MICAP-OES 1000

Multi-elemental high throughput analysis of in-service coolants with a novel N_2 ICP-OES system following ASTM Method D6130

Introduction

Monitoring engine coolants has recently become a very important tool in tracking the health of the critical liquid coolant process in gas and diesel engines. The elemental composition of the coolant fluids provides important information regarding the corrosion protection and stability of these essential engine fluids. Maintaining effective cooling throughout an engine directly impacts the usable lifetime of these engines.

ICP-OES has been used routinely in the monitoring of in-service engine oils for many years, and recently has been applied to the monitoring of engine coolants. This note describes the use of the simultaneous MICAP N2 ICP-OES system for routine analysis of glycol-based coolants following the ASTM Method D6130, which is designed to monitor both new and in-service coolants by ICP-OES. For this work, high throughput sample introduction automation is used to optimize and speed up both the uptake and washout of these critical fluids for an easy multi-elemental analysis of the additive, corrosion, and contaminant elements.

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Instrumentation

As engine coolants are aqueous-based liquids, the Radom Instruments MICAP-OES 1000 was configured with an aqueous sample introduction system. A double-pass cyclonic spray chamber and high-solids concentric nebulizer were coupled to the standard one-piece torch to introduce the samples into the N_2 plasma.

Microwave energy in the MICAP is coupled into the Cerawave™ ring in a highly efficient process that creates the magnetic fields required to inductively couple energy into the robust N_2 plasma emission source. The 4 MP sCMOS camera simultaneously collects the emission lines from the high-resolution spectrometer to detect the trace elemental signals.

The composition of these coolants can vary greatly based on their use, which alters physical properties such as viscosity and surface tension. To ensure consistent uptake and rinse-out of these coolant samples, an Elemental Scientific (ESI, Omaha, NE, USA) 4DXCi autosampler and SampleSense *FAST* discrete sampling valve was coupled to the MICAP.

This automated sampling valve quickly vacuum loads the sample into a loop while the valve optically monitors the arrival of the sample. Once the sample loading is complete (approx. 3 sec), the analysis is automatically triggered to start the collection of the emission spectrum from the plasma. Upon analysis completion, the next sample is automatically loaded while the nebulizer and spray chamber are rinsed out in preparation for the next sample analysis. This automated sampling valve provides the following advantages to the analysis:

- Sample uptake time is greatly shortened
- Uptake of each sample is optimized as coolants of varying viscosities are each optimally loaded
- Washout of coolants is enhanced as the spray chamber rinse is performed simultaneously along with the next sample uptake

Experimental Conditions

The analyses were performed on the MICAP-OES 1000 simultaneous N_2 ICP-OES system utilizing the conditions listed in Table 1. The settings used with the ESI SampleSense *FAST* automation system are also provided here. A complete view of this integrated analysis solution is displayed in Figure 1.

The analysis conditions employed on the MICAP follow closely the procedures outlined in ASTM Method D6130-24, Determination of Silicon and Other Elements in Engine Coolant by ICP-AES[1]. Table 2 provides specifics on the analyte and internal standard (Co) wavelengths used for this analysis.

Table 1. MICAP conditions and FAST automation settings

Parameter	Value
Torch	Quartz 1-piece, 1.5mm injector
Spray Chamber	Double pass cyclonic
Nebulizer	High solids concentric glass
Sample Tubing	Blk/Blk PVC (0.76 mm ID)
Drain Tubing	Blu/Yel PVC (1.52 mm ID)
SampleSense *FAST* Loop	1 mL
FAST Carrier / Rinse	DI Water
Coolant Gas Flow	14 L/min
Auxiliary Gas Flow	0.4 L/min
Nebulizer Gas Flow	0.7 L/min
Peristaltic Pump	30 rpm
Plasma Viewing	Axial
Camera Exposure	10 sec (200 ms @ 50 reps)
# of Repeats	3

Table 2. Analyte and internal standard wavelengths

Analyte Wavelength (nm)	Internal Standard Wavelength (nm)
Al 396.152	Co I 240.725
B 249.677	
Ca 396.847	Co II 238.892
Cu 324.754	Co I 240.725
Fe 259.940	Co II 238.892
K 404.414	Co I 240.725
K 766.490	Co II 238.892
Mg 280.270	
Mo 317.034	Co I 240.725
Na 568.819	
P 213.618	Co II 238.892
Pb 283.305	Co I 240.725
Si 251.611	
Sn 283.998	
Zn 213.857	Co II 238.892

Figure 1. MICAP, SampleSense *FAST* valve & 4DXCi autosampler

Table 3. Analytes and calibration standards, in mg/L (ppm)

Element	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	CCV1	CCV2	CCV3
Al	0.2	2	20				2		
B	0.2	5	100					50	
Ca	0.2	2	20				2		
Cu	0.2	2	20				2		
Fe	0.2	2	20				2		
K	0.5	20	500				5	200	
Mg	0.2	2	20				2		
Na	20	200	1000					200	
P	5	100	200					100	
Pb	0.5	2	20				5		
Zn	0.2	2	20				2		
Mo				0.2	5	100			5
Si				0.2	2	20			2
Sn				0.5	2	20			5

Standard and Sample Preparation

The calibration standards, blanks, and samples were prepared in accordance with the protocols outlined in ASTM Method D6130-24[1]. Multielement standards were prepared from aqueous standards (Inorganic Ventures, Christiansburg, VA, USA). Final standards and blanks were prepared in 18 MΩ deionized water (DI) and 5% ethylene glycol w/v (Sigma-Aldrich, St. Louis, MO, USA). See Table 3 above for the specific concentrations utilized. Note that since K was cross calibrated using two emission lines, a mid-point calibration check was performed for each line to confirm stable response during the analysis.

Thirty in-service coolant samples were sourced from a local heavy equipment supplier laboratory. These were augmented with two new coolant samples sourced commercially. Coolant supplied at usage levels were prepared by diluting 1:10 fold (v/v) in DI water, while concentrated (new) coolant samples were diluted 1:20 fold.

All standards and samples included the element Cobalt (Co) at 10 mg/L (ppm) as an internal standard (Inorganic Ventures). Additionally, 1% (w/v) Cesium (as CsCl, Sigma-Aldrich) was also added to all solutions. The Cs serves as an ionization buffer to eliminate matrix interference observed for coolant samples containing very high Na and K levels. Both the Co and the Cs were added into the diluent to facilitate the sample and standard preparation.

Results

The 30 in-service and 2 new coolant samples were successfully analyzed with MICAP and the results compiled. Figure 2 demonstrates the differences in the measured analytes across 2 in-service and one new extended lifetime coolant (ELC).

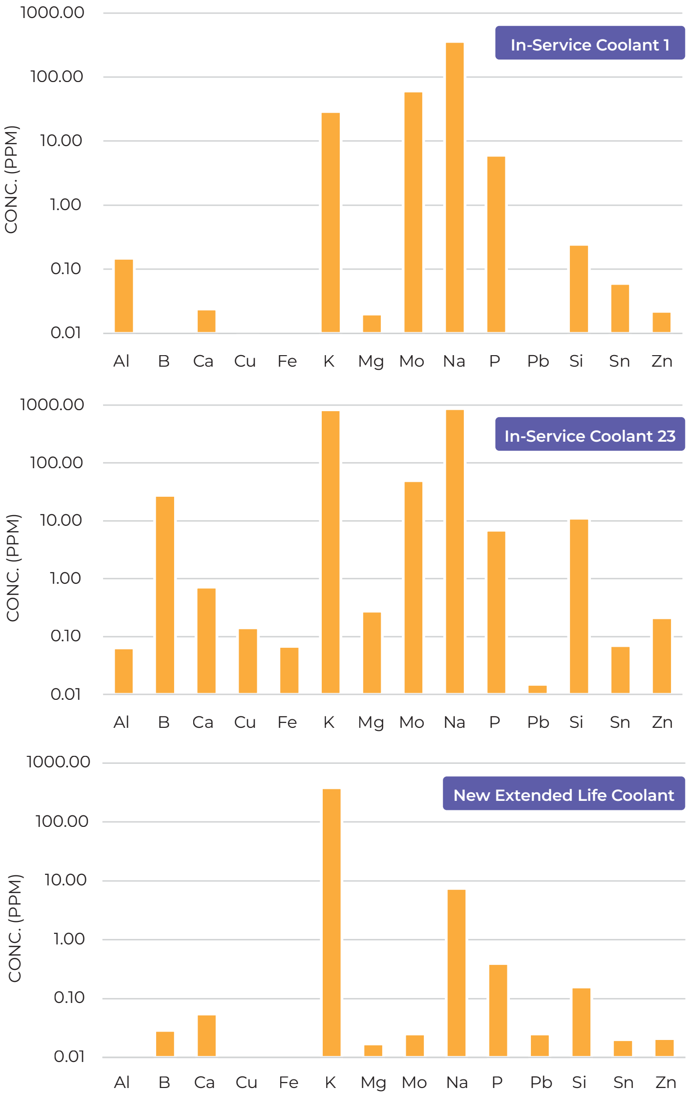


Figure 2. Comparison of elemental concentrations across three coolant samples analyzed

These coolants vary significantly in their makeup. They differ in color from various shades of red, orange, and green (see Figure 3). From general observation, the viscosities also vary from coolant to coolant. It was additionally interesting to observe the wide range of concentrations of elements in various coolant samples. Figure 4 displays the K concentrations across the 32 samples.

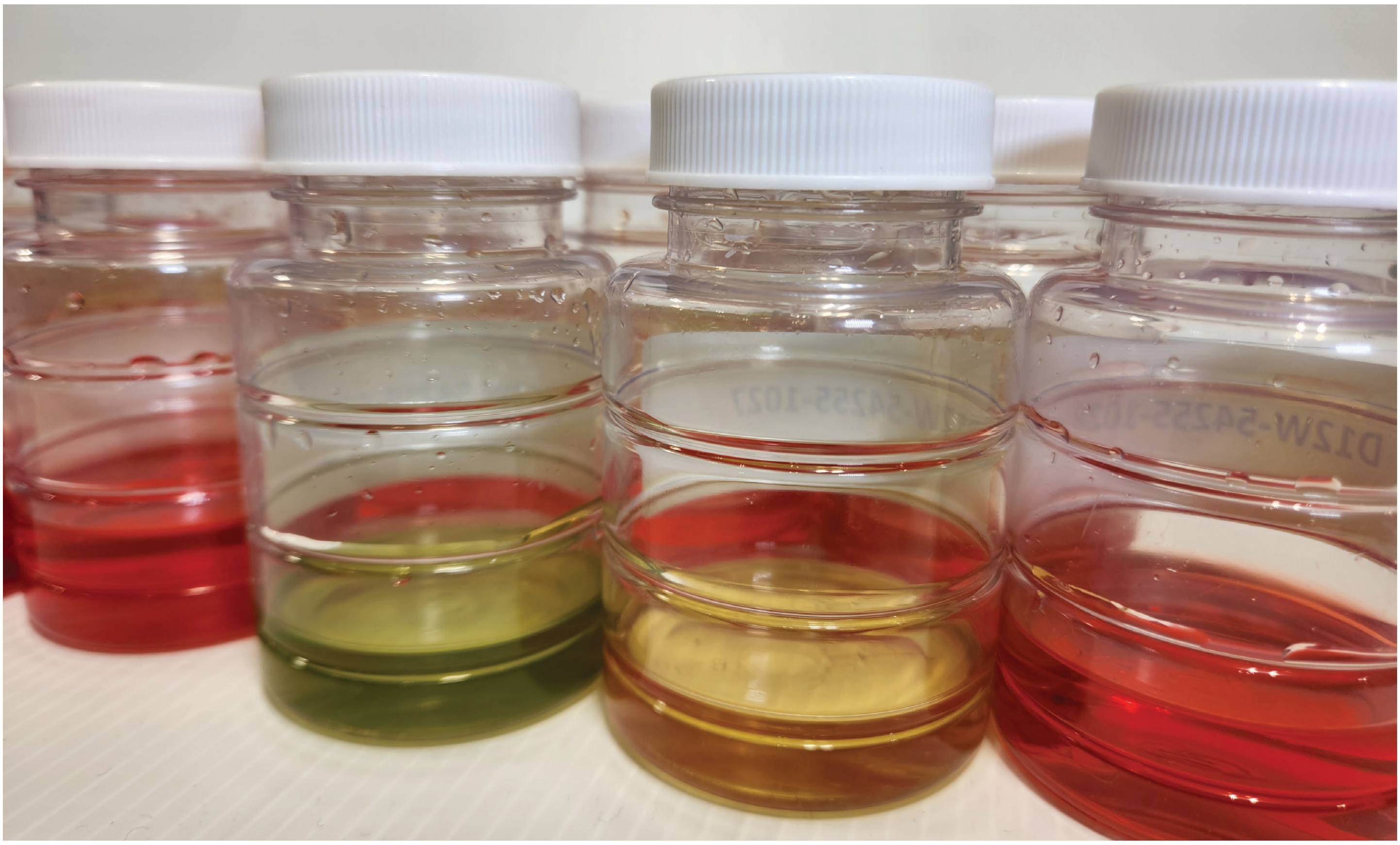


Figure 3. Image of various coolant samples analyzed

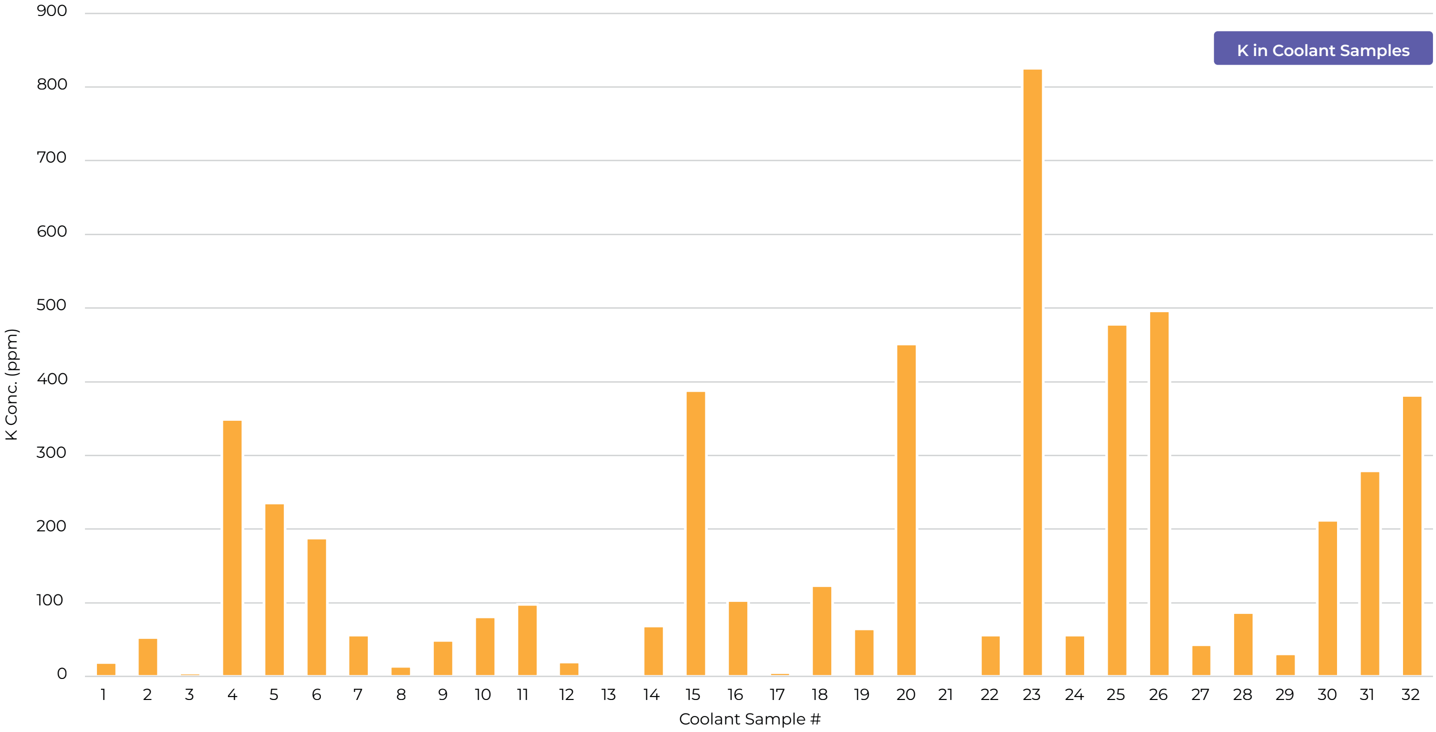


Figure 4. Potassium (K) concentrations measured in coolant samples (ppm)

System Stability

The coolant method was also evaluated for its stability, as many laboratories need to analyze a large number of coolant samples in a single session. Figure 5 displays the QC Sample stability obtained across the over 5-hour sample analysis, with all the recovery values falling within the ± 5% control window required in ASTM Method D-6130[1].

Equally as important is the recovery of the Co internal standard during the analysis of these in-service coolants (Figure 6). This graph demonstrates the importance of the internal standard to correct for the different physical and chemical properties of the coolants.

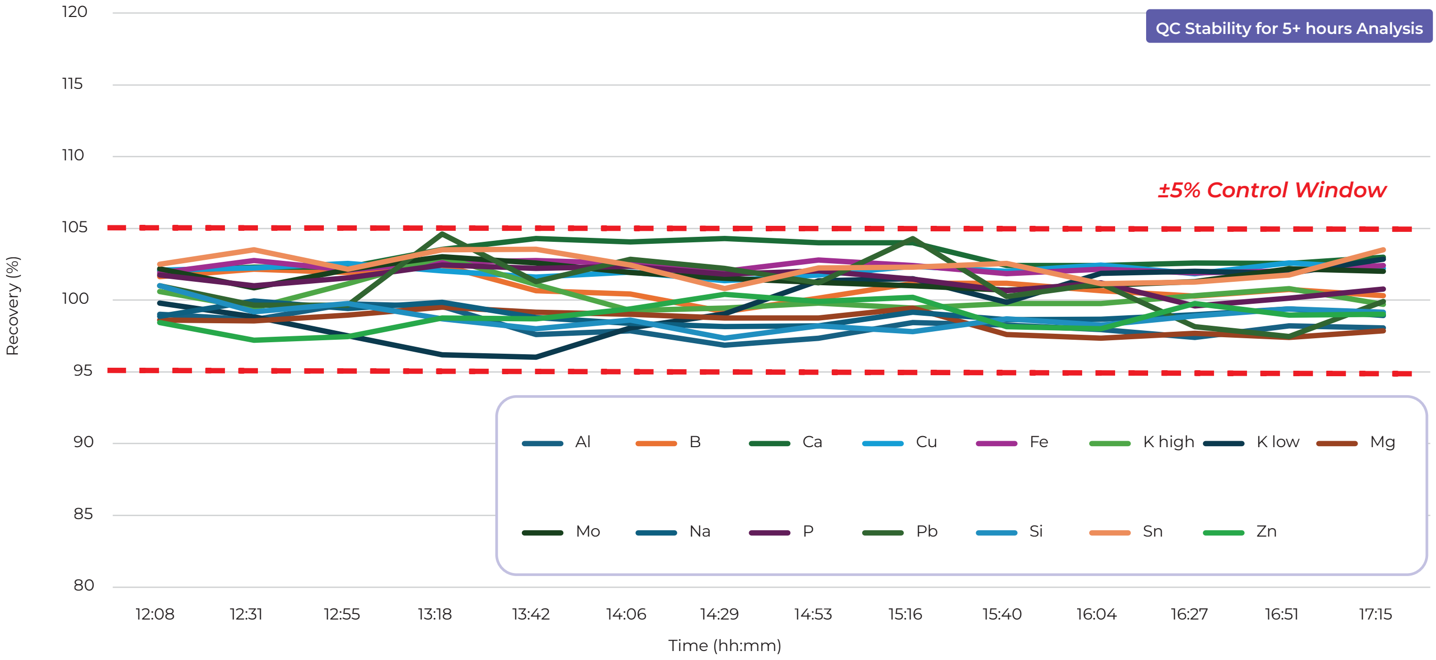


Figure 5. Stability of quality control results analyzed during 5+ hour coolant sample analysis

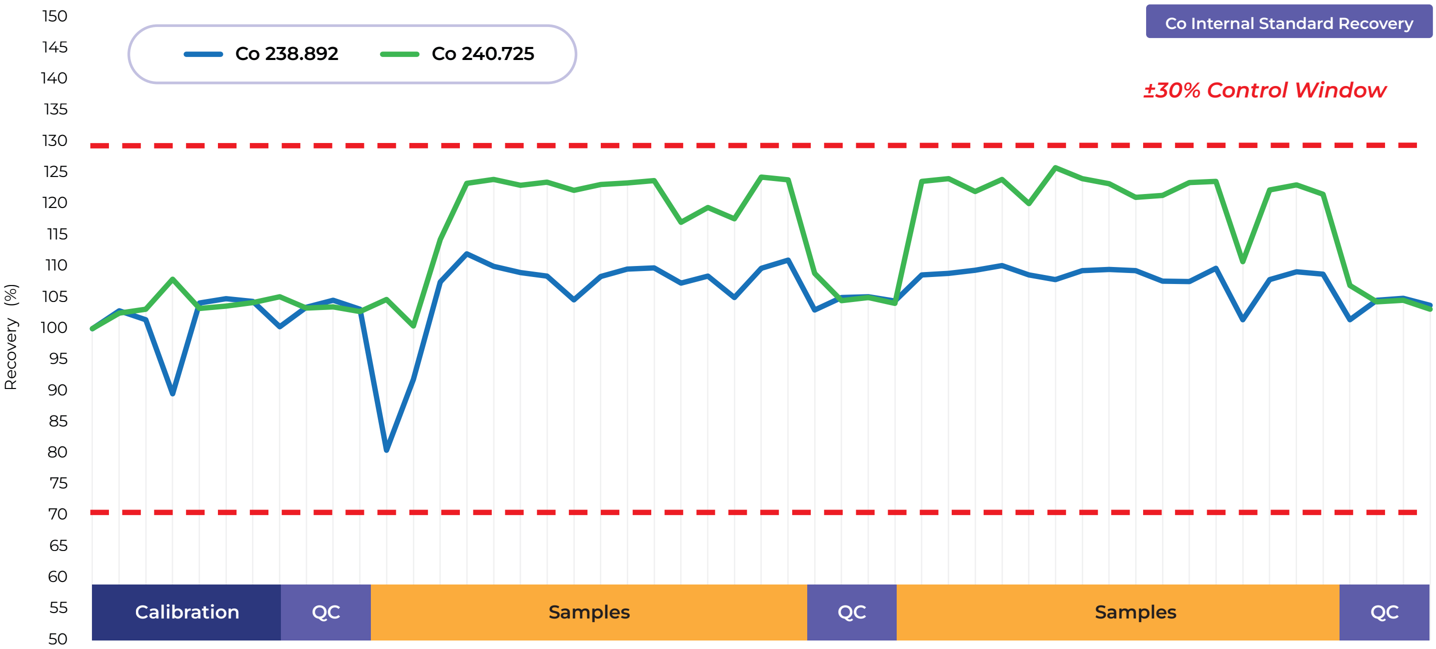


Figure 6. Internal Standard stability observed during coolant sample analysis

Detection Limits

The detection capability of the MICAP in coolants was determined in the glycol matrix utilized for standard preparation. Ten blanks were measured under the method conditions and the detection limits (DL) calculated by:

DL = 3x (Std Dev of 10 blank measurements)

The values obtained are shown in Table 4. These values are presented both as measured and in the actual coolants (reflecting the 10x dilution).

Experimental Conditions

In-service coolant samples often present washout challenges due to their varying composition. The ESI SampleSense *FAST* automation was primarily selected to help address these challenges. With its automated valve sampling, samples are loaded simultaneously into the valve while the MICAP sample introduction system is rinsed. Additionally, more viscous samples (that load slower) are actively monitored during the loading process. Improved analyte washout is a result of using this technology, resulting in faster sample throughput for quicker analysis times. Figure 7 demonstrates the highly effective sample washout to blank levels immediately after analysis of the high standard levels

The sample throughput rate obtained with a basic autosampler was determined to be 2 min 5 sec per sample. Utilizing the ESI SampleSense *FAST* automation significantly reduced this to 1 min 11 sec per sample, providing a 43% increase in sample throughput along with enhanced washout performance.

Table 4. Detection limits in glycol matrix

Analyte Wavelength (nm)	DL In Solution (ppm)	DL In Coolant (ppm)
Al 396.152	0.006	0.065
B 249.677	0.061	0.607
Ca 396.847	0.000	0.000
Cu 324.754	0.002	0.021
Fe 259.940	0.008	0.083
K 766.490	0.011	0.110
Mg 280.270	0.002	0.024
Mo 317.034	0.032	0.325
Na 568.819	0.573	5.726
P 213.618	0.573	5.734
Pb 283.305	0.062	0.618
Si 251.611	0.023	0.232
Sn 283.998	0.059	0.595
Zn 213.857	0.022	0.221

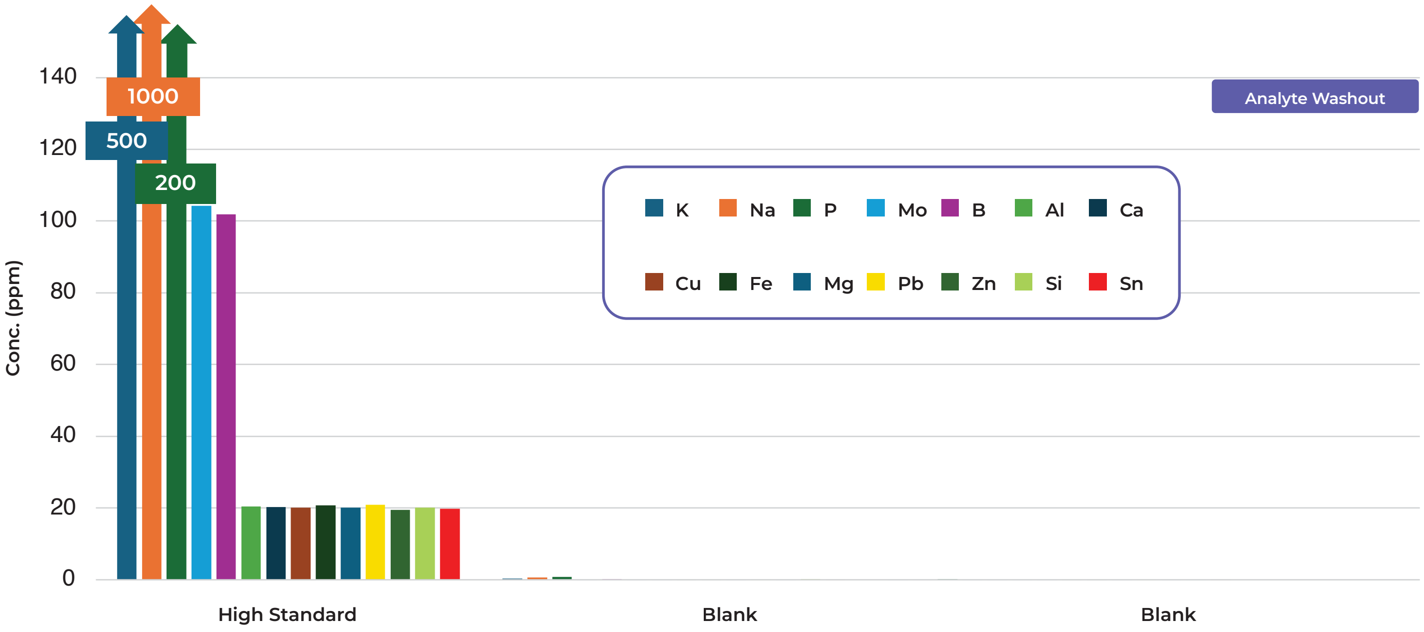


Figure 7. Analyte washout on MICAP with ESI SampleSense *FAST*. Washout to blank levels immediately after high standard levels. Note 500 ppm K, 1000 ppm Na, & 200 ppm P are off scale in the high standard.

Conclusion

The performance of the MICAP-OES 1000 N2 ICP-OES demonstrates its capability for the high throughput analysis of new and in-service coolants in accordance with ASTM Standard Method D6130-24. The high matrix tolerance of the system coupled with the proper application of internal standard correction delivers stable and accurate monitoring of these critical coolants.

Utilization of the ESI SampleSense *FAST* automated introduction system ensured that the varying viscosity coolant samples were each monitored for the optimal sample loading time, while also enhancing the sample washout process. An average analysis time of 71 seconds/sample was obtained with the ESI automation coupled to the MICAP.

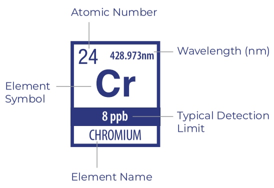
References

1. ASTM D6130-24, Standard Test Method for Determination of Silicon and Other Elements in Engine Coolant by Inductively Coupled Plasma-Atomic Emission Spectroscopy, ASTM International, West Conshohocken, PA, 2024, www.astm.org

MICAP - OES 1000

Typical Limit of Detection and Resolution

Key



Typical Resolution

Wavelength (nm)	Resolution (pm)
Zn 202.584	5
Cr 360.534	11
Ba 455.403	14
Na 588.996	21
Li 610.364	30

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H HYDROGEN																	2 He HELIUM
2	3 610.364nm Li 19 ppb LITHIUM	4 234.860nm Be 2 ppb BERYLLIUM											5 249.772nm B 9 ppb BORON	6 C CARBON	7 N NITROGEN	8 O OXYGEN	9 F FLUORINE	10 Ne NEON
3	11 588.995nm Na 2 ppb SODIUM	12 279.553nm Mg 1 ppb MAGNESIUM											13 396.152nm Al 6 ppb ALUMINUM	14 251.611nm Si 14 ppb SILICON	15 213.618nm P 560 ppb PHOSPHORUS	16 S SULFUR	17 Cl CHLORINE	18 Ar ARGON
4	19 766.490nm K 24 ppb POTASSIUM	20 393.366nm Ca 1 ppb CALCIUM	21 361.383nm Sc 1 ppb SCANDIUM	22 334.940nm Ti 7 ppb TITANIUM	23 311.071nm V 9 ppb VANADIUM	24 428.973nm Cr 8 ppb CHROMIUM	25 259.372nm Mn 2 ppb MANGANESE	26 259.940nm Fe 12 ppb IRON	27 345.350nm Co 21 ppb COBALT	28 346.165nm Ni 27 ppb NICKEL	29 324.754nm Cu 2 ppb COPPER	30 213.857nm Zn 26 ppb ZINC	31 403.298nm Ga 11 ppb GALLIUM	32 265.117nm Ge 32 ppb GERMANIUM	33 228.812nm As 310 ppb ARSENIC	34 196.026nm Se 790 ppb SELENIUM	35 Br BROMINE	36 Kr KRYPTON
5	37 Rb RUBIDIUM	38 407.771nm Sr 1 ppb STRONTIUM	39 437.493nm Y 1 ppb YTTRIUM	40 339.198nm Zr 7 ppb ZIRCONIUM	41 313.079nm Nb 24 ppb NIOBIUM	42 379.825nm Mo 22 ppb MOLYBDENUM	43 Tc TECHNETIUM	44 372.803nm Ru 12 ppb RUTHENIUM	45 369.236nm Rh 10 ppb RHODIUM	46 360.955nm Pd 8 ppb PALLADIUM	47 328.068nm Ag 10 ppb SILVER	48 228.802nm Cd 13 ppb CADMIUM	49 451.130nm In 10 ppb INDIUM	50 303.412nm Sn 110 ppb TIN	51 252.852nm Sb 74 ppb ANTIMONY	52 238.579nm Te 230 ppb TELLURIUM	53 206.163nm I 14,000 ppb IODINE	54 Xe XENON
6	55 Cs CESIUM	56 455.403nm Ba 1 ppb BARIUM	●	72 339.980nm Hf 67 ppb HAFNIUM	73 263.558nm Ta 51 ppb TANTALUM	74 400.871nm W 43 ppb TUNGSTEN	75 346.046nm Re 40 ppb RHENIUM	76 442.047nm Os 39 ppb OSMIUM	77 322.078nm Ir 84 ppb IRIDIUM	78 265.945nm Pt 34 ppb PLATINUM	79 242.795nm Au 16 ppb GOLD	80 253.652nm Hg 37 ppb MERCURY	81 377.572nm Tl 94 ppb THALLIUM	82 283.305nm Pb 65 ppb LEAD	83 306.770nm Bi 83 ppb BISMUTH	84 Po POLONIUM	85 At ASTATINE	86 Rn RADON
7	87 Fr FRANCIUM	88 Ra RADIUM	● ●	104 Rf RUTHERFORDIUM	105 Db DUBNIUM	106 Sg SEABORGIUM	107 Bh BOHRIUM	108 Hs HASSIUM	109 Mt MEITNERIUM	110 Ds DARMSTADTIUM	111 Rg ROENTGENIUM	112 Cn COPERNICIUM	113 Nh NIHONIUM	114 Fl FLEROVIUM	115 Mc MOSCOVIUM	116 Lv LIVERMORIUM	117 Ts TENNESSINE	118 Og OGANESSON
Lanthanide series			●	57 408.672nm La 3 ppb LANTHANUM	58 446.021nm Ce 10 ppb CERIUM	59 440.882nm Pr 6 ppb PRASEODYMIUM	60 401.225nm Nd 7 ppb NEODYMIUM	61 Pm PROMETHIUM	62 428.079nm Sm 3 ppb SAMARIUM	63 420.505nm Eu 3 ppb EUROPIUM	64 342.247nm Gd 12 ppb GADOLINIUM	65 384.873nm Tb 19 ppb TERBIUM	66 394.468nm Dy 4 ppb DYSPROSIUM	67 345.600nm Ho 4 ppb HOLMIUM	68 369.265nm Er 3 ppb ERBIUM	69 384.802nm Tm 2 ppb THULIUM	70 328.937nm Yb 1 ppb YTTERBIUM	71 261.542nm Lu 1 ppb LUTETIUM
Actinide series			● ●	89 Ac ACTINIUM	90 401.913nm Th 10 ppb THORIUM	91 Pa PROTACTINIUM	92 409.013nm U 50 ppb URANIUM	93 Np NEPTUNIUM	94 Pu PLUTONIUM	95 Am AMERICIUM	96 Cm CURIUM	97 Bk BERKELIUM	98 Cf CALIFORNIUM	99 Es EINSTEINIUM	100 Fm FERMIUM	101 Md MENDELEVIUM	102 No NOBELIUM	103 Lr LAWRENCIUM

Detection limits are averaged from multiple systems.
Values are calculated from 3x the standard deviation of 10 measurements of a blank; each with three, 30 second replicates.

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