

## Water Analysis Following U.S. EPA Method 200.7 Using the Teledyne Leeman Lab's Prodigy7 ICP-OES

### Application Note - AN1303

Under the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA), the USEPA is deemed responsible for establishing analytical procedures used for compliance monitoring of both drinking and wastewaters.

In the Safe Drinking Water Act, the EPA outlines National Primary Drinking Water Regulations (NPDWR), which specifies the Maximum Contaminant Levels (MCLs) for drinking water contaminants that are known for causing adverse health effects in people. Contaminants that are known to affect the properties of water (color, taste, smell, etc.) are regulated under the National Secondary Drinking Water Regulations (NSDWR). A third set of contaminants, which fall under the Unregulated Contaminant Monitoring Rule 3 (UCMR-3), must be measured and recorded. The Maximum Contaminant Level (MCL) and Maximum Reporting Limit (MRL) for each contaminant are listed in Table I below.



Figure 1: Prodigy7 ICP-OES

Table I: MCL and MRL Concentrations for Contaminants Monitored Under the Safe Drinking Water Act					
National Primary Drinking Water Regulations		National Secondary Drinking Water Regulations		Unregulated Contaminant Monitoring Rule 3	
Contaminant	MCL (mg/L)	Contaminant	MCL (mg/L)	Contaminant	MCL (mg/L)
As	0.01	Ag	0.1	Co	0.001
Ba	2.0	Al	0.05 - 0.2	Cr (total)	0.0002
Be	0.004	Cu	1	Mo	0.001
Cd	0.005	Fe	0.3	Sr	0.0003
Cr (total)	0.1	Mn	0.05	V	0.0002
Cu	1.3	SO <sub>4</sub>	250		
Hg	0.002	Zn	5		
Pb	0.015				
Sb	0.006				
Se	0.05				
Tl	0.002				
U	0.03				

Protocol for the analysis of drinking water and wastewater is outlined in the USEPA 600 Series of methods (CFR 40 Part 136). All treatment facilities who discharge to surface waters must comply with the appropriate method from this series. For those facilities using Inductively Coupled Plasma (ICP) for compliance monitoring of metals, the required procedure is *Method 200.7: Determination of Metals and Trace Metals in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry*. The sample types covered by this method include: drinking water, surface water, wastewater and solid wastes. Method 200.7 provides a protocol for the analysis of 32 elements.

Each individual treatment facility must analyze for those elements outlined in its issued Natural Pollutant Discharge Elimination System (NPDES) permit. Most facilities are required to determine only a subset of elements outlined in Method 200.7.

As with other USEPA mandated methods, Method 200.7 requires adherence to specific procedures to ensure analytical quality control. Some of these procedures are designed to demonstrate the initial performance of the instrument, while others assess the ongoing performance of the laboratory. This application note describes the capability of the Teledyne Leeman Lab's Prodigy7 ICP-OES for performing analyses of drinking water samples in accordance with USEPA Method 200.7.

## Experimental

### Instrument

A Prodigy7 ICP-OES equipped with CETAC ASX-520 autosampler was used to generate the data for this application note. The system used was dual view which allows for both axial and radial data collection within the same analytical method. The sample introduction setup that was utilized for this work is outlined in Table II.

Parameter	Setting
<b>Nebulizer</b>	Glass Conikal for Low-Dissolved Solids
<b>Spray Chamber</b>	Glass Cyclonic with no Center Knockout Tube
<b>Torch Injector Diameter</b>	2.5 mm
<b>Sample Uptake Tubing</b>	0.76 mm (Black/Black)
<b>Sample Drain Tubing</b>	1.14 mm (Red/Red)

### Operating Parameters

In order to determine the initial performance characteristics of the Prodigy7 as outlined in Method 200.7, an instrument method was created which contained the appropriate wavelengths. Wavelengths for yttrium (Y) were added to allow for the use of an internal standard, if needed. All data was generated using the instrument operating conditions listed in Table III.

Parameter	Setting	
<b>Coolant Gas</b>	12 L/min	
<b>Auxiliary Gas</b>	0.5 L/min	
<b>Nebulizer Gas</b>	40 psi	
<b>RF Power</b>	1.2 kW	
<b>Pump Rate</b>	30 RPM	
<b>Autosampler Rinse Time</b>	60 s	
<b>Integration Time</b>	<b>Axial</b>	30 s
	<b>Radial</b>	15 s

Calibration standards were prepared from multi-element stock solutions (EPA Method Quality Control Standards 7 and 19, VHG Labs, Manchester, NH) which contained all but two of the elements of interest at 100 mg/L. The QC 7 standard contained K at 1000 mg/L and Si at 50 mg/L. The standards were prepared at 0.0, 1.0 and 10 mg/L in an acid concentration that carefully matched that of the prepared water samples.

## Results and Discussion

EPA Method 200.7 requires that instrument performance characteristics such as Instrument Detection Limits (IDL) and Method Detection Limits (MDL) be established before samples can be analyzed. The instrument's stability and upper linear dynamic range must also be established prior to sample analysis. The accuracy and precision of the method were evaluated with the analysis of Certified Reference Materials (CRMs).

### Method Detection Limit (MDL)

MDLs were calculated based upon seven replicate measurements of a fortified calibration blank. The blank was spiked with analytes at concentrations two times the calculated IDLs. Each MDL was calculated by multiplying the standard deviation of the ten replicates by the appropriate Student's t-value. Results for the MDL study are presented in Table IV and indicate that the detection limits for most of the analytes are significantly better than those estimated from Method 200.7.

### Linear Dynamic Range (LDR)

An LDR was established for each analyte in Method 200.7. After calibration, a series of standards of increasing concentration was measured as samples. The upper limit of the LDR was the highest concentration for which the measured concentration was no more than 10% below the true (i.e., known) concentration. Results for the LDR study are shown in Table IV and demonstrate the LDR of the Prodigy7 which allows for the measurement of analytes at widely varying concentrations with minimal or no sample dilution.

While the LDRs exhibited by the Prodigy7 cover a wide concentration range, the results presented in Table IV are a conservative estimate of the LDR for the analytes in this method. The presence of a large number of elements in the same solution can produce interference effects, thus reducing the linear range for a number of elements. For results that more accurately reflect an individual experiment, one is advised to establish the LDR using multi-element standards in a matrix that closely matches that of the samples that are to be analyzed.

**Table IV: Detection Limits and Linear Dynamic Range**

Element	Wavelength (nm)	MDL (ug/L)	LDR Upper Limit (mg/L)	Element	Wavelength (nm)	MDL (ug/L)	LDR Upper Limit (mg/L)
<b>Ag</b>	328.068 r	1.6	100	<b>Mn</b>	257.610 r	0.4	150
<b>Al</b>	308.215 r	21.6	1100	<b>Mo</b>	202.03	0.48	200
<b>As</b>	193.759	3.6	200	<b>Na</b>	588.995 r	24	200
<b>B</b>	249.677 r	2.6	1000	<b>Ni</b>	231.604	0.42	100
<b>Ba</b>	493.409 r	1.6	10	<b>P</b>	214.914	9.5	3000
<b>Be</b>	313.042 r	0.04	5	<b>Pb</b>	220.353	1.3	600
<b>Ca</b>	315.887 r	4.4	1000	<b>Sb</b>	206.833	1.7	400
<b>Cd</b>	226.502	0.07	60	<b>Se</b>	196.09	4	200
<b>Co</b>	228.615	0.47	100	<b>Si</b>	251.611 r	3.5	1300
<b>Cr</b>	205.552	0.19	100	<b>Sn</b>	189.991	1.3	200
<b>Cu</b>	324.754	0.29	100	<b>Sr</b>	421.552 r	0.22	20
<b>Fe</b>	259.940 r	2.4	300	<b>Ti</b>	334.941 r	0.18	300
<b>K</b>	766.491 r	55.2	1000	<b>Tl</b>	190.864	2.21	300
<b>Li</b>	670.791 r	1.1	80	<b>V</b>	292.401 r	0.79	200
<b>Mg</b>	279.078 r	4.2	1400	<b>Zn</b>	213.856	0.24	50

### Interfering Element Correction (IEC)

Due to the wide range of analytes that must be monitored under Method 200.7, sample solutions must be checked for the presence of interfering spectral overlap. If left uncorrected, the spectral overlap from interfering elements will produce biased results. To eliminate this bias, Interfering Element Correction (IEC) factors must be calculated and applied, as necessary. Results from the interference study are presented in Table V. The table contains a list of calculated IEC factors for significant interferences that were observed, and provides helpful guidance for correcting interferences, when necessary.

<b>Table V: IEC Factors for Significant Interferences</b>			
<b>Element</b>	<b>Wavelength (nm)</b>	<b>Interference Solution</b>	<b>IEC Factor</b>
<b>Ag</b>	328.068	V	-0.0031
<b>Ag</b>	328.068	Zr	0.0073
<b>Al</b>	308.215	V	0.3856
<b>Al</b>	308.215	Zr	-0.0072
<b>B</b>	249.677	Zr	-0.0033
<b>Ca</b>	315.887	Zr	-0.0121
<b>P</b>	214.914	Cu	0.0189
<b>P</b>	214.914	Sn	-0.0215
<b>Sb</b>	206.833	Cr	0.0305
<b>Sb</b>	206.833	V	-0.0037
<b>Se</b>	196.090	Fe	-0.0054
<b>Tl</b>	190.856	V	0.0027
<b>V</b>	292.401	Cr	-0.0029
<b>Zn</b>	213.856	Ni	0.0093

### Long-Term Stability

The stability of the instrument was evaluated by periodically measuring a Quality Control (QC) standard during a 10 hour sample run. Results from the stability study are presented graphically in Figure 2. For simplicity, a small number of elements that span across a wide wavelength range have been selected for illustration. All results were normalized against the first measurement taken at the beginning of the 10 hour run. Dashed lines were added to graphically illustrate boundaries between which sample results must fall for the data to be within  $\pm 5\%$  of the true value of the standard. Figure 2 illustrates that all data measured within  $\pm 10\%$  of the true value, a requirement outlined in Method 200.7.

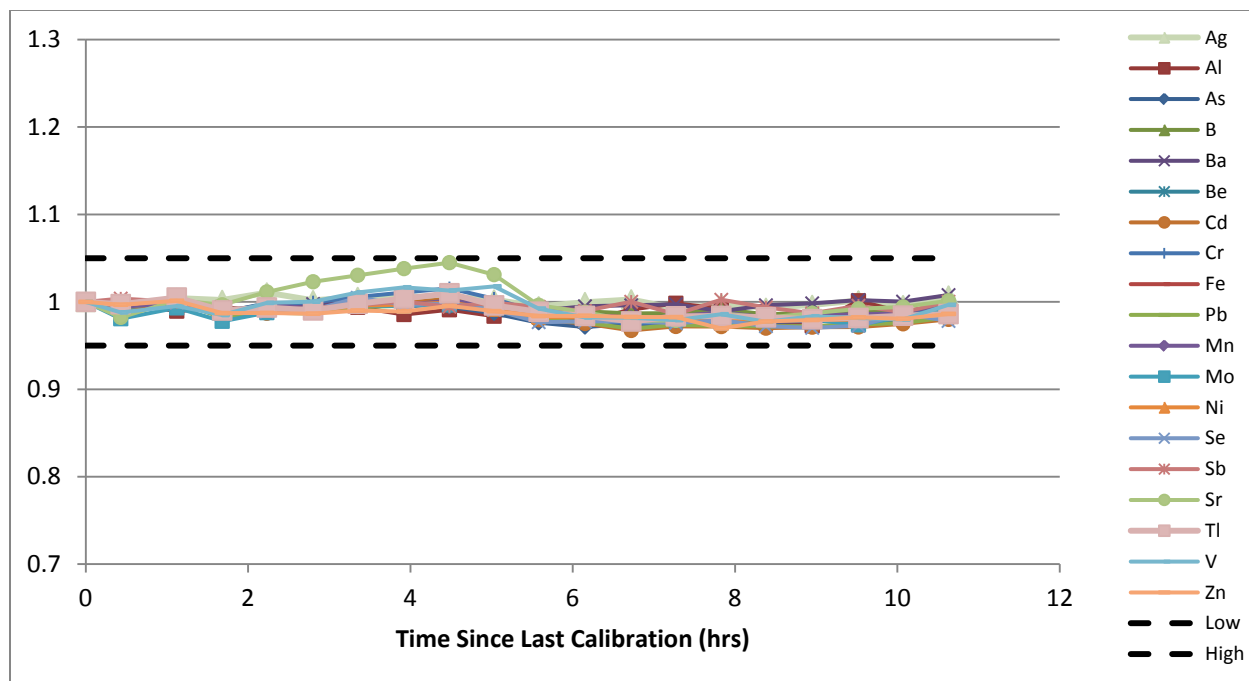


Figure 2: Stability of a quality control sample measured over a 10 hour period

### Quality Control Samples

The accuracy and precision of the method were verified using the following Certified Reference Materials (CRMs): Trace Metals in Water (NIST 1640a) and a PotableWatR™ metals standard (Catalog #697, lot#P213-500, Environmental Resource Associates). CRMs were analyzed without modification to determine the accuracy of the instrument method. Results from the analysis of the CRMs are listed in Table VI.

Table VI: Results For Certified Reference Materials						
Element	NIST 1640a			ERA		
	Measured Conc (µg/L)	Certified Conc (µg/L)	%Rec	Measured Conc (µg/L)	Certified Conc (µg/L)	%Rec
<b>Ag</b>	7.88	8.081	97.5	297	308	96.5
<b>Al</b>	43.71	53	82.5	708	690	102.6
<b>As</b>	6.94	8.075	85.9	471	491	95.9
<b>B</b>	294.0	303.1	97.0	1615	1700	95.0
<b>Ba</b>	153.1	151.8	100.8	326	339	96.3
<b>Be</b>	2.89	3.026	95.4	311	329	94.6
<b>Ca</b>	5522.4	N/A	---	<MDL	N/A	---
<b>Cd</b>	3.76	3.992	94.2	487	498	97.8
<b>Co</b>	20.82	20.24	102.9	287	277	103.5
<b>Cr</b>	37.76	40.54	93.1	293	316	92.6
<b>Cu</b>	84.75	85.75	98.8	404	409	98.8
<b>Fe</b>	34.98	36.8	95.1	624	660	94.6
<b>K</b>	669.0	N/A	---	<MDL	N/A	---
<b>Li</b>	2.43	N/A	---	<MDL	N/A	---
<b>Mg</b>	991.3	N/A	---	<MDL	N/A	---
<b>Mn</b>	40.49	40.39	100.2	1986	1980	100.3
<b>Mo</b>	43.28	45.6	94.9	182	189	96.5
<b>Na</b>	3097.5	N/A	---	<MDL	N/A	---
<b>Ni</b>	26.41	25.32	104.3	2396	2420	99.0
<b>P</b>	<MDL	N/A	---	<MDL	N/A	---
<b>Pb</b>	10.23	12.101	84.6	1430	1460	98.0
<b>Sb</b>	4.57	5.105	89.5	217	246	88.1
<b>Se</b>	20.40	20.13	101.3	480	486	98.7
<b>Si</b>	4907.1	N/A	---	129	N/A	---
<b>Sn</b>	<MDL	N/A	---	<MDL	N/A	---
<b>Sr</b>	113.3	126.03	89.9	165	178	92.5
<b>Ti</b>	<MDL	N/A	---	<MDL	N/A	---
<b>Tl</b>	---	<MDL	---	719	748	96.1
<b>V</b>	16.25	15.05	108.0	279	287	97.2
<b>Zn</b>	53.23	55.64	95.7	1393	1540	90.5

This method was also applied to the analysis of local river and bog water samples. Water samples were spiked with a multi-element standard containing a majority of the analytes of interest. The samples were analyzed and spike recoveries were calculated. Examples of the results obtained from this study are presented in Table VII and VIII.

**Table VII: Results for the Analysis of Spiked River Water Sample**

Element	Spike Conc (mg/L)	River Water		
		Unspiked Conc (mg/L)	Spiked Conc (mg/L)	%Rec
<b>Ag</b>	1.0	<MDL	0.890	89.0
<b>Al</b>	1.0	0.071	0.943	87.2
<b>As</b>	1.0	<MDL	1.017	102.0
<b>B</b>	1.0	0.010	0.975	96.5
<b>Ba</b>	1.0	0.027	0.965	93.8
<b>Be</b>	1.0	<MDL	1.002	100.2
<b>Cd</b>	1.0	<MDL	1.006	100.6
<b>Co</b>	1.0	0.0004	0.963	96.3
<b>Cr</b>	1.0	<MDL	0.990	99.0
<b>Cu</b>	1.0	0.002	0.971	96.9
<b>Fe</b>	1.0	0.606	1.533	92.6
<b>K</b>	10.0	1.323	10.99	96.7
<b>Li</b>	1.0	0.014	1.061	104.7
<b>Mg</b>	1.0	1.100	1.983	88.3
<b>Mn</b>	1.0	0.086	1.041	95.6
<b>Mo</b>	1.0	<MDL	0.997	99.7
<b>Ni</b>	1.0	<MDL	0.958	95.6
<b>P</b>	1.0	<MDL	0.926	91.6
<b>Pb</b>	1.0	<MDL	0.965	97.0
<b>Sb</b>	1.0	<MDL	0.990	100.9
<b>Se</b>	1.0	<MDL	1.033	103.6
<b>Si</b>	1.0	3.368	4.355	98.7
<b>Sn</b>	0.5	<MDL	0.562	112.4
<b>Sr</b>	1.0	0.053	1.104	105.1
<b>Ti</b>	1.0	0.006	1.045	103.9
<b>Tl</b>	1.0	<MDL	0.959	96.2
<b>V</b>	1.0	0.001	1.022	102.0
<b>Zn</b>	1.0	0.011	1.042	103.1



**Table VIII: Results for the Analysis of Spiked Bog Water Sample**

Element	Spike Conc (mg/L)	Bog Water		
		Unspiked Conc (mg/L)	Spiked Conc (mg/L)	%Rec
Ag	1.0	<MDL	0.952	95.1
Al	2.5	4.077	6.411	93.4
As	1.0	0.225	1.315	109.0
B	1.0	0.017	1.052	103.5
Ba	1.0	0.102	1.105	100.3
Be	1.0	<MDL	1.064	106.4
Cd	1.0	0.003	1.063	106.1
Co	1.0	0.004	1.016	101.2
Cr	1.0	0.108	1.143	103.5
Cu	1.0	1.018	2.008	99.0
Fe	2.5	7.211	9.283	82.9
K	10.0	1.921	12.24	103.2
Li	1.0	0.016	1.164	114.8
Mg	1.0	3.011	3.898	88.7
Mn	1.0	0.176	1.184	100.9
Mo	1.0	<MDL	1.040	104.4
Ni	1.0	0.023	1.027	100.5
P	1.0	0.305	1.279	97.4
Pb	1.0	0.591	1.586	99.5
Sb	1.0	<MDL	1.064	108.1
Se	1.0	<MDL	1.109	114.9
Si	0.5	1.204	1.684	95.9
Sn	0.5	<MDL	0.547	109.2
Sr	1.0	0.081	1.215	113.4
Ti	1.0	0.031	1.132	110.1
Tl	1.0	<MDL	1.014	101.7
V	1.0	0.029	1.107	107.8
Zn	1.0	0.592	1.666	107.4

## Conclusions

The results presented in this application note demonstrate that the Prodigy7 ICP produces results that meet the requirements outlined in USEPA Method 200.7, making the Prodigy7 a valuable tool for compliance monitoring of drinking water samples. The instrument provides accurate and precise results on a consistent basis, as demonstrated with the analysis of the CRMs.

The high precision, accuracy and versatility of the Prodigy7 derive from its stable, free-running 40 MHz power supply and high-sensitivity sample introduction system. Additionally, a reliable autosampler provides flexibility and confidence in unattended operation.

The Teledyne Leeman Lab's Prodigy7 ICP, combined with software designed to automatically perform routine tasks such as QC standard checks, spike and duplicate spike analyses, and calibration via the Method of Standard Additions (MSA), represents an outstanding choice for the analysis of drinking water samples in accordance with USEPA Method 200.7.