High-Throughput Analysis of Wear Metals Using the Teledyne Leeman Labs Prodigy Plus ICP-OES

Manuel Almeida, ICP/DCA Technical Product Manager; Teledyne Leeman Labs

Introduction

Used oil-based materials such as engine oils, transmission oils and other lubrication oils are regularly monitored for the presence of particles deposited from the components which they are designed to protect. These particles gradually build-up in the oil due to the normal wear of the component. For this reason, the analysis of used oils is often referred to as "wear metals" or "trend" analysis. This technique can be used to accurately identify and predict component failure, based on the composition of the metals and the speed at which they accumulate over time. Additionally, lubricating fluids must also be monitored for external contaminants (metals from sources such as dust and dirt) which should not be present in the fluid for any reason.

Due to the importance of wear-metal analysis and the large amount of equipment that is typically monitored, many wear metal labs require high productivity and often analyze hundreds of samples a day. This application note will not only demonstrate the Prodigy Plus ICP's ability to analyze wear metals, but will also illustrate two different approaches to reduce analysis time and significantly increase sample throughput. The first approach is based on unique settings in the Prodigy Plus Salsa software, while the second approach configures the autosampler with a Teledyne CETAC ASXPress Plus Rapid Sample Introduction Accessory (Figure 3). It should also be noted that other high sample volume laboratories including geological, agricultural, food and environmental will find the results of this study in increased sample throughput beneficial.

Instrument and Method

Prodigy Plus ICP

A Prodigy Plus Inductively Coupled Plasma (ICP) Spectrometer equipped with a radial-view torch (Figure 1) and a 240-position Teledyne CETAC Oils 7400 Homogenizing Dual Matrix Autosampler (Figure 2) was used to generate the data for this application note.

Figure 1 Prodigy Plus ICP with Radial Torch Configuration

The Prodigy Plus is a compact benchtop simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a mega-pixel CMOS detector. 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 six orders of magnitude. The Prodigy Plus uses a 40.68 MHz rugged, free-running RF Generator, allowing it to handle the most difficult sample matrices, as well as common organic solvents.

Automation

The Teledyne CETAC Oils 7400 Homogenizing Dual Matrix Autosampler allows two sample matrices to be introduced to an ICP instrument from the same system. With a dual-port rinse station fed by two separate peristaltic pumps, the autosampler can easily transition from oil to coolant testing and has improved speed, mixing capability and sample drip capture.

Used oil samples typically contain particulates that settle to the bottom of the sample tube prior to analysis and lead to erroneous results. The Oils 7400 autosampler eliminates this issue by homogenizing each sample using a stirring paddle mounted next to the sample probe, prior to analytical measurement. To prevent cross-contamination, the stirring paddle (along with the sample probe) is cleaned at the rinse station before moving to the next sample. Additionally, sample mixing is configurable via the software dashboard for oil samples that vary in viscosity.

Figure 2 Teledyne CETAC Oils 7400 Homogenizing Dual Matrix Autosampler

The Teledyne CETAC ASXPress Plus Rapid Sample Introduction Accessory increases sample throughput for ICP-OES analysis by reducing sample loading, signal stabilization and washout times. Using proven technology, the ASXPress Plus combines a metal-free, 6-port injection valve and inert, high-speed vacuum pump to rapidly load the sample loop for introduction to the nebulizer. The design of the ASXPress Plus facilitates quick rinsing of the sample loop while simultaneously injecting sample into the ICP-OES nebulizer for analysis. The liquid flow paths are then quickly and thoroughly cleaning using “segmented-stream washout technology”.

Figure 3 ASXPress Plus

Prodigy Plus Sample Introduction

The Prodigy Plus sample introduction system consisted of:

- Cyclonic spray chamber with a knockout tube
- Ryton® V-groove nebulizer
- Four-channel peristaltic pump

The volume of the 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. Virtually impossible to clog, the Ryton V-groove nebulizer is sensitive, inert and requires no adjustment.

The Prodigy Plus torch is mounted using an innovative twist-lock cassette system, shown in Figure 4. This design permits operators to remove and replace the torch in the exact same position, enhancing day-to-day reproducibility and simplified training. Additionally, the twist-lock cassette system automatically connects the coolant and auxiliary gas flows, eliminating potential errors.

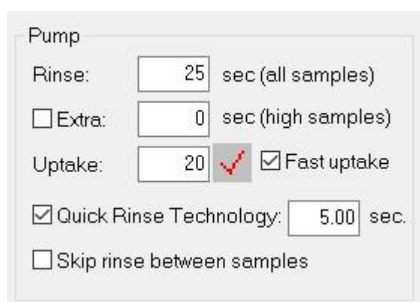
Figure 4 Prodigy Plus Twist-Lock Sample Introduction System

Increasing Sample Throughput Study

A significant portion of sample analysis time consists of uptake and rinse cycles. For this study, two different approaches for increasing sample throughput by reducing uptake and rinse times were demonstrated and corresponding data generated:

- The first approach was entirely software-based and utilized two unique Prodigy Plus Salsa software features (Figure 5). First, the "Fast Uptake" peristaltic pump option was selected, instructing the software to increase pump speed during sample uptake and accelerate the sample's arrival to the nebulizer. In this example, the uptake pump speed was set to 85 rpm while the analytical speed was 25 rpm. Secondly, the "Quick Rinse Technology" option was selected. A user-specified amount of time then determined when the autosampler probe was sent back to the rinse station. By returning the probe to the rinse station prior to completion of the analysis, and the start of the next sample cycle, the Prodigy Plus saved time by performing two actions at once: analyzing the sample while rinsing in preparation for the next.

Figure 5 Salsa Software Pump Panel – Fast Uptake and Quick Rinse Settings



- A second approach configured the system with a Teledyne CETAC ASXPress Plus Rapid Sample Introduction Accessory, in combination with the autosampler. Using a rotary valve and vacuum pump, the ASXPress Plus reduces the sample uptake time while effectively eliminating the sample rinse time. When the ASXPress Plus was used, the "Fast Uptake" and "Quick Rinse Technology" software settings explained in the previous approach were turned off.

Operating Parameters

The instrument operating conditions used for all samples and standards are shown in Table I and Table II. ASXPress Plus settings are given in Table III. The wavelengths used for this analysis are shown in Table IV.

Table I Instrument Operating Conditions		
Parameter	**Value**	**Part Number**
RF Power	1.2 kW	
Coolant Flow	14.0 LPM	
Auxiliary Flow	1.4 LPM	
Nebulizer Pressure	25 PSI	
Torch	Quartz Demountable	318-00167-1
Injector	1.1 mm Bore	318-00161-ORG2

Table II Method Parameters		
Parameter	**Value**	**Part Number**
Sample Uptake Time	20 sec	
Replicates	2	
Integration Time	2 sec	
Rinse Time	25 sec	
Pump Rate	25 RPM	
Fast Pump Rate	85*	
QC Acceptance Limits	±10%	
QC Failure Action	Recalibrate and Rerun	
Sample Uptake Tubing	Black Tab Solvent Flex	309-00069-8
Sample Drain Tubing	Red Tab Solvent Flex	309-00063-5

* This setting is used in conjunction with the Salsa Software “Fast Uptake” and “Quick Rinse Technology” options. When the system is configured with the ASXPress Plus, the “Fast Uptake” option was deselected.

Table III ASXPress Plus Parameters	
Parameter	**Value**
Sample Load	
Loop Load	2 sec
Equalization Delay	2 sec
Stir Delay	0 sec
Post Sample Rinse	
Time to Evacuate Probe	1 sec
Probe Rinse	2 sec
Rinse Station Fill	4 sec

Table IV Analytical Wavelengths, nm	
Analytical Wavelengths	
Ag 328.068 r	Mn 257.610 r
Al 396.152 r	Mo 203.844 r
B 208.956 r	Na 589.592 r
Ba 493.409 r	Ni 231.604 r
Ca 317.933 r	P 214.914 r
Cd 226.502 r	Pb 220.353 r
Cr 205.552 r	Si 288.158 r
Cu 324.754 r	Sn 189.991 r
Fe 259.940 r	Ti 334.941 r
K 766.491 r	V 292.401 r
Mg 279.078 r	Zn 213.856 r

Standard and Sample Preparation

Ten oil samples were obtained from a wear-metal analysis lab and prepared for analysis by diluting 1:10, by weight, with VHG Kerosene Blank.

Calibration standards for all elements at 5, 25 and 50 ppm were prepared by diluting 900 ppm VHG V23 (VHG Labs, Manchester, NH) to the appropriate weight. For the additive elements (Ba, Ca, Mg, P and Zn), calibration standards at 250 and 500 ppm were made by diluting 5000 ppm VHG Metal Additive Standards (MA-5). To minimize viscosity differences, a sufficient quantity of VHG 75cSt Base Oil Blank was added to each standard, such that the final oil concentration was 10% (to match the 1:10 dilution of the samples). To bring the calibration standards to their final weight, VHG Kerosene Blank was used. No internal standard correction was used.

Three quality control (QC) standards were used to monitor instrument stability during the sample run. One QC standard was made at 15 and 25 ppm levels for all elements being determined. A third QC standard for the additive elements was made at 250 ppm.

Two sets of Performance Testing Lube Oil Test Standard (VHG Labs, Manchester, NH), PTPLUBEMO-25, and VPTM0-25 were analyzed to verify the accuracy of the method. These performance samples were also diluted 1:10 using the VHG Kerosene Blank.

Fast Uptake/Quick Rinse Technology Configuration Results (50 Second Sample Time)

After igniting the plasma and allowing 15 minutes for the Prodigy Plus to stabilize, the instrument was calibrated. Immediately following instrument calibration, two QC standards, QC25 and QC250, were analyzed. A QC standard measurement within ±10% of the certified value was required before commencing sample analysis. A summary of all QC standard analysis results is shown in Table VII and Table VIII. All elements were easily within the ±10% acceptance limit and exhibited the high precision expected at these concentration levels. Throughout the remainder of the sample run, the same QC standards were periodically analyzed (every 12 samples for QC25 and every 24 samples for QC250) to ensure analytical accuracy.

Sales/Support: 800-634-9942 • **Main**: 603-886-8400
4736 Socialville Foster Rd., Mason, OH 45040
www.teledyneleemanlabs.com

The Prodigy Plus Salsa software was configured such that should any QC standard result fall outside the ±10% acceptance limit, the Prodigy Plus would automatically recalibrate, rerun both QC standards and after passing the QCs, rerun all samples analyzed following the last successful QC standard.

Immediately following the initial successful analysis of the QC standard, the two Performance Samples, (VPTPMO and PTPLUBEMO), were analyzed. Their results, along with the certified values are shown in Table V and Table VI. The results show an excellent agreement between the "Measured" and "Certified" values and demonstrate the Prodigy Plus's ability to generate both accurate and precise results over the wide concentration range required for oil sample analysis.

All reported concentrations are corrected for any dilution and are in ppm.

Table V Wear Metals Performance Sample Results (VPTPMO), ppm

Element	Measured	Certified Value	% Recovery
Ag	20.0	20.1	99.4
Al	20.1	21.0	95.6
B	126.6	121	104.6
Ca	2136.3	2019	105.8
Cd	25.6	25.0	102.4
Cr	32.0	30.5	104.9
Cu	47.7	45.2	105.5
Fe	69.8	68.1	102.6
K	13.3	13.0	102.3
Mg	423.5	391	108.3
Mn	9.6	10.0	95.5
Mo	15.4	15.0	102.5
Na	75.7	72.0	105.1
Ni	19.8	19.1	103.5
P	1461.3	1500	97.4
Pb	43.7	42.3	103.3
Si	63.2	60.2	105.0
Sn	55.7	58.2	95.8
Ti	12.0	12.1	99.0
V	15.3	15.1	101.1
Zn	757.2	702	107.9

Table VI Wear Metals Performance Sample Results (VPTLUBEMO), ppm			
Element	**Measured**	**Certified Value**	**% Recovery**
Ba	116.6	113	103.2
Ca	1052	1003	104.9
Mg	257.4	251	102.5
Mo	50.9	50	101.8
P	715.8	726	98.6
Si	215.2	202	106.5
Zn	1303	1252	104.1

The ultimate test of a wear metal analysis system is its stability and reproducibility. High sample throughput is meaningless, if samples have to be frequently rerun due to check standard failure caused by drift. Every aspect of an ICP system's design affects its stability - optics, RF power supply and sample introduction being the most crucial. Equally important is the system's ability to compensate for environmental changes due to the lab's location (wear metal labs are often far from an ideal environment for an ICP spectrometer).

The stability of the Prodigy Plus ICP was demonstrated by setting up a complete analytical sequence and repeatedly analyzing the ten used engine oil samples obtained from a wear metals lab. The run resulted in ten analyses of each oil sample, ten analyses of QC25, four analyses of QC250, four analyses of QC15 and a complete calibration. The entire duration of the run was just under 2 hours. Sample-to-sample time for this configuration was 50 seconds.

The stability data for the QC standards is shown in Table VII and Table VIII. There were no QC failures over the course of the run and the results are well within the ±10% acceptance limit. During the analysis, there were no updates of any kind performed, nor was internal standard standardization use.

Sales/Support: 800-634-9942 • **Main**: 603-886-8400
4736 Socialville Foster Rd., Mason, OH 45040
www.teledyneleemanlabs.com

Table VII Check Standard Stability (25.4 ppm Certified Value)				
Element	**Mean**	**SD**	**RSD**	**% Recovery**
Ag	24.7	0.7	2.9	97.1
Al	24.6	0.8	3.2	96.9
B	24.4	0.6	2.6	96.2
Ba	25.1	0.5	1.9	99.0
Ca	25.8	0.4	1.6	101.7
Cd	24.9	0.3	1.4	98.0
Cr	25.1	0.5	1.8	98.7
Cu	24.7	0.8	3.2	97.4
Fe	25.0	0.5	2.1	98.6
K	24.8	1.0	4.1	97.4
Mg	25.1	0.4	1.7	98.8
Mn	25.1	0.4	1.8	98.8
Mo	25.0	0.6	2.2	98.3
Na	24.8	0.8	3.2	97.4
Ni	25.3	0.4	1.6	99.5
P	25.5	0.9	3.8	100.4
Pb	25.4	0.3	1.3	100.0
Si	25.8	0.7	2.8	101.5
Sn	25.3	0.3	1.1	99.6
Ti	24.8	0.7	2.7	97.7
V	24.9	0.5	2.2	98.1
Zn	25.0	0.5	1.9	98.6

Table VIII Check Standard Stability (265.9 ppm Certified Value)				
Element	**Mean**	**SD**	**RSD**	**% Recovery**
Ba 493.409 r	273.0	6.4	2.3	102.7
Ca 317.933 r	259.1	3.7	1.4	97.4
Mg 279.078 r	257.9	3.0	1.1	97.0
P 214.914 r	255.7	5.3	2.1	96.1
Zn 213.856 r	254.4	2.3	0.9	95.6

Table IX contains typical sample data and is the average of the 10 analyses of Sample 1 compared to the results provided by the wear metals lab that supplied the sample. As with the QC data, the sample data exhibited good stability, as well as agreement with the analytical results reported by the wear metals lab. The results for the remaining nine samples analyzed showed similar stability and agreement with the wear metals lab results.

Table IX Long-Term Data for Sample 1 (n = 10)

Line	LT Mean Conc	LT SD Conc	LT RSD Conc	Oil Lab Results
Ag	0	-	-	-1
Al	1.6	0.2	12.7	1
B	2	0.7	35.4	1
Ba	0	-	-	0
Ca	159	4.1	2.6	147
Cd	0	-	-	0
Cr	0	-	-	0
Cu	19.7	0.7	3.4	19
Fe	18.8	0.5	2.9	17
K	2.1	0.4	16.8	2
Mg	4.2	0.3	7.4	5
Mn	0	-	-	-
Mo	0	-	-	0
Na	2	0.1	5.7	2
Ni	0	-	-	0
P	541	15.7	2.9	555
Pb	0	-	-	0
Si	4	0.3	7.5	3
Sn	0	-	-	0
Ti	0	-	-	0
V	0	-	-	0
Zn	789	20.6	2.6	740

ASXPress Plus Configuration Results (31 Second Sample Time)

After installing the ASXPress Plus, the entire sample run was repeated to generate new data for comparison. Using the ASXPress Plus eliminates the need for a rinse time and also reduces the sample uptake time. For the sample data collected using the “standard ICP system” with “Fast Uptake and “Quick Rinse Technology” settings selected, the uptake and rinse times were set to 20 seconds and 25 seconds, respectively as shown in Figure 5.

For the ASXPress Plus configuration, the uptake time was reduced to 13 seconds and the rinse time was eliminated. As a result, the sample-to sample-time was reduced from 50 seconds to 31 seconds. To keep the overall run time approximately the same as that used to obtain the previous data, the number of each sample analyzed was increased to 15. The three QC standards were measured after every 24 samples and the total run time was just over two hours. As with the "standard ICP system" configuration data, there were no updates of any kind used.

The data collected using the ASXPress Plus is shown in Table X, Table XI and Table XII. The quality of the data is equivalent to that obtained using the "standard ICP system" configuration, in that there were no QC failures over the course of the run and the sample results also agreed with the results reported by the wear metals lab.

Table X ASXPress Plus Configuration - Check Standard Stability (26.7 ppm Certified Value)

Element	Mean	SD	RSD	% Recovery
Ag	26.9	0.4	1.6	100.8
Al	26.0	0.4	1.6	97.5
B	27.4	0.5	1.9	102.8
Ba	27.1	0.5	1.8	101.6
Ca	27.3	0.4	1.6	102.3
Cd	26.8	0.4	1.3	100.6
Cr	26.6	0.4	1.4	99.8
Cu	26.4	0.4	1.4	99.1
Fe	26.6	0.4	1.3	99.9
K	26.4	0.4	1.5	99.0
Mg	26.4	0.7	2.6	99.1
Mn	26.9	0.4	1.4	100.8
Mo	26.7	0.4	1.5	100.1
Na	26.5	0.4	1.4	99.4
Ni	26.9	0.3	1.2	101.0
P	27.0	0.6	2.1	101.4
Pb	27.5	0.3	1.1	103.2
Si	26.5	0.4	1.5	99.5
Sn	26.9	0.5	1.7	100.8
Ti	26.5	0.3	1.3	99.4
V	26.7	0.4	1.3	100.0
Zn	26.9	0.5	1.8	100.8

Table XI ASXPress Plus Configuration - Check Standard Stability (261.8 ppm Certified Value)				
Element	**Mean**	**SD**	**RSD**	**% Recovery**
Ba	260.9	5.07	1.94	99.6
Ca	271.2	5.18	1.91	103.6
Mg	280.3	7.07	2.52	107.2
P	272.8	3.79	1.39	104.2
Zn	246.8	5.08	2.06	94.3

Table XII ASXPress Plus Configuration - Long-Term Data for Sample 1 (n = 15)				
Line	**LT Mean Conc**	**LT SD Conc**	**LT RSD Conc**	**Oil Lab Results**
Ag	0	-	-	-1
Al	1.6	0.21	12.7	1
B	1.7	0.5	27.1	1
Ba	1.4	0.2	11.4	0
Ca	153.1	3.3	2.2	147
Cd	0	-	-	0
Cr	0	-	-	0
Cu	18.6	0.5	2.8	19
Fe	18.2	0.4	2.4	17
K	2.1	0.35	16.8	2
Mg	4.2	1.3	31.2	5
Mn	0	-	-	-
Mo	0	-	-	-1
Na	2.4	0.3	11.3	2
Ni	0	-	-	0
P	565	10.5	1.9	555
Pb	0	-	-	0
Si	4.5	0.6	14	3
Sn	0	-	-	0
Ti	0	-	-	0
V	0	-	-	0
Zn	782	8.9	1.1	740

Sales/Support: 800-634-9942 • **Main**: 603-886-8400
4736 Socialville Foster Rd., Mason, OH 45040
www.teledyneleemanlabs.com

Conclusion

This study demonstrates the ability of the Prodigy Plus ICP to perform high-speed wear metal analysis along with two different approaches to increase sample throughput.

The first approach using the "standard ICP system" configuration with Salsa software "Fast Uptake and "Quick Rinse Technology" settings selected, resulted in a sample analysis time of 50 seconds. This time could be further reduced by increasing the "Fast Uptake" pump speed, which was set to 85 rpm for this study, but can be set as high as 200 rpm.

The second approach which configured the system with a Teledyne CETAC ASXPress Plus Rapid Sample Introduction Accessory, resulted in a sample analysis time of 31 seconds. This time savings is achieved by eliminating the rinse time and reducing the sample uptake time. An additional advantage of the ASXPress Plus system is that the sample does not contact the Prodigy Plus peristaltic pump tubing. Once the sample has filled the ASXPress Plus sample loop, the ICP's peristaltic pump simply pushes the contents of the sample loop to the nebulizer. This system characteristic helps to minimize carryover between samples as the ASXPress Plus sample path consists entirely of Polytetrafluoroethylene (PTFE tubing).

The analysis of wear metals in lubricating fluids is a challenging, but common application in ICP spectrometry. Laboratories analyzing samples of this type require accurate, high-throughput analysis, to provide quick turn-around times for their customers.

The Teledyne Leeman Labs Prodigy Plus meets and exceeds these needs with efficient, unattended sample analysis and optimum accuracy and precision. Designed for the most demanding applications, the Prodigy Plus is a true "workhorse" instrument well-suited to the wear metals laboratory due to the following characteristics:

- A high-energy optical system and detector providing precise measurements with short integration times.
- A high-sensitivity sample introduction system designed for rapid equilibration and washout.
- Easy-to-use software that simplifies operation and training.
- A stable, robust RF power supply capable of easily handling the demands of organic samples.

The level of performance exhibited in this application note, demonstrates that the Prodigy Plus ICP will be successful in the most demanding wear metals analysis laboratory.