

ICP - Mass Spectrometry

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fully-automated chemicals
analysis workflows

Automated Analysis of Semiconductor-Grade TMAH with prepFAST 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 for sample handling and analysis.

Tetramethylammonium hydroxide (TMAH) is a basic solvent widely utilized in the semiconductor industry for photoresist development and lithography applications. The reduction of potential contamination on silicon wafers during the manufacturing processes 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 TMAH and other chemicals, if not properly handled.

This work presents the analysis of undiluted semiconductor-grade TMAH using a PerkinElmer NexION® 5000 Multi-Quadrupole ICP-MS working seamlessly with the ESI prepFAST S ultraclean sample introduction system.

Experimental

Reagents and Samples

Commercially available TMAH (25%) was used as the sample for all analyses. All standards were automatically spiked in-line using the on-board reagent supply on the prepFAST S ultraclean sample introduction system. The prepFAST S utilized syringe-driven flow of ultrapure water, HNO_3 , TMAH and standard solutions to automate the method of standard addition (MSA) for standard preparation and sample handling.

All MSA standards were automatically prepared from the stock solutions by the prepFAST S. UPW was used as the carrier solution and samples were introduced at 200 $\mu\text{L}/\text{min}$. For MSA, 200 ppt mixed-element standard in 1% HNO_3 was prepared from a 100-ppb standard. All samples and standards were automatically spiked in-line to a final concentration of 0.5% HNO_3 from an on-board reagent supply vessel (containing 70% HNO_3) to match the sample to the calibration standards and stabilize the spiked elements. Calibrations were automatically performed at 0, 1, 2, 5, 10 and 15 ppt and 1000x higher for Si. 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, but only using the instrumentation discussed below.

The prepFAST S allows automated dilution by volume or weight for direct analysis of concentrated chemicals from their original sample vessels. This feature eliminates sample contamination caused by manual dilution into a secondary container and significantly reduces operator exposure to concentrated and hazardous chemicals.

Instrumentation: Sample Introduction

In this application, a prepFAST S ultraclean system (Elemental Scientific Inc., Omaha, Nebraska, USA) was used to minimize contamination from the environment and sample handling and to deliver inline, 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 prepFAST S ultraclean system.

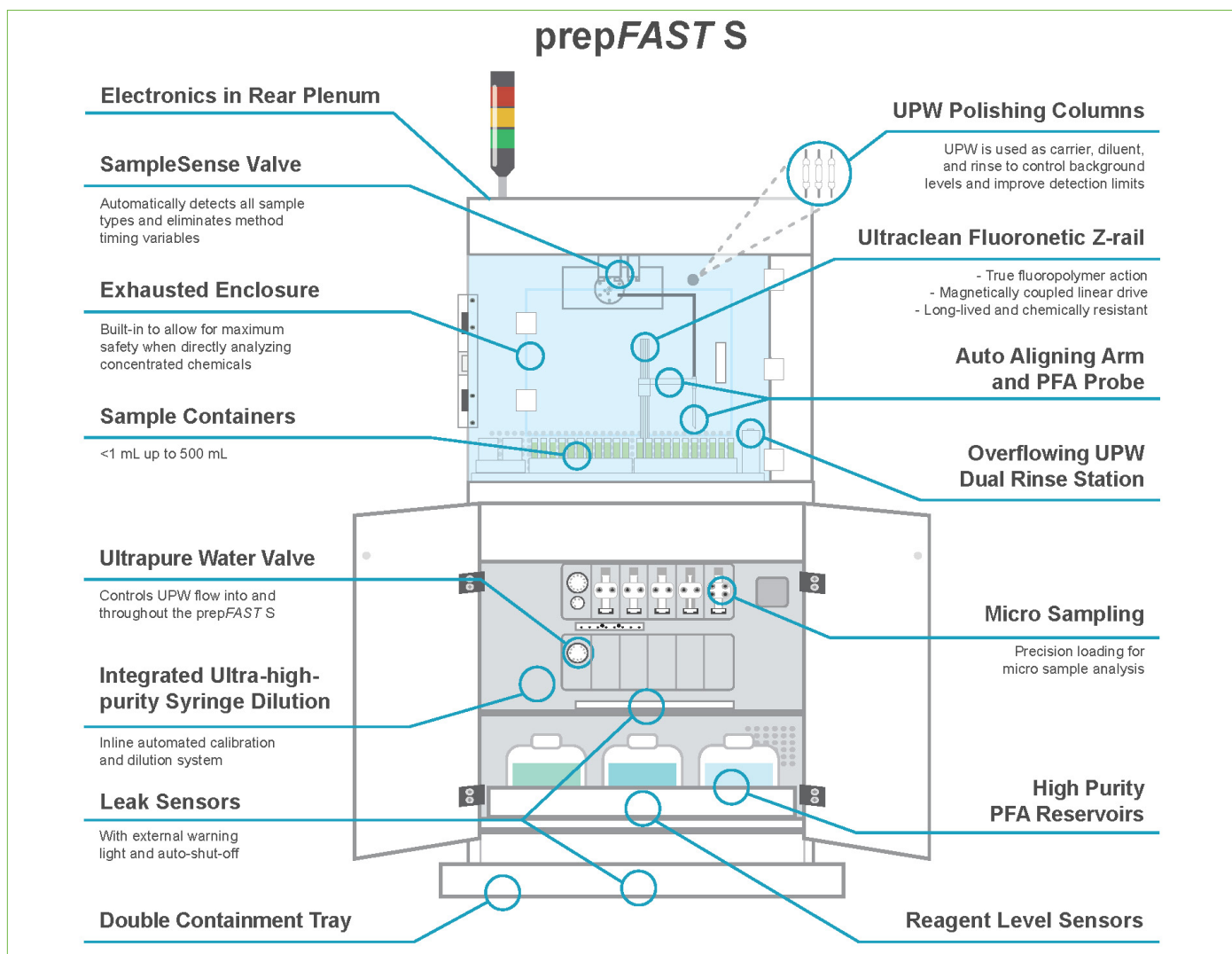


Figure 1. Schematic of prepFAST S ultraclean system.

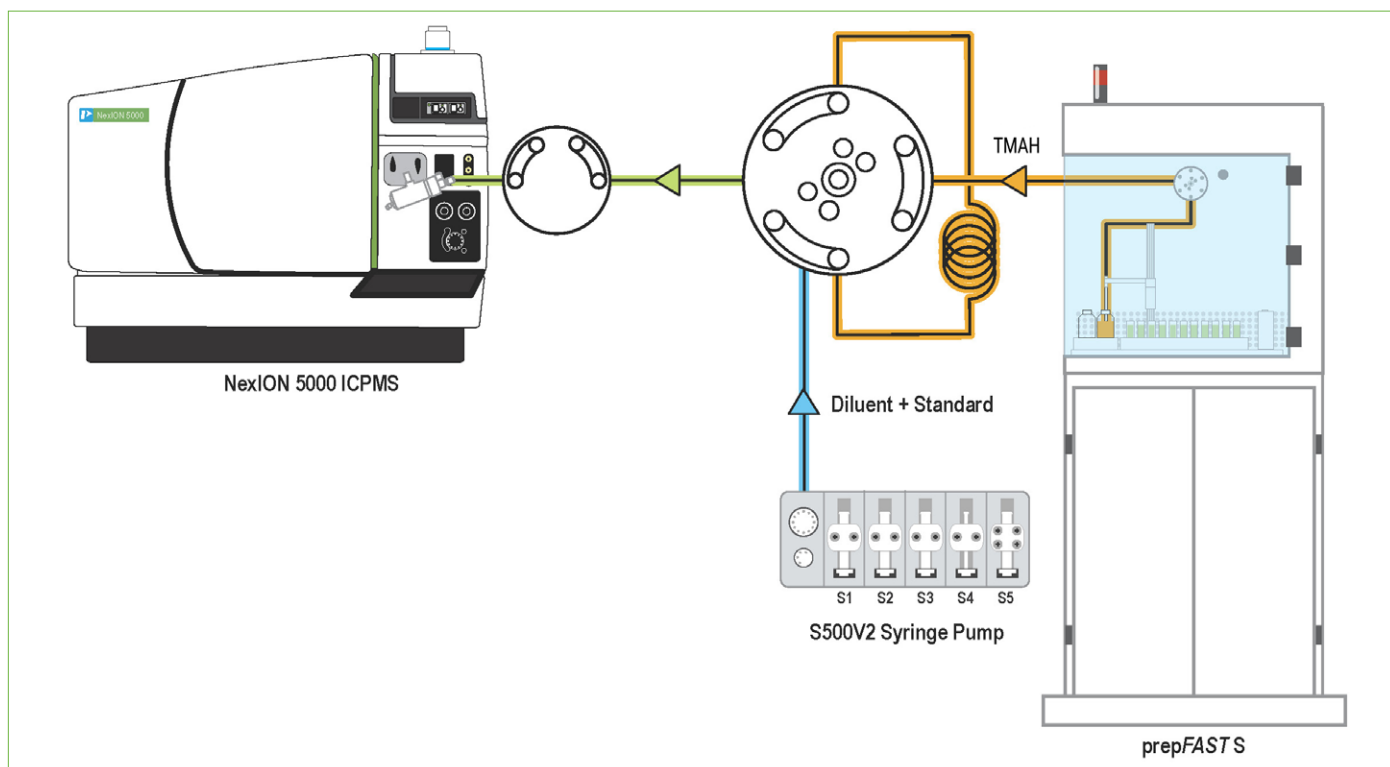


Figure 2. Simplified flow path from prepFAST S ultraclean system to the NexION 5000 ICP-MS.

In order to deliver upon the needs of semiconductor customers 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.

The prepFAST S can also utilize a SampleSense valve to detect all kind of samples – viscous, non-viscous and solvents without timing or method adjustment.

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 TMAH. The NexION 5000 represents a truly significant advancement in ICP mass spectrometry and 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 enhance the

instrument's analytical performance and sensitivity, as well as reliability. The NexION 5000 works seamlessly with the prepFAST S, as shown in Figure 2.

To deliver the best BECs for this application, four plasma powers were used, namely cold, semi-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 or more times (i.e. under cold and hot plasma conditions). Here, cold, warm and hot plasma modes were used in combination with the multi-quadrupole technology of the NexION 5000 and gas phase reactions in the UCT to remove polyatomic ion interferences on certain analytes. Pure reaction gases (NH_3 and O_2) were 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 reaction gas flow rates and bandpass settings were determined experimentally. By combining multiple plasma modes, multi-quad functionality and quadrupole Universal Cell modes, the accurate determination of trace metals in semiconductor chemicals, in this case in TMAH, at extremely low levels was made possible.

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

Table 1. Operating Parameters for TMAH Analysis.

Parameter	Cold Plasma (STD)	Warm Plasma (DRC)	Warm Plasma (DRC)	Hot Plasma (DRC)	Hot Plasma (STD)
ICP RF Power (W)	600	1000	900	1600	
Nebulizer Gas Flow (L/min)	0.93	0.8	0.85	0.94	0.84
Reaction Gas	-	100% O ₂	100% NH ₃		-
AMS Gas Flow (L/min)	0.3				
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	Fluorobore Straight-bore 2.5 mm Pt				
ICP-MS Cones	Platinum-tipped Sampler and Skimmer Nickel Hyper-skimmer and OmniRing Assembly				
Hyper-skimmer Voltage	-30	-50	5		
OmniRing Voltage	-220	-210	-160	-165	

Table 2. ICP-MS Analytical Conditions.

Element	Q1 Mass	Q3 Mass	Power (W)	Reaction Gas	Reaction Gas Flow	RPq
Li	7	7	600	NH ₃	0.1	0.45
Be	9	9	1600	-	0	0.25
B	11	11	1600	-	0	0.25
Na	23	23	600	NH ₃	1.2	0.45
Mg	24	24	600	NH ₃	1.2	0.45
Al	27	27	600	NH ₃	1.2	0.45
Si	28	44	1000	O ₂	3	0.1
K	39	39	600	NH ₃	1.2	0.8
Ca	40	40	600	NH ₃	1.2	0.8
Ti	48	131	900	NH ₃	1	0.3
V	51	67	1000	O ₂	1	0.1
Cr	52	52	600	NH ₃	1.2	0.8
Mn	55	55	600	NH ₃	1.2	0.8
Fe	56	56	600	NH ₃	1.2	0.8
Co	59	110	900	NH ₃	1	0.3
Ni	60	111	900	NH ₃	1	0.3
Cu	65	65	600	NH ₃	1.2	0.45
Zn	64	115	900	NH ₃	1	0.3
Ga	71	71	600	NH ₃	0.1	0.45

Element	Q1 Mass	Q3 Mass	Power (W)	Reaction Gas	Reaction Gas Flow	RPq
As	75	91	1000	O ₂	1	0.45
Sr	88	88	1600	-	0	0.25
Y	89	89	1600	-	0	0.25
Zr	90	90	1600	-	0	0.25
Mo	98	98	1600	-	0	0.25
Ag	107	107	1600	-	0	0.25
Cd	111	111	1600	-	0	0.25
In	115	115	1600	-	0	0.25
Sn	120	120	1600	-	0	0.25
Sb	121	121	1600	-	0	0.25
Ba	138	138	1600	-	0	0.25
Ce	140	140	1600	-	0	0.25
W	184	184	1600	-	0	0.25
Pt	195	195	1600	-	0	0.25
Au	197	197	1600	-	0	0.25
Tl	205	205	1600	-	0	0.25
Pb	208	208	1600	-	0	0.25
Bi	209	209	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 25% TMAH. The correlation coefficients with R values equal or better than 0.999 for most elements demonstrate the accuracy of the prepFAST S automated spike addition, 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, 1, 2, 5, 10 and 15 ppt with the prepFAST S. Si was spiked at 0, 1, 2, 5, 10 and 15 ppb. Figure 3 shows calibration curves for a selection of elements with MSA in 25% TMAH.

As can be seen in Table 3, by combining the prepFAST 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, Mg, K and Ca, in 25% TMAH. These results were achieved in a non-cleanroom environment due to the enclosed and vented sampling area in the prepFAST S automated sample introduction system, and the superior interference removal capabilities of the NexION 5000 Multi-Quadropole ICP-MS.

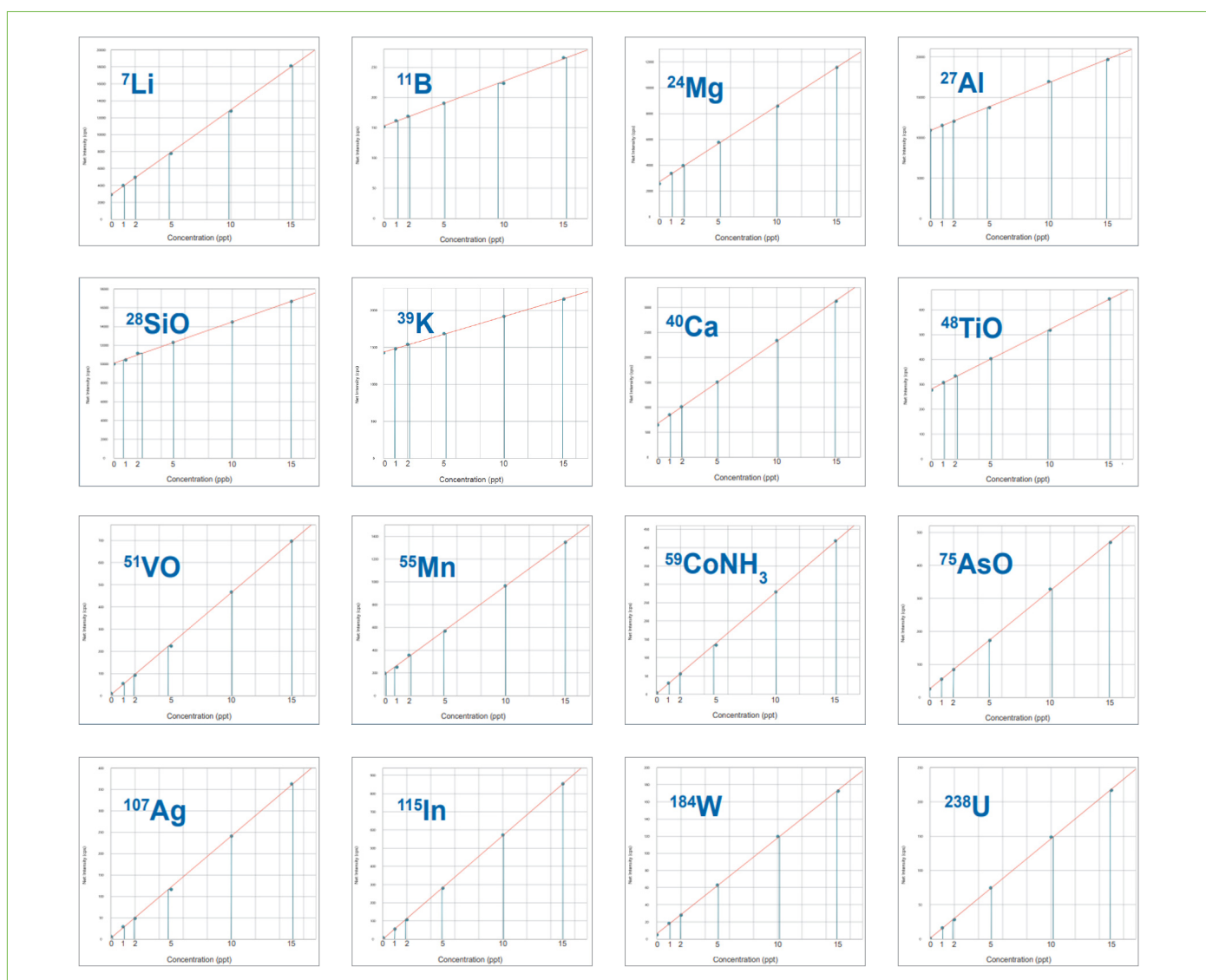


Figure 3. Examples of calibration curves in 25% TMAH obtained by the method of standard addition (MSA).

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

Element	BEC (ppt)	LOD (ppt)	Linearity (R)
Li	2.8	0.6	0.999
Be	0.1	0.4	0.999
B	21.9	1.8	0.999
Na	5.6	1.4	0.999
Mg	4.6	0.9	0.999
Al	18.5	1.3	0.999
Si (ppb)	22.9	1.3	0.999
K	14.9	3.8	0.995
Ca	3.8	1.0	0.999
Ti	11.8	2.2	0.999
V	0.1	0.6	0.999
Cr	21.8	10.8	0.997
Mn	2.5	0.4	0.999
Fe	12.4	8.3	0.998
Co	0.07	0.1	0.999
Ni	15.0	2.6	0.998
Cu	5.0	1.2	0.999
Zn	20.6	6.3	0.997
Ga	0.2	1.1	0.998

Element	BEC (ppt)	LOD (ppt)	Linearity (R)
As	0.8	0.2	0.999
Sr	0.9	1.1	0.999
Y	0.1	0.2	0.999
Zr	1.0	0.3	0.999
Mo	2.1	2.9	0.999
Ag	0.1	0.5	0.999
Cd	0.2	1.0	0.999
In	0.1	0.2	0.999
Sn	9.8	2.2	0.999
Sb	1.6	0.6	0.999
Ce	0.08	0.07	0.999
Ba	1.6	0.7	0.999
W	0.5	0.3	0.999
Pt	4.8	2.6	0.999
Au	2.7	0.7	0.999
Tl	0.05	0.1	0.999
Pb	0.2	0.2	0.999
Bi	0.1	0.2	0.999
U	0.07	0.07	0.999

Conclusions

This application brief describes the fully automated analysis of undiluted TMAH using the ESI prepFAST S and PerkinElmer NexION 5000 Multi-Quadrupole ICP-MS. The automated MSA calibration capabilities of the prepFAST S allowed outstanding calibration linearity to be achieved for all 38 elements. Due to the unique design of the prepFAST S, for a handful of elements which are known to be challenging contaminants to control, 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 NH₃ and O₂, the NexION 5000 ICP-MS effectively eliminated the spectral interferences in the samples, resulting in superb BECs and LODs. It also proved to deliver excellent tolerance to harsh chemicals, in this case, a strong base TMAH.