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Reducing Instrument Downtime in Elemental Analysis of Lubricant Oils as per ASTM 5185

Run samples faster and for longer using the V-groove nebulizer

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Abstract

In this application note, lubricant oil samples were analyzed using an Agilent 5900 Synchronous Vertical Dual View (SVDV) inductively coupled plasma optical emission spectrometer (ICP-OES) coupled with an Agilent Advanced Valve System 6 (AVS 6) and the Agilent V-groove nebulizer to enable the rapid analysis of over 1,000 samples in 6 hours (more than 160 samples per hour). The V-groove nebulizer provides exceptional performance characteristics, robustness, and durability, even when using troublesome samples. It also provides a reduction in sample loading on the plasma, which reduces carbon formation on the injector of the torch, allowing extended run times, while exceeding the sensitivity requirements required for the ASTM D5185-18 standard method.

Introduction

Elemental analysis of lubricant and hydraulic oils is essential for predictive and preventive maintenance, as well as trend analysis in many heavy industries. The ASTM D5185-18 standard method[1] is the gold standard in tribology laboratories globally to quantify additive elements, wear metals, and contaminants. This method uses ICP-OES for the rapid elemental determination of 22 elements in both used and unused lubricating and base oils, providing quick screening of used oils for signs of wear.

Tribology laboratories typically process hundreds of samples daily; therefore, they are constantly searching for ways to enhance efficiency and improve sample throughput. Instrument downtime caused by blockages in the sample introduction system (SIS) can be a common problem in these high-throughput labs. These blockages are typically caused by suspended particles in the samples blocking the nebulizer, and carbon deposits blocking the injector of the torch. Although various methods exist to remove the blockage from the nebulizer and clean the torch, all require extinguishing the plasma to remove and clean the SIS.

The use of a robust nebulizer is a strategy that can enable tribology laboratories to run more samples with reduced blockage. This will improve their workflows and increase sample throughput, reducing both instrument downtime and their running costs. One example of a robust nebulizer that helps to overcome the blockage issues is the inert, high-total-dissolved-solids (high-TDS) Agilent V-groove nebulizer, which is capable of aspirating highly dissolved solids and slurries (up to 30% dissolved solids with a maximum particle size of 350 μm). Its inert construction also ensures that any solvent can be nebulized.

In this application note, used diesel engine lubricant oil samples were analyzed using the 5900 SVDV ICP-OES coupled with the AVS 6 and the V-groove nebulizer, following the ASTM D5185-18 standard method.
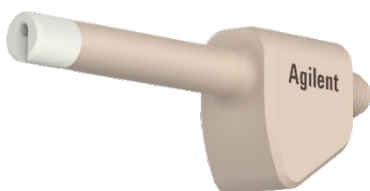

Figure 1. Agilent V-groove nebulizer.

Experimental

All measurements were performed using a 5900 SVDV ICP-OES configured with an AVS 6. The fast, high-capacity Agilent SPS 4 high-speed autosampler was also used. The sample introduction system consisted of the V-groove nebulizer, an Agilent standard, glass, cyclonic action, double-pass spray chamber, and the fully demountable Agilent Easy-fit torch, configured with the outer tube set for organics and a 1.4 mm id Agilent inert alumina injector.

Inert alumina injectors have historically been used for samples containing hydrofluoric acid, but they are also proven to be more robust against devitrification. This means that through repeated analysis and maintenance cycles, the tip of the alumina injector will maintain its surface finish for longer. Quartz injector tips inevitably tend to degrade with prolonged use, resulting in a rough surface that leads to increased rates of carbon buildup; therefore, more frequent cleaning cycles are required, or, in severe cases, replacement of the quartz injector.

To achieve the required sample throughput, the valve of the AVS 6 was fitted with a 0.25 mL loop. Also, uptake, stabilization, and read times were reduced as much as possible. To ensure that the undiluted sample enters the plasma, the valve plumbing was slightly modified by switching the nebulizer (port 2) and the carrier connection (port 3) on the valve, as shown in Figure 2. In this alternative configuration (also called "first in, last out"), the last portion of sample entering the loop is the first to be injected through the nebulizer into the plasma.
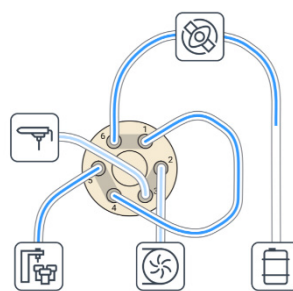

Figure 2. Agilent AVS 6 configuration used.

Adding oxygen into the auxiliary argon gas flow is recommended to further reduce carbon deposition on the tip of the injector in the torch, maintain a stable plasma, and reduce carbon emission from the solvent; however, in this work, oxygen addition was not used.

Instrument and AVS 6 operating parameters and method settings are listed in Table 1. A list of the consumables used can be found in the Appendix.

Preparation of standards and samples

Calibration standards were prepared by serial dilution of 500 µg/g A-21+K organometallic Agilent A21 wear metal standard (part number 5190-8712). High-concentration multi-element standards containing different concentrations of P, Ca, Zn, and S were prepared from the corresponding 5,000 µg/g single-element organometallic Agilent standards (prepared in 75 cSt hydrocarbon oil). Table 2 lists the calibration standards used in this method and the fast, automated curve-fitting technique (FACT) interferent solution used for spectral modeling of the background signal on the sodium (Na) 589.592 nm wavelength used for analysis.

Yttrium (Y 371.029 nm) was used as the internal standard at a concentration of 10 mg/kg for all elements. This was added to all blanks, standards, and oil samples. Agilent A-Solv ICP solvent was used as the diluent. Preparation of all blanks, standards, and oil samples was performed on a weight-to-weight (w/w) basis. To achieve consistent viscosity, additional 75 cSt base mineral oil was added when needed, to give a total oil concentration of 10% w/w. The calibration blank solution was prepared by dilution of the 75 cSt base mineral oil.

Table 1. Instrument and Agilent AVS 6 operating and method parameters.

Parameter	Setting	
RFPower	1.40 kW	
Plasma Gas	15 L/min	
Auxiliary Gas	1.4 L/min	
Nebulizer	Agilent V-groove nebulizer	
Nebulizer Gas Flow	0.5 L/min	
Spray Chamber	Glass double pass	
Torch	Fully demountable 1.4 mm id Agilent inert alumina injector	
Replicates	3	
Read Time	1 s	
Pump Speed	15 rpm	
Stabilization Time	7 s	
Viewing Mode	Radial	
Viewing Height	8 mm	
Peristaltic Pump Tubing	Sample/carrier	White-white
	Waste	Blue-blue
Rinse Time	0 s	
Oxygen Injection	Not used	

AVS Parameter	Setting
Pump Rate—Uptake	30 mL/min
Pump Rate—Inject	15 mL/min
Valve Uptake Delay	6 s
Bubble Injection Time	2 s
Preemptive Rinse Time	0 s
Rinse Time	0 s
Loop Volume	0.25 mL

Table 2. Calibration and FACT standards table.

Element/Standard	Calibration Standards Concentration (mg/kg)								
	1	2	3	4	5	6	7	8	FACT
Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Ti, V	1	5	15						
Ca				90	170	250			
P, Zn				50	85	125			
S							200	500	
B									10

Wavelength selection and background correction

Wavelengths were selected to provide minimal spectral interferences and a wide dynamic range, eliminating the need for time-consuming sample dilutions and reanalysis. Wavelength selection and background correction types used are listed in Table 3.

Table 3. Wavelength selection, background correction, and calibration correlation coefficients.

Wavelength (nm)	Background Correction	Calibration Fit	Calibration Through	Correlation Coefficient
Ag 328.068	Fitted	Linear	Blank	0.99999
Al 396.152	Fitted	Linear	Blank	0.99999
B 249.678	Fitted	Linear	Blank	1.00000
Ba 233.527	Fitted	Linear	Blank	1.00000
Ca 422.673	Fitted	Linear	Blank	1.00000
Cd 228.802	Fitted	Linear	Blank	1.00000
Cr 267.716	Fitted	Linear	Blank	1.00000
Cu 327.395	Fitted	Linear	Blank	1.00000
Fe 259.940	Fitted	Linear	Blank	0.99997
K 766.491	Off-peak right	Linear	Blank	0.99999
Mg 279.553	Fitted	Linear	Blank	0.99999
Mn 257.610	Fitted	Linear	Blank	0.99999
Mo 284.824	Fitted	Linear	Blank	0.99999
Na 589.592	FACT	Linear	Blank	0.99997
Ni 231.604	Fitted	Linear	Blank	1.00000
P 178.222	Fitted	Linear	Blank	0.99999
Pb 220.353	Fitted	Linear	Blank	0.99999
S 180.669	Fitted	Linear	Blank	1.00000
Si 185.005	Fitted	Linear	Blank	0.99996
Sn 189.925	Fitted	Linear	Blank	0.99996
Ti 334.188	Fitted	Linear	Blank	0.99999
V 309.310	Fitted	Linear	Blank	1.00000
Zn 213.857	Fitted	Rational	Blank	0.99994
Y 371.029	Internal standard			

The Agilent FACT[2] is one of the background correction methods available in Agilent ICP Expert software. This easy-to-use spectral modeling technique accurately models complex analytical spectra that are often observed when analyzing challenging organic sample matrices or interferents by ICP-OES. FACT was used as the background correction method for Na 589.492 nm line (Figure 3). In this study, a boron (B) 10 mg/Kg FACT interferent solution was included in the sequence and used to accurately correct the background for the Na content in the sample, as shown in the spike recovery test.
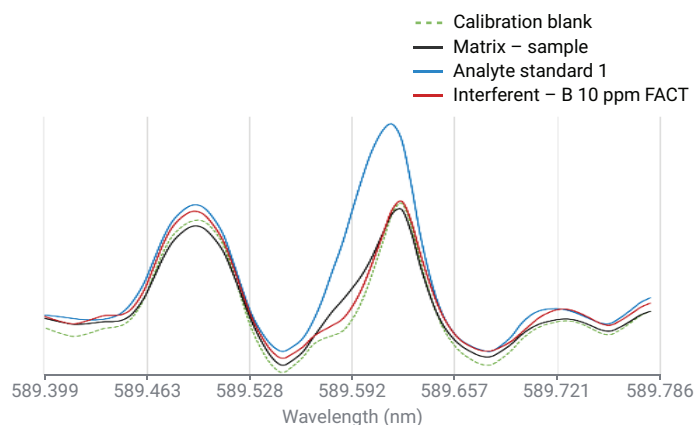

Figure 3. FACT model for Na 589.892 nm.

Results and discussion

Spike recovery study

To assess the robustness of the method, used oil samples were spiked with different elemental concentrations and analyzed. The difference between the concentration found on the spiked samples and the nonspiked samples was used to calculate the spike recoveries. For all the elements included in this study, the spike recoveries were well within ± 10% of the spiked concentration (Table 4).

Table 4. Spike recoveries.

Element Line (nm)	Unspiked Sample (mg/kg)	Spiked Sample (mg/kg)	Difference (mg/kg)	Spike Concentration (mg/kg)	Recovery (%)
Ag 328.068	0.002	0.970	0.968	0.97	100
Al 396.152	0.151	1.18	1.03	0.97	107
B 249.678	3.11	4.11	1.01	0.97	104
Ba 233.527	0.002	0.969	0.967	0.97	100
Ca 422.673	227	237	9.88	9.66	102
Cd 228.802	0.004	0.939	0.935	0.97	96
Cr 267.716	0.040	1.03	0.991	0.97	102
Cu 327.395	0.585	1.56	0.976	0.97	101
Fe 259.940	1.51	2.49	0.976	0.97	101
K 766.491	0.848	1.80	0.951	0.97	98
Mg 279.553	9.97	10.92	0.948	0.97	98
Mn 257.610	0.023	0.981	0.958	0.97	99
Mo 284.824	1.44	2.43	0.996	0.97	103
Na 589.592	0.186	1.16	0.978	0.97	101
Ni 231.604	0.013	0.990	0.978	0.97	101
P 178.222	97.7	108	10.4	9.62	108
Pb 220.353	0.021	0.953	0.932	0.97	96
S 180.669	328	356	27.2	25.8	106
Si 185.005	1.86	2.90	1.03	0.97	107
Sn 189.925	0.028	1.06	1.03	0.97	106
Ti 334.188	0.007	0.968	0.961	0.97	99
V 309.310	0.041	1.02	0.976	0.97	101
Zn 213.857	103	113	9.93	9.63	103

Method detection limits

Method detection limits (MDLs) were determined by running the full calibration, followed by 10 repeat analyses of the calibration blank. The MDL is defined as three times the mean standard deviation of the concentration readings for each element, multiplied by the applied dilution factor (10x). Apart from phosphorus and sulfur, all MDLs were well below 1 mg/kg (Table 5), allowing wear metals and additives to be detected and monitored at low levels. Phosphorous, sulfur, calcium, and zinc are usually present at concentrations much higher than their calculated MDL.

Table 5. Calculated MDLs.

Element/Line	MDL (mg/kg)	Element/Line	MDL (mg/kg)
Ag 328.068	0.60	Mo 284.824	0.22
Al 396.152	0.52	Na 589.592	0.36
B 249.678	0.16	Ni 231.604	0.13
Ba 233.527	0.095	P 178.222	1.4
Ca 422.673	0.72	Pb 220.353	0.80
Cd 228.802	0.17	S 180.669	3.3
Cr 267.716	0.10	Si 185.005	0.68
Cu 327.395	0.18	Sn 189.925	0.36
Fe 259.940	0.19	Ti 334.188	0.33
K 766.491	0.54	V 309.310	0.29
Mg 279.553	0.033	Zn 213.857	0.39
Mn 257.610	0.027		

Long-term stability

To check the system stability, a used oil sample spiked with different elemental concentrations was analyzed continuously over a period of 6 hours (> 1,000 samples). No recalibration or reslope was applied.

Figure 4 shows the relative concentration, normalized against the first sample reading. Excellent long-term stability was achieved throughout the analysis period over 6 hours. All measurements were within ± 10% of the expected value, with replicate precision better than 5% RSD in most cases.
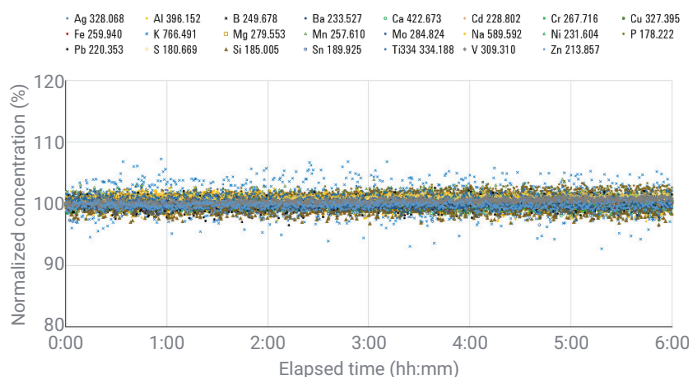

Figure 4. Long-term stability study showing normalized concentration (relative to the first reading) for a used oil sample spiked with different elemental concentrations, over a period of 6 hours (> 1000 samples).

Despite no oxygen injection being used, it is worth noting that there were no signs of injector obstruction or carbon deposition at the conclusion of the test. This demonstrates the stability of the 5900 ICP-OES and the suitability of the inert V-groove nebulizer for high-throughput analysis of used oil samples in tribology laboratories.

The parallel path design of the inert V-groove nebulizer reduces the chances of blockage of the gas orifice, and the 1 mm id sample channel allows any suspended particles to flow through it. Moreover, unlike other nebulizers, there is no risk of damage if the tip is accidentally touched or if the nebulizer is accidentally dropped.

Conclusion

This application note shows the suitability of the Agilent 5900 SVDV ICP-OES used with the Agilent AVS 6 and inert V-groove nebulizer for rapid multi-element analysis of used lubricant oil samples using the ASTM D5185-18 standard method.

Excellent long-term stability was demonstrated when more than 1,000 samples were analyzed over a six-hour period (22 to 23 seconds per sample). All measurements of this spiked oil sample were within ± 10% of the expected value, with precision better than 5% RSD in most cases. The spike recovery study showed how the 5900 ICP-OES, used with the inert V-groove nebulizer, can accurately detect low range concentrations of wear metals and high concentrations of the elements from the additive package in a single analysis. The inert V-groove nebulizer also enabled the samples to be run faster, with excellent accuracy.

Despite no oxygen injection being used, there were no signs of blockage of the injector of the torch, or carbon deposition after the test. The V-groove nebulizer design reduces sample loading on the plasma, minimizing carbon buildup while maintaining the sensitivity required for the ASTM D5185 standard method. No nebulizer blockage was experienced while collecting the data for this study. The inert V-groove nebulizer allows extended run times by reducing the frequency of torch and nebulizer maintenance. This demonstrates the stability of the 5900 ICP-OES and the suitability of the inert V-groove nebulizer for high-throughput tribology laboratories, by reducing instrument maintenance downtime and improving sample throughput.

References

1. ASTM D5185-18, 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 International, West Conshohocken, PA, **2018**.

2. Real-Time Spectral Correction of Complex Samples Using FACT Spectral Deconvolution Software, *Agilent Technologies*, publication number 5991-4837EN, **2021**.

Appendix

Agilent consumables used

Description	Agilent Part Number
V-Groove Nebulizer, Inert, High TDS	G8020-69001
Easy-Fit Torch, Fully Demountable, with 1.4 mm id Inert Alumina Injector	G8020-68020
Double-Pass Glass Cyclonic Spray Chamber	G8010-60256
Peristaltic Pump Tubing, PVC Solvaflex, White/White, 12/pk	3710035000
Peristaltic Pump Tubing, PVC Solvaflex, Blue/Blue, 12/pk	3710067900
SPS 4 Autosampler Probe, 0.8 mm id, Green Markers, Inert, FEP Sleeved	G8410-80102
SPS 3/4 PVC Solvaflex Peristaltic Pump Tubing, 3-Bridged, Purple/White Tabs	5043-0063
Sample Loop for AVS Switching Valve, 0.25 mL Volume, 1/pk	5005-0420
A-Solv ICP Solvent, 1 gal	5190-8717
Base Mineral Oil Blank in 75 cSt Mineral Oil, 500 mL	5190-8715
A21+K Wear Metal Standard, 500 µg/g, 100 g	5190-8712
Calcium (Ca) Standard, 5,000 µg/g, in 75 cSt Hydrocarbon Oil, 50 g	5190-8745
Phosphorus (P) Standard, 5,000 µg/g, in 75 cSt Hydrocarbon Oil, 50 g	5190-8772
Zinc (Zn) Standard, 5,000 µg/g, in 75 cSt Hydrocarbon Oil, 50 g	5190-8798
Boron (B) Standard, 5,000 µg/g, in 75 cSt Hydrocarbon Oil, 50 g	5190-8741
Yttrium (Y) Standard, 5,000 µg/g, in 75 cSt Hydrocarbon Oil, 50 g	5190-8796

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