WHITE PAPER

An Introduction and Overview of FAST-FIAS Coupled to the NexION ICP-MS

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Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is a very sensitive elemental analysis technique capable of analyzing a wide variety of sample types. One of the appeals of ICP-MS is its near-simultaneous nature: a large number of elements can be measured in a short time period. In this technique, predominantly singly-charged positive ions are generated in an argon plasma source and then transferred to and analyzed with a quadrupole mass analyzer. However, with conventional sample introduction (i.e. a peristaltic pump, nebulizer, and spray chamber) the total concentration of dissolved solids should not exceed 0.1-0.5%, otherwise deposition of material within the instrument will occur, causing serious drift and signal suppression.

With modern ICP-MS instrumentation, the total analytical measurement time is on the order of a few minutes or less. This implies that if samples can be introduced to the instrument in a manner such that there is very little idle instrumental time between measurements, sample throughput could be significantly improved.

Flow injection (FI) analysis is a very versatile method of sample introduction that has been used extensively in ICP-MS. The principles of FI were first described by Ruzicka and Hansen[1] and, since then, have been applied in nearly all branches of analytical chemistry to considerably enhance the capabilities of atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and ICP-MS. The advantages of flow injection are well documented in the literature.[2]

Microsampling FI is a mode of FI where small volumes of concentrated sample are injected into a flowing acid carrier stream which is transported to the ICP-MS. Because the ICP-MS is continuously exposed to clean acid, aside from the small volume of sample, the sample introduction, and interface components are continuously rinsed, reducing matrix deposition and the associated instrumental drift. Figure 1 shows a representation of a microsampling flow injection system.

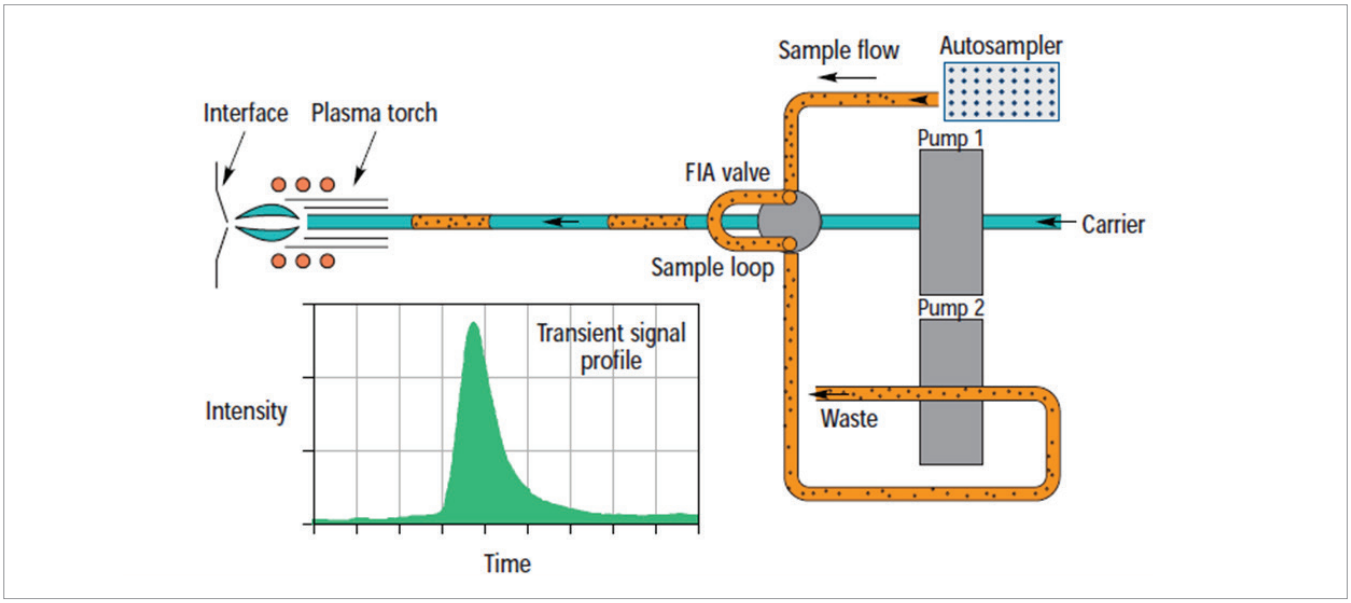

Figure 1. Schematic of a flow injection system used for microsampling.

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Flow Injection

Flow Injection signals are transient, time-dependent signal profiles, similar to chromatographic or nanoparticle signals, but different from the continuous steady-state signals characteristic of conventional solution aspiration techniques.

Flow Injection analysis (FIA) involves the injection of a discrete sample plug into a non-segmented carrier stream which is then analyzed by the ICP-MS. FIA coupled to ICP-MS is widely used in many application fields (i.e. agricultural, environmental, biochemical, biomonitoring, and industrial) because of its extreme flexibility and desirable features for ICP-MS:

- high sampling rate (many discrete injections are made in a given time)
- minimal sample consumption (typically 100 µL per injection)
- ease of automation
- ability to perform rapid, on-line chemistry
- minimal contamination (everything is done within a closed system)
- continuous monitoring of the blank (i.e. the carrier) throughout the whole measurement process.

PerkinElmer pioneered the use of FI-ICP-MS work with FIAS 100 and FIAS 400 systems. While successful in proving the benefits of FI, these systems had limitations. First, there was a long distance from the sample loop to the nebulizer (up to 30 cm), which causes sample dispersion, leading to smaller, broader peaks. Another limitation was that the amount of sample introduced was limited by the size of the sample loop. In addition, both the sample and carrier solutions were transported with peristaltic pumps, which lead to imprecision as the peristaltic pump tubing aged and introduced contamination from the pump tubing.

Many of these limitations have been addressed with the SC-FAST system from Elemental Scientific Inc. (ESI). The basic FAST system consists of an integrated valve mounted just before the nebulizer, a sample loop, a vacuum system for filling the loop, and a peristaltic pump for pumping the spray chamber drain and pushing the carrier solution. The sample never touches peristaltic pump tubing: the sample is only in contact with PTFE tubing, thus eliminating the possibility of contamination from the peristaltic pump tubing. Although referred to as a rapid sample introduction system, the SC-FAST is really a flow injection system that is modified to suit the application needs of busy commercial labs by using the benefits of FI but without having to use transient signals. In fact, with typical sample loop sizes of 1.5-2.0 mL, and flow rates of 250-400 µL/min, a steady signal can be maintained for up to 6 minutes of analysis time per injection.

Although the SC-FAST operates in a similar fashion to FIA, there would be benefits to operating it in a microsampling mode by injecting microliter amounts of sample by switching the loop for short times (milliseconds to a few seconds). In this way, the sample creates a short, transient peak which quickly returns to baseline. The advantage of this is that samples with elevated levels of dissolved solids can be rapidly measured without much deposition on the interface cones.

The possible disadvantage of rapid microsampling is that only a few isotopes can be measured in the short analysis time. However, given the rapid data acquisition capabilities of the PerkinElmer NexION® ICP-MS, this is not an issue, making the NexION ideal for microsampling flow injection.

Combining PerkinElmer's experience with FIAS with the fast data acquisition capabilities of the NexION ICP-MS and the SC-FAST resulted in the concept of FAST-FIAS: operating the SC-FAST in a rapid microsampling manner with the NexION ICP-MS.

Since the main benefit of FAST-FIAS is the ability to analyze samples with high levels of total dissolved solids (TDS), a special PFA nebulizer was designed to resist clogging, as shown in Figure 2. This nebulizer has an internal volume of less than 2 µL and connects directly to the FAST valve.

There are alternative approaches to analyzing samples with high levels of total dissolved solids than with FAST-FIAS. The most common way is sample dilution to a level of 0.1% TDS, followed by conventional, continuous solution aspiration into the ICP-MS. However, this methodology may significantly decrease sample throughput and degrade detection power due to sample dilution. In addition, matrix will deposit on the interface cones, which leads to instrument drift. Gas dilution, with or without an argon humidifier, may be another option, but this also degrades the detection limit and increases the analysis time.

To further improve the capabilities of FAST-FIAS, the FAST system can be connected to an ESI prepFAST system, which incorporates syringe pumps. The result is a prepFAST-FIAS, which consists of 2 valves: a 7-port valve to control the FAST vacuum, prepFAST dilution, in-line addition of internal standards, and a 6-port valve to control sample injections.

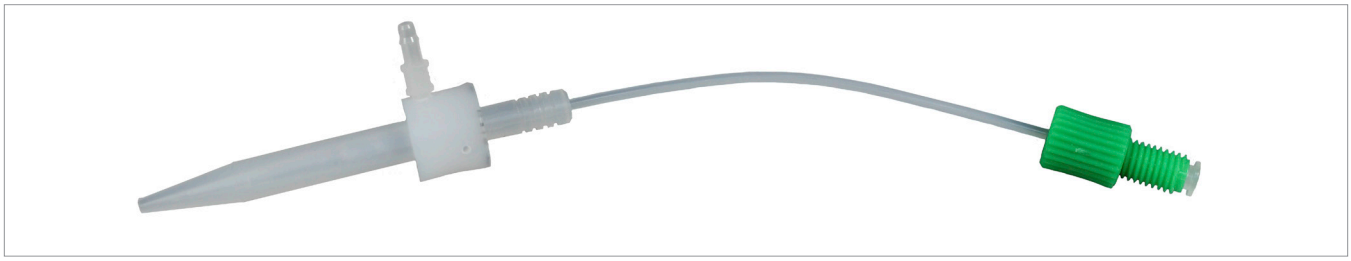

Figure 2. FAST-FIAS PFA nebulizer.

The FIAS injections start after the prepFAST has performed any sample dilution and added internal standard to the sample in the 7-port valve. The diluted sample then enters the loop on the 6-port valve, which then switches to "inject" for a short period of time (1-2 seconds). During this time, the carrier solution pushes the sample from the loop towards the nebulizer. At the same time, a trigger is sent to the ICP-MS to begin data acquisition. The valve then switches back to load so that the sample is followed immediately by the carrier solution. Since the "inject" time is short, only a small portion of the sample in the loop is sent towards the nebulizer. This sampling scheme creates a short transient peak in the instrument, which quickly returns to baseline. This process can be repeated multiple times without emptying the loop. Figure 3 shows a representation of this process, where three injections are made from the loop. After all replicates are finished, the vacuum empties the loop and draws carrier solution through the loop to rapidly rinse any traces of sample.

Because microsampling flow injection is so fast, the instrument has a very short exposure to the sample, resulting in minimal deposition on the interface cones and improving the repeatability of the measurements when compared with conventional sample introduction. As an example, consider the analysis of nine elements across the mass range (spiked at 10 µg/L) in a 3% (m/v) NaCl solution. Using a flow rate of 240 µL/min and a three-second injection time, 12 µL of sample reaches the instrument for each replicate. The injection profiles of three replicate injections of several elements are shown in Figure 4.

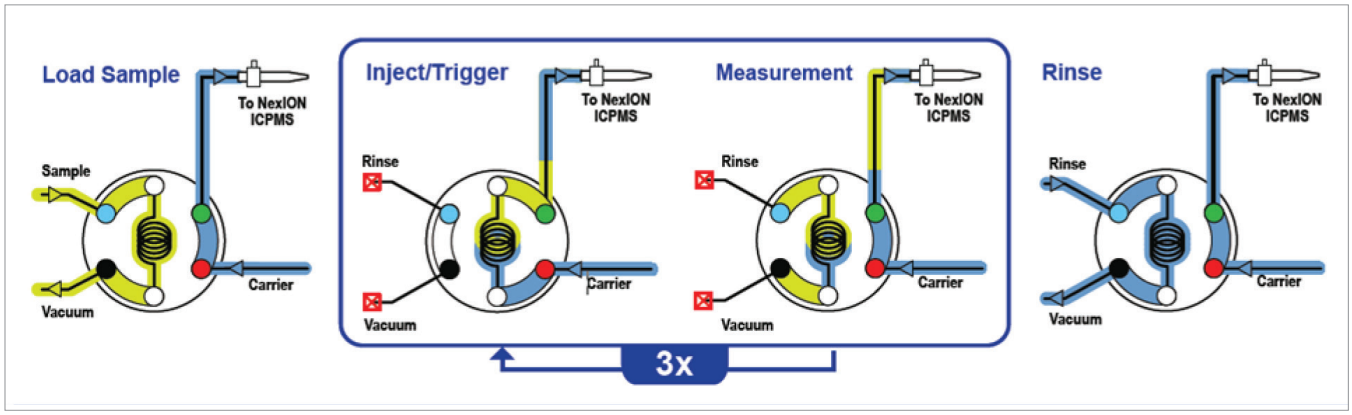

Figure 3. prepFAST scheme of the 6-port valve for rapid microsampling. In this example, three injections are made from a single fill of the sample loop.

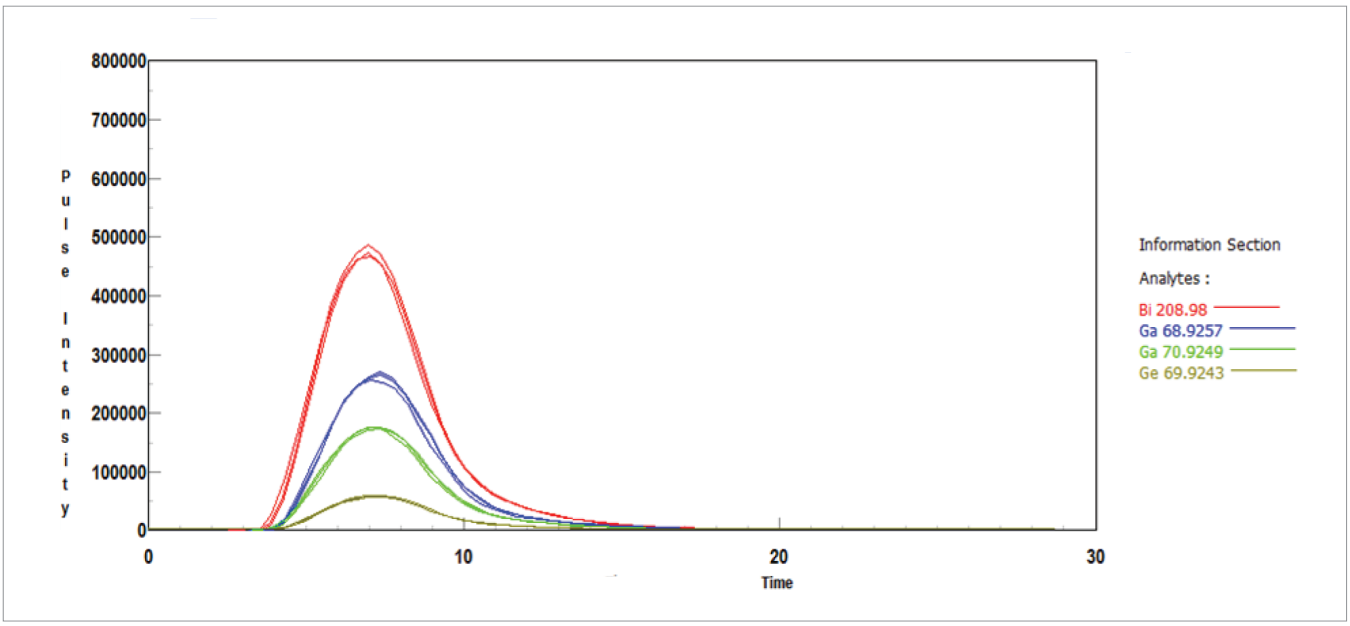

Figure 4. Flow injection profiles of a 3% salt solution (three-second injection time, three replicates).

The robustness of the system was evaluated by measuring solutions with NaCl levels from 0-30% (with 250 µs injections) and comparing the internal standard responses to those in 2% HNO_3. Table 1 shows the internal standard recoveries relative to 2% HNO_3 which indicate minimal signal suppression; although 30% NaCl showed less than 80% recovery for most elements, this is still significantly better than with conventional sample introduction. Table 2 shows the relative standard deviations for the internal standards in the various salt solutions, indicating that the high matrix does not affect the precision.

Table 1. Typical internal standard recoveries as a function of salt content.

% NaCl	Li 7	Sc 45	Ga 69	Ge 72	Y 89	In 115	Lu 175	Bi 209
0	100%	100%	100%	100%	100%	100%	100%	100%
0.1	103%	110%	109%	106%	108%	107%	109%	106%
0.5	103%	104%	104%	103%	106%	102%	106%	102%
1	101%	105%	103%	102%	104%	103%	107%	102%
3	99%	102%	99%	98%	101%	95%	100%	93%
5	98%	99%	94%	94%	95%	89%	96%	88%
10	98%	94%	88%	92%	90%	84%	91%	81%
30	96%	82%	78%	87%	80%	69%	76%	67%

Table 2. Relative standard deviations (RSDs) for the internal standards in different salt solutions, calibrated with 2% nitric standards.

% NaCl	Li 7	Sc 45	Ga 69	Ge 72	Y 89	In 115	Lu 175	Bi 209
0	0.4%	1.2%	1.2%	1.1%	0.4%	0.5%	0.5%	2.7%
0.1	2.6%	1.0%	1.5%	3.6%	4.6%	4.9%	0.9%	0.9%
0.5	1.6%	0.7%	5.2%	1.0%	1.3%	1.8%	4.3%	2.0%
1	2.2%	1.9%	1.7%	0.7%	2.6%	1.7%	1.3%	1.7%
3	2.3%	1.6%	2.2%	0.7%	2.3%	2.9%	1.5%	1.9%
5	2.7%	4.8%	1.4%	3.0%	4.0%	1.6%	1.8%	3.0%
10	2.4%	1.0%	1.5%	2.5%	2.7%	2.2%	1.8%	1.2%
30	0.5%	1.3%	1.5%	1.5%	0.5%	2.5%	0.4%	1.3%

The data in Table 1 shows that matrix suppression is greater at high mass than low mass. As a result, an investigation was performed to study the effect of injection time on the uranium signal in 3% NaCl. The results appear in Figure 5 and indicate that at injection times of one second or less, matrix suppression is eliminated.

The peak shape from a FI injection will vary as a function of injection time and salt content, as shown in Figure 6: longer injection times and higher salt content lead to broader peaks. This broadening effect is a byproduct of the flow injection process and has been observed in the past. As a result, most accurate results are obtained when the peak area is used for quantitation.[3]

Another advantage of the prepFAST-FIAS over standard FAST-FIAS is that it fully automates calibration by making appropriate dilutions from a single multielement standard solution. Figure 7 demonstrates how the prepFAST-FIAS simplifies calibrations by making the appropriate calibration standards in-line. Figure 8 shows typical calibration curves which were prepared from a single standard via in-line dilution with the prepFAST-FIAS using peak areas, as discussed above.

The excellent linearity of the calibration curves in Figure 8 (Pb and As in a multi-mode method) prepared in 2% HNO_3 illustrates the accuracy of rapid 125 ms injections. This calibration curve is used to determine the recovery of Pb

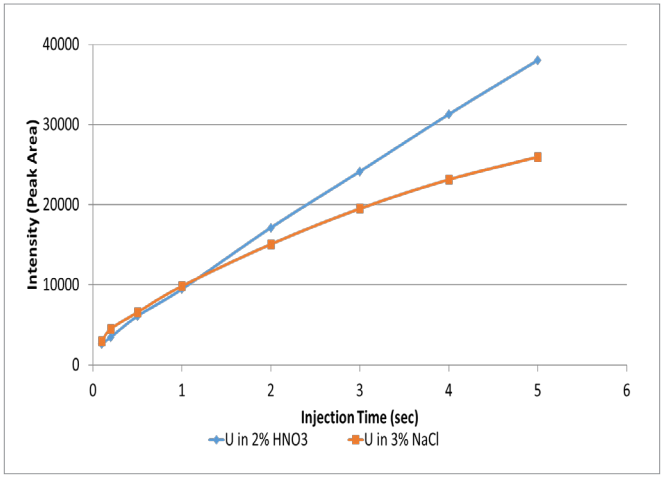

Figure 5. Effect of FAST-FIAS injection time vs. U signal for 2% HNO_3 and 3% NaCl.

spiked into a 30% brine solution. A recovery near 100% indicates that FAST-FIAS eliminates the need to dilute or matrix match high TDS solutions.

To explore the effect of salt content on signal suppression, a multielement 50 ppb standard in 25% NaCl was measured against a calibration curve prepared in 2% nitric acid. Figure 9 shows that the recoveries across the mass ranges are right at 50 ppb, demonstrating the ability of microsampling FIA to overcome the effects of matrix suppression.

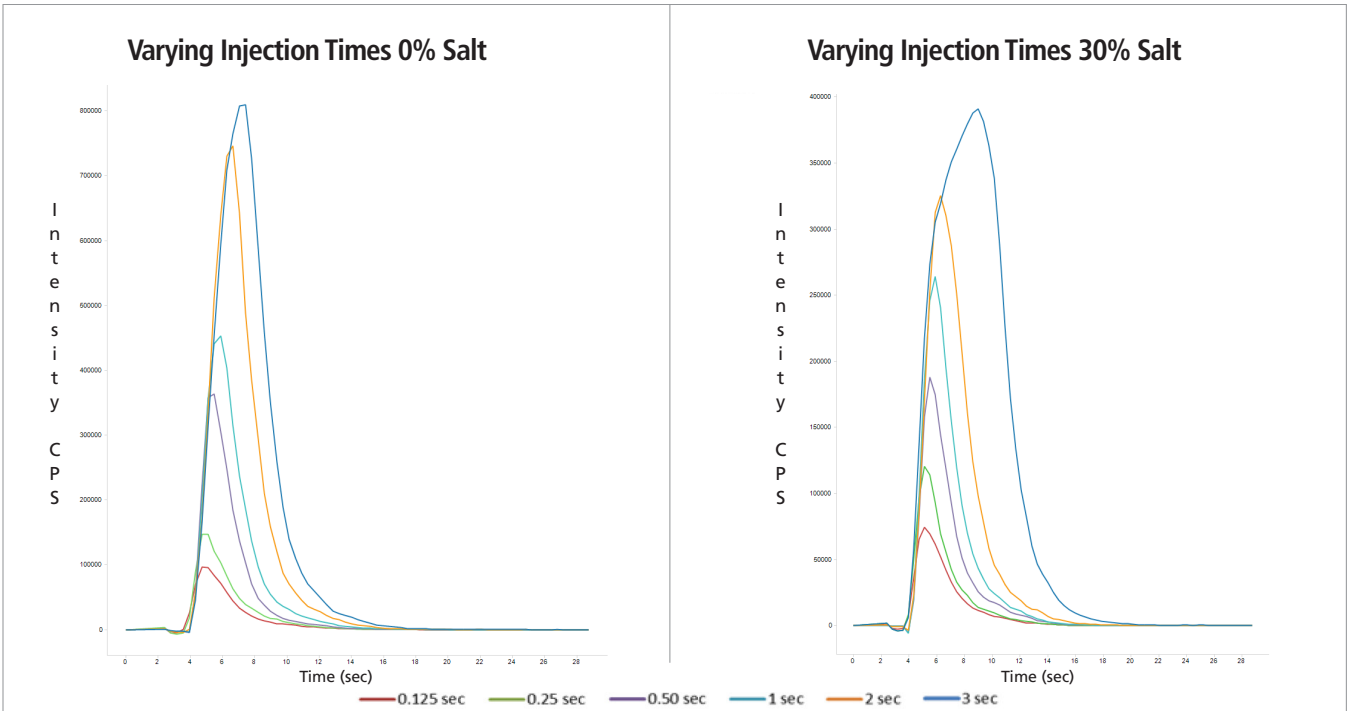

Figure 6. Effect of injection time and salt content on flow injection peak.

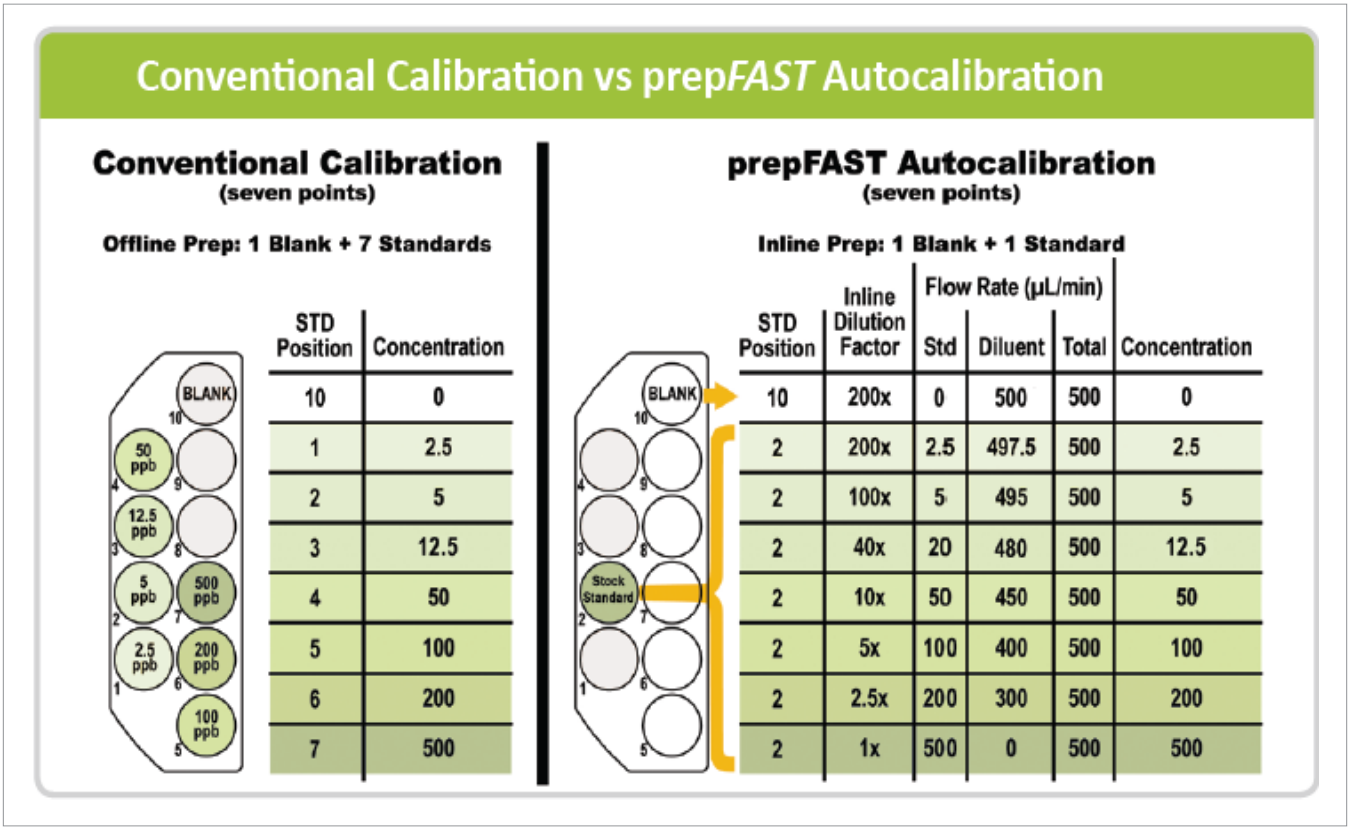

Figure 7. A representation of conventional calibration vs. calibrations produced from in-line preparation of the standards with the prepFAST-FIAS.

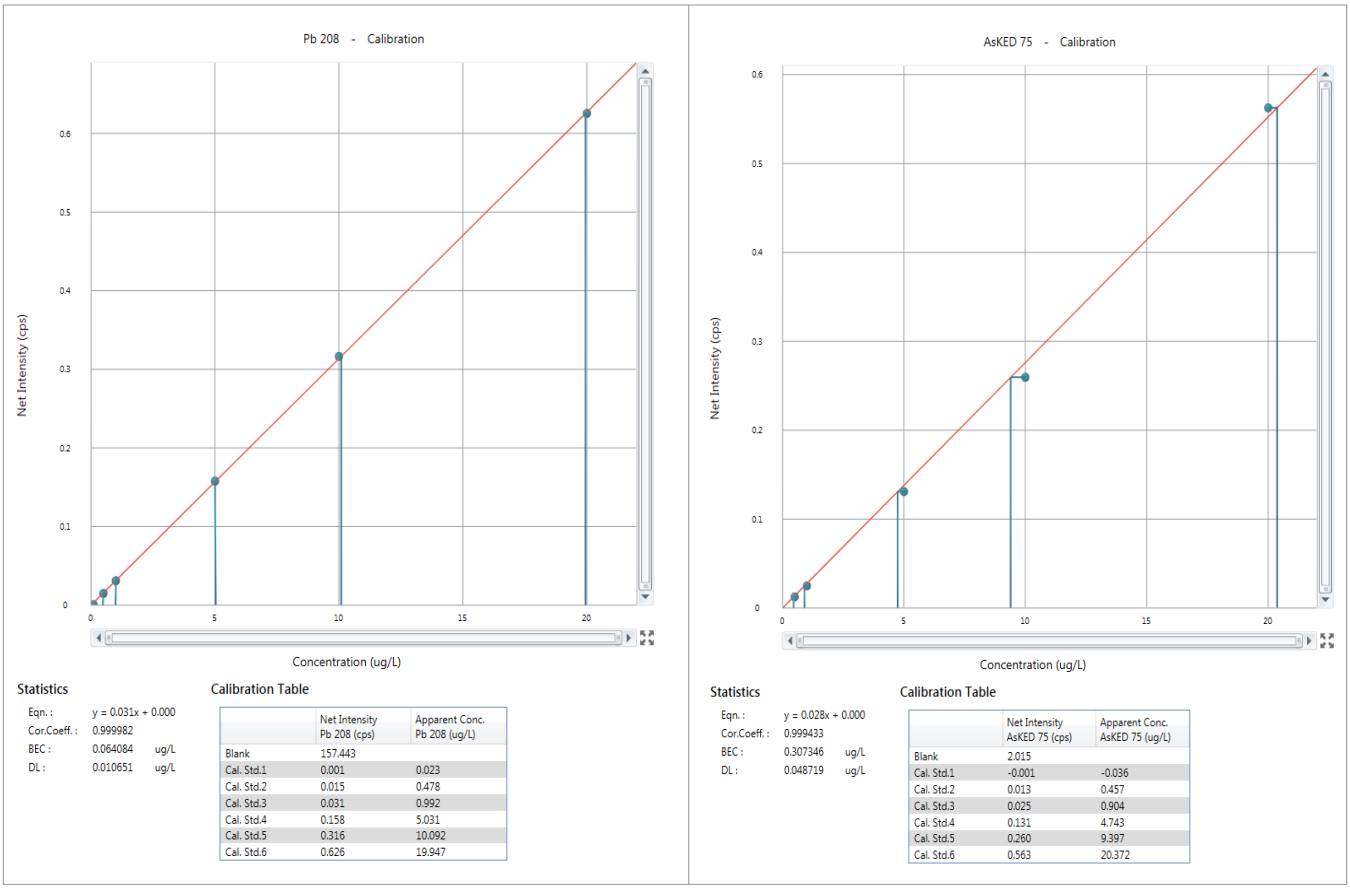

Figure 8. Typical calibration curves prepared in-line from a single calibration standard with the prepFAST-FIAS.

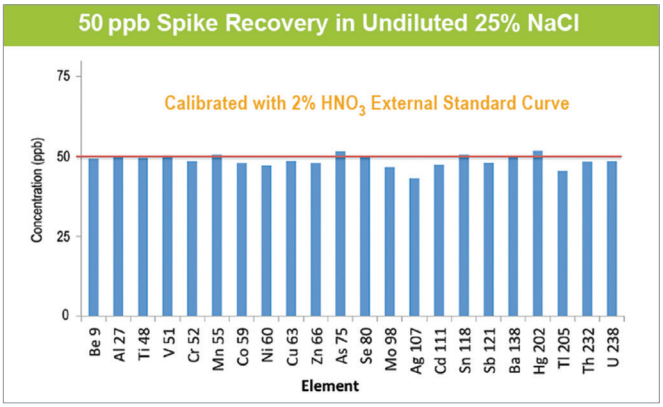

Figure 9. Quantitative recovery of 50 ppb spike in 25% NaCl solution calibrated with 2% nitric standards.

Detection limits (Table 3) were determined as three times the standard deviation of an undiluted 25% NaCl solution measured against a calibration curve prepared in 2% HNO_3. The highest calibration standard used was 20 mg/L for Mg, Al, K, Ca, and Fe and 200 µg/L for all other elements. All measurements were done in Standard mode, except As and Se, which were determined in Reaction mode.

Table 3. prepFAST-FIAS detection limits in 25% NaCl.

Element	Detection Limit	Units
Ti 47	10	µg/L
V 51	3	µg/L
Cr 52	5	µg/L
Mn 55	2	µg/L
Co 59	0.3	µg/L
Ni 60	1	µg/L
Cu 63	3	µg/L
Zn 66	3	µg/L
As 75*	1	µg/L
Se 78*	2	µg/L
Mo 95	2	µg/L
Cd 111	2	µg/L
Sb 121	2	µg/L
Ba 138	0.8	µg/L
Pb 208	0.3	µg/L
Mg 24	0.02	mg/L
Al 27	0.01	mg/L
K 39	0.4	mg/L
Ca 44	1	mg/L
Fe 56	0.02	mg/L

** = Reaction mode; all other elements in Standard mode*

Washout and Dispersion Factor

The prepFAST-FIAS sample introduction system washes out quickly due to both the small sample injection volumes and the vacuum which quickly rinses the sample loop. For example, trace levels of Cd can be measured after direct injection of 35% $CdSO_4$ solution, as shown in Figure 10. This is consistent both with the microsampling nature of the protocol in which a relatively small amount of sample is injected into the carrier stream and the instrument design characteristics of the NexION ICP-MS.

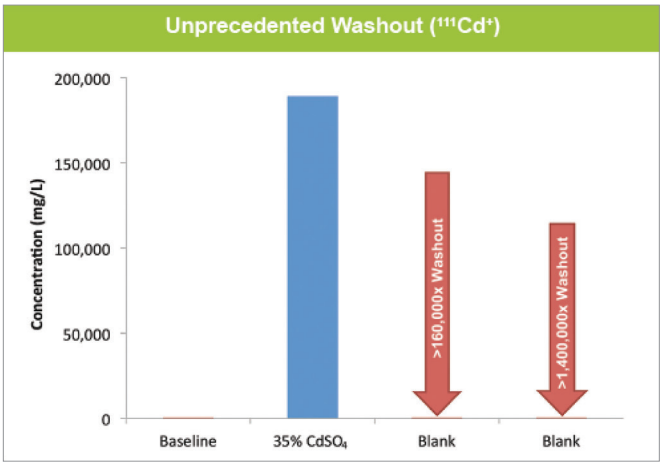

Figure 10. Rapid washout of Cd.

Summary

Coupling FAST-FIAS to the NexION ICP-MS provides the following benefits:

- Excellent precision (1-3% RSD)
- With prepFAST, the ability to automatically prepare calibration standards and add internal standard
- Simplified operation of your ICP-MS
- Reduced instrument maintenance
- Improved internal standard recoveries
- Ability to run any TDS solution with external calibration

The prepFAST-FIAS as a sample introduction system for the NexION ICP-MS has proven to be a unique combination capable of analyzing high-matrix samples with minimal signal suppression, achieved by incorporating syringe pumps, dual valves, and a vacuum pump for loading and washing the sample loop. Unique design characteristics of the NexION ICP-MS minimize matrix deposition within the instrument and eliminate re-ionization of deposits on the interface cones.

Another characteristic of the prepFAST-FIAS which simplifies the user experience is its ability to create a calibration curve from a single calibration standard via in-line dilution. This autodilution capability is further used to provide intelligent dilution of samples which have concentrations beyond the range of the calibration curve.

References

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