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Application Note

Improving Turn-Around Times for ICP-OES Analysis for EPA 200.7

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Introduction

Environmental laboratories frequently analyze samples by EPA 200.7 to determine sample compliance with government regulations. The results of these analyses are often used to protect the environment and the population from potentially hazardous contaminants. Accuracy of this testing is paramount, even though client expected turnaround times (TAT) for laboratories are constantly shrinking. New generations of ICP-OES can rapidly analyze samples to meet these shorter TATs, but their speed can be limited by long sample uptake and rinse times. The *ASXPRESS PLUS* Rapid Sample Introduction System can be easily added to the sample introduction system of the ICP to shorten analysis time by eliminating the rinse time and reducing sample uptake time. These improvements do not impact the critical accuracy of sample results. In this application note, the *ASXPRESS PLUS* will be shown to accurately and precisely deliver samples to the ICP-OES while reducing analysis time by 60%.

Sample Preparation

To demonstrate the effectiveness of the *ASXPRESS PLUS*, two samples representing typical matrices and two NIST standard reference materials (SRMs) were analyzed. A stream sample collected from a local forest and a wastewater influent provided by an environmental laboratory were digested according to EPA 3010. NIST 1640a, Trace Elements in Natural Water, and 1643f, Trace Elements in Water, were digested following EPA 200.7 for all elements except Calcium. The Calcium result was from an undigested aliquot. Samples for both methods were digested by means of a graphite digestion block.

Instrument Conditions

Samples were analyzed using a Perkin Elmer Avio 500 ICP-OES in conjunction with a Teledyne CETAC ASX-560 autosampler and an *ASXPRESS PLUS*. A Meinhardt nebulizer aspirated the samples. The AVIO software included a 200.7 method template which was used for analysis. Minor adjustments were made to uptake and flush times to match our sample introduction system. Avio and *ASXPRESS PLUS* Settings are in Table 1 and Table 2.

Table 1: Avio Settings

Parameter	Setting Standard Run	Setting Xpress Run
Pump Speed	1.0 mL/min	1.5 mL/min
Read Delay	30 s	15 s
Flush Speed	3.0 mL/min	-
Flush Time	30 s	-
Power	1500 W	
Nebulizer	0.7 L/m	
Auxiliary Gas	0.2 L/m	
Plasma	8 L/m	
Replicates	4	

Table 2: Xpress Settings

Parameter	Setting
Loop Size	2.5 mL
Loop Evacuation Delay	0.1 s
Loop Load	3.0 s
Equalization Delay	1.0 s
Time to Evacuate Probe	1.0 s
Probe Rinse	5.0 s
Rinse Station Fill	5.5 s

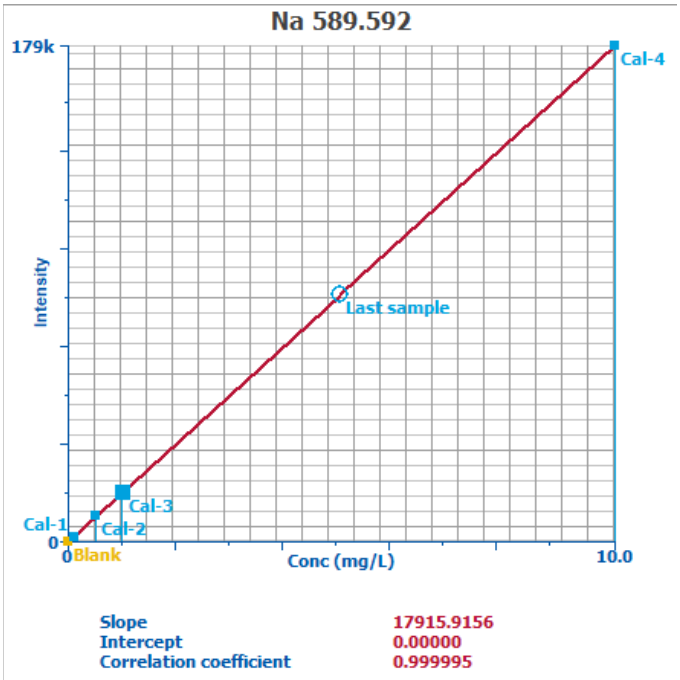
The instrument was calibrated using three to four calibration standards prepared in 2% HNO_3, 2% HCl. Scandium and Yttrium were used as the internal standard (IS) and added on-line such that the final concentration was 1 mg/L. The *ASXPRESS PLUS* run used an optional 7-port valve for on-line internal standard (IS) addition whereas the standard run used a mixing tee. Element wavelengths, calibration standards, and plasma view are in Table 3.

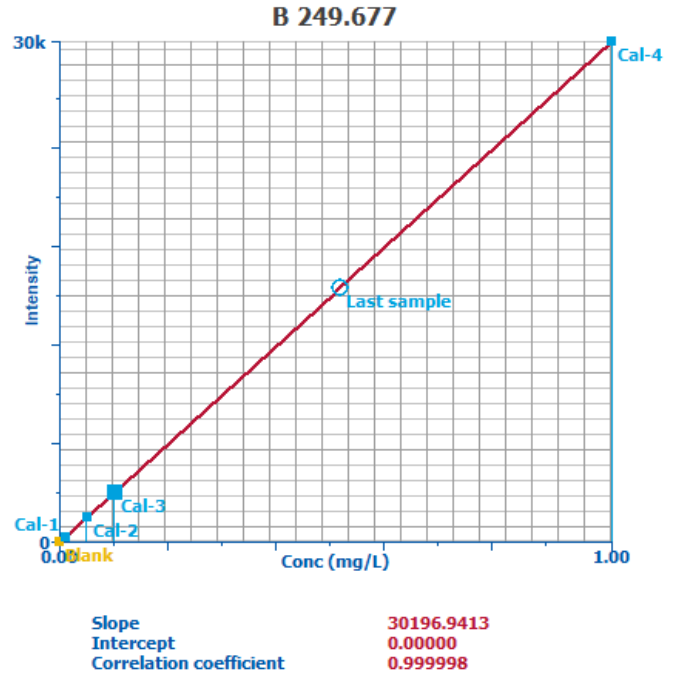
Table 3: Elements, Wavelengths, View, and Standards

Element	Wavelength	Plasma View	Standards
Ag	328.068	Radial	0.025, 0.05, 0.5
Al	394.401	Radial	0.1, 0.5, 1, 10
As	188.979	Axial	0.1, 0.5, 1, 10
B	249.677	Axial	0.01, 0.05, 0.1, 1
Ba	493.408	Radial	0.01, 0.05, 0.1, 1
Be	313.107	Axial	0.01, 0.05, 0.1, 1
Ca	315.887	Radial	0.1, 0.5, 1, 10
Cd	214.440	Axial	0.02, 0.1, 0.2, 2
Co	228.616	Axial	0.02, 0.1, 0.2, 2
Cr	267.716	Axial	0.05, 0.25, 0.5, 5
Cu	324.752	Axial	0.02, 0.1, 0.2, 2
Fe	238.204	Radial	0.1, 0.5, 1, 10
K	766.490	Radial	1, 2, 20
Li	670.784	Radial	0.05, 0.25, 0.5, 5
Mg	285.213	Radial	0.1, 0.5, 1, 10
Mn	257.610	Axial	0.02, 0.1, 0.2, 2
Mo	203.845	Axial	0.1, 0.5, 1, 10
Na	589.592	Radial	0.1, 0.5, 1, 10
Ni	231.604	Axial	0.02, 0.1, 0.2, 2
P	178.221	Axial	0.1, 0.5, 1, 10
Pb	220.353	Axial	0.1, 0.5, 1, 10
Sb	206.836	Axial	0.05, 0.25, 0.5, 5
Se	196.026	Axial	0.05, 0.25, 0.5, 5
SiO_2	251.611	Axial	0.1, 0.5, 1, 10
Sn	189.927	Axial	0.04, 0.2, 0.4, 4
Sr	421.552	Radial	0.01, 0.05, 0.1, 1
Ti	334.940	Axial	0.1, 0.5, 1, 10
Tl	190.801	Axial	0.05, 0.25, 0.5, 5
V	292.402	Axial	0.02, 0.1, 0.2, 2
Zn	206.200	Axial	0.05, 0.25, 0.5, 5
Sc (IS)	361.383	Radial	-
Y (IS)	371.029	Axial	-

All calibration coefficients were 0.9999 or better. Calibrations at the low end and high end are shown in Figure 1. The *ASXPRESS PLUS* consistently delivers sample to the ICP allowing for excellent curve linearity.

Figure 1: Calibration Curves Na and B





Results

Fast

The *ASXPRESS PLUS* significantly reduces analysis time by decreasing sample aspiration time and eliminating the rinse time. To show this savings a batch of samples was analyzed with the *ASXPRESS PLUS* and with standard sample introduction. For the standard method, the rinse was set to use SmartRinse — a feature whereby the instrument analyzes the rinse solution and continues to rinse until the result is below user set concentrations. Thus, rinse time varied from zero to 120 seconds (maximum rinse allowed for this method) depending on the sample. To determine average sample time with this varying rinse, the batch in Table 4 was analyzed using both sample introduction systems. The analysis times are in Table 5. Adding the valve accessory afforded a 62% reduction in analysis time, allowing an additional 23 samples to be analyzed per hour.

Table 4: Typical Batch

Batch
Blank
LCS
Stream
Stream MS
Stream MSD
Influent
Influent MS
Influent MSD

Table 5: Analysis Time and Number of Samples for each system

	Total Run Time	Time per sample	Samples per hour
Standard run	33 min 58 s	4 min 14 s	14
ASXPRESS run	12 min 43 s	1 min 35 s	37
Time Savings	62%		

Most of the time savings is from eliminating the rinse from the total sample time. When using the *ASXPRESS PLUS*, the sample introduction system rinses while the instrument is analyzing the sample. To test the rinsing capability of the system, a standard was prepared at 1 mg/L Ag, 10 mg/L B, Mn, Mo, and 2.5 mg/L Sb. The standard was analyzed 10× with a blank tested before and after analysis. All elements had no change except for B. The boron value in both blanks increased to the same amount (0.030 mg/L). This shows the *ASXPRESS PLUS* was able to rinse the system as efficiently as the standard set-up despite the shorter rinse time. If desired, an additional rinse can be enabled such that the sample introduction system will rinse again prior to aliquoting the sample.

Precise

EPA method 200.7 requires that the RSD of 4 replicates of an instrument performance check (IPC) standard is less than 3%. The IPC was prepared using the same standards as the calibration at a value of half the highest calibration standard. Every 10 samples, at the beginning of runs without the QCS, and at the end of runs, the IPC was analyzed. All elements for all analyses of the IPC had an RSD of less than 2% demonstrating the precision of the *ASXPRESS PLUS*. The average RSD for each element is in Figure 2.

Accurate

For the initial sample run, the calibration was verified with a second source (QCS) analyzed at 1mg/L for most elements with Al and Si at 5 mg/L, Ca, Na, and K at 10 mg/L, and Sn at 2 mg/L. The QCS passed as all elements tested within 5% of actual value. In addition, recoveries of the IPC passed at ±10% of the true value. Results are in Figure 3.

Figure 2: Average RSD of 6 IPC Measurements Using the *ASXPRESS PLUS*

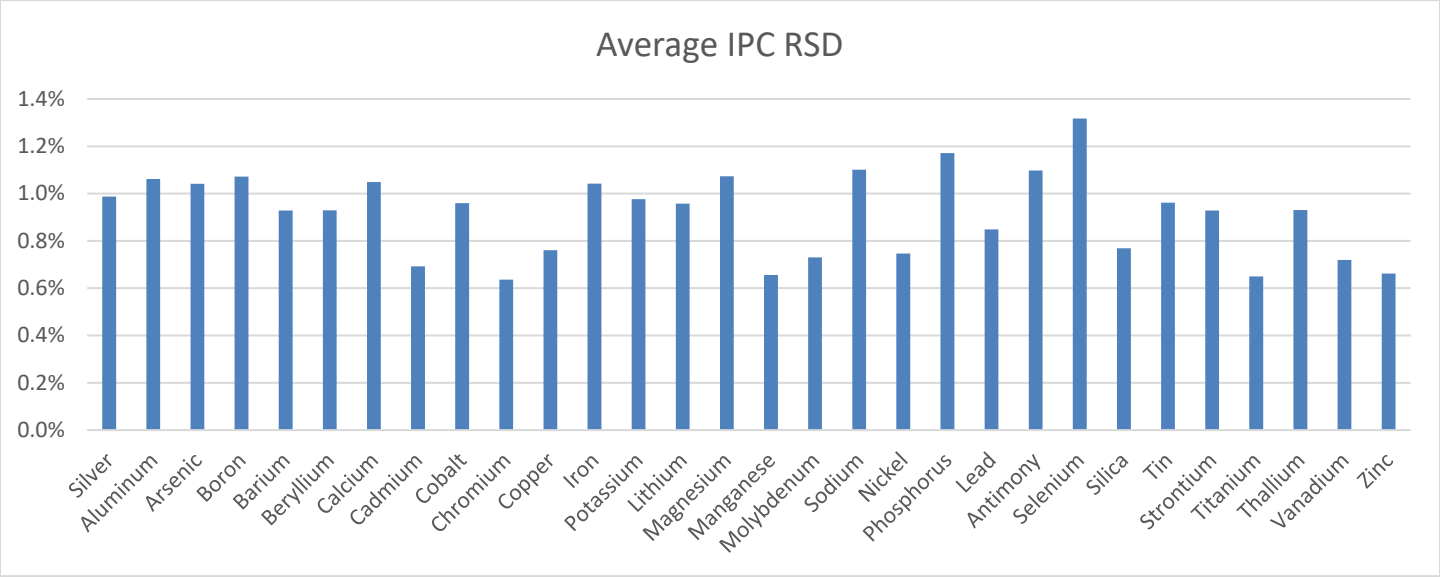
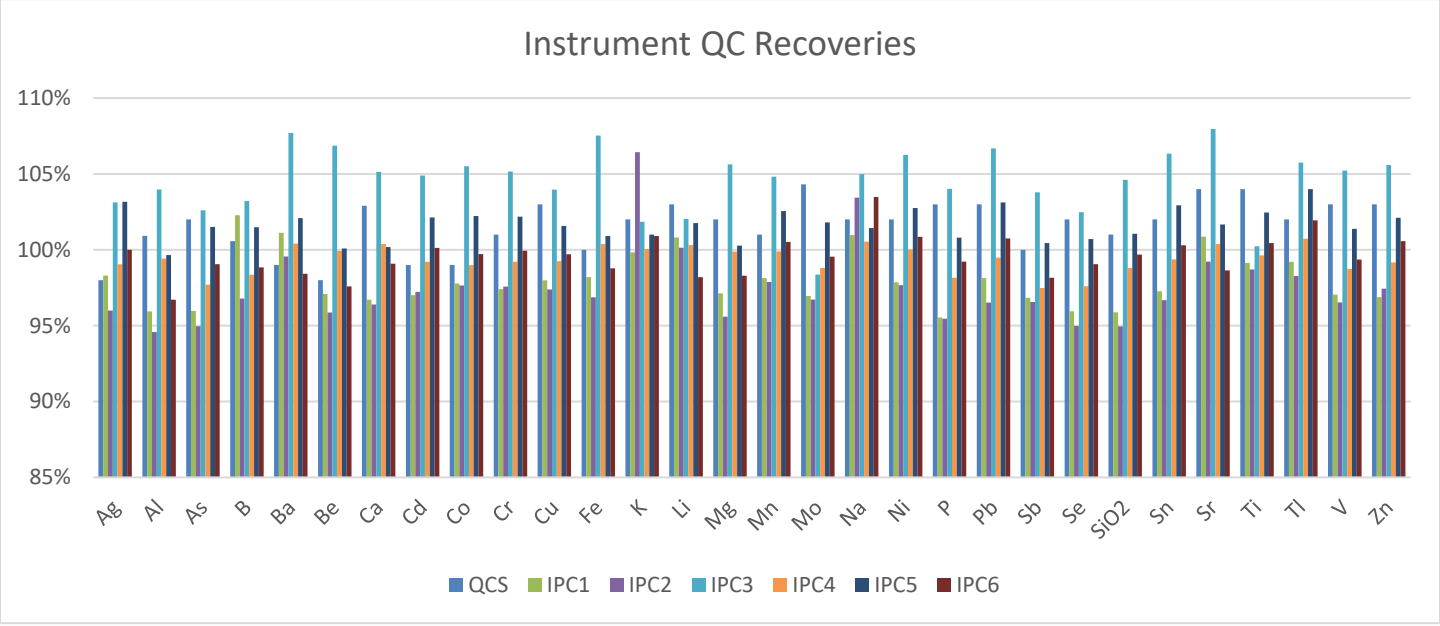


Figure 3: QCS and 6 IPC QC Recoveries



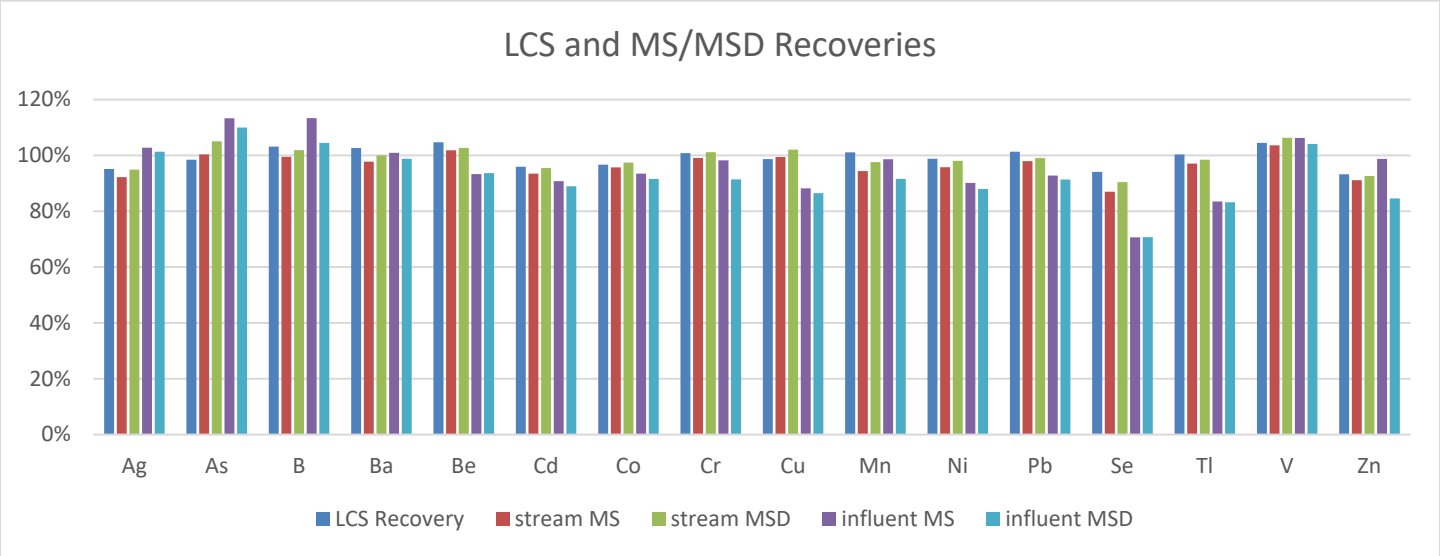
To further demonstrate the accuracy of the *ASXPRESS PLUS*, two NIST standard reference materials, 1640a and 1643f, were analyzed. Recoveries were within 10% for all elements as shown in Table 5. Particularly of note, Ag, Be, Cd, Sb, and Tl have excellent recoveries despite their low certified values.

Spiked samples were also analyzed to demonstrate the accuracy of the *ASXPRESS PLUS*. The stream and influent samples along with a blank were spiked prior to digestion using a second source standard. The final concentration of the spike was 0.2 mg/L. Results for select elements are in Figure 4. All spiked elements had a recovery of 85–115% for the LCS and MS/MSD except for Selenium in the influent. The influent had a recovery of 71% for both the MS and MSD. The result, while low, is still within the 70-130% limits of EPA 200.7. The recoveries show the efficacy of the *ASXPRESS PLUS* in the presence of a complex sample matrix.

Table 5: NIST SRM Results

	1640a			1643f		
	True Value (µg/L)	Measured (µg/L)	% Recovery	True Value (µg/L)	Measured (µg/L)	% Recovery
Ag	8.081	7.414	91.7	0.9606	1.001	104.2
Al	53.0	51.0	96.3	132.5	129.8	97.0
As	8.075	8.101	100.3	56.85	62.56	109.0
B	303.1	314.1	103.6	150.8	160.6	105.4
Ba	151.8	151.3	99.7	513.1	525.6	101.4
Be	3.026	3.078	101.7	13.53	14.09	103.1
Ca	5,615	5,563	99.1	29,140	28,859	98.1
Cd	3.992	3.694	92.5	5.83	6.27	106.1
Co	20.24	19.08	94.2	25.05	24.16	95.5
Cr	40.54	39.20	96.7	18.32	19.11	103.3
Cu	85.75	83.47	97.3	21.44	21.10	97.4
Fe	36.8	38.4	104.3	92.51	98.56	105.5
K	579.9	596	102.8	1,913.3	2,079	107.6
Li	-	-	-	16.42	17.75	107.0
Mg	1,058.6	1,072	101.3	7,380	7,594	101.9
Mn	40.39	40.68	100.7	36.77	37.73	101.6
Mo	45.6	44.7	98.0	114.2	121.3	105.2
Na	3,137	3,183	101.5	18,640	19,763	105.0
Ni	25.32	23.88	94.3	59.2	57.0	95.2
Pb	12.101	12.693	104.9	18.303	19.987	108.1
Sb	5.105	4.782	93.7	54.90	55.38	99.9
Se	20.13	18.53	92.0	-	-	-
SiO_2	5.210	10.180	91.3	-	-	-
Sr	126.03	125.61	99.7	311	327	104.2
Tl	-	-	-	6.823	6.644	96.4
V	15.05	14.590	96.9	35.71	37.98	105.0
Zn	55.64	54.461	97.9	73.7	77.3	103.9

Figure 4: LCS and MS/MSD Results for EPA 3010 Digestion Analyzed by *ASXPRESS PLUS*



Conclusion

The *ASXPRESS PLUS* accessory reduced sample analysis time by 62% while passing the criteria established by EPA 200.7. The system was simple to add to an existing Avio ICP-OES method, only requiring modification to sample introduction and rinse parameters. In addition, the *ASXPRESS PLUS* software provided a user-friendly interface to modify settings such that total method development was minimal. Overall, the *ASXPRESS PLUS* is a perfect addition to laboratories to help meet stringent TATs while maintaining data integrity.

References

1. U.S. EPA. 1994. "Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry," Revision 4.4. Cincinnati, OH. Available from: https://www.epa.gov/esam/method-2007-determination-metals-and-trace-elements-water-and-wastes-inductively-coupled-plasma
2. U.S. EPA. 1992. "SW-846 Test Method 3010A: Acid Digestion of Aqueous Samples and Extracts for Total Metals Analysis by FLAA or ICP Spectroscopy". Available from: https://www.epa.gov/hw-sw846/sw-846-test-method-3010a-acid-digestion-aqueous-samples-and-extracts-total-metals-analysis

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