Determination of Wear Metals using the Teledyne Leeman Lab's Prodigy7 ICP-OES

Application Note – AN1304

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.

Figure 1 Prodigy7 ICP-OES

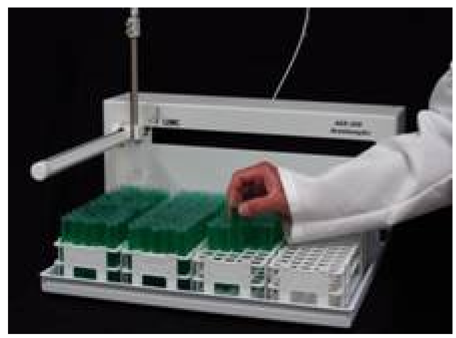

Figure 2 CETAC ASX520 Autosampler

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 Lab's Prodigy7 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

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Experimental

Instrument

A Prodigy7 Inductively Coupled Plasma (ICP) Spectrometer (Figure 1) equipped with a radial 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 mega-pixel Large Format CMOS (L-CMOS). 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 Prodigy7 to achieve higher optical resolution than other solid-state detector-based ICP system. 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.

The Prodigy7 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 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 a newly designed 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 simplifying 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

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Operating Parameters

All samples were analyzed using the Prodigy7 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	1.2 kW	-
Coolant Flow	12 L/min	-
Auxiliary Flow	0.8 L/min	-
Nebulizer Pressure	30 psi	-
Torch	Quartz Demountable	318-00160-1
Injector	1mm bore, Demountable	318-00161-ORG2

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 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	Mo 203.844
Al 396.152	Na 589.592
B 208.956	Ni 231.604
Ba 233.527	P 214.914
Ca 317.933	Pb 220.353
Cd 226.502	Sb 217.581
Cr 205.552	Si 288.158
Cu 324.754	Sn 189.991
Fe 259.940	Ti 334.941
K 766.491	V 292.401
Mg 279.078	Zn 213.856
Mn 257.610	Co 228.615

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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, 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 were prepared for analysis by diluting 1:10 with the kerosene blank oil.

Two sets of Performance Testing Lube Oil Test Standard (VHG Labs, Manchester, NH) (PTPLUBEMO-25, sample ID: 00050007 and 20130014 and VPTM0-25, sample ID: 10073001 and 30066038) 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 Prodigy7 to warm up, the instrument was calibrated using the calibration standards listed above. Immediately after calibration, the two QC standards, QC25 and QC250 were analyzed. To be able to begin sample analysis, it is required that the QC standards be measured to ±10% of the true actual value. Results from the QC standards analysis are shown in Table V and Table VI. All elements are easily within the ±10% interval and exhibit the high precision expected at these concentration level. During the remainder of the sample run, these QC standards were analyzed periodically. The QC25 standard was analyzed after every 12 samples and the QC250 after every 60. The instrument software was setup such that should any QC standard results fall outside the ±10% range, the Prodigy7 would automatically recalibrate, rerun both QC standards and after passing the QCs, rerun all the samples analyzed since the last successful QC standard.

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Table V	Initial QC25 Results (ppm)			
	Mean	SD	RSD	%Recovery
Ag	25.1	0.2	0.8	100.3
Al	25.0	0.3	1.0	99.8
B	24.8	0.2	0.8	99.2
Ba	26.0	0.1	0.4	103.8
Ca	25.4	0.0	0.1	101.6
Cd	25.0	0.1	0.2	99.9
Cr	24.7	0.1	0.4	98.7
Cu	25.0	0.1	0.4	99.9
Fe	24.9	0.1	0.5	99.8
K	24.9	0.2	0.9	99.8
Mg	24.9	0.1	0.4	99.6
Mn	24.9	0.1	0.3	99.7
Mo	25.3	0.2	0.6	101.1
Na	25.9	0.1	0.5	103.7
Ni	25.0	0.1	0.4	99.9
P	25.2	0.1	0.5	100.8
Pb	24.7	0.0	0.1	98.7
Sb	24.6	0.1	0.4	98.5
Si	25.0	0.2	0.6	99.9
Sn	24.4	0.1	0.4	97.6
Ti	25.1	0.1	0.4	100.3
V	25.6	0.2	0.7	102.6
Zn	25.7	0.1	0.2	102.7

Table VI	Initial QC250 Results, ppm			
	Mean	SD	RSD	%Recovery
Ba	253.2	2.3	0.9	101.3
Ca	249.5	0.2	0.1	99.8
Mg	244.9	1.6	0.6	98.0
P	248.8	1.1	0.4	99.5
Zn	249.5	0.3	0.1	99.8

Immediately after the initial successful QC analysis, the two Performance Samples, VPTPMO and PTPLUBEMO, were analyzed. Their results, along with the certificate values are given in Table VII and Table VIII. Agreement between the "Measured" and "Certificate Values" is excellent and indicates the Prodigy7 is capable of providing both accurate and precise results over the wide concentration range required when analyzing oil samples.

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Table VII Wear Metals Performance Sample Results (VPTPMO), ppm			
	Measured	Certificate Value	%Recovery
Ag	31.1	31.7	98.1
Al	12.2	11.8	103.4
B	107	102.4	104.5
Ba	1045	1037	100.8
Ca	2804	2832	99.0
Cd	12.7	12.3	103.3
Cr	4.0	3.7	108.1
Cu	22.6	22.6	100.0
Fe	122	119	102.6
K	20.5	20.4	100.5
Mg	500	490	102.0
Mn	8.6	8.2	104.9
Mo	32.4	31.9	101.6
Na	41.1	42.2	97.4
Ni	6.5	5.9	109.6
P	965.9	984	98.2
Pb	20.9	21.8	95.9
Sb	68	67.3	101.0
Si	43.5	45.1	96.5
Sn	8.9	8.9	99.7
Ti	7.4	7.1	104.2
V	42.8	42.5	100.7
Zn	1007	988	101.9

Table VIII Additive Element Performance Sample Results (PTPLUBEMO), ppm				
	Mean	SD	RSD	%Recovery
Ba	253.2	2.3	0.9	101.3
Ca	249.5	0.2	0.1	99.8
Mg	244.9	1.6	0.6	98.0
P	248.8	1.1	0.4	99.5
Zn	249.5	0.3	0.1	99.8

Table IX displays a typical set of results for the two engine oil samples. In the table, the entry of “ND” indicates the element was not detected in the sample. As expected, precisions for high concentration elements are below 1%. Elements present at low concentrations, such as Pb, will exhibit lower levels of precision.

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Table IX Typical Sample Results, ppm							
High Mileage Oil				Synthetic Oil			
	Mean	Dev.	RSD		Mean	Dev.	RSD
Ag	ND	-	-	**Ag**	ND	-	-
Al	ND	-	-	**Al**	ND	-	-
B	101.5	0.3	0.3	**B**	29.19	0.29	1.0
Ba	ND	-	-	**Ba**	ND	-	-
Ca	2504	17	0.7	**Ca**	1832	5.39	0.3
Cd	ND	-	-	**Cd**	ND	-	-
Cr	ND	-	-	**Cr**	ND	-	-
Cu	6.38	0.1	1.6	**Cu**	2.39	0.03	1.3
Fe	2.79	0.08	3.0	**Fe**	18.35	0.01	0.1
K	ND	-	-	**K**	ND	-	-
Mg	22.09	0.18	0.8	**Mg**	431.6	0.77	0.2
Mn	ND	-	-	**Mn**	ND	-	-
Mo	61.6	1.21	2.0	**Mo**	62.5	0.1	0.2
Na	179.5	0.85	0.5	**Na**	166.4	0.25	0.2
Ni	ND	-	-	**Ni**	ND	-	-
P	817.9	0.53	0.1	**P**	793.3	1.29	0.2
Pb	5.56	0.49	8.8	**Pb**	1.7	0.14	8.2
Sb	ND	-	-	**Sb**	ND	-	-
Si	ND	-	-	**Si**	ND	-	-
Sn	ND	-	-	**Sn**	ND	-	-
Ti	ND	-	-	**Ti**	ND	-	-
V	ND	-	-	**V**	ND	-	-
Zn	916.7	2.36	0.3	**Zn**	937.1	2.05	0.2

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, sample introduction are all crucial. Also critical 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 Prodigy7 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 the analysis of 119 of each of the engine oils, 21 analyses of QC25, 11 analyses of QC250 as well as a complete calibration. The entire duration of the run was 5 hours or just under 55 seconds per sample. For labs with higher throughput needs, a switching valve system, such as the CETAC CETAC ASX520 Autosampler is ideal.

Table X shows the average concentration of all 120 analyses of the two engine oil samples for element that were detected on the samples. Table XI and Table XII contain the average results for each of the two QC check standards.

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Table X	Average Results of Oil Samples Analyzed, ppm (n = 120)							
High Mileage Oil					Synthetic Oil			
	Mean	Dev.	RSD			Mean	Dev.	RSD
B	100.6	2.7	2.7		**B**	29.7	0.8	2.8
Ca	2509	14.6	0.6		**Ca**	1834	12.7	0.7
Cu	6.5	0.2	3.4		**Cu**	2.3	0.1	3.1
Fe	2.9	0.1	4.7		**Fe**	17.8	0.3	1.9
Mg	21.2	0.6	2.8		**Mg**	426.2	8.4	2.0
Mo	62.0	1.1	1.8		**Mo**	61.0	0.9	1.4
Na	184.1	5.2	2.8		**Na**	162.6	8.5	5.2
P	810.5	11.1	1.4		**P**	803.9	10.5	1.3
Pb	5.9	0.3	4.8		**Pb**	1.9	0.2	12.1
Zn	915.5	7.5	0.8		**Zn**	941.0	8.4	0.9

Table XI Average Results for QC25, ppm (n=21)			
	Mean	SD	RSD
Ag	25.6	0.5	1.9
Al	24.8	0.4	1.7
B	24.8	0.5	1.9
Ba	26.3	0.6	2.4
Ca	26.0	0.3	1.3
Cd	24.6	0.2	0.7
Cr	24.2	0.3	1.1
Cu	25.5	0.6	2.4
Fe	25.0	0.2	0.9
K	24.9	0.9	3.6
Mg	24.8	0.5	1.8
Mn	25.0	0.7	2.6
Mo	25.5	0.2	0.8
Na	26.8	1.6	5.8
Ni	25.0	0.2	0.6
P	25.6	0.4	1.4
Pb	24.1	0.5	2.1
Sb	23.6	0.7	2.8
Si	25.1	0.3	1.1
Sn	23.2	1.0	4.1
Ti	25.8	0.4	1.7
V	26.0	0.3	1.0
Zn	25.6	0.3	1.2

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Table XII Average Results for QC250, ppm (n=5)			
	Mean	SD	RSD
Ba	253	4.3	1.7
Ca	250	3.1	1.2
Mg	244	5.4	2.2
P	248	3.8	1.5
Zn	252	2.7	1.1

These data illustrate the outstanding stability of the Prodigy7: over the entire 5 hour run 240 sample analyses were performed without a single check standard failure. No updates or recalibrations were performed during the run. The total number of analyses during this run was 266. This figure includes all samples and check standards.

Conclusion

The analysis of wear metals in lubricating fluids is a challenging but common application in ICP spectrometry. Generally, laboratories analyzing samples of this type require accurate, high throughput analysis, to provide quick turn-around time for their customers. The Teledyne Leeman Lab's Prodigy7 provides a high rate of sample throughput with optimum accuracy and precision, under standard operating conditions.

The Prodigy7 is able to provide this level of performance by paying proper attention to the needs of wear metals analysis labs and then reflecting those needs into the ultimate workhorse instrument.

The design features making this possible are:

- A high energy optical system and detectors ideal for making precise measurements with short integration times
- An 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 able to easily handle the demands of organic samples

With level of performance presented in this application note, the Prodigy7 will be successful in the most demanding wear metals analysis labs.

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