

U.S. EPA SW 846 Método 6010C Mediante el ICP-OES Prodigy 7

Aplicación 024

Introducción

This application note describes the capability of the Teledyne Leeman Lab's Prodigy7 High-Dispersion ICP for performing analysis according to SW-846 Method 6010C. This method is applicable to groundwaters, Toxicity Characteristic Leaching Procedure (TCLP) and Extraction Procedure (EP), industrial organic wastes, soils, sludge and sediments.

As with other USEPA mandated methods, Method 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 Teledyne Leeman Lab's Prodigy7 High-Dispersion ICP. The initial performance parameters to be characterized are:

1. Method Detection Limit (MDL)
2. Linear Dynamic Range (LDR)

Experimental

Instrument

A Prodigy7 Inductively Coupled Plasma (ICP) Spectrometer (Figure 1) equipped with a dual-view torch and a 240-position CETAC ASX-520 autosampler (CETAC Technologies, Omaha, NE) (Figure 2) was used to generate the data for this application note.

The Prodigy7 is a compact benchtop simultaneous ICP-OES system featuring a 500 mm focal length Echelle Optical System coupled with a megapixel CMOS Detector. At 28 x 28 mm, the active area of the CMOS Detector is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows Prodigy7 to achieve 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, nondestructive readout that results in a dynamic range of more than 6 orders of magnitude.

Aqueous, high-solids and organic samples are easily analyzed with the powerful, water-cooled



Figure 2 CETAC ASX-520 Autosampler

40.68 MHz Free-Running Power Supply. The addition of a thoroughly re-engineered Twist-n-Lock Auto-Aligning Sample Introduction System provides exceptional signal transmission to the spectrometer and precisely retains torch settings if removed.

Sample Introduction

The sample introduction system consists of:

- Cyclonic spray chamber with a center knockout tube
- Seaspray™ concentric nebulizer (glass expansion)
- Four-channel peristaltic pump

The volume of cyclonic spray chamber is low to allow for fast washout between samples, while its knockout tube or baffle, efficiently reduces the amount of sample aerosol reaching the torch.

The torch is mounted using a newly designed Twist-n-Lock Auto-Aligning Sample Introduction System, shown in Figure 3. The cassette-based design permits operators to remove and replace the torch in the exact same position, enhancing day-to-day reproducibility and simplifying training. Additionally, the twist-n-lock design automatically connects the coolant and auxiliary gas flows eliminating potential errors.



Figure 3 Twist-n-Lock Sample Intro System

The 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 Prodigy7's innovative Image Stabilization System, which treats the torch as an optical component by rigidly attaching it to the spectrometer.

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 Prodigy7, a method was created containing the elements and wavelengths listed in Table I.

Table I Elements, Wavelengths and Plasma View		
Element	Wavelength	View
Ag	328.068	Axial
As	193.759	Axial
Ba	233.527	Axial
Be	313.042	Axial

Cd	214.441	Axial
Co	228.615	Axial
Cr	267.716	Axial
Cu	324.754	Axial
Mn	257.610	Axial
Ni	231.604	Axial
Pb	220.353	Axial
Sb	206.833	Axial
Se	196.090	Axial
Tl	190.856	Axial
V	309.311	Axial
Zn	213.856	Axial
Al	308.215 r	Radial
Ca	315.887 r	Radial
Fe	259.940 r	Radial
K	766.491 r	Radial
Mg	279.078 r	Radial
Na	589.592 r	Radial

All samples were analyzed using the Prodigy7 equipped with a dual-view torch. Instrument operating parameters are shown below in Table II. Method parameters are displayed in Table III.

Table II Instrument Operating Parameters		
Parameter	Value	Part Number
RF Power	1.2 kW	-
Coolant Flow	12 L/min	-
Auxiliary Flow	0.8 L/min	-
Nebulizer Pressure	30 psi	-
Torch	Quartz Demountable	318-00160-1
Injector	2.5 mm bore, Demountable	318-00161-AQ1

Table III Method Parameters		
Parameter	Value	Part Number
Sample Uptake Time, sec	20	-
Replicates	2	-
Integration Time, sec	5	-
Rinse Time, sec	20	-
QC Limit	±10%	-
QC Failure Action	Recalibrate, Rerun	-

Sample Uptake Rate, L/min	1.2	-
Sample Uptake Tubing	Black Tab 030	309-00069-7
Sample Drain Tubing	Red Tab 045	309-00069-4

Calibration Solutions

Standards

Calibration standards were prepared from multi-element stock solutions (Plasma-Pure® Standards, Teledyne 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 IV.

Table IV Calibration Standard Concentration, mg/mL						
	STD1	STD2	STD3	STD4	STD5	STD6
Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Ti, V, Zn	0	1	5	10	-	-
Al, Ca, Fe, K, Mg, Na	0	-	-	-	10	100

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 Calibration Blank (ICB) and Continuing Calibration Blank (CCB) determinations.

The method blank must contain all of the reagents in the same volumes as those 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 a 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 midpoint 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 (IEC) 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 three to five times the Instrument Detection Limit (IDL). This solution is analyzed seven 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 nonconsecutive days and the MDL values averaged.

The MDLs are presented in Table V.

Table V MDLs and LDRs					
	MDL, µg/L	LDR, mg/L		MDL, µg/L	LDR, mg/L
Ag	0.19	50	Sb	2.45	500
As	4.60	200	Se	5.04	200
Ba	0.22	5	Tl	2.50	250
Be	0.07	5	V	1.98	100
Cd	0.10	30	Zn	0.62	30
Co	0.39	100	Al	18.33	1500
Cr	0.25	100	Ca	7.73	1000
Cu	0.22	50	Fe	1.26	500
Mn	0.03	30	K	48.42	1000
Ni	0.62	100	Mg	8.31	1500
Pb	1.13	500	Na	18.97	500

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 LDR 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 to which the interelement correction was applied may be inaccurately reported.

For this experiment, single element Plasma-Pure® standards of 100, 500 and 1000 mg/L were analyzed. The Prodigy7 was calibrated using the standard mix indicated in Table IV. 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 V. 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 Prodigy7 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 V 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 Prodigy7 will automatically calculate the interfering element correction factors. Table VI 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 (i.e., 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.

Table VI Interfering Elements		
Element	Wavelength, nm	Interferent
Ag	328.068	Fe
As	193.759	
Cd	214.441	Fe
Co	228.615	Fe
Cr	267.716	Fe, Al
Pb	220.353	Al
Sb	206.833	Fe, Al
Se	196.090	Al
V	309.311	Fe
Zn	213.856	Fe

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 VII and Table VIII.

Table VII Typical ICV Data			
	Actual	Measured	% Recovery
Ag	5.0	4.87	97.4
As	5.0	4.90	98.0
Ba	5.0	4.91	98.2
Be	5.0	5.12	102.4

Cd	5.0	4.85	97.0
Co	5.0	4.81	96.2
Cr	5.0	4.86	97.2
Cu	5.0	4.79	95.8
Mn	5.0	4.73	94.6
Ni	5.0	5.04	100.8
Pb	5.0	4.82	96.4
Sb	5.0	4.75	95.0
Se	5.0	4.90	98.0
Tl	5.0	4.73	94.6
V	5.0	4.91	98.2
Zn	5.0	4.85	97.0
Al	5.0	5.51	110.
Ca	5.0	4.82	96.4
Fe	5.0	4.84	96.8
K	5.0	48.94	97.9
Mg	5.0	4.82	96.5
Na	5.0	4.84	96.8

Table VIII Typical CCV Data			
	Actual	Measured	% Recovery
Ag	5.0	4.78	95.6
As	5.0	4.94	98.8
Ba	5.0	4.84	96.8
Be	5.0	4.72	94.4
Cd	5.0	4.75	95.0
Co	5.0	4.71	94.2
Cr	5.0	4.78	95.6
Cu	5.0	4.88	97.6
Mn	5.0	4.67	93.4
Ni	5.0	4.66	93.2
Pb	5.0	4.71	94.2
Sb	5.0	4.67	93.4
Se	5.0	4.87	97.4
Tl	5.0	4.68	93.6
V	5.0	4.89	97.8
Zn	5.0	4.81	96.2
Al	50.0	50.0	100.0
Ca	50.0	50.3	100.5
Fe	50.0	51.6	103.2
K	50.0	49.5	98.9

Mg	50.0	49.8	99.5
Na	50.0	49.9	99.9

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, ICSAB, contained the same matrix elements plus all analyte elements spiked at 500 to 1000 µg/L. The results for these two standards are shown in Table IX. The measured values for the ICSB standard must be with 20% of the true concentrations.

Table IX Interference Check Solution Results				
	ICSA, µg/ml	ICSAB, µg/ml	Actual	% Recovery
Ag	<0.19	1016.3	1000	101.6
As	<4.6	993.5	1000	99.4
Ba	<0.22	521.0	500	104.2
Be	<0.07	535.6	500	107.1
Cd	<0.1	982.2	1000	98.2
Co	<0.39	475.3	500	95.1
Cr	<0.25	502.6	500	100.5
Cu	<0.22	540.8	500	108.2
Mn	<0.03	485.6	500	97.1
Ni	<0.62	985.4	1000	98.5
Pb	<1.13	970.6	1000	97.1
Sb	<2.45	1052.3	1000	105.2
Se	<5.04	980.4	1000	98.0
Tl	<2.5	1092.3	1000	109.2
V	<1.98	465.3	500	93.1
Zn	<0.62	1053.9	1000	105.4

Sample Analysis Results

A certified water sample, ERA WatR™ Pollution Trace Metals, Lot P213-500, and four certified soil samples were prepared and analyzed: ERA Metals in SewageSludG™, Lot. D078-160 (Environmental Resource Associates, Arvada, CO.) and Standard Reference Materials (SRM) 2709, 2710, 2710 (NIST, Gaithersburg, MD). In each case, approximately 1 gram of soil was prepared and diluted to 100 ml. Each of the soils was prepared by following USEPA Method 3050B. Calibration standards were prepared from multi-element stock solutions (Plasma-Pure® Standards, Teledyne 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 Table X through Table XIV.

Table X ERA WatR™ Pollution Trace Metals, Lot P213-500					
Element	Concentration Found, µg/L	RSD	Certified Value, µg /L	% Recovery	QC Performance Acceptable Limits
Ag	292	0.45	308	94.8	275 - 339
As	481	0.78	491	98.0	423 - 545
Ba	323	0.38	339	95.3	307 - 370
Be	321	0.42	329	97.6	296 - 359

Cd	466	0.50	498	93.6	435 - 533
Co	280	0.46	277	101	257 - 307
Cr	307	0.40	319	96.2	285 - 348
Cu	405	0.31	409	99.0	365 - 446
Mn	2037	0.43	1980	103	1800 - 2160
Ni	2418	0.49	2420	99.9	2180 - 2660
Pb	1472	0.45	1460	101	1300 - 1620
Sb	220	1.51	246	89.4	212 - 276
Se	483	0.99	486	99.4	422 - 549
Tl	739	0.87	748	98.8	651 - 838
V	283	0.41	287	98.6	262 - 307
Zn	1535	0.37	1540	99.7	1390 - 1710
Al	609	2.60	690	88.3	594 - 794

Table XI ERA Metals in SewageSludG™, Lot D078-160

Element	Concentration Found, mg/L	RSD	Certified Value, mg/L	% Recovery	QC Performance Acceptable Limits
Ag	86.7	0.57	92.9	93.3	65.4 - 120
As	257	0.55	284	90.3	216 - 351
Ba	938	0.51	1010	92.9	742 - 1270
Be	69.9	0.52	77.1	90.7	65.7 - 88.4
Cd	97.2	0.55	120	81.0	94.6 - 145
Co	29.3	0.47	28.1	104	24 - 32.2
Cr	156	0.52	165	94.7	136 - 195
Cu	738	0.49	867	85.1	738 - 997
Mn	357	0.56	411	86.9	303 - 518
Ni	156	0.40	182	85.5	146 - 218
Pb	136	0.38	146	93.2	114 - 178
Sb	169	0.55	186	90.8	124 - 248
Se	157	0.73	166	94.6	115 - 217
Tl	152	1.11	168	90.7	130 - 205
V	127	0.46	143	88.7	90.7 - 195
Zn	1024	0.50	1180	86.8	945 - 1420
Al	6891	0.79	7510	91.8	6340 - 8690
Ca	38980	0.66	34300	113	27500 - 41000
Fe	22231	0.65	23300	95.4	18500 - 28200
K	1848	0.97	1980	93.3	1380 - 2580
Mg	3739	0.85	4000	93.5	3370 - 4620
Na	1154	0.75	1080	107	787 - 1360

Table XII San Joaquin Soil, NIST 2709 (LCS)

Element	Concentration Found, mg/kg	RSD	Median Value, mg/kg	Range, mg/kg	% Recovery
As	16.5	1.5	<20	-	-
Ba	406	0.24	398	392 - 400	102
Cd	0.85	3.2	<1	-	-
Co	12.6	0.66	12	10.0 - 15.0	105
Cr	69.52	0.34	79	60 - 115	88
Cu	27.84	0.30	32	26 - 40	87
Mn	465.3	0.30	470	360 - 600	99
Ni	70.2	0.32	78	65 - 90	90

Pb	13.5	3.8	13	12.0 - 18.0	104
Sb	4.7	5.3	<10	-	-
Se	ND	-	0.014	-	-
V	52.7	0.34	62	51 - 70	85
Zn	95	0.41	100	87 - 120	95
Al	2.75	0.40	2.6	2.0 - 3.1	106
Ca	1.61	0.27	1.5	1.4 - 1.7	107
Fe	2.72	0.28	3	2.5 - 3.3	90.7
K	0.314	0.34	0.32	0.26 - 0.37	98.1
Mg	1.35	0.38	1.4	1.2 - 1.5	96.4
Na	0.076	0.35	0.068	0.063 - 0.11	112

Table XIII Montana Soil (Elevated), NIST 2710

Element	Concentration Found, mg/kg	RSD	Median Value, mg/kg	Range, mg/kg	% Recovery
Ag	25.8	1.2	28	24 - 30	92.1
As	561	0.83	590	490 - 600	95.1
Ba	364	0.97	360	300 - 400	101
Cd	23	1.9	20	13 - 26	115
Co	7.79	2.5	8.2	6.3 - 12	95.0
Cr	20.9	1.2	19	15 - 23	110
Cu	2889	0.86	2700	2400 - 3400	107
Mn	7084	0.74	7700	6200 - 9000	92.0
Ni	10.6	1.08	10.1	8.8 - 15	105
Pb	5202	0.87	5100	4300 - 7000	102
Sb	8.3	4.5	7.9	3.4 - 12	105
Se	ND	-	0.002	-	-
Tl	ND	-	0.63	0.5 - 0.76	-
V	43.4	0.94	43	37 - 50	101
Zn	5782	0.78	5900	5200 - 6900	98.0
Al	1.99	0.51	1.8	1.2 - 2.6	111
Ca	0.38	0.48	0.41	0.38 - 0.48	92.7
Fe	2.9	0.47	2.7	2.2 - 3.2	107
K	0.48	0.63	0.45	0.37 - 0.50	107
Mg	0.52	0.43	0.57	0.43 - 0.60	91.2
Na	0.056	0.73	0.054	0.049 - 0.062	104

Table XIV Montana Soil (Moderate), NIST 2711

Element	Concentration Found, mg/kg	RSD	Median Value, mg/kg	Range, mg/kg	% Recovery
Ag	4.8	2.73	4	2.5 - 5.5	120
As	88.6	3.0	90	88 - 110	98.4
Ba	184	0.56	200	170 - 260	92.0
Cd	40.8	0.81	40	32 - 46	102
Co	7.79	1.5	8.2	7.0 - 12.0	95.0
Cr	19	0.83	20	15 - 25	95.0
Cu	97.3	0.47	100	91 - 110	97.3
Mn	564	0.90	490	400 - 620	115
Ni	17.1	0.84	16	14 - 20	107
Pb	990	0.50	1100	930 - 1500	90.0
Sb	4.88	5.1	<10	-	-
Se	ND	-	0.009	-	-

V	45.1	0.559	42	34 - 50	107
Zn	298	0.593	310	290 - 340	96.1
Al	1.93	0.465	1.8	1.2 - 2.3	107
Ca	2.42	0.483	2.1	2.0 - 2.5	115
Fe	1.87	0.481	2.2	1.7 - 2.6	85.0
K	0.35	0.689	0.38	0.26 - 0.53	92.1
Mg	0.82	0.575	0.81	0.72 - 0.89	101
Na	0.027	0.469	0.026	0.020 - 0.029	104

Conclusion

The Prodigy7 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 soil 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 Prodigy7 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 Prodigy7, allowed easy selection of highly sensitive wavelengths.

The Prodigy7's ability to perform this type of analysis derives from its thorough design. The combination of a powerful, field-proven power supply with a high-sensitivity sample introduction system produces exceptional results. A reliable autosampler provides flexibility and confidence in unattended operation.

The heart of the Prodigy7 is its CMOS Array Detector and 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 and sensitivity. The use of the CMOS 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 Teledyne Leeman Lab's Prodigy7 ICP spectrometer represents an outstanding choice for analysis of these sample types. The Prodigy7 ICP equipped with the optional dualview 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.