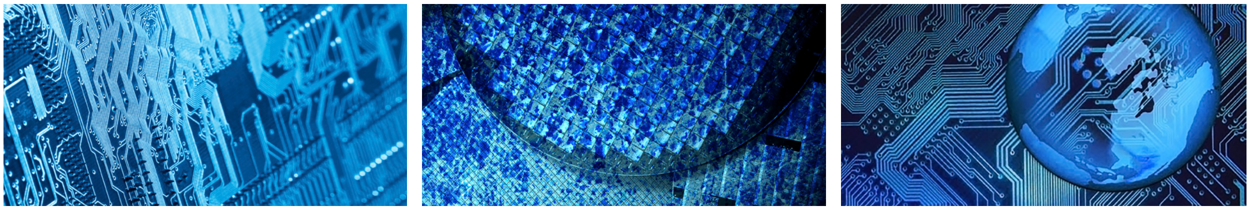

Elemental Scientific
ICP | ICPMS | AA

Hydrofluoric Acid

Automated Analysis of Semiconductor Grade HF with prep*FAST* S and NexION 5000® ICPMS

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Introduction

Advances in semiconductor technology and decreasing tolerances in microchip design require simultaneous improvements in both chemical purity and fabrication. As manufacturers move to <10 nm geometry, while seeking improved yield, the chemicals and process reagents must maintain minimal trace metal contamination. The demand for lower detection limits in reagents requires new approaches to sample handling and trace elemental analysis – within the fab and throughout the supply chain.

Hydrofluoric Acid is widely utilized in the semiconductor industry. The reduction of potential contamination of silicon wafers during the cleaning process is crucial as trace metal, particulate, and organic contaminants can alter the functionality of the semiconductors. At the ppt level, environmental contaminants are difficult to control and can easily contaminate a HF sample if not properly handled.

The prep*FAST* S ultraclean sample preparation and introduction system minimizes contamination from the environment and sample handling, enabling semiconductor manufacturers and laboratories to easily analyze these critical samples. The prep*FAST* S features inline, automated calibration and dilution technology that automates sample and standard preparation. Samples are analyzed directly from their original containers in an exhausted and fully enclosed environment, eliminating manual sampling errors and operator variability and providing sub-ppt detection limits for critical semiconductor elements.

Figure 1. prep*FAST* S.

prep*FAST* S

The prep*FAST* S utilizes a robust PFA probe, CTFE AutoAlign Arm, and sealed PTFE vertical probe drive assembly combined with high-purity, chemically conditioned fluoropolymer flow paths to minimize contamination and maximize chemical resistance. When combined with an exhausted, enclosed sample environment, these features allow automated dilution, acidification, and spiking of concentrated semiconductor chemicals resulting in high-quality calibrations and accurate, precise determination of background equivalent concentrations and detection limits.

Calibrations are generated by automatically spiking from an enclosed multi-element stock standard using either automated inline method of standard addition (MSA) or external calibration for over 50 elements that are typically controlled in semiconductor manufacturing processes. When combined with the interference reduction modes and multi-quadrupole functionality of the NexION 5000 ICPMS, the result is low to sub-ppt calibrations.

For sample analysis, the prep*FAST* S allows automatic 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.

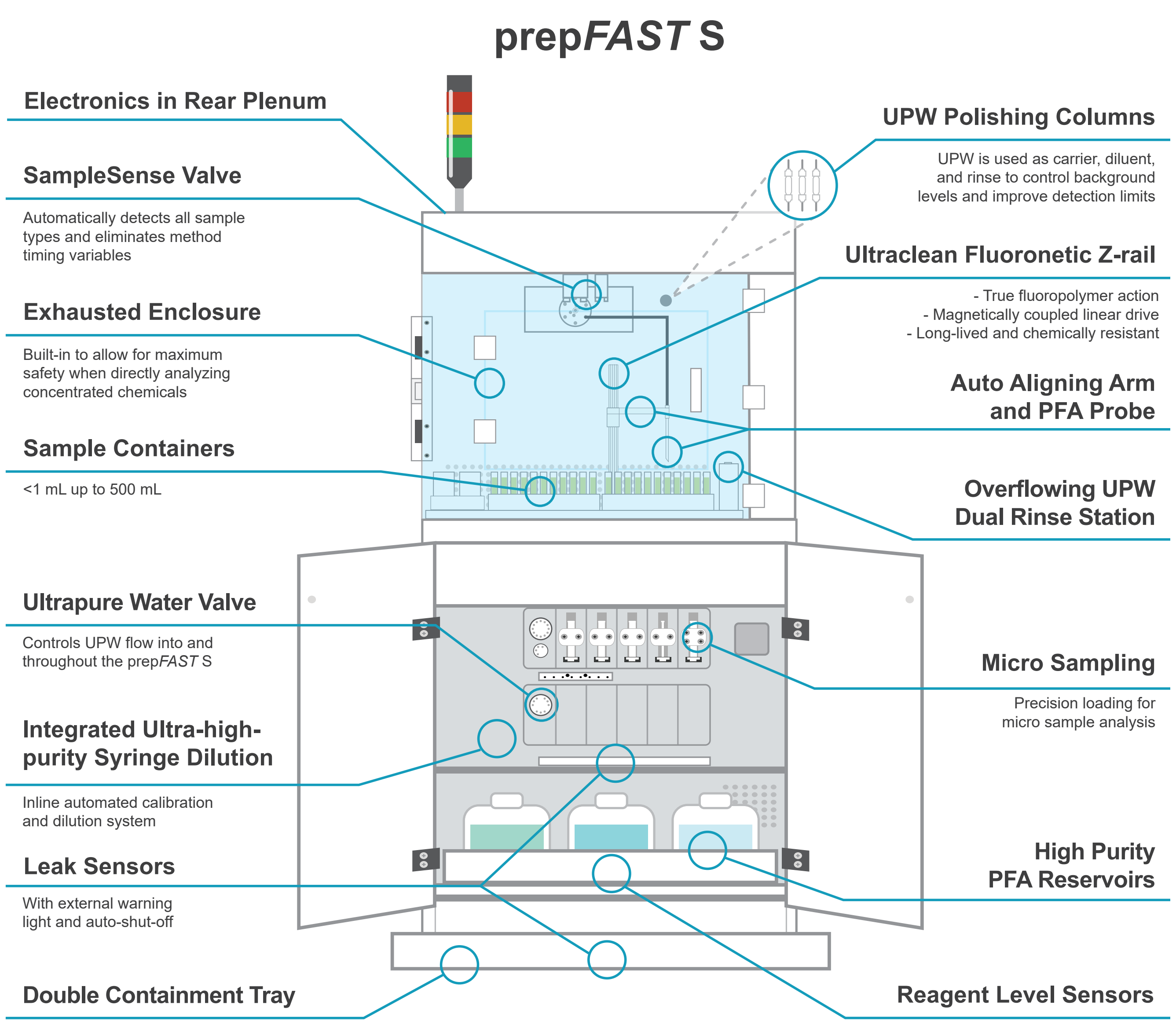


Figure 2. prep*FAST* S features diagram.

Fluorospray Sample Introduction

The Fluorospray sample introduction kit for the NexION 5000 is a new, HF-resistant technology offering enhanced precision and sensitivity for the analysis of semiconductor-grade ultrapure chemicals. Designed for demanding, multichemical analysis, the Fluorospray chamber combined with an o-ring free Fluorobore platinum injector provides complete high-performance sample introduction for the semiconductor laboratory.

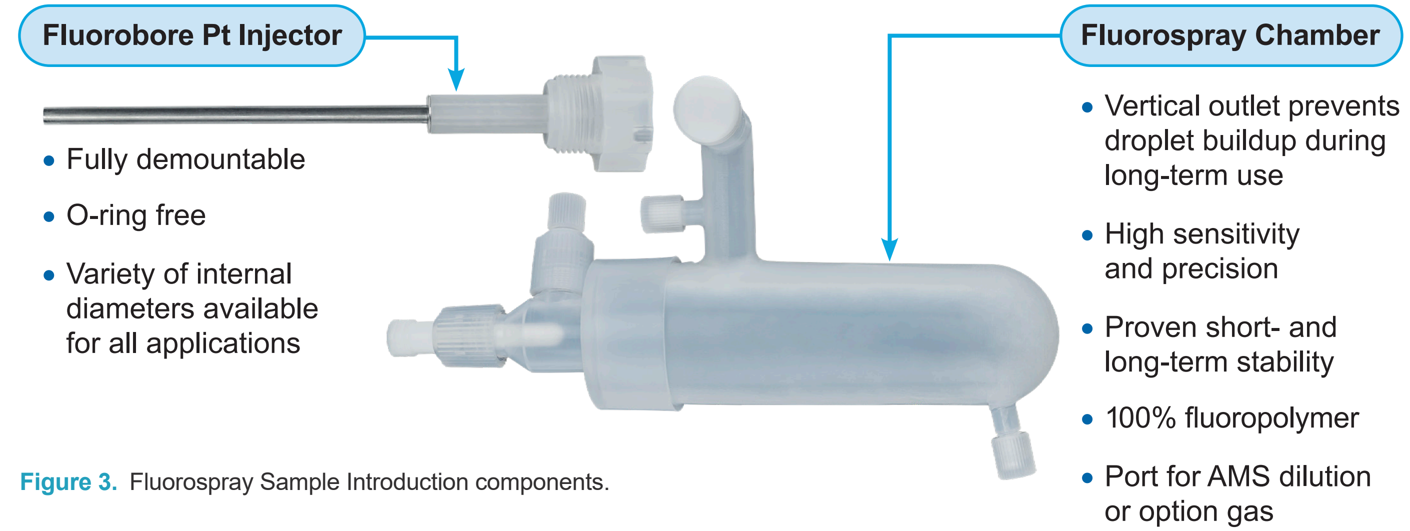


Figure 3. Fluorospray Sample Introduction components.

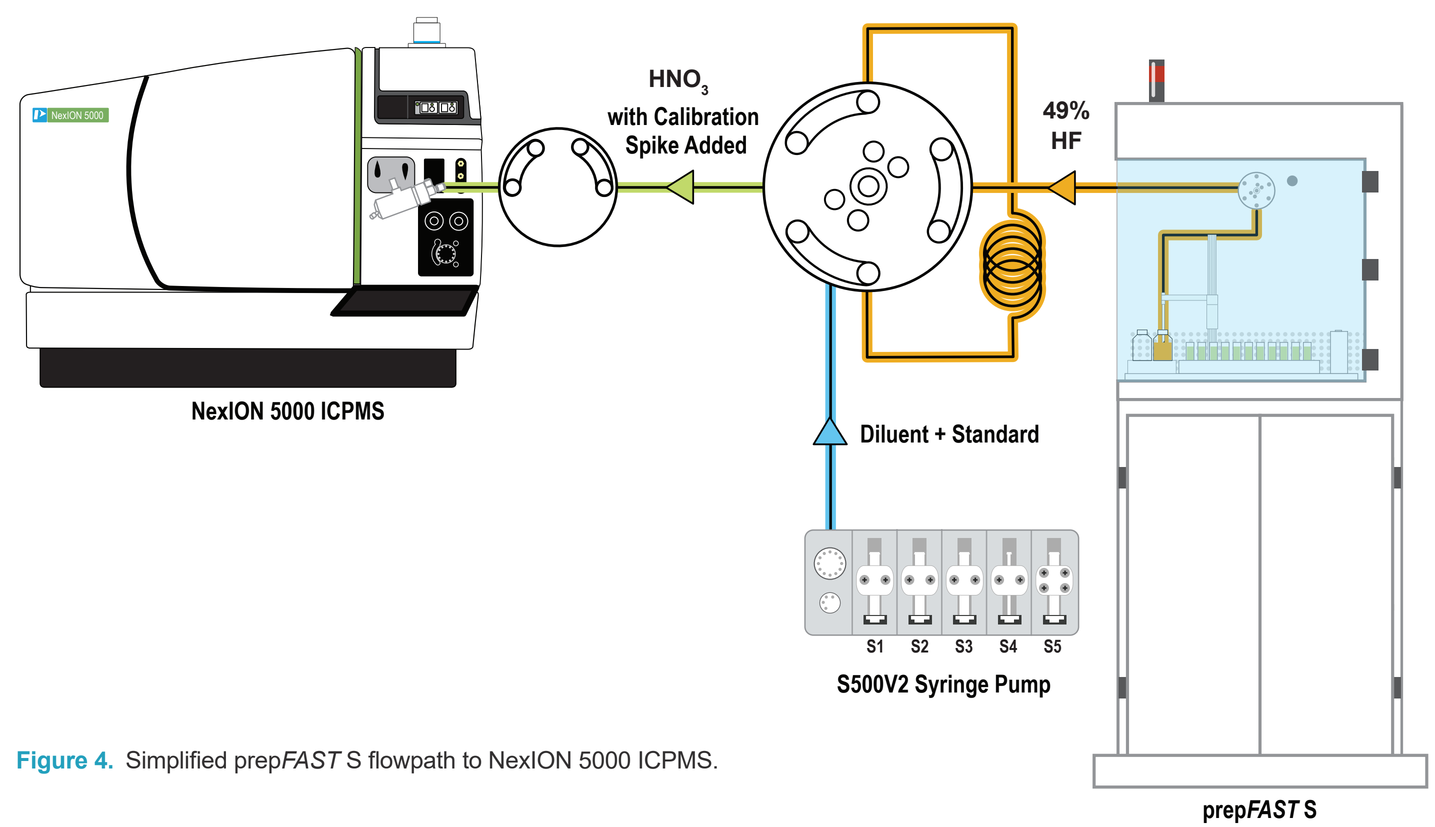


Figure 4. Simplified prep*FAST* S flowpath to NexION 5000 ICPMS.

Experimental: Reagents and Samples

Commercially available 49% HF was used as sample for all analyses. A 200 ppt, 1% HNO_3 mixed-element standard was prepared from a 100 ppb standard; P was spiked at 200 ppb. 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 standard and stabilize the spiked elements.

The prep*FAST* S utilized syringe-driven flow of ultrapure water, semiconductor grade HNO_3, and standard solution to automate sample and MSA standard preparation. All MSA standards were prepared from the stock solutions automatically by the prep*FAST* S. UPW was used as the carrier solution and samples were introduced at 200 µL/min.

Experimental: Instrumentation

The NexION 5000 multi-quadrupole ICPMS was used with the Fluorospray sample introduction kit and a microflow PFA-ICN concentric integrated capillary nebulizer. The NexION 5000 automatically switches between cool, warm, and hot plasma conditions to optimize the analysis of all analytes. Cool plasma works in tandem with the multi-quadrupole technology of the NexION 5000 to reduce polyatomic ion interferences while simultaneously reducing background from the ICPMS interface for elements that can be thermally ionized. Hot plasma ensures ionization of refractory and high ionization-potential elements and maintains high matrix tolerance, allowing for analysis of nearly the entire periodic table. Combining multiple plasma conditions, QQQQ filtering and DRC technology allows for excellent detection limits and accurate determination of trace metals in semiconductor chemicals. Instrumental parameters and sample introduction hardware are listed in Table 1. NexION method parameters are shown in Table 2. DRC gas flow rates and RPq values were determined experimentally.

Table 1. Operating Parameters for HF Analysis.

Parameter	Cool Plasma (STD)	Cool 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	SilQ Ultra High Purity Quartz				
Injector	Fluorobore Straight-bore 2.5 mm Platinum				
ICPMS Cones	Platinum-tipped Sampler and Skimmer with Nickel Hyperskimmer				
Hyperskimmer Voltage	-50		5		
OmniRing Voltage	-210	-245	-165	-205	
Inner Target Lens Voltage	6		5	4.5	
Outer Target Lens Voltage	0		-17	-10	

Table 2. ICPMS Analytical Conditions.

Element	Q1 Mass	Q3 Mass	Power (W)	Reaction Gas	Reaction Gas Flow	QID Fixed Voltage	RPq	Axial Field Voltage
Li	7	7	600	-	0	-20	0.45	0
Be	9	9	1600	-	0	-16.5	0.25	0
B	11	11	600	-	0	-20	0.45	0
Na	23	23	600	NH_3	1.5	-18.5	0.45	250
Mg	24	24	600	NH_3	0.5	-18.5	0.45	250
Al	27	27	600	NH_3	1.5	-18.5	0.45	250
K	39	39	600	NH_3	0.5	-18.5	0.8	250
Ca	40	40	600	NH_3	0.3	-18.5	0.8	250
P	31	47	1600	O_2	1.0	-16.5	0.1	150
Sc	45	61	1600	O_2	0.4	-16.5	0.45	150
Ti	48	64	1600	O_2	1.0	-16.5	0.1	150
V	51	51	1600	NH_3	0.2	-16.5	0.45	90
Cr	52	52	600	NH_3	0.5	-18.5	0.8	250
Mn	55	55	600	NH_3	0.5	-18.5	0.8	250
Fe	56	56	600	NH_3	1	-18.5	0.8	250
Ni	58	58	600	NH_3	0.7	-18.5	0.8	250
Co	59	59	600	NH_3	0.7	-18.5	0.3	250
Cu	63	63	600	NH_3	0.3	-18.5	0.45	250
Zn	66	66	1600	NH_3	0.2	-16.5	0.45	90
Ga	71	71	1600	-	0	-16.5	0.45	0
As	75	91	1000	O_2	1	-16.5	0.1	150
Rb	85	85	1600	NH_3	0.2	-16.5	0.45	90
Sr	88	88	1600	-	0	-16.5	0.25	0
Y	89	89	1600	-	0	-16.5	0.25	0
Zr	90	90	1600	-	0	-16.5	0.25	0
Nb	93	93	1600	-	0	-16.5	0.25	0
Mo	98	98	1600	-	0	-16.5	0.25	0
Ru	101	101	1600	-	0	-16.5	0.25	0
Rh	103	103	600	-	0	-20	0.25	0
Ag	107	107	600	-	0	-20	0.25	0
In	115	115	1600	-	0	-16.5	0.25	0
Sn	118	118	1600	NH_3	0.2	-16.5	0.45	90
Ba	137	137	1600	NH_3	0.5	-16.5	0.45	90
Ce	140	140	1600	-	0	-16.5	0.25	0
Ta	181	181	1600	-	0	-16.5	0.25	0
W	184	184	1600	-	0	-16.5	0.25	0
Os	189	189	1600	-	0	-16.5	0.25	0
Ir	193	193	1600	-	0	-16.5	0.25	0
Tl	205	205	1600	-	0	-16.5	0.25	0
Pb	208	208	1600	-	0	-16.5	0.25	0
Bi	209	209	1600	-	0	-16.5	0.25	0
U	238	238	1600	-	0	-16.5	0.25	0

49% HF

Calibrations were automatically performed at 0, 0.5, 1, 2, 5 and 10 ppt (P 1000x higher)

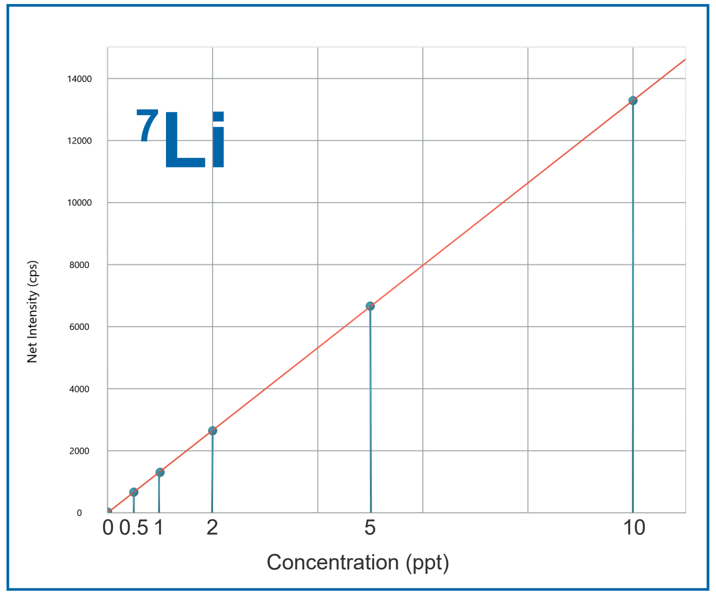
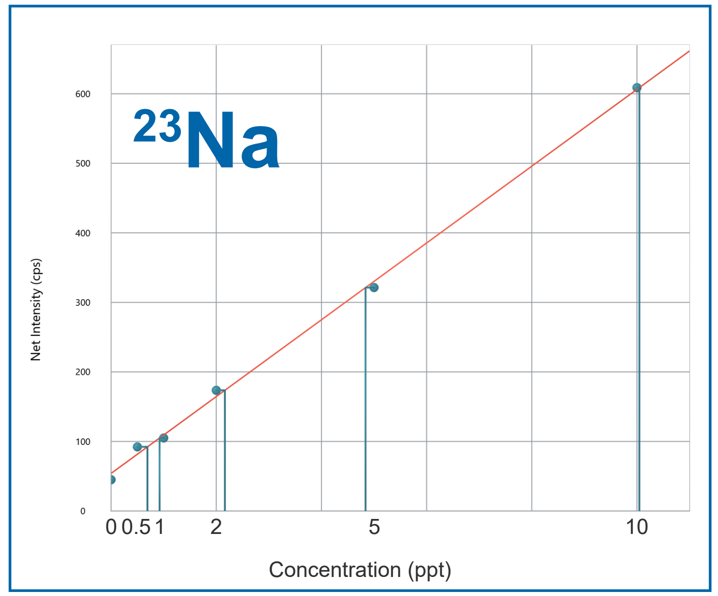


Figure 5



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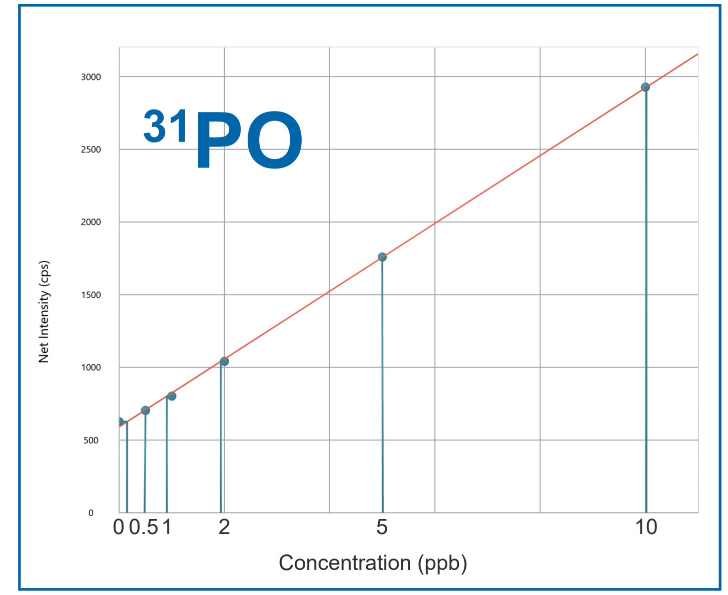

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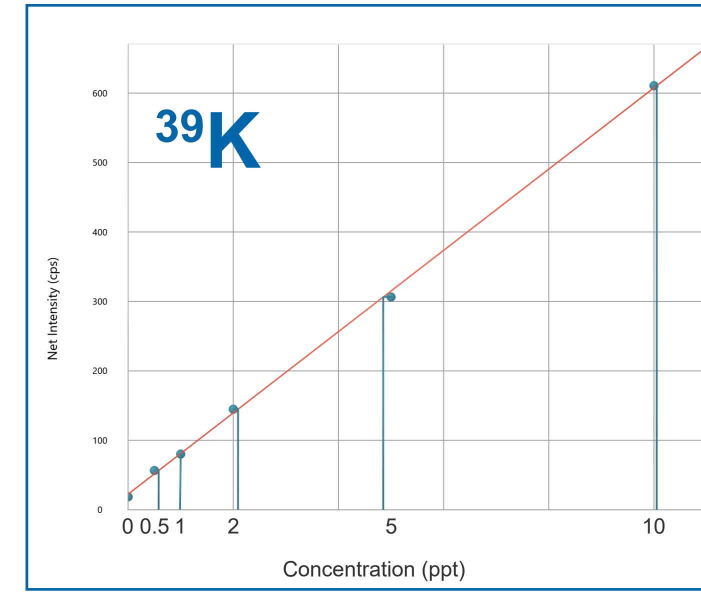

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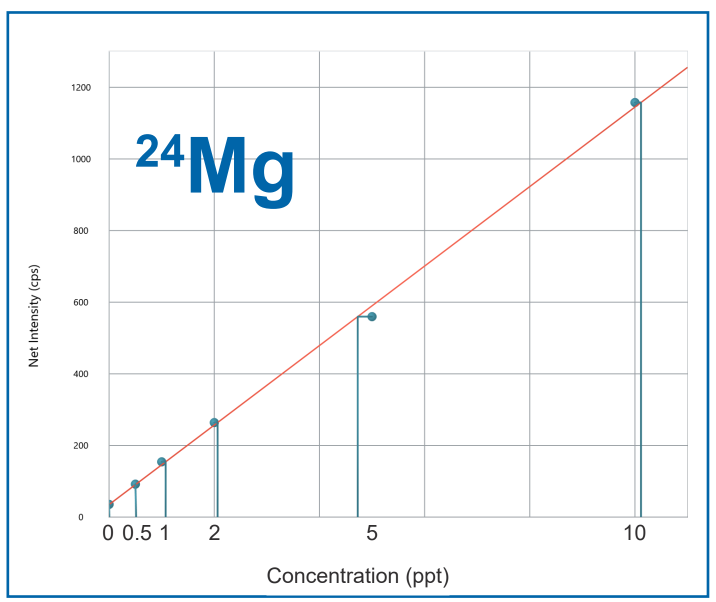

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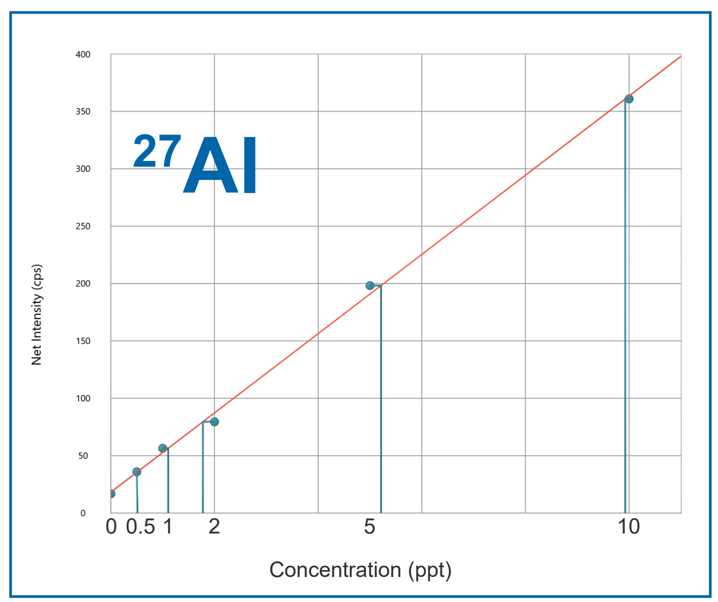

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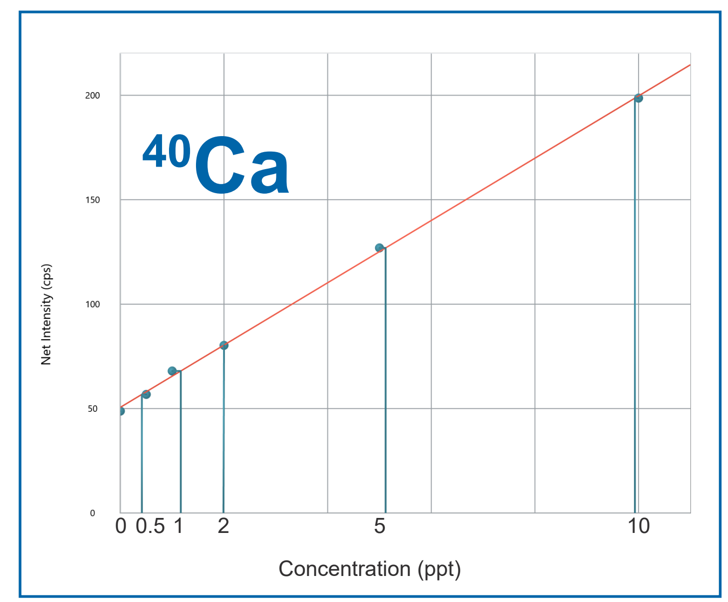

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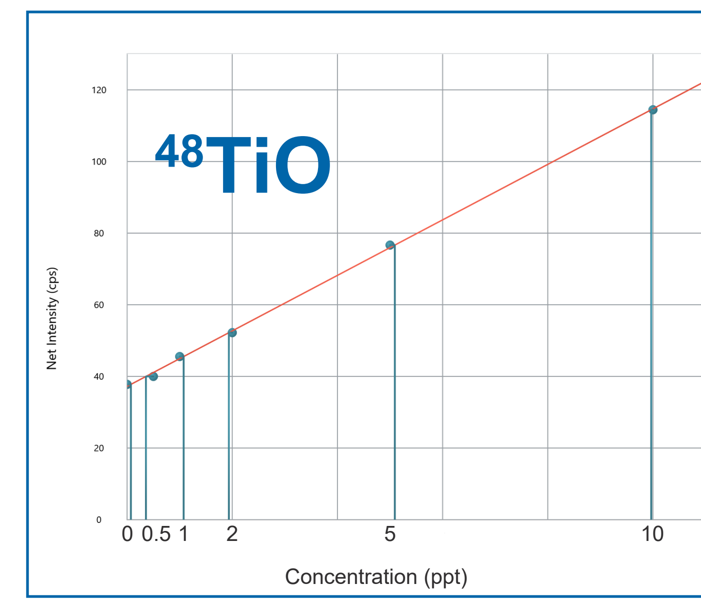
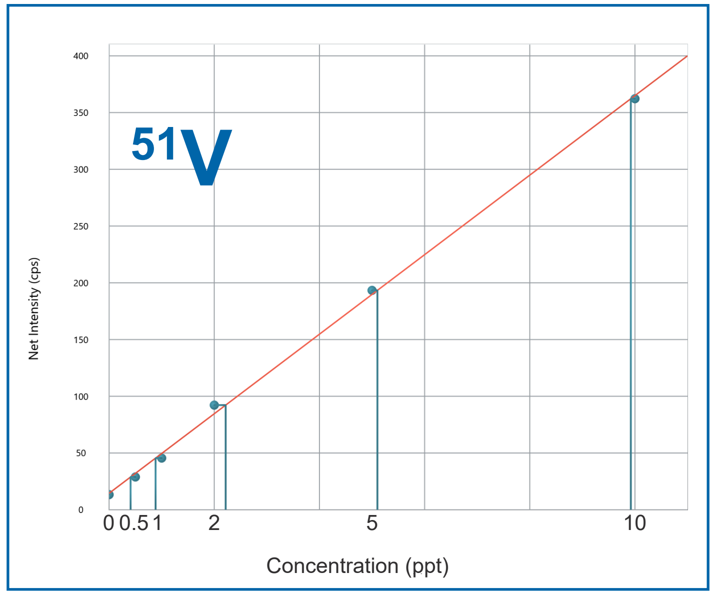


Figure 12

49% HF

Calibrations were automatically performed at 0, 0.5, 1, 2, 5 and 10 ppt



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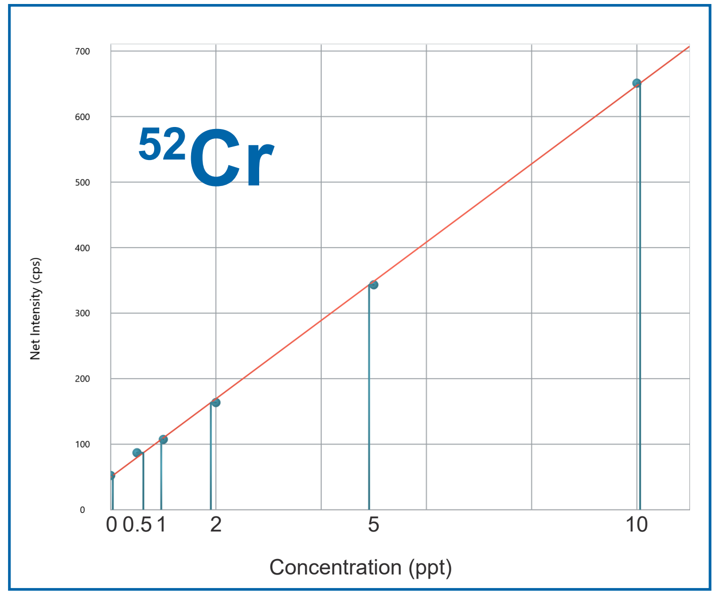

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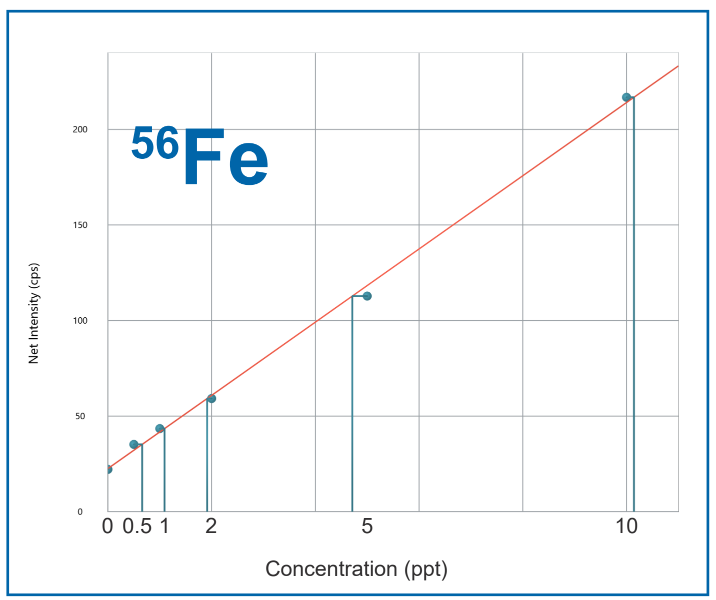

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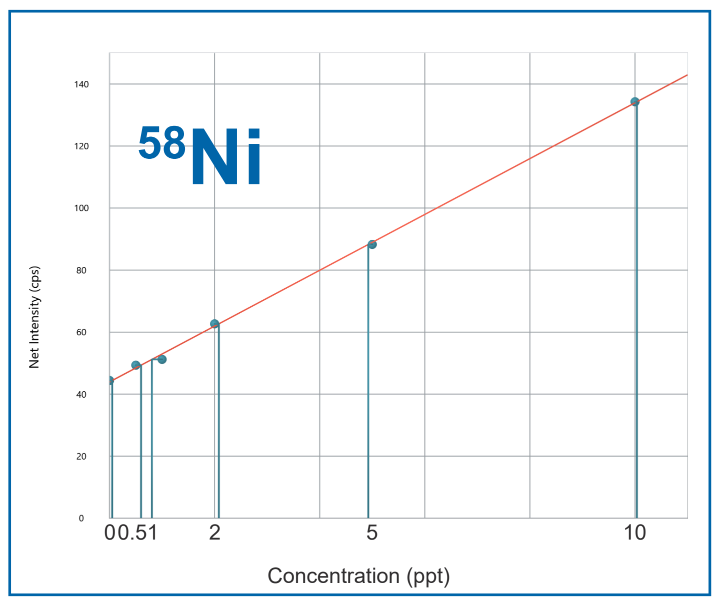

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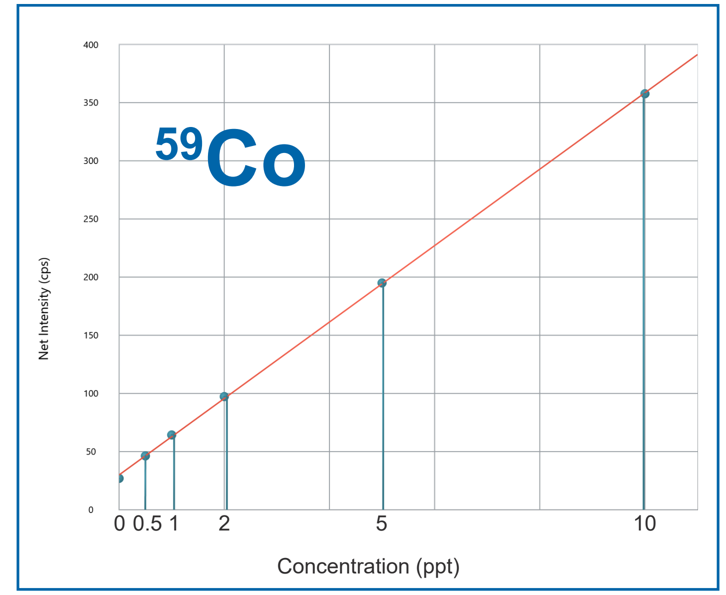

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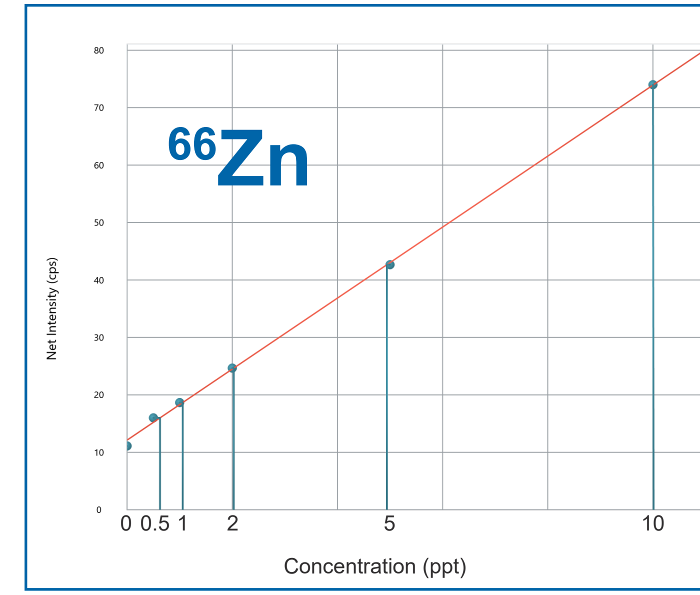

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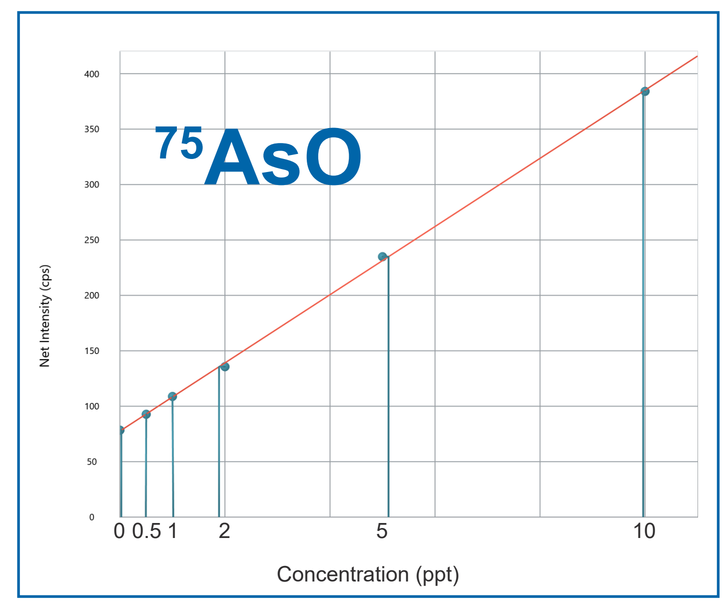

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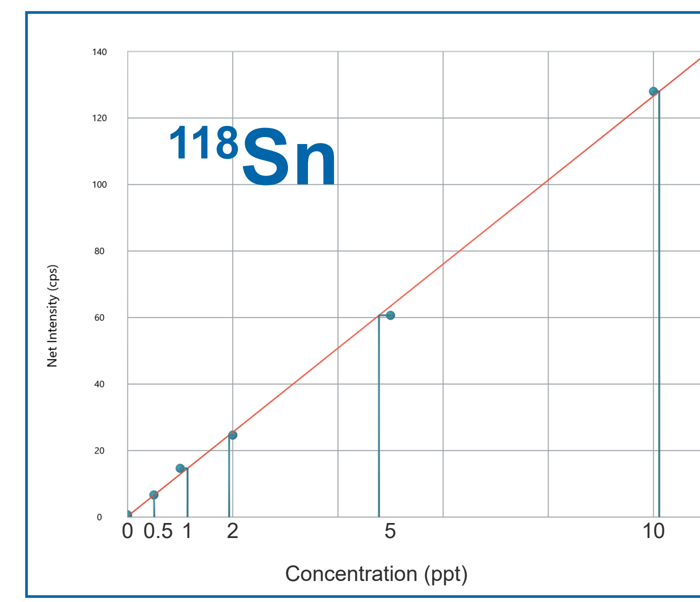

Figure 20

Results and Discussion

Table 3 shows background equivalent concentrations (BEC), limits of detection (LOD) and correlation coefficient (R) for all elements measured in undiluted HF. Blank subtraction was not used for the determination of BECs or LODs in this study.

Calibrations were automatically prepared at 0, 0.5, 1, 2, 5 and 10 ppt automatically with the prep*FAST* S (P was spiked at 0, 0.5 1, 2, 5 and 10 ppb). Figures 5-20 show calibration curves for a selection of elements with MSA in undiluted HF.

Combining the prep*FAST* S with the advantages of various plasma modes, QQQQ filtering and DRC technology allows major contamination-prone elements to be analyzed in the low-ppt range. These advantages make it possible to achieve single-digit-ppt BEC and LOD levels for historically difficult elements such as Na, Mg and Ca in undiluted HF. By utilizing the enclosed and vented sampling area in the prep*FAST* S, these results were achieved in a non-clean room environment. The correlation coefficients demonstrate the accuracy of the prep*FAST* S automatic dilution and spike addition, which enables calibrations in complicated matrices with excellent results.

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

Element	BEC (ppt)	LOD (ppt)	Linearity (R)	Element	BEC (ppt)	LOD (ppt)	Linearity (R)
Li	0.006	0.009	0.999	Rb	0.06	0.4	0.999
Be	0.1	0.3	0.999	Sr	0.02	0.06	0.999
B	8.4	10.0	0.998	Y	0.02	0.1	0.999
Na	0.7	0.2	0.999	Zr	0.5	0.7	0.999
Mg	0.2	0.2	0.999	Nb	0.8	0.7	0.999
Al	0.4	0.9	0.999	Mo	1.4	2.0	0.999
K	0.3	0.2	0.999	Ru	0.3	0.5	0.999
Ca	2.2	1.2	0.999	Rh	0.1	0.1	0.999
P (ppb)	0.9	1.7	0.999	Ag	0.06	0.03	0.999
Sc	0.8	1.0	0.999	In	0.02	0.04	0.999
Ti	2.6	2.0	0.999	Sn	0.06	0.3	0.999
V	0.2	0.3	0.999	Ba	0.07	0.08	0.999
Cr	0.9	0.7	0.999	Ce	0.004	0.2	0.999
Mn	0.05	0.1	0.999	Ta	0.05	0.07	0.999
Fe	0.9	0.9	0.999	W	1.6	1.3	0.999
Ni	4.3	3.0	0.999	Os	0.06	0.1	0.999
Co	0.6	0.2	0.999	Ir	0.1	0.2	0.999
Cu	0.4	0.2	0.999	Tl	0.1	0.1	0.999
Zn	1.8	3.0	0.999	Pb	0.2	0.2	0.999
Ga	1.5	1.0	0.999	Bi	0.1	0.5	0.999
As	2.5	0.5	0.999	U	0.02	0.7	0.999

Conclusions

Fully automated analysis of Hydrofluoric Acid samples was performed using the prep*FAST* S and NexION 5000 Triple Quad ICPMS. The automated dilution and MSA calibration capabilities of the prep*FAST* S achieved linear calibration curves for all elements analyzed. The triple quadrupole ICPMS allowed for elimination of key polyatomic interferences, and detection limits for 40 elements were low ppt, while P was low ppb.

Summary

prep*FAST* S fully automates sample analysis in an ultraclean enclosed system:

- Offers ultrapure semiconductor-grade chemical preparation, dilution, and analysis with detection limits in ppt/ppq range with ICPMS
    - Allows for direct analysis of concentrated chemicals without pre-dilution
- Automatically performs calibration using MSA or external calibration
- Includes a magnetically coupled PTFE/CTFE drive as part of the most chemically resistant autosampler on the market
- Utilizes SampleSense valve to detect all samples – viscous, non-viscous, solvents – without timing or method adjustment