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Enhanced Automation using SampleSense prep*FAST* and PerkinElmer NexION 2000 ICPMS for U.S. EPA Method 200.8

Introduction

The measurement of trace metals in environmental waters is of great importance to ecosystems and human health, not only for the provision of safe drinking water to communities, but also to protect the natural world from the toxic effects of excess pollution from industrial discharge and treated wastewater effluent. Therefore, the levels of many trace metals are often regulated by law for waters discharged into the environment as a result of human activities. One of the most widely used regulated analytical methods for these measurements is United States Environmental Protection Agency Method 200.8: *Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma-Mass Spectrometry (1).*

This work demonstrates the Elemental Scientific prep*FAST* automated sampling system featuring novel SampleSense™ technology coupled with a PerkinElmer NexION 2000 ICPMS performing analysis with this U.S. EPA method.

Figure 1. NexION 2000 equipped with a 4DX SampleSense prep*FAST* autodilution and autocalibration system with *pergo* 2000.

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Experimental

SampleSense prep*FAST*

The prep*FAST* is a sample preparation system consisting of an intelligent autosampler (2, 4, 8, or 14-rack capacities available) coupled with a syringe pump module and DXi integrated valve and peripump assembly mounted on the NexION 1000/2000. prep*FAST* fully automates laboratory dilutions while providing high sample throughput. It offers high-precision inline autodilution up to 400x and autocalibration from one or more stock standards.

SampleSense combines an auto-correcting DXCi autosampler with an inert injection valve featuring integrated optical sensors that automatically detect both the arrival of a sample in the valve and when the loop is completely filled. This allows rapid sample loading using a high-speed vacuum pump. The sensed sample is automatically injected from the valve loop and the analysis is triggered in a tightly timed analytical sequence free of predetermined delay timings.

This technology is available for Elemental Scientific's *FAST* and prep*FAST* systems to further increase instrument productivity and fully automate the sample uptake process. Key highlights of the system include:

- Eliminates all sample uptake method development – no uptake delays required
- Optimizes loading conditions for each sample matrix
- Allows sample loop sizes to be changed without needing to alter method settings
- Automatically compensates for drift caused by kinked lines or partial blockages
- Provides positive confirmation of sample loading – if a sample fails to load for any reason, the failed sample is logged and the user is alerted.
- Automatically goes to the correct sample location every time – even in extreme laboratory environments.

Samples and Sample Preparation

Several reference water samples were obtained from the U.S. Geological Survey Standard Reference Sample project (https://bqs.usgs.gov/srs/) and analyzed according to U.S. EPA Method 200.8 as dissolved water samples.

The prep*FAST* system automatically prepared the 6 calibration standard levels from the two stock calibration standards shown in Table 1. As required by the EPA method, calibration and Quality Control stock solutions were obtained from two separate suppliers. The dilution of the stock standards is defined by the coding in the calibration tab, which indicates the location of the stock standard and the dilution factor (see Figure 2). Gold at 200 µg/L was added to Stock A to stabilize mercury. Since the best accuracy is obtained when blanks, standards, and samples have the same acid concentration, all stock and prep*FAST* carrier, diluent, and internal standard solutions were prepared in 2% (vol/vol) ultrapure nitric acid.

Table 1. Calibration stock standards used on prep*FAST* (Numbers in parentheses are PerkinElmer stock standard part numbers).

Solution ID	Elements	Concentration
Stock A – Traces Only (N9301721, N9307807, N9300253)	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn, B, Th, U……	5 µg/L
Stock B – Traces + Majors (N9301721, N9307807)	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn, B, Th, U……	200 µg/L
(N9307805)	Ca, Mg, Na, K……	50 mg/L

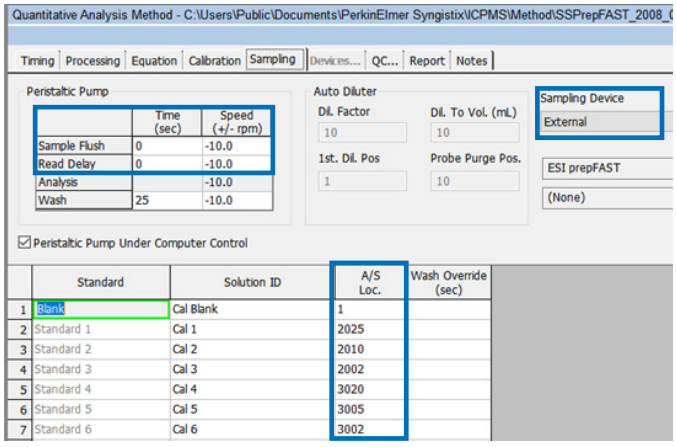

Figure 2. Syngistix software sampling tab showing programming of 6 calibration standards from 2 stock solutions. First number is stock location, next 3 digits are the dilution factor.

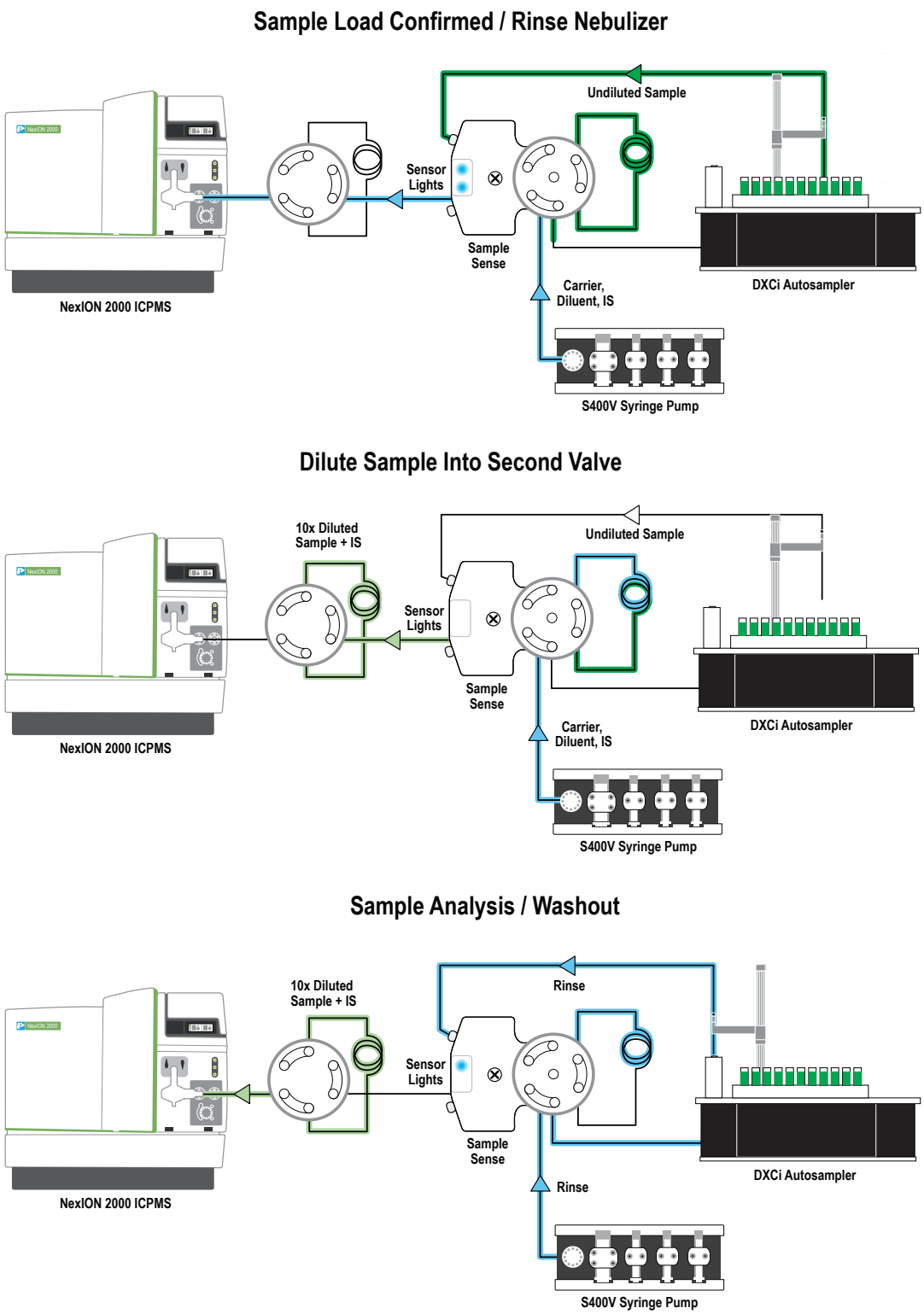

Figure 3. Schematic overview of the SampleSense prep*FAST* shows the following steps: (i) sample loading, with the valve automatically injecting upon detection of a full loop; (ii) dilution and addition of internal standard; (iii) analysis of the sample and simultaneous washing of the probe and SampleSense valve.

Instrument Conditions

Table 2. Instrument analysis settings (PerkinElmer part numbers given in parentheses).

Parameter	Value
Nebulizer	ESI PFA with Integrated Capillary
Spray Chamber	Baffled glass cyclonic with AMS port – (N8152389)
Sample Uptake Rate	~180 µL/min (MP2 pump speed -10 rpm)
RF Power	1600 W
Torch/Injector	Quartz with integrated 2.0 mm id injector – (N8152472)
Argon Humidifier	*pergo* 2000 with AMS (N8150498)
Nebulizer Gas Flow	1.04 L/min
Auxiliary Gas Flow	1.2 L/min
Plasma Gas Flow	15 L/min
Sample Uptake Tubing	Black/Black PVC (0.76 mm id), flared - (N8145202)
Drain Tubing	Grey/Grey Santoprene (1.14 mm id) - (N8145173)
Replicates	3

Table 3. Elements and masses monitored in this work. Masses that are reported are underlined.

Analyte	Mass	Analyte	Mass
Be	9	Cd	111, 114
Al	27	Sb	121, 123
V	51	Ba	135, 137
Cr	52, 53	Hg	202
Mn	55	Tl	203, 205
Co	59	Pb	206, 207, 208
Ni	60, 62	Th	232
Cu	63, 65	U	238
Zn	66, 67, 68	Na	23
As	75	Mg	24
Se	77, 78 82	K	39
Mo	95, 97, 98	Ca	43
Ag	107, 109	Fe	54, 57
Internal Standard	**Mass**	**Internal Standard**	**Mass**
Sc	45	In	115
Ge	72	Tb	159
Rh	103	Ir	193

The prep*FAST* was configured with 1.5 mL loops and automatically triggered the NexION 2000 analysis after the sample was loaded and diluted. SampleSense's automated loading and triggering function actively monitors the loading of each sample, automatically compensating for changes in sample viscosity (i.e. between clean water samples and digested solid samples). As a result, method development in the host instrument is greatly simplified – all uptake and stabilization delays were set to "0" in the PerkinElmer Syngistix™ software (Figure 2). The PFA-ICN integrated capillary nebulizer minimizes the number of connections between the valve and the nebulizer, reducing dead volume and uptake time. Total sample consumption for each analysis was < 4 mL, leaving sufficient sample volume for reanalysis or QC-triggered autodilution without the need to refill any sample vials. An overview of the prep*FAST* operation is given in Figure 3.

The instrument was also fitted with a *pergo* 2000 argon humidifier to improve long-term stability. *pergo* continually dissolves micro-crystal deposits in the nebulizer tip to maintain steady nebulizer efficiency (samples contained ~ 50-100 ppm Ca, Mg, Na and K) (3).

The ICPMS system was tuned according to the manufacturer's recommendations. The instrument conditions are summarized in Table 2. Since Na and K were anticipated to be at fairly high levels in the water samples analyzed, these elements were determined using Extended Dynamic Range (EDR) mode. EDR mode is a unique feature of the NexION ICPMS systems where the RPa setting on the mass-filtering quadrupole located in the reaction cell can be adjusted to attenuate the signal for a particular element or mass without time penalty or reduction in sensitivity of other analytes determined in the method.

Since U.S. EPA Method 200.8 does not allow for the use of collision/reaction cells for drinking water analysis (2), all determinations were carried out in Standard Mode without use of a cell reaction gas.* The masses monitored and reported in this work are given in Table 3.

The instrument was calibrated using a blank and 6 levels of calibration standards prepared by the prep*FAST*. The trace elements were calibrated at 0.2, 0.5, 2.5, 10, 40, and 100 µg/L. Mercury was calibrated at 0.2, 0.5, and 2.5 µg/L. Increasing levels of the major cations (Na, Mg, Ca, and K) were added to the highest 3 calibration standards to both compensate for matrix effects caused by Easily Ionizable Element (EIE) effects and calibrate for these major cations, which were determined even though they are not included as analytes in U.S. EPA Method 200.8. The levels of the major cations spiked into calibration standards 4, 5, and 6 were 2.5, 10, and 25 mg/L, respectively.

** EPA 200.8 does permit the use of collision/reaction cell technology for the analysis of waste waters. With NexION's Universal Cell Technology, improved Detection Limits can be achieved for elements impacted by polyatomic interferences.*

Results and Discussion

The calibration was verified using a second-source Quality Control Sample (QCS) prepared at the midpoint of the calibration range for each element. A continuing calibration verification standard (CCV) was prepared from the same stock as the calibration standards at a concentration at the mid-point of the calibration curve for each element. A continuing calibration blank (CCB) and the CCV were analyzed at the beginning of the run after the QCS sample, after every 10 samples, and at the end of the run. In all cases, the limits for the QCS and CCV were within the ± 10% acceptance limits. Sample washout for all elements was excellent – even for mercury – using the prep*FAST*. After running a 5 µg/L linear range check standard for mercury, the next sample, a CCB, read back at less than the calculated method detection limit (MDL) of 0.008 µg/L, even when using just 2% nitric acid without the addition of gold as the wash solution.

After calibration and initial QC, a series of eight blank solutions were analyzed as samples in order to calculate the estimated detection limits. Calibrations prepared using the prep*FAST* were very linear, as illustrated by the example calibration plot for Mo in Figure 4. The calibration linearity and calculated estimated detection limits are given in Table 4.

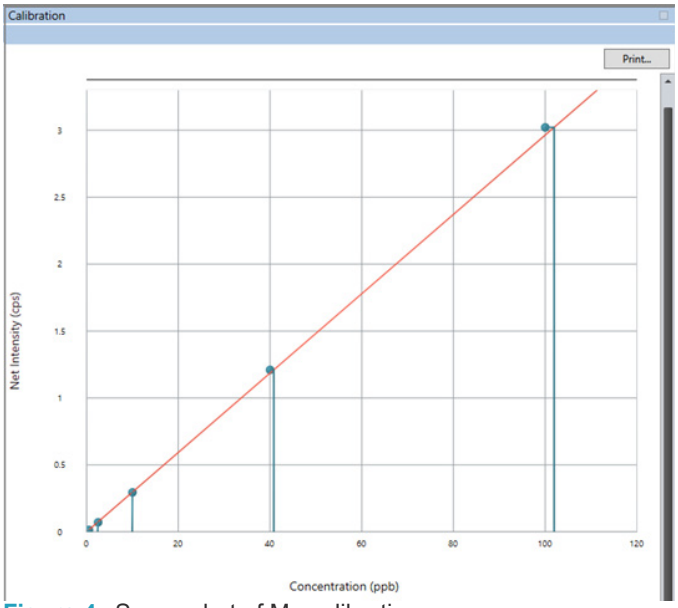

Figure 4. Screenshot of Mo calibration curve.

Table 4. Summary of estimated detection limits, calculated as 3 * standard deviation of 8 blank measurements, and calibration linearity, shown by the correlation coefficient, R.

Element	Correlation Coefficient (R)	Estimated IDL (µg/L)
Be 9	0.99998	0.001
Al 27	0.99997	0.006
V 51	0.99972	0.03
Cr 52	0.99977	0.09
Mn 55	0.99974	0.004
Co 59	0.99944	0.002
Ni 60	0.99999	0.003
Cu 63	0.99996	0.03
Zn 66	0.99996	0.04
As 75	0.99999	0.03
Se 82	0.99999	0.03
Mo 95	0.99999	0.008
Ag 109	0.99986	0.004
Cd 111	0.99994	0.006
Sb 121	0.99999	0.003
Ba 135	0.99996	0.003
Hg 202	0.99996	0.008
Tl 205	0.99921	0.008
Pb 208	0.99997	0.0009
Th 232	0.99879	0.0009
U 238	0.99894	0.0005
Na 23 (EDR Mode)	0.99999	0.4
Mg 24	0.99999	0.2
K 39 (EDR Mode)	0.99999	1.2
Ca 43	0.99999	0.6
Fe 54	0.99776	2

Results and Discussion *(continued)*

Example results for three of the six U.S. Geological Survey reference water samples are given in Table 5. For the majority of elements where a round-robin MPV (Most Probable Value) was given, the obtained results from this study were within ± 10% of the reported MPV.

Figure 5 shows the internal standard stability obtained over the course of the run. Although this run was fairly short in duration, the internal standard drift was negligible, even after running several samples with fairly high total dissolved solids.

Another advantage of using prep*FAST* to prepare and analyze the calibration standards is reduced contamination of the blank. Blank levels for some elements, such as Zn, were improved by a factor of up to 4 with the prep*FAST* compared to analysis with manually prepared standards on a standard autosampler. As Figure 6 illustrates, the Zn calibration blank when using the prep*FAST* was only 145 cps as compared to 622 cps when performing a manual calibration. Use of the prep*FAST* minimizes handling of the various solutions and prevents potential contamination because the sample solution never touches peristaltic pump tubing, which is a common source of contamination. Figure 6 shows that in the case of Zn, the Background Equivalent Concentration (BEC) with the prep*FAST* is two times better than that for the manually prepared calibration curve.

Table 5. Results for USGS reference water samples showing Most Probable Value (MPV) and obtained result as a percent recovery. All elements reported in µg/L unless otherwise noted. Elements with an * were analyzed using Extended Dynamic Range (EDR) Mode. MPV = Most Probable Value, as determined by a round-robin study of over 100 reporting laboratories.

	T221		T225		T229	
Element	MPV	% Recovery	MPV	% Recovery	MPV	% Recovery
Ag	14	101.3%	2.6	94.5%	3.5	100.3%
Al	374	99.8%	245	93.6%	680	97.7%
As	17.7	100.4%	0.786	109.1%	12.8	98.5%
Ba	29	102.2%	118	102.3%	76.7	105.3%
Be	0.383	104.9%	0.96	96.8%	1.2	101.1%
Ca (mg/L)	16.7	95.2%	114	90.1%	44	95.2%
Cd	0.038	91.0%	0.969	103.6%	1.89	103.7%
Co	2.24	97.1%	1.07	97.6%	2.88	96.8%
Cr	1.71	91.7%	1.17	100.7%	7.51	95.7%
Cu	3.78	96.7%	2.45	96.4%	21.6	98.1%
Fe	328	90.4%	38.8	61.6%	847	92.5%
K* (mg/L)	1.9	95.3%	2.5	84.8%	4.52	91.5%
Mg (mg/L)	3.77	97.5%	14.8	92.7%	22	96.5%
Mn	33.6	93.0%	43.2	93.1%	670	96.7%
Mo	0.522	95.9%	1.8	95.3%	10.9	96.3%
Na* (mg/L)	17.4	95.2%	115	85.0%	25.3	94.5%
Ni	0.6	108.6%	6.89	113.5%	8.83	103.5%
Pb	0.49	103.6%	4.27	99.0%	13.8	104.7%
Sb	1.04	96.0%	1.84	93.3%	3.17	98.4%
Se	3.8	104.3%	5.33	102.9%	5.09	101.2%
Tl	3.31	94.6%	6.55	91.4%	2.9	96.6%
U	1.49	98.8%	9.52	94.9%	8.31	102.9%
V	0.508	87.3%	12.9	96.8%	25.4	97.8%
Zn	25.2	106.2%	10.1	95.6%	230	98.4%

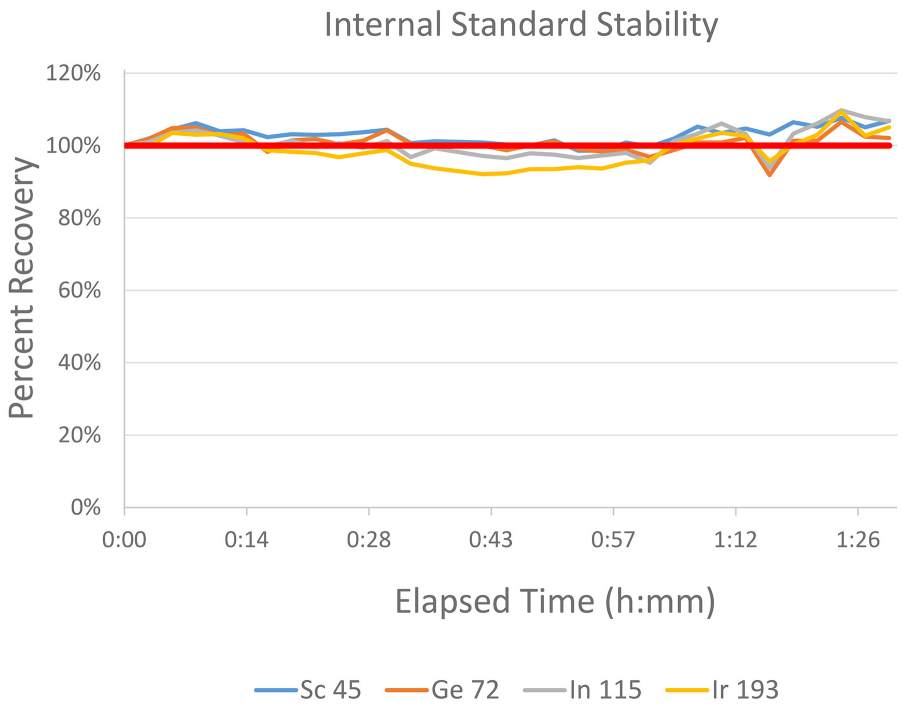

Figure 5. Stability of internal standards over the analytical run, relative to the calibration blank.

Use of the prep*FAST* minimizes blank levels by minimizing handling of the various solutions and eliminating sample contact with peristaltic pump tubing, which is a common contamination source. In the example shown in Figure 6, the Background Equivalent Concentration (BEC) for Zn with the prepFAST is two times better than that for the manually prepared calibration curve.

prep*FAST* Autocalibration

BEC: 0.046066 ppb

	Net Intensity Zn 66 (cps)	Apparent Conc. Zn 66 (ppb)
Blank	145.3	
Cal. Std.1	0.0	0.210
Cal. Std.2	0.0	0.548
Cal. Std.3	0.2	2.583
Cal. Std.4	0.8	10.554
Cal. Std.5	3.0	40.631
Cal. Std.6	7.3	99.690

Manual Calibration

BEC: 0.113000 ppb

	Net Intensity Zn 66 (cps)	Apparent Conc. Zn 66 (ppb)
Blank	622.0	
Cal. Std.1	0.0	0.191
Cal. Std.2	0.1	0.505
Cal. Std.3	0.1	1.057
Cal. Std.4	0.6	5.212
Cal. Std.5	2.2	19.530
Cal. Std.6	11.5	100.083

Figure 6. Lower background levels and improved BEC for Zn using prep*FAST*.

Conclusions

The integration of SampleSense prep*FAST* with the PerkinElmer NexION 2000 ICPMS provides the ultimate performance for elemental analysis of environmental waters and waste samples. The SampleSense technology coupled with the powerful autocalibration and autodilution capabilities of the prep*FAST* offers unmatched automation for high-throughput analysis of challenging environmental samples.

Following the US EPA Method 200.8 protocols with three replicates per sample, the sample-to-sample cycle time with SampleSense prep*FAST* is 2 minutes and 49 seconds as compared to 4 minutes and 20 seconds using conservative sample uptake and wash times. Over the course of analysis for 100 samples, using the prep*FAST* can save over 3 hours, increasing laboratory productivity while lowering both argon gas consumption and laboratory support costs. Manual sample reanalysis is all but eliminated, and positive confirmation of sample loading ensures the highest confidence in data quality.

Summary

SampleSense prep*FAST* fully automates sample analysis:

- Eliminates all method uptake timing parameters and automatically triggers each ICPMS analysis
- Optimizes loading conditions for each sample matrix, independent of changing viscosities
- Reduces sample consumption, allowing for reanalysis or autodilution of samples
- Actively detects and reports any sample loading issues
- Automatically compensates for drift in vacuum uptake time caused by kinked lines or partial blockages
- Autocalibrates the ICP with real-time preparation of calibration standards from one or more stock standards
- Autodilutes both prescribed samples and overrange samples automatically during the analysis run

References

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