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Analysis of Oil Additives Following ASTM D4951 with the Avio 200 ICP-OES

Introduction

When blending base oils and additives for use as lubricants, it is important to know and control the concentrations of certain elements for optimal performance and

longer engine life. Because this process is so crucial, ASTM developed a method for monitoring this procedure: ASTM method D4951, which covers barium (Ba), boron (B), calcium (Ca), copper (Cu), magnesium (Mg), molybdenum (Mo), phosphorus (P), sulfur (S), and zinc (Zn). However, not all these elements need to be measured all the time – the blends and additives are specified to meet certain performance specifications which can vary among oil types, depending on their final use.

Oil blending facilities typically analyze 10-40 samples per day to support manufacturing. As a result of the low sample load, small number of elements, and relatively high concentrations, analysis is most commonly performed either by X-ray or ICP-OES, with each technique having its advantages and limitations.

This work will focus on the analysis of additives in new oils using PerkinElmer's Avio™ 200 ICP Optical Emission Spectrometer¹ (ICP-OES), which overcomes limitations of other ICP-OES systems and X-ray analyses.

Experimental

Samples and Standards Preparation

New oil samples were obtained and diluted 10x by weight with V-Solv™ containing 40 ppm cobalt (Co) as an internal standard. Calibration curves were made from a 75 cSt base oil as a blank, two V-23 stock solutions at 100 and 500 ppm (PerkinElmer), and a Metals Additives Standard (MA4) (PerkinElmer) which contains Ca at 5000 ppm as well as P, Mg, and Zn at 1600 ppm. The blank and all standards were prepared the same way as the samples. The MA4 standard was used as the QC sample during the analysis of samples.

Instrument Conditions

All analyses were performed on the Avio 200 ICP-OES running in radial mode, using the conditions in Table 1 along with the analytes and wavelengths listed in Table 2. 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 1. Avio 200 ICP-OES instrumental parameters and conditions.

Parameter	Value
Nebulizer	MEINHARD® K-1
Spray Chamber	Baffled glass cyclonic
RF Power	1500 W
Torch	3-Slot Avio torch for organics
Injector	1.2 mm
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	1.3 mL/min
Sample Uptake Tubing	Black/Black (0.76 mm id), Viton
Drain Tubing	Red/Red (1.14 mm id), SolvaFlex
Replicates	3
Rinse Between Samples	40 sec (flush, read delay, AS rinse)
Auto Integration Time	Min 0.5 secs, Max 2.0 secs

Table 2. Analytes and wavelengths.

Element	Wavelength (nm)
Ca	315.887
Mg	279.077
P	214.914
Zn	213.857
Co (internal standard)	228.616

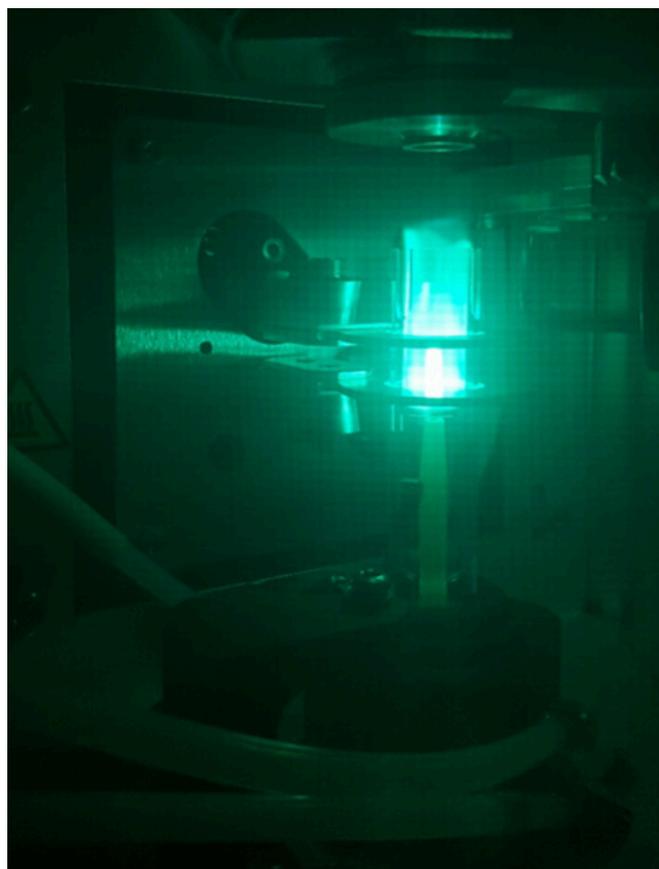


Figure 1. Correct position of green carbon "bullet" just below the second plate of Avio's unique Flat Plate plasma technology, when aspirating V-Solv.

Results and Discussion

Five new oil samples with different formulations were analyzed, and the concentrations compared to those obtained from X-ray analysis using ASTM D6443. Table 3 shows the results, which indicate that both analyses gave similar results, thus demonstrating agreement of the results with X-ray. In addition, the relative standard deviations (RSDs) for each measurement were generally 1% or less, with the exception of the low-level analytes (Mg in Oil 3 and 5), where the low intensities resulted in statistically slightly higher RSDs.

Compared to X-ray analysis, the Avio 200 ICP-OES provides several advantages including price, sample throughput, ease of use, and the ability to measure different oil formulations with calibration standards that do not have to be matched to the composition of each oil. In addition, X-ray analysis of additives in oils suffers from interferences, which require either mathematical or physical corrections, both of which necessitate running additional standards. However, ICP-OES does not suffer from interferences for this analysis, resulting in simpler, faster, and more accurate measurements. Another major difference between X-ray and ICP-OES is the ability to measure high-level samples. X-ray techniques require further dilutions of the sample, while on the Avio 200, the same sample can be run in attenuation mode, which selectively suppresses the signal of only the analyte of interest, without affecting other analytes.

Table 3. Results from five new oil samples with different formulations.

Oil Sample	Element	Concentration (ppm)	X-Ray Results (ppm)
1	Ca	1136	1131
	Mg	1017	1045
	P	1114	1131
	Zn	1284	1291
2	Ca	1372	1404
	Mg	842	863
	P	1141	1170
	Zn	1321	1353
3	Ca	2457	2494
	Mg	19	11
	P	710	756
	Zn	875	843
4	Ca	1338	1342
	Mg	827	838
	P	994	991
	Zn	1142	1139

Since a typical blending plant may run about 20 samples per day, a 20-sample stability run was performed where each oil sample was run, followed by the QC sample (MA4) after every five samples. This sequence was repeated so that each oil sample was analyzed four times. All QC values were within $\pm 2\%$, with the first and last QC samples appearing in Table 4. These results demonstrate the stability of the methodology, allowing a typical oil blending plant to easily perform their daily analyses with the Avio 200 ICP-OES.

Several instrumental considerations of the Avio 200 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, which causes quicker buildup of carbon on the injector and torch. 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 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.

Another important use of the ICP for an oil blending plant is to check other additives used in the oil formulation (such as detergents, dispersants, and viscosity improvers, to name a few) for elemental contamination that could change the additive levels in the final product.

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Table 4. First and last QC check samples of a 20-sample analytical run.

Sample	Element	Experimental (ppm)	% Recovery
First QC	Ca	4994	100
	Mg	1614	101
	P	1602	100
	Zn	1587	99
Last QC	Ca	5093	102
	Mg	1631	102
	P	1630	102
	Zn	1625	102

Conclusion

This work has demonstrated the ability of the Avio 200 ICP-OES to analyze a variety of lubricating oil samples for oil additives in accordance with ASTM method D4951. Instrumental design considerations allow for accurate and stable analysis of different oil formulations against an external calibration curve which did not have to be matched to the specific oil compositions.

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, 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

References

- <http://www.perkinelmer.com/product/avio-200-icp-optical-emission-spectrometer-avio200>

