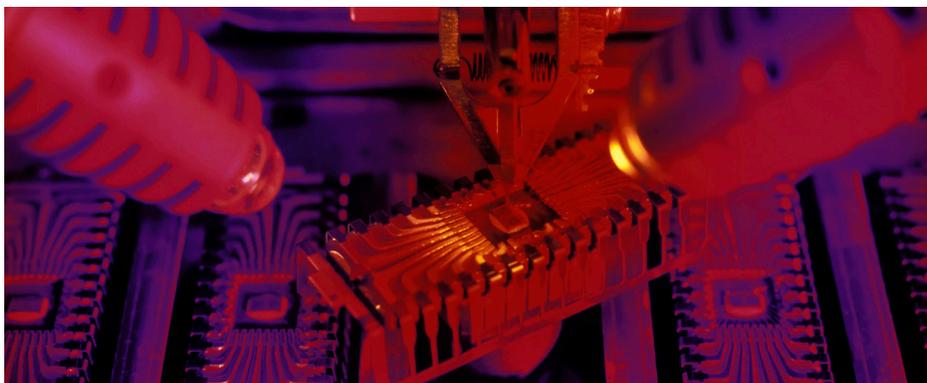


Automated Analysis of Semiconductor Grade Hydrogen Peroxide and DI Water using ICP-QQQ

Online MSA calibration using prepFAST S automated sample introduction and Agilent 8900 ICP-QQQ



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Introduction

Maximizing product yield and performance of semiconductor devices requires manufacturers to address the potential for contamination at every stage of the production process. Contamination from particles, metals, and organic residues can affect the electrical properties of the semiconductor, reducing the quality and reliability of the final product. For example, following each photolithography step during wafer processing, the organic photoresist mask must be completely removed from the silicon wafer surface. A mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) known as a sulfuric/peroxide mix (SPM) is used for this cleaning procedure. SPM is also used for degreasing the wafer surface. H_2O_2 is also used in the RCA Standard Clean steps (SC-1 and SC-2) used to clean silicon wafers, and for etching metallic copper on printed circuit boards.

Ultrapure water (UPW) is used throughout the wafer fabrication process. As well as working as a rinse solution between processing steps, UPW is also the diluent for many process chemistries such as SC-1 and SC-2 solutions. As these chemicals are in frequent and prolonged contact with the wafer surface, minimizing metal impurities is essential to prevent wafer surface contamination.

Semiconductor Equipment and Materials International (SEMI) publishes standards for semiconductor process chemicals. The standard for H₂O₂ is SEMI C30-1110 – Specifications for Hydrogen Peroxide (1). SEMI Grade 5 is the highest purity level, with maximum contamination levels of 10 ppt for most trace elements.

Quadrupole ICP-MS (ICP-QMS) is the standard technique used to monitor trace element contaminants in the semiconductor industry. However, the drive for ever smaller device architectures and higher yields requires an increasing number of contaminant elements to be monitored at lower concentrations.

In addition to trace elements, SEMI Standard C30-1110 specifies the maximum concentration of sulfate and phosphate allowed in high purity H₂O₂, with a limit of 30,000 ppt. This limit equates to an elemental concentration of sulfur (S) and phosphorus (P) of 10,000 ppt. Due to the relatively high detection limits achievable with conventional single quadrupole ICP-MS, these two elements are not currently measured using ICP-MS.

Triple quadrupole ICP-MS (ICP-QQQ) provides much lower limits of detection for S and P (among many other elements). Uniquely, the technique offers the potential for the sulfate and phosphate analysis to be combined with the other trace metals. The adoption of ICP-QQQ therefore enables all SEMI specified elements to be monitored using a single technique (2, 3).

Contamination control

Ultratrace analysis at the pg/g (ppt) or fg/g (ppq) level is susceptible to contamination from the lab environment, reagents, or errors arising from manual tasks, such as pipetting. To deliver consistently accurate results at these ultratrace concentrations, a skilled and experienced analyst is typically required.

One approach to simplifying the analysis for less expert analysts is to use an automated sample introduction system. These systems automate typical sample handling steps such as dilution, acidification, and spiking. They can also automatically generate a calibration curve using either external standards or Method of Standard Additions (MSA).

In this study, an automated procedure was developed to quantify ultratrace elemental impurities in de-ionized (DI) water and H₂O₂ using an Agilent 8900 ICP-QQQ fitted with an ESI prepFAST S automated sample introduction system. The prepFAST S automates sample preparation and calibration, saving time and minimizing the risk of sample-contamination from manual sample handling operations.

Experimental

Reagents and samples

TAMAPURE-AA-10 hydrogen peroxide (35%, Tama Chemicals, Japan) and ultrapure DI water (Milli-Q water, Molsheim, France) were used as the samples.

Standard stock solution for MSA: a 1000 ppt mixed multi-element standard solution was prepared by diluting a 10 ppm mixed multi-element standard solution (SPEX CertiPrep, NJ, US) with 1% HNO₃.

Nitric acid for sample acidification: a 10% nitric acid solution was prepared by diluting 68% ultrapure HNO₃ (TAMAPURE-AA-10) with DI water. HNO₃ was automatically added to the H₂O₂ samples, giving a final concentration of 0.5% HNO₃ to stabilize the spiked elements. UPW samples are often also acidified to ensure trace element stability (see reference 2). However, in this work, the DI water was analyzed unacidified, without the addition of a HNO₃ spike, providing results that can be compared with the earlier work.

The standard stock and HNO₃ spike solutions were loaded on the prepFAST S. All solutions run in the analysis were automatically prepared from these stock solutions by the prepFAST S system. The prepFAST S method used DI (Milli-Q) water as the carrier solution, at a flow rate of 100 µL/min.

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

Instrumentation

A standard Agilent 8900 semiconductor configuration ICP-QQQ instrument was equipped with a PFA concentric nebulizer that is included with the prepFAST S automated sample introduction system. The semiconductor configuration ICP-QQQ is fitted with a Peltier cooled quartz spray chamber, quartz torch (2.5 mm id), platinum-tipped sampling and skimmer cones, and s-lens.

The 8900 ICP-QQQ was connected to the ESI prepFAST S automated sample introduction system. The prepFAST S is a specialized, semiconductor version of the standard ESI prepFAST. The S version has a high purity, low-contamination, inert sample path and features an automated MSA spike addition mode. ICP-QQQ instrument operating conditions are given in Table 1.

Table 1. ICP-QQQ operating conditions.

Tune	Cool-no gas	Cool-NH ₃ (1)	Cool-NH ₃ (2)	No gas	H ₂	He	O ₂ (1)	O ₂ (2)
Acquisition mode	Single Quad	MS/MS						
RF power (W)	600			1500				
Carrier gas (L/min)	0.70							
Makeup gas (L/min)	0.90			0.48				
Sampling depth (mm)	18.0			8.0				
Ext 1 (V)	-150.0		-100.0	4.2	4.7	4.2	4.5	3.5
Ext 2 (V)	-18.0	-17.0	-12.0	-250.0			-120.0	
Omega bias (V)	-70.0			-140.0				-70
Omega lens (V)	2.0			10.0	8.0	10.0	10.5	4.0
Q1 entrance (V)	-15.0		-50.0					
NH ₃ flow (mL/min)*	-	3.0 (30%)**		-	-	-	-	-
He flow (mL/min)	-	1.0		-	-	5.0	-	-
H ₂ flow (mL/min)	-	-	-	-	7.0	-	-	-
O ₂ flow (mL/min)	-	-	-	-	-	-	4.5 (45%)**	
Axial acceleration (V)	0.0	1.5			0.0		1.0	
Energy discrimination (V)	15.0	-5.0		5.0	0.0	3.0	-7.0	

*10% NH₃ balanced with 90% He

** Values in parentheses are % of the maximum flow of the gas controller, as displayed in the tuning pane of ICP-MS MassHunter software

The most advanced semiconductor manufacturing facilities require the lowest possible levels of contamination, so they require analytical techniques that can deliver the lowest possible detection limits (DLs). This requirement is critical in the analysis of trace contaminants in process chemicals such as UPW and H₂O₂, which are used at multiple stages of the wafer fabrication process. UPW and H₂O₂ also come into direct contact with the wafer surface.

The 8900 ICP-QQQ satisfies this requirement by offering the flexibility to optimize the measurement parameters (plasma conditions, quadrupole scan mode, cell gas type, and flow rate) to give the highest sensitivity and lowest background for each analyte.

In this work, several reaction cell gases (He, H₂, O₂, and NH₃) were used in the collision/reaction cell (CRC) of the 8900, as appropriate for the large number of analytes being measured. Since DI water and H₂O₂ are low-matrix samples, cool plasma conditions were also applied for the elements where this mode provides the lowest background equivalent concentrations (BECs).

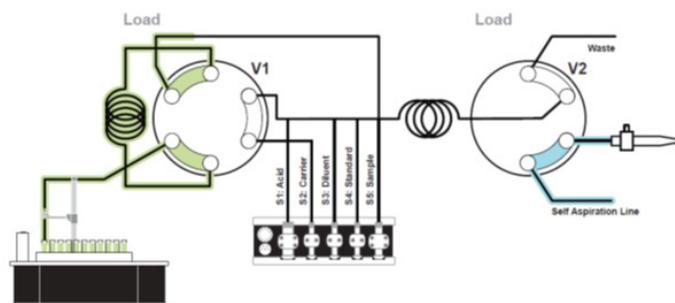
The tuning steps were applied sequentially during the measurement of each solution. This approach allows the tuning conditions to be optimized for the removal of different types of interferences, while maintaining maximum sensitivity for the analytes. Q1 and Q2 settings are shown in Table 2 along with DLs, BECs, and quantification results.

ESI prepFAST S operation

The prepFAST S automated sample introduction system combines an autosampler with a system of ultrapure valves (S1 -5), and a set of high precision syringe pumps. Undiluted chemicals can be placed on the autosampler and the system will perform the actions—such as dilution, acidification, and spiking—required to prepare the sample for introduction to the ICP-MS or ICP-QQQ. The operation of the prepFAST S is outlined in the four schematics shown in Figure 1.

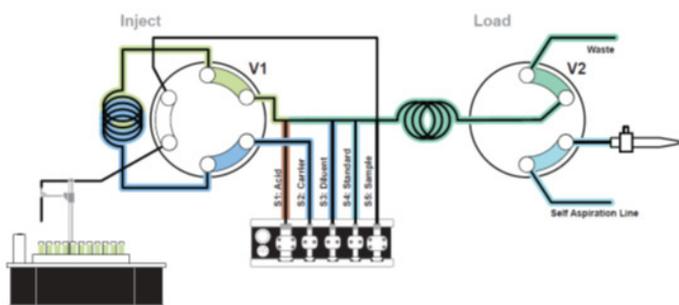
1. Loading of sample: Syringe S5 loads a precise amount of sample to the loop of valve 1 (V1).

Step 1: Fill Loop



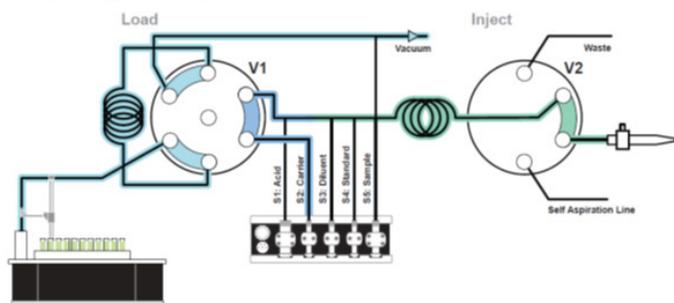
2. Sample dilution and sample spiking: Syringes S1, S2, S3, and S4 mix the acid, sample, diluent, and spike solution into a loop connecting V1 and V2.

Step 2: Dilute Sample



3. Sample injection: The prepared sample is introduced into the ICP-QQQ via the carrier solution pumped by S2. S2 provides a precise flow rate regardless of sample type. The V1 loop is washed simultaneously.

Step 3: Inject Sample



4. Valve wash: UPW or acidified UPW is used to clean the lines between V1 and V2.

Step 4: Clean Valves

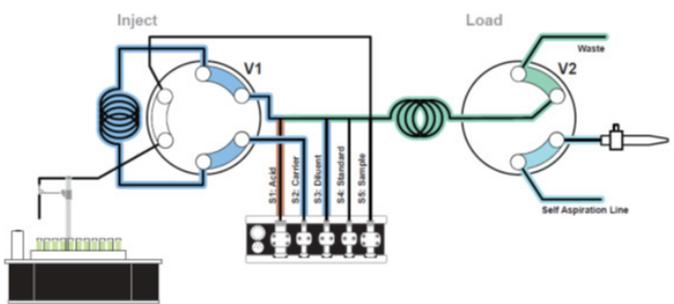


Figure 1. ESI prepFAST S system schematic, illustrating four distinct steps: sample loading during spray chamber rinse, sample preparation, injection, and cleaning.

The prepFAST S removes the need for analyst intervention in the analysis of semiconductor grade chemicals, reducing the risk of sample contamination. The integrated system offers the following advantages for the ultratrace elemental analysis of semiconductor samples:

1. Automated dilution of samples
2. Automated creation of external or MSA calibrations
3. Automated acidification of samples
4. Injection of samples at a precise flow rate
5. High speed rinsing of the ICP-MS sample introduction system

Results and Discussion

Figures 2 and 3 show calibration curves for Na, K, Si, P, and S in DI water and Ca, Zn, and As in H₂O₂, respectively. All elements were measured using the MSA calibration prepared automatically using the prepFAST S. These elements are difficult to analyze at low levels due to raised backgrounds. The analytes Si, P, and S are not commonly measured with conventional single quadrupole ICP-MS, due to the presence of intense polyatomic interferences. However, the controlled reaction chemistry of the 8900 ICP-QQQ operating in MS/MS mode gives far superior control of background interferences. MS/MS mode allows these elements to be calibrated and quantified at ppt concentrations.

Good linearity at the ppt level was observed for all elements measured in both sample matrices, although Si, P, and S had relatively high BECs of 85, 10, and 118 ppt, respectively. These elements are typically present at higher levels than the trace metals, as they are more difficult to control in the lab environment and in reagents. They are also less critical contaminants, as reflected in the higher levels for P and S (of 30 ppb for phosphate and sulfate) permitted in high purity H₂O₂. However, despite the higher BECs, the calibration curves for Si, P, and S were still linear over the calibration range from 10 to 50 ppt. The same calibration levels were used for all analytes, as the mixed stock standard contained all elements at the same concentration.

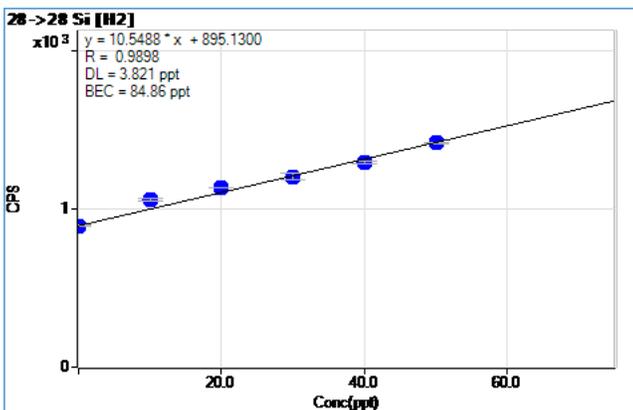
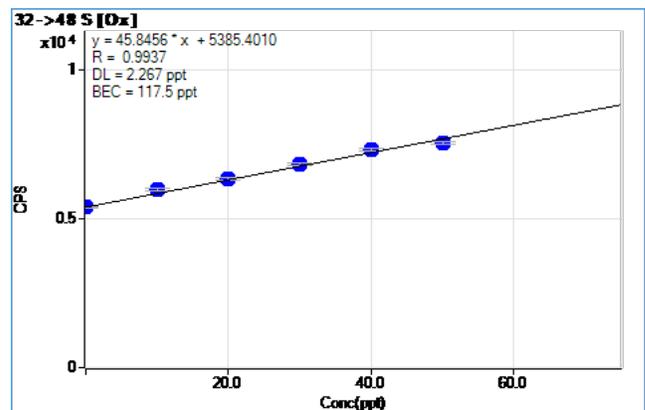
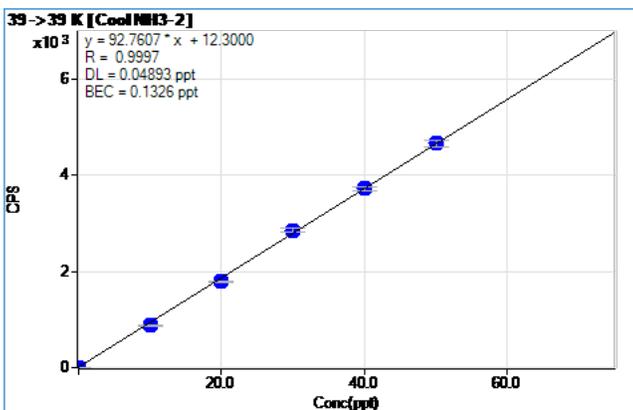
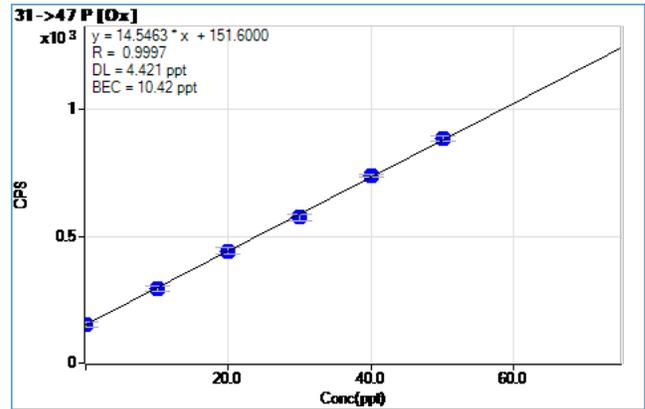
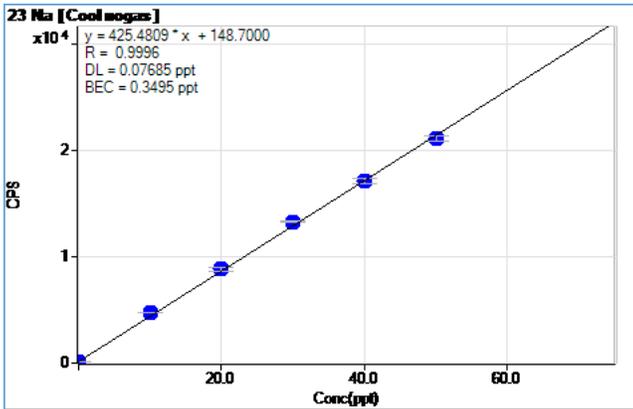


Figure 2. Calibration plots for Na, K, Si, P, and S in DI water. All values in ng/L (ppt).

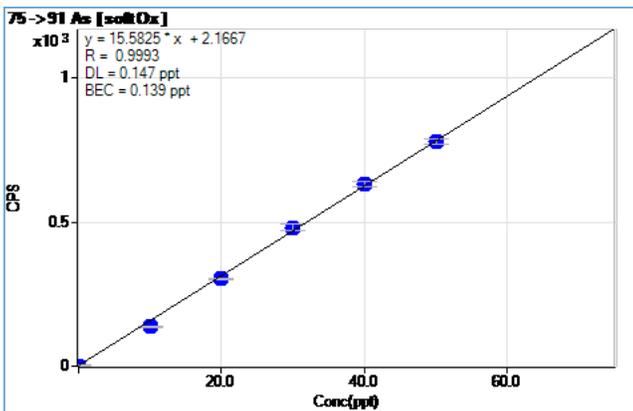
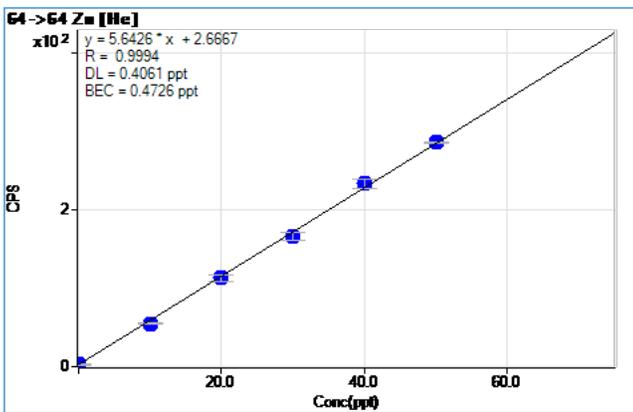
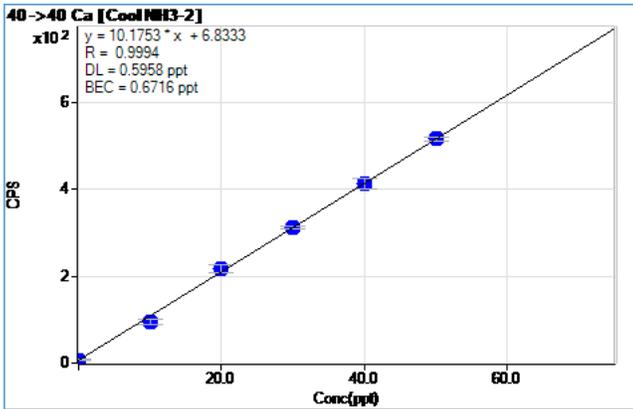


Figure 3. Calibration plots for Ca, Zn, and As in H₂O₂. All values in ng/L (ppt).

DLs and quantitative results

Forty-nine elements in total, including all the elements listed in SEMI C30-1110, were measured by MSA in DI water and H₂O₂, using the 8900 multi-tune mode method. Data was acquired in an automated sequence of cool plasma, no gas, and gas modes, during a single visit to the sample vial. Data for each of the modes was combined automatically into a single report for each sample.

Quantitative results, DLs, and BECs for all analytes—including all the SEMI specified elements—are shown in Table 2. Detection limits were calculated as 3-sigma of 10 replicate measurements of the blank DI water or H₂O₂ sample.

DLs <1 ng/L (ppt) were obtained for 46 elements in DI water. The DLs for the remaining 3 elements, Si, P, and S, were at the single-ppt level. Measured concentrations of all elements apart from B, Si, P, and S were <1 ng/L or <DL, confirming the purity of the sample. This analytical performance easily meets the requirements for monitoring UPW in semiconductor manufacturing.

In H₂O₂, DLs <1 ng/L were obtained for 45 elements. The DLs for B, P, and S, were at the single-ppt level, while the DL for Si was 26 ppt. All elements were measured at <1 ng/L or <DL apart from B (22 ppt), Na (1.1 ppt), Si (500 ppt), P (9.4 ppt), and S (220 ppt) in 35% H₂O₂. Only B and Si exceed the 10 ppt maximum limit in the SEMI specifications, and of these, only B is a SEMI specified element. P and S were quantified well below the 10,000 ppt SEMI specified limit in H₂O₂.

Table 2. Quantification of trace elements in DI water and 35% H₂O₂. SEMI specification elements are in bold.

	Q1	Q2	Scan type	Tune mode	DI Water			H ₂ O ₂		
					DL ng/L	BEC ng/L	Conc ng/L	DL ng/L	BEC ng/L	Conc ng/L
Li		7	SQ	Cool no gas	0.003	0.001	<DL	0.025	0.022	<DL
Be	9	9	MS/MS	No gas	0.096	0.040	<DL	0.089	0.017	<DL
B	11	11	MS/MS	No gas	0.52	1.7	1.7	1.9	22	22
Na		23	SQ	Cool no gas	0.077	0.35	0.35	0.11	1.1	1.1
Mg		24	SQ	Cool no gas	0.015	0.009	<DL	0.040	0.053	0.053
Al		27	SQ	Cool no gas	0.040	0.028	<DL	0.22	0.63	0.63
Si	28	28	MS/MS	H ₂	3.8	85	85	26	500	500
P	31	47	MS/MS	O₂	4.4	10	10	2.6	9.4	9.4
S	32	48	MS/MS	O₂	2.3	120	120	7.5	220	220
K	39	39	MS/MS	Cool NH ₃ (2)	0.049	0.13	0.13	0.19	0.45	0.45
Ca	40	40	MS/MS	Cool NH ₃ (2)	0.082	0.044	<DL	0.60	0.67	0.67
Ti	48	64	MS/MS	O₂ (2)	0.042	0.021	<DL	0.24	0.21	<DL
V	51	67	MS/MS	O₂ (2)	0.021	0.026	0.026	0.058	0.068	0.068
Cr	52	52	MS/MS	Cool NH ₃ (1)	0.085	0.047	<DL	0.24	0.69	0.69
Mn	55	55	MS/MS	Cool NH ₃ (1)	0.010	0.010	0.010	0.039	0.020	<DL
Fe	56	56	MS/MS	Cool NH ₃ (1)	0.070	0.076	0.076	0.29	0.17	<DL
Co	59	59	MS/MS	Cool NH ₃ (1)	0.017	0.002	<DL	0.025	0.005	<DL
Ni	60	60	MS/MS	Cool NH ₃ (1)	0.080	0.016	<DL	0.24	0.18	<DL
Cu	63	63	MS/MS	Cool NH ₃ (1)	0.12	0.11	<DL	0.17	0.12	<DL
Zn	64	64	MS/MS	He	0.063	0.28	0.28	0.41	0.47	0.47
Ga		71	SQ	Cool no gas	0.011	0.001	<DL	0.032	0.031	<DL
Ge	74	74	MS/MS	He	0.36	0.32	<DL	0.27	0.20	<DL
As	75	91	MS/MS	O₂ (2)	0.072	0.035	<DL	0.15	0.14	<DL
Se	78	78	MS/MS	H ₂	0.20	0.14	<DL	0.40	0.13	<DL
Rb		85	SQ	Cool no gas	0.031	0.015	<DL	0.052	0.035	<DL
Sr	88	88	MS/MS	He	0.024	0.002	<DL	0.000*	0.000*	0.000*
Nb	93	93	MS/MS	He	0.018	0.010	<DL	0.030	0.029	<DL
Mo	98	98	MS/MS	He	0.093	0.045	<DL	0.065	0.063	<DL
Ru	101	101	MS/MS	He	0.077	0.058	<DL	0.075	0.014	<DL
Rh	103	103	MS/MS	O ₂ (2)	0.057	0.10	0.10	0.018	0.097	0.097
Pd	105	105	MS/MS	No gas	0.078	0.12	0.12	0.055	0.090	0.090
Ag	107	107	MS/MS	No gas	0.099	0.14	0.14	0.031	0.016	<DL
Cd	114	114	MS/MS	No gas	0.045	0.021	<DL	0.047	0.009	<DL
In	115	115	MS/MS	No gas	0.009	0.003	<DL	0.022	0.019	<DL
Sn	118	118	MS/MS	No gas	0.038	0.059	0.059	0.20	0.17	<DL
Sb	121	121	MS/MS	H₂	0.029	0.032	0.032	0.028	0.005	<DL
Te	125	125	MS/MS	No gas	0.18	0.043	<DL	0.000*	0.000*	0.000*
Cs		133	SQ	Cool no gas	0.074	0.020	<DL	0.088	0.059	<DL
Ba	138	138	MS/MS	H₂	0.023	0.014	<DL	0.039	0.018	<DL
Ta	181	181	MS/MS	No gas	0.024	0.041	0.041	0.12	0.28	0.28

Table continues....

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	Q1	Q2	Scan type	Tune mode	DI Water			H ₂ O ₂		
					DL ng/L	BEC ng/L	Conc ng/L	DL ng/L	BEC ng/L	Conc ng/L
W	182	182	MS/MS	No gas	0.037	0.009	<DL	0.044	0.044	0.044
Re	185	185	MS/MS	No gas	0.040	0.037	<DL	0.062	0.056	<DL
Ir	193	193	MS/MS	No gas	0.023	0.016	<DL	0.040	0.027	<DL
Pt	195	195	MS/MS	H ₂	0.28	0.33	0.33	0.088	0.39	0.39
Au	197	197	MS/MS	No gas	0.051	0.048	<DL	0.22	0.15	<DL
Tl	205	205	MS/MS	No gas	0.036	0.082	0.082	0.015	0.010	<DL
Pb	208	208	MS/MS	No gas	0.042	0.066	0.066	0.056	0.035	<DL
Bi	209	209	MS/MS	No gas	0.034	0.048	0.048	0.027	0.054	0.054
U	238	238	MS/MS	No gas	0.004	0.001	<DL	0.012	0.008	<DL

SQ: single quadrupole. *Measured value was zero counts in all replicates.

Conclusions

By combining superior detection limits with a high degree of automation, the Agilent 8900 ICP-QQQ fitted with ESI's prepFAST S automated sample introduction system provides unmatched performance. The method also simplifies the elemental analysis of semiconductor process chemicals.

User handling of the samples is limited to loading the multielement stock standards, acid used for spiking, and samples into the prepFAST S automated sample introduction system. All subsequent steps, including introduction of the sample to the ICP-QQQ, are performed automatically by the prepFAST S. Benefits of the method include:

- Autodilution of samples
- Auto-acidification of samples
- Auto-creation of MSA calibrations
- Injection of samples at a precise flow rate
- High-speed rinsing of the ICP-MS sample introduction system.

A complete analysis of the two samples, measured using separate, automated MSA calibrations, was achieved in less than 30 minutes.

Automating the sample handling steps speeds up the analytical procedure, while also making the overall analysis easier for the analyst to perform. Eliminating manual tasks such as sample dilution and spiking lowers the risk of contamination during ultratrace analysis. Limiting the

handling of reagents and samples also reduces the likelihood of errors arising during the experimental procedure, leading to an increased confidence in the data quality.

All the elements specified in SEMI C30-1110, including P and S, were measured at sub-ppt to ppt levels in DI water and high purity 35% H₂O₂. The results easily meet the current SEMI Grade 5 specifications for H₂O₂.

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