



## APPLICATION NOTE

### ICP-Optical Emission Spectroscopy

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## Rapid Water Analysis Following U.S. EPA 200.7 Using the Avio 560 Max ICP-OES

### Introduction

The U.S. EPA developed Method 200.7 to address the determination of 30 metals and trace elements

in waters, wastewaters, and solid wastes by ICP-OES<sup>1</sup>. Having been around since 1994, Method 200.7 has been implemented routinely in environmental labs throughout the United States.

With the growth of industry, pollution and wastes continue to be produced in greater and greater quantities, resulting in an increasing number of samples which require analysis per Method 200.7. In an effort to meet this increased demand, PerkinElmer's Avio® 560 Max fully simultaneous ICP-OES incorporates a built-in High Throughput System (HTS) for rapid sample-to-sample times. The HTS is a valve-and-loop system which minimizes the time required for the sample to reach the nebulizer and washout time after analysis by using a vacuum to both rapidly fill and wash the sample loop.

This work describes the analysis of wastewaters following Method 200.7 using the Avio 560 Max ICP-OES, building on previous work<sup>2</sup>.

## Experimental

### Samples and Sample Preparation

Development and evaluation of the methodology were accomplished with four different wastewater certified reference materials:

- Wasterwaters C, D, and H (High Purity Standards™, Charleston, South Carolina, USA)
- WasteWatR™, Trace Metals (ERA, Golden, Colorado, USA)

These standards were supplied as concentrates and diluted as directed on the certificates. Samples were prepared in accordance with Method 200.7: 50 mL were acidified with 2 mL of 1:1 HNO<sub>3</sub> and 1 mL of 1:1 HCl, then placed in a hot block and heated to a temperature of  $\approx 85$  °C. The solutions were removed with  $\approx 20$  mL final volume, allowed to cool, and diluted to 50 mL with deionized water for analysis.

All measurements were made against external calibration curves, where the standards were prepared at the concentrations in Table 1 in 2% HNO<sub>3</sub> (v/v). The internal standard (yttrium, Y) was prepared in 2% HNO<sub>3</sub>(v/v) and added to the sample stream via a port in the HTS valve.

Interelement corrections (IECs) were applied to all measurements. The IEC solutions were run at the concentrations specified within Method 200.7, except

Table 1. Calibration Standards

Element	Standard 1 (mg/L)	Standard 2 (mg/L)
Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ti, Tl, V, Zn	0.5	1
Na, Mg, K, Ca	10.5	21

Table 2. Avio 560 Max ICP-OES with HTS Instrumental Parameters

Parameter/Component	Value/Description
Sample Uptake Tubing	Black/Black (0.76 mm id) PVC
Internal Standard Tubing	Green/Orange (0.38 mm id), PVC
Drain Tubing	Gray/Gray (1.30 mm id), Santoprene
Nebulizer	MEINHARD® K1
Spray Chamber	Baffled Glass Cyclonic
Carrier	2% HNO <sub>3</sub> (v/v)
Carrier Flow Rate	0.8 mL/min
Sample Loop Volume	1 mL
Injector	2.0 mm id Alumina
Nebulizer Gas Flow	0.70 L/min
Auxiliary Gas Flow	0.2 L/min
Plasma Gas Flow	8 L/min
Torch Depth	-3
Integration	Auto
Read Time Range	0.5-5 sec
Loop Fill Time	4 sec
Loop Rinse Time	3 sec
Replicates	2

where they were outside the linear range. In these cases, the concentrations of the IEC solutions were adjusted to be within the linear range.

### Instrumental Conditions

All analyses were performed on an Avio 560 Max ICP optical emission spectrometer (OES), using the High Throughput System (HTS)<sup>3</sup> for sample introduction connected to an S23 Autosampler. Instrument parameters and conditions are shown in Table 2, along with the analytes, analytical wavelengths, and plasma view modes in Table 3. Standard sample introduction components and conditions were used, including a total argon flow of 9 L/min.

Although Method 200.7 states that four replicates must be used, a common implementation is to use two or three replicates to increase sample throughput. To make this work more relevant to commercial labs, two replicates were used

Table 3. Analytes, Wavelengths, and Plasma View Mode

Element	Wavelength (nm)	Plasma View Mode
Ag	328.068	Axial
Al	308.215	Radial
As	188.979	Axial
B	249.677	Axial
Ba	493.408	Radial
Be	313.107	Radial
Ca	315.887	Radial
Cd	214.440	Axial
Ce	413.764	Axial
Co	228.616	Axial
Cr	267.716	Axial
Cu	324.752	Axial
Fe	238.204	Radial
K	766.490	Radial
Li	670.784	Radial
Mg	285.213	Radial
Mn	257.610	Axial
Mo	203.845	Axial
Na	589.592	Radial
Ni	231.604	Axial
P	178.221	Axial
Pb	220.353	Axial
Sb	206.836	Axial
Se	196.026	Axial
Si	251.611	Radial
Sn	189.927	Axial
Sr	421.552	Radial
Ti	334.940	Axial
Tl	190.801	Axial
V	292.402	Axial
Zn	206.200	Axial
Y (Internal Standard)	371.029	Axial and Radial

for all measurements. All analyses were performed using auto-integration with a read-time range of 0.5-5 seconds, which provided fast analysis for high-level analytes while also allowing for accurate measurements of low-level analytes. To simplify analysis, auto background correction was used.

Using these conditions, sample-to-sample time was approximately 60 seconds. Because auto integration with variable read times was used for optimum performance, the sample-to-sample time varies depending on the analyte concentrations in the samples: for higher concentrations, sample-to-sample time will be less than 60 seconds; for samples with lower concentrations, the sample-to-sample time can be slightly longer than 60 seconds. Three or four replicates can also be implemented to meet standard operating procedures with minimal sample-to-sample time gain.

## Results and Discussion

In order to be compliant with Method 200.7, quality control (QC) criteria accounting for sample handling/preparation and the instrumental analysis must be satisfied. The following criteria relate specifically to instrumental analysis and will be assessed to determine the viability of the Avio 560 Max system: linear dynamic range, method detection limits (MDLs), instrument performance checks (IPCs), spectral interference checks (SICs), accuracy, and stability.

### Using Smart Software to Facilitate Data Analysis

Syngistix for ICP software (version 5.1 or higher) includes a host of smart features to facilitate data analysis and interpretation, including smart workflow, smart methods, smart monitoring, and smart data. While all of these were used when acquiring data for Method 200.7, only a couple of the features will be discussed here.

One of the most important aspects of acquiring solid data is reviewing and assuring good linearity for calibration curves. This is easily done in Data Viewer, as shown in Figure 1.

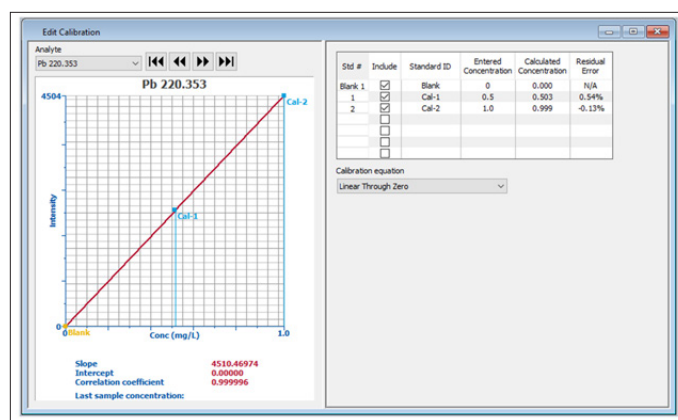


Figure 2. Detailed calibration information displayed in the Edit Calibration window.

When data is acquired in Data Viewer, thumbnails of the calibration curves appear which provide the user a quick overview. For more detailed analyses, when each thumbnail is clicked, details of the calibration curve appear, which show the correlation coefficients, equation, corrected intensities, entered concentrations, calculated concentrations for each standard, and the residual error for each standard. If, for any reason, the calibration curve needs to be modified (for example, if a standard was out of range), the same information is displayed in the Edit Calibration window (Figure 2), which allows the calibration information to be edited.

When running long-term stability, it is also important to monitor the stability of the internal standard. The normalized internal standard response (normalized to the calibration blank) is displayed automatically in Data Viewer in real-time (Figure 3), allowing the user to monitor the real-time performance of an active run.

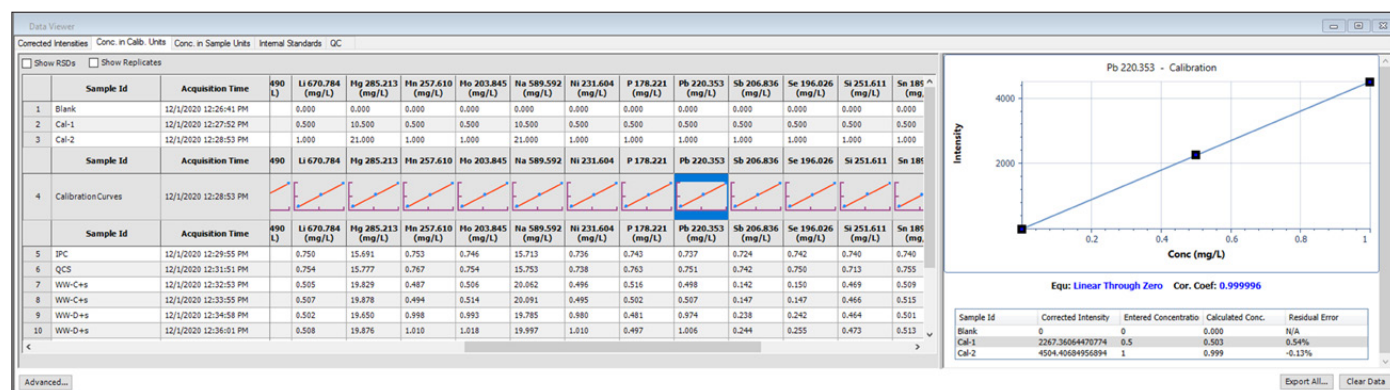


Figure 1. Calibration information displayed in Data Viewer.

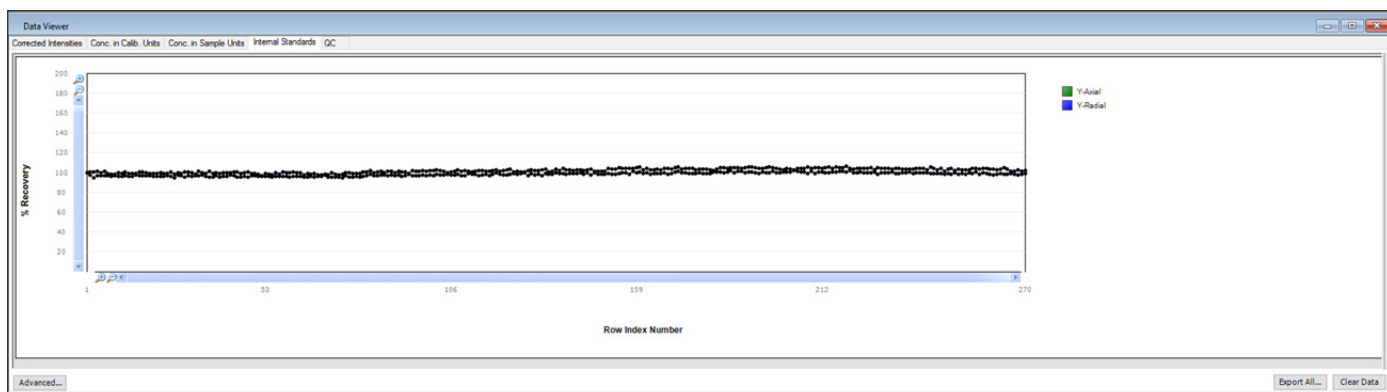


Figure 3. Internal standard plot in Data Viewer.

### Initial QC: Initial Performance Check and Quality Control Sample

To verify the quality of the calibration curve, an initial performance check (IPC) must be analyzed immediately after the calibration. The IPC must be a separate standard made from the same stock standard as the calibration standards. In addition, a quality control sample (QCS) must be made to the same concentration as the IPC, but from a second-source standard to validate the concentration of the stock solutions used for the calibration standards. Both the IPC and QCS must recover within 5% of their true values for the analysis to proceed.

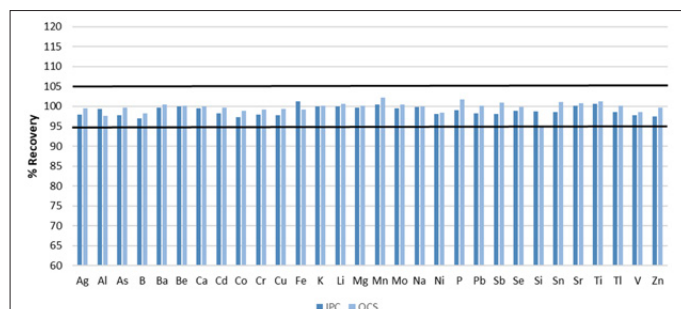


Figure 4. Recoveries for initial IPC and QCS.

For this evaluation, all elements were present at 0.75 ppm, except the minerals (Ca, K, Mg, Na) which were added at 21 ppm. Figure 4 shows that both the QCS and IPC recovered within the required 5% for all analytes.

### Method Detection Limits

Method 200.7 states that method detection limits (MDLs) are determined by measuring a standard seven times which has been spiked with analytes at 2-3 times the instrumental detection limits (IDLs). The standard deviation of these seven measurements is then multiplied by 3.14 to obtain MDLs at the 99% confidence level. Before the MDLs can be measured, the IDLs must be determined. IDLs were calculated by multiplying the standard deviation of 10 blank measurements by three. Figure 5 shows the determined MDLs plotted alongside the certified analyte concentrations in the four reference materials analyzed in this study. (Note that not all analytes were contained in the reference materials.) The MDLs are significantly lower than the certified values, demonstrating the ability of the methodology to easily measure low-level analytes in wastewaters.

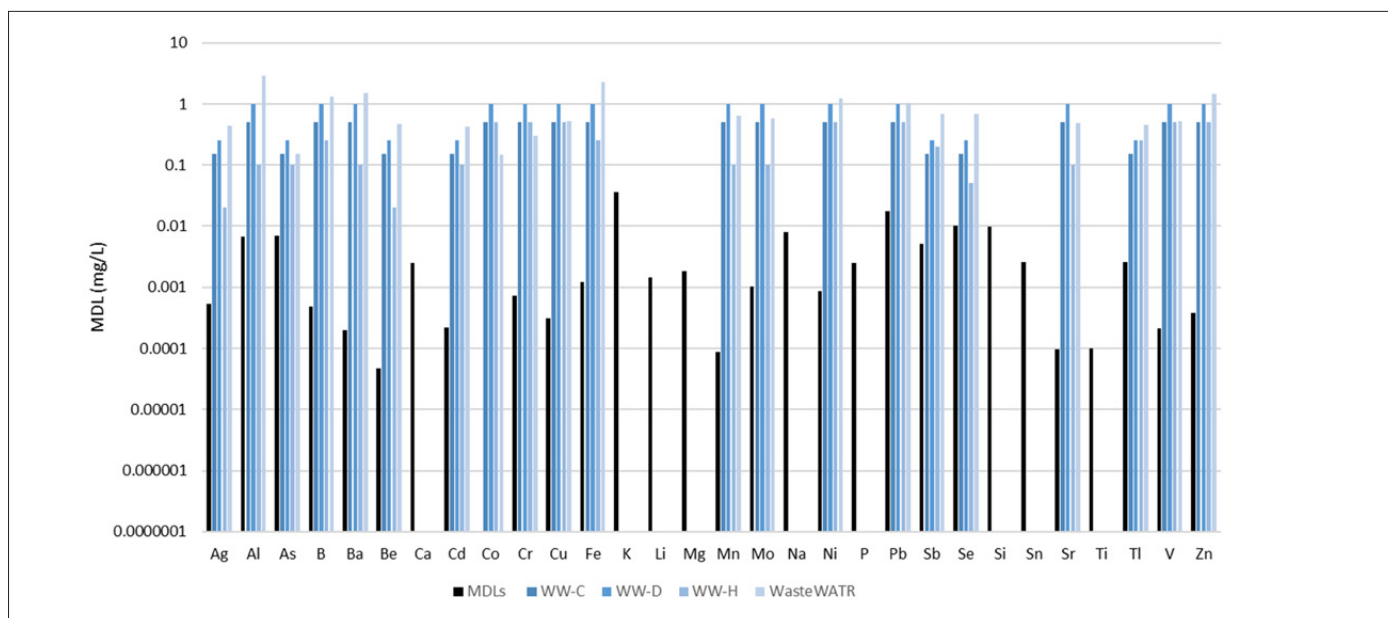


Figure 5. Method detection limits (black) along with certified concentrations in four reference materials (shades of blue). Not all analytes were certified in the reference materials.



## Linear Dynamic Range

Method 200.7 defines the linear dynamic range as the highest concentration which recovers within 10% of its true value as measured against the calibration curve used for analysis. All linear dynamic range measurements were made in multi-element solutions to make them more relevant to sample analyses, which are always multi-element solutions.

As shown in Table 4, the linear dynamic range is the highest concentration analyzed for most elements, which represents the highest typical concentrations in wastewaters, not the limit of the Avio 560 Max ICP-OES. The linear range of the Avio 560 Max can be extended further, if needed, by the selection of less sensitive wavelengths, changing the plasma viewing mode (i.e axial/radial), varying the torch position, changing the viewing height in the plasma to radial mode, using high-resolution mode, and/or using a less sensitive sample introduction system.

Table 4. Linear Dynamic Range

Elements	Linear Range (mg/L)
Cd, Mn, Sr	30
Ba	40
Co, Cr, Ni, Sn, Ti, Tl	50
Be	70
Ag, Al, As, B, Cu, Fe, Li, Mg, Mo, P, Pb, Sb, Se, Si, V, Zn	100*
Ca, K, Na	500*

\*= highest concentration evaluated

## Accuracy

With the fundamental characteristics of the methodology established, the accuracy was determined through the analysis of four reference materials, whose certified values are shown in Table 5. The analyte recoveries for all of the certified elements appear in Figure 6. With all recoveries within 10% of their certified values, the accuracy of the methodology is established.

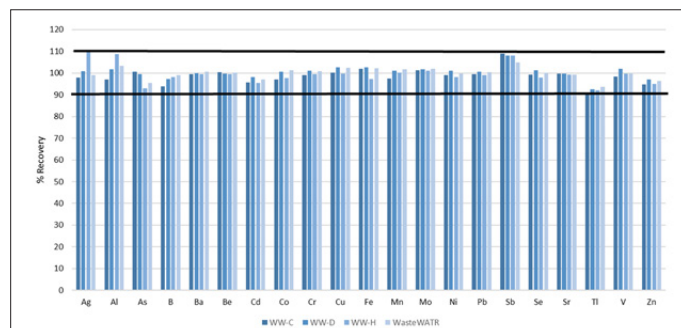


Figure 6. Certified analyte recoveries in four different wastewater reference materials.

However, not all the elements specified in Method 200.7 are certified in the reference materials. These elements were spiked into the reference materials (prior to digestion) at the concentrations shown in Table 6, and their recoveries appear in Figure 7. Again, all recoveries are within 10%, further demonstrating accuracy.

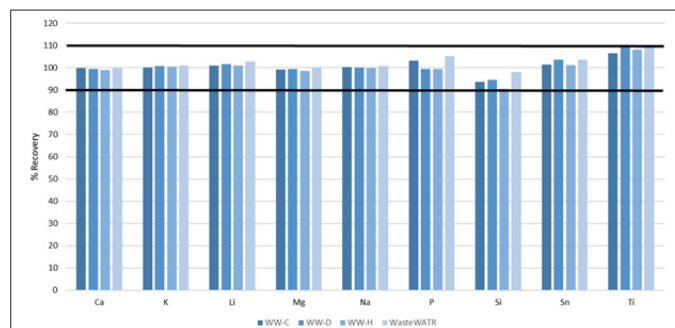


Figure 7. Recoveries of non-certified elements spiked into four wastewater CRMs.

Table 5. Certified Values in Wastewater Reference Materials (all units in mg/L)

Element	Wastewater C	Wastewater D	Wastewater H	WasteWATR
Ag	0.15	0.25	0.02	0.444
Al	0.5	1	0.1	2.91
As	0.15	0.25	0.1	0.151
B	0.5	1	0.25	1.33
Ba	0.5	1	0.1	1.5
Be	0.15	0.25	0.02	0.468
Cd	0.15	0.25	0.1	0.430
Co	0.5	1	0.5	0.147
Cr	0.5	1	0.5	0.302
Cu	0.5	1	0.5	0.526
Fe	0.5	1	0.25	2.25
Mn	0.5	1	0.1	0.636
Mo	0.5	1	0.1	0.578
Ni	0.5	1	0.5	1.21
Pb	0.5	1	0.5	1.05
Sb	0.15	0.25	0.2	0.693
Se	0.15	0.25	0.05	0.678
Sr	0.5	1	0.1	0.489
Tl	0.15	0.25	0.25	0.461
V	0.5	1	0.5	0.525
Zn	0.5	1	0.5	1.46

Table 6. Spiked Concentrations of Non-Certified Elements in Wastewater CRMs

Analyte	Concentration (mg/L)
Li, P, Si, Sn, Ti	0.75
Ca, K, Mg, Na	20

## Stability

With the accuracy established, stability was determined by measuring wastewater samples and monitoring the recoveries of the IPC standards, which are run every 10 samples. Figure 8 shows that all IPCs recover within 10% of their certified values over the 4-hour run, with a sample-to-sample time averaging 1 minute, demonstrating the exceptional stability of the system, despite the rapid sample-to-sample time of  $\approx 60$  seconds. Instrumental design considerations, including the vertical torch and Flat Plate™ plasma technology, result in excellent stability, while taking advantage of the dual view capability and continuously switching between axial and radial plasma viewing modes for each sample.

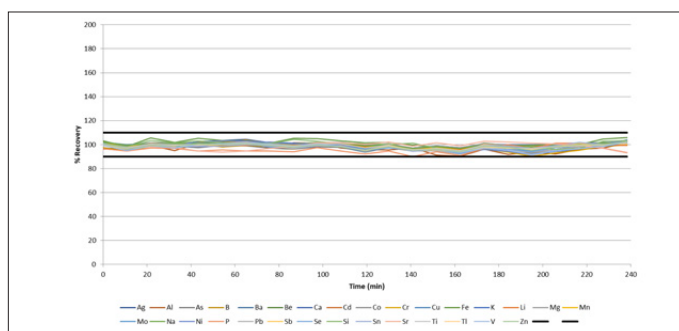


Figure 8. IPC recoveries during a 4-hour run of wastewaters, with a sample-to-sample time of  $\approx 60$  seconds.

## Conclusion

This work demonstrates the ability of the Avio 560 Max ICP-OES to perform rapid analysis – 60 sec sample-to-sample time – of wastewater following the guidelines provided in U.S. EPA Method 200.7. With accuracy, reliability, robustness, and stability demonstrated through the analysis of reference materials and QC checks, the Avio 560 Max ICP-OES with built-in HTS provides a robust solution for wastewater analysis, while using a total argon flow of 9 L/min. The low argon consumption (9 L/min plasma flow) of the Avio 560 Max ICP-OES provides a faster return on investment for all laboratories, while the HTS significantly reduces sample uptake and washout times compared to conventional sample introduction, further increasing sample throughput.

## References

1. Method 200.7, Revision 4.4: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma- Atomic Emission Spectrometry”, United States Environmental Protection Agency, 1994.
2. “Analysis of Wastewaters Following U.S. EPA 200.7 using the Avio 550 Max ICP-OES”, Application Note, PerkinElmer Inc., 2020.
3. “High Throughput System for ICP-MS/OES”, Product Note, PerkinElmer Inc., 2020.

## Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black, (0.76 mm id), PVC, flared	N8152407
Internal Standard Tubing, Orange/Green (0.38 mm id), PVC, flared	N8152403
Drain Tubing, Gray/Gray (1.30 mm id), Santoprene	N8152415
Instrument Calibration Standard 1: 5000 mg/L Ca, K, Mg, Na	N9300218 (125 mL)
Instrument Calibration Standard 2: 100 mg/L 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	N9301721 (125 mL)
Boron Standard, 1000 mg/L	N9300016 (125 mL) N9303760 (500 mL)
Lithium Standard, 1000 mg/L	N9303781 (125 mL) N9300129 (500 mL)
Phosphorus Standard, 1000 mg/L	N9303788 (125 mL) N9300139 (500 mL)
Silicon Standard, 1000 mg/L	N9303799 (125 mL) N9300150 (500 mL)
Yttrium Standard, 1000 mg/L	N9303810 (125 mL) N9300167 (500 mL)
DigiTUBES, 50 mL	N9308008 (Racklock with caps) N9308340 (Racklock without caps) N9308037 (non-Racklock with caps)
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)