Determination of Ultra Trace Elements in High Purity Reagents by Automatic Standard Addition Methods Using prep*FAST* S - ICP-MS/MS.

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Introduction

- Ultratrace analysis at the pg/g (ppt) or fg/g (ppq) level using a highly sensitive instrument such as ICP-MS is susceptible to contamination from the lab environment or reagents.
- Given the challenging nature of the (SEMI) publishes standard specifications for semiconductor process chemicals, including H_2O_2 (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.
- SEMI Standard C30-1110 specifies the maximum concentration of sulfate and phosphate allowed in high purity H_2O_2, with a limit of 30,000 ppt. This equates to an elemental concentration of sulfur (S) and phosphorus (P) of 10,000 ppt.
- Currently, ICP-QMS isn't used to measure these two elements, but triple quadrupole ICP-MS (ICP-MS/MS or ICP-QQQ) permits much lower limits of detection for S and P.
- The development of ICP-MS/MS means all SEMI specified elements can now be monitored using a single technique [2].

In this study, impurities in deionized water (DIW) and H_2O_2 were quantified by automatic Method of Standard Addition (MSA) using a prep*FAST* S (Elemental Scientific, USA) and Agilent 8900 ICP-MS/MS (Agilent Technologies, USA).
The method allows the quantification of ultra-trace level impurities in H_2O_2 and DIW regardless of the skill level of the analyst.

Experimental

Reagents and sample

- TAMAPURE-AA-10 hydrogen peroxide (35% H_2O_2, Tama Chemicals, Japan) and DIW (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% HNO_3.
- Standard stock solution for acid spiking (10%): a 10% nitric acid solution was prepared by diluting 68% ultrapure HNO_3 (TAMAPURE-AA-10) with DIW. HNO_3 was used to stabilize the spiked elements in the H_2O_2 sample.
- The two stock solutions were loaded on the *prepFAST* S autosampler.
- All target concentration solutions required for the analysis were automatically prepared by the prep*FAST* S system.
- 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 coaxial nebulizer that is included with the prep*FAST* S system. This configuration of 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 automated sample preparation and injection system. Instrument operating conditions are given in Tables 1,2 and 3. And Figure 1 shows an illustration of the prep*FAST* S .

Table 1. ICP-MS/MS operating conditions.

	Cool no gas	Cool NH_3	Cool NH_3 soft	No gas	H_2	He	O_2	Soft O_2
Scan type	Single	MS/MS						
RF power (W)	600			1500				
Sample Depth (mm)	18			8				
Carrier gas flow rate (L/min)	0.7							
Makeup gas flow rate (L/min)	0.9			0.48				
Extract 1 (V)	-150		-100	4.2	4.7	4.2	4.5	3.5
Extract 2 (V)	-18	-17	-12	-250				120
Omega bias (V)	-70			-140				-70
Omega lens (V)	2.0			10.0	8.0	10.0	10.5	4.0
Q1 entrance (V)	-15		-50					
He gas flow rate (mL/min)	-	1		-	-	5	-	-
H_2 gas flow rate (mL/min)	-	-	-	-	7	-	-	-
NH_3 gas flow rate (mL/min)	-	3		-	-	-	-	-
O_2 gas flow rate (mL/min)	-	-	-	-	-	-	4.5	
OctP bias (V)	-20	-10		-8	-18		-3	
Axial Acceleration (V)	0	1.5		0			1	
Energy discrimination (V)	15	-5		5	0	3	-7	

Table 2. Acquisition parameters.

Parameter	Setting
Q2 peak pattern	1 point
Replicates	3 (spiked solution)
	10 (unspiked solution)
Sweeps/Replicate	10
Integration time	1 s for all isotopes

Table 3. prepFAST S operating conditions.

	DIW	H_2O_2
Carrier flow rate (µL/min)	100	
Dilution factor	1 (no-dilution)	
Stock standard conc. (ng/L)	1000 (1.0 % HNO_3)	
Conc. of HNO_3 used for spike (%)	-	10
Conc. of HNO_3 in the sample after acid spiking (%)	0	0.5

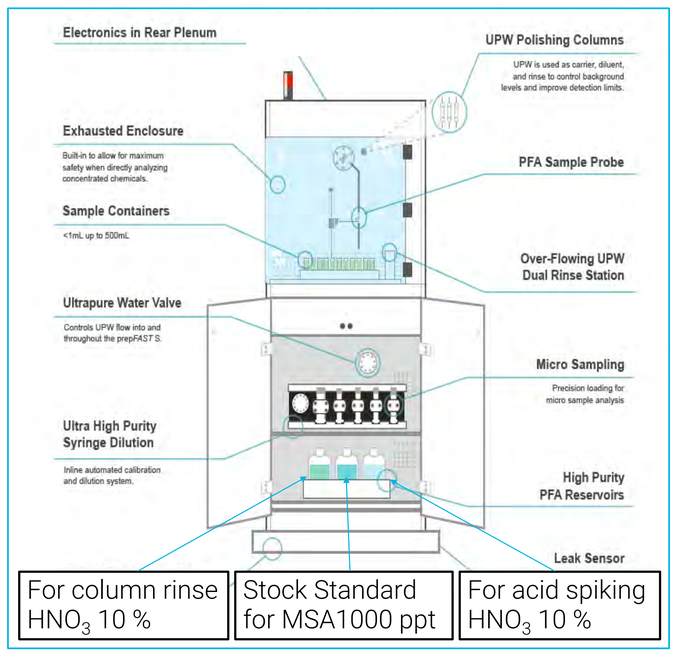

Figure 1. prepFAST S system.

ESI prep*FAST* S operation

The prep*FAST* S combines an autosampler with a system of ultrapure valves (S1 -S5), and a set of high precision syringe pumps. Undiluted chemicals can be placed on the autosampler and the system will perform the actions required to prepare the sample for injection to the ICP-MS or ICP-QQQ. The operation of the prep*FAST* S is outlined in the four schematics shown in Figure 2.

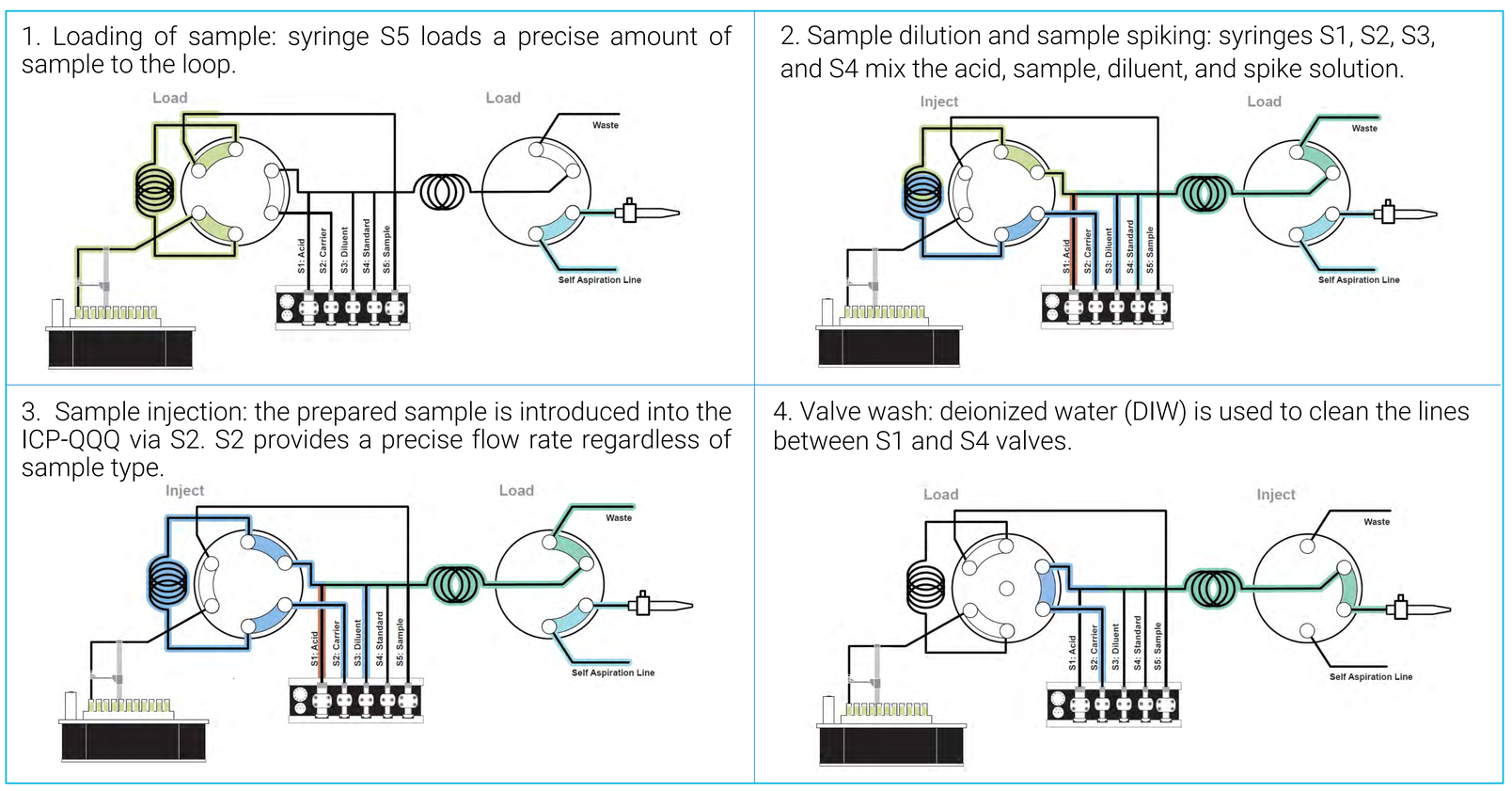

Figure 2. ESIprepFAST S system schematic, illustrating four distinct steps: sample loading during spray chamber rinse, sample preparation, injection, and cleaning.

Results and Discussion

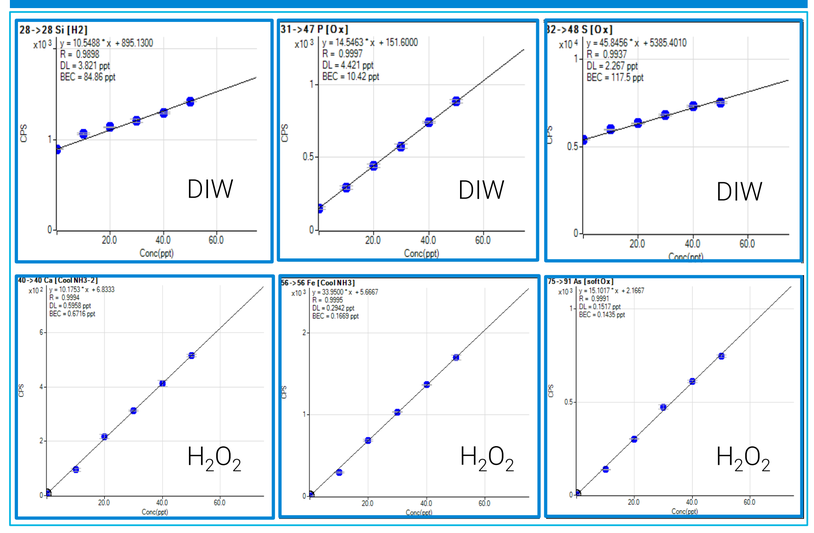

Figure 3. MSA calibration curves.

Table 4. DLs and BECs in DIW and H_2O_2. Analytes shown in bold are SEMI C30-1110 Grade 5 elements.

	Q1	Q2	Tune Mode	DIW		H_2O_2	
				conc. ng/L	D.L. ng/L	conc. ng/L	D.L. ng/L
Li		7	Cool no gas	< D.L.	0.003	< D.L.	0.025
Be	9	9	No Gas	< D.L.	0.096	< D.L.	0.089
B	11	11	No Gas	1.7	0.52	22	1.9
Na		23	Cool no gas	0.35	0.077	1.1	0.11
Mg		24	Cool no gas	< D.L.	0.015	0.053	0.040
Al		27	Cool no gas	< D.L.	0.040	0.63	0.22
Si	28	28	H_2	85	3.8	500	26
P	31	47	O_2	10	4.4	9.4	2.6
S	32	48	O_2	120	2.3	220	7.5
K	39	39	Cool NH_3 soft	0.13	0.049	0.45	0.19
Ca	40	40	Cool NH_3 soft	< D.L.	0.082	0.67	0.60
Ti	48	64	soft O_2	< D.L.	0.042	< D.L.	0.24
V	51	67	soft O_2	0.026	0.021	0.068	0.058
Cr	52	52	Cool NH_3	< D.L.	0.085	0.69	0.24
Mn	55	55	Cool NH_3	0.010	0.010	< D.L.	0.039
Fe	56	56	Cool NH_3	0.076	0.070	< D.L.	0.29
Co	59	59	Cool NH_3	< D.L.	0.017	< D.L.	0.025
Ni	60	60	Cool NH_3	< D.L.	0.080	< D.L.	0.24
Cu	63	63	Cool NH_3	< D.L.	0.12	< D.L.	0.17
Zn	64	64	He	0.28	0.063	0.47	0.41
Ga		71	Cool no gas	< D.L.	0.011	< D.L.	0.032
Ge	74	74	He	< D.L.	0.36	< D.L.	0.27
As	75	91	soft O_2	< D.L.	0.072	< D.L.	0.15
Se	78	78	H_2	< D.L.	0.20	< D.L.	0.40
Rb		85	Cool no gas	< D.L.	0.031	< D.L.	0.052
Sr	88	88	He	< D.L.	0.024	0.000*	0.000*
Nb	93	93	He	< D.L.	0.018	< D.L.	0.030
Mo	98	98	He	< D.L.	0.093	< D.L.	0.065
Ru	101	101	He	< D.L.	0.077	< D.L.	0.075
Rh	103	103	soft O_2	0.10	0.057	0.097	0.018
Pd	105	105	No Gas	0.12	0.078	0.090	0.055
Ag	107	107	No Gas	0.14	0.099	< D.L.	0.031
Cd	114	114	No Gas	< D.L.	0.045	< D.L.	0.047
In	115	115	No Gas	< D.L.	0.009	< D.L.	0.022
Sn	118	118	No Gas	0.059	0.038	< D.L.	0.20
Sb	121	121	H_2	0.032	0.029	< D.L.	0.028
Te	125	125	No Gas	< D.L.	0.18	0.000*	0.000*
Cs		133	Cool no gas	< D.L.	0.074	< D.L.	0.088
Ba	138	138	H_2	< D.L.	0.023	< D.L.	0.039
Ta	181	181	No Gas	0.041	0.024	0.28	0.12
W	182	182	No Gas	< D.L.	0.037	0.044	0.044
Re	185	185	No Gas	< D.L.	0.040	< D.L.	0.062
Ir	193	193	No Gas	< D.L.	0.023	< D.L.	0.040
Pt	195	195	H_2	0.33	0.28	0.39	0.088
Au	197	197	No Gas	< D.L.	0.051	< D.L.	0.22
Tl	205	205	No Gas	0.082	0.036	< D.L.	0.015
Pb	208	208	No Gas	0.066	0.042	< D.L.	0.056
Bi	209	209	No Gas	0.048	0.034	0.054	0.027
U	238	238	No Gas	< D.L.	0.004	< D.L.	0.012

DLs were calculated as 3-sigma of 10 replicate measurements of unspiked samples.
*DLs and BECs for Sr and Te could not be calculated, as the background signal mean and SD were 0 counts per second.

Conclusions

- By providing a high degree of automation, the Agilent 8900 ICP-QQQ fitted with ESI's prep*FAST* S autodilution system simplifies the elemental analysis of DIW and 35% H_2O_2.
- Once the multielement standards, acid used for spiking, and samples have been loaded into the prep*FAST* S autosampler, the system performs all required steps including introduction of the sample to the ICP-QQQ.
- Automating the sample handling steps speeds up the analytical procedure and is easier for the analyst to perform. Eliminating manual tasks during ultratrace analysis lowers the risk of contamination. It 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 (and many other elements), were measured at sub-ppt to ppt levels in DIW and high purity 35% H_2O_2. The results exceeded current SEMI specifications for H_2O_2.

Referencess

1. SEMI C30-1110, Specifications for hydrogen peroxide (2010).
2. Kazuo Yamanaka, Determination of ultra trace elements in high purity hydrogen peroxide with Agilent 8900 ICP-QQQ, Agilent publication (2016), 5991-7701EN.