

## Rapid-Throughput Analysis for EPA Methods 6010C, 200.7 and 200.8 by ICP-AES and ICP-MS

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### ABSTRACT

When coupled to a compatible autosampler, the CETAC *ASXPRESS<sup>®</sup> PLUS* Rapid Sample Introduction System optimizes sample introduction to increase productivity for the analysis of environmental samples. Sample throughput for ICP-AES and ICP-MS can be more than doubled with no change to analytical instrument parameters, except for the elimination of rinse times and a reduction of overall read delay times. These improvements can be achieved with various instrument platforms from multiple manufacturers across a number of environmental methods. Additionally, instrument stability is improved by use of the *ASXPRESS<sup>®</sup> PLUS* for long run times while meeting calibration and method QC requirements.

### INTRODUCTION

The US Environmental Protection Agency (EPA) maintains various methods for the analysis of environmental samples which are relied upon by many regulatory agencies. The EPA's methods are often lengthy and detailed with provision of specific instructions concerning sample collection, preservation, and treatment as well as required and recommended procedures for instrument calibration, tuning, and interference corrections. Compliance usually requires the methods be adhered to with no changes or modifications.

Even with rigorous compliance standards in place, it is desirable in most laboratories to increase productivity. More productive analyses make better use of funds and provide a lower cost of instrument ownership. By employing an advanced sample introduction system to reduce sample delivery, stabilization, and washout times, the amount of time spent by the analytical instrument on the entire analysis can be optimized. Such a system can be introduced into the analysis without altering method parameters such as elements, measurement times, and number of replicates.



## EXPERIMENTAL

The experiments reported here test an accelerated sampling system, consisting of a CETAC *ASXPRESS*<sup>®</sup> *PLUS* Rapid Sample Introduction System, coupled to a CETAC autosampler. The accelerated system optimizes sample introduction by significantly increasing sample throughput and reducing costs of argon, electricity, and maintenance (e.g. sample exposure to ICP torch, sampling cones, etc.) for ICP-AES or ICP-MS analysis. The system allows multiple functions to occur simultaneously which would otherwise take place separately. See Figures 1 through 3 for the setup of the *ASXPRESS*<sup>®</sup> *PLUS* with various ICP-AES and ICP-MS instruments.

A standard analysis system relies upon a single peristaltic pump to both deliver samples to the nebulizer and rinse the sample flow path between sample deliveries. The *ASXPRESS*<sup>®</sup> *PLUS* system comprises a high speed vacuum pump with a 6-port switching valve in addition to the ICP instrument's peristaltic pump, as illustrated in Figure 4. The 6-port valve allows the use of both pumps simultaneously, significantly reducing total sample analysis time.

The use of a 6-port valve effectively divides each analysis into two stages:

First, while the valve is in the "load" position, the vacuum pump rapidly fills the sample loop, while the ICP peristaltic pump simultaneously transports carrier solution to the nebulizer to maintain plasma stability. The carrier stream is segmented by introducing air bubbles. This facilitates faster, more effective washout of the sample flow path.

In the second or "inject" position, the loaded sample is transported to the nebulizer by the carrier solution flowing through the ICP peristaltic pump. Simultaneously, the autosampler probe is moved to the rinse station and the uptake flow path is flushed with rinse solution via the vacuum pump.

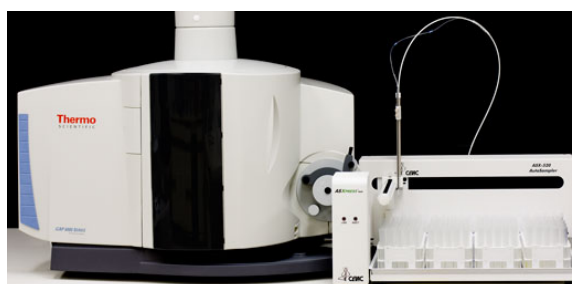


Figure 1. *ASXPRESS*<sup>®</sup> *PLUS* with Thermo Scientific iCAP 6500 ICP-AES

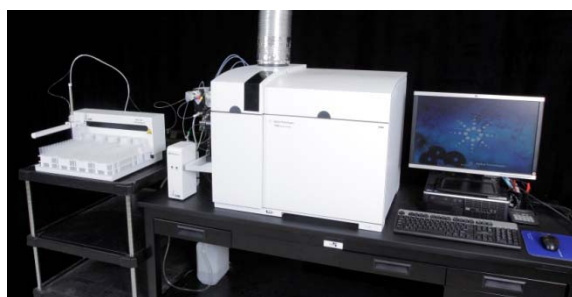


Figure 2. *ASXPRESS*<sup>®</sup> *PLUS* with Agilent 7700 ICP-MS

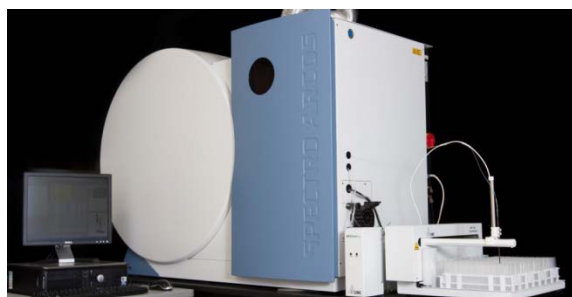


Figure 3. *ASXPRESS*<sup>®</sup> *PLUS* with SPECTRO ARCOS ICP-AES

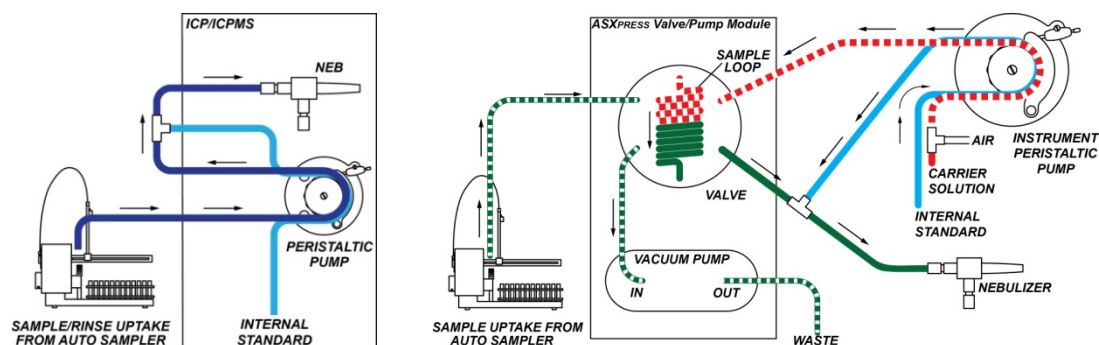


Figure 4. Standard analysis system setup (Left); Analysis setup with *ASXPRESS*<sup>®</sup> *PLUS* (Right)

**Table 1. ASXPRESS® PLUS Configuration Parameters**

Parameter	Time (s) – 6010C	Time (s) – 200.7	Time (s) – 200.8
Loop Rinse	2.0	1.0	0.5
Rinse Evacuation	2.0	1.0	1.0
Loop Load	10.0	1.0	0.5
Equalization	2.0	1.0	1.0
Time to Evacuate	1.0	1.0	1.0
Probe Rinse	5.0	1.0	1.0
Rinse Station Refill	4.0	3.5	3.0
Loop Volume	5.0 mL	2.5 mL	1.5 mL

**Table 2. Approximate analysis times per sample before and after implementation of ASXPRESS® PLUS system**

EPA Method	Initial Analysis Time (min per sample)	Analysis Time w/ ASXpress® PLUS (min per sample)	Time Savings (%)
6010C	6	3.5	40
200.7	4	2	50
200.8	7.5	3.5	55

Since most environmental laboratories need to cope with large numbers of samples, the sample introduction approach used by the ASXPRESS® PLUS has particular application to environmental analyses. It can dramatically increase sample throughput without affecting method requirements or negatively impacting data quality.

Initial configuration parameters developed for the accelerated system allow it to be integrated without modification to the analysis method. A Windows® based configuration tool is used to store parameters shown in Table 1.

Instrument parameters such as gas flows, plasma power, mode stabilization times, measurement times, and number of replicates were not manipulated with the addition of the ASXPRESS® PLUS. The flush and rinse times were not necessary with the accelerated system and the delay time was reduced.

Each method used the nebulizer and spray chamber already in place on the respective ICP instrument.

## RESULTS

Testing of the ASXPRESS® PLUS system showed good precision for 3 replicate measurements over all elements covered by each EPA Method. Most RSD's are well below 1%.

The accelerated system achieved a time savings of 40–55%, as shown in Table 2, while preserving the original data quality.

### CARRYOVER

Following EPA Method 200.8 using an Agilent 7700 ICP-MS equipped with the ASXPRESS® PLUS system, carryover was tested by running a high standard followed by five replicate blanks. The results given below in Table 3 were calculated using the following formula:

$$\text{Carryover} = \frac{\text{Blank Value}}{\text{Standard Value}} \times 100\%$$

(Data was supplied by a laboratory using a CETAC QuickTrace<sup>®</sup> Mercury Analyzer for Hg; Hg was not measured by ICP-MS. Th and U were not reported.)

Carryover was also reduced following EPA Method 6010C using the CETAC ASXPRESS<sup>®</sup> PLUS with the Thermo Scientific iCAP 6500 ICP-AES. Carryover was tested using highly concentrated Fe and Na samples and found to be less than 0.02%.

In addition to the use of a segmented carrier stream and a simultaneous analysis and rinsing scheme, the sample never comes into contact with the peristaltic pump tubing. This feature further helps to minimize carryover.

#### CALIBRATION & PERFORMANCE

EPA Method 6010C guidelines state that calibration correlation coefficients of 0.998 or better must be achieved. With the ASXPRESS<sup>®</sup> PLUS system in use on a Thermo iCAP 6500 ICP-AES, this is easily obtained. Correlation coefficients for all elements except Hg are listed in Table 4. (Data was supplied by a laboratory using a CETAC QuickTrace<sup>®</sup> Mercury Analyzer for Hg; Hg was not measured by ICP-AES.)

Calibration is sometimes the most frustrating and time consuming part of the analysis for the user. A run cannot begin until a calibration has been performed and the subsequent necessary checks have verified calibration and overall instrument performance to be within specifications and acceptable limits. A user will

**Table 3. Carryover Data for EPA 200.8 using an Agilent 7700 ICP-MS equipped with ASXPRESS<sup>®</sup> PLUS**

Element	m/z	Average Measured Carryover (%)	Element	m/z	Average Measured Carryover (%)
Be	9	0.0148	As	75	0.0130
Na	23	-0.0080	Se	78	0.0499
Mg	24	0.0054	Mo	95	0.0151
Al	27	-0.5152	Mo	98	0.0122
K	39	0.0050	Ag	107	-0.0068
Ca	44	0.0047	Cd	111	-0.1023
V	51	0.0059	Sb	121	0.0070
Cr	52	0.0044	Sb	123	0.0075
Mn	55	0.0031	Ba	137	0.0040
Fe	56	0.0056	Tl	205	0.0111
Co	59	0.0051	Pb	206	0.0040
Ni	60	-0.0161	Pb	207	0.0048
Cu	63	0.0094	Pb	208	0.0047
Zn	66	-0.0046			

**Table 4. Calibration correlation coefficients for EPA 6010C**

Element	$\lambda$ (nm)	Coefficient	Element	$\lambda$ (nm)	Coefficient
Al	308.215	0.99998	Mn	260.569	0.99993
Sb	206.833	0.99976	Mo	202.095	0.99983
As	189.042	0.99996	Ni	231.604	0.99995
Ba	455.404	0.99994	P	178.287	0.99989
Be	313.107	0.99977	K	766.491	0.99998
B	249.773	0.99998	Se	196.090	0.99982
Cd	214.438	0.99956	Si	251.612	0.99997
Ca	317.933	0.99911	Ag	328.068	0.99800
Cr	267.716	0.99994	Na	589.592	0.99986
Co	228.616	0.99999	Sr	407.771	0.99998
Cu	324.754	0.99958	Tl	190.864	0.99929
Fe	259.941	0.99974	Sn	189.991	0.99991
Pb	220.353	0.99992	Ti	334.941	0.99995
Li	670.780	0.99970	V	292.464	0.99997
Mg	279.079	0.99997	Zn	206.200	0.99942

have to tend to the instrument during this process to ensure that the instrument is ready for the sample set. If an initial check is not passed for whatever reason, the user will have to rerun the calibration before the samples can be allowed to run unattended. The accelerated system greatly reduces the calibration time which is significant and appreciable in the eyes of the user. Below, Figure 8 shows some EPA 200.7 calibration data obtained using the *ASXPRESS<sup>®</sup> PLUS* on a SPECTRO Analytical ARCOS ICP-AES.

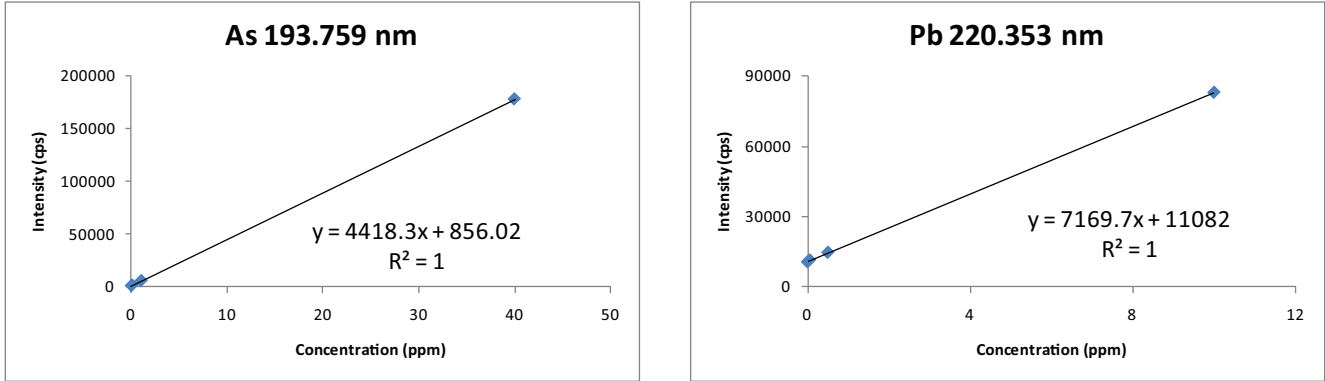


Figure 5. Calibration Plots Showing Linearity for EPA 200.7 elements with *ASXPRESS<sup>®</sup> PLUS* on SPECTRO ARCOS ICP-AES

A set of eight production samples were analyzed on the Thermo iCAP 6500 ICP-AES before and after the *ASXPRESS<sup>®</sup> PLUS* was installed. Correlation plots were then generated to establish how well the two sample introduction setups agreed with one another. The data obtained from the original setup was plotted against that obtained from the accelerated system setup. The closer the slopes and correlation coefficients are to 1.0 for each element graphed, the closer in agreement the two sets of data are. A selection of graphs is displayed in Figure 6.

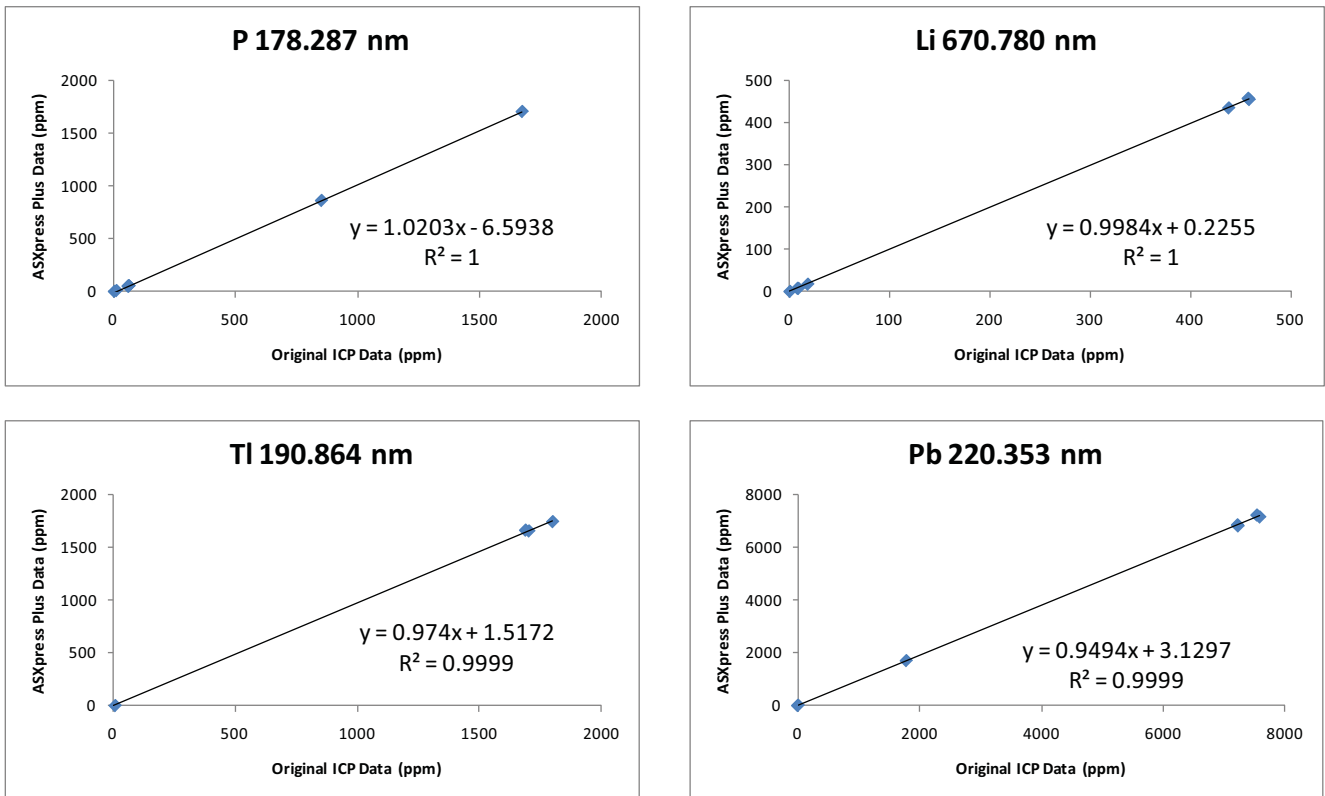


Figure 6. Reproducibility for EPA 6010C elements with *ASXPRESS<sup>®</sup> PLUS*



**PRECISION, ACCURACY, & STABILITY**

Over time or sample volume, ICP-MS signal can drift. One of the main reasons for such drift is directly related to the sample matrix coming into contact with the sampling cones. With the use of the *ASXPRESS® PLUS*, the instrument only comes into contact with the matrix during data acquisition. This dramatically reduces the instrument exposure to the matrix thereby reducing drift. Since the system is also able to run many more samples per unit time, the drift per unit number of samples is also reduced. Precision and accuracy were tested by running a continuing calibration verification (CCV) standard thirty consecutive times on an Agilent 7700 ICP-MS. Data is shown in Table 5.

Precision and accuracy were also tested on a Thermo iCAP 6500 ICP-AES by running a CCV standard five consecutive times. The precision was 1% or better for all elements analyzed across the five standard measurements. The stability can be better visualized with the graphs shown in Figure 7.

**CONCLUSION**

Existing analysis methods for EPA 6010C have been found to require 6 minutes per sample to meet analysis criteria such as throughput, precision, passing QCs and accuracy of results. Various time tests were conducted using the CETAC *ASXPRESS® PLUS* with the Thermo Scientific iCAP 6500 ICP-AES. Sampling time was cut to ~3.5 minutes per sample when using the accelerated system while still meeting all analysis criteria. A time saving of greater than 40% was realized.

Similarly, the existing analysis methods for EPA 200.7 were found to require approximately 2 minutes per sample in order to meet analysis criteria. Time tests conducted using the CETAC *ASXPRESS® PLUS* with the SPECTRO ARCOS ICP-AES found analysis time reduced to 1 minute per sample while still meeting all the criteria, realizing a 50% time savings.

**Table 5. Repeatability Data for EPA 200.8**

Element	m/z	Average Measured Result (ppb)	RSD (%)	Known Value (ppb)	Average Recovery (%)
Be	9	23.1	1.2	25	92.2
Na	23	2491.8	0.8	2500	99.7
Mg	24	2507.5	0.8	2500	100.3
Al	27	23.9	2.2	25	95.4
K	39	2516.2	1.4	2500	100.6
Ca	44	2426.2	0.9	2500	97.0
V	51	23.5	0.7	25	94.1
Cr	52	23.9	0.9	25	95.7
Mn	55	23.4	0.7	25	93.5
Fe	56	2491.0	0.6	2500	99.6
Co	59	24.8	0.9	25	99.2
Ni	60	25.1	1.0	25	100.6
Cu	63	24.5	1.0	25	98.1
Zn	66	25.2	1.1	25	100.8
As	75	24.8	0.7	25	99.2
Se	78	25.7	2.2	25	102.7
Mo	95	22.9	1.2	25	91.6
Mo	98	23.1	1.2	25	92.3
Ag	107	2.5	3.2	2.5	101.3
Cd	111	24.9	1.2	25	99.7
Sb	121	24.2	1.1	25	96.8
Sb	123	24.3	1.1	25	97.1
Ba	137	24.5	1.1	25	98.2
Tl	205	25.1	1.1	25	100.2
Pb	206	24.5	1.1	25	98.1
Pb	207	24.5	1.1	25	97.9
Pb	208	24.6	1.0	25	98.5

Analysis time for EPA 200.8 was reduced from 7.5 minutes per sample to 3.5 minutes per sample when using the Agilent 7700 ICP-MS. A 55% time savings was realized while meeting all criteria.

As shown in the data comparison, use of the ASXPRESS® PLUS results in the same quality of data with a significant analysis time reduction of 40 to 55%

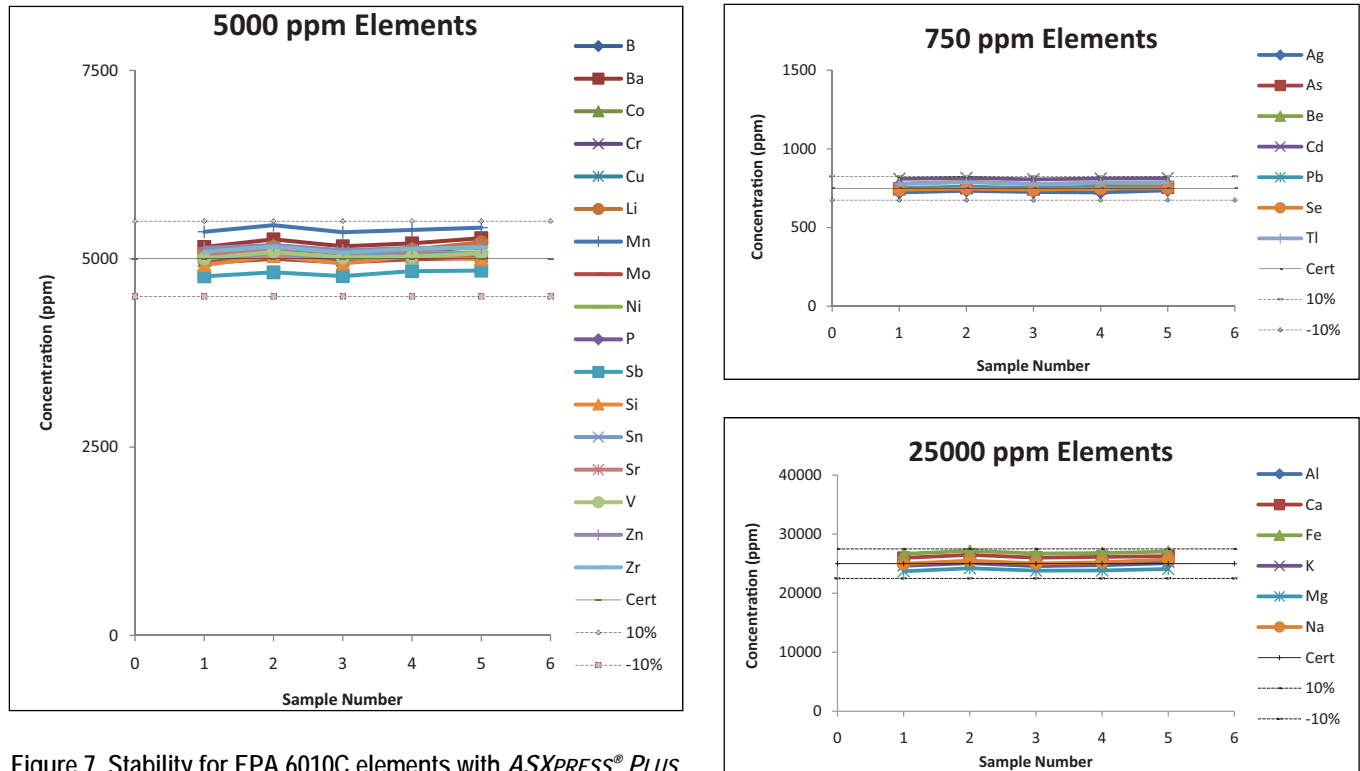


Figure 7. Stability for EPA 6010C elements with ASXPRESS® PLUS

## REFERENCES

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2. EPA Method 200.8, "Methods for the Determination of Metals in Environmental Samples – Supplement 1", EPA-600/R-94-111, May 1994, Available at NTIS, PB 94-184942.
3. USEPA SW-846 Method 6010C, Revision 3, November 2000.