

## ICP - Mass Spectrometry

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## Analysis of Semiconductor-Grade Chemicals Using Automated Standard Addition System (ASAS)-ICP-MS

### Introduction

Various chemicals are used in semiconductor manufacturing processes and the required concentration of metallic impurities to be determined within these chemicals is getting lower and lower. Inductively coupled plasma

mass spectrometry (ICP-MS) is one of the most sensitive techniques for the analysis of metallic impurities in various chemicals and is an indispensable analytical tool in the semiconductor industry. Most chemicals are analyzed with minimal dilution in order to determine ultra-trace levels of metallic impurities. However, the sensitivity of ICP-MS is affected by higher concentrations of chemicals and the method of standard addition (MSA) needs to be used to compensate for the variation in sensitivity.

In the MSA, different amounts of a standard solution are added to a sample solution. This can be done by either preparing the spiked sample solutions in different bottles, or by spiking the standard solution into only one bottle and adding more standard solution after each analysis to prepare different concentration levels. When samples at single- or sub-ppt levels are of interest, the one-bottle approach is preferred because it is extremely challenging to keep and maintain contamination-free bottles. In order to do this with sufficient accuracy, a system which is capable of delivering highly-accurate low volumes of standard solution into a sample solution with auto-calibrating functionality would be highly advantageous.

This paper describes the analysis of metallic impurities in semiconductor-grade  $\text{H}_2\text{SO}_4$  and HCl by using an Automated Standard Addition System (ASAS) coupled to a PerkinElmer NexION® 5000 ICP-MS.

## Experimental

### Reagents and Samples

Stock standard solutions (2 ppb in 1% HNO<sub>3</sub> and 0.1 ppb in 0.5% HNO<sub>3</sub>) were prepared from a 10 ppm multi-element standard solution (XSTC-622B, SPEX CertiPrep, New Jersey, USA) for ASAS. TAMAPURE AA-100 HNO<sub>3</sub> (Tama Chemicals Co., Ltd., Kanagawa, Japan) was used for acidifying the standard solution.

Purified deionized water (DIW) (Organo Corp., Tokyo, Japan) was used and all chemicals were prepared in an ISO Class 5 clean draft installed in a clean room. Semiconductor-grade hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were purchased in a market in Japan.

### Instrumentation

The ASAS injects a few  $\mu\text{L}/\text{min}$  of standard solution into a sample solution line to create calibration curves from the standard solution. The ASAS is installed between an autosampler and the NexION 5000 Multi-Quadrupole ICP-MS. A sample solution is self-aspirated from a vial (on an autosampler) to the nebulizer of the ICP-MS via a PFA tube

and two PCTFE connectors. A multi-element standard solution in a loop is injected into the sample line by a special syringe pump, which can generate calibration curves automatically. A peristaltic pump can also be used to deliver the sample solution, but self-aspiration is preferred as this prevents contamination which can be introduced via the use of peristaltic pump tubing.

When self-aspiration is used, the sample uptake rate depends upon the viscosity of the chemicals, so it is very important to have an exact knowledge of the sample uptake rate. ASAS equips two photo sensors in the sample line that detect a small air bubble introduced from Valve C, where the time taken to travel between the two photosensors has a linear relationship with the sample uptake rate. The photosensors are attached to the outside of the PFA sample line and measure the intensity of the transmission of light. This simple sample path configuration minimizes contamination and memory effects for sub-ppb-level metal analysis in various chemicals.

The key patented technology of ASAS is that there is no valve from the loop to the sample solution line. The process can be described as shown in as follows and per Figure 1:

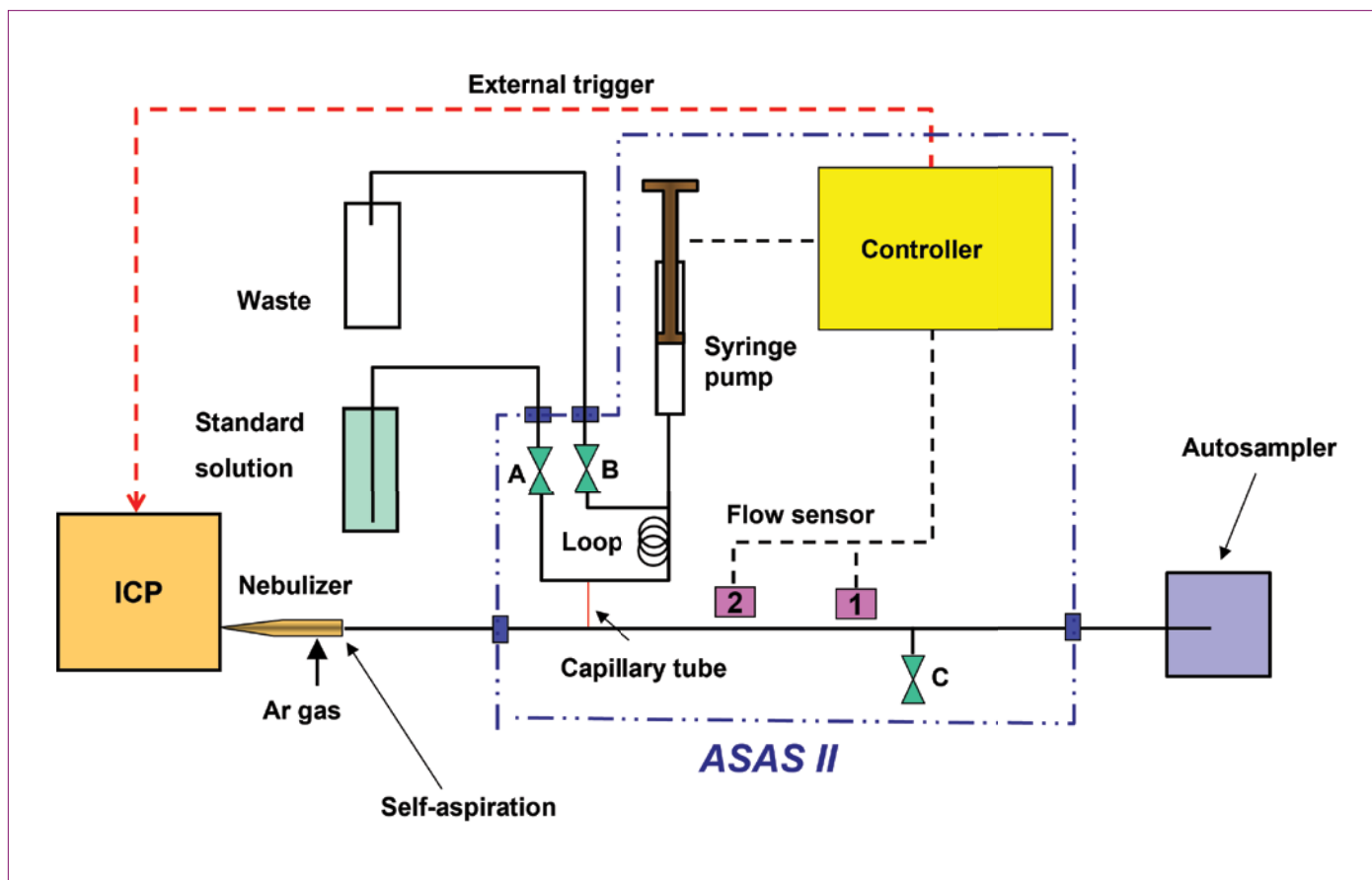


Figure 1: Schematic diagram of ASAS.

- Valve A opens and the syringe aspirates only the standard solution from a stock standard solution bottle to the loop through a wider inner diameter of the PFA tube.
  - The sample solution is not aspirated to the loop because the sample solution line is at negative pressure, and there is a small capillary tube between the loop and the sample solution line.
  - The volumes of syringe and loop are at 1000 and 800  $\mu\text{L}$ , respectively.
- One syringe aspiration fills the standard solution in the loop, and then Valve A closes, and Valve B opens to discharge the standard solution in the syringe to a waste bottle via Valve B.
- The above steps are repeated to clean the loop
  - Only clean standard solution is filled and kept in the loop.
- When the addition of the standard is needed, the syringe pushes the standard solution in the loop to the sample solution line.
- When the volume of the remaining solution in the syringe gets lower than the specified value, refilling of standard solution is performed automatically right after completing the current standard addition sequence.

The standard solution injection amount by ASAS is from 0.1 to 99.99  $\mu\text{L}/\text{min}$ , but a practical range is between 0.5 to 10  $\mu\text{L}/\text{min}$ . This is because injection volumes that are too low have longer stabilization times to pressurize the injection line, and higher injection volumes dilute the sample solution.

### Instrumental Conditions

Table 1 shows the instrument conditions of the NexION 5000 ICP-MS. For DIW analysis, a quartz sample introduction system with higher sample uptake rates was used to avoid adsorption by the PFA tube. For  $\text{H}_2\text{SO}_4$  and HCl analysis, a PFA sample introduction system with C-Flow S-Type nebulizer (Savillex, Minnesota, USA) was used.

$\text{NH}_3$  and  $\text{O}_2$  reaction gases were used to overcome interference issues.

ASAS software communicated with Syngistix™ software's development kit, which allowed the creation of the dataset and switching the acquisition method from ASAS software to the Syngistix one. The sample solution was placed on a SC- $\mu$  autosampler (Elemental Scientific Inc., Omaha, Nebraska, USA) and a sequence was set up in the ASAS software. Following were the analysis steps:

- The autosampler probe was moved to a sample bottle.
- The ASAS software opened an acquisition method in Syngistix software and the NexION 5000 waited for a trigger signal from the ASAS.
- The ASAS sent the trigger signal to the NexION 5000 after waiting for the replacement of the sample solution in the sample introduction tube.
- The analysis of unspiked sample was performed, and a count report file was generated by Syngistix software after completing the analysis.
- ASAS software retrieved the count report file from Syngistix software and stopped the trigger signal.
- The ASAS introduced a small air bubble in the sample introduction line and measured the sample uptake rate.
- The ASAS started the injection of standard solution to get the concentration of first standard level specified in the ASAS software. If a sample uptake rate is 100  $\mu\text{L}/\text{min}$  and the concentration of ASAS stock standard solution is 1 ppb, a 1  $\mu\text{L}/\text{min}$  of ASAS stock standard solution is injected from ASAS to get a 10 ppt concentration.
- The ASAS sent the trigger signal to the NexION 5000 after waiting for a stabilization time.
- Steps 4 to 8 were repeated until the analysis of all standard levels was completed and the autosampler probe moved to a rinse port.

Table 1: NexION 5000 ICP-MS Instrumental Conditions

Parameter	Samples		
	$\text{H}_2\text{SO}_4$	HCl	DIW
Torch	Demountable 2 mm I.D. Pt Injector		2 mm I.D. Quartz
Spray Chamber	PFA Cyclonic		Quartz Cyclonic
RF Power	1600 W Hot Plasma	1500 W Hot Plasma	1200 W Hot Plasma
	700 W Cold Plasma	700 W Cold Plasma	700 W Cold Plasma
Nebulizer Gas Flow (L/min)	0.97	0.96	1.01
Sample Uptake Rate ( $\mu\text{L}/\text{min}$ )	165	165	447
Integration Time/Isotope	1 sec		
Dwell Time	50 msec		
Number of Replicates	3		

## Results and Discussion

Figure 2 shows the stability of the signal on the NexION 5000 ICP-MS using ASAS sample introduction. A 0.5 ppb In standard solution in 1% HNO<sub>3</sub> solution was self-aspirated at 202  $\mu\text{L}/\text{min}$ , and 100 ppb of Li, Mg, Ge, Sr and Zr in 5% HNO<sub>3</sub> solution was added at 10, 5.0, 2.5 1.0, 0.5 and 0.25  $\mu\text{L}/\text{min}$  from the ASAS syringe. As can be clearly seen, sample introduction using ASAS showed a very stable signal even at 0.25  $\mu\text{L}/\text{min}$  when analyzed on the NexION 5000 ICP-MS.

## Deionized Water (DIW) Analysis

DIW was self-aspirated by the nebulizer, then ASAS measured the sample uptake rate by injecting a small volume of air into the sample line, and ASAS added the standard solution to achieve the concentrations of 0, 0.1, 0.5, 1, 2 and 5 ppt respectively. Table 2 shows the results from the analysis and NexION 5000 conditions, and Figure 3 shows the calibration curves.

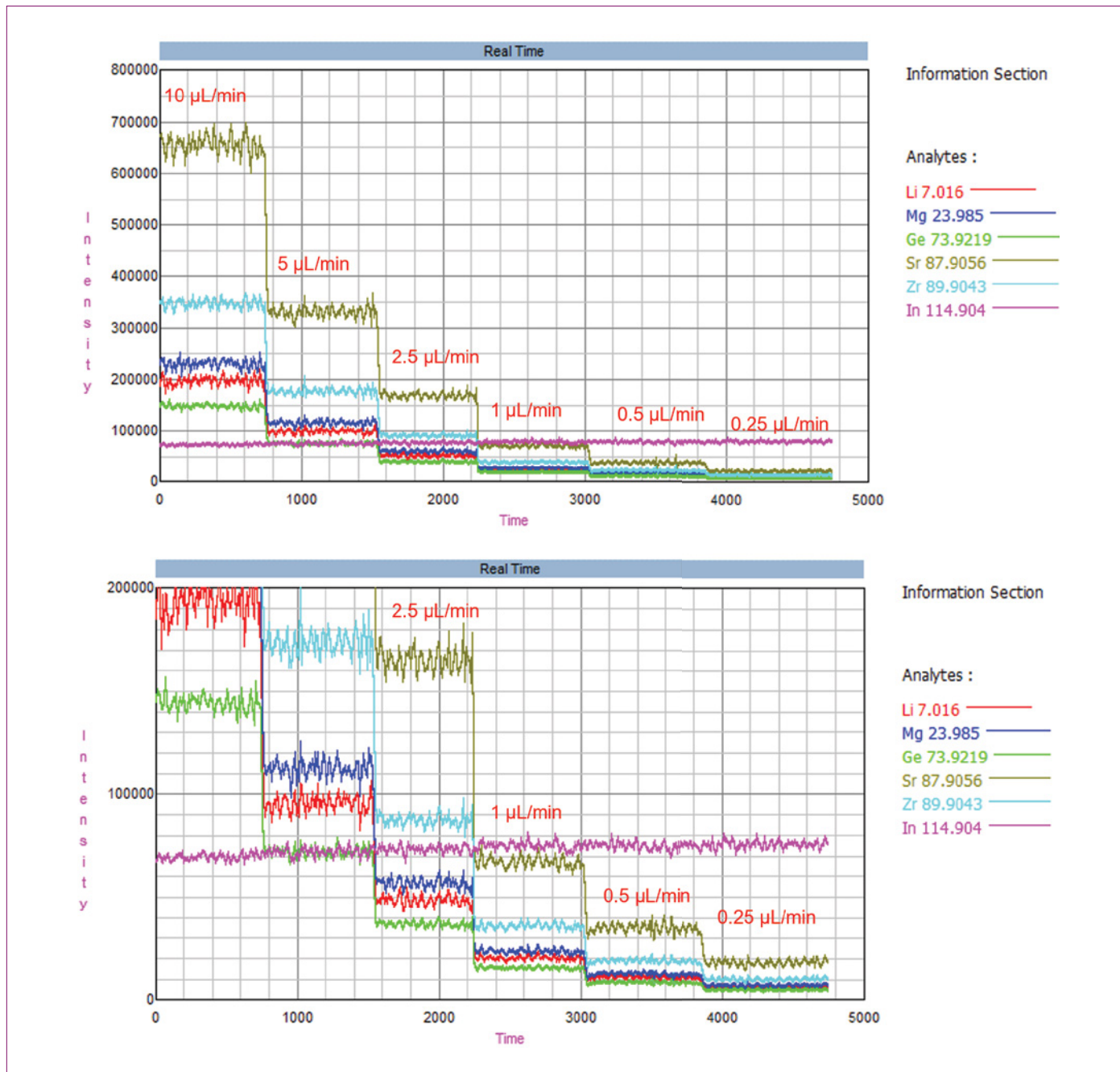
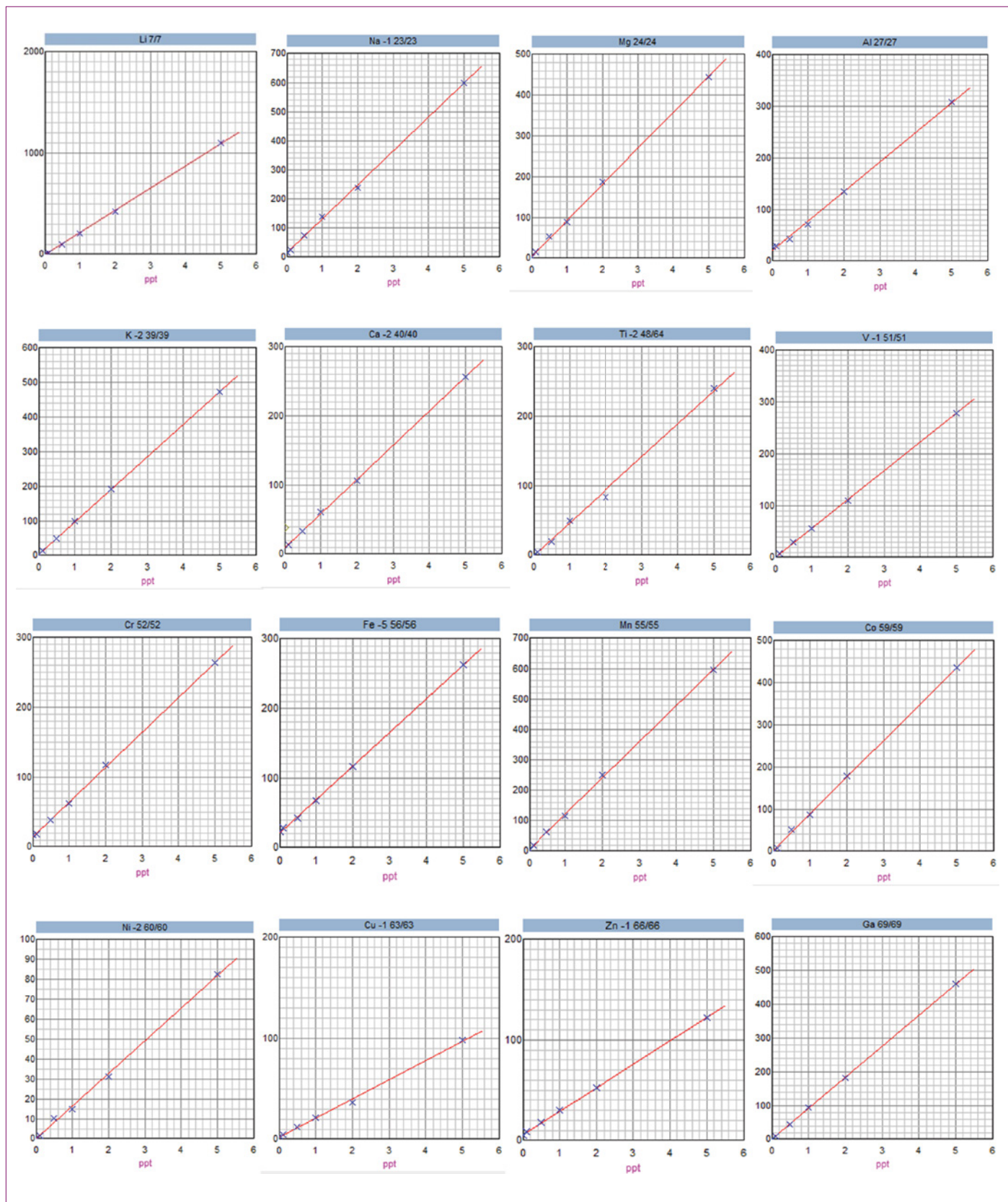


Figure 2: Stability of ASAS.

Table 2: Results of DIW

Element	Q1/Q3	IGM	Profile	NH <sub>3</sub> (mL/min)	O <sub>2</sub> (mL/min)	RPq	Slope (cps/ppt)	BEC (ppt)	DL (ppt)	Correlation Coefficient
Li	7/7	Cold Plasma	Std Cold	0	0	0.25	214	< DL	0.008	1.000
Na	23/23	Cold Plasma	Std Cold	0	0	0.25	111	0.14	0.1	1.000
Mg	24/24	Cold Plasma	Std Cold	0	0	0.25	82	< DL	0.02	0.999
Al	27/27	Extraction	Ammonia DRC	0.6	0	0.45	58	0.48	0.05	0.998
K	39/39	Cold Plasma	Ammonia DRC Cold	0.6	0	0.45	95	< DL	0.06	1.000
Ca	40/40	Cold Plasma	Ammonia DRC Cold	0.6	0	0.45	50	< DL	0.1	1.000
Ti	48/64	Extraction	Oxygen DRC	0	1.1	0.45	42	< DL	0.04	0.998
V	51/51	Extraction	Ammonia DRC	0.3	0	0.45	58	< DL	0.000 (*1)	0.999
Cr	52/52	Extraction	Ammonia DRC	1.0	0	0.45	44	< DL	0.4	0.998
Mn	55/55	Extraction	Ammonia DRC	0.6	0	0.45	128	< DL	0.07	1.000
Fe	56/56	Cold Plasma	Ammonia DRC Cold	0.9	0	0.6	23	< DL	0.3	0.998
Co	59/59	Extraction	Ammonia DRC	0.6	0	0.45	88	< DL	0.02	0.999
Ni	60/60	Cold Plasma	Ammonia DRC Cold	0.3	0	0.45	17	< DL	0.000 (*1)	0.999
Cu	63/63	Cold Plasma	Ammonia DRC Cold	0.3	0	0.45	43	< DL	0.04	0.998
Zn	66/66	Extraction	Ammonia DRC	0.3	0	0.45	23	< DL	0.3	0.999
Ga	69/69	Extraction	Ammonia DRC	0.6	0	0.6	94	< DL	0.000 (*1)	1.000
Ge	74/90	Extraction	Ammonia DRC	0.6	0	0.45	9	< DL	0.2	1.000
As	75/91	Extraction	Oxygen DRC	0	0.7	0.45	7.8	< DL	0.2	0.999
Se	80/96	Extraction	Oxygen DRC	0	0.7	0.45	1.3	< DL	1	0.997
Sr	88/88	Extraction	Ammonia DRC	0.6	0	0.45	156	< DL	0.000 (*1)	1.000
Zr	90/90	Extraction	Standard	0	0	0.25	30	< DL	0.06	0.998
Mo	98/98	Extraction	Ammonia DRC	0.6	0	0.6	19	< DL	0.09	1.000
Ag	107/107	Extraction	Ammonia DRC	0.6	0	0.6	81	< DL	0.02	1.000
Cd	111/111	Extraction	Standard	0	0	0.25	13	< DL	0.000 (*1)	0.998
Sn	118/118	Extraction	Ammonia DRC	0.6	0	0.45	37	0.76	0.6	0.998
Sb	121/121	Extraction	Ammonia DRC	0.6	0	0.45	32	< DL	0.1	0.998
Ba	138/138	Extraction	Standard	0	0	0.25	93	< DL	0.000 (*1)	0.999
W	184/184	Extraction	Standard	0	0	0.25	16	< DL	0.000 (*1)	0.999
Pb	208/208	Extraction	Ammonia DRC	0.6	0	0.45	70	< DL	0.07	1.000

\*1: The counts were 0.



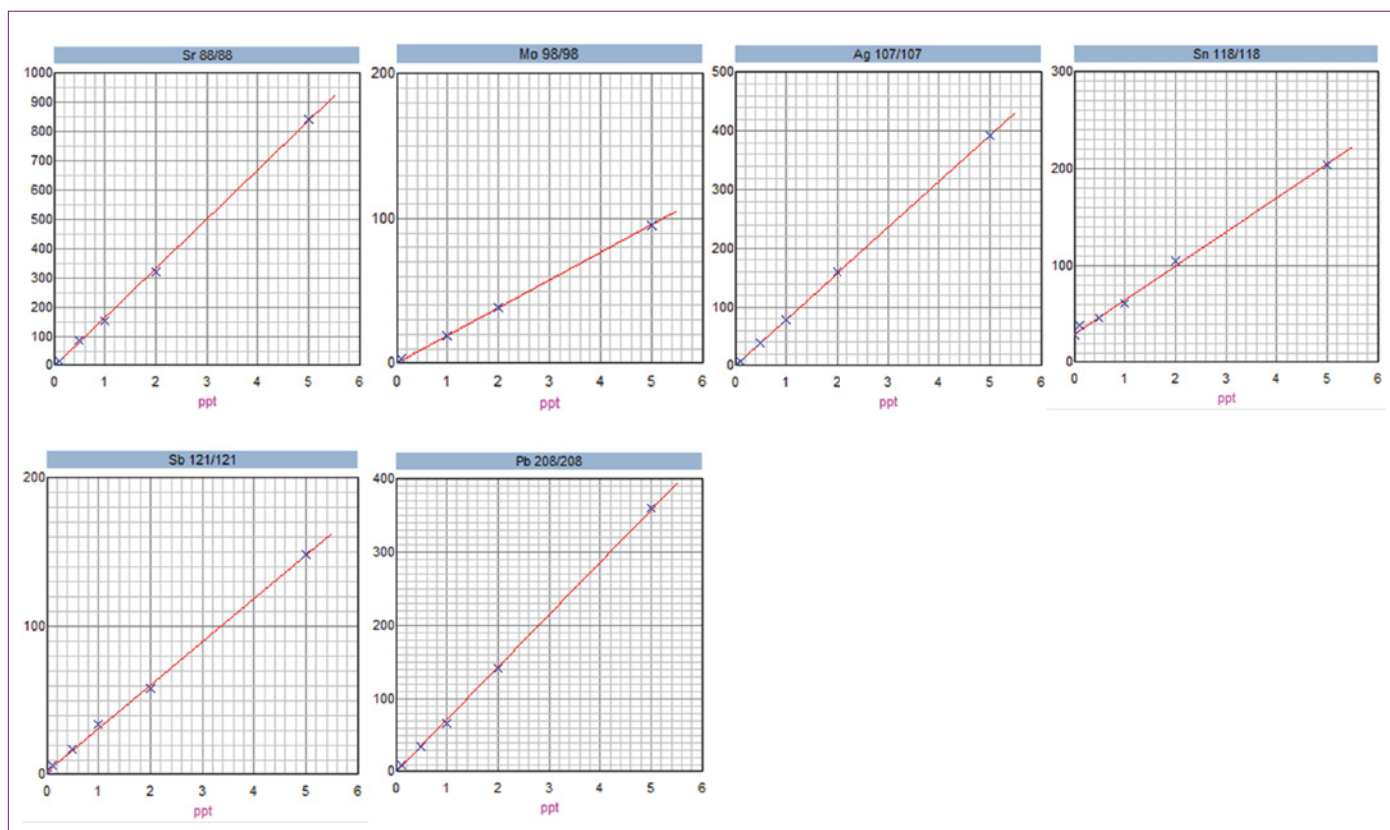


Figure 3: Standard addition calibration curves of DIW.

All elements showed excellent linear calibration curves at single- and sub-ppt levels. One of the features of the NexION 5000 ICP-MS is ion guide mode that can use the optimal Quadrupole Ion Deflector (QID) voltages for different plasma conditions. The QID uses different voltages from lower masses to higher masses because the kinetic energy of ions from the plasma depends on the mass and is greatly affected by the plasma temperature. For this experiment, two of the ion guide modes, i.e. Cold Plasma and Extraction, were used. Taking advantage of the multi-quadrupole technology and Universal Cell combination, Mass Shift mode was used for some elements, such as Ti, Ge, As and Se, which showed lower background equivalent concentrations (BECs) than other modes.

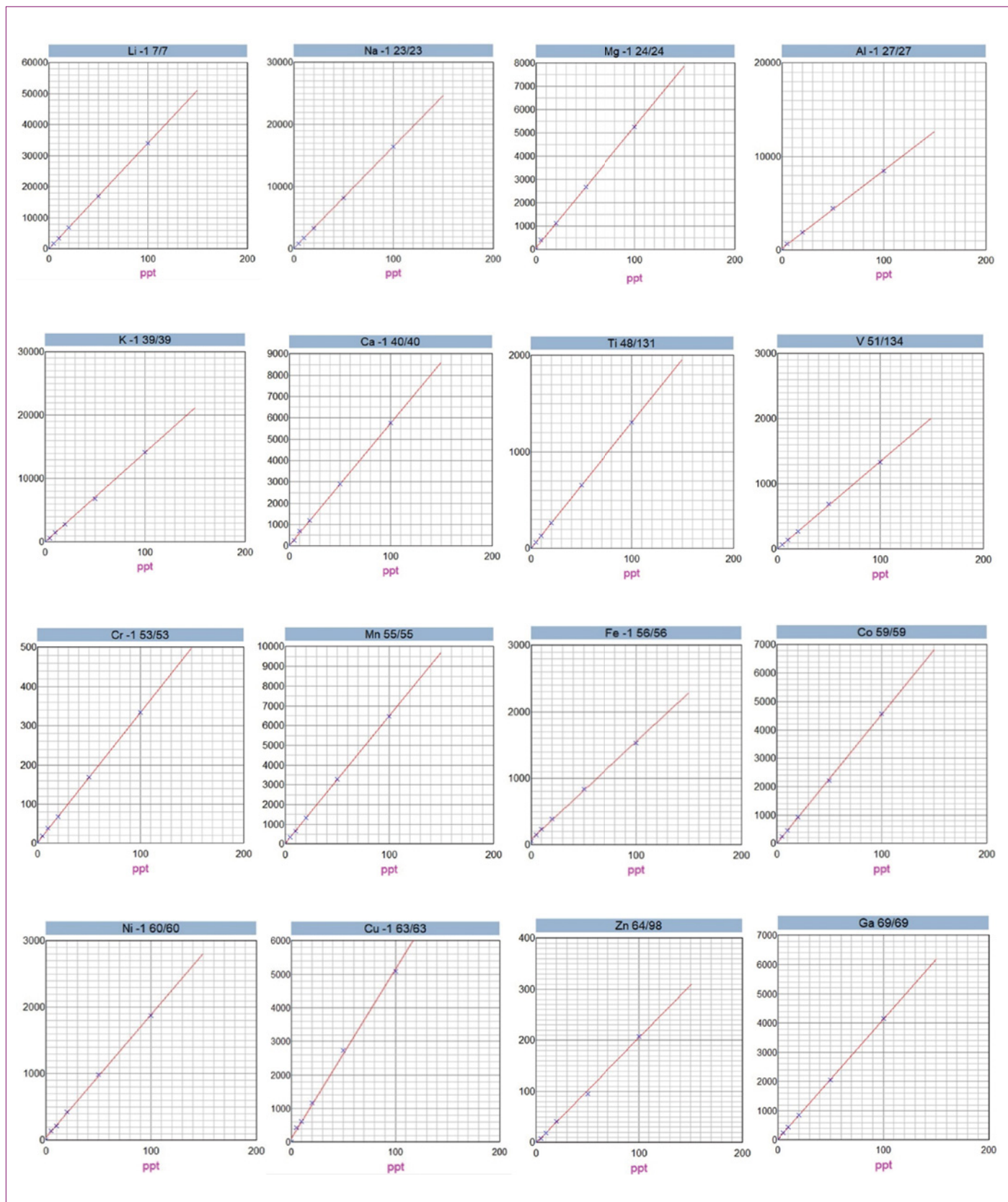
### Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) Analysis

A 10% (wt/wt) H<sub>2</sub>SO<sub>4</sub> was analyzed using self-aspiration and the standard addition calibration curves were created using ASAS. The spike concentrations were 0, 5, 10, 20, 50 and 100 ppt, and good linear calibration curves were obtained, as shown in Figure 4. Different masses and IGM modes were used for each element and the results demonstrating the lowest BECs were summarized in Table 3. All elements except Fe and Se had lower than 1 ppt BEC. The background of Fe was found to gradually decrease with the introduction of H<sub>2</sub>SO<sub>4</sub>, so much lower BECs can be expected after thorough cleaning. Several elements showed better BECs with the Focusing ion guide mode. Sulfur-related polyatomic interferences on V, Cr, Zn, Ge and Mo were also eliminated using Reaction mode on the NexION 5000 ICP-MS.

Table 3: Results of 10% H<sub>2</sub>SO<sub>4</sub>

Element	Q1/Q3	IGM	Profile	NH <sub>3</sub> (mL/min)	O <sub>2</sub> (mL/min)	RPq	Slope (cps/ppt)	BEC (ppt)	DL (ppt)	Correlation Coefficient
Li	7/7	Cold Plasma	Std Cold	0	0	0.25	340	< DL	0.4	1.000
Na	23/23	Cold Plasma	Std Cold	0	0	0.25	164	0.71	0.5	1.000
Mg	24/24	Cold Plasma	Ammonia DRC Cold	0.5	0	0.45	52	0.14	0.1	1.000
Al	27/27	Cold Plasma	Ammonia DRC Cold	0.5	0	0.45	83	0.64	0.5	0.999
K	39/39	Cold Plasma	Ammonia DRC Cold	0.9	0	0.45	141	< DL	0.2	1.000
Ca	40/40	Cold Plasma	Ammonia DRC Cold	0.9	0	0.6	57	0.68	0.2	1.000
Ti	48/131	Extraction	Ammonia DRC	0.6	0	0.45	13	< DL	0.4	1.000
V	51/134	Extraction	Ammonia DRC	1.0	0	0.45	13	< DL	0.3	1.000
Cr	53/53	Focusing	Ammonia DRC	1.0	0	0.45	3	< DL	2	1.000
Mn	55/55	Focusing	Ammonia DRC	0.6	0	0.45	65	< DL	0.4	1.000
Fe	56/56	Cold Plasma	Ammonia DRC Cold	0.9	0	0.6	15	3.7	1.0	0.999
Co	59/59	Focusing	Ammonia DRC	0.6	0	0.45	45	< DL	0.5	1.000
Ni	60/60	Cold Plasma	Ammonia DRC Cold	0.5	0	0.45	19	0.21	0.2	1.000
Cu	63/63	Cold Plasma	Ammonia DRC Cold	0.5	0	0.45	50	< DL	0.2	0.999
Zn	64/98	Extraction	Ammonia DRC	1.4	0	0.35	2	< DL	3	0.999
Ga	69/69	Focusing	Ammonia DRC	0.6	0	0.6	41	< DL	0.4	1.000
Ge	74/90	Extraction	Ammonia DRC	0.6	0	0.45	16	< DL	0.5	1.000
As	75/91	Extraction	Oxygen DRC	0	0.7	0.45	26	< DL	0.5	1.000
Se	78/94	Extraction	Oxygen DRC	0	0.7	0.45	1	1.5	1.0	1.000
Sr	88/88	Focusing	Ammonia DRC	0.6	0	0.45	86	< DL	0.4	1.000
Zr	90/90	Extraction	Ammonia DRC	0.3	0	0.45	11	0.50	0.3	1.000
Mo	95/95	Focusing	Ammonia DRC	0.6	0	0.6	10	< DL	0.4	1.000
Ag	107/107	Focusing	Ammonia DRC	0.6	0	0.6	52	< DL	1.0	0.999
Cd	111/111	Focusing	Oxygen DRC	0	0.7	0.45	3	< DL	1.0	1.000
Sn	118/118	Focusing	Ammonia DRC	0.6	0	0.45	21	< DL	0.4	1.000
Sb	121/121	Focusing	Ammonia DRC	0.6	0	0.45	22	0.32	0.2	1.000
Ba	138/138	Focusing	Standard	0	0	0.25	48	< DL	0.3	1.000
W	184/184	Extraction	Standard	0	0	0.25	16	< DL	0.3	1.000
Pb	208/208	Focusing	Standard	0	0	0.25	14	< DL	0.6	1.000





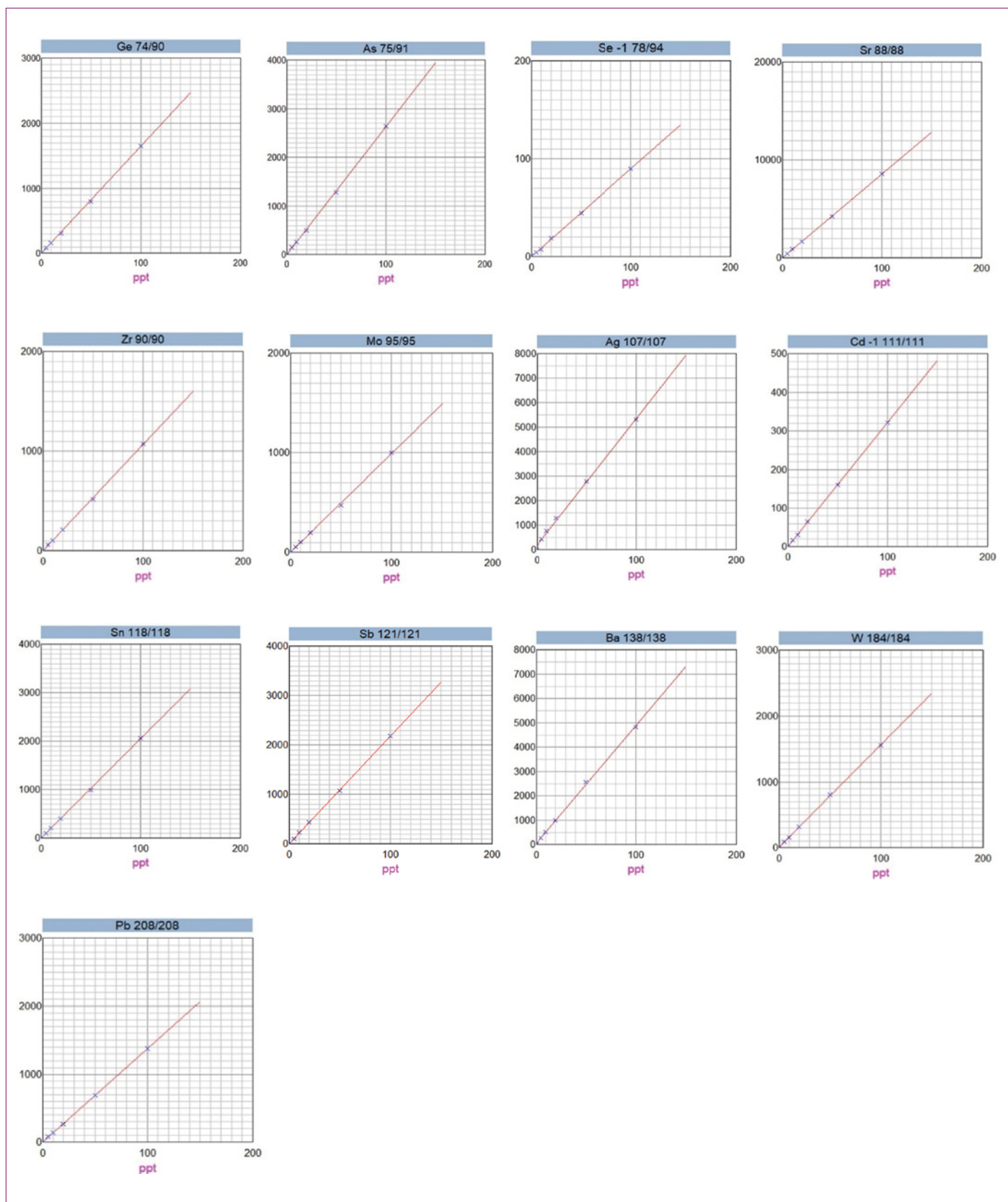


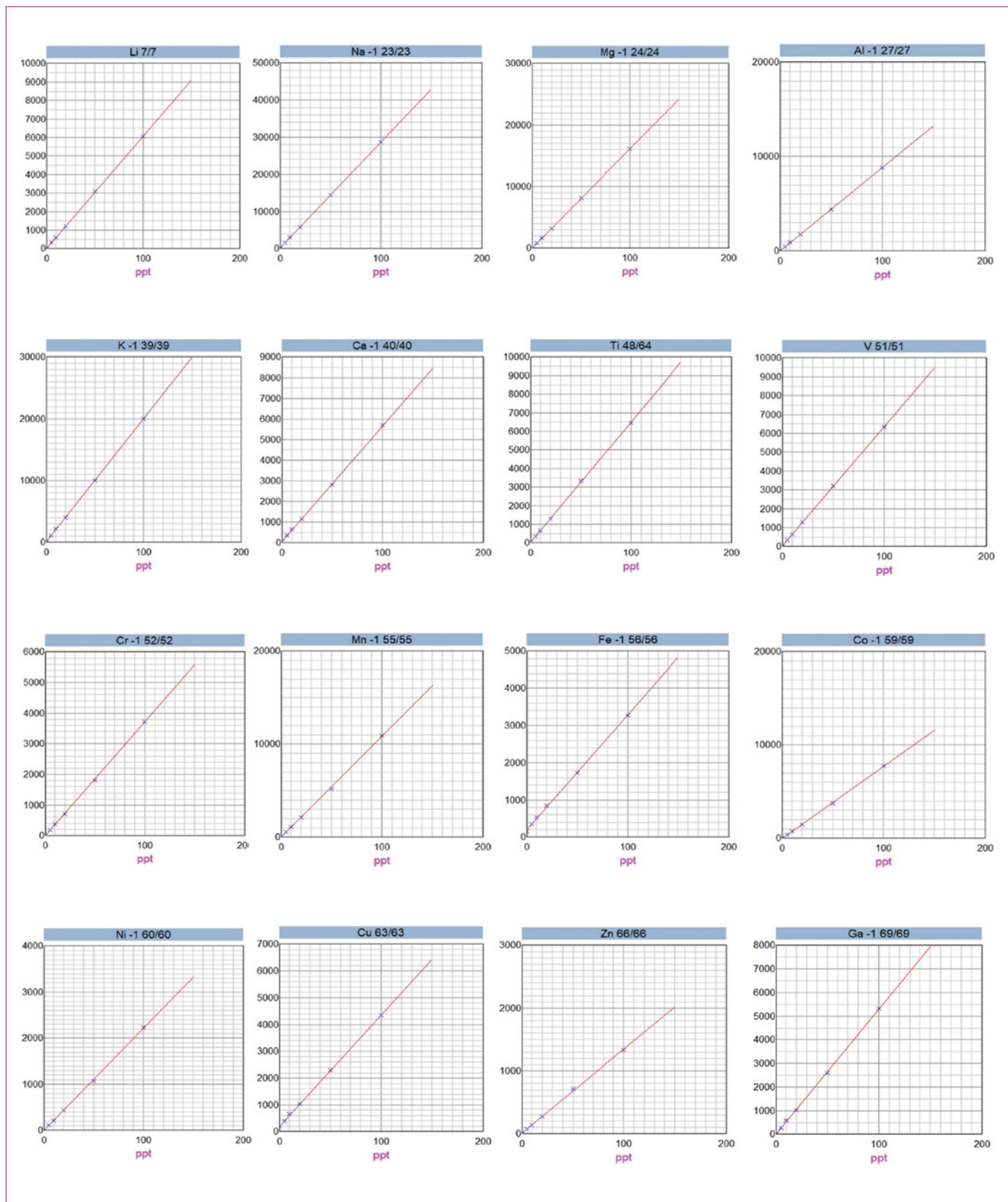
Figure 4. Standard addition calibration curves of 10 % H<sub>2</sub>SO<sub>4</sub>.

## Hydrochloric Acid (HCl) Analysis

A 15% (wt/wt) HCl was analyzed by self-aspiration and standard addition calibration curves were created using ASAS. The concentrations spiked were 0, 5, 10, 20, 50 and 100 ppt respectively, and good linear calibration curves were obtained, as shown in Figure 5. Different masses and ion guide modes were analyzed for each element and the lowest BECs are summarized in Table 4. Chloride-related interferences on K, V, Cr, Ga, Ge and Se were eliminated using Reaction mode on the NexION 5000 ICP-MS. Sn was not reported in the table because the detected concentration was over 200 ppt and was too high compared with the spiked concentrations.

Table 4: Results of 15% HCl

Element	Q1/Q3	IGM	Profile	NH <sub>3</sub> (mL/min)	O <sub>2</sub> (mL/min)	RPq	Slope (cps/ppt)	BEC (ppt)	DL (ppt)	Correlation Coefficient
Li	7/7	Cold Plasma	Std Cold	0	0	0.25	597	< DL	0.2	1.000
Na	23/23	Cold Plasma	Std Cold	0	0	0.25	285	0.39	0.3	1.000
Mg	24/24	Cold Plasma	Std Cold	0	0	0.25	161	< DL	0.2	1.000
Al	27/27	Cold Plasma	Ammonia DRC Cold	0.6	0	0.45	88	0.45	0.3	1.000
K	39/39	Cold Plasma	Ammonia DRC Cold	0.6	0	0.45	199	< DL	0.5	1.000
Ca	40/40	Cold Plasma	Ammonia DRC Cold	1.0	0	0.45	56	1.4	0.7	1.000
Ti	48/64	Focusing	Oxygen DRC	0	1.1	0.45	64	< DL	0.6	1.000
V	51/51	Focusing	Ammonia DRC	0.6	0	0.45	63	< DL	0.6	1.000
Cr	52/52	Cold Plasma	Ammonia DRC Cold	0.6	0	0.45	37	< DL	0.6	1.000
Mn	55/55	Cold Plasma	Ammonia DRC Cold	0.6	0	0.45	109	< DL	0.4	1.000
Fe	56/56	Cold Plasma	Ammonia DRC Cold	0.6	0	0.45	91	3.0	0.3	1.000
Co	59/59	Cold Plasma	Ammonia DRC Cold	0.3	0	0.45	78	< DL	0.6	1.000
Ni	60/60	Cold Plasma	Ammonia DRC Cold	0.3	0	0.45	22	< DL	0.9	1.000
Cu	63/63	Focusing	Ammonia DRC	0.3	0	0.45	41	4.6	0.5	1.000
Zn	66/66	Focusing	Ammonia DRC	0.3	0	0.45	13	< DL	0.7	0.999
Ga	69/69	Cold Plasma	Ammonia DRC Cold	0.6	0	0.45	53	< DL	0.4	1.000
Ge	74/90	Extraction	Ammonia DRC	0.3	0	0.45	23	0.58	0.5	1.000
As	75/91	Focusing	Oxygen DRC	0	1.1	0.45	12	25	3	1.000
Se	80/96	Extraction	Oxygen DRC	0	1.1	0.45	2	2.6	0.6	0.999
Sr	88/88	Focusing	Ammonia DRC	0.6	0	0.45	136	< DL	0.5	1.000
Zr	90/106	Extraction	Oxygen DRC	0	1.1	0.45	94	< DL	0.4	1.000
Mo	98/98	Focusing	Ammonia DRC	0.6	0	0.45	25	2.2	1	1.000
Ag	107/107	Focusing	Standard	0	0	0.25	42	< DL	0.4	1.000
Cd	111/111	Focusing	Standard	0	0	0.25	9	< DL	0.9	1.000
Sb	121/121	Focusing	Ammonia DRC	0.6	0	0.45	28	0.95	0.3	1.000
Ba	138/138	Focusing	Standard	0	0	0.25	67	0.43	0.2	1.000
W	184/184	Focusing	Standard	0	0	0.25	18	< DL	0.3	1.000
Pb	208/208	Focusing	Ammonia DRC	0.6	0	0.45	44	< DL	0.7	1.000



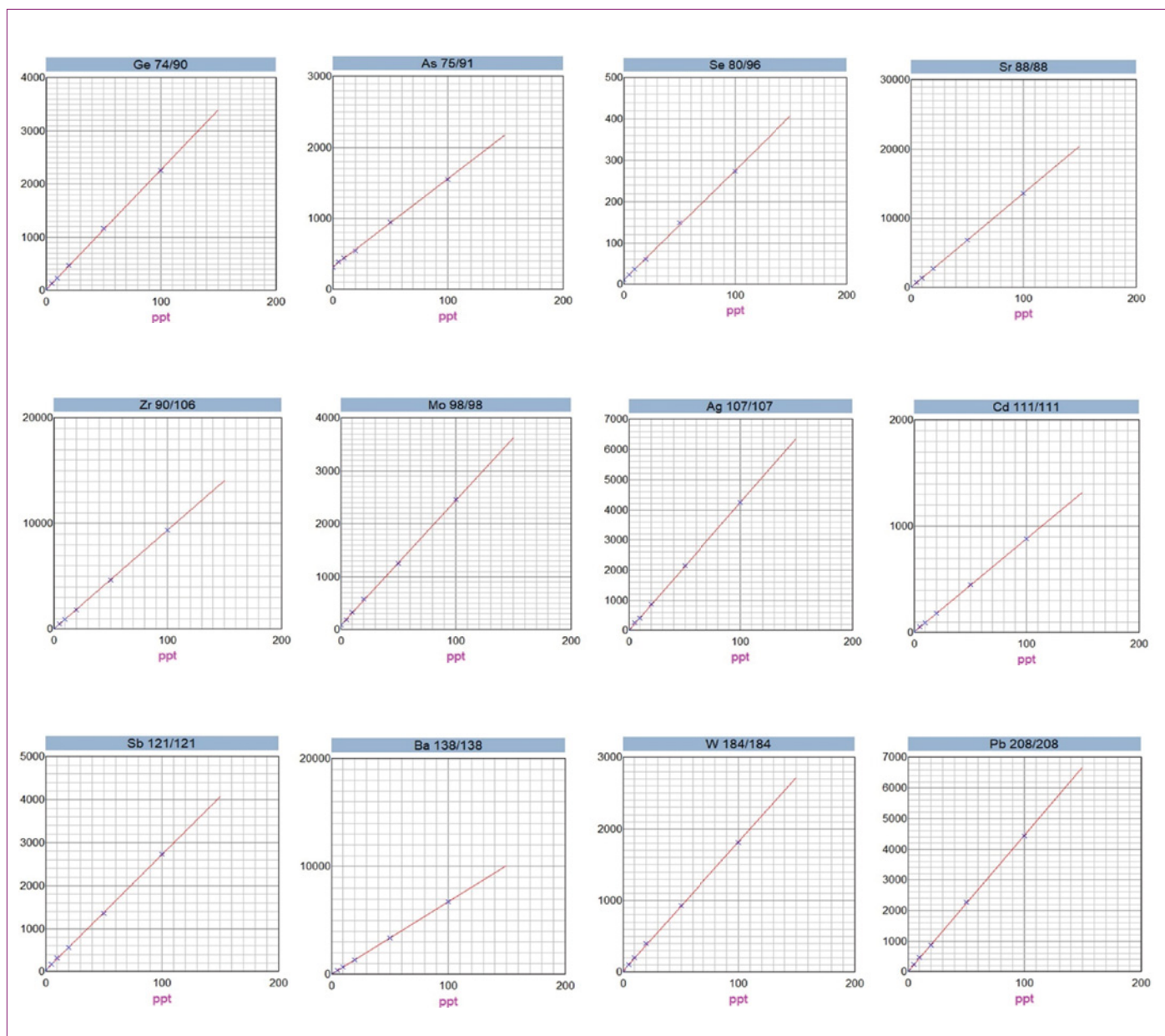


Figure 5. Standard addition calibration curves of 15 % HCl.

In terms of analysis, outstanding BECs and DLs of  $\leq 1$  ppt, for all elements (even alkali earth elements) were found in DIW under hot plasma conditions, demonstrating the superior interference removal capabilities of the NexION 5000 ICP-MS. Sulfuric acid was found to have excellent BECs below 1 ppt for all elements except Fe and Se, indicating potential contamination by these elements. DLs in 10%  $\text{H}_2\text{SO}_4$  were found to be  $\leq 1$  ppt for all elements except Cr and Zn. In 15% HCl, BECs for all elements were found to be  $< 1$  ppt except Ca, Fe, As, Se, and Mo, and the DLs were  $\leq 1$  ppt for all elements except As and Se where HCl is well-known for being harder to purify than acids, such as  $\text{HNO}_3$ , and generally having higher levels of contaminants.

## Conclusion

This work demonstrates the integration of ASAS with the NexION 5000 Multi-Quadrupole ICP-MS for the low- and sub-ppt analysis of 28 elements in DIW, 10% H<sub>2</sub>SO<sub>4</sub> and 15% HCl.

ASAS was able to provide automated and on-line MSA calibrations via easy integration with Syngistix for ICP-MS software. This user-friendly sample introduction system does not require the use of a valve, thereby minimizing the risk of memory effects and sample contamination. Since various chemicals were analyzed over the course of the sample run, each having different viscosities, vapor pressures, boiling points and surface tensions, calibration using MSA methods was required in order to perform accurate quantitative analyses. The use of ASAS, in combination with the NexION 5000 Multi-Quadrupole ICP-MS was able to provide:

- Fast, simple and efficient MSA calibration and sample measurement;
- Easy integration of ASAS with Syngistix for ICP-MS software;
- Outstanding interference removal capabilities of the NexION 5000 ICP-MS, leading to sub-ppt BECs for all elements in DIW, even under hot plasma conditions;
- Outstanding BECs and DLs for all matrices evaluated, even concentrated acids such as H<sub>2</sub>SO<sub>4</sub> and HCl.