Challenge

Reliable and effective assessment of elemental composition in additive packages and unused lubricating oils for process monitoring and quality control

Solution

High-resolution ICP-OES for the interference-free and accurate analysis of elemental parameters relevant to composition and quality of lubricating oils and additives directly after dilution in an organic solvent

Determination of Additive Elements in Lubricating Oils according to ASTM D4951 with HR ICP-OES

Introduction

Lubricating oils are the essence of oil-wetted machinery. Elements like barium, boron, calcium, copper, magnesium, molybdenum, phosphorus, sulfur, and zinc are used as additives in lubricating oils to enhance their lubricating capacity and properties, like anti-wear, anticorrosive, antioxidant, and anti-friction property. The amount of those elements greatly impacts how the lubricant acts. As such, a fast and accurate measurement is critical as an aspect of its manufacture.

Elemental analysis is most commonly performed by X-ray fluorescence spectrometry, atomic absorption spectrometry (AAS), or inductively coupled plasma optical emission spectrometry (ICP-OES).

ICP-OES is a formidable device for elemental assessment due to its capacity for fast multi-elemental analysis, elevated sensitivity, and a broad linear dynamic analysis range. This prowess means ICP-OES is the recommended technique for new oil study and additive packages in ASTM D4951 technique. The difficulties for ICP-OES, however, are characteristics of lubricating oil, such as high viscosity and matrix intricacy.

These challenges can be avoided by diluting the sample with a solvent that is less viscous and employing an appropriate sample introduction system, therefore diminishing detection limits. The elevated organic load may trigger plasma instability and extinction. Inadequate carbon combustion causes soot formation on the torch injector, which needs urgent cleaning, producing downtime. Spectral interferences may have a significant effect on the condition of the baseline fitting practices, causing substandard accuracy and detection boundaries.

Because of this, oil analysis by ICP-OES needs an instrument that provides superb plasma performance, spectral resolution, and sensitivity. The PlasmaQuant 9100 Elite by Analytik Jena is ideal for economical oil evaluation, with

its robust plasma, excellent resolution, and distinctive sensitivity.
These excellent analytical capacities occur from its four main components. A free-running high-frequency generator with a heavy-duty four-winding induction coil provides dependable plasma performance for lubricating oil samples. The robust plasma can effortlessly accept high organic sample loadings and offer long-term stability.
High-resolution optics and a charge-coupled device (CCD) detector offer excellent spectral resolution, which permits interference-free measurement by well-separated lines. The CCD detector depicts emission line and background intensities concurrently; this allows the automatic background correction. The vertical plasma geometry of the V Shuttle Torch means soot development and memory impacts are no longer an issue. In a normal analysis, the V Shuttle Torch design means maintenance is easy and decreases instrument downtime and consumable costs.

A further beneficial point is that the DualView PLUS plasma observation will enhance the ease of oil analysis substantially, as the suggested wavelengths from ASTM D4951 method can be used without running into optical saturation while analyzing elements in high concentrations. Furthermore, trace elements and major constituents can often be quantified from a single sample measurement, which reduces the need for tedious sample preparation.
Here we present the analysis of lubricant oils following ASTM D4951 method. The basic technique ASTM D4951 is for "determination of additive elements in lubricating oils by inductively coupled plasma atomic emission spectrometry"[1]. This test technique encompasses nine elements and can be employed to ascertain if additive packages and unused lubricating oils meet requirements regarding to elemental composition.

Materials and Methods

Samples and reagents

Elemental analysis was performed on gear oil, engine oil, and three different lubricant additives, covering a wide range of viscosity. The following chemicals were employed for standards and sample preparation: CONOSTAN® Standard S21+K multi-element organometallic standard at 885 mg/kg (SCP Science), 1000 mg/kg sulfur oil-based standard (SCP Science), 1000 mg/kg yttrium oil-based standard (SCP Science), 20 and 75 cSt blank oil (SCP Science), and low odor kerosene (Fisher Scientific).

Sample and standard preparation

Sample preparation was created to be straightforward, consistent across analytes, show lowered sample viscosity, and reduce possible interferences. Yttrium was employed as the internal standard. The yttrium standard was diluted with kerosene to achieve a final concentration of 2 mg/kg. This yttrium solution was used as a diluent for each sample and standard. To reduce the viscosity disparity between samples and standards, 75 cSt blank oil was included if necessary, resulting in the final solution comprising of 5% oil by weight. According to method D4951 the mass % sample in diluent must be constant and in the range of 1% to 5%. Since the element concentrations in additive packages are typically very high compared to the final lubricating oil, a ten times dilution by mass was performed, if necessary, with 20 cSt blank oil before adding the diluent.
The calibration blank was made by diluting the 75 cSt blank oil in the yttrium solution. Each standard was prepared by diluting the stock standard by weight to offer the necessary concentration. The multi-element organometallic standard is made from metal sulfonates and therefore separate calibration standards were prepared from the 1000 mg/kg sulfur oil-based standard.

Calibration

A two-point calibration using blank and 40 mg/kg multi-element, respectively sulfur, working standards was performed to analyze samples and check standards. Following method D4951, the linear range of all calibration curves must be determined once by running intermediate standards lower and higher concentrated than the chosen working standards. The concentrations of those standards can be seen in Table 1.

Table 1: (mg/kg) of calibration standards for determination of linear calibration range

Element	Concentration									
	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6	Std. 7	Std. 8	Std. 9	Std. 10
S	1	5	10	25	50					
B, Ba, Ca, Cu, Mg, Mo, P, Zn						1	5	10	25	50

Instrument settings

The PlasmaQuant 9100 Elite ICP-OES, equipped with organic sample introduction kit, was employed for this analysis. Just 10 minutes of warm up time was necessary prior to the sample analysis. No oxygen was inserted into the plasma. A Teledyne CETAC Oils 7400 Homogenizing Dual Matrix Autosampler was employed to ensure good homogeneity of the samples. The instrument parameters can be seen in Table 2.

Table 2: Instrument settings

Parameter	Setting
RF Power	1350 W
Plasma gas flow	14 L/min
Auxiliary gas flow	1.5 L/min
Nebulizer gas flow	0.4 mL/min
Nebulizer	borosilicate concentric nebulizer, 1 mL/min
Spray chamber	borosilicate cyclonic spray chamber with dip tube, 50 mL
Outer tube/inner tube	quartz/quartz
Injector	quartz, inner diameter 1 mm
Pump tubing	viton (black, black)
Sample pump rate	1 mL/min
Fast mode	2 mL/min
Read delay	60 s
Rinse time	60 s
Torch position*	-2 mm

* Spacing between injector and coil further suppresses carbon deposits on the injector tip

Method and evaluation parameters

In the ASTM method, analysis wavelengths are recommended as a standard. With the outstanding spectral resolution of the Analytik Jena PlasmaQuant 9100 Elite, each line can be chosen with no issue of interference. In the Analytik Jena ASpect PQ software, the automatic background correction (ABC) purpose was utilized for data evaluation. The ABC function automatically sits in a global baseline to the whole spectral background concurrently throughout the sample analysis. The evaluation parameters for method ASTM D4951 can be seen in Table 3.

Table 3: Method parameters

Element	Line [nm]	Plasma view	Integration mode	Replicates	Read time [s]	Evaluation		
						No. of pixels	Baseline fit	Correction
Y	371.030	axial/radial	peak	3	1	3	ABC*	-
B	249.678	axial	peak	3	1	3	ABC	Y
Ba	233.527	radial	peak	3	1	3	ABC	Y
Ca	315.887	attenuated axial	peak	3	1	3	ABC	Y
Cu	324.754	radial	peak	3	1	3	ABC	Y
Mg	285.213	radial	peak	3	1	3	ABC	Y

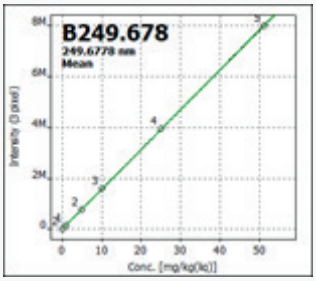
Table 3 (continued): Method parameters

Element	Line [nm]	Plasma view	Integration mode	Replicates	Read time [s]	Evaluation		
						No. of pixels	Baseline fit	Correction
Mo	202.030	axial	peak	3	1	3	ABC	Y
P	213.618	axial	peak	3	1	3	ABC	Y
S	180.672	axial	peak	3	1	3	ABC	Y
Zn	213.856	radial	peak	3	1	3	ABC	Y

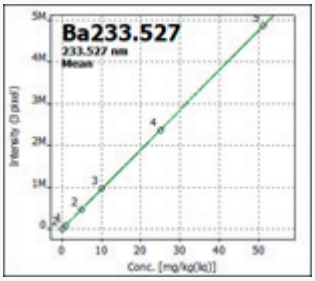
* Automated baseline correction

Results and Discussion

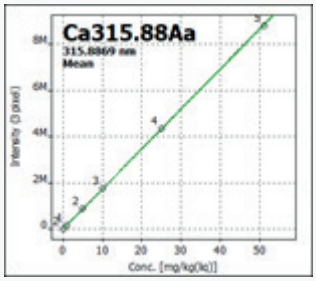
Linear calibrations were obtained with correlation coefficient greater than 0.9999 for all elements. Calibration curves for the method are shown in Figure 1 together with the adjusted coefficient of correlation (R^2_{adj}). ASTM D4951 expects detectability in the low mg/kg range for most elements to be sufficient.



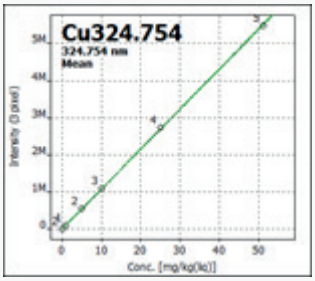
R^2(adj):0.99999



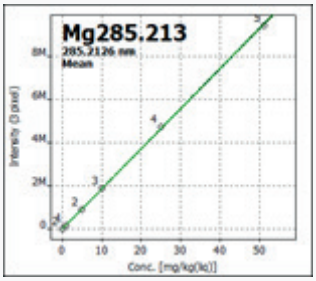
R^2(adj):0.99999



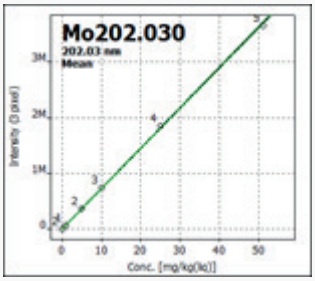
R^2(adj):0.99999



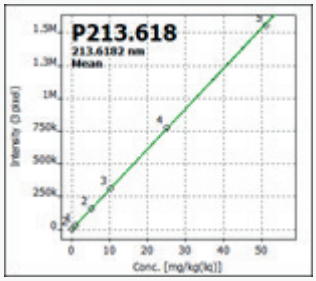
R^2(adj):0.99999



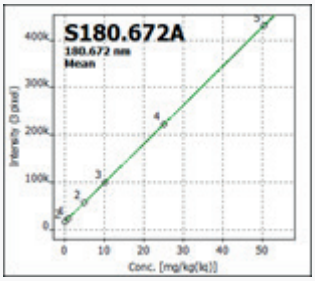
R^2(adj):0.99998



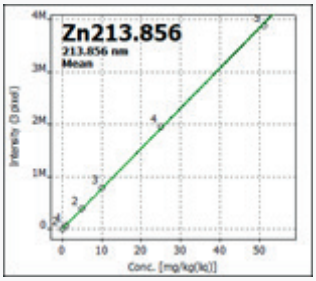
R^2(adj):0.99995



R^2(adj):0.99999



R^2(adj):0.99999



R^2(adj):0.99997

Figure 1: Determination of the linear calibration range with correlation coefficients greater than 0.9999 for all elements

Table 4 shows the obtained concentrations for two unused oil samples and three lubricant additives, as well as the method detection limits (MDL). Instrument detection limits (IDL) were determined using three times standard deviation from eleven measurements of the calibration blank. The MDLs, comprising the instrument detection limits and the sample preparation, were all in the lower µg/kg range. Relative standard deviations (RSDs) were obtained from three replicates for each measurement and were generally less than 2%.

Table 4: Results for investigated lubricating oils and additive packages as well as method detection limits (MDL) for analytical lines

Element	MDL [mg/kg]	Concentration [mg/kg]				
		Gear oil	Engine oil	Additive 1	Additive 2	Additive 3
B	0.034	2.25	274	173	2387	873
Ba	0.006	<MDL	<MDL	<MDL	<MDL	0.118
Ca	0.028	<MDL	1134	1348	22010	11330
Cu	0.036	<MDL	<MDL	<MDL	<MDL	<MDL
Mg	0.016	0.06	12.6	626	107	2681
Mo	0.024	<MDL	513	17.6	777	444
P	0.080	2478	488	750	7946	6826
S	0.090	<MDL	1721	2797	28130	18100
Zn	0.016	0.05	553	819	8960	7914

To achieve consistent and precise results and reduce the need for recalibration or remeasurement of samples, the ICP-OES system must provide good long-term stability. Long-term stability was tested by measuring quality control standards after the batch of five samples. The sequence was repeated ten times resulting in a run of 50 samples.
No recalibration was performed in between the different sample batches. For all the elements, the recovery of quality control standards was within ± 5% of the expected value as required by method D4951 (Figure 2). Over the whole period of sample measurements, no soot formation and carbon deposits were observed. The excellent long-term stability was achieved without adding oxygen to the plasma illustrating that the PlasmaQuant 9100 Elite ICP-OES is ideally suited for the routine oil analysis. Those results demonstrate that the analyzer can be easily used for routine oil analysis with excellent plasma and signal stability.

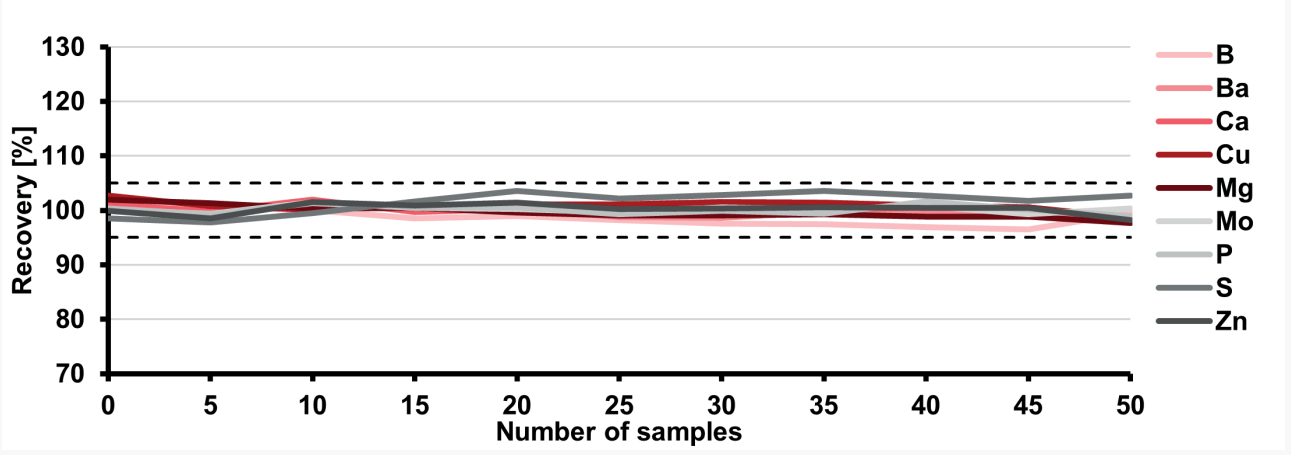


Figure 2: Percentage recoveries of quality control standards were within ± 5% of the expected value during a 50 samples measurement run

Conclusion

The exceptional precision and accuracy in lubricating oil analysis has been demonstrated by Analytik Jena's PlasmaQuant 9100 Elite ICP-OES in this study. The analyzer can easily fulfill the requirements of method ASTM D4951. The robust plasma and the high matrix tolerance make the PlasmaQuant 9100 Elite the ideal instrument for routine oil analysis. The unique V Shuttle Torch minimizes maintenance due to minimal carbon deposition. The high-resolution optics easily separate analytical lines from interferences, such as carbon-based emission. In summary, Analytik Jena PlasmaQuant 9100 Elite ICP-OES provides an easy solution for evaluating lubricating oil accurately, effectively, and timely.

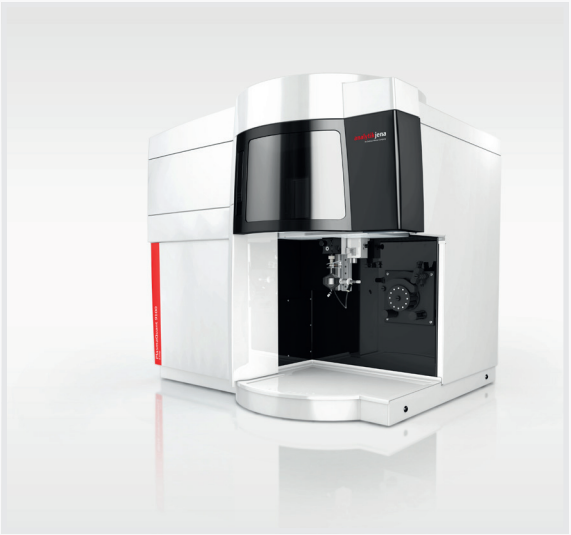


Figure 3: PlasmaQuant 9100 Elite

References

[1] ASTM D4951-14(2019), Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

Headquarters
Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.0 · Author: SSun/AB
en · 08/2022