Analysis of Crude Oil by ASTM Procedures D5708 and D1548 Using the Teledyne Leeman Labs' Prodigy Plus ICP-OES

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Introduction

Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) has been an important technique in the petroleum/petrochemical analysis laboratory since the 1970s due to its ability to determine a range of elements and concentrations in both aqueous and organic samples. Additionally, because ICP is compatible with many organic solvents, it permits the preparation of a wide range of sample types using only a simple dilution.

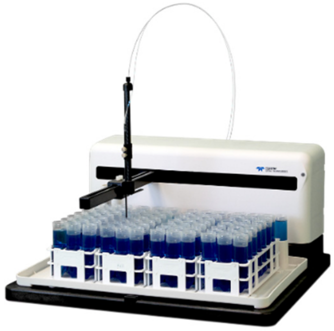
This application note will demonstrate the ability of the Teledyne Leeman Labs' Prodigy Plus ICP-OES to meet the criteria of ASTM procedures D1548, Test Method for Vanadium in Heavy Fuel Oils and D5708 Determination of Nickel, Vanadium, and Iron in Crude Oils. These elements are of interest to the refining industry as V can form corrosive compounds during combustion and both Fe and Ni at trace levels can deactivate catalysts used in the process.

Instrument

A Prodigy Plus Inductively Coupled Plasma (ICP) Spectrometer equipped with a radial-view torch (Figure 1) 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.

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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's 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

A radial analytical viewing zone was used for all samples. The operating conditions used for all sample analyses are shown in Table I.

Table I Instrument Operating Conditions

Parameter	Value	Part Number
RF Power	1.3 kW	
Coolant Flow	16.0 LPM	
Auxiliary Flow	1.2 LPM	
Nebulizer Pressure	21 PSI	
Pump Rate	25 RPM	
Torch	Quartz Demountable	318-00167-1
Injector	1.1 mm Bore	318-00161-ORG2
Integration Time	30 sec	

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Sample Preparation

Sample dilutions were performed on a weight-to-weight basis. All samples were diluted with high-purity kerosene containing 5 ppm of Cobalt (Co) as an internal standard to overcome potential nebulization effects caused by different oil viscosities.

Two sets of samples were diluted according to Table II. The first preparation was analyzed without further modification, while the second preparation was spiked with a multi-element standard such that the concentrations of the spiked elements was 2 ppm. Spike recoveries were calculated for all spiked samples to verify the accuracy of the method.

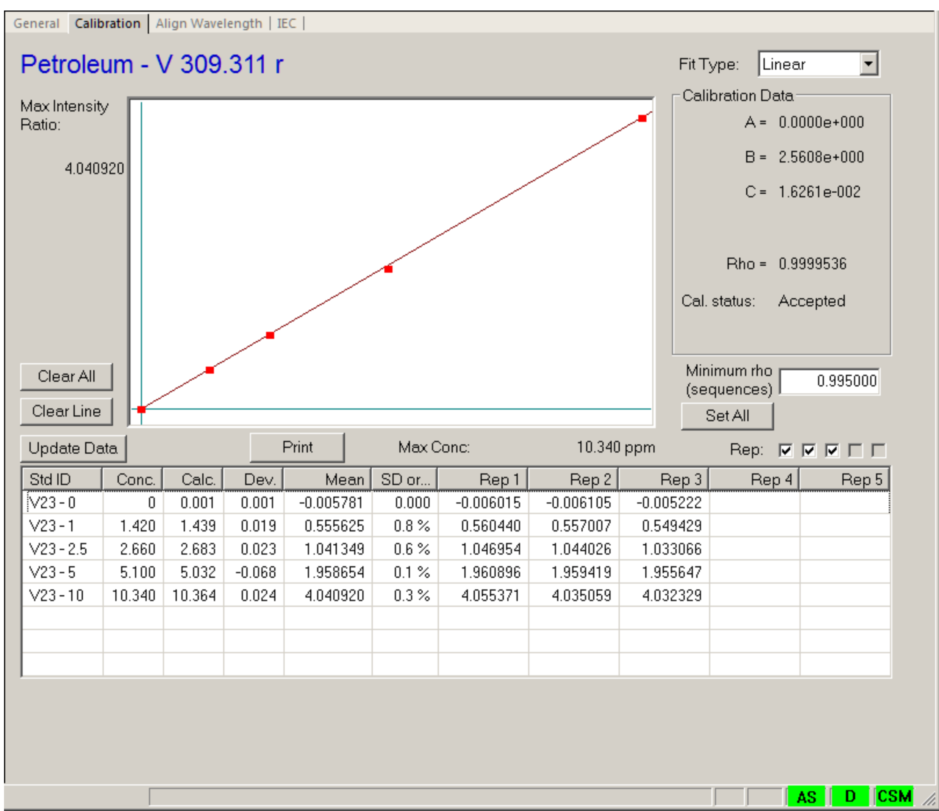
Table II Sample Preparation

Preparation	Sample	Dilution	Internal Standard	Spike
Set #1	Crude Oil	1:100	5 ppm Co	None
Set #2	Crude Oil	1:100	5 ppm Co	2 ppm

Calibration

Standard dilutions were performed on a weight-to-weight basis. Calibration standards for all elements were prepared by diluting 100 ppm VHG V23 standard (VHG Labs, Manchester, NH) with high-purity kerosene containing 5 ppm of Cobalt (Co) as an internal standard to overcome potential nebulization effects caused by different oil viscosities. The oil concentration in the standards was 10%. Standard concentrations were 0, 1.0, 2.5, 5.0 and 10.0 ppm.

Figure 4 Typical Calibration Curve



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Results

Detection Limits

A study was performed to determine the Instrument's Detection Limits (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 analytes of interest, background correction was performed simultaneously with the peak measurement, resulting in improved precision and detection limits. Results for the detection limit study have been corrected for the sample dilution and are shown in Table III.

Table III Instrument Detection Limit Results

Element	Wavelength (nm)	DL (mg/g)
Fe	259.94	0.015
Ni	221.648	0.050
V	309.311	0.010

Samples

After igniting the plasma and allowing 15 minutes for the Prodigy Plus to warm up, the instrument was calibrated using the calibration blank and standards. After the calibration, a Quality Control (QC) Check Standard was analyzed, followed by samples. Results for the crude oil samples are presented in Table IV. Results for the sample are reported in units of parts per million (mg/g). Results are also presented for the recoveries of the 2 ppm spike, along with %RSD values for the measured spike concentrations. Elements were reported as ND, if the measured concentration was at or below the IDL shown in Table III.

Table IV Crude Oil Results

Element	Measured Conc. (mg/g)	Spike Recovery	%RSD
Fe	1.00	100.7	0.1
Ni	9.74	101.4	0.3
V	18.8	101.4	0.3

Conclusions

The analysis of crude oil samples was successfully performed using the Teledyne Leeman Labs' Prodigy Plus ICP-OES. The spike recovery results presented in this application note 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 to provide accurate and reliable analysis of this subset of elements in this matrix. The use of the cobalt internal standard minimized differences related to sample nebulization efficiency and resulted in improved precision values. The image stabilized plasma combined with the simultaneous collection of both peak and background data provided exceptionally precise and stable results.

The Prodigy Plus ICP-OES was well suited to the determination of elements in crude oil samples due to the high precision, accuracy and versatility provided by its stable, free-running 40 MHz power supply and high-sensitivity sample introduction system. The addition of a reliable autosampler provided flexibility and confidence in unattended operation.

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