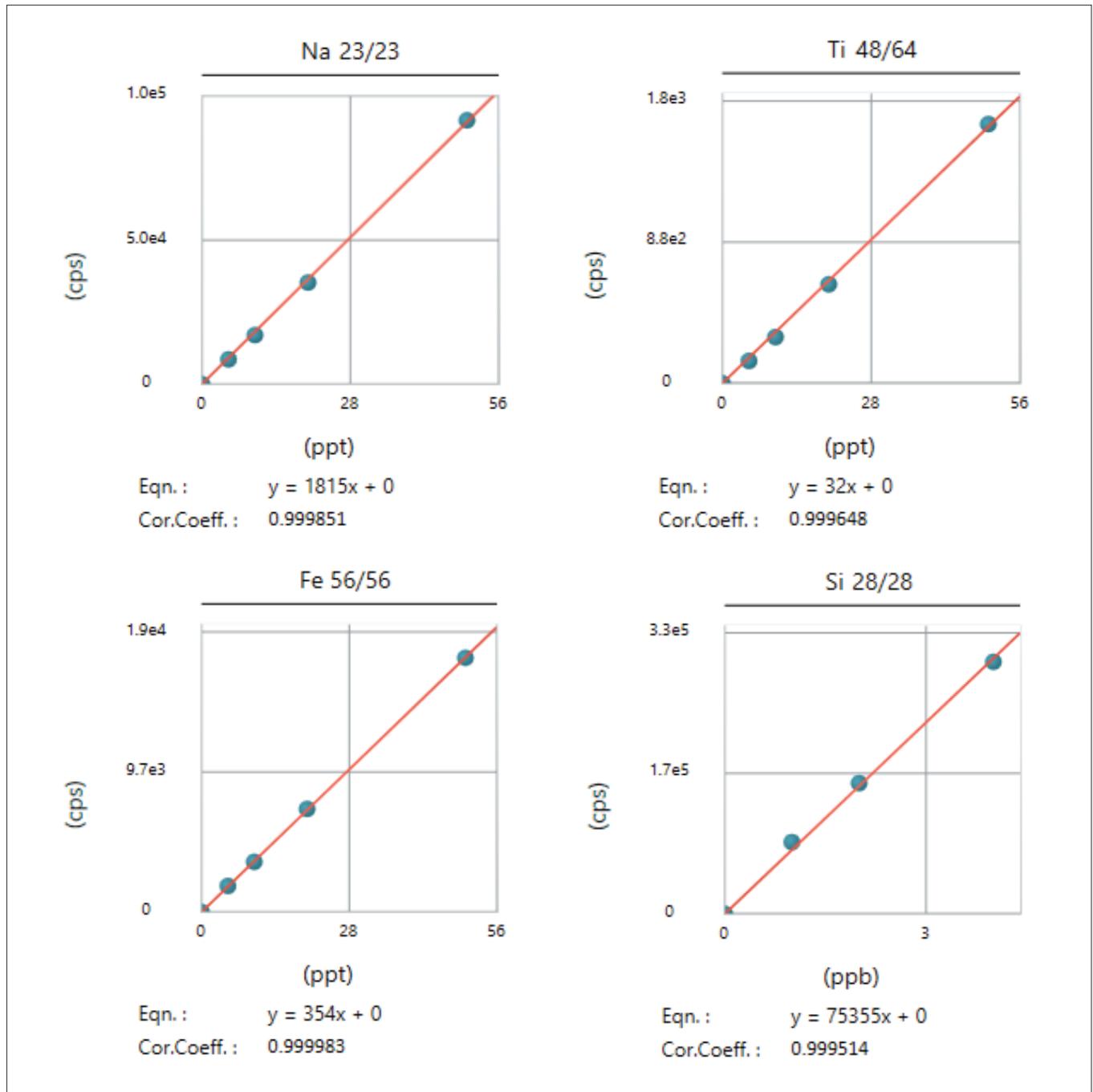


Figure 3. Calibration curves for Na, Fe, Ti and Si in 35% H₂O₂.

Quantitative Results

The measurement of all elements was carried out by MSA in undiluted 35% H₂O₂ acidified by 0.2% HNO₃. The NexION 5000 ICP-MS provides the flexibility to measure these elements using multiple modes within a single method. BECs, DLs and recoveries of 5 ppt spike (1ppb for Si and S) are shown in Table 3. Detection limits were calculated as 3-sigma of seven replicate measurements of the H₂O₂ blank sample. With the exception of B, Si, P and S, DLs less than 1 ng/L (ppt) were obtained for all other elements, with many of them even below 0.1 ppt. The DLs for B and P were at the single-digit ppt level, while the DLs for Si and S were at 16 and 26 ppt respectively.

More importantly, BECs were below 1 ppt for most elements, with many well below the detection limits. The exceptions were non-metals, B and P with BECs at single-digit ppt and Si and S with BECs <1 ppb.

Spike recoveries were performed at 5-ppt level (1 ppb for Si and S) with all elements achieving recoveries within ±25% as required by SEMI standard SEMI C1-0310.

Table 3. Quantification of Trace Elements in 35% H₂O₂.

Element	Isotope Selection (Q1/Q3)	Scan Type	Cell Mode	BEC (ppt)	DL (ppt)	5-ppt Recovery %
Li	7/7	MS/MS	Standard Cold	<DL	0.005	103.7
Be	9/9	MS/MS	Standard	<DL	0.1	105.5
B	11/11	MS/MS	Standard	5	2	124.1
Na	23/23	MS/MS	Standard Cold	0.17	0.05	103.6
Mg	24/24	MS/MS	Standard Cold	0.04	0.01	104.1
Al	27/27	MS/MS	Reaction Cold NH ₃	0.12	0.05	103.3
Si*	28/28	MS/MS	Reaction H ₂	810	16	101.5
P	31/47	Mass Shift	Reaction O ₂	<DL	6	111.0
S*	32/48	Mass Shift	Reaction O ₂	830	26	102.6
K	39/39	MS/MS	Reaction Cold NH ₃	0.13	0.07	102.9
Ca	40/40	MS/MS	Reaction Cold NH ₃	0.4	0.2	110.3
Ti	48/64	Mass Shift	Reaction O ₂	<DL	0.2	101.6
V	51/51	MS/MS	Reaction NH ₃	<DL	0.02	105.6
Cr	52/52	MS/MS	Reaction Cold NH ₃	0.10	0.07	105.8
Mn	55/55	MS/MS	Reaction Cold NH ₃	<DL	0.006	103.4
Fe	56/56	MS/MS	Reaction Cold NH ₃	0.21	0.07	101.3
Co	59/59	MS/MS	Reaction Cold NH ₃	<DL	0.02	101.5
Ni	60/60	MS/MS	Reaction Cold NH ₃	<DL	0.06	102.5
Cu	63/63	MS/MS	Reaction Cold NH ₃	<DL	0.01	99.8
Zn	64/64	MS/MS	Reaction NH ₃	<DL	0.4	96.4
Ga	69/69	MS/MS	Reaction Cold NH ₃	<DL	0.001	101.7
Ge	74/90	Mass Shift	Reaction NH ₃	<DL	0.007	113.0
As	75/91	Mass Shift	Reaction O ₂	<DL	0.06	97.3
Se	80/96	Mass Shift	Reaction O ₂	<DL	0.7	95.7
Sr	88/88	MS/MS	Reaction NH ₃	<DL	0.01	100.7
Zr	90/90	MS/MS	Standard	<DL	0.04	97.6
Nb	93/93	MS/MS	Standard	<DL	0.02	101.9
Mo	98/98	MS/MS	Reaction NH ₃	<DL	0.01	106.0
Ru	102/102	MS/MS	Standard	<DL	0.07	104.1
Rh	103/103	Q3 Only	Standard Cold	<DL	0.001	101.9
Pd	106/106	MS/MS	Standard	<DL	0.09	113.4
Ag	107/107	MS/MS	Standard	<DL	0.05	103.6
Cd	111/111	MS/MS	Standard	<DL	0.06	88.0

Table 3. Quantification of Trace Elements in 35% H₂O₂ - CONTINUED.

Element	Isotope Selection (Q1/Q3)	Scan Type	Cell Mode	BEC (ppt)	DL (ppt)	5-ppt Recovery %
In	115/115	MS/MS	Standard	<DL	0.006	108.2
Sn	118/118	MS/MS	Standard	<DL	0.1	100.6
Sb	121/121	MS/MS	Reaction NH ₃	<DL	0.01	96.0
Ba	138/138	MS/MS	Standard	<DL	0.04	105.0
Hf	180/180	MS/MS	Standard	<DL	0.03	110.0
Ta	181/181	MS/MS	Standard	<DL	0.03	107.4
W	184/184	MS/MS	Standard	<DL	0.1	107.0
Pt	195/195	Q3 Only	Standard Cold	<DL	0.3	85.7
Au	197/197	MS/MS	Standard	<DL	0.1	95.1
Tl	205/205	MS/MS	Standard	<DL	0.009	95.7
Pb	208/208	MS/MS	Reaction NH ₃	<DL	0.02	101.2
Bi	209/209	MS/MS	Standard	<DL	0.01	97.6
U	238/238	MS/MS	Standard	<DL	0.01	103.1

* 1 ppb spike for Si and S

It is imperative that besides producing the best BECs and DLs, the ICP-MS must also be able to provide good long-term stability. A five-hour analysis of H₂O₂ was performed with a QC (H₂O₂ spiked with 10 ppt) measured at 20-minute intervals.

Figure 4 demonstrates exceptional stability for all elements in all modes with the NexION 5000 ICP-MS. Relative standard deviations (RSDs) were less than 5% for all elements and the drift was within ±15% against an average value.

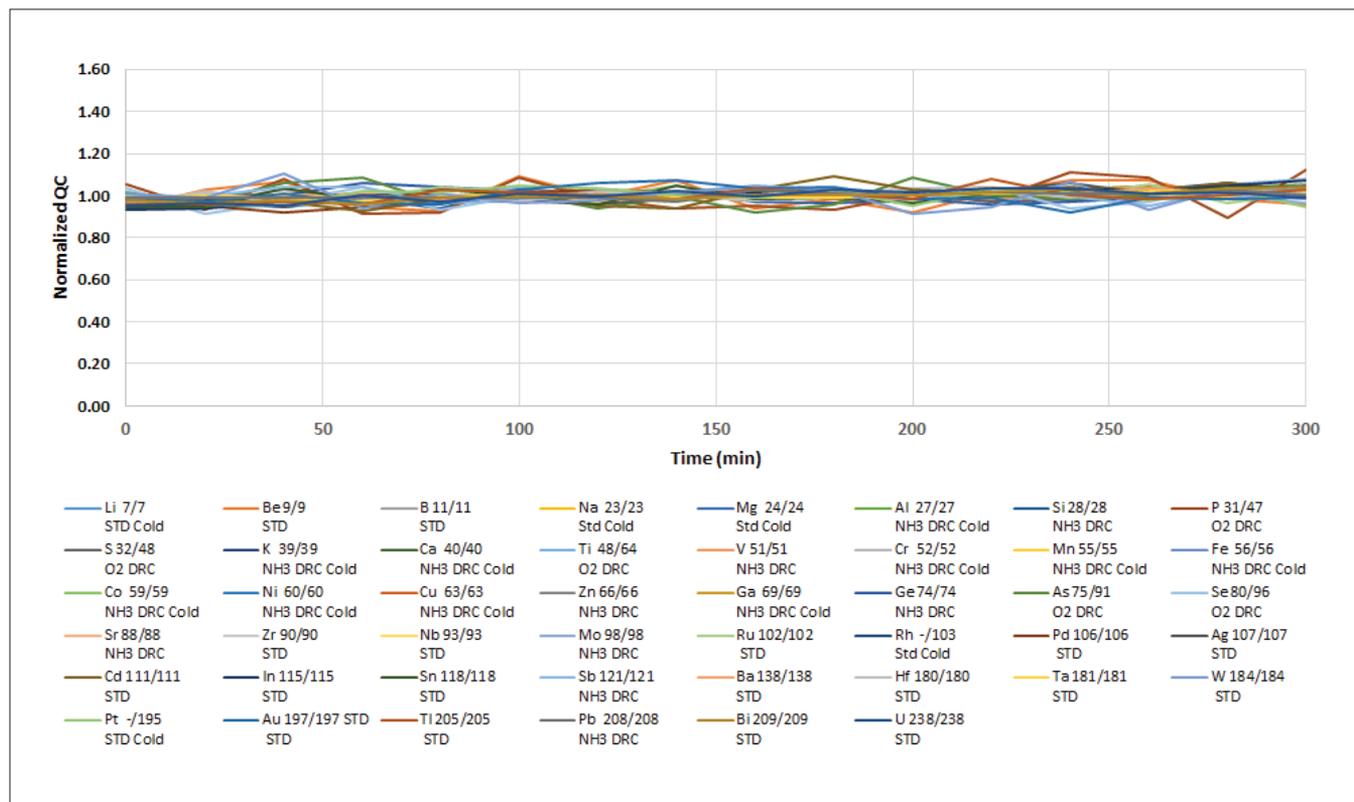


Figure 4. Long-term stability (5 hours) of 10 ppt spiked in 35% H₂O₂.

Conclusions

The NexION 5000 Multi-Quadrupole ICP-MS has shown to be robust and suitable for the routine quantification of ultra-trace impurities at the ng/L level in 35% H₂O₂. Syngistix for ICP-MS software simplifies the optimization procedure of different operating modes, allowing various modes of operation in MS/MS, Mass Shift as well as Hot and Cold Plasma with and without the use of cell gas flow to be used in a single method. All the elements specified in SEMI C30-1110, including Si, P and S, were measured at sub-ppt to ppt levels in high-purity 35% H₂O₂.

References

1. SEMI C30-1110 – Specifications for Hydrogen Peroxide, 2010.
2. Badiei H. et al, "Advantages of a Novel Interface Design for NexION 5000 ICP-MS" PerkinElmer Technical Note, 2020.