MICAP-OES 1000

In-service oil analysis for metals following ASTM Method D5185 utilizing air as the nebulizer gas

Introduction

The analysis of wear metals, additives, and ingress elements in new and in-service oils is critical in monitoring ongoing lubrication needs of heavy equipment engines. Unscheduled maintenance can be very expensive, in both repair costs and lost productivity. Monitoring the status of the engine, gear, transmission, and hydraulic oils provides indication when preventative maintenance is required. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is used routinely to monitor metal levels in these essential fluids.

This note describes the use of the simultaneous MICAP OES-1000 N_2 ICP-OES system for routine analysis of used and unused in-service oils following the procedures outlined in ASTM Method D5185. The oil samples are diluted ten-fold in a kerosene-based solvent prior to analysis. A MICAP option that introduces air as the sample nebulization gas is demonstrated here, enhancing performance for several key elements of interest.

Many laboratories performing this work analyze hundreds of samples per shift, so the speed of analysis becomes very important. A high-throughput Teledyne Cetac sample automation system is interfaced to automatically stir each sample prior to vacuum uptake into an injection valve - shortening the total sample analysis time. Analytical performance is presented to demonstrate accurate and stable performance for these lubrication oils.

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Instrumentation

This method outlines the procedures utilized for determining additive elements, wear metals, and contaminates in both used (in-service) and new lubricating oils. The procedures follow those outlined in ASTM standard test method D5185[1], Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The lubricant samples are simply diluted into a kerosene-based solvent for direct introduction into the plasma. The MICAP-OES 1000 is configured with an organic solvent introduction system.

In this work lab-grade compressed air is utilized as the nebulizer gas, demonstrating the performance enhancements observed from reduction in the carbon emission background from within the plasma.

The MICAP patented design efficiently drives microwave energy into the Cerawave™ ring to create magnetic fields required to inductively couple energy into the robust N_2 plasma source. The high efficiency of the Cerawave ring ensures there is no change in the stability of the plasma when air is injected into the middle of the discharge. The 4 MP sCMOS camera collects the resulting emission lines from the high-resolution simultaneous spectrometer.

Experimental Conditions

The analyses were performed on the MICAP system shown in Figure 1 utilizing the conditions listed in Table 1. Since many laboratories that analyze in-service oils typically run hundreds of oil samples daily, high sample throughput is a paramount requirement. Additionally, the widely varying viscosities of engine oils present several challenges to optimally introduce samples in and out of the instrument while supporting high-throughput analysis. To help obtain these goals, a Teledyne Cetac Technologies (Cetac, Omaha, NE, USA) Oils 7400 autosampler and ASXpress Plus rapid sample introduction system were interfaced to the MICAP. This sample automation system provides several unique features:

- Sample stirring of the sample prior to uptake
- Vacuum loading of samples into valve loop
- Enhanced washout of spray chamber with solvent during sample valve loading

The Cetac sample automation system is integrated together with the MICAP operation. When a sample is loaded into the valve, the MICAP analysis timing is automatically triggered. The autosampler probe line is then rinsed and the next sample is stirred while the current sample is loaded into the ASXpress Plus loop.

Figure 1. MICAP-OES 1000 N_2 ICP-OES with Teledyne Cetac Oils 7400 & ASXpress Plus automation system

Table 1. Operational conditions for oil analysis

Parameter	Value
Torch	Quartz 1-piece, 1.5mm injector
Spray Chamber	Double pass glass cyclonic
Nebulizer	Glass V-Groove
Sample Tubing	Solvaflex Blk/Blk (0.76 mm ID)
Drain Tubing	Solvaflex Blu/Yel (1.52 mm ID)
ASXpress Valve Loop	1.02 mL
Sample uptake Time	20 sec
Rinse & Diluent	PremiSolv™
Power	1000 W
Coolant Gas Flow	16 L/min N2
Auxiliary Gas Flow	0.4 L/min N2
Nebulizer Gas Flow	0.55 L/min Air
Peristaltic Pump	45 rpm
Plasma Viewing	Axial
Camera Exposure	4.5 sec (50 ms @ 90 reps)
# of Repeats	2

The ICP-OES analysis conditions employed on the MICAP follow closely the procedures outlined in ASTM Method D5185[1] for the measurement of 22 elements in used and new lubricating oils. Table 2 provides specifics on the analyte and internal standard (Co) wavelengths used for this analysis. In the case of the elements of Ca and Zn, the MICAP was configured to perform an automated cross calibration using two emission lines for each element to address the wide concentration range commonly present in these oil samples.

The automation capabilities of the Cetac Oils 7400 & ASXpress system significantly speed up the rate at which oil samples can be processed. The paddle stirs the next sample while the current sample is quickly vacuum loaded. Without this mixing, some oil samples settle out from the dilution solvent which negatively impacts the results. With the optimized sample handling provided by this automation system, oil samples can be analyzed on the MICAP at a rate of approximately every 45 seconds.

Table 2. Analyte and internal standard wavelengths

Analyte Wavelength (nm)	Internal Standard Wavelength (nm)
Ag 328.068	Co I 240.725
Al 396.152	
B 249.772	
Ba 614.171	Co II 238.892
Ca 422.673	Co I 240.725
Ca 430.253	
Cd 266.501	Co II 238.892
Cr 428.973	Co I 240.725
Cu 324.754	
Fe 259.940	Co II 238.892
K 766.490	Co I 240.725
Mg 277.983	
Mn 403.076	
Mo 281.615	Co II 238.892
Na 569.033	Co I 240.725
Ni 300.249	
P 213.618	
Pb 238.305	
Si 251.611	
Sn 283.998	
Tl 323.451	Co II 238.892
V 309.310	Co I 240.725
Zn 206.200	Co II 238.892
Zn 213.857	Co I 240.725

Table 3. Calibration standards and quality control levels in mg/Kg (ppm)

Analyte Wavelength (nm)	Low Std (mg/Kg)	High Std (mg/Kg)	QC Std (mg/Kg)
Ag 328.068	50	500	100
Al 396.152	50	500	100
B 249.772	50	500	100
Ba 614.171	50	500	100
Ca 422.673*	50	100	100
Ca 430.253*	100	5000	200
Cd 226.501	50	500	100
Cr 428.973	50	500	100
Cu 324.754	50	500	100
Fe 259.940	50	500	200
K 766.490	50	500	200
Mg 277.980	50	500	200
Mn 403.076	50	500	100
Mo 281.615	50	500	100
Na 569.033	50	500	200
Ni 300.249	50	500	100
P 213.618	100	1600	200
Pb 283.305	50	500	100
Si 251.611	50	500	100
Sn 283.998	50	500	100
Ti 323.451	50	500	100
V 309.310	50	500	100
Zn 213.857*	50	100	200
Zn 206.200*	100	1600	100

**Ca & Zn obtained from 2 cross-calibrated wavelengths*

Standard and Sample Preparation

The calibration standards, blanks, and samples were prepared in accordance with the protocols outlined in ASTM Method D5185[1]. Working standards were prepared by diluting (w/w) oil-based stock standards (VHG, LGC Standards, Manchester, NH, USA) while maintaining a constant oil content with added Base Oil. Blanks and QC samples were prepared in the same manner.

All standards and oil samples were diluted in PremiSolv™ (Conostan, AnalytiChem, Bale-D'Urfe, QC, Canada) prepared by weight, with the 30 ppm Cobalt (Co) internal standard[2] also included at this time. A quality control sample (Conostan) was also analyzed to provide an external check for calibration accuracy. Table 3 provides the concentration levels of the standards and QC sample.

A total of 25 in-service oils were obtained for this work. These samples consisted of 10 engine, 5 gear, 5 transmission and 5 hydraulic oil samples. Examples of these samples are displayed in Figure 2. All these oil samples were diluted 1:10 (w/w) using the same procedures outlined above.

Figure 2. Examples of engine, gear, transmission, and hydraulic oils analyzed in this work, prior to dilution.

Results

The MICAP was calibrated as previously described and quality control checks were performed every 20 samples to ensure stable and accurate response. All wavelengths were viewed in the Radom Intuitive Software (RIS) Profiles View to ensure no spectral interferences and to set peak integration points. Example emission signals are shown in Figure 3.

Additional external quality control checks were prepared and analyzed to further validate the accuracy of the MICAP results. The successful results of these external quality control checks can be found in Table 4 below, displayed in % recovery of the certificate values. These checks were:

- 2nd Source QC- Conostan Standard S-21+K+Sb, 500 ppm (AnalytiChem, Bale-D'Urfe, QC, Canada)
- QC Check Standard – at end of sample analysis

Detection limits (LODs) were measured by analyzing ten replicate measurements of the blank. LODs were calculated by multiplying the standard deviation by 3. The average LOD values obtained from three separate analysis sessions are shown in Table 4. These values are presented on the basis of the actual oil samples, multiplied by the 10x dilution applied to the oil samples. Where two wavelengths are "cross-calibrated" (Ca & Zn), the more sensitive emission line DL value is reported.

Table 4. QC results & limits of detection (LODs)

Analyte	2nd Source QC (%Rec)	End of Run QC (% Rec)	Oil LOD (mg/Kg)
Ag	109	101	0.045
Al	97	95	0.18
B	103	101	0.64
Ba	105	103	0.052
Ca	102	102	0.056
Cd	101	99	5
Cr	98	95	0.076
Cu	108	104	0.048
Fe	105	101	0.42
K	92	91	0.3
Mg	97	94	3.7
Mn	96	97	0.077
Mo	101	98	1.1
Na	101	97	3.6
Ni	96	95	0.55
P	100	107	24
Pb	100	95	1.1
Si	99	98	0.76
Sn	101	97	0.63
Ti	104	102	0.074
V	102	100	0.34
Zn	99	97	0.53

**Ca & Zn obtained from 2 cross-calibrated wavelengths*

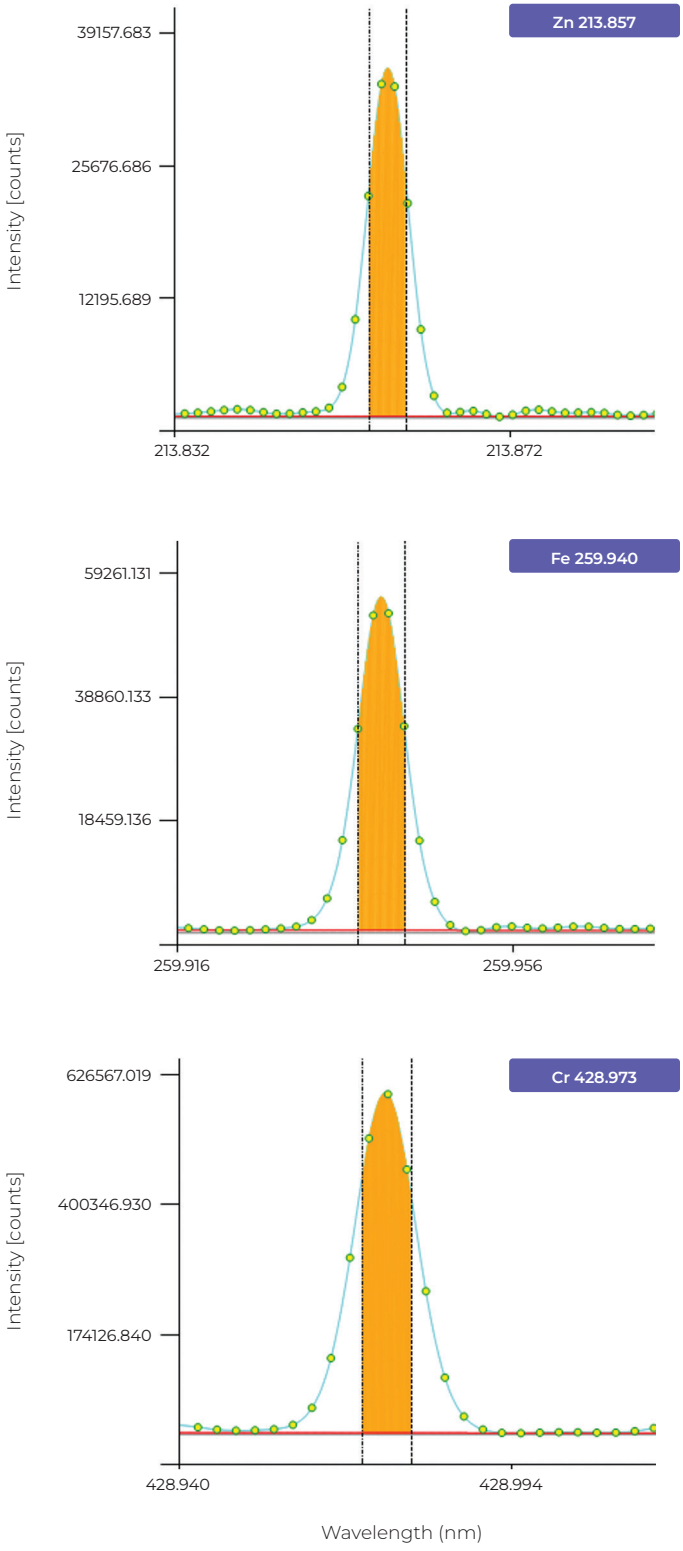

Figure 3. MICAP profiles view of signals for Zn, Fe & Cr obtained from an in-service engine oil analysis

Selected results obtained for the in-service oils are displayed in Figure 4 below. They are displayed on a logarithmic scale due to the wide range of concentrations of the additives, wear metals, and ingress elements in all four types of the oil samples analyzed.

The Co internal standard performance demonstrated the robustness of the calibration and analysis procedures, with the internal standard recovery values within +/- 10% or better. Several of the engine oils did exhibit reduced recoveries (within +/- 15%) for both Co lines monitored, indicating the importance of utilizing this correction to maintain accuracy across a wide range of lubricant samples (with different viscosities). Figure 5 at the right shows typical internal standard recoveries across the various oil sample types.

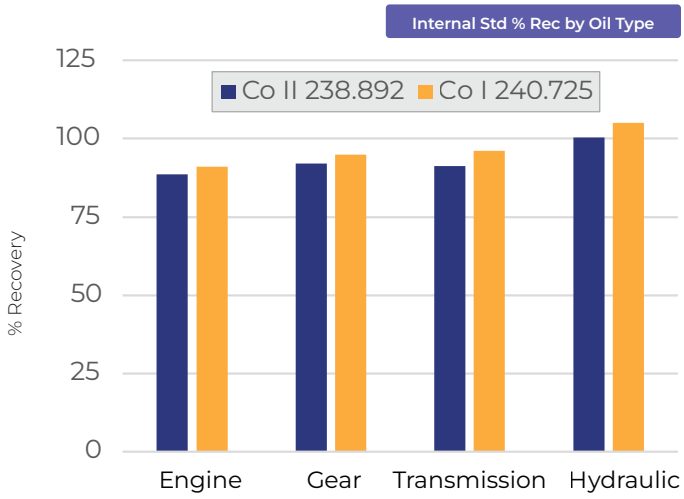

Figure 5. Averaged internal standard (Co) recoveries in oil samples analyzed

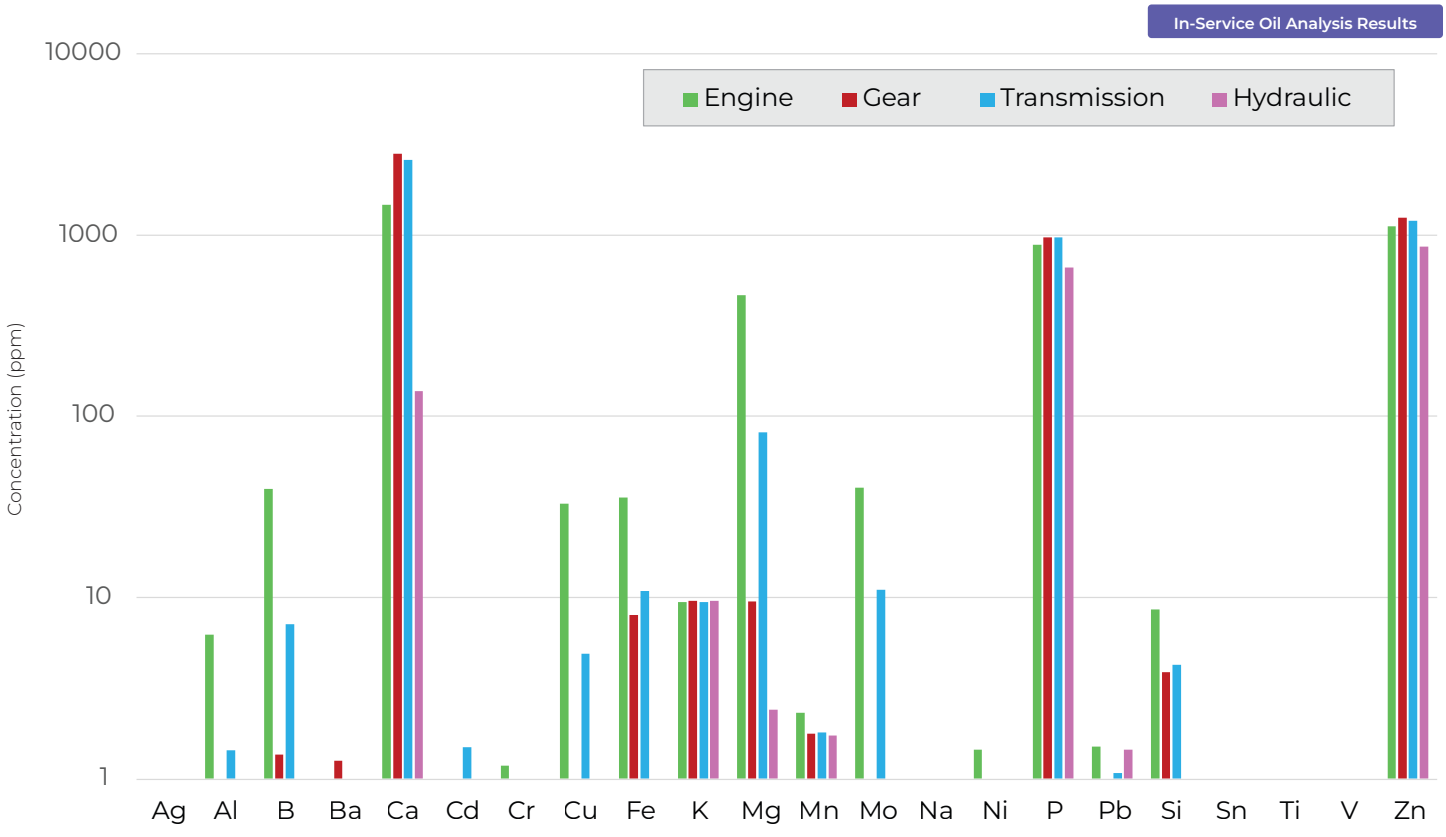

Figure 4. Selected In-Service Oil results with MICAP-OES 1000, concentrations displayed in logarithmic scale

System Stability

As many in-service oil laboratories analyze hundreds of samples per day, the stability of the instrument response is a critical factor to delivering high sample throughput. If the oil samples cause carbon deposits on the torch injector to form, then this causes drift in the signal obtained as an analysis progresses. Eventually this can require an ICP-OES analysis to be stopped prematurely and the torch removed for cleaning, replaced, and the system recalibrated before continuing more sample analysis.

Figures 6 & 7 display the QC Sample stability obtained for a 4.5-hour analysis session. These QC Samples were run every 20 oil samples and are typically monitored at a ± 10% control window in high throughput laboratories. The analytes have been split into two groups to aid viewing, with Figure 6 displaying the higher concentration elements and Figure 7 showing the lower concentration elements.

Excellent stability is observed for the QC samples across this 4.5+ hour session. During multiple weeks of analyzing oil samples and optimizing these procedures, no carbon deposition was observed on the MICAP torch.

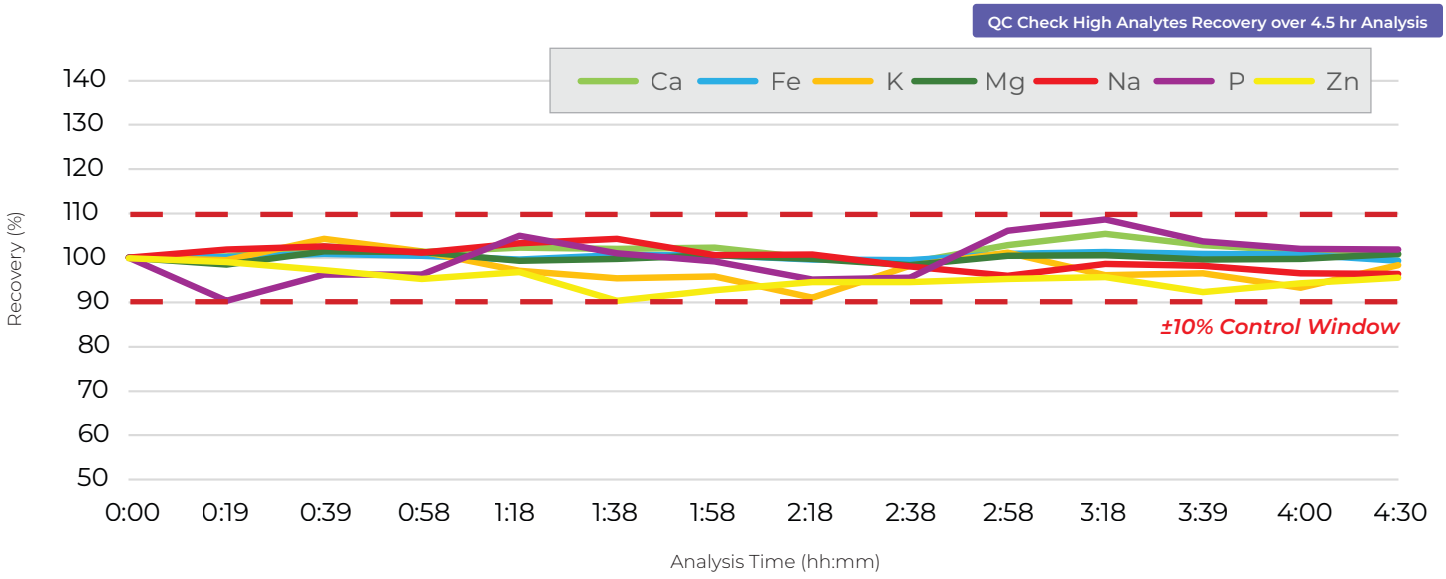

Figure 6. QC stability for high concentration elements (200ppm) during 4.5-hour oil analysis session

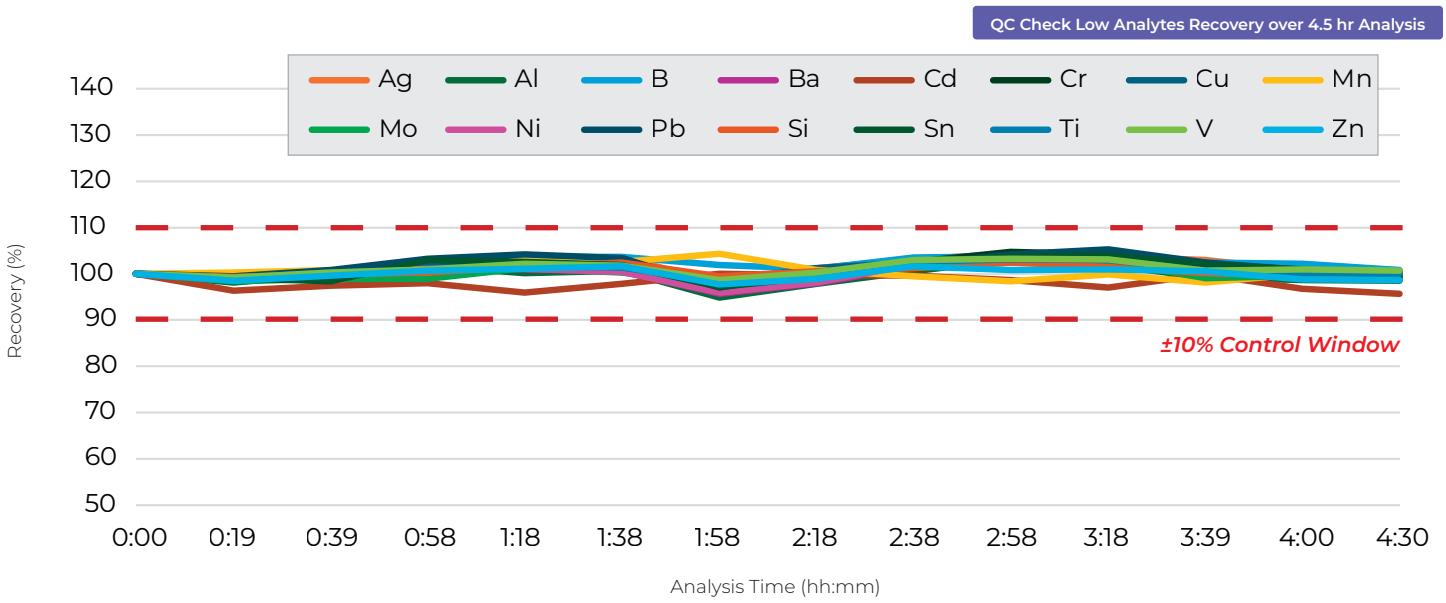

Figure 7. QC stability for low concentration elements (100ppm) during 4.5-hour oil analysis session

High Throughput Automation

In order to meet the demands for running hundreds of oil samples every shift, the MICAP and the Cetac Oils 7400 autosampler + ASXpress Plus valve are fully integrated to deliver rapid sample analysis. The Oils 7400 autosampler first mixes the samples with a rotating paddle stirrer. In the 2nd step the sample is quickly vacuum loaded into a sample valve loop. While this is happening, the nebulizer and spray chamber are being simultaneously rinsed with segmented solvent and air bubbles to wash out the previous sample.

When the sample loading is completed, the ASXpress Plus valve automatically injects the sample into the MICAP for analysis. A summary of these automation actions is shown in Figure 8 below. The speed of analysis for In-Service Oils following ASTM Method D5185 with this integrated system is a sample every 45 seconds.

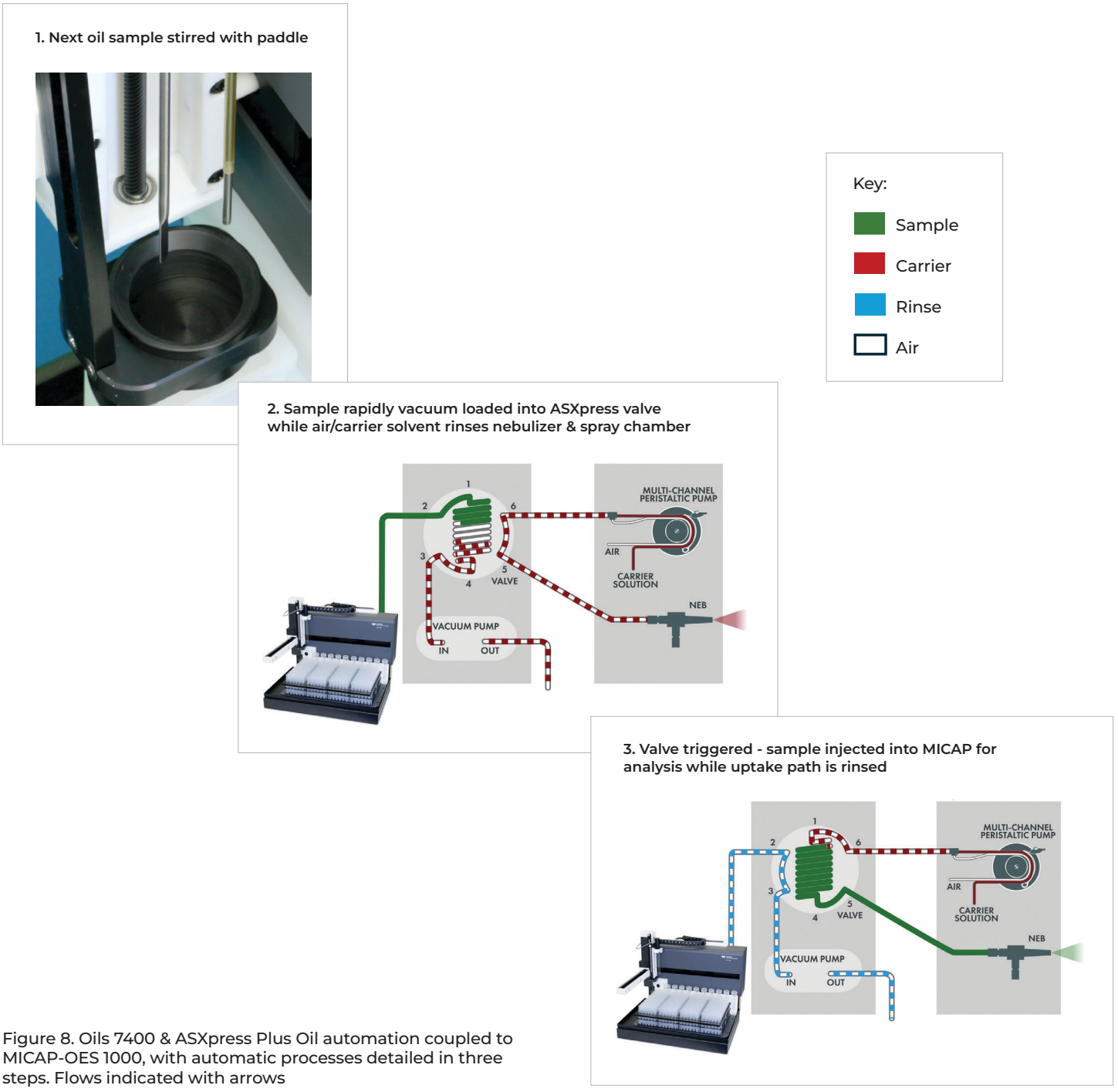

Figure 8. Oils 7400 & ASXpress Plus Oil automation coupled to MICAP-OES 1000, with automatic processes detailed in three steps. Flows indicated with arrows

Conclusions

The MICAP-OES 1000 N_2 ICP-OES system demonstrated its capability to successfully analyze in-service and new oil samples following the procedures outlined in ASTM Standard Method D5185. The unique use of air as a nebulizer gas reduces the plasma emission background in the visible wavelength range, which improves detection for several elements (ie Na & K)[3].

High throughput capability and stable long-term performance was exhibited with the MICAP coupled with the Cetac Oils 7400 autosampler and the ASXpress Plus valve system. No carbon deposition was observed on the MICAP torch throughout the length of this application work for in-service lubrication oils.

References

1. ASTM D5708, Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), ASTM Intn, West Conshohocken, PA, 2024, **www.astm.org**

2. ASTM D4951, Standard Test Method for Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry, ASTM Intn, West Conshohocken, PA, 2024, **www.astm.org**

3. Lubricant Oil Analysis for Wear Metals, Additives, and Ingress Elements with the MICAP N2 ICP-OES system, Application Note, Radom Instruments, Pewaukee, WI, 2024, **www.radominstruments.com**

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