



U.S. EPA SW-846 Method 6010C using the Prodigy High Dispersion ICP

Introduction

This Application Note describes the capability of the Teledyne Leeman Labs Prodigy High Dispersion ICP for performing analysis according to SW-846 Method 6010c. This method is applicable to ground waters, TCLP and Extraction Procedure (EP) toxicity extracts, industrial organic wastes, soils, sludge, and sediments.

As with other USEPA mandated methods, 6010c 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. The purpose of this application note is to demonstrate the initial performance of the Leeman Labs Prodigy High Dispersion ICP. The initial performance parameters to be characterized are 1) Instrument Detection Limit (IDL), 2) Method Detection Limit (MDL), 3) Linear Dynamic Range (LDR) and 4.) Performance on a Laboratory Control Sample (LCS).

Experimental

Instrument

A Prodigy High Dispersion Inductively Coupled Plasma (ICP) Spectrometer equipped with a dual view torch and an 88 position autosampler was used to generate the data for this application note.

The Prodigy is a compact bench-top simultaneous ICP-OES featuring an 800 mm focal length Echelle optical system coupled with a mega-pixel Large Format Programmable Array Detector (L-PAD). At 28 x 28 mm, the active area of the L-PAD is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows Prodigy to achieve significantly higher optical resolution than other solid-state detector based ICP systems. The detector also provides continuous wavelength coverage from 165 to 1100 nm permitting measurement over the entire ICP spectrum in a single reading without sacrificing wavelength range or resolution. This detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than 6 orders of magnitude.

The Prodigy uses a 40.68 MHz free running, water-cooled oscillator, allowing it to handle the most difficult sample matrices. A high sensitivity sample introduction system ensures that sufficient and steady emission signals are transmitted to the spectrometer. The torch and sample introduction system are uniquely integrated into the optical system through Prodigy's innovative Image Stabilization system, which treats the torch as an optical component by rigidly attaching it to the spectrometer.

The sample introduction system consists of a four-channel peristaltic pump, cyclonic spray chamber with a knockout tube, single piece quartz torch and a Glass Expansion SeaSpray™ AR30 nebulizer.

Operating Parameters

The initial performance parameters measured for this application note were determined as specified in Method 6010c.

In order to determine the initial performance characteristics of the Prodigy, a method was created containing the wavelengths listed in **Table 1**.

Element	View	Wavelength, nm	Left Background Pixel Position	Left Background Width	Right Background Pixel Position	Right Background Width
Ag	Axial	328.068	5	1	11	1
As	Axial	188.977	3	1	13	1
Ba	Axial	455.403	2	1	13	1
Be	Axial	313.042	3	1	12	1
Cd	Axial	214.438	3	1	13	1
Co	Axial	228.616	3	1	13	1
Cr	Axial	267.716	3	1	13	1
Cu	Axial	324.754	3	1	13	1
Mn	Axial	257.610	3	1	13	1
Ni	Axial	231.604	3	1	15	1
Pb	Axial	220.353	2	1	13	1
Sb	Axial	206.833	5	1	13	1
Se	Axial	196.026	2	3	-	-
Tl	Axial	190.801	5	1	11	1
V	Axial	310.230	1	1	13	1
Zn	Axial	213.856	3	1	13	1
Al	Radial	308.215	3	1	13	1
Ca	Radial	315.887	3	1	13	1
Fe	Radial	259.940	3	1	13	1
K	Radial	766.490	3	1	13	1
Mg	Radial	285.213	3	1	13	-1
Na	Radial	589.592	4	1	13	1

Table 1. Element Parameters

This table also includes the background correction and plasma view information. The integration times used were 30 and 10 seconds for the axial and radial views, respectively. For all elements, background correction points and the analytical peak measurement are made simultaneously, resulting in improved detection limits. Off-peak background correction is a requirement in Method 6010c.

Instrument operating parameters are contained in **Table 2**.

Parameter	Value
RF Power	1.2 kW
Coolant Flow	19 L/min
Auxiliary Flow	0.8L/m
Nebulizer Pressure	34 psi
Nebulizer Type	Concentric
Sample Uptake Rate	1.0 mL/min
Spray Chamber	Cyclonic
Torch	Wide Bore, 1 piece
Purge Gas	Argon
Purge Gas Flow	0.7 l/min

Table 2. Instrument Parameters

Calibration Solutions

Standards

Calibration standards were prepared from multielement stock solutions (PlasmaPure® Standards, Leeman Labs) in appropriate concentrations to cover the linear range for each element. The acid concentration of the standards was carefully matched to the acid concentration of the prepared soil samples.


The suggested element mix in Method 6010c was used, and is shown in **Table 3**.

Solution	Elements
I	Be, Cd, Mn, Se and Zn
II	Ba, Co, Cu, Fe and V
III	As and Mo
IV	Al, Ca, Cr, K, Na, Li and Sr
V	Ag, Mg, Sb, and Tl
VI	P

Table 3. Calibration Standards

Blanks

Two types of blanks are required for the analysis of samples prepared by any method other than Method 3050. The calibration blank is used in establishing the analytical curve and the method blank is used to identify possible contamination resulting from either the reagents (acids) or the equipment used during sample processing, including filtration.



The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. A sufficient quantity should be prepared to flush the system between standards and samples. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations.

The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

QC/Check Standards

The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve.

The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve.

The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will provide an adequate test of the interfering element correction factors. The sample is spiked with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/l.

Performance Characteristics

Method Detection Limits (MDL)

The Method Detection Limit (MDL) is defined as the minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDLs are measured by analyzing a solution with analytes at a concentration 3 to 5 times the Instrument Detection Limit (IDL). This solution is analyzed 7 times and the standard deviations of the analyte concentrations are multiplied by 3.14 (the student's t-statistic for a 99% confidence interval). To obtain a better estimate of the MDL, the procedure can be repeated on three non-consecutive days and the MDL values averaged.

The average of the MDLs collected over the three days are presented in **Table 4**.


	MDL, $\mu\text{g/l}$	LDR, mg/l
Ag	0.5	10
As	5	10
Ba	0.3	1
Be	0.04	1
Cd	0.4	10
Co	0.3	100
Cr	0.5	10
Cu	0.3	10
Mn	0.08	10
Ni	0.4	100
Pb	1.4	500
Sb	2.6	10
Se	4.5	10
Tl	2.2	100
V	0.6	100
Zn	0.1	50
Al	25	1000
Ca	20	1000
Fe	10	900
K	45	900
Mg	10	1000
Na	15	900

Table 4. MDL and LDR Data

Linear Dynamic Range (LDR)

Method 6010c requires that the upper limit of the Linear Dynamic Range (LDR) be established. This is accomplished by analyzing increasingly higher concentration analyte standards. The LDR is considered exceeded when the measured concentration is more than 10% below the true concentration.

The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum of three, different concentration standards across the range. The ranges that may be used for the analysis of samples should be judged by the analyst from the resulting data. A standard at the upper limit must be prepared, analyzed and quantitated against the normal calibration curve. The calculated value must be within 10% ($\pm 10\%$) of the true value. New upper range limits should be determined whenever there is a significant change in instrument response. At a minimum, the range should be checked every six months. The analyst should be aware that if an analyte present above its upper limit is used to apply an interelement correction, the correction may not be valid and those analytes where the interelement correction has been applied may be inaccurately reported.



For this experiment single element PLASMA-PURE™ standards of 100, 500 and 1000 mg/l were analyzed. The Prodigy was calibrated using the standard mix indicated in **Table 3**. Other concentration standards were prepared as necessary if the LDR was not determined or exceeded using the 100, 500 and 1000 mg/l standards.

Results of the LDR study are shown in **Table 4**. These LDR values emphasize one of the advantages of using ICP for compliance monitoring. ICP is known for its excellent linear range, particularly when compared with Atomic Absorption Spectrometry (AAS). The LDRs exhibited by the Prodigy permit the analysis of samples with wide concentration ranges for a particular element without the need to dilute samples frequently. The limited linear range of AAS requires multiple dilutions to cover such wide concentration ranges.

The LDRs presented in **Table 4** were determined using single element solutions. In real samples, LDRs may be affected by the presence of multiple elements at high concentrations or different sample matrices. Analysts are advised to use caution in apply LDR data determined using single element standards. For the most accurate LDRs, multi-element standards in a matrix similar to that of the sample should be used.

Interelement Corrections

The types of samples analyzed under the scope of Method 6010c may exhibit considerable spectral complexity. As a result, interferences due to spectral overlaps may be observed. When present and uncorrected, these interferences will produce biased determinations. For this study, checks are performed for the major matrix elements, Al, Ca, Fe, Mg, Si and P on the other analyte elements. This is done using single element solutions. Once the interferences are identified, the Prodigy will automatically calculate the interfering elements correction factors. **Table 5** lists the interferences that were found.

When interelement corrections are applied, their accuracy must be verified daily, by analyzing spectral interference check solutions (ICSA and ICSB). All interelement spectral correction factors must be verified and updated every six months or when an instrument configuration change occurs, such as one in the torch, nebulizer, injector, or plasma conditions. Standard solutions should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

Element	Wavelength, nm	Interferent
Ag	328.068	Fe
As	188.977	
Ba	455.403	
Be	313.042	
Cd	214.438	Fe
Co	228.616	Fe
Cr	267.716	Fe, Al
Cu	324.754	
Mn	257.610	
Ni	231.604	
Pb	220.353	Al
Sb	206.833	Fe, Al
Se	196.026	Al
Tl	190.801	
V	310.230	Fe
Zn	213.856	Fe
Al	308.215	
Ca	315.887	
Fe	259.940	
K	766.490	
Mg	285.213	
Na	589.592	

Table 5 Interfering Elements

Results and Discussion

Initial and Continuing Calibration Verification (ICV and CCV)

After initial calibration, the calibration curve must be verified by use of an initial calibration verification (ICV) standard. The ICV standard must be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for the ICV standard must be $\pm 10\%$ of its true value. If the calibration curve cannot be verified within the specified limits, the cause must be determined and the instrument recalibrated before samples are analyzed.

The calibration curve must be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB). The CCV should be made from the same material as the initial calibration standards at or near mid-range. The acceptance criteria for the CCV standard must be $\pm 10\%$ of its true value and the CCB must not contain target analytes above 2 - 3 times the MDL for the curve to be considered valid. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed.

Typical results for the ICV and CCV standards are given in **Table 6 and 7**.

	Actual	Measured	% Recovery
Ag	1.0	1.05	105
As	1.0	1.01	101
Ba	5.0	5.25	105
Be	0.5	0.51	102.2
Cd	0.5	0.48	95.3
Co	5.0	4.89	97.9
Cr	1.0	0.97	97.0
Cu	2.0	1.98	98.8
Mn	2.0	2.05	102.4
Ni	5.0	4.92	98.4
Pb	5.0	5.21	104
Sb	5.0	4.90	97.9
Se	5.0	5.14	102.9
Tl	5.0	4.85	97.1
V	5.0	5.14	103
Zn	5.0	5.21	104
Al	100	98.5	98.5
Ca	100	99.8	99.8
Fe	100	100.5	100.5
K	100	100.0	100.0
Mg	100	98.7	98.7
Na	100	97.3	97.3

Table 6. Typical ICV Results

	Actual	Measured	% Recovery
Ag	0.5	0.53	106.7
As	0.50	0.46	92.9
Ba	2.50	2.43	97.4
Be	0.25	0.255	102.1
Cd	0.25	0.244	97.5
Co	2.50	2.53	101.2
Cr	0.50	0.53	105.9
Cu	1.00	1.03	103.4
Mn	1.00	0.96	96.4
Ni	2.50	2.53	101.3
Pb	2.50	2.46	98.6
Sb	2.50	2.36	94.4
Se	2.50	2.62	105.0
Tl	2.50	2.54	101.7
V	2.50	2.35	93.9
Zn	2.50	2.60	104.0
Al	50.0	50.5	101.0
Ca	50.0	48.5	96.9
Fe	50.0	48.5	97.0
K	50.0	49.8	99.5
Mg	50.0	51.5	103.0
Na	50.0	52.2	104.5

Table 7. Typical CCV Data

Interference Check Solutions (ICS)

In order to verify the validity of the interfering element correction (IEC) factors, interference check solutions must be analyzed prior to the start of sample analysis.

Two Interference Check Standards were prepared and used. The first, ICSA, contained Fe at 200 mg/l and Al, Ca and Mg at 500 mg/l. The second, ICSB, contained the same matrix element plus all analyte elements spiked a 0.5 to 1.0 mg/l.

The results for these two standards are shown in **Table 8**. The measured values for the ICSB standard must be with 20% of the true concentrations.

	ICSA	ICSB	Actual	% Recovery
Ag	<0.5	98.5	100	98.5
As	<5	96.5	100	96.5
Ba	<0.3	192.0	200	96.0
Be	<0.04	102.0	100	102.0
Cd	<0.4	103.7	100	103.7
Co	<0.3	485.9	500	97.2
Cr	<0.5	483.8	500	96.8
Cu	<0.3	490.1	500	98.0
Mn	<0.08	488.6	500	97.7
Ni	<0.4	514.5	500	102.9
Pb	<1.4	52.6	50	105.2
Sb	<2.6	491.7	500	98.3
Se	<4.5	45.9	50	91.8
Tl	<2.2	48.6	50	97.2
V	<0.6	105.3	100	105.3
Zn	<0.1	97.1	100	97.1

Table 8. Interference Check Solution Results

Sample Analysis Results

Five certified soil samples were prepared and analyzed: ERA 212 and 228 (Environmental Resource Associates, Arvada, CO.) and Standard Reference Materials (SRM) 2709, 2710, 2710 (NIST, Gaithersburg, MD). The NIST SRM 2709 was used as the Laboratory Control Sample (LCS) sample.

In each case, approximately 1 gram of soil was prepared and diluted to 100 ml. Each of the soils was prepared by following U.S. EPA Method 3050B. Calibration standards were prepared from multi-element stock solutions (PlasmaPure® Standards, Leeman Labs) at appropriate concentrations. The acid concentration of the standards was carefully matched to the acid concentration of the prepared soil samples. The results for the analyses are given in **Tables 9-13**.

Element	Concentration Found, mg/kg	RSD, %	Certified Value, mg/kg	Performance Acceptance Limits (PAL), mg/kg
Ag	62.1	1.11	89	130-40.5
As	77.6	3.91	65.4	97.4-32
Ba	169	0.12	161	211-11.3
Be	127	0.19	122	171-78.1
Cd	86.2	0.23	85.4	123-44
Co	111	0.31	94.2	134-56.5
Cr	76.1	0.60	71.6	101-38.7
Cu	169	0.17	173	251-98.6
Mn	323	0.04	298	402-209
Ni	74.9	0.88	68.5	100-37.7
Pb	72.1	0.34	70.4	100-37.3
Sb	38.6	6.82	38.1	68.6-11.4
Se	157	2.19	152	226-79
Tl	78.1	2.51	71.8	117-26.4
V	121	0.38	105	142-73.5
Zn	123	0.12	110	134-59.4
Al	8102	0.27	6070	8668-2730
Ca	3820	0.02	3710	5230-2340
Fe	17853	0.07	12500	18800-6380
K	3700	0.43	3250	4290-2010
Mg	2840	0.30	2490	3590-1490
Na	254	1.23	167	262-71.1

Table 9: ERA 228

Element	Concentration Found, mg/kg	RSD, %	Certified Value, mg/kg	Performance Acceptance Limits (PAL), mg/kg
Ag	39.8	1.45	37	56-18
As	15.7	1.75	15	25-5.6
Ba	136	0.06	134	174-93
Be	16.5	0.75	15	21-9.5
Cd	106	1.41	109	142-76
Co	197	0.77	211	274-148
Cr	48.2	2.51	41	62-20
Cu	20.9	1.57	20	32-8
Mn	312	0.19	310	403-217
Ni	25.1	2.16	28	48-8
Pb	62.4	4.21	74	111-37
Sb	48.7	1.74	52	160-0
Se	84.5	1.01	91	136-45
Tl	87.9	1.53	99	150-48
V	59.8	0.43	57	74-40
Zn	72.9	0.27	71	80-26
Al	12930	0.21	11500	16500-6530
Ca	7520	0.12	7130	9270-4990
Fe	17500	0.31	14500	20150-10100
K	3640	0.41	3790	4930-2650
Mg	3920	0.27	3620	4710-2530
Na	502	0.64	400	627-173

Table 10. ERA 212

Element	Concentration Found, mg/kg	RSD, %	Median Value, mg/kg	Range, mg/kg
Ag	26.3	0.23	28	30-24
As	523	0.66	590	600-490
Ba	338	0.29	360	400-300
Cd	20.6	0.13	20	26-13
Co	10.1	2.01	8.2	12-6.3
Cr	21.0	2.21	19	23-15
Cu	2820	0.33	2700	3400-2400
Mn	8140	0.18	7700	9000-6200
Ni	9.14	2.97	10.1	15-8.8
Pb	5370	0.23	5100	7000-4300
Sb	7.41	10.46	7.9	12-3.4
Se	ND		0.002	-
Tl	ND		0.63	0.76-0.5
V	48.7	0.47	43	50-37
Zn	6280	0.18	5900	6900-5200
Al (Wt.%)	2.17	0.32	1.8	2.6-1.2
Ca (Wt.%)	0.407	0.42	0.41	0.48-0.38
Fe (Wt.%)	2.83	0.36	2.7	3.2-2.2
K (Wt.%)	0.481	0.39	0.45	0.50-0.37
Mg (Wt.%)	0.560	0.52	0.57	0.60-0.43
Na (Wt.%)	0.059	1.07	0.054	0.062-0.049

Table 11. Montana Soil (Elevated) NIST 2710

Element	Concentration Found, mg/kg	RSD, %	Median Value, mg/kg	Range, mg/kg
Ag	4.28	7.21	4	5.5-2.5
As	102	2.06	90	110-88
Ba	211	0.24	200	260-170
Cd	40.1	0.35	40	46-32
Co	10.1	1.19	8.2	12-7
Cr	23.4	1.68	20	25-15
Cu	109	0.39	100	110-91
Mn	534	0.25	490	620-400
Ni	15.8	3.77	16	20-14
Pb	1130	0.05	1100	1500-930
Sb	3.66	6.74	<10	-
Se	ND		0.009	-
V	46.4	0.35	42	50-34
Zn	337	0.14	310	340-290
Al (Wt.%)	2.23	0.14	1.8	2.3-1.2
Ca (Wt.%)	2.14	0.21	2.1	2.5-2.0
Fe (Wt.%)	2.33	0.24	2.2	2.6-1.7
K (Wt.%)	0.529	0.31	0.38	0.53-0.26
Mg (Wt.%)	0.791	0.26	0.81	0.89-0.72
Na (Wt.%)	0.028	0.98	0.026	0.029-0.020

Table 12. Montana Soil (Moderate) NIST 2711

Element	Concentration Found, mg/kg	RSD, %	Median Value, mg/kg	Range, mg/kg	% Recovery
As	17.6	1.91	<20	-	-
Ba	400	0.20	398	400-392	101
Cd	0.83	1.57	<1	-	-
Co	12.8	4.22	12	15-10	107
Cr	75.9	0.26	79	115-60	96
Cu	29.5	1.14	32	40-26	92
Mn	496	0.10	470	600-360	106
Ni	78.2	0.42	78	90-65	100
Pb	14.2	4.18	13	18-12	109
Sb	0.689	2.69	<10	-	-
Se	ND		0.014	-	-
V	64.4	0.28	62	70-51	104
Zn	97.8	0.18	100	120-87	98
Al (Wt.%)	2.79	0.23	2.6	3.1-2.0	107
Ca (Wt.%)	1.43	0.31	1.5	1.7-1.4	95.3
Fe (Wt.%)	3.03	0.20	3.0	3.3-2.5	101
K (Wt.%)	0.335	0.56	0.32	0.37-0.26	105
Mg (Wt.%)	1.33	0.09	1.4	1.5-1.2	95
Na (Wt.%)	0.072	0.84	0.068	0.11-0.063	106

Table 13. San Joaquin Soil (NIST 2709)



Conclusion

The Prodigy ICP readily accommodated all of the soil samples for analysis. Examination of the data indicates the results for all elements lie well within the Performance Acceptance Limits (PAL) for the ERA soils or the range specified for the NIST SRM soils. In addition, the results are in good agreement with the certified values for all samples. The results demonstrate excellent precision, as indicated by the low Relative Standard Deviation (RSD) data in each table, indicating the Prodigy is operating well above the detection limit (DL) and limit of quantitation (LOQ) for the elements determined. This means the analysis can be performed with a high degree of confidence. The versatility of unlimited wavelength selection coupled with the excellent resolution and dispersion of the Prodigy system allowed easy selection of highly sensitive wavelengths.

The Prodigy's ability to perform this type of analysis derives from its robust design. A stable, free-running 40 MHz power supply and high sensitivity sample introduction system ensures that sufficient and steady emission signals are introduced into the spectrometer. A reliable autosampler provides flexibility and confidence in unattended operation.

The heart of the Prodigy is in its large format programmable array detector (LPAD) and an advanced high dispersion Echelle spectrometer. The high resolution and dispersion inherent in the design result in a compact optical system that offers outstanding long-term stability as shown above. The use of the LPAD detector allows all the analytes to be measured simultaneously and gives the largest dynamic range with true simultaneous background correction.

With software designed to automatically perform the necessary QC tasks, including spikes, duplicates and method of standard additions, the Leeman Labs Prodigy ICP spectrometer represents an outstanding choice for analysis of these sample types.

The Prodigy ICP equipped with the option Dual View capability is an appropriate choice to increase the versatility of the instrument. The additional capability permits the analysis of samples that would otherwise have to be analyzed on multiple instrument types that may require additional digestion procedures, decreasing overall productivity and increasing waste disposal costs.