# Analysis of Oil Additives in Petroleum Samples Using the Teledyne Leeman Labs' Prodigy Plus ICP-OES

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## Introduction

Nearly all commercially available motor oils contain additives to modify properties and improve performance. These additives can typically make up 1-25% of the total liquid volume. A majority of motor oils contain "anti-oxidant" additives, which help prevent the oil from burning at high temperatures. 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 inhibitors. 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 oil viscosity so that it does not thicken in low temperatures and prevent engines from starting.

Wear inhibiting additives contain high concentrations of phosphorus, sulfur and zinc, and are used to reduce premature wear in 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 whose engines are operated at extremely high temperatures and pressures.

Analysis by ICP can be used to quantify particular elements in these additives. The method developed for this application note was used to determine a range of elements in Performance Testing Lube Oil Standard (PTPLUBEMO-25) using the Teledyne Leeman Labs' Prodigy Plus Simultaneous ICP-OES.

## Instrument

A Prodigy Plus Inductively Coupled Plasma (ICP) Spectrometer (Figure 1) equipped with a radial view torch and a 240-position Teledyne CETAC ASX-560 autosampler (Omaha, NE) (Figure 2) were used to generate the data for this application note.

**Figure 1** Prodigy Plus ICP-OES

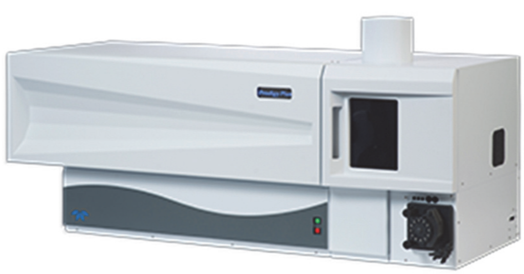
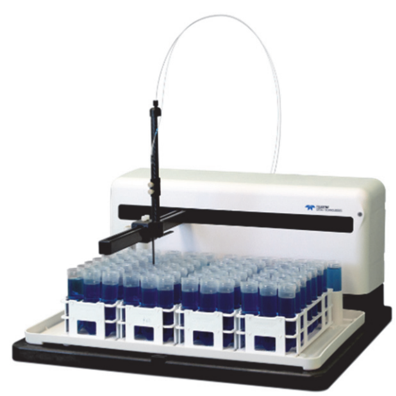


**Figure 2** Teledyne CETAC ASX-560 Autosampler



The Prodigy Plus is a compact benchtop simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a mega-pixel Large Format CMOS (L-CMOS) detector. At 28 x 28 mm, the active area of the L-CMOS is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows the Prodigy Plus 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 Prodigy Plus uses a 40.68 MHz rugged, free-running RF Generator, allowing it to handle the most difficult sample matrices, as well as common organic solvents.

## Sample Introduction

A high-sensitivity sample introduction system ensures that sufficient and steady emission signals are transmitted to the spectrometer.

The sample introduction system consisted of:

- Cyclonic spray chamber with a center knockout tube
- Ryton™ V-groove nebulizer
- 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 Plus torch is mounted using an innovative twist-n-lock cassette system, shown in Figure 3. This design permits operators to remove and replace the torch to the exact same position, providing day-to-day reproducibility and simplified training. Additionally, the twist-lock design automatically connects the coolant and auxiliary gas flows, eliminating potential errors.

**Figure 3** Radial Twist-n-Lock Sample Introduction System

## Method

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 Conditions**

| Parameter | Value | Part Number |
|---|---|---|
| **RF Power** | 1.2 kW | |
| **Coolant Flow** | 16.0 LPM | |
| **Auxiliary Flow** | 1.4 LPM | |
| **Nebulizer Pressure** | 25 PSI | |
| **Pump Rate** | 20 RPM | |
| **Torch** | Quartz Demountable | 318-00167-1 |
| **Injector** | 1.1 mm Bore | 318-00161-ORG2 |
| **Integration Time** | 20 sec | |

## Instrument Detection Limit

A study was performed to determine the Instrument's Detection Limit (IDL) in radial view for the elements of interest. Detection limits were calculated based on three times the standard deviation of 10 replicate measurements of the calibration blank. For all elements of interest, background correction was performed simultaneously with the peak measurement, resulting in improved detection limits. Results for the detection limit study are shown in Table II in units of parts per million (ppm) and are corrected for the sample dilution.

**Table II Instrument Detection Limits**

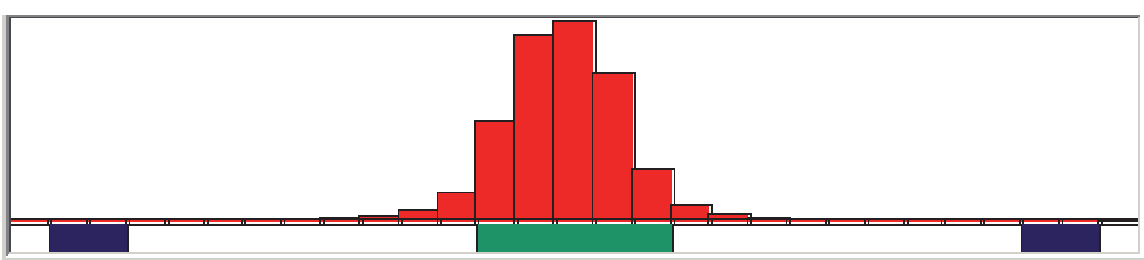
| Element | Wavelength (nm) | DL (ppm) |
|---|---|---|
| **Ca** | 315.887 | 0.032 |
| **Ba** | 233.527 | 0.075 |
| **Mg** | 279.078 | 0.109 |
| **P** | 214.914 | 0.078 |
| **S** | 182.034 | 0.520 |
| **Zn** | 206.200 | 0.018 |

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.

The Prodigy Plus 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. All data in the subarrays is collected simultaneously. Additionally, all pixel data is saved, permitting future recalculation of results.

Figure 4 illustrates the element parameters for the Ca 315.887 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 4** Ca 315.887 nm Wavelength Parameter Example



## 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: 40117023) was diluted 10-fold in kerosene and 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 of 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.

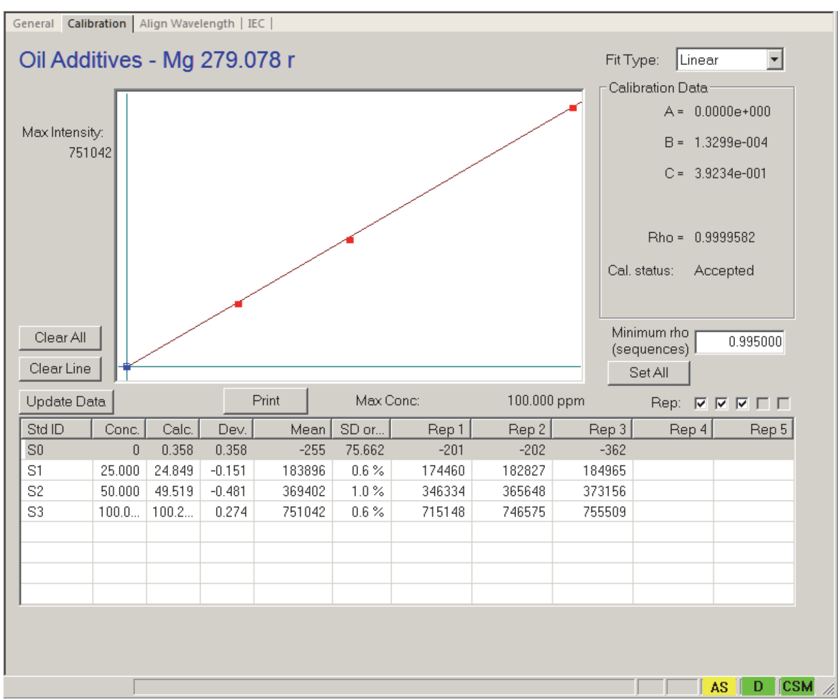
## Calibration Standards

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 and base oil solution was used for a calibration blank. The concentrations of the standards are listed in Table III. Figure 5 illustrates a typical calibration curve.

**Table III Calibration Standards**

| Element | Blank ppm | Std1 ppm | Std2 ppm | Std3 ppm | Std4 ppm | Std5 Ppm | Std6 ppm |
|---|---|---|---|---|---|---|---|
| **Ca** | 0 | 25 | 50 | 100 | 200 | - | - |
| **Ba** | 0 | 25 | 50 | - | - | - | - |
| **Mg** | 0 | 25 | 50 | 100 | - | - | - |
| **P** | 0 | 25 | 50 | 100 | - | - | - |
| **S** | 0 | - | - | - | - | 250 | 500 |
| **Ca** | 0 | 25 | 50 | 100 | 200 | - | - |

**Figure 5** Mg 279.078 nm Calibration Curve



## Results

After igniting the plasma and allowing a 15-minute warm-up period, the Prodigy Plus was calibrated. Once the calibration was complete, a set of QC Standards were 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 shown in Table IV, the results for each analyte of interest fluctuated by less than 1.5% over the course of the study. The measured concentration in Table V represents an average of all analyses of the Performance Testing Lube Oil Standard (PTPLUBEMO-25). The differences between the measured and certified concentrations are expressed as percentages in the Difference (%) Column, 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 (nm) | Day 1 Conc. | Day 2 Conc. | Day 3 Conc. | Day 4 Conc. | Day 5 Conc. | Day 6 Conc. | Day 7 Conc. |
|---|---|---|---|---|---|---|---|---|
| **Ca** | 315.887 | 1576 | 1579 | 1586 | 1606 | 1598 | 1576 | 1584 |
| **Ba** | 233.527 | 101.5 | 100.5 | 100.3 | 101.4 | 100.9 | 101.2 | 100.5 |
| **Mg** | 279.078 | 127.3 | 126.2 | 126.1 | 128.0 | 126.9 | 124.3 | 125.0 |
| **P** | 214.914 | 754.9 | 746.3 | 754.7 | 765.6 | 754.3 | 747.3 | 753.0 |
| **S** | 182.034 | 3936 | 3929 | 3936 | 4001 | 3981 | 3894 | 3899 |
| **Zn** | 206.200 | 920.8 | 916.2 | 919.2 | 924.9 | 919.7 | 922.8 | 909.3 |

**Table V PTPLUBEMO-25 (ID 40117023)**

| Element | Wavelength (nm) | Certified (ppm) | Found (ppm) | Difference (%) | Spike Recovery (%) | % RSD |
|---|---|---|---|---|---|---|
| **Ca** | 315.887 | 1589 | 1586 | 0.2 | 91.4 | 0.7 |
| **Ba** | 233.527 | 100 | 100.8 | 0.8 | 92.8 | 0.5 |
| **Mg** | 279.078 | 125 | 126.1 | 0.9 | 102.8 | 1.0 |
| **P** | 214.914 | 752 | 752.9 | 0.1 | 95.5 | 0.8 |
| **S** | 182.034 | 3932 | 3937 | 0.1 | 90.3 | 0.9 |
| **Zn** | 206.200 | 924 | 919.7 | 0.5 | 90.3 | 0.6 |

## Conclusion

The analysis of Performance Testing Lube Oil Standard (PTPLUBEMO-25) using the Teledyne Leeman Labs' Prodigy Plus 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 Prodigy Plus can be used for accurate and reliable analysis of a suite of elements present in a wide range of concentrations in viscous sample matrices.