RADOM™

DETERMINATION OF WEAR METALS IN LUBRICATING OILS UTILIZING MICROWAVE INDUCTIVELY COUPLED ATMOSPHERIC PRESSURE PLASMA

MICAP-OES 1000 Optical Emission Spectrometer:

- Robust nitrogen plasma with superior matrix tolerance
- Simultaneous measurement for fast analysis times
- Smallest footprint and light-weight design
- Reduced running cost/analysis

REIMAGINE PLASMA™

Introduction

Proper maintenance scheduling for critical engine and machines should be considered to minimize cost, extend lifetime, and maximize performance. Over and under maintaining can lead to unnecessary repair or replacement of the engine or the vehicle. The determination of wear metal profile can help isolate areas for maintenance. Table 1 describes the target elements and the associated wear to their presence.[1]

Table 1. Wear Metal Indicator[2]

Elements	Wear Indication
Aluminum	Piston and bearings wear, push rods, air cooler, pump hosings, oil pumps, gear castings, box castings
Antimony	Crankshaft and camshaft bearings
Boron	Coolant leakage in system
Cadmium	Bearings
Chromium	Ring wear, cooling system leakage, chromium-plated parts in aircraft engines, cylinder liners, seal rings
Copper	Wear in bushings, injector shields, coolant core tubes, thrust washers, valve guides, connecting rods, piston rings, bearings, sleeves, bearing cages
Iron	Wear from engine block, cylinder, gears, cylinder liners, valve guides, wrist pins, rings, camshaft, oil pump, crankshaft, ball and roller, bearings rust
Lead	Bearings, fuel blowby, thrust bearings, bearing cages, bearing retainers
Magnesium	Cylinder liner, gear box housing in aircraft engines
Molybdenum	Wear in bearing alloys and in oil coolers; various molybdenum-alloyed components in aircraft engines, piston rings
Nickel	Bearings, valves, gear platings
Silicon	Dirt intrusion from improper air cleaner, seal materials
Silver	Wrist pin bearings in railroad and auto engines, silver plotted spline lubricating pump
Sodium	Antifreeze leakage
Tin	Bearings and coatings of connecting rods and iron pistons
Titanium	Various titanium-alloyed components in aircraft engines
Tungsten	Bearings
Zinc	Neoprene seals, galvanized piping

Traditionally Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES) is used to determine wear metals in lubricating oils. In this application brief, the MICAP-OES 1000 was utilized to determine elements prepared by ASTM Method D5185. The acceptance criteria outlined in the standard test method was used evaluate the results.

Experimental

Samples and Sample Preparation

Samples included one in-service oil (unknown) and one Matrix Reference Material (MRM) HU-1, which were diluted 10x with ICP Solvent PremisolvTM (refined kerosene). Each sample and standard contained 10 ppm Co and 10 ppm Y.

The unknown in-service oil was synthetic oil from a 2006 Dodge Durango (130,000 miles) with service frequency of change/3000 miles.

The MRM HU-1 test article was acquired from SCP Science cat # 140-025-041. This was prepared and analyzed two times at 2-week intervals.

Quantitative measurements were obtained against external calibration curves made from Conostan S-21 (commercial organometallic standard) stock solutions diluted to the appropriate concentrations (1.0, 5.0, 10 ppm) with PresolveTM, with 75 centistoke (cSt) base oil serving as a blank. Co (10 ppm) and Y (10 ppm) were also added to the blank and calibration standards.

The method was standardized with a blank and a 5 ppm standard. The 1 ppm and 10 ppm standard were analyzed as samples to establish criteria below and above the 5 ppm standard.

Experimental Conditions

All analyses were performed on a microwave inductively coupled atmospheric pressure plasma - optical emission spectrometer system (MICAP-OES). MICAP-OES 1000 is a microwave plasma source paired with a simultaneous optical spectrometer with a sCCD camera for detection. The plasma source is coupled to the spectrometer via fiber optic connection.

Instrument Setup and Conditions

The instrument setup is depicted in Figure 1 which summarizes the nebulizer, spraychamber and torch used for sample analysis.

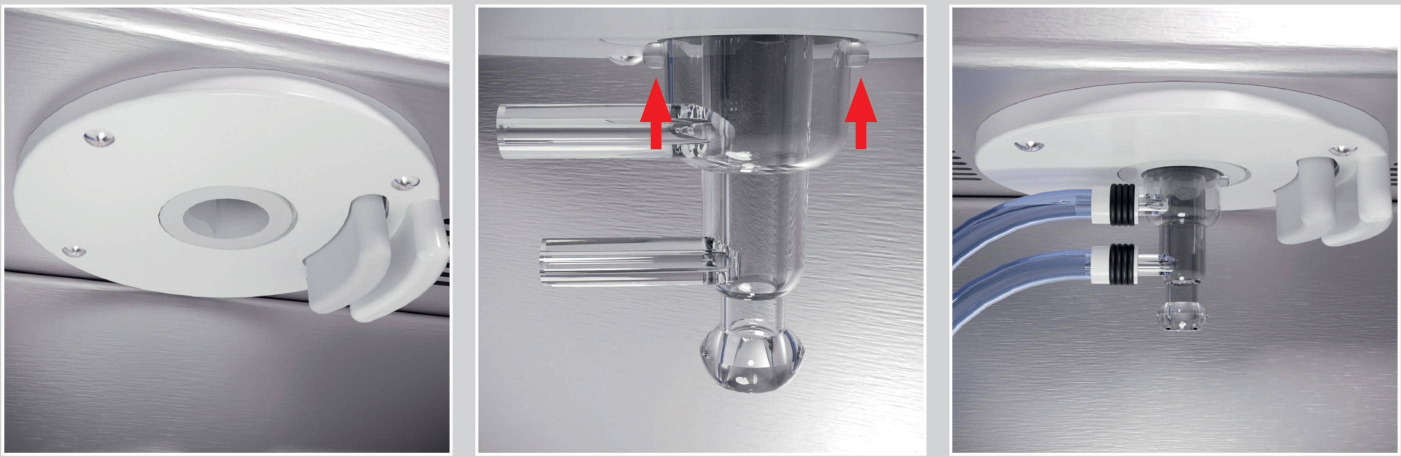
MICAP-OES 1000

Sample Introduction Assembly (SIA)

- Glass Expansion 0.2mL/min Micromist nebulizer
- Double pass cyclonic spraychamber
- 2.5mm injector torch
- No oxygen addition required

Figure 1. Sample Introduction Assembly (SIA)

MICAP-OES 1000 plasma is axially viewed. The plasma tail removal system automatically sheers the recombination zone without user intervention. This system is comprised of an air sheer gas and reproducible torch installation assembly pictured in Figure 2.



1. Torch guide 2. Torch alignment pegs 3. Completed assembly

Figure 2. MICAP-OES Torch Guide

The method parameters are presented in Table 2.

Table 2. Method Conditions

Parameters	Teledyne Cetac Technologies ASX-560
Coolant (L/min)	14
Auxiliary (L/min)	0.40
Nebulizer (L/min)	0.70
Power (W)	1000
Exposure time (ms)	1000
Replicates	
# of Exposures	10
# of Repeats	3
Time/sample	2 min 50 sec
Internal Standard	Co 238.892

Results and Discussion
Advantages of MICAP-OES

Typically, ICP-OES is used for simplicity, ease of use and matrix tolerance. The sample introduction design is well understood and with continuous flow or value injection present the sample to the plasma. The linear range, wavelength flexibility and ease of reporting makes the ICP-OES a great tool for wear metal analysis. The highest consumable for traditional ICP-OES is the argon gas used to create and sustain the plasma.

MICAP-OES 1000 uses a patented technology Radom Cerawave™ which creates and sustains a robust plasma using nitrogen gas. The plasma source is coupled via fiber optic to a research grade spectrometer using sCCD camera.

Analysis of in-Service Oils following ASTM D5185

The analysis of the MRM test sample was performed on two non-consecutive days. The table summarizes the elements, wavelength, measured results for both analysis sessions (2-week interval), consensus value and confidence interval.

Table 3. Matrix Reference Material Summary of Results for Two Non-Consecutive Days

Catalogue No.: 140-025-041		EnviroMAT™	Lot No.: HU-1	Used Oil	First run	Second run
Element	Wavelength nm	Consensus Value (mg/kg)	Confidence Interval (mg/kg)	Tolerance Interval (mg/kg)	MICAP-OES Measured (mg/kg)	MICAP-OES Measured (mg/kg)
Ag	338.289	17.4	15.5 – 19.4	4.33 – 30.6	17.3	17.3
Al	396.152	28.9	27.8 – 29.9	20.7 – 37.0	29.5	32.2
Ba	493.408	18.7	18.0 – 19.4	13.5 – 23.9	18.8	18.8
Ca	317.933	62.7	59.7 – 65.8	39.9 – 85.6	64.4	74.9
Cd	228.802	19.5	18.7 – 20.2	14.2 – 24.8	19.7	19.7
Cr	425.435	18	17.3 – 18.7	12.8 – 23.1	17.9	17.1
Cu	327.396	4182	4002 – 4362	2932 – 5431	3089	4782
Fe	259.94	94.5	91.1 – 98.0	68.6 – 120	96.3	96.3
Mg	279.553	18.6	17.8 – 19.3	12.9 – 24.3	20.9	20.9
Mn	259.372	19.9	19.3 – 20.6	14.6 – 25.2	20.7	21.1
Mo	281.615	18	17.5 – 18.6	14.0 – 22.1	18.8	18.8
Na	588.995	35.1	32.0 - 38.2	12.3 - 57.9	36.3	36.3
Ni	341.476	64	60.6 – 67.4	38.8 – 89.3	66.9	64.0
P	-----	-48	-----	-----	-----	-----
Pb	283.305	25.1	23.5 – 26.7	12.5 – 37.6	20.3	22.3
Si	251.611	21.3	20.4 - 22.2	14.5 - 28.2	22.3	22.3
Sn	303.412	510	474 - 546	269 - 751	528	552
Ti	334.94	16.8	16.0 – 17.6	10.5 – 23.0	17.1	18.5
V	311.071	17.1	16.4 – 17.9	11.4 – 22.9	18	19.1
Zn	213.857	58.5	56.5 – 60.6	44.0 – 73.1	60.7	60.7

The results for the in-service used oil with matrix spike recoveries are summarized in Table 4. The spike recovery for some elements could not be calculated due to the fact that the spike concentration was equal to or significantly less than the inherent concentration of the element measured.

Table 4. In-Service Syntenic Engine Oil Matrix Spike Results and Recovery

In-service Oil, engine 130,000 miles with oil change every 3000 miles. Synthetic oil. Spike concentration 2.57 mg/kg

Element	Wavelength nm	Initial Result Sample (mg/kg)	Initial Result Spike (mg/kg)	Spike recovery (%)
Ag	328.068	0.032	2.32	89
Al	396.152	0.283	2.80	98
B	249.772	2.425	4.46	80
Ba	455.403	-0.018	2.45	96
Ca	317.933	73.5	983	*
Cd	228.802	-0.466	2.45	114
Cr	428.973	0.146	2.73	100
Cu	327.396	1.36	2.48	44
Fe	259.94	2.03	4.59	100
Mg	279.553	29.3	392	*
Mn	257.610	0.022	2.46	95
Mo	281.615	7.36	10.2	111
Na	588.995	1.41	4.21	109
Ni	341.476	0.341	2.88	99
P	253.560	45.0	49.5	*
Pb	283.305	-0.37	2.57	115
Sn	283.998	-0.034	2.52	99
Ti	336.121	0.069	2.32	87
V	309.31	-0.045	2.47	98
Zn	213.857	53.1	707	*

* spike concentration is less than the inherent element concentration

The QC recoveries for the 1ppm, 5 ppm and 10 ppm quality control check standard solutions are presented in Figure 3.

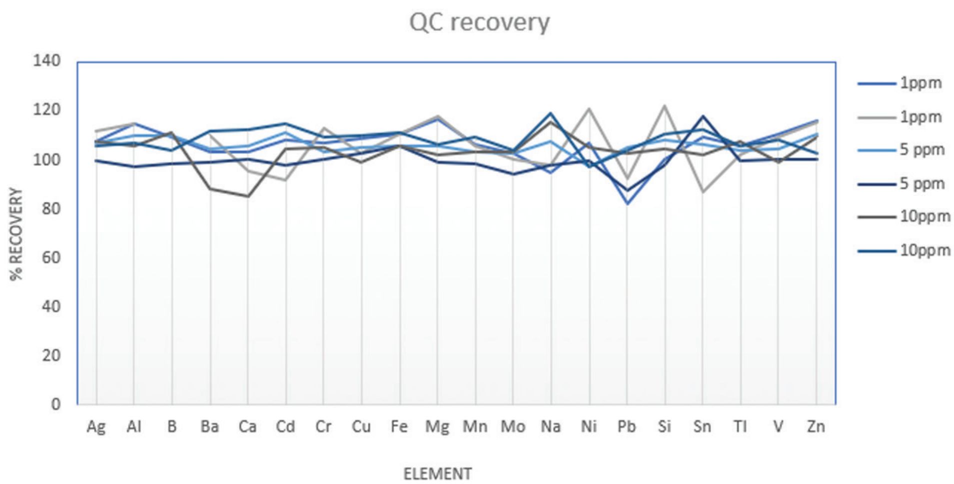


Figure 3. Quality Control Standards Plotted For Analysis 1

Conclusion

MICAP-OES 1000 was used to determine metals for in-service unknown sample, matrix spike and Material Reference Material, HU-1. The results were in the expected range and the unknown sample results were verified with a matrix spike sample.

Notes

1, 2 ASTM D5185 “Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry,” ASTM.