

ICP - Optical Emission Spectroscopy

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Analysis of Oil Additives Following ASTM D4951 with the Avio 220 Max 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® 220 Max hybrid simultaneous 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 220 Max hybrid simultaneous 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 220 Max 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 |

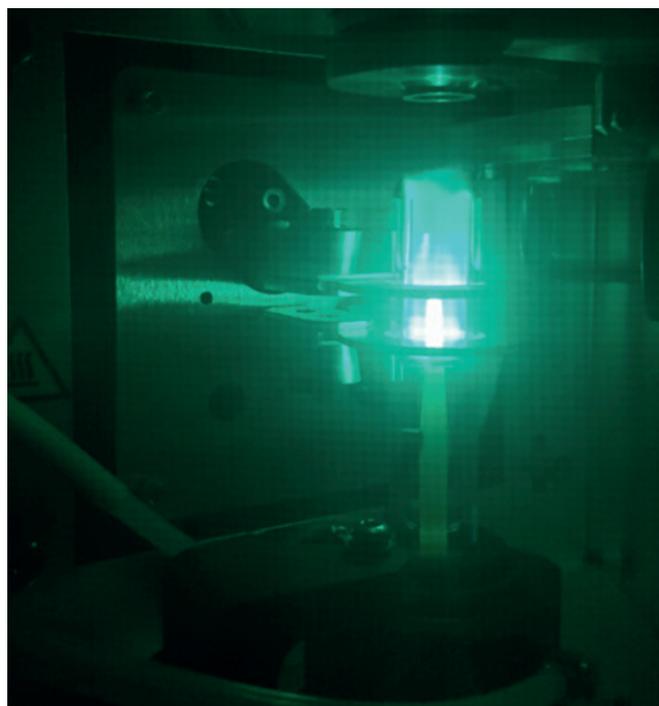


Figure 1. Correct position of green carbon "bullet" just below the second plate of Avio's unique Flat Plate plasma technology, when aspirating V-Solv.

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 220 Max 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 220 Max, the same sample can be run in attenuation mode, which selectively suppresses the signal of only the analyte of interest, without affecting other analytes.

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

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 |
| 5 | Ca | 2822 | 2845 |
| | Mg | 15 | 9 |
| | P | 715 | 734 |
| | Zn | 846 | 828 |

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 220 Max ICP-OES.

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, 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 220 Max hybrid simultaneous 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

- "Avio 220 Max Hybrid Simultaneous ICP-OES", PerkinElmer Product Note, 2020.

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