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

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Introduction

Wear metals analysis using Inductively Coupled Plasma Spectrometers (ICP-OES) has been an important component of predictive maintenance programs for many years. Used oil-based materials, such as engine oils, transmission oils, and engine coolants, are regularly monitored for the presence of particles deposited from the components that they are designed to protect.

These particles gradually build up in the oil due to normal wear of the component (Table I). For this reason, the analysis of used oils and coolants is often referred to as "wear metals analysis" or "fluids 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 overtime. By analyzing the various metals in the fluids and applying trend analysis, expensive breakdowns can be prevented and service life increased.

Fluid analysis can also be used to maximize the usable life of oils by monitoring the health of any additive packages by determining the depletion of particular elements. Among the most widely used additive types are those used for anti-wear. These additives typically contain high concentrations of calcium, phosphorus, and zinc, and are used to reduce premature wear of vehicle engines. The additives in the oil bond to metal surfaces in the engine and help reduce friction between the moving parts. These additives are particularly important for oil used in racing vehicles, as the engines are operated at extremely high temperatures and pressures.

This application note will demonstrate the ability of the Teledyne Leeman Labs' Prodigy Plus ICP to determine a range of elements, both wear and additive, in used oil samples.

Table I Potential Problems Revealed Using Wear Metal Analysis

Wear Metal	Source	Potential Effect
Cr, Fe, Mo	Broken or Stuck Piston Rings	Ring, Liner Wear
Al, Cr, Fe, Si	Dirt Ingestion, Poor Air Filtration	Piston, Ring or Liner Wear
Al, Fe, Pb, Si	Dirt in Lower Engine	Crankshaft Bearing Wear
Al, Cu, Fe	Oil Degradation or Contamination	Piston, Ring and Liner Wear
Al, Cr, Fe	Abnormal Operating Temp, Oil Degradation	Crankshaft Bearing Wear
Al, Pb	Oil Degradation or Contamination	Bearing Damage, Piston, Ring Liner Wear
Na, K, Cu	Engine Coolant	Indicates Coolant Leak

Experimental

Instrument

A Prodigy Plus Inductively Coupled Plasma (ICP) Spectrometer equipped with a radial view torch (Figure 1) and a 240-position Teledyne CETAC ASX-560 autosampler (Omaha NE) (Figure 2) was used to generate the data for this application note.

Figure 1 Prodigy Plus ICP-OES

Figure 2 Teledyne CETAC ASX-560 Autosampler

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 Large Format CMOS (L-CMOS) detector. At 28 x 28 mm, the active area of the L-CMOS is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows the Prodigy Plus 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, 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. A high-sensitivity sample introduction system ensures that sufficient and steady emission signals are transmitted to the spectrometer.

Sample Introduction

The sample introduction system consists of:

- Cyclonic spray chamber with a center 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 torch is mounted in the instrument using an innovative twist-lock cassette system, shown in Figure 3. 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 design automatically connects the coolant and auxiliary gas flows, eliminating potential errors.

Figure 3 Twist-n-Lock Sample Intro System

Operating Parameters

All samples were analyzed using a Prodigy Plus ICP equipped with a radially viewed torch. Instrument operating parameters are shown below in Table II. Method parameters are displayed in Table III.

Table II Instrument Operating Conditions

Parameter	Value	Part Number
RF Power	1.30 kW	
Coolant Flow	16.0 LPM	
Auxiliary Flow	1.2 LPM	
Nebulizer Pressure	22 PSI	
Torch	Quartz Demountable	318-00167-1
Injector	1.1 mm Bore, Demountable	318-00161-ORG2

Table III Method Parameters

Parameter	Value	Part Number
Sample Uptake Time, sec.	50	
Replicates	2	
Integration Time, sec.	15	
Rinse Time, sec.	20	
QC Limit	± 10%	
QC Failure Action	Recalibrate and rerun	
Sample Uptake Rate	25 RPM	
Sample Uptake Tubing	Black Tab Solvent Flex	309-00069-8
Sample Drain Tubing	Red Tab Solvent Flex	309-00063-5

Table IV Analytical Wavelengths, nm

Analytical Wavelengths	
Ag 328.068 r	Mo 203.844 r
Al 396.152 r	Na 589.592 r
B 208.956 r	Ni 231.604 r
Ba 413.066 r	P 214.914 r
Ca 317.933 r	Pb 220.353 r
Cd 226.502 r	Sb 217.581 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
Mn 257.610 r	Co 228.615 r

Standard and Sample Preparation

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). In order to minimize viscosity differences, sufficient 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. Cobalt (Co) was added to the kerosene blank at a concentration of 5 ppm to be used as an internal standard.

Two Quality Control (QC) standards were made to monitor instrument stability during the sample run. One QC standard was made at the 25 ppm level for all elements being determined. A second QC standard, at 250 ppm, was made for the additive elements.

Used automotive engine oils were used as samples:

- 10W-30 High Mileage
- 5W-30 Synthetic

Both samples were prepared for analysis by diluting 1:10 with the kerosene.

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 kerosene blank.

Results

After igniting the plasma and allowing 15 minutes for the Prodigy Plus to warm up, the instrument was calibrated using the calibration standards listed in Table IV. Immediately after calibration, the two QC standards, QC25 and QC250 were analyzed. QC standard measurements within ±10% of the true actual value was required before commencing sample analysis. A summary of all QC standard analysis results are shown in Table VIII and Table IX. All elements are easily within the ±10% interval and exhibit the high precision expected at these concentration levels. Throughout the remainder of the sample run, these QC standards were analyzed periodically (every 60 samples) to ensure accuracy.

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

Immediately after the initial successful QC analysis, the two Performance Samples, (VPTPMO and PTPLUBEMO), were analyzed. Their results, along with the certificate values are shown in Table V and Table VI. Agreement between the "Measured" and "Certificate Values" is excellent and indicates the Prodigy Plus is capable of providing both accurate and precise results over the wide concentration range required when analyzing oil samples.

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

Element	Measured	Certified Value	% Recovery
Ag	20.8	20	104.0
Al	26.6	25	106.3
B	154	150	102.5
Ba	15.0	15	99.7
Ca	2411	2500	96.4
Cd	12.4	12	103.3
Cr	30.4	28	108.4
Cu	52.4	50	104.7
Fe	77.6	75.1	103.3
K	19.2	18	106.5
Mg	350	351	99.7
Mn	21.2	20	106.2
Mo	26.9	26	103.5
Na	126	118	107.0
Ni	18.3	17.8	102.7
P	1184	1200	98.7
Pb	46.3	45	103.0
Sb	34.0	35.1	97.0
Si	36.4	38.4	94.7
Sn	53.3	50.1	106.4
Ti	24.8	24	103.3
V	17.3	16.7	103.3
Zn	631	650	97.1

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Table VI Additive Element Performance Sample Results (PTPLUBEMO), ppm			
Element	**Measured**	**Certified Value**	**% Recovery**
Ba	97.6	98	99.6
Ca	1613	1583	101.9
Mg	121	120	100.7
Mo	51.8	50	103.6
P	729	717	101.7
Si	218	205	106.2
Zn	866	875	98.9

The ultimate test of a wear metal analysis system is its stability. High sample throughput is meaningless, if samples have to be frequently rerun because of check standard failure caused by drift. Every aspect of a system's design affects stability - optics, RF power supply, and sample introduction are all crucial. Equally important is the system's ability to compensate for changes in its environment (wear metal labs are not always ideal locations for an ICP spectrometer).

The stability of the Prodigy Plus was tested by setting up a complete analytical sequence and repeatedly analyzing the two used engine oils obtained from a wear metals lab. The run resulted in 120 analyses of each engine oil type, 5 analyses of QC25 and QC250 and a complete calibration. The entire duration of the run was 7 hours or just under 2 minutes per sample. For labs requiring higher levels of throughput, a switching valve system, such as the Teledyne CETAC ASXExpress is ideal.

Table VII shows the average concentration of all 120 analyses of the two engine oil samples for elemental determination. Elements that were below the detection limit are not included in this table. Table VIII and Table IX contain the average results for each of the two QC check standards.

Table VII Average Results of Oil Samples Analyzed, ppm (n=120)								
High Mileage Oil					Synthetic Oil			
Element	**Mean**	**Dev.**	**RSD**		**Element**	**Mean**	**Dev.**	**RSD**
B	7.66	0.10	0.1		**B**	29.8	0.2	0.7
Ca	183.30	0.90	0.9		**Ca**	1751	16	0.9
Cu	0.50	0.01	0.01		**Cu**	2.72	0.03	1.2
Fe	0.28	0.01	0.01		**Fe**	19.3	0.1	0.3
Mg	2.65	0.04	0.04		**Mg**	429	1.8	0.4
Mo	4.75	0.26	0.3		**Mo**	59.4	0.5	0.8
Na	14.18	0.36	0.4		**Na**	145	2.5	1.7
P	46.45	1.29	1.3		**P**	763	4.2	0.5
Zn	60.13	0.82	0.8		**Zn**	876	3.5	0.4

Table VIII Average Results for QC25, ppm, (n=5)				
Element	**Measured**	**Certified**	**% Recovery**	**RSD**
Ag	25.1	25.0	100.2	1.9
Al	24.4	25.0	97.4	1.8
B	26.1	25.0	104.4	1.7
Ba	25.3	25.0	101.3	2.3
Cd	24.9	25.0	99.6	1.0
Cr	25.3	25.0	101.1	2.4
Cu	25.3	25.0	101.3	2.4
Fe	25.1	25.0	100.2	0.6
K	24.1	25.0	96.4	2.9
Mg	25.8	25.0	103.2	2.1
Mn	24.7	25.0	98.9	1.7
Mo	24.9	25.0	99.7	1.5
Na	24.6	25.0	98.6	2.6
Ni	24.5	25.0	98.0	2.8
P	24.9	25.0	99.6	3.2
Pb	25.4	25.0	101.7	1.3
Sb	24.5	25.0	98.2	1.5
Si	24.4	25.0	97.8	2.0
Sn	24.8	25.0	99.4	1.5
Ti	25.2	25.0	100.8	2.9
V	24.8	25.0	99.1	0.6
Zn	25.5	25.0	102.0	2.6

Table IX Average Results for QC250, ppm, (n=5)				
Element	**Measured**	**Certified**	**% Recovery**	**RSD**
Ba	247.4	250.0	99.0	0.6
Ca	243.8	250.0	97.5	2.9
Mg	246.6	250.0	98.6	1.2
P	245.3	250.0	98.1	1.7
Zn	251.4	250.0	100.6	1.9

This data illustrates the outstanding stability of the Prodigy Plus over the entire run of 240 sample analyses without a single QC check standard failure. No updates or recalibrations were performed during the run. In total, 266 analyses were performed including samples and check standards.

Conclusion

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 time for their customers.

The Teledyne Leeman Labs' Prodigy Plus meets 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 because of 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 will be successful in the most demanding wear metals analysis labs.