Application Note

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Multi-element Analysis of Used Lubricant Oils

Evaluating an Agilent Easy-fit fully demountable ICP-OES torch for oil analysis, according to ASTM D5185-18

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Introduction

Elemental analysis of lubricant and hydraulic oils is important for predictive/preventive maintenance and trend analysis. The data helps users avoid the expense and downtime caused by damage to engines, transmissions, turbines, and other important equipment. In lubricant manufacturing, analysts routinely assess the metal content of base oils and lubricants, as well as the homogeneity of any additive-blends.

Standard method ASTM D5185-18 is the gold standard test used by oil-testing (tribology) laboratories around the world for the rapid determination of 22 elements in used and unused lubricating and base oils. The method uses Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for the determination of additive elements, wear metals, and contaminants. Many laboratories that use this method process hundreds of samples per day, so high sample throughput is critical. A major challenge faced by high throughput tribology labs is instrument downtime from

blockage of the injector in the ICP torch caused by carbon deposits. To clean the torch, it must be removed from the instrument. The deposits are usually removed by baking the quartz components in a muffle furnace at high temperatures (> 600 °C) or using a handheld blow torch to "flame" the injector. Another challenge is the potential for premature cracking of the outer tube of the torch, around the portion of the outer tube that is close to the induction coil. Outer tubes (or the complete torch) that are affected must be replaced once the physical structure has been damaged.

Agilent has developed an Easy-fit fully demountable torch for Agilent 5100 or 5110 and 5800 or 5900 ICP-OES instruments (Figure 1). The fully demountable torch is designed to improve laboratory workflows, reduce instrument downtime, and lower running costs. All the quartz components of the torch can be easily removed for maintenance or to change the injector when switching applications. No tools are required. Also, Agilent has developed an outer quartz tube-set for Agilent semi- and fully demountable torches that improve the robustness of the torch when analyzing samples prepared in organic solvents. The new torch and outer quartz tube-set have been extensively tested in customer laboratories with positive feedback. Analysts who have used the new products have found them more cost effective and convenient than alternatives, such as using a torch with a ceramic outer tube.

Figure 1. Agilent Easy-fit fully demountable torch for 5100 or 5110 and 5800 or 5900 ICP-OES, fitted with the outer quartz tube-set for organic solvents.

In this study, a series of used lubricant and hydraulic oil samples were analyzed using an Agilent 5110 Radial View (RV) ICP-OES. The instrument was equipped with the Easy-fit fully demountable torch and the outer tube-set for organic samples.

Experimental

All measurements were performed using an Agilent 5110 RV ICP-OES configured with an SPS 4 autosampler. The standard sample introduction system and Easy-fit fully demountable RV torch fitted with the outer quartz tube-set for organic solvents and a removable 1.4 mm i.d. quartz injector (part number G8020-68002) were used. Instrument method parameters and analyte settings are listed in Table 1.

Table 1. 5110 RV ICP-OES instrument and method parameters.

Parameter	Setting	
RF Power (kW)	1.30	
Plasma Gas Flow (L/min)	12.0	
Auxiliary Gas Flow (L/min)	1.40	
Torch	Easy-fit fully demountable torch	
Outer Tube-set	Quartz RV outer tube-set for organic solvents	
Injector	Quartz 1.4 mm i.d., tapered	
Viewing Mode	Radial	
Viewing Height (mm)	7	
Nebulizer	SeaSpray U-series concentric glass nebulizer	
Spray Chamber	Glass double pass	
Uptake Time (s)	12	
Stabilization Time (s)	25	
Rinse Time (s)	45	
Peristaltic Pump Tubing	Sample	PVC white-white
	Waste	PVC blue-blue
	Internal Standard	PVC black-black

Preparation of calibration standards and samples

Three multi-element standards were prepared at 5, 10, and 50 ppm by serial dilution of Agilent 500 µg/g A-21+K organometallic wear metal standard (part number 5190-8712). Three more high concentration multi-element standards containing different concentrations of P, Ca, Zn, and Mg were prepared from the respective Agilent 5000 µg/g single element standards. All of Agilent's organometallic oil standards are prepared in 75 cSt hydrocarbon oil.

All standards and samples were prepared on a weight-weight basis. To achieve consistent viscosity, 75 cSt base mineral oil

(part number 5190-8715) was added when needed, to give a total oil concentration of 10 % w/w. The calibration blank was prepared by dilution of the 75 cSt base mineral oil. Agilent A-Solv ICP (kerosene type distillate) solvent (part number 5190-8717) was used as the diluent for preparation of all blanks, standards, and oil samples.

A National Institute of Standards and Technology (NIST) SRM 1085c Wear Metals in Lubricating Oil (Gaithersburg MD, USA) was analyzed to validate the method. The SRM was diluted 10-fold by weight using the A-Solv ICP solvent.

Wavelength selection and background correction

Table 2 lists the emission lines selected for the analysis, together with the background correction method used for each line. All wavelengths were suggested in ASTM D5185-18, except for cadmium, which is not included in D5185-18, and tin. Sulfur was not determined in this study as this analyte was not present in the SRM. The selected wavelengths provide minimal spectral interferences and a wide dynamic range, eliminating the need for time-consuming sample dilutions and reanalysis. An internal standard (ISTD) of 25 mg/kg cobalt in hydrocarbon oil was prepared by dilution of an Agilent 5000 µg/g organometallic oil ISTD (part number 5190-8714) on a weight-weight basis using the A-Solv solvent. The ISTD was delivered online to the sample before nebulization using a Y-connector.

Linear calibrations were obtained for all selected wavelengths as shown by the correlation coefficients in Table 2. The 5110 ICP-OES can accurately detect low range concentrations of wear metals and high concentrations of the elements from the additive package in a single analysis. The Agilent ICP Expert software for ICP-OES allows simultaneous monitoring of multiple wavelengths of the same element to extend the measurement range. Using the MultiCal feature, low detection limits were achieved; it was also possible to extend the linear dynamic range to high concentrations. Figure 2 shows a calibration curve for Zn 206.200 nm, up to 220 mg/kg (ppm). The correlation coefficient was 0.99994 and calibration error on each calibration point was ≤3 %.

Table 2. Line selection and calibration data. Co 230.786 nm was used as the internal standard.

Element and Wavelength (nm)	Calibration Fit	Background Correction	Correlation Coefficient (R)	Calibration Range (mg/kg)
Ag 328.068	Linear	Fitted	1.0000	0–50
Al 308.215	Linear	Fitted	1.0000	0–50
B 249.678	Linear	Fitted	0.9999	0–50
Ba 493.408	Linear	Fitted	1.0000	0–50
Ca 422.673	Linear	Fitted	0.9997	0–380
Cd 228.802	Linear	Fitted	1.0000	0–50
Cr 267.716	Linear	Fitted	1.0000	0–50
Cu 324.754	Linear	Fitted	0.9999	0–50
Fe 259.940	Linear	Fitted	1.0000	0–50
K 766.491	Linear	Fitted	0.9999	0–50
Mg 285.213	Linear	Fitted	1.0000	0–120
Mn 293.305	Linear	Fitted	1.0000	0–50
Mo 202.032	Linear	Fitted	1.0000	0–50
Na 589.592	Linear	Fitted	0.9999	0–50
Ni 231.604	Linear	Off-peak right	1.0000	0–50
P 178.222	Linear	Fitted	0.9997	0–160
Pb 220.353	Linear	Fitted	1.0000	0–50
Si 288.158	Linear	Fitted	0.9999	0–50
Sn 283.998	Linear	Fitted	0.9999	0–50
Ti 334.941	Linear	Fitted	1.0000	0–50
V 310.229	Linear	Fitted	1.0000	0–50
Zn 206.200	Linear	Fitted	0.9994	0–220

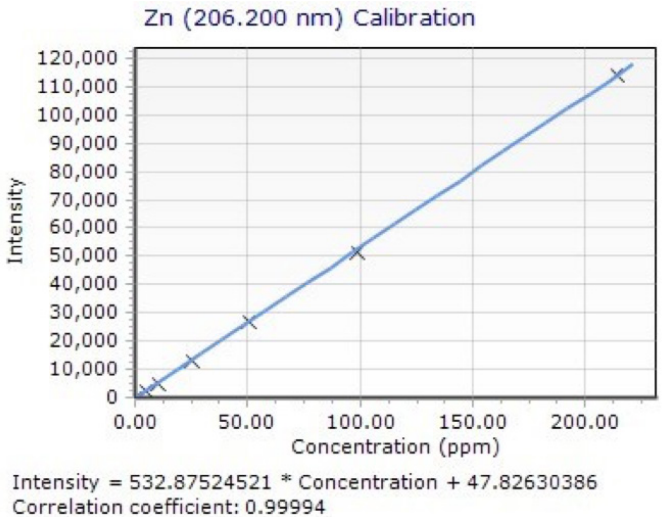

Figure 2. Calibration graph for Zn using the 206.200 nm emission line.

Results and discussion

SRM recoveries

The recoveries for the 22 elements measured in the wear metal oil SRM were all within ±10 % (Table 3). The results are the average of five determinations of different preparations of two ampoules of the SRM. The measurements were performed on two, nonconsecutive days, three weeks apart. The relative standard deviation of the results was below 3 %.

Table 3. Mean measured recoveries for elements determined in the NIST 1085c Wear Metals in Lubricating Oil SRM. n = 10.

Element	Certified Concentration (mg/kg)	Mean Measured Concentration (mg/kg)	% Recovery
Ag	298	301	101
Al	292	309	106
B	304	301	99
Ba	306	306	100
Ca	299	318	106
Cd	301	309	103
Cr	302	310	103
Cu	302	316	105
Fe	301	314	104
K	301	325	108
Mg	300	298	99
Mn	299	303	101
Mo	299	305	102
Na	300	306	102
Ni	306	310	101
P	304	304	100
Pb	303	314	104
Si	293	306	104
Sn	298	305	102
Ti	300	311	104
V	285	303	106
Zn	285	284	99

Spike recoveries

To assess the robustness of the method, used oil samples of different types and viscosities were obtained. Each used oil sample (2 g) was spiked with known amounts of the organometallic oil standards. The wear metal elements were spiked at low concentrations, while Ca, Mg, P, and Zn were spiked at a higher concentration. Base mineral oil (75 cSt) was added to give a total oil concentration of 10 % w/w. The samples were diluted to 40 g using the A-Solv solvent.

Excellent spike recoveries were obtained for all elements in all the different oil sample types (Tables 4–6). The recoveries for all elements are within ±10 % of the expected values, despite the different viscosities of the oil samples.

Table 4. Spike concentrations and spike recoveries for a sample of used diesel engine oil SAE 15W-40.

Element	Engine Oil (mg/kg)	Spiked Engine Oil (mg/kg)	Measured Spike Concentration (mg/kg)	Spike Concentration (mg/kg)	% Recovery
Ag	0.002	4.770	4.769	5.11	93
Al	0.077	4.726	4.650	5.11	91
B	1.061	6.031	4.970	5.11	97
Ba	0.007	4.786	4.779	5.15	93
Ca	124.1	137.5	13.46	14.97	90
Cd	0.000	5.508	5.509	5.11	108
Cr	0.023	5.317	5.294	5.11	104
Cu	0.227	4.848	4.621	5.11	90
Fe	0.662	5.800	5.138	5.12	100
K	0.012	4.761	4.749	5.11	93
Mg	0.607	15.08	14.47	15.18	95
Mn	0.018	5.222	5.205	5.11	102
Mo	1.611	6.823	5.212	5.11	102
Na	0.083	4.781	4.697	5.12	92
Ni	0.030	5.423	5.393	5.11	106
P	51.45	66.52	15.07	14.69	103
Pb	0.126	5.538	5.412	5.11	106
Si	0.217	5.045	4.829	5.13	94
Sn	0.040	5.031	4.991	5.11	98
Ti	0.004	5.032	5.029	5.11	98
V	0.003	5.045	5.042	5.11	99
Zn	62.04	77.99	15.95	14.97	107

Table 5. Spike concentrations and spike recoveries for a sample of used hydraulic oil SAE 10W.

Element	Hydraulic Oil (mg/kg)	Spiked Hydraulic Oil (mg/kg)	Measured Spike Concentration (mg/kg)	Spike Concentration (mg/kg)	% Recovery
Ag	0.043	5.301	5.257	5.26	100
Al	0.168	5.363	5.195	5.26	99
B	0.086	5.359	5.273	5.26	100
Ba	0.022	5.325	5.302	5.30	100
Ca	9.196	24.33	15.14	14.48	105
Cd	0.001	5.266	5.266	5.26	100
Cr	0.041	5.318	5.277	5.26	100
Cu	0.291	5.526	5.236	5.26	100
Fe	0.640	5.925	5.285	5.27	100
K	0.040	5.401	5.361	5.26	102
Mg	0.252	15.20	14.95	14.68	102
Mn	0.015	5.285	5.270	5.26	100
Mo	0.046	5.309	5.263	5.26	100
Na	0.106	5.555	5.449	5.38	101
Ni	0.006	5.266	5.260	5.26	100
P	26.01	40.66	14.65	14.21	103
Pb	0.163	5.283	5.120	5.26	97
Si	0.377	5.611	5.233	5.27	99
Sn	0.025	5.259	5.234	5.26	100
Ti	0.013	5.324	5.312	5.26	101
V	0.008	5.289	5.281	5.26	100
Zn	27.57	42.54	14.97	14.00	107

Table 6. Spike concentrations and spike recoveries for a sample of used differential oil SAE 85W-140.

Element	Differential Oil (mg/kg)	Spiked Differential Oil (mg/kg)	Measured Spike Concentration (mg/kg)	Spike Concentration (mg/kg)	% Recovery
Ag	0.003	4.978	4.975	5.03	99
Al	0.105	5.053	4.947	5.03	98
B	0.160	5.254	5.094	5.03	101
Ba	0.002	5.030	5.028	5.08	99
Ca	201.3	216.9	15.50	14.49	107
Cd	0.000	5.053	5.053	5.03	100
Cr	0.015	5.045	5.030	5.03	100
Cu	0.727	5.589	4.862	5.03	97
Fe	1.186	6.223	5.037	5.05	100
K	0.020	5.071	5.050	5.03	100
Mg	0.861	15.771	14.911	14.69	101
Mn	0.027	5.051	5.024	5.03	100
Mo	0.019	5.038	5.020	5.03	100
Na	0.074	5.326	5.252	5.16	102
Ni	0.000	5.063	5.063	5.03	101
P	47.24	62.02	14.78	14.22	104
Pb	0.181	5.064	4.883	5.03	97
Si	0.894	5.882	4.988	5.05	99
Sn	0.053	5.056	5.003	5.03	99
Ti	0.006	5.022	5.016	5.03	100
V	0.010	5.042	5.032	5.03	100
Zn	52.68	68.19	15.51	14.49	107

Method detection limits (MDLs)

Method detection limits (MDL) were determined by running the full calibration, followed by 10 repeat analyses of the sample blank. The MDL is defined as three times the mean standard deviation of the concentration readings for each element. All MDLs were well below 0.5 mg/kg, allowing wear metals to be detected and monitored at low levels (Table 7).

The limit of quantification (LOQ) for this analysis was estimated as 10 times the standard deviation of the concentration readings multiplied by the dilution factor (10 x).

Long-term stability

To check instrument stability, a 5 mg/kg organometallic calibration standard was analyzed after every 10 measurements of the used oil samples, over a period of 10 hours. No recalibration or reslope was applied. Excellent long-term stability was achieved over 10 hours, as shown in Figure 3. All measurements were within ±10 % of the expected value, with precision better than 3 % RSD.

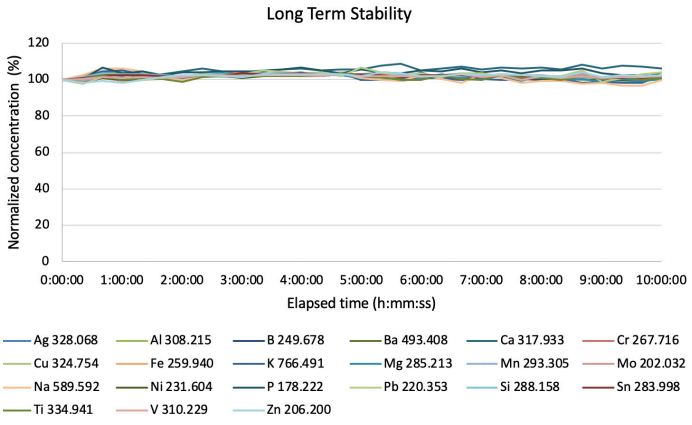

Figure 3. Long-term stability: recoveries of a 5 mg/kg organometallic calibration standard analyzed over the course of the 10-hour sequence.

Table 7. Method detection limits and estimated limits of quantification.

Element and Wavelength (nm)	MDL (mg/kg)	LOQ (mg/kg)
Ag 328.068	0.0013	0.045
Al 308.215	0.012	0.40
B 249.678	0.0056	0.19
Ba 493.408	0.00012	0.0041
Ca 422.673	0.0032	0.11
Cd 228.802	0.0054	0.18
Cr 267.716	0.0038	0.13
Cu 324.754	0.0021	0.069
Fe 259.940	0.008	0.27
K 766.491	0.042	1.4
Mg 285.213	0.0019	0.063
Mn 293.305	0.0029	0.098
Mo 202.032	0.012	0.40
Na 589.592	0.016	0.52
Ni 231.604	0.025	0.84
P 178.222	0.14	4.8
Pb 220.353	0.11	3.6
Si 288.158	0.013	0.45
Sn 283.998	0.036	1.2
Ti 334.941	0.00072	0.024
V 310.229	0.0044	0.15
Zn 206.200	0.017	0.56

Conclusion

The Agilent 5110 RV ICP-OES fitted with the Easy-fit fully demountable torch is ideally configured for fast multi-element analysis of new and used lubricant and hydraulic oils according to ASTM D5185-18. Excellent recoveries were obtained for all elements present in the NIST Wear Metals in Lubricating Oil SRM.

The long-term stability test showed the robustness and stability of the sample introduction system and Easy-fit fully demountable torch. Wear metal oil samples were analyzed continuously for 10 hours without any loss in precision or accuracy. The removable quartz injector did not show any signs of blockage during the extended analysis period. Also, the outer tube of the torch remained intact during the analysis.

A spike recovery test highlighted the dynamic range of the 5100's Vista Chip II detector. Excellent recoveries were achieved for analytes ranging from low mg/kg to several hundred mg/kg spiked into different types of used oil samples. Having a large dynamic range of up to eight orders of magnitude is important for the application. It allows low concentrations of wear metals and high concentrations of additive-elements to be analyzed in oils prepared using a single sample preparation method, in a single reading.

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, 2017, www.astm.org/Standards/D5185.htm

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