

ICP - Mass Spectrometry

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fully-automated chemicals
analysis workflows

Automated Analysis of Semiconductor-Grade Hydrofluoric Acid 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 to sample handling and analysis.

Hydrofluoric acid (HF) is widely utilized in the semiconductor industry during the cleaning process of silicon wafers in order to reduce contamination by trace metals, particulates, and organic contaminants which would otherwise alter the functionality of the semiconductors. As such, the use of high-quality acids and the control of contaminants in the acid itself are important to the use of these chemicals in the semiconductor industry. Since the control of environmental contaminants at the parts per trillion (ppt) level is challenging, special handling is often required and the acids need to be regularly analyzed for trace metals as part of quality control.

This work presents the analysis of undiluted semiconductor-grade hydrofluoric acid 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 HF (49%) 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 prepFAST 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 prepFAST S utilized syringe-driven flow of ultrapure water, semiconductor-grade HNO_3 , and standard solution to automate sample introduction and method of standard addition (MSA) standard preparation.

For MSA, a 200 ppt multi-element standard in 1% HNO_3 was prepared from a 100-ppb standard (P was prepared from a 200 ppb standard). Dilutions for calibration were automatically performed at concentrations of 0, 0.5, 1, 2, 5 and 10 ppt (P 1000x higher). 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 the typical cleanroom-infrastructure using the instrumentation discussed below.

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.

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.

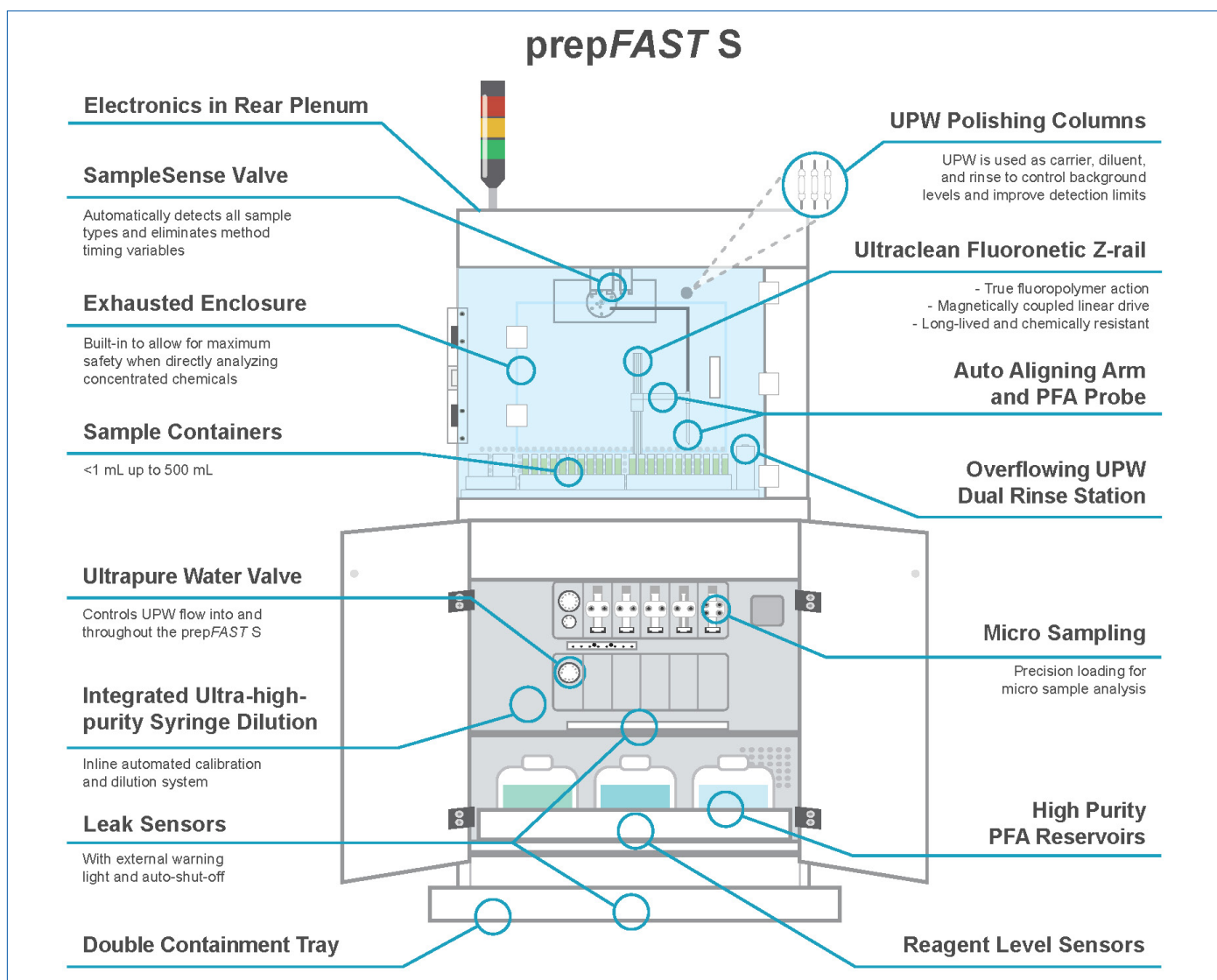


Figure 1. Schematic of prepFAST S ultraclean system.

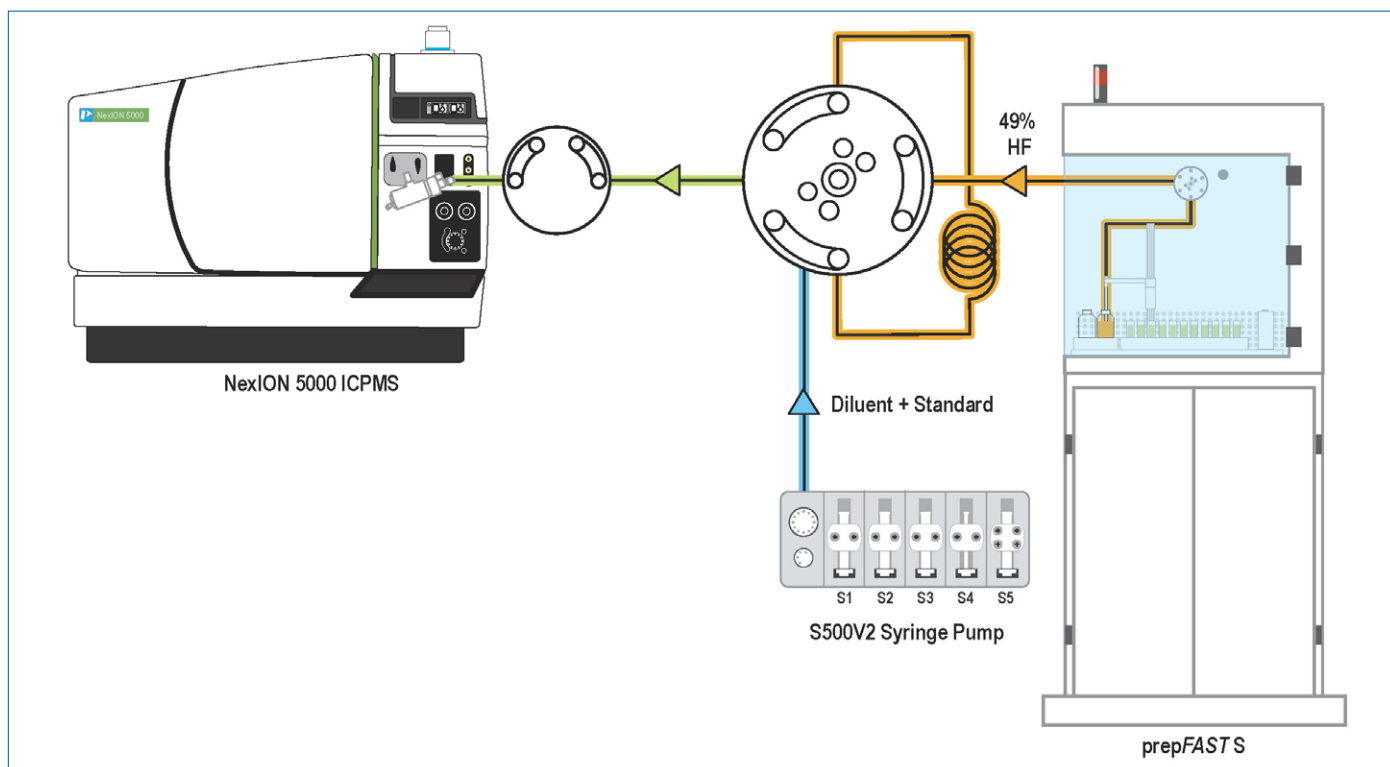


Figure 2. Simplified flow path from prepFAST S ultraclean system to the NexION 5000 ICP-MS.

The Fluorospray sample introduction kit of the NexION 5000 ICP-MS with HF-resistant technology was used to enhance precision and sensitivity for the analysis of semiconductor-grade ultrapure chemicals. In order to further improve performance for semiconductor applications, the Fluorospray PFA 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 HF. 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 (UTC) with dynamic bandpass tuning and multi-quad technology enhance the instrument's analytical performance and sensitivity, as well as reliability.

In order 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 (under cold and hot plasma conditions). Here, cold plasma was 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.

In cold, warm, and hot plasma conditions, pure reaction gases (NH_3 and O_2) were used in the Universal Cell to assist in the removal of interferences, which, 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 conditions and Multi Quad mode, the accurate determination of trace metals in semiconductor chemicals, in this case HF, 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 HF Analysis.

Parameter	Cold Plasma (STD)	Cold Plasma (DRC)	Warm Plasma (DRC)	Hot Plasma (DRC)	Hot Plasma (STD)
ICP RF Power (W)	600		1000	1600	
Nebulizer Gas Flow (L/min)	0.99	1.04	0.85	0.98	1.01
Reaction Gas	-	NH ₃	O ₂	NH ₃ or O ₂	-
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	SiIQ Ultra High Purity Quartz				
Injector	Fluorobore Straight-bore 2.5 mm Platinum				
ICP-MS Cones	Platinum-tipped Sampler and Skimmer Nickel Hyper-Skimmer and OmniRing Assembly				
Hyper-skimmer Voltage	-50		5		
OmniRing Voltage	-210	-245	-165	-205	

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
B	11	11	600	-	0	0.45
Na	23	23	600	NH ₃	1.5	0.45
Mg	24	24	600	NH ₃	0.5	0.45
Al	27	27	600	NH ₃	1.5	0.45
K	39	39	600	NH ₃	0.5	0.8
Ca	40	40	600	NH ₃	0.3	0.8
P	31	47	1600	O ₂	1.0	0.1
Sc	45	61	1600	O ₂	0.4	0.45
Ti	48	64	1600	O ₂	1.0	0.1
V	51	51	1600	NH ₃	0.2	0.45
Cr	52	52	600	NH ₃	0.5	0.8
Mn	55	55	600	NH ₃	0.5	0.8
Fe	56	56	600	NH ₃	1	0.8
Ni	58	58	600	NH ₃	0.7	0.8
Co	59	59	600	NH ₃	0.7	0.3
Cu	63	63	600	NH ₃	0.3	0.45
Zn	66	66	1600	NH ₃	0.2	0.45
Ga	71	71	1600	-	0	0.45
As	75	91	1000	O ₂	1	0.1

Element	Q1 Mass	Q3 Mass	Power (W)	Reaction Gas	Reaction Gas Flow	RPq
Rb	85	85	1600	NH ₃	0.2	0.45
Sr	88	88	1600	-	0	0.25
Y	89	89	1600	-	0	0.25
Zr	90	90	1600	-	0	0.25
Nb	93	93	1600	-	0	0.25
Mo	98	98	1600	-	0	0.25
Ru	101	101	1600	-	0	0.25
Rh	103	103	600	-	0	0.25
Ag	107	107	600	-	0	0.25
In	115	115	1600	-	0	0.25
Sn	118	118	1600	NH ₃	0.2	0.45
Ba	137	137	1600	NH ₃	0.5	0.45
Ce	140	140	1600	-	0	0.25
Ta	181	181	1600	-	0	0.25
W	184	184	1600	-	0	0.25
Os	189	189	1600	-	0	0.25
Ir	193	193	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 the background equivalent concentrations (BECs), limits of detection (LODs) and correlation coefficients (R) for all elements measured in undiluted HF. 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 prepFAST S (P was spiked at 0, 0.5, 1, 2, 5 and 10 ppb). Figure 3 shows calibration curves for a selection of elements prepared using automated MSA in undiluted HF, where all exhibited R values of > 0.999 . These findings demonstrate the exceptional linear regression, accuracy of injection and reliability which can be achieved using the prepFAST S automatic dilution and spike addition on the NexION 5000 ICP-MS, further demonstrating that complicated matrices can be evaluated using this solution with outstanding results.

As can be seen in Table 3, by combining the prepFAST S sample introduction system with multiple plasma conditions and Multi Quad mode on the NexION 5000 ICP-MS, elements which typically have large polyatomic interferences and/or are likely affected by contaminants in lab environments can easily be analyzed. Here, it was possible to achieve sub-ppt BECs and LODs for most ($> 80\%$) of the elements analyzed. Nonetheless, it was still possible to achieve single-digit ppt BECs and LODs for historically challenging elements such as Na, Mg and Ca in undiluted HF due to the enclosed and vented sampling area in the prepFAST S automatic sample introduction system and the superior interference removal capabilities of the NexION 5000 Multi-Quadrupole ICP-MS.

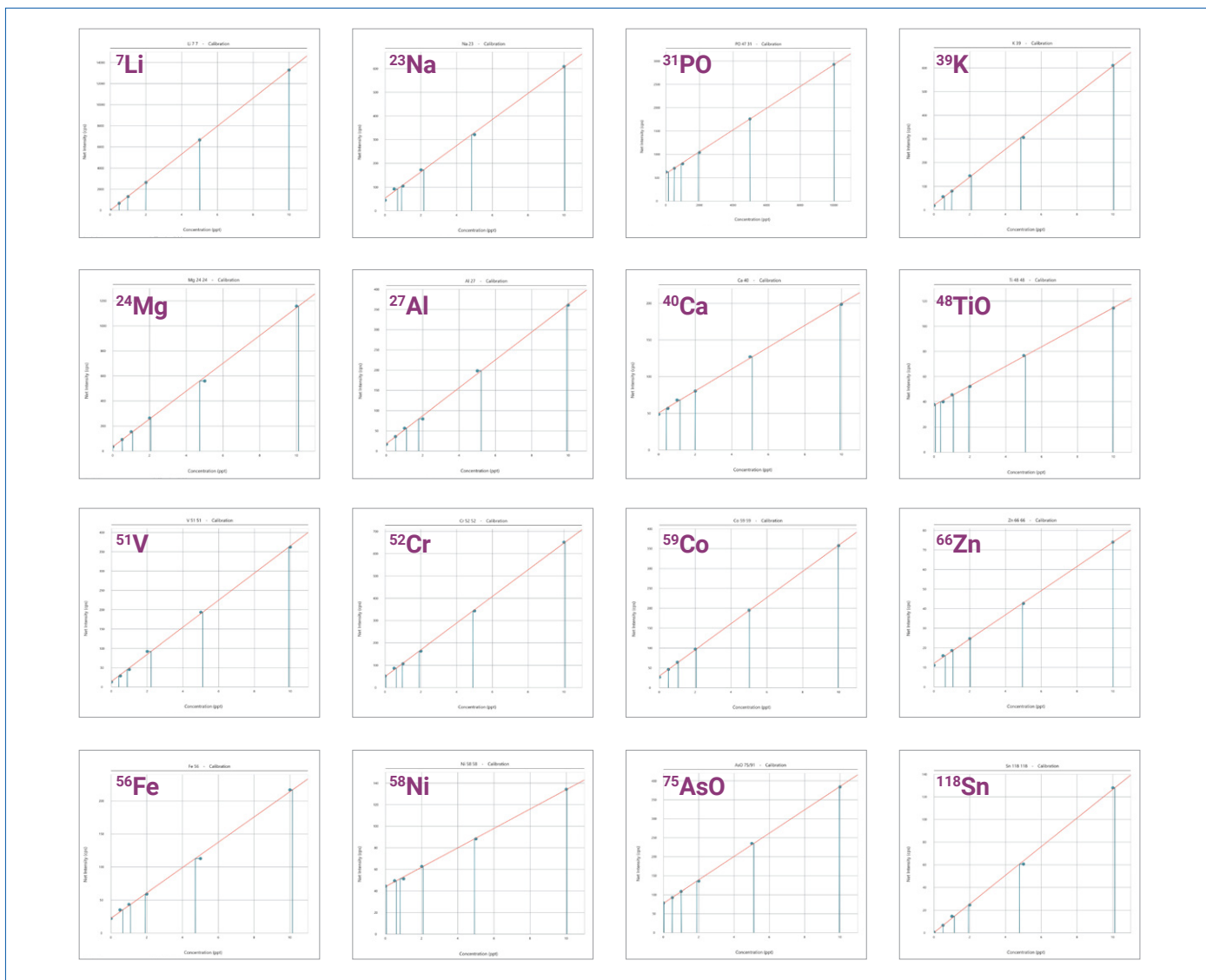


Figure 3. Examples of calibration curves in undiluted HF obtained by the method of standard addition (MSA).

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

Element	BEC (ppt)	LOD (ppt)	Linearity (R)
Li	0.006	0.009	0.999
Be	0.1	0.3	0.999
B	8.4	10.0	0.998
Na	0.7	0.2	0.999
Mg	0.2	0.2	0.999
Al	0.4	0.9	0.999
K	0.3	0.2	0.999
Ca	2.2	1.2	0.999
P (ppb)	0.9	1.7	0.999
Sc	0.8	1.0	0.999
Ti	2.6	2.0	0.999
V	0.2	0.3	0.999
Cr	0.9	0.7	0.999
Mn	0.05	0.1	0.999
Fe	0.9	0.9	0.999
Ni	4.3	3.0	0.999
Co	0.6	0.2	0.999
Cu	0.4	0.2	0.999
Zn	1.8	3.0	0.999
Ga	1.5	1.0	0.999
As	2.5	0.5	0.999

Element	BEC (ppt)	LOD (ppt)	Linearity (R)
Rb	0.06	0.4	0.999
Sr	0.02	0.06	0.999
Y	0.02	0.1	0.999
Zr	0.5	0.7	0.999
Nb	0.8	0.7	0.999
Mo	1.4	2.0	0.999
Ru	0.3	0.5	0.999
Rh	0.1	0.1	0.999
Ag	0.06	0.03	0.999
In	0.02	0.04	0.999
Sn	0.06	0.3	0.999
Ba	0.07	0.08	0.999
Ce	0.004	0.2	0.999
Ta	0.05	0.07	0.999
W	1.6	1.3	0.999
Os	0.06	0.1	0.999
Ir	0.1	0.2	0.999
Ti	0.1	0.1	0.999
Pb	0.2	0.2	0.999
Bi	0.1	0.5	0.999
U	0.02	0.7	0.999

Conclusions

In summary, the fully automated analysis of hydrofluoric acid samples was performed using the ESI prepFAST S and PerkinElmer NexION 5000 Multi-Quadrupole ICP-MS. The automated dilution and MSA calibration capabilities of the prepFAST S achieved outstanding linearity of the calibration curves for all of the 42 elements analyzed. Thanks to its multi-quadrupole technology and a true quadrupole Universal Cell, the NexION 5000 ICP-MS effectively eliminated the spectral interferences in the samples, delivering superb BECs and LODs,

and proved to deliver excellent tolerance to harsh chemicals, in this case hydrofluoric acid. Thanks to the ability of the NexION 5000 to be able to use pure reaction gases – including pure ammonia – for extended periods of time, the sub-ppt detection for more than 80 of the elements analyzed was made possible. For a handful of elements which are known to be challenging contaminants to control, the single-digit ppt detection was achieved, despite the absence of a cleanroom for this application.