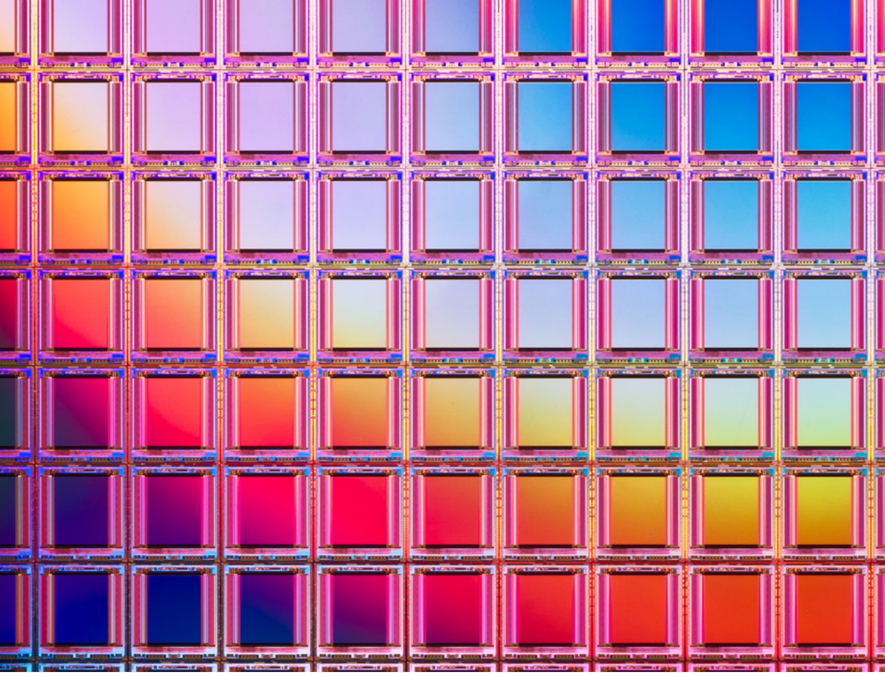

APPLICATION BRIEF

ICP - Mass Spectrometry

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Partnered solutions for fully-automated chemicals analysis workflows

Automated Analysis of Semiconductor-Grade Sulfuric Acid with prep*FAST* S and NexION 5000 ICP-MS

Introduction

Advances in semiconductor technology and decreasing tolerances in microchip design require improvements to be made in both the purity of the chemicals being used and fabrication processes. Since manufacturers are moving to < 10 nm geometry, while seeking improved yield, the chemicals and process-reagents used must contain minimal trace metal contaminants. Consequently, the demand for lower detection limits in reagents to allow the accurate quantification of trace elemental contaminants requires new approaches to sample handling and analysis.

Sulfuric acid (H_2SO_4) is used in the semiconductor industry to clean, etch impurities on silicon wafers and strip photoresist during the chip production processes. The reduction of potential contamination on silicon wafers is crucial, as trace-metal, particulate, and organic contaminants can alter the functionality of semiconductors. At the sub-ppt level, environmental contaminants are difficult to control and can easily contaminate H_2SO_4 and other chemicals if not properly handled.

This work presents the analysis of automatically diluted semiconductor-grade sulfuric acid using a PerkinElmer NexION® 5000 Multi-Quadrupole ICP-MS working seamlessly with the ESI prep*FAST* S ultraclean sample introduction system.

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Experimental

Reagents and Samples

Commercially available H_2SO_4 (98%) was used as the sample for all analyses. All samples and standards were automatically spiked in-line using the on-board reagent supply on the prep*FAST* S ultraclean sample introduction system to a final concentration of 0.5% HNO_3. This was done in order to match the sample to the calibration standard and stabilize the spiked elements. Thereafter, the prep*FAST* S utilized syringe-driven flow of ultrapure water, semiconductor-grade HNO_3, and standard solution to automate sample dilution and method of standard addition (MSA) for standard preparation.

All MSA standard preparations from the stock solutions were automated by the prep*FAST* S. UPW was used as the carrier solution and samples were introduced at 200 µL/min. For MSA, 200 ppt mixed-element standard in 1% HNO_3 was prepared from a 100-ppb standard. Calibrations were automatically performed at 0, 0.5, 1, 2, 5 and 10 ppt and 1000x higher for Si and P. All analyses took place in a non-cleanroom environment to demonstrate the limits of detection (LODs) and background equivalent concentrations (BECs) which could be achieved even without this typical infrastructure using the instrumentation discussed below.

Instrumentation: Sample Preparation and Introduction

In this application, a prep*FAST* S ultraclean system (Elemental Scientific Inc., Omaha, Nebraska, USA) was used to minimize contamination from the environment and sample handling and to deliver in-line, automated calibration and dilutions (Figure 1). In order to eliminate manual sampling errors and operator variability, samples were analyzed directly from their original containers in the exhausted and fully enclosed environment of the prep*FAST* S ultraclean system.

In order to minimize contamination and maximize chemical resistance, a robust PFA probe, CTFE auto-aligning arm, and sealed PTFE vertical probe drive assembly combined with high-purity, chemically-conditioned fluoropolymer flow paths were used.

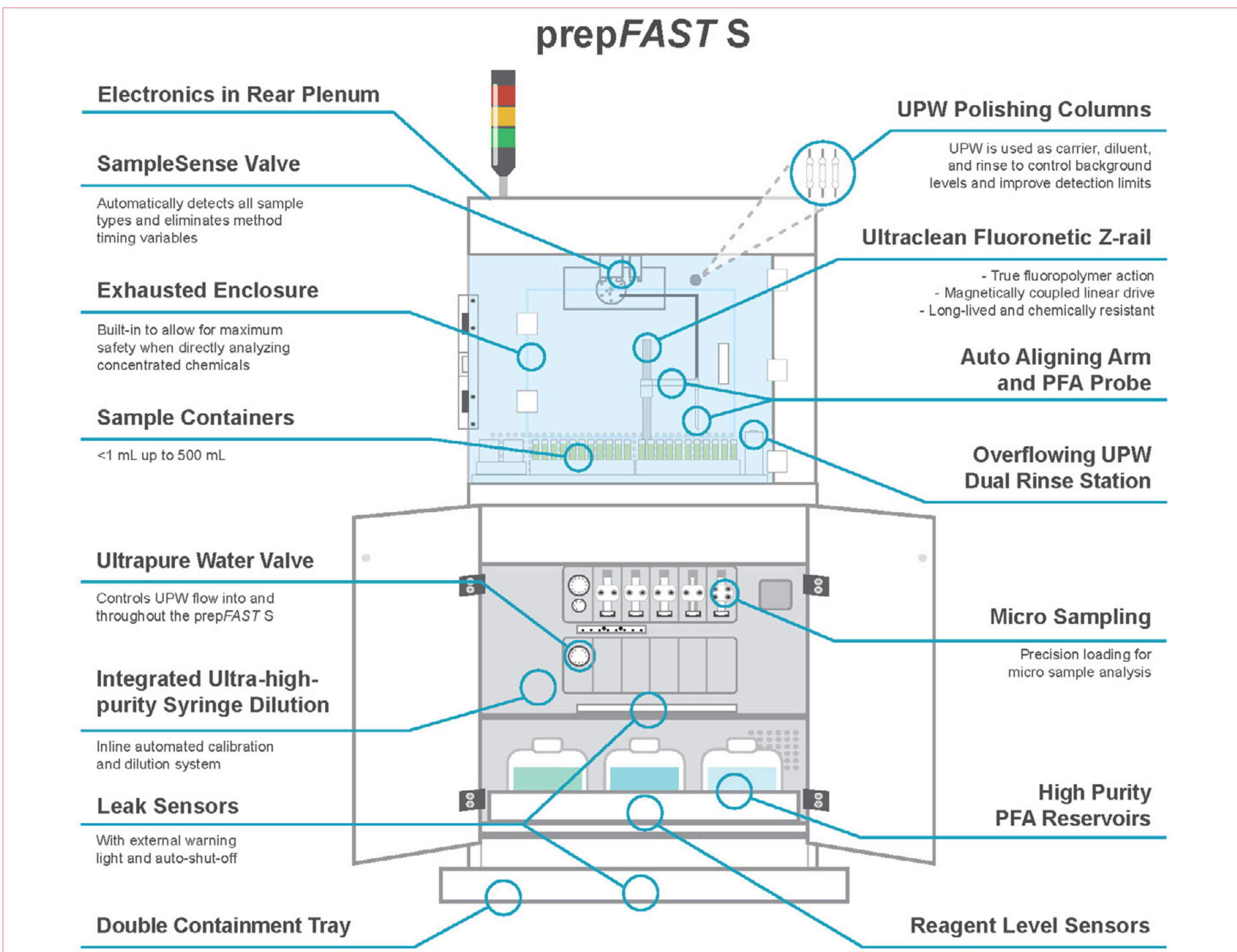

Figure 1. Schematic of prepFAST S ultraclean system.

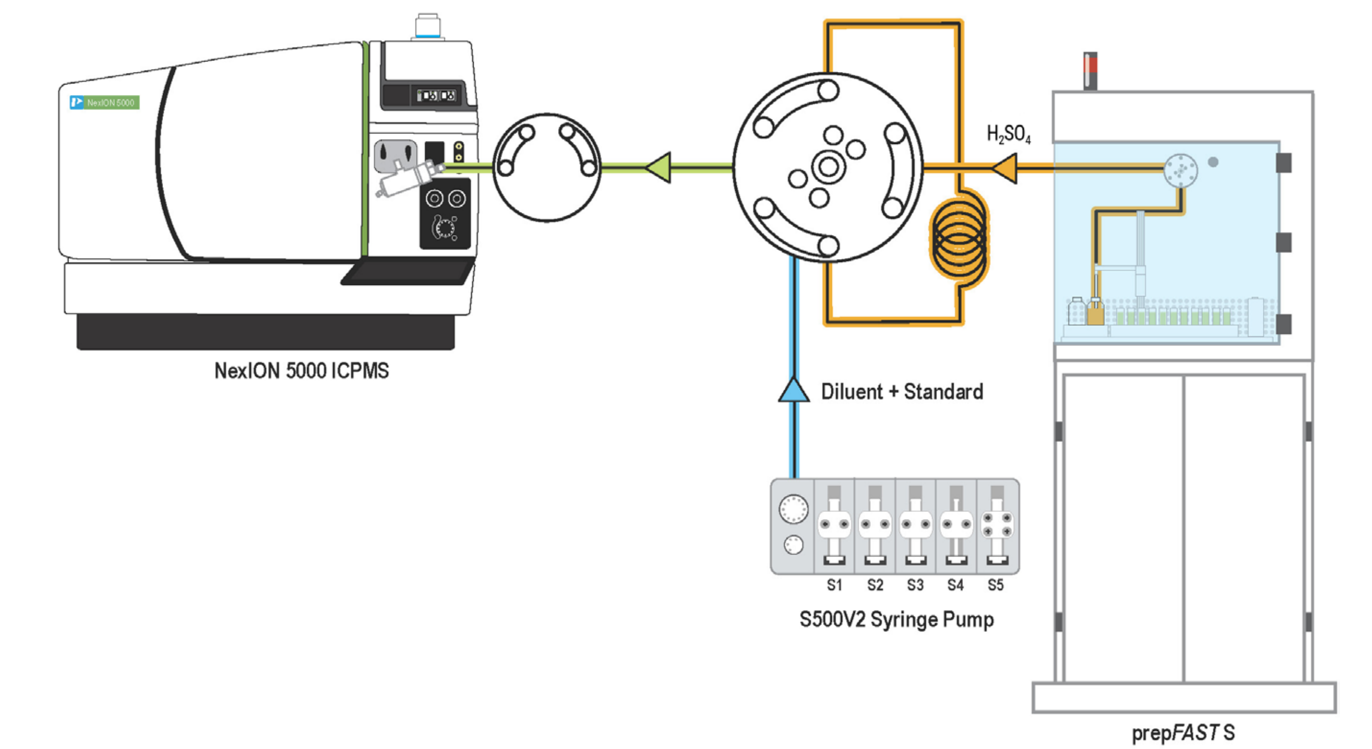

Figure 2. Simplified flow path from prepFAST S ultraclean system to the NexION 5000 ICP-MS.

The HF-resistant Fluorospray sample introduction kit for the NexION 5000 ICP-MS was used to enhance precision and sensitivity for the analysis of semiconductor-grade ultrapure chemicals. To further improve performance for semiconductor applications, the Fluorospray spray chamber was used with an O-ring-free platinum injector and a microflow PFA-ICN concentric integrated capillary nebulizer.

Instrumentation: ICP Mass Spectrometer

The NexION 5000 Multi-Quadrupole ICP-MS was used to accurately quantify the concentration of impurities in diluted H_2SO_4. The NexION 5000 represents a truly significant advancement in ICP mass spectrometry for the removal of spectral interferences. The combination of its novel, second-generation Triple Cone Interface (TCI) with OmniRing™ technology, patented plasma generator, LumiCoil™ RF coil, Universal Cell Technology (UCT) with dynamic bandpass and multi-quad technology enhances analytical performance and sensitivity, as well as reliability. The NexION 5000 works seamlessly with the prep*FAST* S, as shown in Figure 2.

To deliver the best BECs for this application, three plasma powers were used, namely cold, mid-range/warm and hot plasma conditions. Due to the novel design of the NexION's RF generator, switching between these modes can be easily accomplished in a single sample acquisition, eliminating the need to run the samples twice (i.e. under cold and hot plasma conditions). Here, cold and hot plasma modes were used in combination with the multi-quadrupole technology of the NexION 5000 and gas phase reactions (for selected isotopes) in the UCT to remove polyatomic ion interferences on certain analytes. A pure reaction gas (NH_3) was used in the Universal Cell for the removal of interferences and, along with dynamic bandpass tuning, actively prevented new interferences from forming in the cell. The optimal reaction gas flow rates and bandpass settings were determined experimentally. By combining multiple plasma modes, multi-quad functionality and the quadrupole Universal Cell modes, the accurate determination of trace metals in semiconductor chemicals, in this case in H_2SO_4, at extremely low levels was made possible.

For this application, instrumental and sample introduction parameters can be found in Table 1. NexION 5000 ICP-MS method parameters are shown in Table 2.

Table 1. Operating Parameters for H_2SO_4 Analysis.

Parameter	Cold Plasma (STD)	Cold Plasma (DRC)	Hot Plasma (DRC)	Hot Plasma (STD)
ICP RF Power (W)	600		1600	
Nebulizer Gas Flow (L/min)	0.99	1.04	0.98	1.01
Reaction Gas	-	NH_3	NH_3	-
AMS Gas Flow (L/min)	0.1		0.05	
Auxiliary Gas Flow (L/min)	1.2			
Plasma Gas Flow (L/min)	16			
Sample Flow Rate (mL/min)	0.2			
Nebulizer	Fluoroneb PFA-ICN			
Spray Chamber	Fluorospray PFA			
Torch	SilQ Ultra High Purity Quartz			
Injector	SilQ Ultra High Purity Quartz 2mm			
ICP-MS Cones	Platinum-tipped Sampler and Skimmer Nickel Hyper-Skimmer and OmniRing Assembly			
Hyper-skimmer Voltage	-30	-50	5	
OmniRing Voltage	-210		-165	

Table 2. ICP-MS Analytical Conditions.

Element	Q1 Mass	Q3 Mass	Power (W)	Reaction Gas	Reaction Gas Flow	RPq
Li	7	7	600	-	0	0.45
Be	9	9	1600	-	0	0.25
Na	23	23	600	-	0	0.45
Mg	24	24	600	NH_3	1.5	0.45
Al	27	27	600	NH_3	0.5	0.45
Si	28	44	600	NH_3	1.5	0.1
P	31	47	600	NH_3	0.5	0.1
K	39	39	600	NH_3	0.3	0.8
Ca	40	40	600	NH_3	0.3	0.8
Ti	48	131	600	NH_3	0.3	0.1
V	51	51	1600	NH_3	1.0	0.45
Cr	52	52	600	NH_3	0.3	0.8
Mn	55	55	600	NH_3	0.5	0.8
Fe	56	56	600	NH_3	0.5	0.8
Ni	58	58	600	NH_3	1	0.8
Co	59	59	600	NH_3	0.7	0.3
Cu	63	63	600	NH_3	0.7	0.45
Zn	64	115	600	NH_3	0.3	0.1
Ga	71	71	1600	NH_3	0.2	0.45
Rb	85	85	1600	-	0	0.45
Sr	88	88	1600	NH_3	0.2	0.25
Y	89	89	1600	-	0	0.25
Nb	93	93	1600	-	0	0.25
Ru	101	101	1600	-	0	0.25
Rh	103	103	1600	-	0	0.25
Pd	106	106	1600	-	0	0.25

Element	Q1 Mass	Q3 Mass	Power (W)	Reaction Gas	Reaction Gas Flow	RPq
Ag	107	107	1600	-	0	0.25
In	115	115	1600	-	0	0.25
Sn	118	118	1600	NH_3	0.2	0.25
Sb	121	121	1600	-	0	0.25
Cs	133	133	1600	NH_3	0.5	0.25
Ba	137	137	1600	-	0	0.25
La	139	139	1600	-	0	0.25
Ce	140	140	1600	-	0	0.25
Pr	141	141	1600	-	0	0.25
Nd	146	146	1600	-	0	0.25
Sm	147	147	1600	-	0	0.25
Eu	153	153	1600	-	0	0.25
Gd	157	157	1600	-	0	0.25
Tb	159	159	1600	-	0	0.25
Dy	164	164	1600	-	0	0.25
Ho	165	165	1600	-	0	0.25
Tm	169	169	1600	-	0	0.25
Yb	174	174	1600	-	0	0.25
Lu	175	175	1600	-	0	0.25
Hf	178	178	1600	-	0	0.25
Ta	181	181	1600	-	0	0.25
Re	185	185	1600	-	0	0.25
Os	189	189	1600	-	0	0.25
Tl	205	205	1600	-	0	0.25
Pb	208	208	1600	-	0	0.25
U	238	238	1600	-	0	0.25

Results and Discussion

Table 3 shows background equivalent concentrations (BECs), limits of detection (LODs) and correlation coefficients (R) for all elements measured in 9.8% H_2SO_4. The correlation coefficients with R values equal or better than 0.999 demonstrate the accuracy of the prep*FAST* S automated dilutions and spike additions, which enables calibrations in complicated matrices with excellent results. Blank subtraction was not used for the determination of BECs or LODs in this study.

As mentioned previously, calibrations were automatically prepared at 0, 0.5, 1, 2, 5 and 10 ppt with the prep*FAST* S. Si and P were spiked at 0, 0.5, 1, 2, 5 and 10 ppb. Figure 3 shows calibration curves for a selection of elements with MSA in 9.8% H_2SO_4.

As can be seen in Table 3, by combining the prep*FAST* S sample introduction system with multiple plasma modes and the Universal Cell Technology of the NexION 5000 ICP-MS, elements which typically have spectral interferences and/or are likely affected by contaminants in lab environments can easily be analyzed. It was possible to achieve sub-ppt or single-digit-ppt BECs and LODs even for historically difficult elements, such as Na, Al, K, Ca and Fe, in 9.8% H_2SO_4. These results were achieved in a non-cleanroom environment due to the enclosed and vented sampling area in the prep*FAST* S automated sample introduction system and the superior interference removal capabilities of the NexION 5000 Multi-Quadrupole ICP-MS.

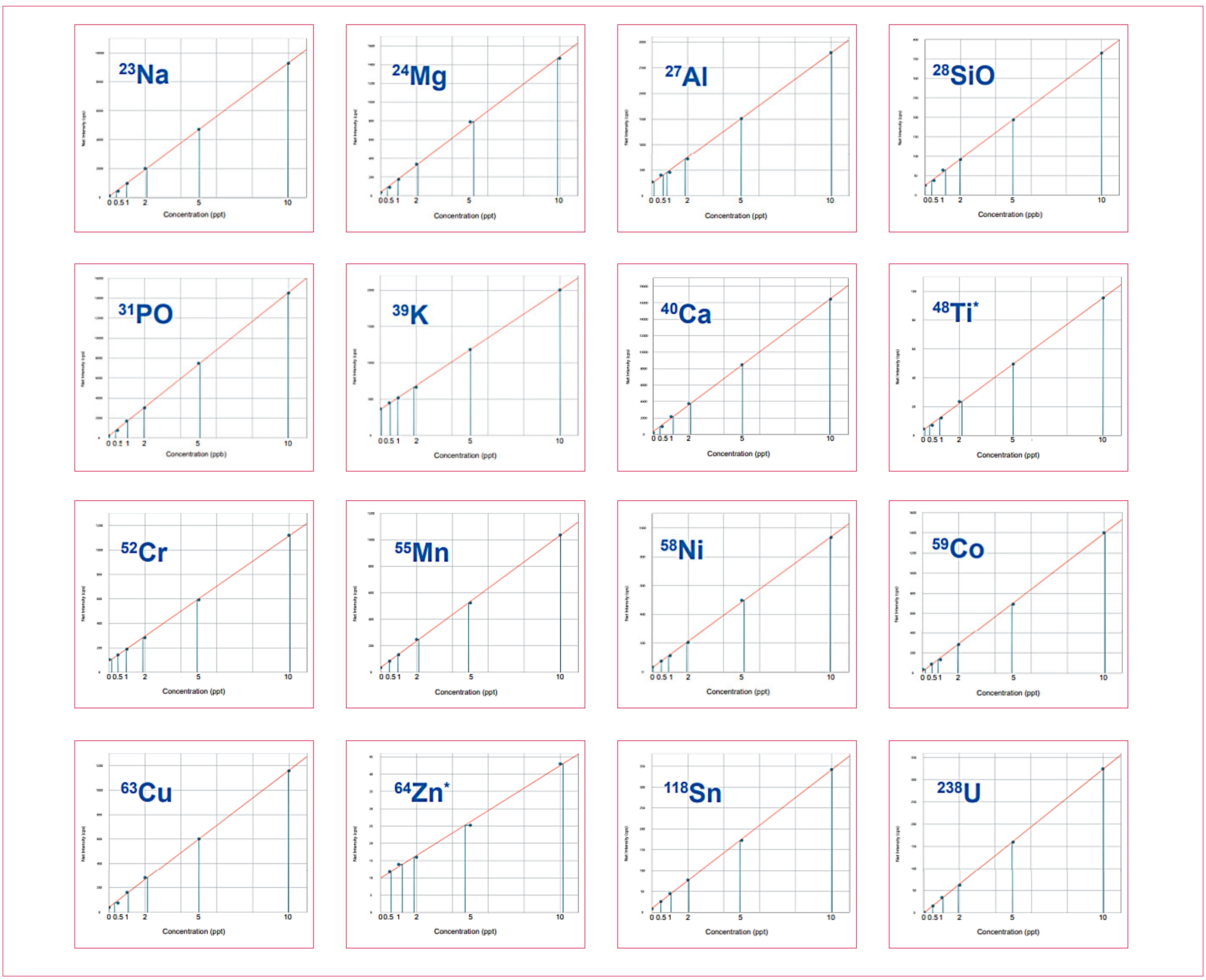

Figure 3. Examples of calibration curves in 9.8% H_2SO_4 obtained by the method of standard addition (MSA).

Table 3. BECs, Calibration Linearity, and LODs in H_2SO_4.

Element	BEC (ppt)	LOD (ppt)	Linearity (R)
Li	0.1	0.1	0.999
Be	0.1	0.4	0.999
Na	0.08	0.3	0.999
Mg	0.3	0.3	0.999
Al	0.9	0.4	0.999
Si	369	481	0.999
P	194	302	0.999
K	2.1	0.3	0.999
Ca	0.2	0.3	0.999
Ti	0.4	0.8	0.999
V	1.6	0.7	0.999
Cr	0.9	0.2	0.999
Mn	0.3	0.1	0.999
Fe	0.9	0.4	0.999
Ni	0.3	0.4	0.999
Co	0.1	0.3	0.999
Cu	0.4	2.1	0.999
Zn	3.3	4.1	0.998
Ga	0.03	0.2	0.999
Rb	0.03	0.3	0.999
Sr	0.06	0.02	0.999
Y	0.1	0.07	0.999
Nb	0.1	0.1	0.999
Ru	0.4	0.3	0.999
Rh	0.3	0.2	0.999
Pd	0.08	0.06	0.999

Element	BEC (ppt)	LOD (ppt)	Linearity (R)
Ag	0.05	0.1	0.999
In	0.06	0.04	0.999
Sn	0.3	0.3	0.999
Sb	0.4	0.2	0.999
Cs	0.07	0.05	0.999
Ba	0.09	0.1	0.999
La	0.01	0.03	0.999
Ce	0.03	0.02	0.999
Pr	0.02	0.1	0.999
Nd	0.07	0.2	0.999
Sm	0.2	0.2	0.999
Eu	0.008	0.1	0.999
Gd	0.01	0.1	0.999
Tb	0.05	0.2	0.999
Dy	0.02	0.1	0.999
Ho	0.02	0.1	0.999
Tm	0.01	0.1	0.999
Yb	0.2	0.2	0.999
Lu	0.009	0.05	0.999
Hf	0.03	0.1	0.999
Ta	0.03	0.06	0.999
Re	0.1	0.2	0.999
Os	0.01	0.1	0.999
Tl	0.01	0.05	0.999
Pb	0.2	0.1	0.999
U	0.2	0.06	0.999

Conclusions

This application brief describes the fully automated analysis of sulfuric acid samples using the ESI prep*FAST* S and PerkinElmer NexION 5000 Multi-Quadrupole ICP-MS. The automated dilution and MSA calibration capabilities of the prep*FAST* S allowed outstanding calibration linearity for all 52 elements. Due to the unique design of the prep*FAST* S, for a handful of elements which are known to be challenging to analyze due to their ubiquity, the sub-ppt or single-digit-ppt detection was still made possible, despite the absence of a cleanroom for this application. Thanks to its multi-quadrupole technology and a quadrupole-based Universal Cell pressurized with pure reaction gases, such as NH_3, the NexION 5000 ICP-MS effectively eliminated the spectral interferences in the samples, resulting in superb BECs and LODs while demonstrating excellent tolerance to harsh chemicals, such as sulfuric acid.

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