Get the FACCS Before Preparing Your Lubricating Oils

Introduction

Properly maintaining heavy machinery is critical in this time of increasing demand. The key to maintenance is the analysis of lubricating oils - including gear, engine, transmission and hydraulic fluids - to determine wear metal content for directing preventative maintenance prior to component failure. This type of analysis has become very important to the marketplace, prompting the ASTM to create method D5185[1] specifically for quantifying the amount of wear metals in lubricating oils.

The ASTM method calls for every sample to be diluted prior to analysis. Preparing these samples can be a time-consuming task for wear metals and in-service laboratories. Even with experienced technicians, samples can only be made so quickly by hand without encountering a loss in accuracy and precision. As the volume of samples and demand for faster turnaround increases, wear metal analysis labs must find a solution that is Fast, Affordable, Capable, Clean, and Simple: FACCS.

Automated sample preparation can help meet the demands of higher sample volume without any sacrifice to the quality of analytical data. Laboratories can improve their sample throughput and remove opportunities for error by automating the sample dilution step. Automation frees up laboratory staff to focus more time and effort on other areas of greater importance.

The new Teledyne CETAC APS-7450V has incredibly fast preparation times (under 20s per sample) and high levels of accuracy and precision. Labs can be confident in its integration because of the easy-to-use software. This note demonstrates the system's performance across a broad range of criteria.

What are the FACCS?

Fast

Affordable

Capable

Clean

Simple

Experimental

Sample Preparation

Calibration curves and standards were prepared several ways to analyze for accuracy, precision and cleanliness of the system. Check standards, including an internal calibration verification (ICV), continuous calibration verifications (CCV), and standard reference materials (SRMs) were prepared and analyzed to demonstrate system capabilities.

All of the standards and samples were prepared in kerosene spiked with 40 ppm of cobalt to serve as the internal standard.

Multi-element oil standards were purchased to prepare the calibration curves. The elements and concentrations of the standard solutions can be seen in Table 1. All standards were prepared using a 1:10 dilution with spiked kerosene as is typically done to allow for sample matrix matching.

One set of standards, serving as the control, was prepared on a scale using a 1:10 dilution (1g of standard plus 9g of diluent).

Two other sets of standards were prepared on the APS 7450V using 1:10 volumetric dilutions with and without applying density correction. This feature is an option in the OilEase software that adjusts a sample's final volume to more accurately match the dilution ratio of the standards that are prepared by weight. The densities (standard and diluent) used to determine the final volume are programmable in the software. While a discrepancy between samples prepared by volume and by weight will always exist, this feature is designed to improve data accuracy by more closely matching the preparation of the samples (v/v) to the preparation of the standards (w/w).

Next, an ICV and 9 CCVs were prepared using a 500 µg/g (ppm), 75cST oil standard to examine reproducibility of the autodilutor.

Standard Reference Materials were prepared and analyzed (NIST 1085c Wear Metals in Lubricating Oil and NIST 1634c Wear Metals in Fuel Oil). NIST 1085c is made using a 75 cSt base mineral oil, making it the ideal choice to do a direct comparison to the oil standards of the calibration curve. NIST 1634c is a high viscosity sample. Based on the certificate of analysis provided, it is recommended that the oil be brought up to 40°C to raise the viscosity to 301 cST. This is the certified value in which testing was performed on NIST 1634c. The standards and SRMs were all prepared using a 1:10 volume to volume dilution. Additional attention was provided for NIST 1634c to ensure that it was mixed thoroughly prior to analysis.

Finally, a carryover study was conducted to analyze different rinse factors, including the volume of rinse used and the

Table 1. Standard concentration by element

	Std 1	Std 2	Std 3
Ag	10 µg/g	100 µg/g	500 µg/g
Fe	10 µg/g	100 µg/g	500 µg/g
Mg	10 µg/g	100 µg/g	500 µg/g
Mo	10 µg/g	100 µg/g	500 µg/g
Pb	10 µg/g	100 µg/g	500 µg/g
P	10 µg/g	100 µg/g	500 µg/g
V	10 µg/g	100 µg/g	500 µg/g
Mn	10 µg/g	100 µg/g	500 µg/g
Bi	10 µg/g	100 µg/g	N/A
In	10 µg/g	100 µg/g	N/A
Li	10 µg/g	100 µg/g	N/A
Zn	10 µg/g	100 µg/g	500 µg/g
Ba	10 µg/g	100 µg/g	500 µg/g
K	10 µg/g	100 µg/g	500 µg/g
B	10 µg/g	100 µg/g	500 µg/g
Na	10 µg/g	100 µg/g	500 µg/g
Sn	10 µg/g	100 µg/g	500 µg/g
Al	10 µg/g	100 µg/g	500 µg/g
Ca	10 µg/g	100 µg/g	500 µg/g
Cd	10 µg/g	100 µg/g	500 µg/g
Cr	10 µg/g	100 µg/g	500 µg/g
Cu	10 µg/g	100 µg/g	500 µg/g
Ni	10 µg/g	100 µg/g	500 µg/g
Sb	10 µg/g	100 µg/g	500 µg/g
Si	10 µg/g	100 µg/g	500 µg/g
Ti	10 µg/g	100 µg/g	500 µg/g

dispense rate. During sample analysis, one of the variables was kept constant to isolate which of the two variables is more effective in reducing carryover.

For each variable, 10 samples were prepared using a 1:10 dilution on the APS-7450V. A 500 µg/g oil standard was prepared in triplicate along with a clean mineral oil to serve as a blank in the other 7 samples. The samples were tested for the presence of 10 elements, chosen for their high carryover potential (Ba, Ca, Cd, Fe, Mn, Mg, Ni, Ti, V, Zn). Every oil standard dilution was directly followed by one or more mineral oil samples. Samples were rearranged to differentiate carryover related to the dilution step from carryover that occurs as part of sample introduction on the ICP. This established a baseline value for the mineral oil and provided 3 samples to evaluate for carryover within each set of method parameters.

Carryover was determined by analyzing the intensity values for the blanks that were prepared after the standard solutions and subtracting the baseline. The remaining value was then taken as a percentage of the standard solution intensity. These were averaged across all elements and replicates to evaluate the average carryover for the method.

The impact of rinse factors on carryover used the following parameters:

- varying rinse volumes from 4 to 12 mL in 2 mL increments
- varying dispense rates from 250 to 450 mL/min in 50 mL increments

All other parameters were set to the default settings.

Instrument Conditions

Analyses were performed using a Thermo Scientific™ iCAP™ PRO XPS Duo ICP-OES paired with Teledyne CETAC Technologies Oils-7400 Homogenizing Autosampler and Teledyne CETAC Technologies ASXPRESS PLUS Rapid Sample Introduction System. The ASXPRESS PLUS was used to reduce the sample delivery and rinse times through its ability to perform multiple sample introduction steps simultaneously.

With the iCAP PRO XPS Duo instrument, both the radial and axial viewing modes provide robust and stable analysis when running organic samples. However, for this work the higher sensitivity of the axial mode was not required, so radial viewing was used.

Generally, default parameters for the APS-7450V were used in this study, except for the SRMs preparation, where the uptake was lowered to 10 mL/min to enhance accuracy and precision due to the high viscosity of the NIST 1634c. All instrument conditions and settings can be found in Tables 2, 3, 4, and 5.

Table 2. Thermo Scientific iCAP PRO XPS Duo ICP-OES Parameters

ICP-OES Parameter	Setting
Exposure Time	2 seconds
Sample Repeats	3
RF Power	1250 W
Nebulizer Flow	0.40 L/min
Nebulizer Type	Noordermeer V-Groove
Supplemental Oxygen Flow	0.052 L/min

Table 3. Teledyne CETAC Oils-7400 Autosampler Settings

Oils-7400 Parameter	Setting
Uptake Time	10 Seconds
Wash Time	4 Seconds

Table 4. ASXPRESS PLUS Vacuum Pump Settings

ASXPRESS PLUS Parameter	Setting
Extra Loop Rinse	Yes
Loop Rinse Delay	2 Seconds
Loop Evacuation Delay	2 Seconds
Load Loop Time	5 Seconds
Equalization Delay	2 Seconds
Evacuation of Probe	2 Seconds
Probe Wash	2 Seconds
Rinse Station Fill	10 Seconds

Table 5. APS-7450V Autodilutor Default Settings

Autodilutor Parameter	Setting
Uptake Rate	20 mL/min (10 mL/min for SRM checks)
Dispense Rate (Sample/Diluent)	100 mL/min
Volume of Rinse	8.0 mL
Dispense Rate (Rinse)	350 mL/min
Split Rinse	4x
Standard Oil Density	0.863 g/mL
Kerosene Density	0.82 g/mL

Results

Calibration

The correlation coefficient of the element calibration curves must be 0.995 or better to be considered valid for analysis. Coefficients for all elements are shown in Figure 1. The average correlation coefficient across all three curves was 0.99999.

Another criteria examined was the mode of preparation. All three preparation methods were analyzed the same day as part of the same sequence to keep the data consistent. In order to compare the volumetric preparation to the hand prep, the intensity values (counts per second) for the 100 ppm standard across all elements were evaluated comparing the automated sample prep to the manual prep.

Each reading was calculated as a percentage of the intensity of the hand prepared standard to highlight the variance between the methods of preparation.

When comparing the hand-made standards to those prepared on the autodilutor with the density correction applied, very similar results were achieved. On average, the standards prepared with density correction had 101% of the intensity of the standards prepared by weight. However, intensities from the volumetric preparation without density correction applied show a significant discrepancy. On average, those standards had 108% of the intensity and some elements were as much as 15% high (Figure 2).
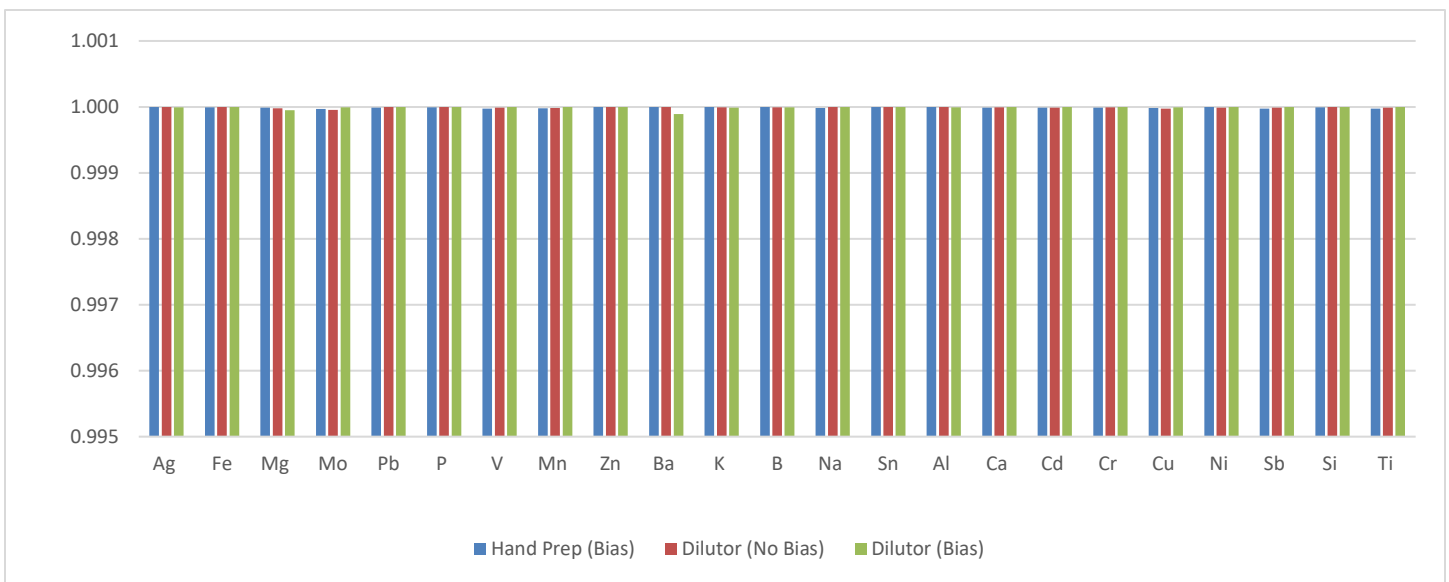

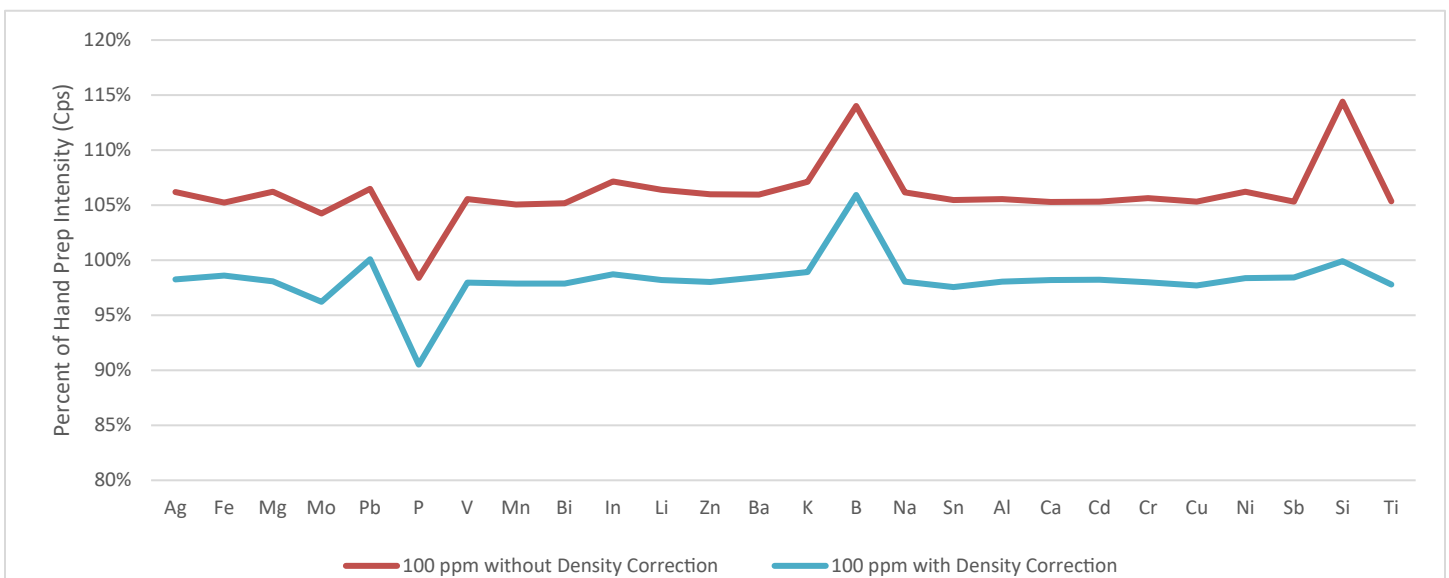*Figure 1. Graph of Correlation Coefficients*

Figure 2. A 100ppm standard comparison with and without density correction

This variance is seen because the density of the diluent used is less than that of the oil standard causing the dilution factors to be different between weight-based and volumetric-based dilutions. The density correction feature in the OilEase software allows a user to simulate a weight-based dilution and more accurately match their standard solutions without the extended time required to prepare samples by hand.

Calibration Verification/Reproducibility

A calibration curve was prepared volumetrically (without density correction) as in the previously discussed experiment, followed by an ICV and a series of samples including 9 more CCVs. These check standards were all the same 500 µg/g standard, prepared at a 1:10 dilution. All samples were then placed on the Oils-7400 and analyzed on the iCAP PRO XPS ICP-OES.

All recoveries were within 2% of the mean value, demonstrating the high level of reproducibility (Figure 3).

Standard Reference Materials

To further demonstrate the dilution accuracy, two different NIST SRMs were prepared and analyzed, NIST 1085c and NIST 1634c.

The APS-7450V was used to prepare NIST 1085c at a 1:10 v/v dilution. A secondary standard of the same concentration and viscosity as the NIST 1085c served as a control sample. The control sample served two purposes; the first was to ensure that the instrument did not drift from its calibration, the second was to cross-check the SRM to a second source standard. All elements were within the method criteria range of 95-105% for the SRM and the control sample (Table 6).

Similar to the NIST 1085c sample, NIST 1634c sample was prepared on the APS-7450V at a 1:10 volume to volume dilution. NIST 1634c was analyzed separately due to its viscosity. Following the certificate of analysis guide, the NIST 1634c was heated up to 40°C. At this temperature, the fuel oil standard is 301cSt. Despite the higher viscosity, the autodilutor was able to prepare the sample accurately. All recovered values were within the method criteria range of 95-105% of the expected value (Table 7).
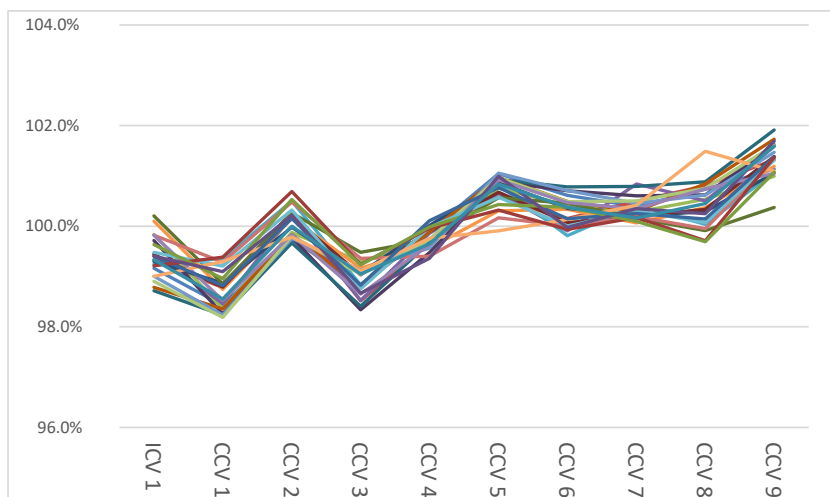

Figure 3. Line Plot of ICV and CCV Recovery

Table 6. NIST 1085c Recovery

Analyte	NIST 1085c Concentration Value (ppm)	NIST 1085c Reported Value (ppm)	NIST 1085c Certified Value	QC Recovery
Ag	291.7	298.0	97.9%	100.7%
Fe	314.8	301.0	104.6%	98.8%
Mg	296.3	300.0	98.8%	100.2%
Mo	308.4	305.0	101.1%	101.4%
Pb	315.7	303.0	104.2%	98.7%
V	297.2	285.0	104.3%	98.6%
Mn	305.9	299.0	102.3%	100.3%
Zn	288.8	285.0	101.3%	100.4%
Ba	299.3	306.0	97.8%	100.1%
K	299.5	295.0	101.5%	98.0%
B	312.3	304.0	102.7%	99.5%
Na	310.6	300.0	103.5%	101.1%
Sn	300.1	298.0	100.7%	100.6%
Ca	303.2	299.0	101.4%	99.1%
Cd	306.5	301.0	101.8%	100.0%
Cr	309.1	302.0	102.4%	99.7%
Cu	308.1	298.0	103.4%	96.8%
Ni	314.8	306.0	102.9%	102.0%
Si	302.8	293.0	103.4%	102.1%
Ti	310.4	300.0	103.5%	99.6%
Al	305.2	292.0	104.5%	98.6%
P	297.9	295.0	101.0%	98.7%

Table 7. NIST 1634c Recovery

Analyte	NIST Certified Concentration (ppm)	NIST Reported Value (ppm)	NIST Recovery Value
Ni	17.6	17.54	100.5%
V	28.3	28.19	100.3%

Carryover Study

We examined the cleanliness of the APS-7450V system by testing for carryover using a highly concentrated solution with varying rinse volumes and dispense rates. Both variables had an impact on carryover, though the rinse volume had a significantly larger impact than the rinse dispense rate. The two variables tested were analyzed separately to simplify data collection and analysis.

A direct correlation can be seen between the amount of rinse used and the average carryover. Increasing the rinse volume leads to a decrease in carryover in an almost linear fashion. Based on this study, 8mL was chosen as the default rinse volume as this produced <1%, maintaining cleanliness while minimizing time and solvent usage (Figure 4).

Once the default value of 8 mL of rinse was determined, it was used to examine the impact that the rinse dispense rate would have on carryover. Increasing the dispense speed by 200 mL/min only reduced the carryover by roughly 0.2%, but there is clearly a positive impact from using higher flow rates. Using a faster rinse dispense rate not only improves sample throughput, but also sample washout. When considered in combination with the rinse volume data, it is clear that a combination of the rinse volume and dispense rate can easily keep carryover under 1% even on difficult elements (Figure 5).

Conclusion

The APS-7450V Volumeteric Sample Prep Station was designed to meet the growing needs of wear metals and in-service laboratories. The simple design and user friendly software allow it to be easily integrated into a laboratory workflow becoming an essential part of daily work.

With this system, samples can be prepared 5 times faster than a chemist preparing samples by hand, while maintaining a high level of accuracy and precision. Users can be confident that the autodilutor can prepare a series of samples and get reliable and consistent results even with less than ideal samples.
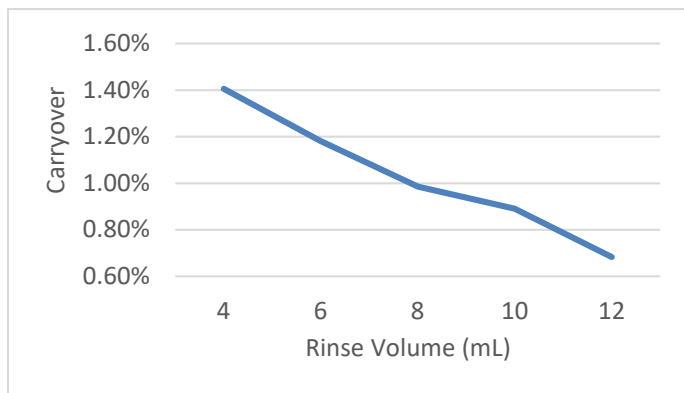

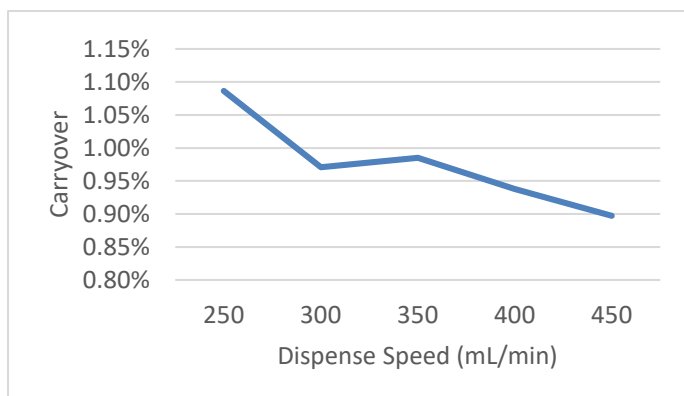*Figure 4. Average Carryover vs Rinse Volume*

Figure 5. Average Carryover vs Dispense Rate

The APS-7450V autodilutor software, OilEase, is simple and intuitive which minimized the time needed to conduct this work. The APS-7450V has been designed in every aspect to meet the challenges of oils samples and provide clean, robust, and consistent sample preparation to the wear metals market.

References

1) ASTM International Standard D5185 Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

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