APPLICATION NOTE

ICP-Optical Emission Spectroscopy

AUTHORS

Ruth Merrifield

Sandy Kanapilly

Cory Schomburg

PerkinElmer, Inc., Shelton, CT USA

Analysis of In-Service Coolants Following ASTM D6130 with the Avio 550 Max ICP-OES

Introduction

Engines are particularly complicated pieces of machinery. Not only do they need lubricants to prevent the moving parts from creating too much friction, they also produce a lot of heat and require cooling. To maintain a healthy engine, both the lubricants and coolants need to be changed or monitored regularly. Lubricant analysis for additives and wear metals by ICP-OES is standardized and has been occurring for years. However, it is only more recently that companies have focused on the cooling system as a point of failure in engines. Consequently, many in-service lubricant laboratories are being asked to measure the elemental concentrations of engine coolant samples to determine if the coolant is still fit for use. This has presented some challenges for labs since coolants are aqueous and must be treated differently than the organic lubricant samples.

Coolants are analyzed for different metals to monitor the additive levels (B, K, Mo, Na, P and Si), corrosion metals (Al, Cu, Fe, Pb, Sn and Zn), and contaminants (Ca and Mg). Monitoring these metals can determine if coolants have been mixed, if part of the cooling system needs replacing due to corrosion, or if the coolant has been diluted with tap water, which, in turn, could lead to engine corrosion.

Regular testing of coolant samples, combined with an effective maintenance program, can minimize corrosion, scale formation, and contamination within the cooling system. However, the composition of coolants can vary depending on their use, which type of engine they are intended for, and the type of coolant (i.e. conventional technology, hybrid technology, organic additive technology). Even the climate (i.e. hot vs. cold) will affect the coolant blend used. Therefore, testing laboratories may encounter samples with varying matrices and compositions. In this work, we discuss a robust method to handle the dynamic analyte composition and viscosity differences from one sample to the next.

As with lubricant testing, ASTM International established a test method for coolants: D6130[1]. Like the ASTM lubricant method, D6130 is intended for both new and in-service coolants to be tested by ICP-OES. This work demonstrates the analysis of coolants with PerkinElmer's Avio® 550 Max fully simultaneous ICP-OES system following a common implementation of method D6130.

Experimental

Samples and Sample Preparation

Samples, standards and QCs were diluted 1:10 (v/v) with deionized (DI) water. Since coolants are not acidic, it is important that the standards and QCs do not contain acid to more closely matrix match the samples. Analytical concentrations were measured against external calibration curves prepared from six custom standard stock solutions at varying analyte concentrations and an additional solution of 1000 ppm Mo. The combination of standard solutions used provides a three-point calibration curve for the analytes listed in Table 2 and utilizes the mid-range standard as a QC check. The additional high standard for Mo is included to cover the working range of extended-life coolants, which typically have higher Mo concentrations.

Yttrium (Y) was used as an internal standard to correct for transport variations and matrix differences from sample to sample. The internal standard solution was prepared at 20-40 ppm in DI water and added inline via a mixing Tee.

Instrument Conditions

Analyses were performed on the Avio 550 Max fully simultaneous ICP-OES using the conditions listed in Table 1, and the wavelengths for each element listed in Table 2. The element list includes the 12 elements specified in ASTM D6130 plus K and Sn, which are commonly measured by in-service oil labs. Because of the Avio Max series' Flat Plate™ plasma technology, the system operates on <10 L/min of total argon. This, in combination with the vertical torch, enhances the ability to analyze challenging matrices. Wavelengths were chosen to eliminate spectral interferences from other metals, necessitating the use of less sensitive lines, especially for Al. As a result, Multicomponent Spectral Fitting (MSF) correction is used to remove the noisy backgrounds and optimize the analytical signal[2].

Samples were introduced into the plasma using a CETAC ASX-7400 autosampler equipped with a stir paddle. Each sample was stirred prior to analysis to ensure that the analytes were suspended in solution, as they could settle out over time while sitting in the autosampler prior to analysis. Additionally, the rinse speed between samples is set to 5.00 mL/min, effectively reducing carryover for problematic analytes such as Si and Mo.

Table 1: Avio 550 Max ICP-OES instrumental parameters and conditions.

Parameter	Value
Nebulizer	High Solids GemCone™
Spray Chamber	Baffled Glass Cyclonic
RF Power	1500 W
Torch	Single-slot Avio Torch
Injector	2.0 mm Alumina
Plasma Gas Flow	8 L/min
Aux. Gas Flow	0.2 L/min
Nebulizer Gas Flow	0.7 L/min
Torch Position	-3
Sample Uptake Rate	1.00 mL/min
Flush Time	10 sec
Sample Uptake Tubing	Black/Black (0.76 mm ID)
Internal Standard Tubing	Green/Orange (0.38 mm ID)
Drain Tubing	Red/Red (1.14 mm ID)
Plasma View	Radial
Read Delay	15 sec
Replicates	2
Integration Range	0.2-5 sec
Rinse Rate	5.00 mL/min
Rinse Time	10 sec

Table 2: Analytes and wavelengths.

Analyte	Wavelength (nm)	Analyte	Wavelength (nm)
Al	394.401	Mo	202.031
B	249.772	Na	589.592
Ca	396.847	P	214.914
Cu	324.752	Pb	220.353
Fe	259.939	Si	288.164
K	766.490	Sn	189.927
Mg	280.271	Zn	206.200
Internal Standard			
Y		371.029	

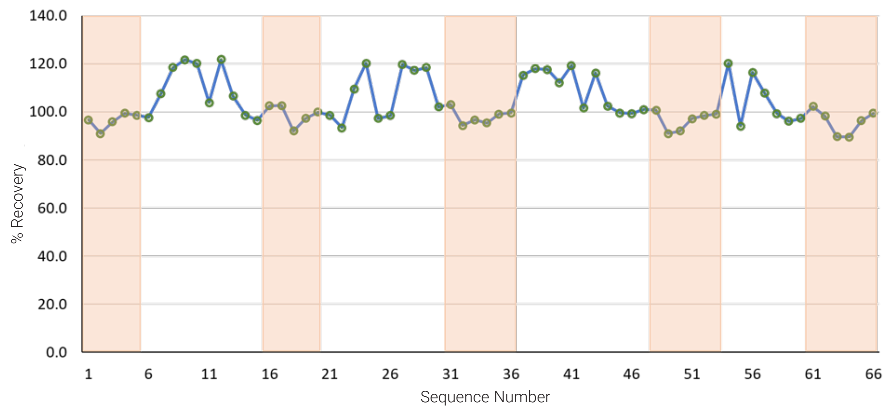

Figure 1: Internal standard (Y) recovery of QCs (orange area) and coolant samples (white area).

Results and Discussion

The use of an internal standard is required to account for matrix differences between the samples, standards, and QCs. The diluted standards and QCs have an acid concentration of 0.2%, while the samples contain glycol. Additionally, the transport efficiency is greatly affected by sample viscosity, which changes depending on the coolant and amount of glycol it contains. Figure 1 shows the internal standard recovery in the QCs and samples during an analytical run of 40 coolants. Because different coolants were analyzed, the internal standard recovery varied throughout the analysis. In Figure 1, the orange sections depict the QC samples, which all recover around 100% relative to the initial calibration. However, when samples are analyzed (white sections), the internal standard recovery can vary up to 120% because of the different viscosities and compositions of the samples. Applying an internal standard ensures accurate quantitative measurements by accounting for the differences between samples.

Conventional and extended-life coolants contain different additives whose levels vary by brand and by the intended use. Additives in coolants are B, K, Mo, Na, P and Si and can range in concentration from a few ppm up to thousands of ppm. Figure 2 shows the concentrations of these six additive elements in 10 randomly selected samples, demonstrating a wide range in additive concentrations.

Corrosion-metal analysis in coolants provides information about the health of an engine's coolant system. While no industry standard exists for acceptable levels of these elements, in general, anything above 10 ppm for Al and Cu and above 25 ppm for Fe, Pb, Sn and Zn are considered dangerous levels, indicating a high risk of engine failure. Figure 3 shows the output from Syngistix™ for ICP software's Data Viewer for the analysis of 10 coolant samples and associated QCs. By using the Limit Setting feature in Data Viewer, samples which are above or below user-defined values will be highlighted. The elements in green in Figure 3 are present at concentrations below threshold values indicating danger, while the

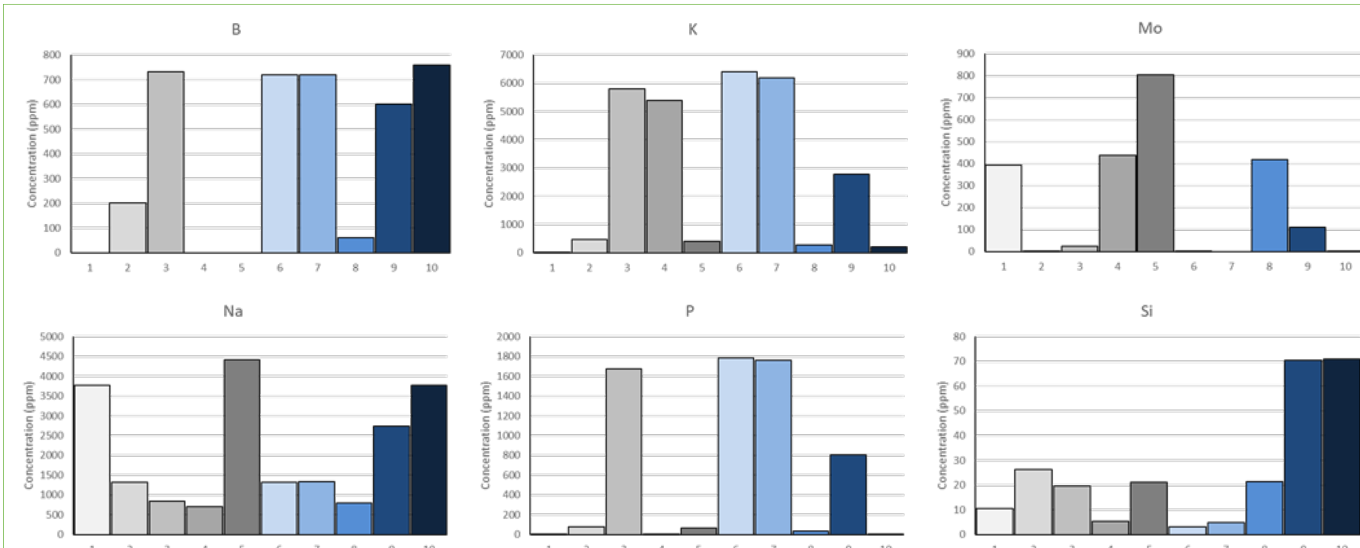

Figure 2: Concentration (ppm) of B, K, Mo, Na, P, and Si additives from 10 randomly selected in-service coolant samples.

	Sample Id	Y 371.029... (%)	Al 394.401 (mg/L)	Cu 324.752 (mg/L)	Fe 259.939 (mg/L)	Pb 220.353 (mg/L)	Sn 189.927 (mg/L)	Zn 206.200 (mg/L)
127	Calibration Curves							
128	Blank	99.1	0.176	0.041	-0.004	0.137	0.222	-0.088
129	QC 1A	89.1	5.171	5.145	25.140	24.850	0.220	20.134
130	QC 1B	98.1	0.247	0.055	0.129	-0.182	10.350	0.065
131	Blank	100.0	2.544E-16	0.000	9.252E-18	-7.401E-17	9.252E-18	-1.156E-17
132	Sample 1	105.5	26.149	0.683	1.100	-0.562	4.132	19.731
133	Sample 2	102.3	0.394	1.799	11.452	0.884	0.515	6.224
134	Sample 3	101.9	0.643	0.262	0.272	0.444	0.919	0.643
135	Sample 4	121.7	0.240	2.111	0.042	-0.843	0.687	0.463
136	Sample 5	106.8	0.569	0.968	0.030	-1.577	0.520	0.275
137	Sample 6	99.2	0.494	0.303	0.123	-0.035	0.600	0.159
138	Sample 7	99.9	0.425	0.237	0.024	0.064	0.614	0.154
139	Sample 8	102.9	0.477	19.100	26.238	-0.635	0.302	0.734
140	Sample 9	102.7	0.587	0.437	2.636	-0.065	0.259	0.423
141	Sample 10	99.4	0.714	0.305	70.107	65.067	0.759	1.597
142	Blank	103.1	0.050	0.005	-0.009	-0.203	0.183	0.083
143	QC 1A	94.2	5.012	5.218	25.304	25.532	0.051	20.529
144	QC 1B	99.6	0.385	0.124	0.317	0.460	10.508	0.060
145	Blank	101.1	0.019	-0.007	-0.035	0.265	0.255	-0.050

Figure 3: Syngistix software's Data Viewer during an analysis of coolant samples. Analytes in green are below danger thresholds, while those in orange are above danger thresholds, indicating an issue with the coolant system.

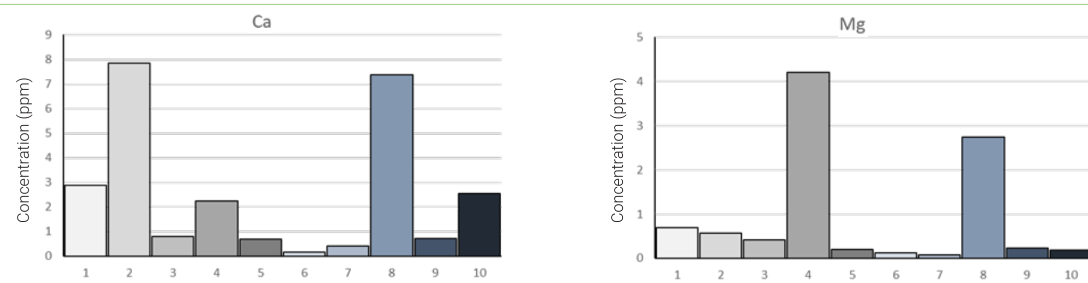

Figure 4: Concentrations of Ca and Mg in 10 coolant samples, all below concentrations which indicate potential damage to the coolant system of an engine.

analytes in orange are above the threshold for dangerous amounts of corrosion metals. The Limit Setting feature in Syngistix software flags problem samples in real-time during an analysis, providing the analyst important information at a glance, allowing these samples to be given a priority status.

The third component of metals testing in coolants pertains to the contaminants Ca and Mg, which can cause scale formation, decrease effectiveness of heat transfer, and precipitate additives, thereby decreasing the effectiveness of the coolants and shortening engine life. These contaminants generally enter the system when water is used to top up or dilute coolant. Samples analyzed in this study showed no elevation in these contaminant levels, as seen in Figure 4.

To assess the accuracy and stability of the method, the QC stability was measured throughout a 6-hour run of coolant samples, with QC standards analyzed every 10 samples.

The plot in Figure 5 shows the stability of the QC standards, where all elemental concentrations recover within +/- 10% of their true values. The results further demonstrate the robustness and stability of the methodology and the Avio 550 Max ICP-OES in accordance with ASTM method D6130.

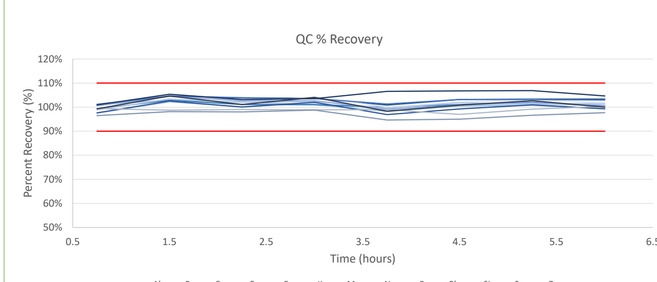

Figure 5: QC stability during a six-hour analytical run of in-service coolant samples.

Conclusion

This work has demonstrated the ability of PerkinElmer's Avio 550 Max fully simultaneous ICP-OES to measure in-service coolant samples in accordance with ASTM method D6130. Instrument design along with the implementation of internal standards, increased rinse speeds, and Multicomponent Spectral Fitting, allow for the accurate multi-element determination and long-term stability analysis of a variety of in-service coolant samples.

References

1. ASTM D6130 "Standard Test Method for the Determination of Silicon and Other Elements in Engine Coolant by Inductively Coupled Plasma-Atomic Emission Spectroscopy", ASTM.
2. "Multicomponent Spectral Fitting", Technical Note, PerkinElmer, 2017.

Consumables Used

Component	Part Number
Custom Standard LO 1A, 500 mL	N9308343
Custom Standard HI 1A, 500 mL	N9308341
Custom Standard LO 1B, 500 mL	N9308345
Custom Standard HI 1B, 500 mL	N9308346
Custom Standard QC 1A, 500 mL	N9308342
Custom Standard QC 1B, 500 mL	N9308344
Molybdenum (Mo) Pure Standard (500 mL)	N9300134
Yttrium (Y) Pure Standard 1000 ppm	N9304128
GemCone™ High Dissolved Solids Nebulizer	N0690670
Baffled Glass Cyclonic Spray Chamber	N0791352
Standard Single-Slot Torch	N0790131
2.0 m Alumina Injector	N0791183
Sample Tubing (Black/Black 0.76 mm ID, PVC)	N0777043
Internal Standard Tubing (Green/Orange 0.38 mm ID, PVC)	N0777042
Drain Tubing (Red/Red 1.14 mm ID, PVC)	09908585
PTFE-Coated Carbon Fiber CETAC Autosampler Probe	N0777547
Tee-Connector	N0777867

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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