Analysis of Petroleum Samples by ICP-OES

Karolina Carpenter, Applications Chemist; Teledyne Leeman Labs

Introduction

Nearly all commercially available motor oils contain additives to modify various properties of the oil and improve its performance. A wide range of additives are used in motor oil and typically make up 1-25% of the total liquid volume. Most motor oils contain “anti-oxidant” additives which help prevent the oil from burning when it gets hot. These additives contain detergents and dispersants to suspend and neutralize impurities in the oil and prevent them from coagulating in the engine.

Some of the most important additives include viscosity modifiers and wear inhibiting additives. Viscosity modifiers are used to help engine oil maintain a consistent viscosity as the temperature and pressure within the engine changes. These additives can also be used to reduce the viscosity of the oil which prevents it from thickening at lower temperatures and allows engines to be started at lower temperatures.

The wear inhibiting additives contain high concentrations of phosphorus, sulfur and zinc, and are used to reduce premature wear of vehicle engines. The additives in the oil bond to metal surfaces in the engine and help reduce friction between the moving parts. These additives are particularly important for oil used in racing vehicles, as those engines are operated at extremely high temperatures and pressures.

The method developed for this application note was applied to determine a range of elements in Performance Testing Lube Oil Standard (PTPLUBEMO-25) using the Teledyne Leeman Lab’s Prodigy7 Simultaneous ICP-OES.

Instrument and Method

This study was performed using a Teledyne Leeman Lab’s Prodigy7 ICP configured for radial viewing. The conditions used in this study are given in Table I and were found to be optimal for this application.

The Prodigy7 is a compact bench-top simultaneous optical emission instrument featuring a 500 mm focal length Echelle optical system coupled with a mega-pixel Large Format CMOS (L-CMOS) detector. At 28 mm^2, the active area of the L-CMOS detector is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows the Prodigy7 to achieve higher optical resolution than other solid-state detector based ICP systems. The detector also provides continuous wavelength coverage from 165 to 1100 nm permitting measurement over the entire ICP spectrum in a single reading, without sacrificing wavelength range or resolution. This detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than six orders of magnitude. The Prodigy7 also uses a 40.68 MHz rugged, water-cooled, free-running RF Generator, allowing it to handle the most difficult sample matrices as well as common organic solvents.

Sales/Support: 800-634-9942 • **Main**: 603-886-8400
110 Lowell Rd, Hudson, NH 03051
www.teledyneleemanlabs.com

Sample Introduction

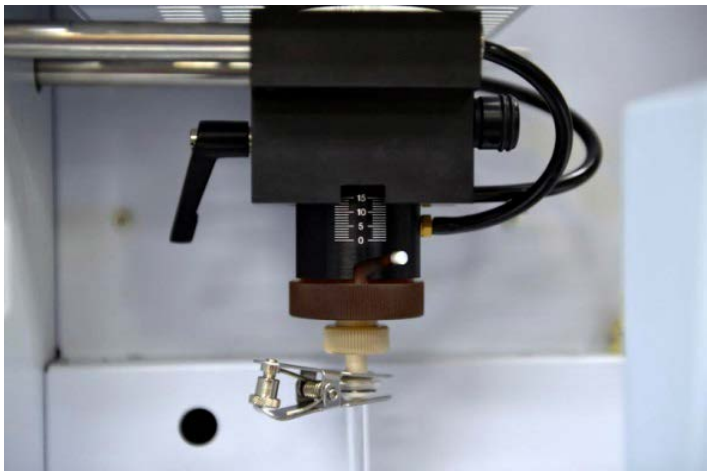
For this study the sample introduction system consisted of:

- Cyclonic spray chamber with a center knockout tube (PN 120-00475-1)
- Ryton™ V-groove nebulizer (PN 120-00045)
- Four-channel peristaltic pump

The volume of the cyclonic spray chamber is low allowing for fast washout between samples, while its knockout tube efficiently reduces the amount of sample aerosol that reaches the plasma torch. The Ryton™ V-groove nebulizer is sensitive, inert, requires no adjustment and is virtually impossible to clog.

The Prodigy 7's torch is mounted using an innovative twist-n-lock cassette system, shown in Figure 1. This design permits operators to remove and replace the torch to the exact same position, providing day-to-day reproducibility and simplified training.

Figure 1 Twist-n-Lock Sample Introduction System



Operating Parameters

For all elements of interest, background correction was performed simultaneously with the peak measurement, resulting in improved detection limits. All samples were analyzed with a radial instrument. The operating conditions used for all data collection are listed in Table I.

Table I Instrument Operating Parameters	
Instrument	
RF Power	1.20 kW
Coolant Flow	19 L/min
Auxiliary Flow	1.2 L/min
Nebulizer Pressure	35 psi
Uptake Rate	25 rpm
Sample Introduction	
Torch	Quartz Demountable
Injector	1.5 mm bore
Sample	
Integration Time	20 seconds

Calibration Standards

Calibration standards were prepared by dilution on a weight-to-weight basis from single and multi-element stock standards (VHG Labs, Manchester, NH) in kerosene. A kerosene solution was used for a calibration blank. The concentrations of the standards are listed in Table II.

Table II Calibration Standards

Element	Blank (ppm)	STD 1 (ppm)	STD 2 (ppm)	STD 3 (ppm)	STD 4 (ppm)	STD 5 (ppm)	STD 6 (ppm)
Ca	0	100	200	-	-	-	-
Mg	0	100	200	-	-	-	-
Na	0	-	-	-	-	100	200
P	0	100	200	-	-	-	-
S	0	-	-	500	1000	-	-
Zn	0	100	200	-	-	-	-

Sample Preparation

A Performance Testing Lube Oil Test Standard (VHG Labs, Manchester, NH) containing Ba, Ca, Cl, Mg, Mo, P, S, Si and Zn (PTPLUBEMO-25, sample ID: 40117014) was diluted 10-fold in kerosene and was prepared in triplicate. The first preparation was analyzed without the further modification.

The second and third preparations were spiked for purposes of calculating spike recoveries. The second preparation was spiked with a VHG Labs metallo-organic multi-element standard MA5 containing 5000 µg/g Ba, Ca, Mg, P and Zn. The third preparation was spiked with a single element standard containing 5000 µg/g of S. Both preparations were spiked such that the final concentration of each element was 50 ppm.

A preparation containing a sulfur spike was prepared separately due to the MA5 multi-element standard containing metal sulfonates. Spike recoveries were calculated for all spiked samples to verify the accuracy of the method.

Wavelength Parameters

The Prodigy7 typically uses a 29 pixel wide subarray, centered on the wavelength of interest, to collect data for each analyte. However, subarrays can be up to 57 pixels in width if needed. The analytical peaks and background correction points are defined in each subarray with pixel position and width values. In Table III below, wavelength and background correction position data are listed. All data in the subarrays is collected simultaneously. Additionally, all pixel data are saved, permitting recalculation of results at a later time.

Table III Wavelength Parameters

Element	Wavelength, nm	Left Background Correction		Right Background Correction	
		Position	Width	Position	Width
Ca	422.673	2	2	27	2
Mg	279.078	2	2	27	2
Na	589.592	2	2	27	2
P	214.914	2	2	27	2
S	182.034	2	2	27	2
Zn	481.053	2	2	27	2

The wavelengths chosen for Ca, Mg and Zn are not the most sensitive emission wavelengths for those elements. The most sensitive wavelengths for these elements produce intense emission which results in short linear dynamic ranges. Therefore, weaker emission lines were selected for Ca, Mg and Zn to increase the linear working range for these elements over a wide concentration range.

Figure 2 illustrates the element parameters for the Ca 422.673 nm line as an example. The left and right background regions begin at pixel positions 2 and 27, respectively. The width of both positions is 2 pixels. The analytical region of interest, where the "Ca" peak is found, begins at pixel position 13 and has a width of 5 pixels.

Figure 2 Ca 422.673 nm Wavelength Parameter Example

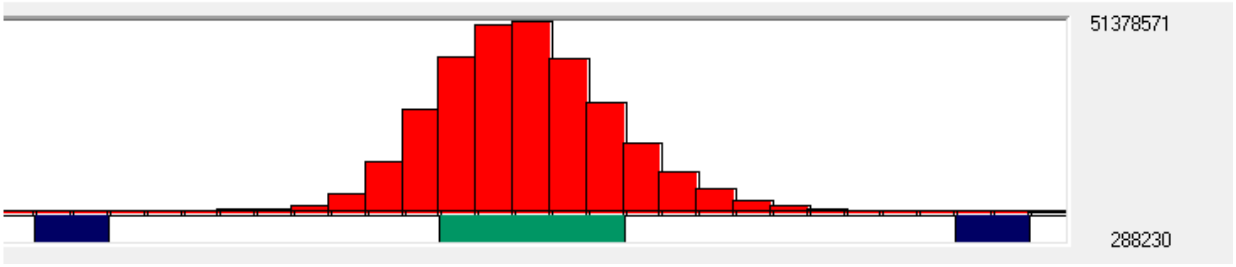
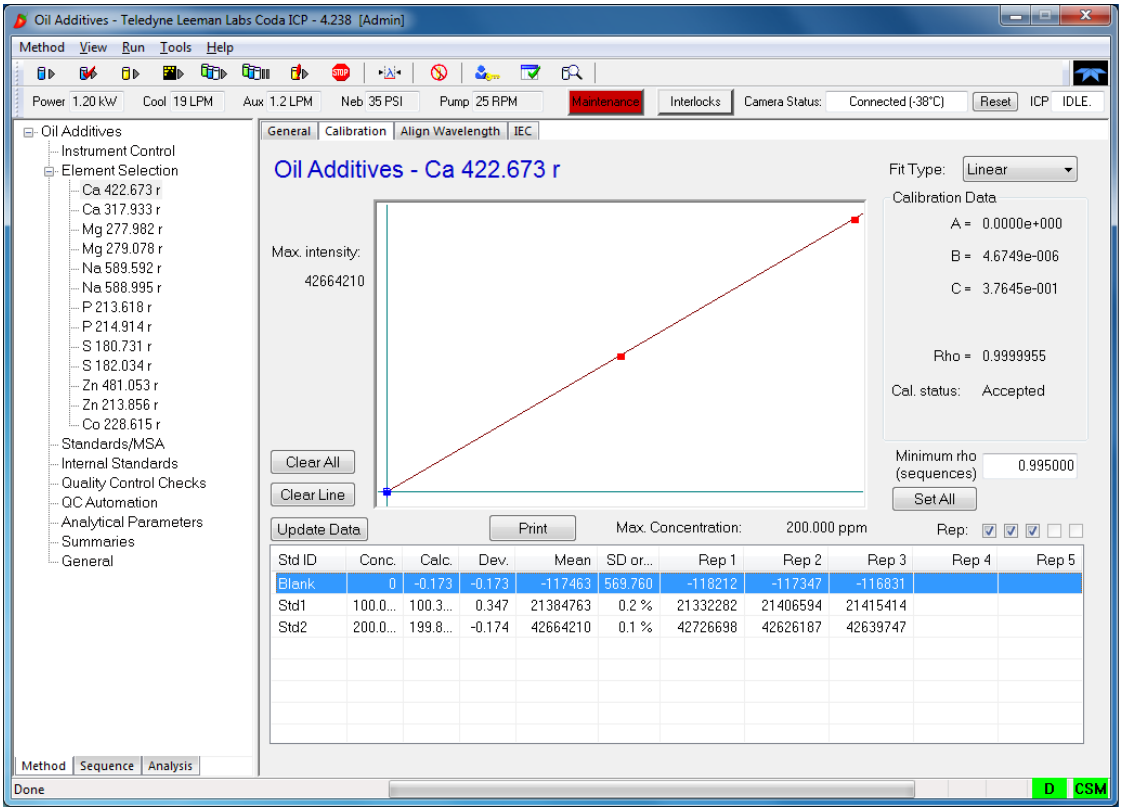


Figure 3 illustrates a typical calibration curve.

Figure 3 Ca 422.673 nm Calibration Curve



Results

After igniting the plasma and allowing a 15 minute warm-up period, the Prodigy7 was calibrated. Once the calibration was complete, a set of QC Standards was analyzed with acceptance criteria of ±10%. Upon successful completion of the QC Standard analysis, the reference sample was then analyzed.

The Performance Testing Lube Oil Standard (PTPLUBEMO-25) was analyzed over 7 days to demonstrate day-to-day precision. As presented in Table IV, the results for each analyte of interest fluctuated by less than 1.5% over the course of the test. The measured concentration in Table V represents an average of all analyses of the performance testing standard. The differences between the measured and certified concentrations are expressed as percentages in the last column of the table, and indicate that all analytes of interest were measured within ±10% of the certified concentrations. Results are also presented for the recoveries of the 50 ppm spikes, along with the %RSD values for the measured spike concentration. All results are reported in units of parts per million (ppm) unless specified otherwise.

Table IV PTPLUBEMO-25 DAY-TO-DAY REPRODUCIBILITY

Element	Wavelength	Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7	
	(nm)	Conc.	% RSD	Conc.	% RSD	Conc.	% RSD	Conc.	% RSD	Conc.	% RSD	Conc.	% RSD	Conc.	% RSD
Ca	422.673	1539	0.2	1539	0.2	1525	0.4	1515	0.5	1526	0.8	1505	0.3	1530	0.04
Mg	279.078	112	0.2	110	0.1	111	0.3	114	0.3	113	0.4	111	0.2	111	0.1
P	214.914	703	0.3	690	0.3	692	0.3	702	0.2	695	0.4	681	0.2	685	0.1
S	182.034	4043	0.1	4063	0.2	4076	0.2	4067	0.3	4020	0.8	4053	0.1	4053	0.02
Zn	481.053	845	0.4	834	0.07	833	0.2	837	0.3	836	0.3	823	0.2	825	0.2

Table V PTPLUBEMO-25 (ID: 40117014)

Element	Wavelength (nm)	Certified (ppm)	Found (ppm)	Difference %	Spike Recovery %	RSD %
Ca	422.673	1583	1526	3.6	94.8	0.2
Mg	279.078	120	112	6.8	96.6	0.1
P	214.914	717	693	3.4	98.0	0.1
S	182.034	3778	4054	7.3	100.3	0.1
Zn	481.053	875	834	4.7	97.0	0.2

Detection Limits

A study was performed to determine the Instrument's Detection Limit (IDL) in radial view mode for the elements of interest. Detection limits were calculated based on 3 times the standard deviation of 10 replicate measurements of the calibration blank. Results for the detection limit study are listed in Table VI and are in units of parts per million (ppm).

Table VI Detection Limits (DLs)

Element	Wavelength (nm)	DL (ppm)
Ca	422.673	0.009
Mg	279.078	0.016
Na	589.592	0.023
P	214.914	0.034
S	182.034	0.356
Zn	481.053	0.101

Conclusion

The analysis of the performance testing lube oil using the Teledyne Leeman Labs Prodigy7 ICP was successful. Additionally, the results presented in this application note demonstrate that the method can be applied to various oil additive samples. While the use of an internal standard was not necessary to generate accurate results for this application note, it can be used when analyzing different types of additives to correct for potential matrix and sample transport-based interferences. The spike recovery results presented indicate that all analytes were measured within ±10% of the spiked concentrations. These results, along with their associated %RSD values, demonstrate that the Prodigy7 can be used for accurate and reliable analysis of a suite of elements present in a wide range of concentrations in viscous sample matrices.