Application Note

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High-Throughput Analysis of Additive-Elements and Wear Metals in Lubricants by ICP-OES

Fast analysis times using the Agilent 5900 ICP-OES with AVS and oil autosampler referencing ASTM D5185-18

Author

Paul D. Krampitz

Agilent Technologies, Inc.

Introduction

Tribology is an interdisciplinary area of science that studies how different surfaces interact together. Better understanding of friction, wear, and lubrication has many practical applications within engineering, manufacturing, transport, energy, and sport.[1]

Oils and lubricating fluids are vital for the ongoing performance of machinery and equipment as they minimize wear on components and extend the life of parts. Since oils deteriorate during use and over time, it is important to monitor their composition to prevent equipment failures and optimize maintenance schedules and costs. Due to its exceptional robustness and stability, ICP-OES is often used for the multi-element analysis of wear metals and additive-elements in oils and lubricants in various industries.[2]

Tracking the elemental profile of wear metals is an important safety control procedure for predictive/preventive maintenance purposes. If certain metals, such as the ones listed in Table 1, are identified in the oil or are seen to be changing in concentration over time, action can be taken before the equipment is damaged by further wear.

Table 1. Potential sources of wear metals in lubricating oils, depending on the use of the oil.

Aluminum	Piston and bearings wear, push rods, air cooler, pump, hosing oil pumps, gear castings, box castings
Antimony	Crankshaft and camshaft bearings
Boron	Coolant leakage in system
Cadmium	Bearings
Chromium	Ring wear, cooling system leakage, chromium-plated parts in aircraft engines, cylinder liners, seal rings
Copper	Wear in bushings, injector shields, coolant core tubes, thrust washers, valve guides, connecting rods, piston rings, bearings, sleeves, bearing cages
Iron	Wear from engine block, gears, cylinder liners, valve guides, wrist pins, camshaft, oil pump, crankshaft
Lead	Bearings, fuel blowby, thrust bearings, bearing cages, bearing retainers
Magnesium	Cylinder liner, gear box housings, and aircraft engines
Molybdenum	Wear in bearing alloys and in oil coolers, various molybdenum alloyed components in aircraft engine piston rings
Nickel	Bearings, valves, gear platings
Silicon	Dirt intrusion from improper air cleaner, seal materials
Silver	Wrist pin bearings in railroad and auto engines, silver plotted, spline lubricating pump
Sodium	Antifreeze leakage
Tin	Bearings and coatings of connecting rods and iron pistons
Titanium	Various titanium-alloyed components in aircraft engines
Tungsten	Bearings
Zinc	Polychloroprene seals, galvanized piping

Oil additives such as antioxidants, corrosion inhibitors, demulsifying, antifoam agents, detergents, metal deactivators, and tackiness agents are used to improve existing properties or provide desirable properties. Some other chemicals, such as pour point suppressors and VI improvers, are used to suppress undesirable properties. Monitoring the inorganic components of these types of chemicals can be a useful way to check for the presence of additives in oil and their level of depletion over time.

Zinc (Zn) typically indicates the presence of zincdialkyl-dithiophosphate (ZDDP), an antiwear additive. Molybdenum dithiocarbamate (Mo DTC) is another common additive that is used to reduce friction. Extreme pressure (EP) additives typically include phosphorus (P) and sulfur (S). Detergents include calcium (Ca) and magnesium (Mg), and sometimes barium (Ba). Detergents work by suspending particulates in oil so they can be removed by a filter. Antifoam agents typically include silicon (Si).

Wear metals and additive elements are included in the list of 22 elements specified in ASTM D5185-18 Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils. ASTM D5185-18 is widely used in the industry for the elemental analysis of used and unused oils by ICP-OES.[3]

The goal of this application was to develop a simple, fast, ASTM 5185-18-compatible method for the analysis of both wear metals and additives. To achieve these objectives, an Agilent 5900 Synchronous Vertical Dual View (SVDV) ICP-OES was used for the analysis of 140 used engine oils and lubricating fluids referencing ASTM D5185-18.

To meet the sample-to-sample throughput goal of under 30 s, including rinsing, the integrated Agilent Advanced Valve System (AVS 6) of the 5900 and external Cetac Oils 7400 Homogenizing Autosampler were used. The AVS 6/7 is standard on the 5900 ICP-OES.[4]

The 5900 uses smart software tools within the Agilent ICP Expert Pro software to help the analyst develop methods that produce accurate data. The following smart tools were used in this study:

- IntelliQuant Screening: the fast acquisition mode allows analysts to perform a full semiquantitative spectrum scan of up to 78 elements in just a few seconds.[5] IntelliQuant Screening automatically identifies the best element wavelength for each type of sample matrix that is analyzed, indicates the level of dilution to use, and suggests the concentration range of calibration standards.
- Fitted Background Correction (FBC): the software routine automatically corrects simple and complex background structures without requiring time-consuming investigation of the sample matrix.[6]

The ICP-OES method followed criteria set out in ASTM D5185-18, which included analyzing a NIST oil standard reference material (SRM) to assess its accuracy.

Experimental

Standard and sample preparation

All solutions were prepared using a diluent that included cobalt (Co) as the internal standard (IS). The diluent was prepared by adding 39 g of 5000 ppm Co (Agilent part number 5190-8751) to 3.79 L (1 gallon) of A-Solv (p/n 5190-8717) and mixing well. The concentration of Co in the diluent was approximately 51 ppm. It is important that the concentration of Co is the same in all solutions.

Weight to weight (w/w) preparation is always recommended for oil analysis because of the wide range of viscosities of reagents and samples.

A calibration blank was prepared by diluting 4 g of 75 cSt base oil (p/n 5190-8716) to 40 g using the diluent. Standards were prepared at 10, 50, and 90 ppm for all analytes (apart from Ca). The standards were prepared 1:10 by weight with the diluent using Agilent 100 ppm S21+K (p/n 5190-8710), Agilent 500 ppm S21+K (p/n 5190-8712), and Agilent 900 ppm S21+K (p/n 5190-8713) solutions, respectively. Calcium was calibrated to 500 ppm using a 5000 ppm Ca stock (p/n 5190-8745).

A 30 ppm quality control (QC) check was prepared from Agilent 300 ppm S21+K (p/n 5190-8711). NIST 1085c Wear Metals in Lubricating Oil SRM was also prepared 1:10 by weight.

Any mass differences noticed during dilutions were accounted for using base oil. For example, if 2 g of standard was used instead of 4 g, 2 g of base oil was added so that the same amount of diluent (Co) was added—36 g to each solution.

The 140 samples that were analyzed in this study were oils formulated for railroad maintenance equipment. The samples included new and used engine oils, transmission oils, pump drive oils, gear box oils, front and rear differential fluids, and synthetics. Most oils were SAE 15W-40 and SAE 80W-90 fluids as well as EP fluids.

All 140 field samples were diluted 1:10 by weight. Before analysis, the samples were mixed thoroughly by shaking vigorously for two minutes, vortexing for two minutes, and additional manual shaking for one minute. All samples were reanalyzed on the second day without further shaking.

Instrumentation

The Agilent 5900 SVDV ICP-OES operating in radial view (RV) mode was used for analysis of all samples. The instrument was fitted with a glass cyclonic spray chamber, a SeaSpray nebulizer, and an Easy-fit fully demountable RV torch fitted with a removable 1.4 mm i.d. quartz injector. The alignment of the torch is optimized automatically, ensuring reproducible instrument performance irrespective of the analyst.

To provide the robustness and stability of the plasma over long analytical runs of complex organic samples, the 5900 uses a vertical plasma, a solid-state radio frequency (SSRF) generator operating at 27 MHz, and a Cooled Cone Interface (CCI).

To increase speed of analysis, the 5900 includes an integrated AVS 6-port switching valve. The AVS 6 improves cost-of analysis of measurements through faster sample throughput and reduced argon gas consumption. The Cetac 7400 Oils Autosampler (Teledyne Labs, USA) was used in its standard setup to automatically mix (homogenize) each solution before measurement. The autosampler also included a drip tray that automatically followed the probe to capture any droplets, eliminating the risk of cross-contamination between samples.

Instrument operating conditions are shown in Tables 2 and 3.

Table 2. Agilent 5900 SVDV ICP-OES operating parameters.

Parameter	Setting
Power (kW)	1.4
Plasma Flow (L/min)	12
Nebulizer Flow (L/min)	0.8
Auxiliary Flow (L/min)	0.6
Viewing Height (mm)	11
O_2 (L/min)	0.3 (80% argon, 20% O_2 mix)
Pump Speed (rpm)	15
Pump Tubing	Solvaflex, black/black
Drain Tubing	Solvaflex, gray/gray
Read Time (s)	1
Replicates	2
Stabilization Time (s)	10

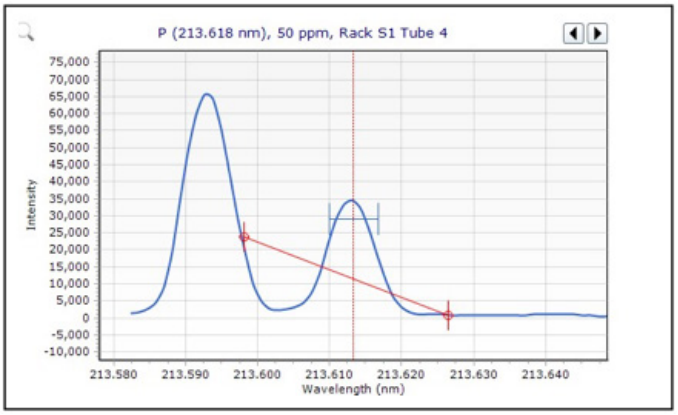
Table 3. Agilent AVS 6 switching valve system parameters.

Parameter	Setting
Pump Rate Uptake (mL/min)	39
Pump Rate Inject (mL/min)	9
Valve Uptake Delay (s)	4.5
Sample Loop Size (mL)	0.25
Bubble Injection Time (s)	0.5
Preemptive Rinse (s)	0
Rinse (s)	0

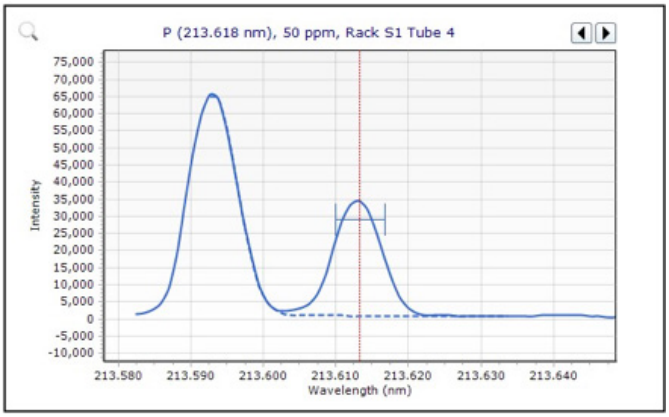
Automatic background correction

FBC was selected in the ICP Expert software to correct for background structures on all analyte wavelengths. Variable background structures are common in oil and lubricating fluids samples, making FBC highly suitable for this application. As there is no need to manually select points for each element in each sample when using FBC, it saves analyst time and removes any bias between different analysts.

Figure 1 shows the accurate background correction of a Cu emission line at P 213.618 nm by FBC, enabling the low-level detection of P 213.618 nm. The automatically applied FBC technique avoids the need to manually place off-peak correction markers, which can produce the wrong result in the presence of unexpected peaks.



Standard two-point background correction. Copper causes an inaccurate phosphorus measurement.



FBC automatically models the background resulting in an accurate measurement of phosphorus.

Figure 1. Top: Spectral overlap by copper on phosphorus at 213.618 nm. Bottom: FBC spectrum of P 213.618 nm, allowing accurate measurement of phosphorus.

Results and discussion

Calibration

A full semiquantitative spectrum scan of randomly selected samples was performed using IntelliQuant Screening, which required a few seconds acquisition time.[5] The scan data provides valuable information on up to 78 elements, helping to decide dilution factors, calibration range, and selection of the best wavelengths for the 22 elements included in the quantitative methods. Typically, wear metals are present in used oils at low concentrations, while elements in oil additive packages are usually present at high concentrations.

For the quantitation of the oils, representative calibration curves of B 208.956 and Mo 202.032 up to 100 ppm, and Ca 315.887 up to 500 ppm are shown in Figure 2.

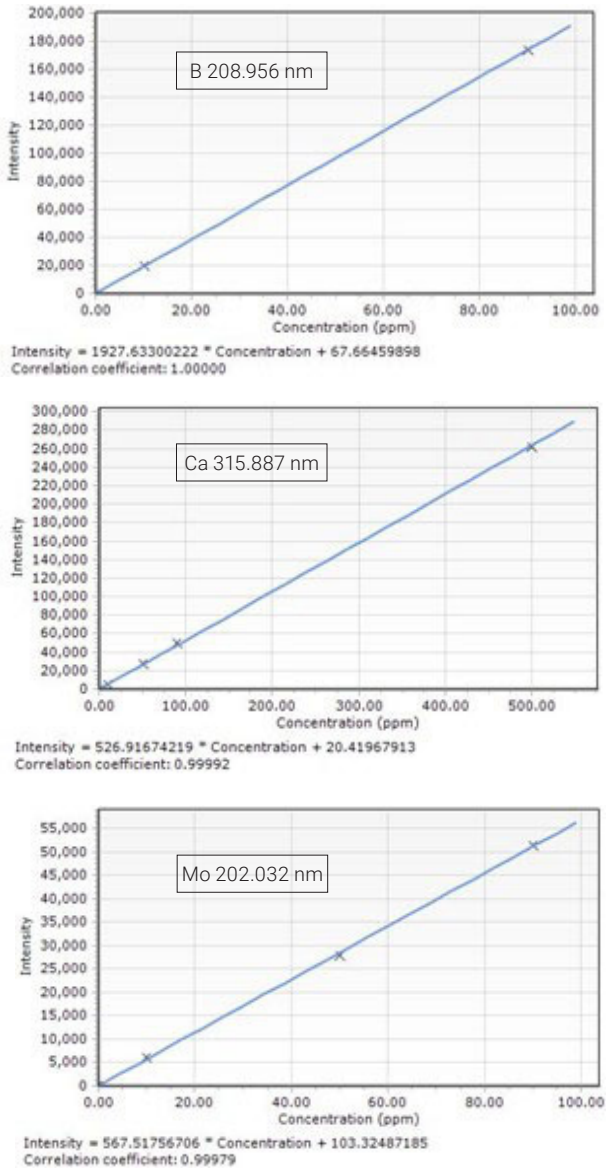


Figure 2. Calibration curves for boron 208.956 nm, calcium 315.887 nm, and molybdenum 202.032 nm.

Figure 3 shows representative calibration curves of P 213.618 (500 ppm) and Zn 213.857 up to 100 ppm for the quantitation of the railroad lubricating fluids. Correlation coefficients were greater than 0.999 for all elements.

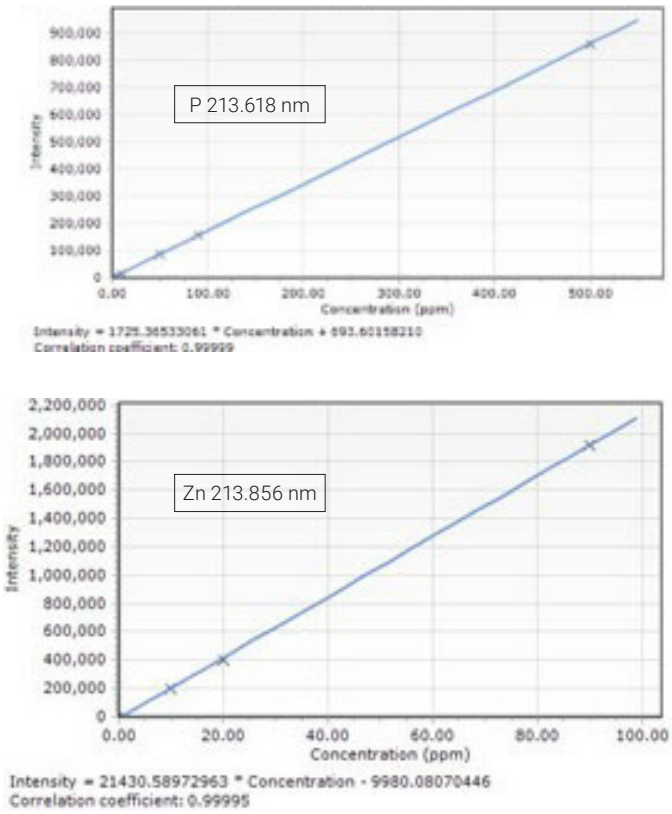


Figure 3. Calibration curves for phosphorus 231.618 nm and zinc 213.857 nm calibration curves used for quantitation of elements in railroad lubricating fluids.

Method detection limits

The method blank solution included 0.065 mg/kg for all analytes. Table 4 shows the method detection limits (MDLs), which were determined by analyzing three sets of 10 method blank solutions, and calculated as three sigma of the spike measurements.

Table 4. Method detection limits.

Element	Wavelength, nm	MDL (mg/kg)
Silver	328.068	0.001
Aluminum	396.152	0.021
	237.312	0.067
Boron	208.956	0.012
	249.772	0.004
Barium	233.527	0.003
	455.403	0.002
Calcium	315.887	0.02
	317.933	0.006
Cadmium	214.439	0.004
Chromium	267.716	0.004
Copper	327.395	0.005
Iron	259.940	0.007
Potassium	766.491	0.075
Magnesium	285.213	0.003
Manganese	257.610	0.002
Molybdenum	202.032	0.006
Sodium	588.995	0.002
Nickel	231.607	0.005
Phosphorus	213.618	0.022
Lead	220.253	0.043
Silicon	251.611	0.016
Tin	189.925	0.055
Titanium	336.122	0.002
Vanadium	292.401	0.005
Zinc	213.856	0.003

Method accuracy and precision

The recoveries for the 22 elements measured in the NIST 1085c Wear Metals in Lubricating Oil SRM were all within 100 ±10% (Table 5). The results are the average of nine determinations of the SRM. The relative standard deviation of the results was below 0.68%, highlighting the excellent precision of the quantitative method.

Table 5. Mean measured recoveries for elements determined in the NIST 1085c Wear Metals in Lubricating Oil SRM by the Agilent 5900 SVDV ICP-OES, n=9

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Element and Wavelength	Average Measured Concentration (mg/kg)	Certified Value (mg/kg)	Standard Deviation (%RSD)	Recoveries %
Ag 328.068	28.0	29.8	0.31	94
Al 394.401	27.9	29.2	0.51	96
B 208.956	28.9	30.4	0.30	95
Ba 455.403	28.3	30.6	0.27	92
Ca 315.887	30.8	30.8	0.16	100
Cd 228.802	29.1	30.1	0.40	97
Cr 267.716	28.9	30.2	0.25	96
Cu 327.39	29.0	29.8	0.48	97
Fe 259.940	29.1	30.1	0.38	97
K 766.491	26.9	29.5	0.41	91
Mg 285.215	27.8	30.0	0.33	93
Mn 257.610	29.0	29.9	0.37	97
Mo 203.846	29.0	30.5	0.25	95
Na 588.995	28.9	30.0	0.68	96
Ni 231.604	29.6	30.6	0.29	97
P 213.618	29.5	30.4	0.24	97
Pb 220.353	29.4	30.3	0.32	97
Si 251.611	28.0	29.3	0.37	96
Sn 189.925	28.8	29.8	0.24	97
Ti 336.122	29.5	30.0	0.45	98
V 292.401	28.0	28.5	0.30	98
Zn 213.857	27.8	28.5	0.15	98

Control charts

For trend analysis of components such as detergents and additives in oils and lubricants, the concentration of representative elements can be measured over time and their levels can be monitored using control charts.

Figure 4 shows that the concentration of Ca and Mo remained within the three sigma limits over time, indicating a steady level of detergent and additive in the engine oil. If the data for ether elements begins to exceed the three sigma range, it may be an indication that the detergent or additive is being depleted. The plots are based on quantitative measurements of every third sample in a block of 60 engine oil samples that were analyzed by the 5900 ICP-OES. The combination of the oil autosampler and integrated AVS 6 sampling valve enabled the 5900 to achieve a sample analysis time of 29 s, including rinse.

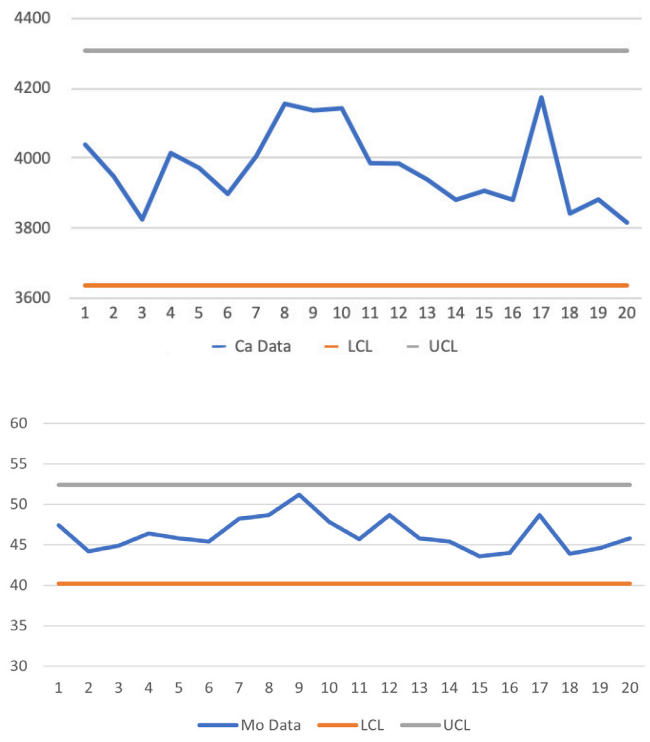

Figure 4. Three sigma control charts for calcium (top) and molybdenum (bottom) in engine oils.

H Uncal																He
Li	Be										B (14.9)	C Uncal	N Uncal	O Uncal	F	Ne
Na	Mg (12.2)										Al (0.1)	Si (1.7)	P (118.5)	S Uncal	Cl	Ar Uncal
K	Ca (189.5)	Sc	Ti (2.2)	V	Cr	Mn (0.0)	Fe (1.4)	Co (47.9)	Ni	Cu	Zn (113.2)	Ga	Ge	As	Se	Br	Kr
Rb	Sr Uncal	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Figure 5. IntelliQuant Screening elemental heat map, showing which elements are present in the engine oil sample and the semiquantitative concentration (ppm).

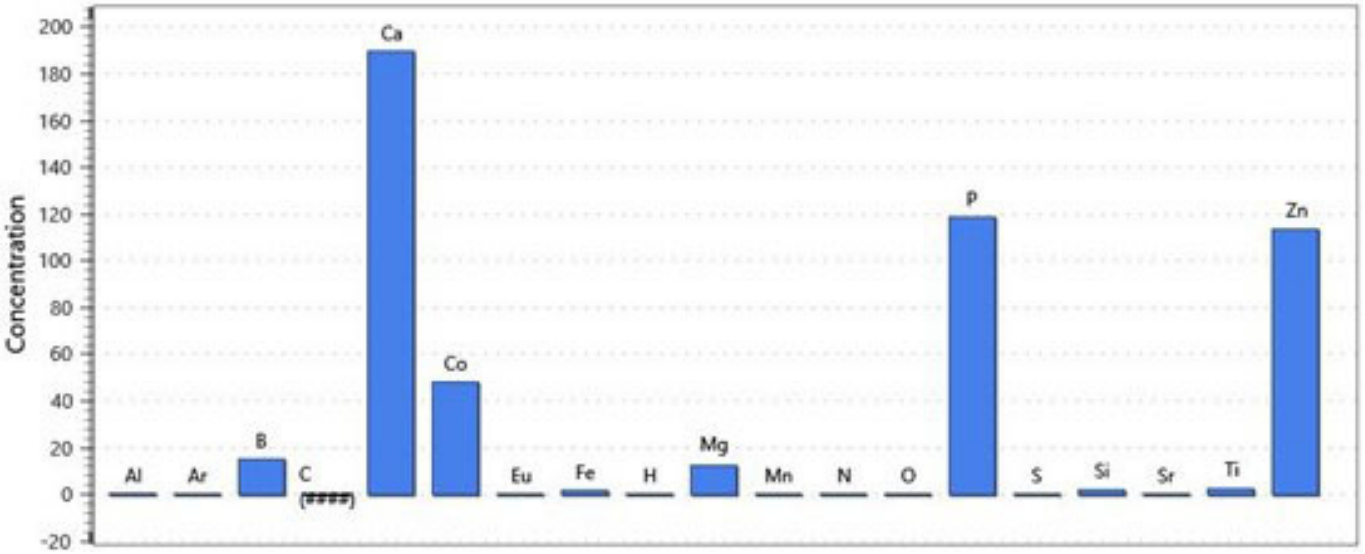

Figure 6. Bar graph showing relative concentrations of elements in an engine oil sample.

IntelliQuant Screening data

The IntelliQuant Screening program took 12 s sample-to-sample to acquire semiquantitative data for each sample. As shown in Figures 5 to 7, the IntelliQuant data can be displayed in different ways to aid interpretation, which is especially useful for trend analyses of wear metals in oils.

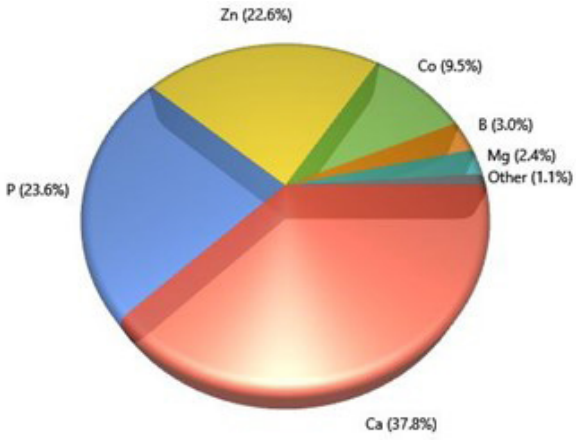

Figure 7. A pie graph showing relative concentrations of elements in an engine oil sample.

Conclusion

The study has outlined a fast, simple, and robust method for analyzing new and used oils according to ASTM 5185–18 using the Agilent 5900 SVDV ICP-OES and Cetac 7400 Oil autosampler. Wear metals, additives, and contaminants were measured in a wide range of 140 real-world railroad samples.

The oil autosampler improved the consistency of mixing samples using a stirring paddle for each sample and an automated drip tray helped to minimize cross contamination between samples. The integrated AVS 6 valve system of the 5900 enabled automated sample introduction, reducing the sample analysis time to 29 s including rinse. To maintain a high level of productivity, interactive, real-time control of instrument parameters was used to monitor the analysis during each run, including monitoring of the RF generator and internal standard responses.

The IntelliQuant Screening program is an invaluable tool for the analysis of wear metals and additives in engine oils and fluids. Full-wavelength scans of samples were acquired for each sample within 12 s sample-to-sample. The data was used to determine the calibration range, sample dilution factors, and to identify or confirm the best wavelengths to use for some elements in the quantitative method. Analysts can also display the semiquantitative data in different ways, helping with trend analyses of metals in oils and lubricating fluids.

The quantitative method met the requirements of ASTM 5185 standard method. Excellent recoveries were obtained for the wear metals in the NIST lubricating oil SRM, and repeated analysis of the SRM nine times throughout the run showed a good level of precision. The control charts for Ca and Mo obtained by plotting the results for every third sample in a block of 60 engine oil samples showed that the elements remained within the three sigma control limits.

The speed, robustness, and simple operation of the 5900 make it highly suited to the routine analysis of unused and used oils and lubricants. Analysts can conduct trend analysis of key elements in used oils based on either semiquantitative or quantitative measurements of samples over time. The availability of flexible and clear presentation tools for trend data enables engineers to make well-informed decisions regarding maintenance actions or adjustments to operating conditions.

www.agilent.com/chem/5900icpoes

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5. Agilent IntelliQuant Screening, Agilent publication 5994-1518EN
6. Fitted Background Correction (FBC) - Fast, Accurate and Fully Automated Background Correction, Agilent publication 5991-4836EN

Agilent part numbers

Description	Part Number
Base oil	5190-8716
A-Solv ICP solvent	5190-8717
Cobalt, 5000 ppm	5190-8751
S21 + K, 100 ppm	5190-8710
S21 + K, 300 ppm	5190-8711
S21 + K, 500 ppm	5190-8712
S21 + K, 900 ppm	5190-8713
Sample loop for AVS switching valve, 0.25 mL volume	G8010-60338
Sample tubing (black/black)	3710034800
Drain tubing (blue/blue)	3710067900
SeaSpray nebulizer	CP959366
Double-pass glass cyclonic spray chamber	G8010-60256
Easy-fit fully demountable torch, with 1.4 mm inner diameter tapered quartz injector for organics	G8020-68002

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