

## ICP - Optical Emission Spectroscopy

Author:

Dave Hilligoss

PerkinElmer, Inc.  
Shelton, CT



## Analysis of In-Service Oils Following ASTM D5185 with the Avio 500 ICP-OES

the equipment also increase, meaning that breakdowns can be costly, both in equipment repair and lost revenue. As a result, preventive maintenance is paramount. Lubricants are among the key fluids that can be tested, especially the oil used in engines. By monitoring the elemental concentration of the oil or other lubricants (hydraulics, transmission, gear), the status of that compartment can be determined. The increase in concentration of key wear metals indicates when maintenance is required. ASTM created a method specifically addressing this analysis, D5185<sup>1</sup>, because the analysis of oil as a diagnostic for engine maintenance is so common.

### Introduction

Globally, heavy machinery is used in construction, mining, and a variety of other areas. As the scale of the operations increase, the size, complexity, and cost of

When monitoring wear metals in oils, typical concentrations which serve as diagnostics are about 1 ppm, making inductively coupled plasma optical emission spectroscopy (ICP-OES) the preferred analytical technique (as specified in D5185) due to its speed, matrix tolerance, and ability to easily and accurately measure these concentrations. To ensure high-quality data, method D5185 has stringent criteria. However, through years of implementation, labs have developed their own criteria for the analysis, which makes it easier to run a large number of samples while still maintaining high-quality data. Table 1 shows several parameters, along with their specifications in D5185 and common implementations.

Table 1. Parameters of ASTM D5185 and Common Implementation.

Parameter	Specified in 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	Every 10-25 samples
QC Limits	± 5%	± 10%

Previous work has demonstrated that the Avio® 200 ICP-OES successfully meets the criteria of method D5185<sup>2</sup>, as it would be applicable for low-volume labs. However, in high-throughput environments, a simultaneous ICP-OES is essential. This work demonstrates the ability of PerkinElmer's Avio 500 ICP-OES system to analyze in-service oil samples following a common implementation of method D5185.

## Experimental

### Samples and Sample Preparation

In-service oil samples were prepared by diluting 10x with V-Solv™, spiked with cobalt (Co) at 40 ppm. The Co serves as an internal standard, and spiking into the diluent is the fastest, most accurate way to add it to all standards and samples. (Please note all consumable part numbers are included in a Consumables Used table at the end of this document.)

Quantitative measurements were made against external calibration curves prepared from three V-23 oil stock solutions at 50, 100, and 500 ppm, along with a Metals Additive Oil Standard (MA3), which contains Ca at 5000 ppm and P and Zn at 1600 ppm each. Alternately, if Mg is an additive, Metal Additive Oil Standard 4 (MA4) also contains Mg at 1600 ppm and may be used instead. The Blank was 75 cSt base oil. The QC standards consisted of the 50 ppm standard for all wear metals, and the MA3 standard for the additive elements.

### Instrument Conditions

All analyses were performed on the Avio 500 ICP-OES running in radial mode using the conditions in Table 2 and the elements and wavelengths in Table 3. The nebulizer flow was adjusted so that the tip of the green carbon "bullet" in the center of the plasma was just below the top flat plate. The ability to use a total of only 11 L/min of argon is the result of Avio's Flat Plate™

plasma technology, which, in combination with the vertical torch, enhances the ability to analyze challenging matrices. The chosen wavelengths have proven stable and interference-free over years of analysis.

Samples were introduced into the Avio using a CETAC ASX-1400 autosampler in conjunction with a CETAC ASXpress. The ASX-1400 autosampler stirs the diluted samples just before analysis, while the ASXpress increases sample throughput through the incorporation of a valve-and-loop.

Table 2. Avio 500 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	1.60 mL/min
Sample Uptake Tubing	Black/Black (0.76 mm id), Viton
Drain Tubing	Red/Red (1.14 mm id), SolvaFlex
Read Delay	16 sec
Replicates	2
Rinse Time Between Samples	None with ASXpress
Integration Range	0.5 – 2 sec

Table 3. Analytes and Wavelengths.

Analyte	Wavelength
Ag	328.063
Al	394.398
B	249.675
Ba	233.529
Ca	315.889
Cd	228.799
Co (int std)	228.613
Cr	205.558
Cu	324.749
Fe	259.937
K	766.508
Mg	279.085
Mn	257.612
Mo	203.845
Na	588.974
Ni	232.002
P	214.913
Pb	220.352
Si	288.151
Sn	189.927
Ti	334.936
V	292.397
Zn	213.861

## Results and Discussion

Many labs following method D5185 are high-throughput environments looking to maximize sample throughput. During the analysis process of in-service oil samples, sample uptake and washout require more time than the actual measurement time. Therefore, anything that reduces sample uptake and washout without reducing data quality is beneficial. With this goal in mind, the ASXpress Rapid Sample Introduction System was used in this work.

A schematic of the ASXpress is shown in Figure 1. A sample loop is rapidly filled by vacuum while carrier solution is delivered to the nebulizer (Figure 1A). After the loop is filled, the valve switches, allowing the carrier solution to push the sample to the nebulizer (Figure 1B) for analysis, while, at the same time, the autosampler probe is rinsed via vacuum. After analysis is complete, the valve switches to its original position so that carrier solution rinses the nebulizer while the sample loop is filled with the next sample. Combining the ASXpress with the Avio 500 ICP-OES, sample-to-sample analysis time is 25 seconds – ideal for high-throughput labs, as this increases sample throughput to two samples per minute.

Figure 2 shows the concentrations of seven elements in 10 randomly selected samples (although 23 elements were measured for each sample, for clarity, only seven elements are shown.) These data clearly show variations between samples, as well as the range of concentrations measured: from 1 ppm to greater than 1000 ppm. While most elements vary greatly between samples, the phosphorus concentration is relatively constant, demonstrating that the methodology is capable of detecting both large and small changes, sample-to-sample.

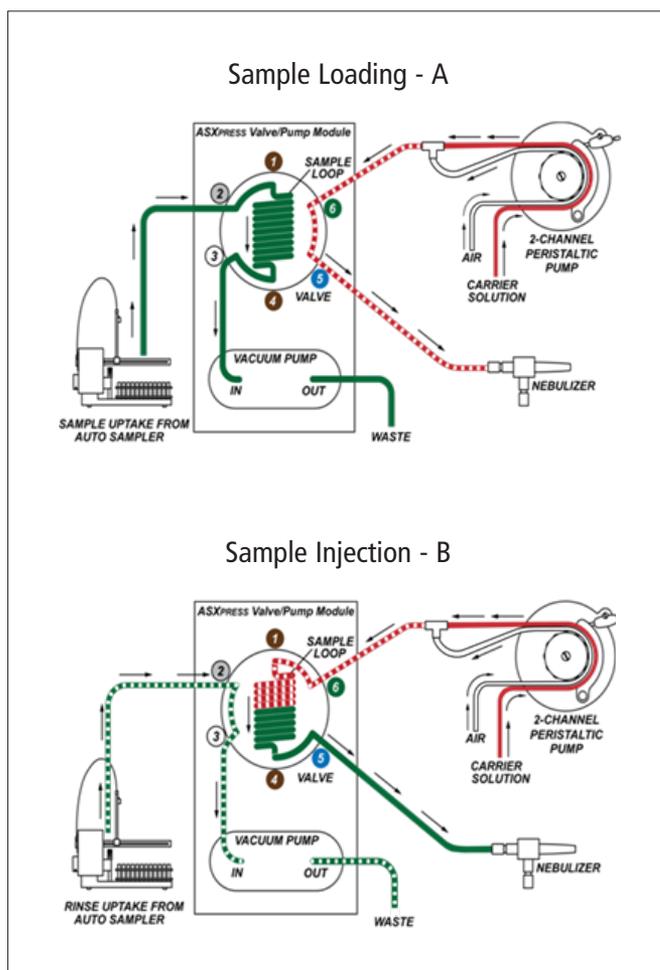


Figure 1. ASXpress system operation: (A) Sample loading; (B) Sample injection. (Used with permission of Teledyne CETAC Technologies).

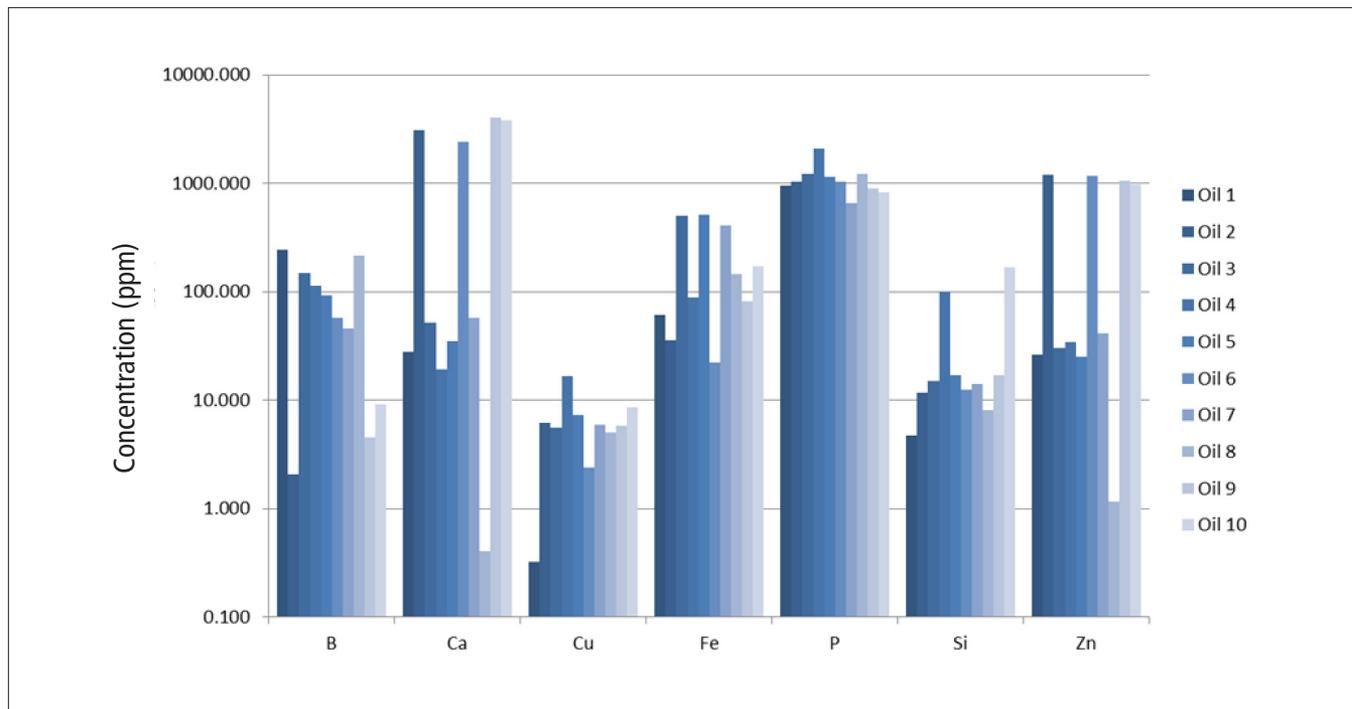


Figure 2. Concentrations of B, Ca, Cu, Fe, P, Si, and Zn in ten randomly selected in-service oil samples.

To assess the stability of the method, 332 in-service oil samples were analyzed, along with QC standards every 11 samples, over six hours. The plot in Figure 3 shows the stability for the QC standards, where all elements recovered within 10% of the true value. The results demonstrate the robustness and stability of the Avio 500 ICP-OES in accordance with ASTM method

D5185 in a high-throughput environment. An important factor to achieving this stability is the incorporation of a vertical torch which allows non-ionized sample to drain back down the torch rather than pooling in the injector, causing carbon build-up on both the injector and torch.

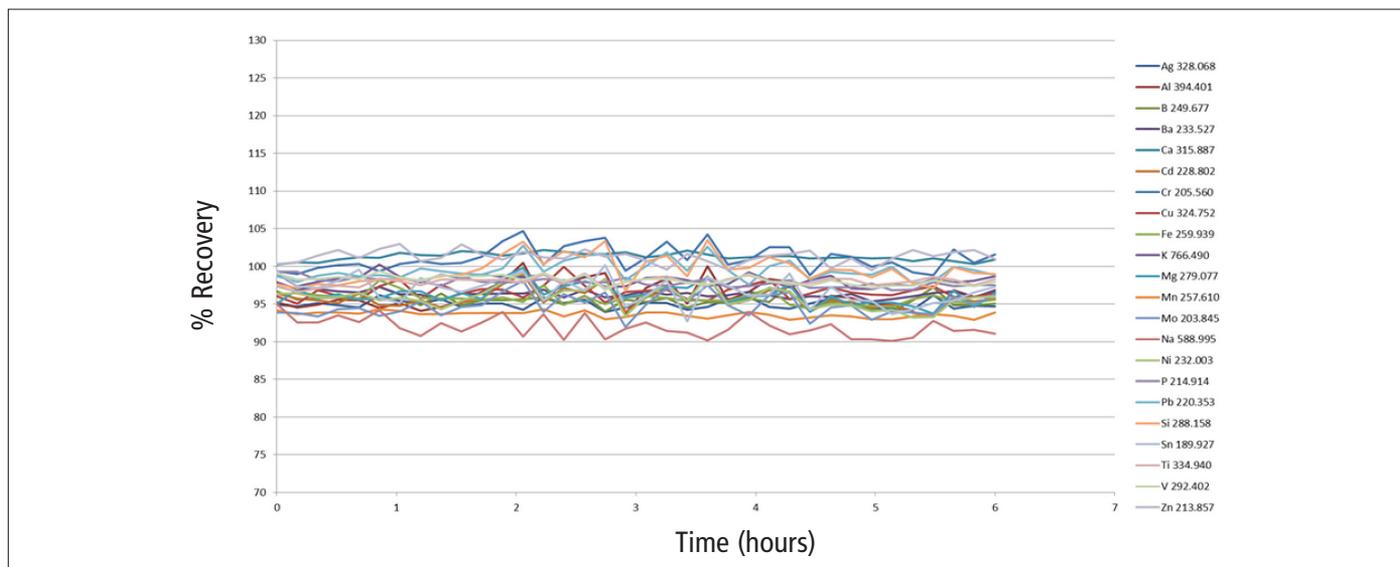


Figure 3. QC stability during a six-hour analytical run of 332 in-service oil samples.

## Conclusion

This work has demonstrated the ability of the Avio 500 ICP-OES to measure in-service oil samples in accordance with ASTM method D5185 in a high-throughput environment. Instrument design characteristics and an enhanced sample introduction module designed specifically for oil analysis allow for multi-element long-term stability when analyzing a wide variety of in-service oils.

## References

1. 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.
2. Hillgoss, D. "Analysis of In-Service Oils Following ASTM D5185 with the Avio 200 ICP-OES", PerkinElmer application note, 2016.

## 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, MA3	N9308369 (100 g) N9308370 (200 g) N9308552 (400 g)
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, 17 x 100 mL, 1200	N0777167