APPLICATION NOTE

ICP - Optical Emission Spectroscopy

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Analysis of In-Service Oils Following ASTM D5185 with the Avio 220 Max ICP-OES

Introduction

With heavy machinery, it is important to assess its status during operation to prevent breakdowns and costly repairs. A key aspect is monitoring the status of the oil or lubricants used to lubricate various components such as engines, transmissions, gearboxes and many other important areas: if the oil degrades too much or becomes highly contaminated, it can damage various components. While many aspects of in-service oils need to be monitored, the metal content provides information about the condition of both the engine and the oil itself to help determine the health of the engine and when the oil needs changing. Because of its importance, ASTM created a method for the analysis of in-service oils: method D5185.

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Since metal concentrations are typically greater than 1 ppm, D5185 specifies ICP-OES as the analytical technique, along with specific criteria, as outlined in Table 1. However, many labs that run D5185 process hundreds of samples a day, making strict adherence to the method a burdensome task. As a result, shortcuts are often taken to improve sample throughput while maintaining quality data. The most common modifications are also shown in Table 1.

Table 1. Highlights of ASTM D5185 and common implementation.

Parameter	Specified by D5185	Common Implementation
Elements	Al, Ba, B, Ca,Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, P, K, Na, Si, Ag, S, Sn, Ti, V, Zn	Elements important to the components being tested
Sample Preparation	By weight	By volume
Internal Standard	Cd, Co, or Y	Co
QC Frequency	Every 5 samples	Varies between 10-25 samples
QC Limits	± 5%	± 10%

For high-throughput labs, fully simultaneous ICP-OES instruments, such as PerkinElmer's Avio® 550 Max Oils configuration, are preferred for their ability to run many wavelengths at the same time.[1] However, there are a fair number of labs with lower sample volumes where analytical speed is not as important. In these instances, a lower-cost, hybrid simultaneous ICP-OES, only available in the Avio 220 Max from PerkinElmer, is the ideal alternative.

This work will focus on the analysis of in-service oils using the Avio 220 Max ICP-OES, following a common implementation of ASTM D5185.[2]

Experimental

Samples and Standards Preparation

In-service oil samples were obtained and diluted 10x by volume with V-Solv™ as a diluent, which was spiked with 40 ppm cobalt (Co) (to act as an internal standard). Pre-mixed V-Solv™ with Co added is also available, reducing the chance of error when spiking the solution. Calibration curves were made from a 75 cSt base oil as a blank, three V-23 stock solutions at 50, 100, and 500 ppm (PerkinElmer), and a Metals Additives Standard (MA4) (PerkinElmer) which contains Ca at 5000 ppm and P, Mg, and Zn at 1600 ppm. The blank and all standards were prepared the same way as the samples. The 50 ppm V23 and the MA4 standards were used as QC samples during sample analysis. The 50 ppm QC was used for all wear and contaminant metals, while the MA4 was used as the QC for the additive elements.

Instrument Conditions

All analyses were performed on the Avio 220 Max ICP-OES running in radial mode using the conditions in Table 2, with the analytes and wavelengths listed in Table 3. These wavelengths have proven over many years to be interference-free in this application when using a spectrometer whose measured resolution is equal to or less than 0.008 nm at 200 nm. The nebulizer gas flow was adjusted so that the tip of the "green bullet" in the central channel was just below the top flat plate, as shown in Figure 1.

Table 2. Avio 220 Max ICP-OES instrumental parameters and conditions.

Parameter	Value
Nebulizer	GemCone™ (modified Babbington)
Spray Chamber	Baffled glass cyclonic
RF Power	1500 W
Torch	3-Slot Avio torch for organics
Injector	1.2 mm ceramic
Plasma Gas Flow	10 L/min
Aux Gas Flow	0.8 L/min
Nebulizer Gas Flow	0.40 L/min
Torch Position	-4
Sample Uptake Rate	2.0 mL/min
Sample Uptake Tubing	Black/Black (0.76 mm id), Viton
Drain Tubing	Red/Red (1.14 mm id), SolvaFlex
Read Delay	18 sec
Replicates	2
Rinse Between Samples	12 sec (fast pump at 6 mL/min)
Auto Integration Range	0.2 - 1.0 sec

Table 3. Analytes and wavelengths.

Element	Wavelength (nm)
Al	394.401
Ag	328.068
B	249.677
Ba	232.527
Ca	315.887
Cd	228.802
Cr	205.560
Cu	324.752
Fe	259.939
K	766.490
Mg	279.077
Mo	203.845
Mn	257.610
Na	588.995
Ni	232.003
P	214.914
Pb	220.353
Sb	217.582
Si	288.158
Sn	189.927
Ti	334.940
V	292.464
Zn	213.857
Co (internal standard)	228.616

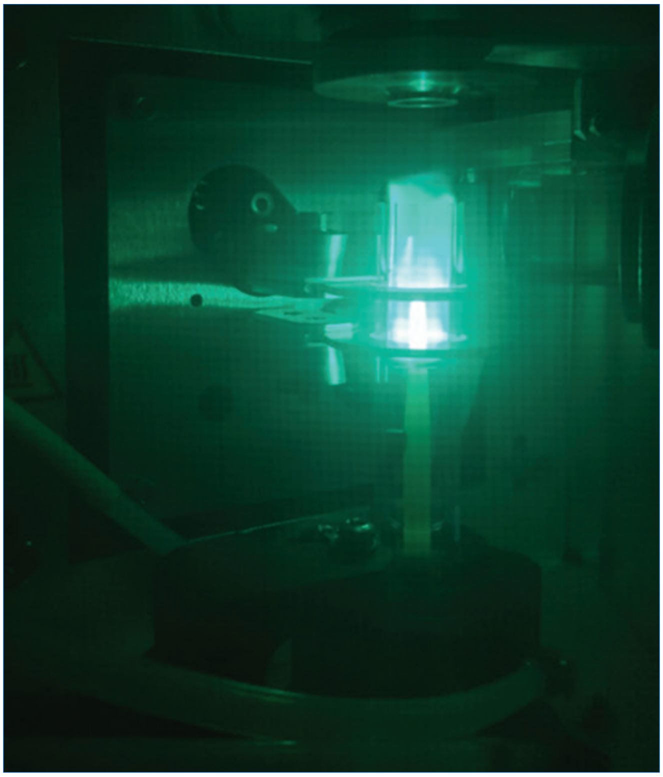

Figure 1. Correct position of green carbon "bullet" just below the second plate of Avio's unique Flat Plate plasma technology, when aspirating V-Solv.

Results and Discussion

With the instrumental parameters in Table 2, the Avio 220 Max ICP-OES can run a sample in five minutes, which includes measuring the 23 elements listed in Table 3 and the internal standard in two replicates. When fewer elements are measured, the analysis time is further reduced. For a low-volume, in-service oil lab running 10-50 samples a day, this analytical speed is all that is required. The results from a typical in-service oil sample are shown in Table 4.

Stability was determined by measuring the QC samples both at the beginning and end of a run consisting of 15 in-service oil samples. The results of the final QC sample appear in Table 5 and show that all elements recovered within ± 10% of the true value, meeting the acceptance criteria of typical in-service oil labs. These results demonstrate the stability of the methodology, allowing a low-volume, in-service oil lab to easily perform their daily analyses with the Avio 220 Max spectrometer.

Several instrumental considerations of the Avio 220 Max ICP-OES contribute to its stability. First, the vertical torch means that any non-ionized sample will drain back down the torch rather than pooling in the injector, leading to few carryover effects. The shear gas cuts off the end of the plasma, preventing deposition on the axial window. Although axial mode is not used in this analysis, this feature allows the Avio 220 Max to be used for other analyses without having to worry about deposition or cone maintenance. Finally, Avio's unique Flat Plate™ plasma technology, which forms the plasma (as shown in Figure 1), is very robust and requires no cooling, which leads to the increased stability. The flat plates also reduce argon consumption: only 11.2 L/min of total argon were used for these analyses.

Table 4. Results from a typical in-service oil sample.

Element	Concentration (ppm)	RSD (%)
Al	16	3.1
Ag	< 0.5*	-
B	81	2.8
Ba	< 0.5*	5.9
Ca	2441	0.21
Cd	< 0.5*	-
Cr	1	2.6
Cu	1	0.26
Fe	27	0.44
K	5	8.0
Mg	17	2.2
Mo	25	0.87
Mn	1	0.69
Na	236	0.44
Ni	2	12
P	847	1.9
Pb	7	0.65
Sb	< 0.5*	-
Si	9	4.2
Sn	< 0.5*	-
Ti	< 0.5*	-
V	< 0.5*	-
Zn	974	2.8

* = lower quantification limit

Table 5. Final QC check samples of a 20 sample analytical run.

Element	Final QC	
	Concentration (ppm)	% Recovery
Al	50	100
Ag	48	96
B	54	108
Ba	49	98
Ca	45	90
Cd	50	100
Cr	50	100
Cu	50	100
Fe	53	106
K	49	98
Mg	46	92
Mo	49	98
Mn	49	98
Na	49	98
Ni	49	98
P	46	92
Pb	50	100
Sb	50	100
Si	48	96
Sn	49	98
Ti	50	100
V	49	98
Zn	47	94

Conclusion

This work has demonstrated the ability of the Avio 220 Max hybrid simultaneous ICP-OES to analyze in-service oils following a common implementation of ASTM method D5185. Although not as appropriate for high-throughput labs running hundreds of samples a day, the five-minute analysis time is fast enough for low-volume labs. However, as the number of elements decreases, analysis time improves, making the Avio 220 Max an appropriate choice for labs wanting to implement D5185 while taking advantage of the Avio 220 Max benefits.

References

1. Hilligoss, D. "Analysis of In-Service Oils Following ASTM D5185 with the Avio 550 Max ICP-OES", PerkinElmer application note, 2021.
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.

Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black (0.76 mm id), Viton	N0773118
Drain Tubing, Red/Red (1.14 mm id), SolvaFlex	09923037
Metal Additives Standard, MA4	N9308259 (100 g) N0776108 (200 g) N9308333 (400 g)
V-23 Wear Metals Standard, 50 µg/g	N9308243 (100 g) N0776104 (200 g) N9308317 (400 g)
V-23 Wear Metals Standard, 100 µg/g	N9308245 (100 g) N0776105 (200 g) N9308318 (400 g)
V-23 Wear Metals Standard, 500 µg/g	N9308249 (100 g) N0776106 (200 g) N9308320 (400 g)
Cobalt Internal Standard, 6% in hydrocarbon oil	N0776107 (200 g) N9304168 (400 g)
V-Solv Solvent	N9308265 (1 gallon) N9308378 (5 gallons)
Sample Tubes, 17x100 mm, 1200	N0777167
Pre-Mixed ICP Solvent + Cobalt: Co @ 40.0 µg/g in V-Solv™	N9308198 (1 gallon) N9308199 (5 gallons)
Sample Tubes Free-Standing, 28 mm x 115 mm	B0193234

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