

Mass Spectrometry & Spectroscopy

Analysis of In-Service Oils with ICP-OES/AES Following ASTM D5185

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Throughout the world, heavy machinery is used in a variety of areas, including construction and mining. As the size, complexity, and cost of the equipment increases, breakdowns can be costly, both in equipment repair and lost revenue. Therefore, preventive maintenance is paramount, but taking equipment off-line for unneeded maintenance can be just as costly. As a result, a diagnostic must be used to determine the optimum time to perform maintenance, both to maximise up-time and minimise breakdowns and repairs.

Engine oil is a key component for keeping heavy machinery up and running and serves as a diagnostic of engine health. While many aspects of in-service oils need to be monitored, the metal content serves as a key indicator of the engine's condition. While sudden spikes in the concentration of a certain metal can indicate the imminent failure of a component, it is more important to monitor the trends of the metal content in the oil over time, as increasing metal levels in the oil indicate when maintenance is needed. Because of the importance of using in-service oil analysis as a diagnostic for heavy equipment maintenance, ASTM created a method specifically addressing this analysis: D5185 [1].

When monitoring wear metals in oils, typical concentrations which serve as diagnostics are greater than 1 ppm, making ICP-OES the preferred analytical technique (as specified in D5185) due its speed, matrix tolerance, and ability to easily and accurately measure these concentrations. To ensure high quality data, method D5185 contains stringent criteria, although, through years of implementation, labs have developed their own criteria, facilitating the analysis of a large number of samples while still maintaining high-quality data. *Table 1* shows several parameters specified in D5185 along with their 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%

Labs may analyse anywhere from less than 50 to hundreds of in-service oil samples per day. Although simultaneous ICP-OES instruments are ideal for high throughput labs, labs with lower daily sample requirements can opt for lower cost, slower simultaneous or hybrid scanning ICP-OES instruments to meet their requirements. This study will focus on the analysis of in-service oils using both a truly simultaneous ICP-OES with enhanced sample introduction capabilities to maximise sample throughput and a hybrid scanning ICP-OES with conventional sample introduction, a more cost-effective solution for labs with lower sample requirements.

Experimental

Samples and Sample Preparation

In-service oil samples were prepared by diluting 10x with V-Solv (a modified version of kerosene, with the lower molecular weight compounds removed), 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.

Quantitative measurements were made against external calibration curves consisting of a 75 cSt base oil blank and three V-23 oil stock solutions at 50, 100, and 500 ppm, along

with a metals additive oil standard containing Ca at 5000 ppm and Mg, P, and Zn at 1600 ppm each. A QC standard consisting of 50 ppm for all wear metals and the metal additive standard for the additive elements was analysed every 11 samples.

Instrument Conditions

All analyses were performed on either a PerkinElmer Avio® 500 (simultaneous) or Avio® 200 (hybrid scanning) ICP-OES, using the conditions and parameters in *Table 2*. The position of the plasma and carbon Swan bands within the plasma is critical to prevent carbon deposition on the injector, so nebuliser flow was adjusted accordingly. The read time range is shorter on the Avio 200 due to its enhanced sensitivity.

To maximise sample throughput on the simultaneous system, a CETAC ASX-1400 autosampler was used in conjunction with a CETAC ASXpress. The autosampler stirs the diluted samples just before analysis, while the ASXpress increases sample throughput through the incorporation of a valve-and-loop. Although the ASXpress can also be used on the hybrid scanning system, it was not used in this work to better mimic what a low-volume lab may use. Instead, rapid pumping between samples was used.

Table 2. Instrumental Parameters and Conditions

Parameter	Value
Nebuliser	GemCone™ (modified Babbington)
Spray Chamber	Baffled glass cyclonic
RF Power	1500 W
Torch	3-slot torch for organics
Injector	1.2 mm ceramic
Plasma Gas Flow	10 L/min
Aux. Gas Flow	0.8 L/min
Nebuliser Gas Flow	0.40 L/min
Torch Position	-4
Plasma View	Radial
Sample Uptake Rate	1.60 mL/min (Avio 500) 2.0 mL/min (Avio 200)
Sample Uptake Tubing	Black/Black (0.76 mm id), Viton
Drain Tubing	Red/Red (1.14 mm id), SolvaFlex
Read Delay	16 sec (Avio 500) 18 sec (Avio 200)
Replicates	2
Rinse Time Between Samples	None with ASXpress (Avio 500) 12 sec at 6 mL/min (Avio 200)
Read Time Range	0.5-2 sec (Avio 500) 0.2-1 sec (Avio 200)

Results and Discussion

With the instrumental parameters in *Table 2*, the sample-to-sample time for a hybrid scanning ICP-OES is 5 minutes. For a low-volume, in-service oil lab running up to 50 samples a day, this analytical speed is all that is required.

However, many labs following ASTM D5185 are high-throughput environments requiring maximum sample throughput. With a simultaneous ICP-OES (Avio 500), sample uptake and washout require more time than the actual measurement time. These times were minimised with the ASXpress, which uses a loop and vacuum to minimise sample uptake and washout times. Combining the ASXpress with the simultaneous ICP-OES, sample-to-sample analysis time is 25 seconds – ideal for high throughput labs.

Figure 1 shows the concentrations of seven elements in 10 randomly selected samples (although 23 elements were measured for each sample, only seven elements are shown for clarity). 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.

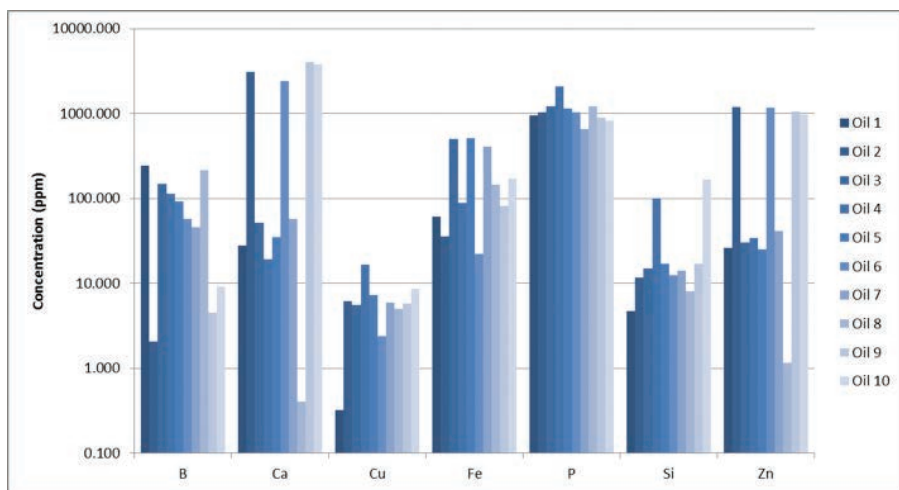


Figure 1. Concentrations of Al, B, Ca, P, Si, and Zn in 10 randomly selected in-service oil samples with the Avio 500 ICP-OES (simultaneous).

To assess the stability of the method, 332 in-service oil samples were analysed, along with QC standards every 11 samples, over 6 hours. The plot in *Figure 2* 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 simultaneous ICP-OES in accordance with ASTM D5185 in a high-throughput environment. An important factor for achieving this stability is the incorporation of a vertical torch which allows non-ionised sample to drain back down the torch rather than pooling in the injector, causing carbon build-up on both the injector and torch.

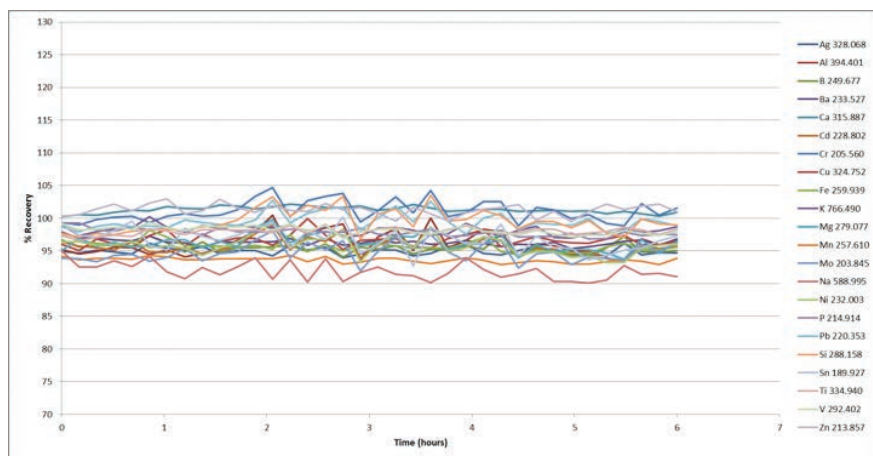


Figure 2. QC stability during a 6-hour analytical run of 332 in-service oil samples with the Avio 500 ICP-OES (simultaneous).

The stability for the hybrid scanning ICP-OES was determined by measuring the QC samples both at the beginning and end of a run consisting of 20 in-service oil samples. The results of the last QC sample appear in *Table 3* and show that all elements recovered within +/- 10% of 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 a hybrid scanning ICP-OES.

Table 3. Initial and Final QC Check Samples of a 20-Sample Analytical Run with the Avio 200 ICP-OES (hybrid scanning)

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 both hybrid scanning and simultaneous ICP-OES instruments to measure in-service oil samples in accordance with ASTM method D5185 in both low and high-throughput environments to meet the specific needs of the lab. Sample throughput is maximised for both instruments by using an enhanced throughput sample introduction system, which eliminates the rinse time between samples. Both accuracy and stability are achieved, showing that ICP-OES is the ideal technique for the analysis of metals in 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.



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