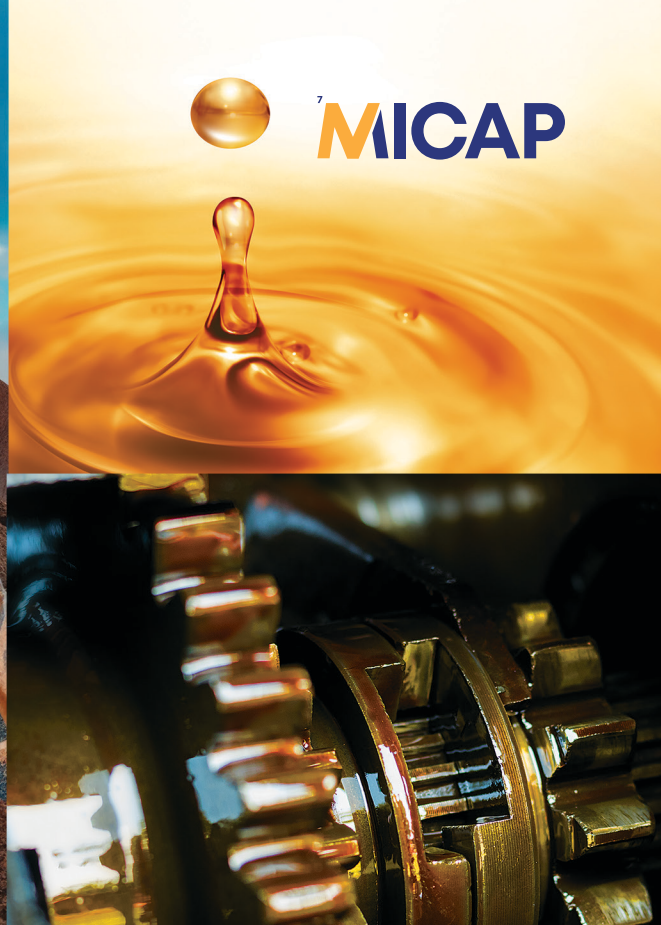




 **MICAP**

MICAP-OES 1000

Lubricant Oil Analysis for Wear Metals, Additives, and Ingress Elements with the MICAP N₂ ICP-OES system

Introduction

The analysis of new and in-service oils is critical in ensuring both the initial and ongoing lubrication needs of heavy equipment engines. The costs incurred from unscheduled maintenance can be very high in both lost productivity and repair expenses. To monitor the quality of these oils, the analysis of lubricant additives, ingress elements, and wear metals helps indicate when preventative maintenance is required. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) has been used routinely for this analysis.

This note describes the use of the simultaneous MICAP OES-1000 N₂ ICP-OES system for routine analysis of new and in-service oils following the procedures outlined in ASTM Method D5185. Oil standards and samples are simply diluted ten-fold in an organic solvent prior to multielement ICP analysis.

As many laboratories performing this work analyze hundreds of samples per shift, the speed of analysis becomes a very important factor. This work demonstrates use of a high-throughput sample automation system that stirs each sample followed by monitored loading into the MICAP for the fastest analysis speed. Analytical performance is presented to demonstrate accurate and stable performance for these lubrication oils.

RADOM
INSTRUMENTS

Instrumentation

This method outlines the procedures that are utilized for determining additive elements, wear metals, and contaminants in both used (In-service) and new lubricating oils. The procedures follow those outlined in ASTM standard test method D5185¹, Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The oil and lubricant samples are simply diluted into a kerosene-based solvent for introduction into the plasma. The MICAP-OES 1000 is configured with an organic solvent introduction system. This includes a double-pass cyclonic spray chamber and a high-solids V-Groove nebulizer connected to the standard one-piece torch for introduction of samples into the N₂ plasma. No addition of air or oxygen is required, as carbon deposition on the torch is not a common occurrence.

The MICAP patented design efficiently drives microwave energy into the Cerawave™ ring to create magnetic fields required to inductively couple energy into the robust N₂ plasma source. 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 large challenges to optimally introduce samples in and out of the instrument while supporting high-throughput analysis. To obtain these goals, an Elemental Scientific Inc. (ESI, Omaha, NE, USA) SampleSense Oil automation system was interfaced to the MICAP. This sample automation system provides several unique features:

- Quick sample stirring with gas infusion from sample probe just prior to uptake
- High-speed vacuum loading of samples into an optically-monitored sample valve loop
- Enhanced washout of spray chamber with solvent during sample valve loading

The SampleSense Oil system is integrated together with the MICAP operation. When a sample is loaded into the valve, the MICAP analysis is automatically triggered. The autosampler probe is then rinsed and the next sample gas infusion mixed while the current analysis is underway.



Figure 1. MICAP-OES 1000 N₂ ICP-OES with ESI SampleSense Oil automation system

Table 1. Operational conditions for oil analysis

Parameter	Value
Torch	Quartz 1-piece, 1.5mm injector
Spray Chamber	Meinhard double pass cyclonic
Nebulizer	Meinhard glass V-Groove
Sample Tubing	Solvaflex Blk/Blk (0.76 mm ID)
Drain Tubing	Solvaflex Blu/Yel (1.52 mm ID)
FAST Valve Loop	750 µL
Sample stirring time	4 seconds
Carrier & Rinse	PremiSolv™
Coolant Gas Flow	14 L/min
Auxiliary Gas Flow	0.4 L/min
Nebulizer Gas Flow	0.3 L/min
Peristaltic Pump	75 rpm
Sample Flow Rate	1.6 mL/min
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 D5185¹ 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 additive element Zn, the MICAP was configured to perform an automated cross calibration using two Zn lines to address the wide concentration range commonly present in these oil samples.

The automation capabilities of the ESI SampleSense Oil system significantly impact the speed at which oil samples can be processed. The gas infusion option was selected, which mixes each sample with nitrogen just prior to their uptake into the valve. Without this mixing, some oil samples settle out from the dilution solvent which negatively impacts the sample uptake. With the optimized sample handling of this automation system, oil samples can be analyzed on the MICAP at a rate of one sample every 32 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 585.368	Co II 238.892
Ca 317.933	
Cd 266.501	
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 285.213	
Mn 257.610	Co II 238.892
Mo 281.615	
Na 588.995	Co I 240.725
Ni 300.249	
P 213.618	Co II 238.892
Pb 283.305	Co I 240.725
Si 251.611	
Sn 283.998	
Ti 323.451	Co II 238.892
V 309.310	Co I 240.725
Zn 206.200	Co II 238.892
Zn 213.857	

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 585.368	50	500	100
Ca 317.933	50	5000	200
Cd 266.501	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 285.213	50	500	200
Mn 257.610	50	500	100
Mo 281.615	50	500	100
Na 588.995	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 206.200*	100	1600	100
Zn 213.857*	50	100	200

* Zn response 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 D5185¹. Working standards were prepared by diluting (w/w) oil-based stock standards (VHG, LGC Standards, Manchester, NH, USA) while maintaining the oil level with a 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) by weight, with the 30 ppm Cobalt (Co) internal standard 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. Four used (in-service) oil samples and one unused engine oil were selected for analysis in this work (see Figure 2). The oil samples were diluted 1:10 (w/w) using the same procedures outlined above.

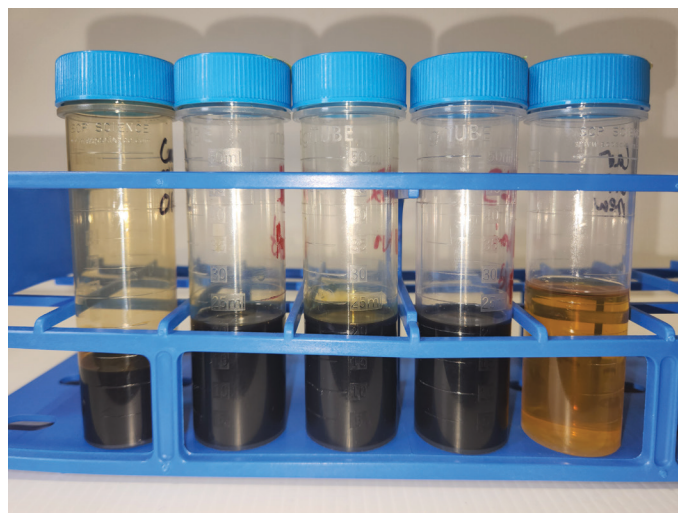


Figure 2. Four used and one new engine oil analyzed in this work, prior to dilution.

Results

The MICAP was calibrated as previously described and quality control checks were performed every 15 oil samples to ensure stable and accurate response. All wavelengths were viewed in the Radom Instruments Software (RIS) Profiles View to ensure no spectral interferences and to set peak integration points. Examples of these emission signals are presented 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:

- NIST CRM 1085c, Wear Metals in Lubricating Oil, (Gaithersburg, MD, USA)
- Conostan Standard S-21+K+Sb, 500 ppm (Analyt-iChem, Bale-D'Urfe, QC, Canada)

Detection limits (LODs) were measured by analyzing ten replicate measurements of the blank. LODs were calculated by multiplying the standard deviation by 3. The LOD values obtained 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.

Table 4. External quality control results and limits of detection (LODs)

Analyte	NIST CRM (%Rec)	2nd source (% Rec)	Oil LOD (mg/Kg)
Ag	98	103	0.12
Al	102	104	1.05
B	86*	103	1.00
Ba	98	103	0.63
Ca	99	100	3.04
Cd	101	104	1.91
Cr	103	102	0.92
Cu	102	101	0.09
Fe	105	101	0.67
K	100	104	5.15
Mg	92	95	0.08
Mn	96	95	0.10
Mo	103	103	1.27
Na	98	100	0.31
Ni	100	97	1.85
P	98	101	10.8
Pb	102	102	2.24
Si	96	98	0.43
Sn	99	101	1.10
Ti	99	100	0.20
V	95	97	0.61
Zn	98	103	0.35

* Boron values for the NIST CRM 1085c recovered low during all this work, including at alternate wavelengths. Satisfactory performance observed on 2nd Source QC for Boron.

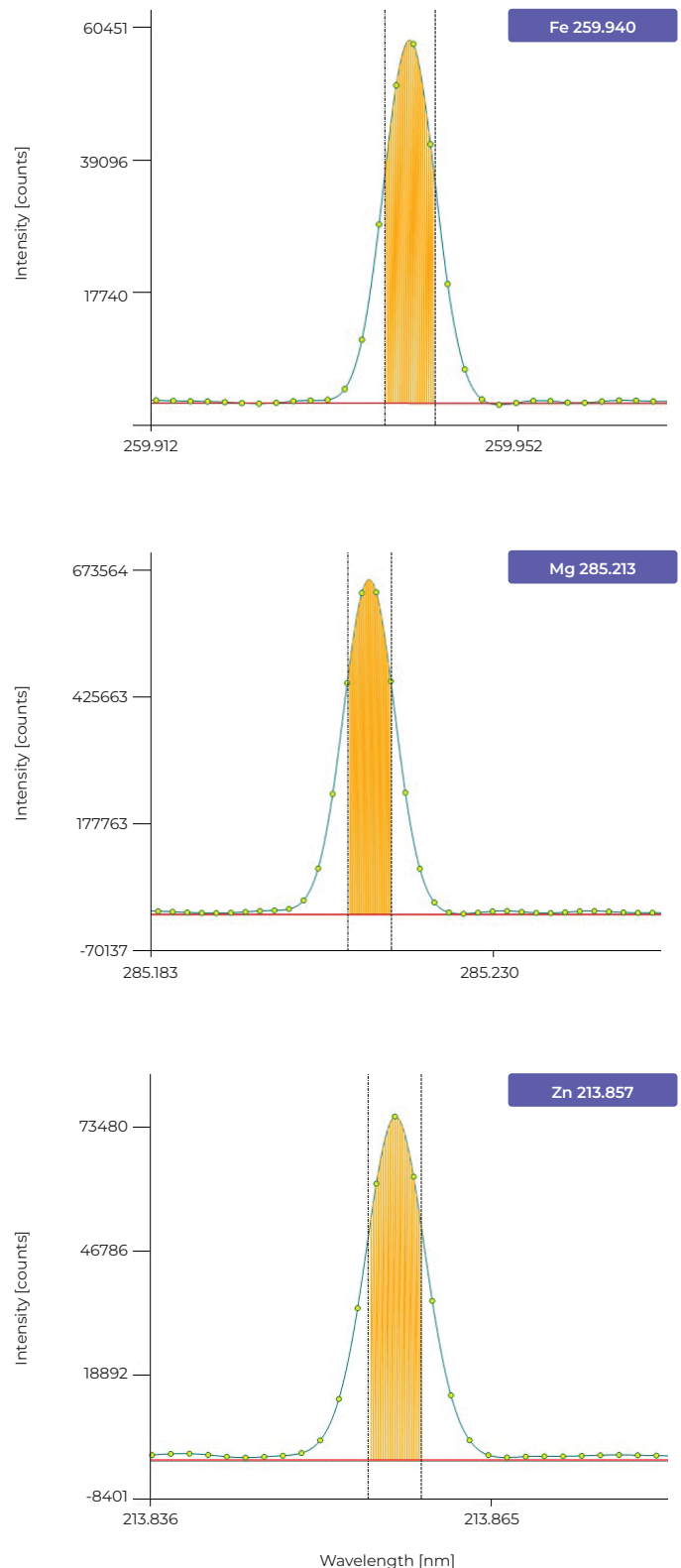


Figure 3. MICAP profiles view of signals for Fe, Mg, & Zn obtained from an in-service oil sample

The results obtained for the five engine 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 these oils.

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

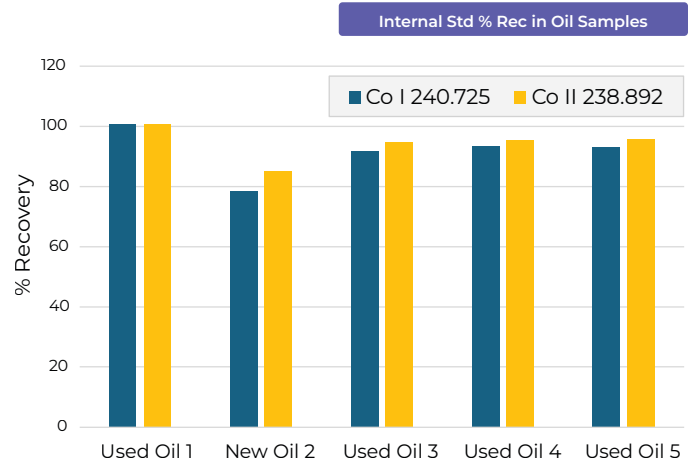


Figure 5. Internal standard (Co) recoveries across engine oil samples analyzed.

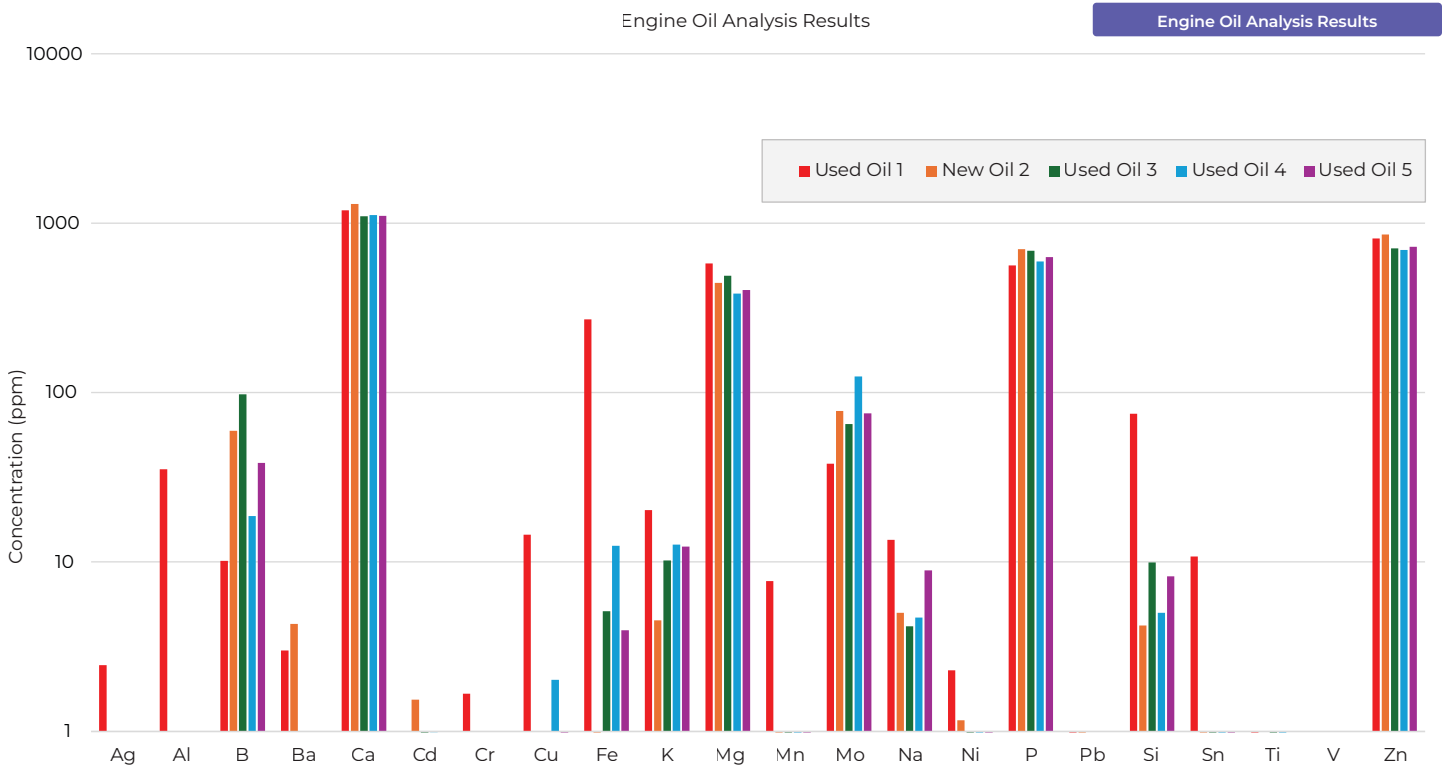


Figure 4. Engine oil results with MCIAP-OES 1000, concentrations displayed in logarithmic scale.

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 eventually 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 5 hour analysis session. These QC Samples were run every 15 oil samples and are typically monitored at a $\pm 10\%$ 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 5+ hour session. During multiple weeks of analyzing oil samples and optimizing these procedures, no carbon deposition was observed on the MICAP torch.

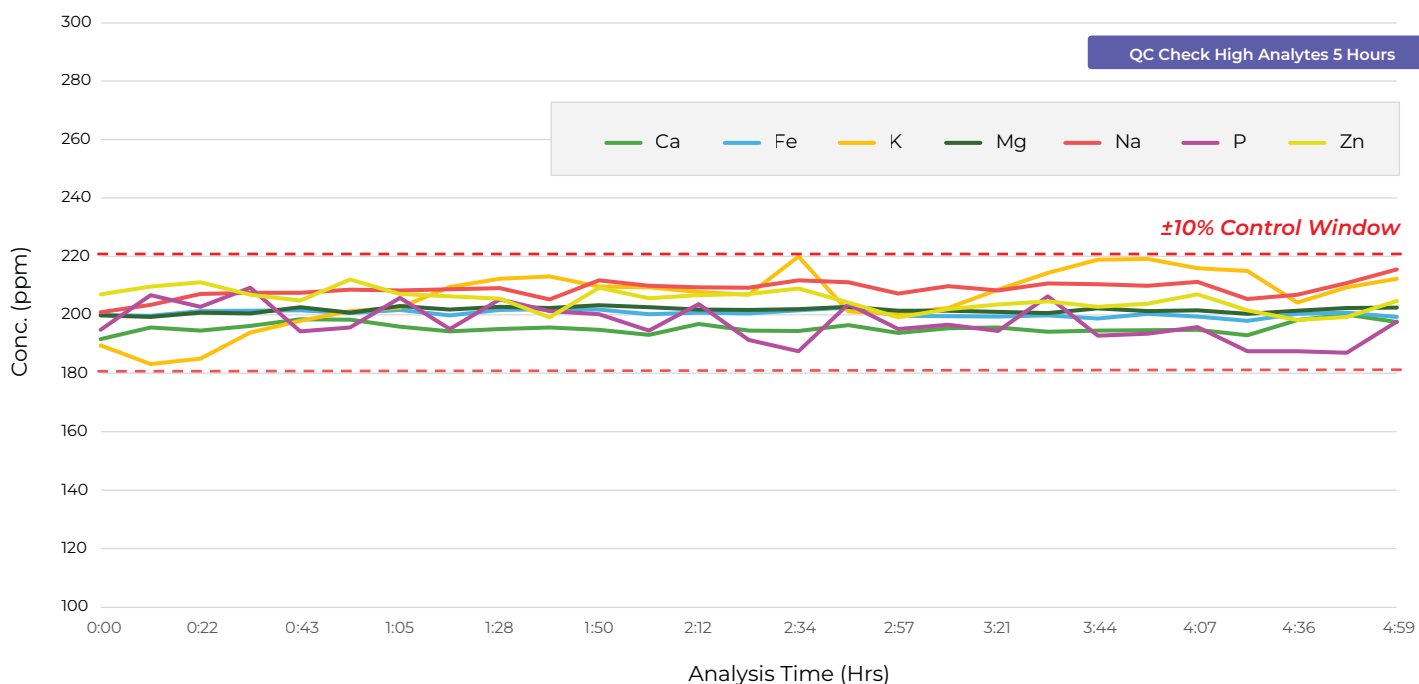


Figure 6. QC stability for high concentration elements during 5-hour oil analysis session

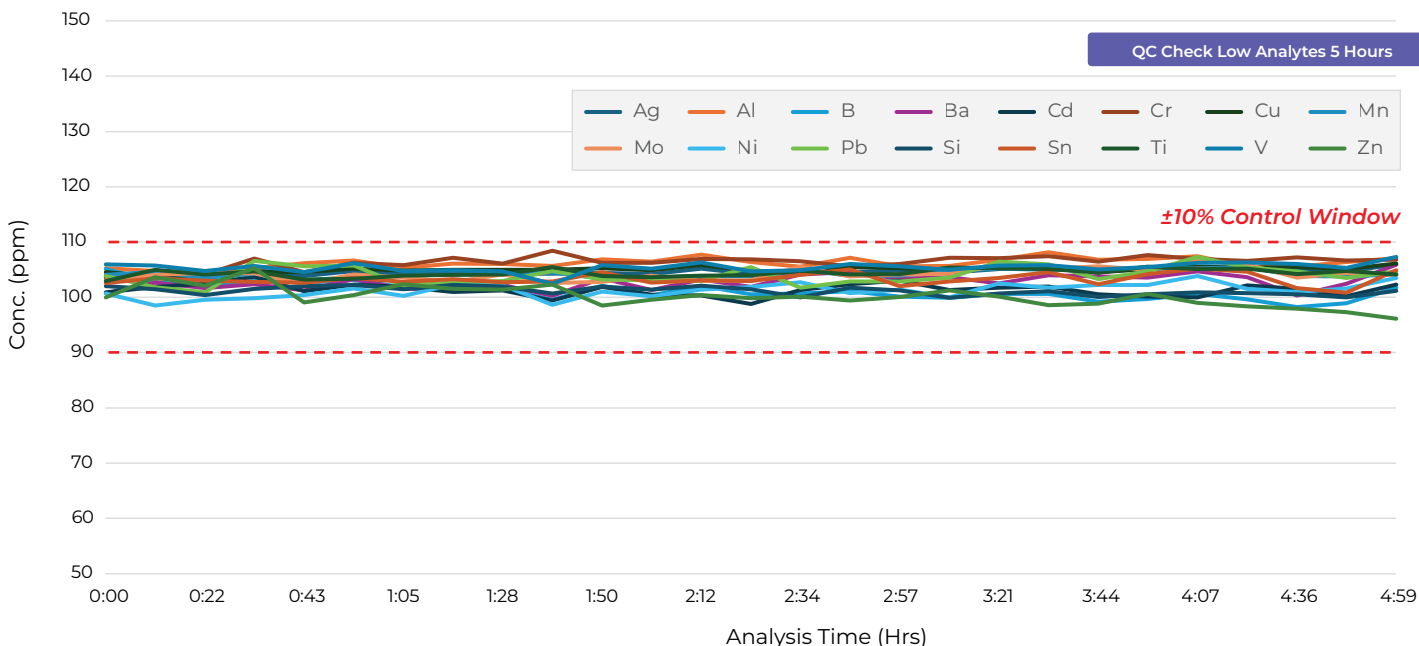


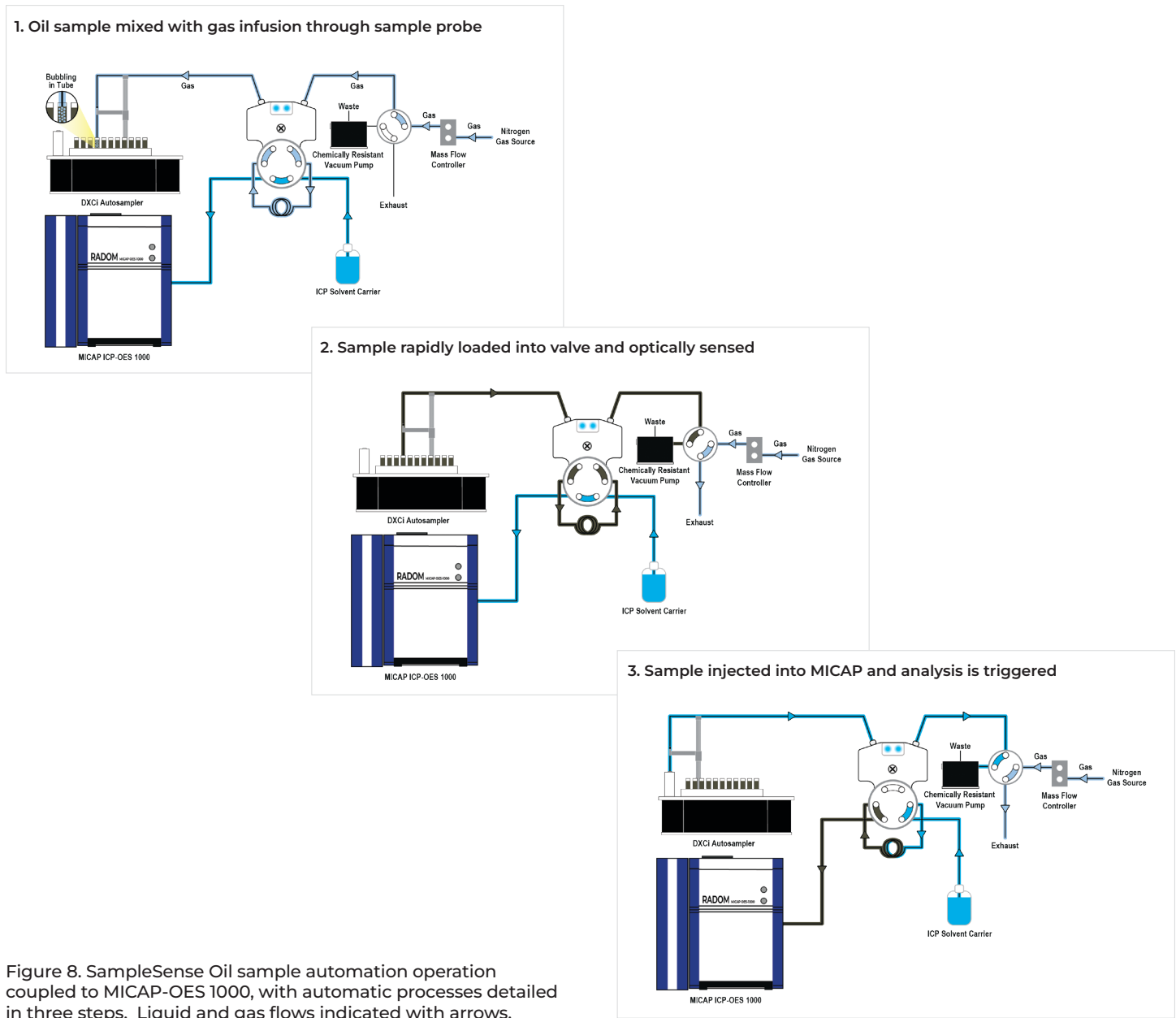
Figure 7. QC stability for low concentration elements during 5-hour oil analysis session

High Throughput Automation

In order to meet the demands for running hundreds of oil systems every shift, the MICAP and ESI SampleSense Oil systems have been fully integrated to deliver this capability. The SampleSense Oil automation system first uniquely automates sample mixing by delivering gas through the sample probe directly into the sample/standard container. Next the sample is quickly vacuum loaded into a sample valve loop. This optically monitored loading provides the optimum loading time for each sample, even with the varying oil viscosity present in

different samples. Simultaneously to this sample loading, the spray chamber is being rinsed with solvent to wash out the previously analyzed sample.

When the sample loading is completed, the SampleSense Oil system automatically triggers the MICAP data acquisition. A summary of these automation actions is shown in Figure 8 below. The speed of analysis for oils following ASTM Method D5185 with this integrated system is a sample every 32 seconds.



Conclusions

The MICAP-OES 1000 N₂ ICP-OES demonstrated its capability to successfully analyze in-service and new oil samples following the procedures outlined in ASTM Standard Method D5185. High throughput capability and stable long-term performance was exhibited with the MICAP coupled to the ESI SampleSense Oil automation 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 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), 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

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