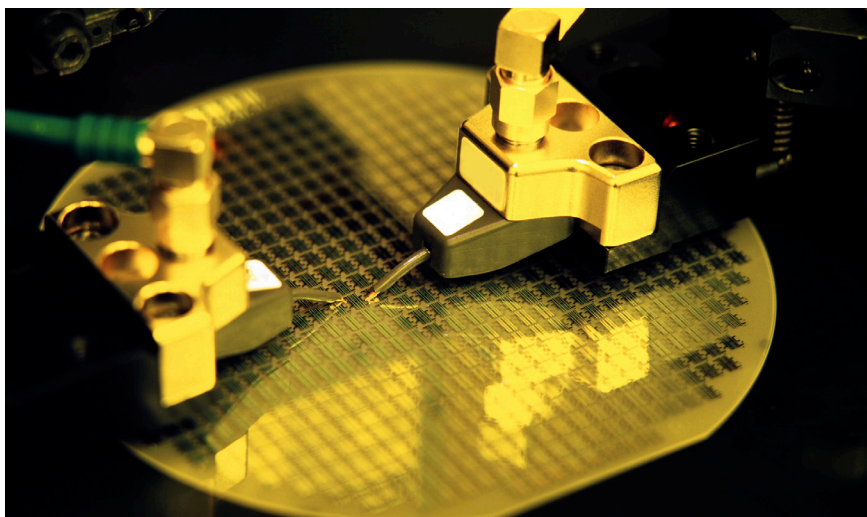# Determination of ultra trace elements in high purity hydrogen peroxide with Agilent 8900 ICP-QQQ

Application note

Semiconductor

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Introduction

Hydrogen peroxide (H_2O_2) is one of the most important process chemicals used in semiconductor device manufacturing. H_2O_2 is a strong oxidizer that is used for cleaning silicon wafers, removing photoresists, and etching metallic copper on printed circuit boards. As the chemical comes into direct contact with the silicon wafer, it is essential that trace metal contamination is controlled at the lowest possible level, to maintain device performance and production yield.

Semiconductor Equipment and Materials International (SEMI) publishes standards regarding the specifications for semiconductor process chemicals including H_2O_2 (SEMI C30-1110 – Specifications for Hydrogen Peroxide). SEMI Grade 5 is the highest purity level, with maximum contamination levels of 10 ppt for most trace elements. The semiconductor industry standard method for monitoring trace element contaminants is quadrupole ICP-MS (ICP-QMS), but the drive for ever-smaller device architectures and further improvement in device performance has led to demands to monitor a greater number of contaminant elements at lower concentrations. Current industry requirements therefore require analytical methods capable of measuring a wide range of trace elements at single- or sub-ppt level background equivalent concentration (BEC).

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SEMI Standard C30-1110 includes specifications for the maximum concentrations of sulfate and phosphate allowed in high purity H_2O_2, with a limit of 30 ppb. This equates to elemental concentrations of sulfur and phosphorus of 10 ppb. These two contaminants are not currently measured by ICP-QMS, but the recent development of triple quadrupole ICP-MS (ICP-QQQ) permits much lower limits of detection for S and P, making it possible to monitor all SEMI elements using a single technique.

This application note presents results for the determination of ppt to sub-ppt level impurities in H_2O_2 using an Agilent 8900 ICP-QQQ. All SEMI specification elements and several additional elements were measured. In addition, compliance with the SEMI specification for sulfate and phosphate was evaluated via the measurement of the S and P elemental concentrations.

The 8900 ICP-QQQ is Agilent's 2nd generation ICP-QQQ, following on from the successful Agilent 8800 ICP-QQQ released in 2012. The 8900 uses a tandem mass spectrometer layout, with two quadrupole mass spectrometers enabling it to operate in MS/MS mode. The 8900 model used in this work features higher sensitivity, a new ORS[4] collision/reaction cell (CRC) with axial acceleration, and a specialized argon gas flow path to provide lower sulfur and silicon backgrounds.

ICP-QQQ offers a more reliable and consistent approach to resolving spectral interferences compared to conventional ICP-QMS, since ICP-QQQ has an additional quadrupole mass filter (Q1) in front of the CRC. In MS/MS mode, Q1 controls the ions that can enter the cell, ensuring that the reaction processes in the cell are consistent, and thereby minimizing the risk of non-target product ions being formed from the matrix elements or other analyte ions. This control of reaction processes not only ensures more consistent results, but also allows the use of highly reactive cell gases, without the risk of creating inter-element product ion overlaps.

In the case of ICP-QMS, non-target ions enter the cell and may pass through it and appear in the spectrum as overlaps on target analyte product ions, or may react with the cell gas to form new interfering product ions. In either case, there is a risk of non-target ions or product ions appearing in the spectrum and causing errors. This risk is reduced or eliminated when ICP-QQQ is used for such applications, making ICP-QQQ suitable for accurate multi-element determinations in complex matrix samples. The ability to use highly selective reaction chemistry also enables more efficient removal of background interferences, so ICP-QQQ also offers superior performance for the analysis of ultra-trace level contaminants in high-purity reagents such as semiconductor grade H_2O_2, as discussed in this note.

Experimental

A standard Agilent 8900 #200 Semiconductor configuration ICP-QQQ instrument was used. The 8900 #200 is 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 peristaltic pump tubing.

In advanced semiconductor applications, the key requirement is to deliver the absolute lowest possible detection limits for every analyte. To achieve this, laboratories measuring ultra-trace 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 the analytes. In this work, several reaction cell gases (He, H_2, O_2 and NH_3) were used as appropriate for the large number of analytes being measured. Since H_2O_2 is a low-matrix sample, cool plasma conditions were also applied for the elements where this mode provides the lowest BECs. Tuning parameters are shown in Table 1, and other acquisition parameters are shown in Table 2. Q1 and Q2 settings are shown in Table 3 and Table 4 along with quantification results.

TAMAPURE-AA-10 hydrogen peroxide (35%, Tama Chemicals, Japan) was used as the sample matrix. To stabilize the spiked elements, ultrapure nitric acid (TAMAPURE-AA-10) was added to the H_2O_2 samples at 1 part of 70% HNO_3 to 1000, giving a final acid concentration of 0.07%. As is typical for high-purity semiconductor samples, calibration was by the Method of Standard Additions (MSA). A mixed multi element standard solution (SPEX CertiPrep, NJ, US) was prepared and spiked into the blank H_2O_2 matrix at 10, 20, 30, 40 and 50 ppt to create the standard addition calibration solutions. Sample solutions were prepared just before the analysis.

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

Table 1. ICP-QQQ tuning parameters.

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 (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)*	-	2.0 (20%)**		-	-	-	-	-
He flow (mL/min)	-	1.0		-	-	5.0	-	-
H$_2$ flow (mL/min)	-	-	-	-	7.0	-	-	-
O$_2$ flow (mL/min)	-	-	-	-	-	-	0.3 (30%)**	
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% NH$_3$ 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

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

Results and discussion

Calibration curves along with the calibration equation, correlation coefficient, detection limit and BEC of several SEMI specification elements are shown in Figure 1. Good linearity was obtained for all SEMI target elements, including P and S, in all of the tune modes used.

Quantitative results and detection limits of the SEMI elements are shown in Table 3. Results of other elements that are not specified in the SEMI standard are shown in Table 4. Each detection limit is calculated as 3-sigma of 10 replicate measurements of a blank H$_2$O$_2$ sample. Quantitative results and detection limits are also shown for all of these elements in pure water, for comparison purposes.

Long term stability was evaluated by measuring a H$_2$O$_2$ sample spiked at 10 ppt for most elements and 100 ppt for sulfur. Calibration curves were made at the beginning of the sequence and the spiked samples were then run as unknown samples for a total analysis period of 3 h 40 min. The analytical results for the spiked samples are plotted in Figure 2, and the RSDs of the 13 analysis results are shown in Table 3 and Table 4 (Stability Test RSD (%)). Good stability was obtained, with RSDs between 1.0% (for Pb in no gas mode) and 8.1% (for B in no gas mode). The spiked sample results of boron and sulfur slowly increased during the run, possibly due to boron and sulfur contamination from the clean room air and air filtration system.

Table 3. Quantification of trace elements and stability test results for SEMI specification elements in high purity 35% H_2O_2 and pure water

	Q1	Q2	Acquisition mode	Tune	Hydrogen Peroxide			Pure Water	
					Conc. (ppt)	DL (ppt)	Stability Test[*] RSD (%)	Conc. (ppt)	DL (ppt)
Li		7	Single Quad	Cool	< DL	0.003	4.7	< DL	0.004
B	11	11	MS/MS	No gas	7.7	0.69	8.1	4.6	0.57
Na		23	Single Quad	Cool	0.39	0.031	3.3	0.50	0.069
Mg		24	Single Quad	Cool	0.017	0.017	4.1	< DL	0.012
Al		27	Single Quad	Cool	0.39	0.071	2.9	0.11	0.11
P	31	47	MS/MS	$O_2(1)$	4.2	0.89	3.3	3.4	0.91
S	32	48	MS/MS	$O_2(1)$	190	5.1	7.8**	41	3.8
K	39	39	MS/MS	Cool+NH$_3$(2)	0.21	0.11	2.2	0.20	0.088
Ca	40	40	MS/MS	Cool+NH$_3$(2)	< DL	0.23	1.9	< DL	0.10
Ti	48	64	MS/MS	$O_2(2)$	0.097	0.045	2.6	< DL	0.028
V	51	67	MS/MS	$O_2(2)$	0.067	0.027	2.6	< DL	0.023
Cr	52	52	MS/MS	Cool+NH$_3$(1)	0.13	0.075	3.5	< DL	0.031
Mn	55	55	MS/MS	Cool+NH$_3$(1)	< DL	0.012	2.7	< DL	0.004
Fe	56	56	MS/MS	Cool+NH$_3$(1)	0.13	0.074	3.3	< DL	0.027
Ni	60	60	MS/MS	Cool+NH$_3$(1)	0.16	0.14	3.7	< DL	0.030
Cu	63	63	MS/MS	Cool+NH$_3$(1)	< DL	0.048	5.0	0.19	0.18
Zn	64	64	MS/MS	He	0.22	0.14	4.5	0.35	0.17
As	75	91	MS/MS	$O_2(2)$	< DL	0.087	3.5	< DL	0.081
Cd	114	114	MS/MS	No gas	< DL	0.020	2.3	< DL	0.017
Sn	118	118	MS/MS	No gas	0.088	0.063	2.0	< DL	0.037
Sb	121	121	MS/MS	H_2	< DL	0.015	1.6	< DL	0.022
Ba	138	138	MS/MS	H_2	0.061	0.033	1.2	< DL	0.004
Pb	208	208	MS/MS	No gas	0.081	0.053	1.0	0.056	0.035

SEMI C30-1110 Grade 5, maximum concentration of listed elements: 10 ppt

* Analyte elements were spiked at 10 ppt

** Sulfur was spiked 100 ppt

Table 4. Quantification of trace elements and stability test results for other (non-SEMI specification) elements in high purity 35% H_2O_2 and pure water

	Q1	Q2	Acquisition mode	Tune	Hydrogen Peroxide			Pure Water	
					Conc. (ppt)	DL (ppt)	Stability Test[*] RSD (%)	Conc. (ppt)	DL (ppt)
Be	9	9	MS/MS	No gas	< DL	0.037	4.7	< DL	0.036
Si**	28	28	MS/MS	H_2	260	25		120	5.9
Sc	45	61	MS/MS	O_2(1)	< DL	0.006	2.4	< DL	0.004
Co	59	59	MS/MS	Cool+NH_3(1)	< DL	0.045	3.6	< DL	0.012
Ga		71	Single Quad	Cool	< DL	0.017	4.1	<DL	0.000
Ge	74	74	MS/MS	He	0.16	0.14	4.4	< DL	0.21
Se	78	78	MS/MS	H_2	< DL	0.26	3.5	< DL	0.15
Rb		85	Single Quad	Cool	< DL	0.012	2.2	< DL	0.008
Sr	88	88	MS/MS	He	< DL	0.015	3.5	< DL	0.006
Zr	90	106	MS/MS	O_2(1)	0.031	0.027	1.3	0.15	0.047
Nb	93	93	MS/MS	He	0.18	0.061	2.8	< DL	0.005
Mo	98	98	MS/MS	He	0.10	0.10	3.4	< DL	0.053
Ru	101	101	MS/MS	He	0.76	0.35	4.2	0.27	0.16
Rh	103	103	MS/MS	O_2(2)	0.29	0.054	1.7	0.066	0.03
Pd	105	105	MS/MS	No gas	0.08	0.052	2.1	0.039	0.037
Ag	107	107	MS/MS	No gas	< DL	0.01	2.2	0.14	0.037
In	115	115	MS/MS	No gas	< DL	0.004	1.8	0.004	0.004
Te	125	125	MS/MS	No gas	< DL	0.16	5.0	< DL	0.19
Cs		133	Single Quad	Cool	< DL	0.014	2.4	< DL	0.016
Hf	178	178	MS/MS	No gas	0.035	0.032	1.6	< DL	0.12
W	182	182	MS/MS	No gas	0.048	0.03	1.9	< DL	0.011
Re	185	185	MS/MS	No gas	< DL	0.049	1.4	< DL	0.011
Ir	193	193	MS/MS	No gas	0.041	0.038	1.6	< DL	0.033
Pt	195	195	MS/MS	H_2	1.7	0.55	2.1	0.85	0.33
Au	197	197	MS/MS	No gas	0.22	0.097	1.5	0.095	0.065
Tl	205	205	MS/MS	No gas	0.017	0.015	1.1	0.03	0.024
Bi	209	209	MS/MS	No gas	< DL	0.008	1.2	< DL	0.007
Th	232	232	MS/MS	No gas	< DL	0.007	1.3	< DL	0.013
U	238	238	MS/MS	No gas	< DL	0.003	1.2	< DL	0.002

[*] Analyte elements were spiked at 10 ppt

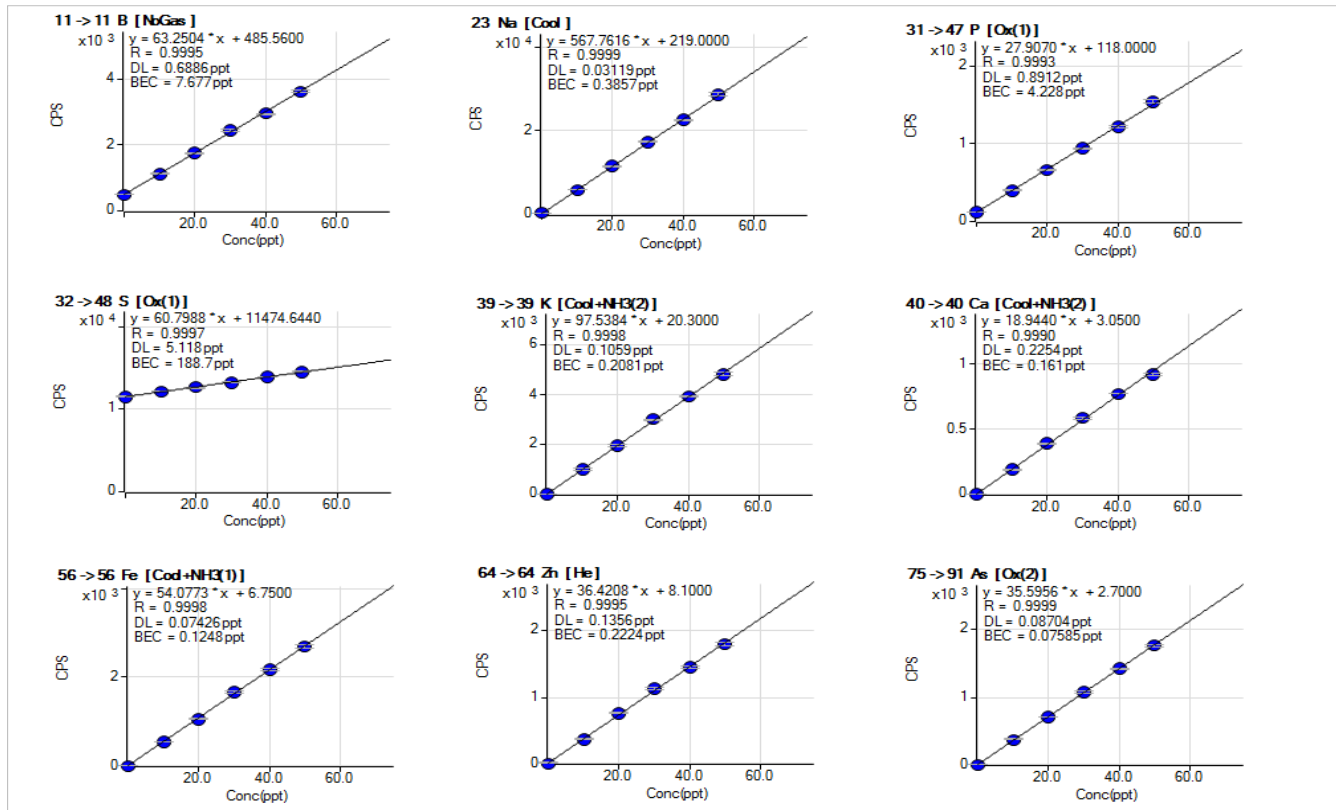** Si concentration in the mixed spike (10 ppt) was too low for reliable quantification above the blank (260 ppt).

Figure 1. Calibration curves for several SEMI specification elements in high purity 35% H₂O₂
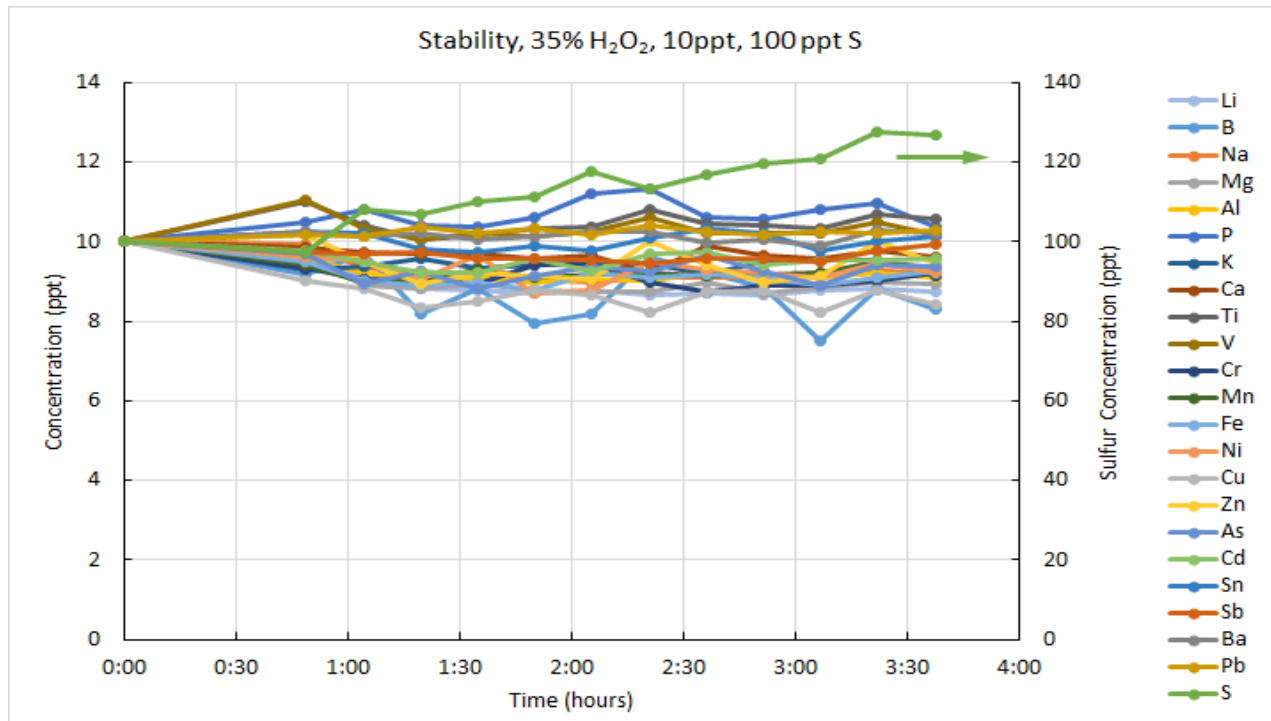

Figure 2. Stability test result of 10 ppt spiked analytes (and 100 ppt sulfur) in high purity 35% H₂O₂. Total analysis time of 3 h 40 min following initial calibration standards. Note: Si concentration in the mixed spike (10 ppt) was too low for reliable quantification above the blank (260 ppt).

Conclusions

Many elements, including all the elements specified in SEMI C30-1110, together with other trace elements, were measured at sub-ppt to ppt levels in high purity 35% hydrogen peroxide, using the Agilent 8900 ICP-QQQ. Excellent linear calibration curves from 0 ppt to 50 ppt concentration range were obtained. For almost all elements, sub ppt quantitative results were obtained, with the remaining elements having single-ppt detection limits (except Si, 25 ppt). Reproducibility between 1.0 – 8.1 % RSD was obtained at the 10 ppt level (100 ppt for S) for the spiked analytes, for a high purity 35% hydrogen peroxide sample analysis sequence lasting 3 hours 40 minutes. This demonstrates the suitability of the Agilent 8900 Semiconductor configuration ICP-QQQ instrument for routine analysis of the highest-purity semiconductor reagents and process chemicals.

Reference

1.SEMI C30-1110, Specifications for hydrogen peroxide (2010)

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