

## Prodigy ICP

## Application Note: # 1060



# Analysis of Oil Additives using the Teledyne Leeman Labs Prodigy High Dispersion ICP

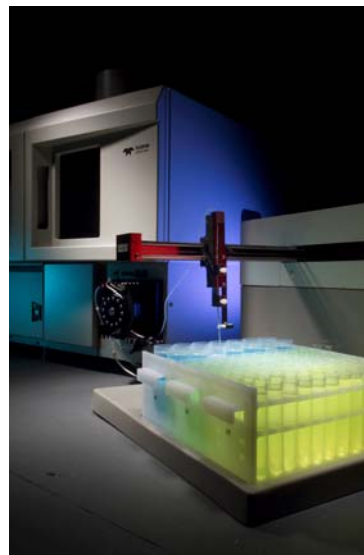
## Introduction

Nearly all commercially available motor oils contain additives. Oil additives are used to modify various properties of the oil to 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 helps 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 motor oils contain additional additives to modify the viscosity of the oil or to prevent the buildup of acids. 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. Acid inhibitors help combat the formation of rust and corrosion as a result of incomplete fuel combustion or from the presence of water in the crankcase.

Among the most widely-used additive types are those used for “anti-wear.” These additives typically 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.

This application note will demonstrate the ability of the Teledyne Leeman Labs **Prodigy High Dispersion ICP** to determine a range of elements in two oil additive sets. The Prodigy provides high sensitivity and dispersion which, combined with appropriately chosen wavelengths and background correction points, can be used to provide accurate and reliable results for a suite of elements in oil additive samples using a radial plasma.



## Experimental

### Instrumentation

A radial Prodigy High Dispersion Inductively Coupled Plasma (ICP) Spectrometer was used to generate the data for this application note. The Prodigy is a compact bench-top simultaneous optical emission instrument featuring an 800 mm focal length Echelle optical system and a mega-pixel Large Format Programmable Array Detector (L-PAD). At 28 mm<sup>2</sup>, the active area of the L-PAD is significantly larger than that of all other solid-state detectors currently used in optical emission spectrometers.

The long focal length, combined with the large array detector, create a solid-state detection system that provides continuous wavelength coverage from 165 to 1100 nm. Well-resolved analytical signals can be measured and background corrected in a single instrument reading, a feature unseen in other emission spectrometers with solid-state detectors.

An additional benefit of the L-PAD is its charge injection device (CID) design which allows random access to each pixel in the detector array and non-destructive readout of its stored charge. These features prevent detector saturation blooming over a linear working range that can cover 6 orders of magnitude.

The Prodigy uses a 40.68 MHz free running, water-cooled oscillator which produces a robust plasma that is stable even with the most challenging sample matrices. An efficient sample introduction system produces and transports a constant, steady aerosol to the plasma which is reflected in stable emission signals.

The Prodigy's innovative Image Stabilization system uniquely integrates the sample introduction components into the optical system which further improves signal stability. In this system, the torch is rigidly attached to the spectrometer and, thus, becomes part of the optical path.

In this work, the sample introduction system consisted of a Ryton™ V-groove nebulizer, glass cyclonic spray chamber with a center knockout tube, and a single-piece quartz torch. The instrument was equipped with an 88 position autosampler. All analytical data presented was collected using the autosampler.

### Operating Parameters

For all analytes 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 1.

Parameter	Instrument Setting
RF Power	1.3 kW
Coolant Gas Flow	19 L/min
Auxiliary Gas Flow	1.2 L/min
Nebulizer Pressure	40 psi
Nebulizer Type	V-Groove
Spray Chamber	Glass Cyclonic with Center Knockout Tube
Torch	Single Piece Radial
Sample Uptake Rate	1.0 mL/min

*Table 1. Plasma Operating Conditions*

## Method

### Calibration Standards

Two sets of calibration standards were prepared to match the matrix in two sets of additive samples. Each set of standards was prepared by dilution on a weight to weight basis from a multi-element stock standard. The standard for the first additive was diluted 1:50, 1:100 and 1:200 in kerosene. The standard for the second additive was diluted 1:50, 1:100 and 1:150 in kerosene. A kerosene solution was used for a calibration blank for both sample sets. The concentration of the standards used for additive #1 and #2 are listed in Tables 2 and 3, respectively. A Mn internal standard was added to all blanks, standards and samples to correct for differences in sample homogeneity and in nebulization efficiency. The internal standard was added such that the ratio between the mass of the internal standard and the total mass of solution was 1:100.

Element	Std 1 (%)	Std 2 (%)	Std 3 (%)	Std 4 (%)
Ca	0	0.009	0.018	0.036
Mg	0	0.005	0.010	0.020
Na	0	0.005	0.010	0.020
Mg	0	0.005	0.010	0.020
P	0	0.007	0.014	0.028
S	0	0.019	0.037	0.075
Zn	0	0.008	0.015	0.030

Table 2. Calibration Standards for Additive Sample #1

Element	Std 1 (%)	Std 2 (%)	Std 3 (%)	Std 4 (%)
P	0	0.0655	0.0968	0.1973
S	0	0.1359	0.2007	0.4093
Zn	0	0.0717	0.1060	0.2161

Table 3. Calibration Standards for Additive Sample #2

### Sample Preparation

Two oil additive samples were prepared for analysis by dilution with high-purity kerosene. The first additive sample contained Ca, Mg, Na, P, S and Zn at concentrations that ranged from 0.5–4.0%. The second additive sample contained P, S and Zn at concentrations that ranged from 10-22%. Each additive sample was prepared by removing a 1 g aliquot, combining it with 1 g of the internal standard solution and 98 g of kerosene, and mixing thoroughly.

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: 70865004) was analyzed to verify the accuracy of the method. The standard was diluted 10-fold in kerosene and a Mn internal standard was added such that the ratio between the mass of the internal standard and the total mass of solution was 1:100. This solution was prepared fresh daily and analyzed periodically during sample analysis.

Each additive sample was prepared in triplicate. The first preparation was analyzed without further modification. The second and third preparations were spiked for purposes of calculating spike recoveries. The second preparation was spiked with a Conostan metallo-organic multi-element standard (Custom Blend, AM Special, SCP Science, Champlain, NY) containing 1000 ppm Ba, Ca, Mg, P and Zn, and a single-element standard containing 5000 ppm sodium. The third preparation was spiked with a single-element standard containing 1000 ppm sulfur. Both preparations were spiked such that the final

concentration of each element was 0.01%. Preparations containing sulfur spikes were prepared separately because the Conostan multi-element standard contains metal sulfonates. Spike recoveries were calculated for all spiked samples to verify the accuracy of the method.

In addition, the first additive sample was prepared and analyzed over the course of 14 days to verify the precision of the method. A single preparation of this additive sample was prepared daily as described above. Spiked solutions were not prepared for this study.

## Wavelength Parameters

The Prodigy typically uses a 3 x 15 pixel subarray, centered on the wavelength of interest, to collect data for each analyte. However, subarrays can be up to 27 pixels in width if needed. The analytical peaks and background correction points are defined in each subarray with pixel position and width values. The wavelength and background correction points used in this method are outlined in Table 4. For elements in which background correction included more than 1 pixel on the same side, multiple values are listed to indicate the positions for all the pixels used. The starting position and pixel width used for all analytical peaks was 7 and 3, respectively. For each analyte of interest, an integration time of 15 seconds was used and background correction was performed simultaneously with the peak measurement. Additionally, all pixel data are saved which allows for future data recalculation.

Element	Wavelength (nm)	Left Background Position	Right Background Position
Ca	422.673	3	11
Mg	277.982	3	15
Na	589.592	5	14
P	213.618	1	12-13
S	182.034	2	11
Zn	481.053	3	11
Mn	403.075	1-3	13-15

*Table 4. Wavelengths and Background Correction Points Used*

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 chosen for Ca, Mg and Zn to increase the linear working range for these elements over a wide concentration range.

An example of the data collection that takes place in each subarray is illustrated graphically in Figure 1. This figure represents the data collected for calibration standard 2 for additive set #1 at the Zn 481.053 nm line. In Figure 1, the left and right background correction points are illustrated at pixel positions 3 and 11, with a width of 1. The pixels used for integrating the analytical peak are at positions 7, 8 and 9.

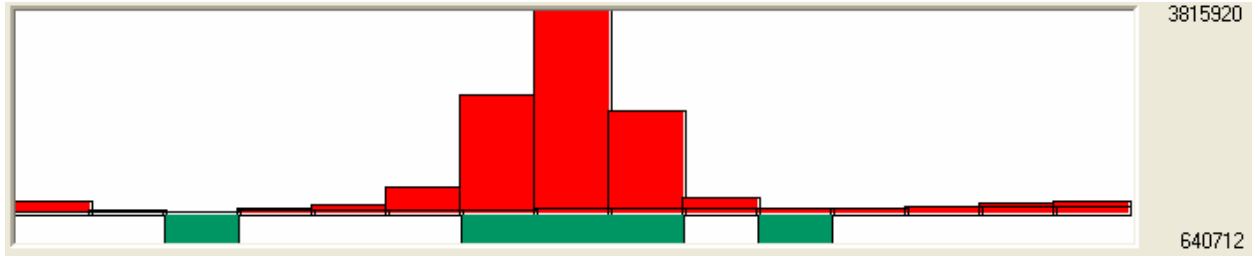


Figure 1. Graphical Representation of the Zn 481.053 nm Subarray for Std 2 in Radial View Mode

Examples of typical calibration curves are illustrated in Figures 2 and 3. The figures are based on calibration data for the Zn 481.053 nm line for additive set #1 and additive set #2, respectively. Both figures demonstrate typical precision and linearity for the range of concentrations included in the calibrations.

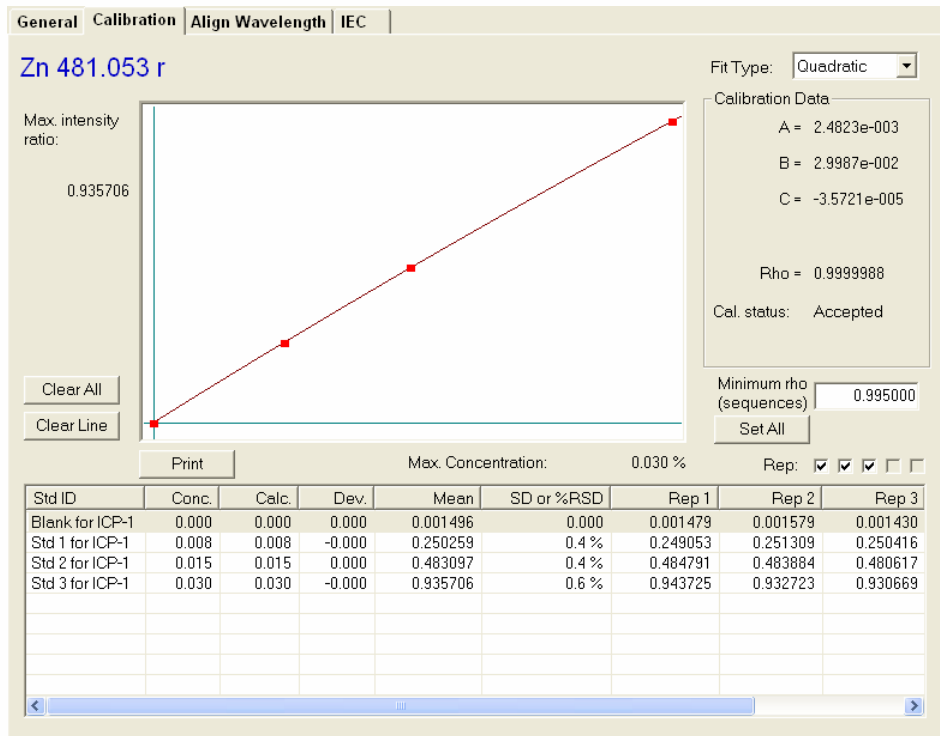


Figure 2. Typical Calibration Curve for Zn 481.053 nm for Additive Set #1

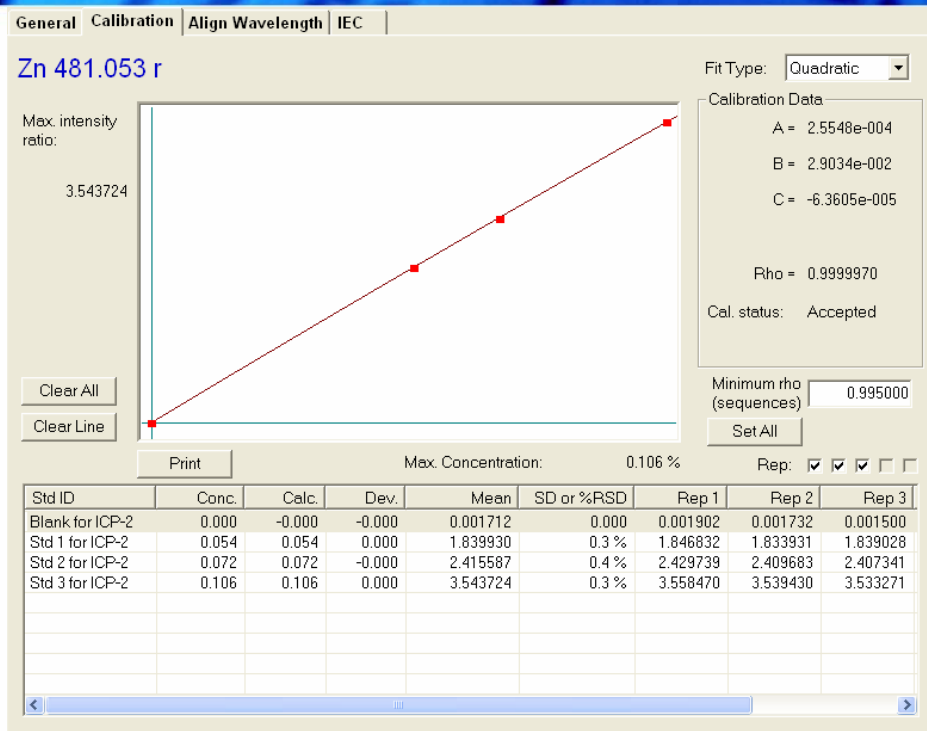


Figure 3. Typical Calibration Curve for Zn 481.053 nm for Additive Set #2

## Results and Discussion

### Detection Limits

A study was performed to determine the instrument's detection limits 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 5 and are listed in units of elemental weight percent (%).

Element	Wavelength (nm)	Detection Limit (%)
Ca	422.673	0.0000013
Mg	277.982	0.0000013
Na	589.592	0.0000043
P	213.618	0.0000024
S	182.034	0.0000082
Zn	481.053	0.000017

Table 5. Detection Limits (DLs) in Kerosene Matrix

## Samples

After igniting the plasma and allowing 15 minutes for the instrument to warm up, the instrument was calibrated using the appropriate calibration blank and standards listed in Tables 2 and 3. Following calibration, the performance test standard and oil additive samples were analyzed.

Results for the Performance Testing Lube Oil Standard (PTPLUBEMO-25, Standard ID: 70865004) are listed in Table 6. The performance testing standard was analyzed immediately after calibration and after every tenth sample for the duration of sample analysis. The measured concentrations in Table 6 represent 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  $\pm 10\%$  of the certified concentrations.

Results for the first and second additive samples are presented in Tables 7 and 8, respectively. Results are also presented for the recoveries of the 0.01% spikes, along with the %RSD values for the measured spike concentrations. All results reported in Tables 6-8 are listed in units of elemental weight percent (%).

Results for the additive sample measured over 14 days are listed in Table 9. Results are reported in units of elemental weight percent (%) and demonstrate day-to-day precision. As seen in Table 9, the results for each analyte of interest fluctuated by less than 2% over the course of 14 days.

Element	Wavelength (nm)	Avg. Measured Conc. (%)	Certified Conc. (%)	Difference (%)
Ca	422.673	0.315	0.318	0.82
Mg	277.982	0.053	0.049	7.6
P	213.618	0.084	0.086	2.7
S	182.034	1.7	1.8	5.6
Zn	481.053	0.1346	0.1410	4.5

*Table 6. Results For the Analysis of Performance Testing Standard, ID: 70865004*

Element	Wavelength (nm)	Measured Conc. (%)	Spike Recovery (%)	Recovery RSD (%)
Ca	422.673	1.284	100.0	0.2
Mg	277.982	0.745	96.6	0.3
Na	589.592	0.525	100.1	0.1
P	213.618	1.180	100.4	0.2
S	182.034	4.148	90.0	0.7
Zn	481.053	1.273	97.8	0.08

*Table 7. Results For the Analysis of Oil Additive Sample #1*

Element	Wavelength (nm)	Measured Conc. (%)	Spike Recovery (%)	Recovery RSD (%)
P	213.618	10.46	109.1	0.4
S	182.034	21.81	90.9	0.04
Zn	481.053	11.25	109.1	0.2

Table 8. Results For the Analysis of Oil Additive Sample #2

Element	Wavelength (nm)	Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7	
		Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD
Ca	422.673	1.297	0.2	1.289	0.4	1.309	0.5	1.304	0.5	1.295	0.4	1.266	0.4	1.321	0.2
Mg	277.982	0.5336	0.06	0.5057	0.6	0.5200	0.4	0.5251	0.5	0.5200	0.5	0.5080	0.2	0.5224	0.3
Na	589.592	0.7571	0.2	0.7662	0.1	0.7663	0.3	0.7679	0.3	0.7585	0.5	0.7432	0.04	0.7790	0.6
P	213.618	1.137	0.3	1.155	0.1	1.180	0.2	1.205	0.05	1.181	0.7	1.150	0.4	1.189	0.2
S	182.034	3.806	0.5	3.839	0.3	3.877	0.3	3.964	0.2	3.865	0.8	3.796	0.3	3.933	0.4
Zn	481.053	1.257	0.3	1.294	0.2	1.299	0.08	1.314	0.2	1.290	0.7	1.264	0.2	1.329	0.2

Table 9. Results For the Analysis of Oil Additive Sample #1 (Days 1-7)

Element	Wavelength (nm)	Day 8		Day 9		Day 10		Day 11		Day 12		Day 13		Day 14	
		Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD	Conc (%)	% RSD
Ca	422.673	1.306	0.2	1.242	0.2	1.276	0.2	1.296	0.4	1.275	0.1	1.288	0.07	1.281	0.4
Mg	277.982	0.5190	0.03	0.5018	0.4	0.5021	0.3	0.5147	0.3	0.5097	0.3	0.5227	0.1	0.5078	0.2
Na	589.592	0.7543	0.2	0.7301	0.1	0.7427	0.2	0.7530	0.3	0.7493	0.1	0.7612	0.06	0.7408	0.2
P	213.618	1.181	0.3	1.138	0.2	1.152	0.2	1.167	0.2	1.166	0.3	1.188	0.3	1.155	0.3
S	182.034	3.911	0.08	3.728	0.6	3.808	0.2	3.820	0.5	3.865	0.07	3.881	0.4	3.772	0.4
Zn	481.053	1.287	0.4	1.242	0.3	1.275	0.2	1.283	0.3	1.286	0.2	1.294	0.4	1.258	0.2

Table 9. Results For the Analysis of Oil Additive Sample #1 (Days 8-14)



## Conclusions

The analysis of oil additive samples has been successfully performed using the Teledyne Leeman Labs ***Prodigy High Dispersion ICP***. The spike recovery results presented in this work indicate that all analytes were measured within  $\pm 10\%$  of the spiked concentrations. Those results, along with their associated %RSD values, demonstrate that the Prodigy can be used to provide accurate and reliable results for a suite of elements that are present at a wide range of concentrations in viscous sample matrices. The use of an internal standard minimized differences in nebulization efficiencies between samples which resulted in improved precision values.

The image stabilized plasma and the simultaneous data collection of both peak and background data combine to provide exceptionally precise and stable results. The high precision, accuracy and versatility of the Prodigy derive from its stable, free-running 40 MHz power supply and high sensitivity sample introduction system. In addition, a reliable autosampler provides flexibility and confidence in unattended operation.