Aplicación 042

Análisis de muestras petroquímicas mediante ICP-OES

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 Prodigy7 ICP-OES to determine a range of elements in petroleum samples. By combining the Prodigy7's high sensitivity and dispersion with appropriately chosen wavelengths and background correction points, accurate and reliable results can easily be obtained for a suite of elements.

Experimental

All samples and calibration standards 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 each sample type were diluted according to Table I. 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 were 2 ppm. Spike recoveries were calculated for all spiked samples to verify the accuracy of the method.

Table I Sample Preparation

	Sample	Dilution	Internal Standard *	Spike **
Preparation #1	Diesel Fuel	1:10	5 ppm Cobalt (Co)	None
	Fuel Oil	1:10	5 ppm Cobalt (Co)	None
	Crude Oil	1:100	5 ppm Cobalt (Co)	None
Preparation #2	Diesel Fuel	1:10	5 ppm Cobalt (Co)	Multi-Element Standard
	Fuel Oil	1:10	5 ppm Cobalt (Co)	Multi-Element Standard
	Crude Oil	1:100	5 ppm Cobalt (Co)	Multi-Element Standard

* The Cobalt (Co) internal standard was added to the high-purity kerosene used to dilute all samples and calibration standards.
** Concentrations of the spiked elements were 2 ppm.

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Instrument Operating Conditions

For all analytes of interest, background correction was performed simultaneously with the peak measurement, resulting in improved precision and detection limits. A radial analytical viewing zone was used for all samples. The operating conditions used for all sample analyses are shown in Table II.

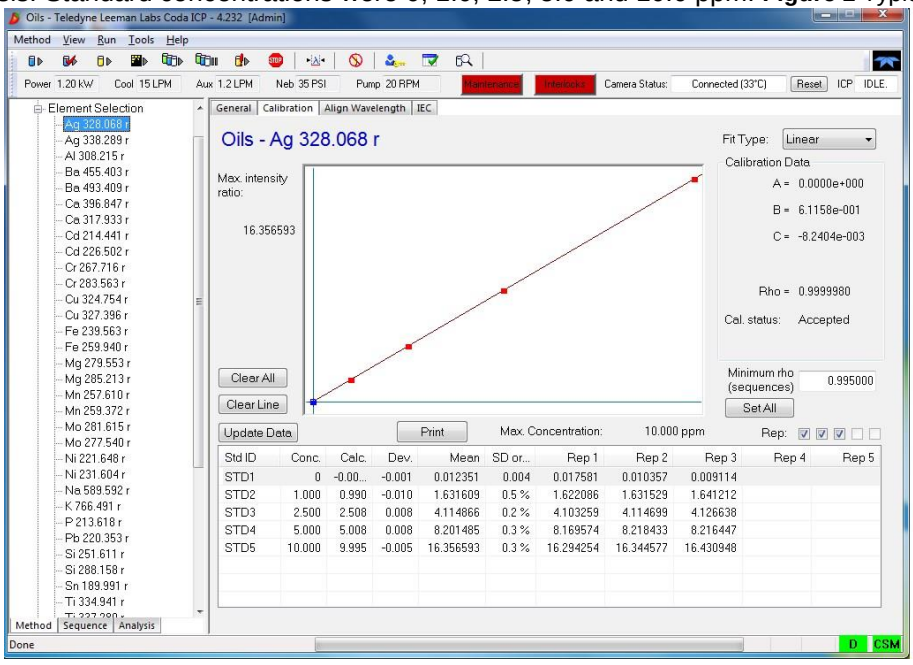
Table II Instrument Operating Parameters

Instrument*	
RF Power	1.20 kW
Coolant Flow	12 L/min
Auxiliary Flow	1.2 L/min
Nebulizer Pressure	35 psi
Uptake Rate	25 rpm
Sample Introduction	
Nebulizer Type	Ryton V-groove
Spray Chamber	Glass cyclonic with a center knockout tube
Torch	Quartz Demountable
Injector	1.1 mm bore
Sample	
Internal Standard	Cobalt (Co)
Integration Time	30 Seconds

* Radial analytical viewing zone.

Calibration

Calibration standards for all elements were prepared by diluting 100 ppm VHG V23 standard. The oil concentration in the standards was 10%. Standards and sample dilutions were performed on a weight-to-weight basis. Standard concentrations were 0, 1.0, 2.5, 5.0 and 10.0 ppm. **Figure 1** Typical Calibration Curve



Results

Detection Limits

A study was performed to determine the instrument's typical detection limits in radial view mode for the elements of interest. Detection limits were calculated based on three times the standard deviation of 10 replicate measurements of the calibration blank. Results for the detection limit study are shown in Table III.

Table III Detection Limits (DLs) in 1:10 Oil:Kerosene Matrix

Element	Wavelength (nm)	DL (mg/L)
Ag	328.068	0.001
Al	308.215	0.001
Ba	455.403	0.0004
Ca	396.847	0.0004
Cd	214.441	0.001
Cr	267.716	0.001
Cu	324.754	0.002
Fe	259.94	0.001
Mg	279.553	0.0001
Mn	257.61	0.0004
Mo	281.615	0.003
Ni	221.648	0.004
Na	589.592	0.024
P	213.618	0.012
Pb	220.353	0.029
Si	251.611	0.006
Sn	189.991	0.030
Ti	334.941	0.001
V	309.311	0.001
Zn	202.548	0.001

Samples

After igniting the plasma and allowing 15 minutes for the Prodigy7 to warm up, the instrument was calibrated using the calibration blank and standards listed in Table III. Following calibration, the samples were analyzed. Results for the fuel oil, diesel fuel, and crude oil samples are presented in Table IV, Table V, and Table VI respectively. Results for each sample are reported in units of parts per million (mg/L). Results are also presented for the recoveries of the 2 ppm spikes, along with %RSD values for the measured spike concentrations. Elements were reported as <DL if the measured concentration was at or below the instrument's detection limits (Table III).

Table IV Fuel Oil Results

Element	Measured Conc. (mg/L)	Spike Recovery %	RSD %
Ag 328.068 r	<DL	93.9	0.2
Al 308.215 r	7.00	96.4	0.2

Ba 455.403 r	<DL	97.2	0.1
Ca 396.847 r	0.74	97.3	0.1
Cd 214.441 r	<DL	95.6	0.2
Cr 267.716 r	<DL	98.5	0.2
Cu 324.754 r	<DL	96.1	0.2
Fe 259.940 r	4.27	96.8	0.1
Mg 279.553 r	<DL	99.8	0.2
Mn 257.610 r	<DL	98.5	0.1
Mo 281.615 r	<DL	98.3	0.3
Ni 221.648 r	3.33	97.5	0.1
Na 589.592 r	1.03	98.8	0.07
P 213.618 r	0.12	96.6	0.7
Pb 220.353 r	<DL	98.6	0.5
Si 251.611 r	0.15	97.3	0.2
Sn 189.991 r	<DL	99.1	0.2
Ti 334.941 r	<DL	97.6	0.1
V 309.311 r	7.08	97.1	0.2
Zn 202.548 r	<DL	97.1	0.1

Table V Diesel Fuel Results

Element	Measured Conc. (mg/L)	Spike Recovery %	RSD %
Ag 328.068 r	<DL	93.1	0.5
Al 308.215 r	<DL	93.6	0.4
Ba 455.403 r	<DL	94.7	0.4
Ca 396.847 r	<DL	94.7	0.3
Cd 214.441 r	<DL	93.9	0.4
Cr 267.716 r	<DL	95.5	0.4

Cu 324.754 r	<DL	95.2	0.3
Fe 259.940 r	<DL	95.1	0.4
Mg 279.553 r	<DL	97.2	0.4
Mn 257.610 r	<DL	96.3	0.4
Mo 281.615 r	<DL	95.1	0.7
Ni 221.648 r	<DL	94.8	0.4
Na 589.592 r	0.95	89.9	0.2
P 213.618 r	<DL	93.9	0.1
Pb 220.353 r	<DL	96.2	0.08
Si 251.611 r	<DL	93.4	0.7
Sn 189.991 r	<DL	91.1	0.5
Ti 334.941 r	<DL	94.9	0.4
V 309.311 r	<DL	94.6	0.4
Zn 202.548 r	<DL	95.2	0.5

Table VI Crude Oil Results

Element	Measured Conc. (mg/L)	Spike Recovery %	RSD %
Ag 328.068 r	<DL	107.6	0.9
Al 308.215 r	1.86	105.9	0.6
Ba 455.403 r	<DL	110.8	0.6
Ca 396.847 r	7.09	109.6	0.4
Cd 214.441 r	<DL	104.6	0.5
Cr 267.716 r	<DL	107.8	0.4
Cu 324.754 r	<DL	107.1	0.5
Fe 259.940 r	<DL	109.6	0.4
Mg 279.553 r	<DL	110.6	0.4
Mn 257.610 r	<DL	109.4	0.7

Mo 281.615 r	<DL	109.1	0.4
Ni 221.648 r	<DL	105.8	0.4
Na 589.592 r	18.7	108.0	0.1
P 213.618 r	<DL	107.5	0.5
Pb 220.353 r	<DL	109.2	0.2
Si 251.611 r	<DL	106.8	0.2
Sn 189.991 r	<DL	108.2	0.8
Ti 334.941 r	<DL	110.5	0.4
V 309.311 r	0.18	109.4	0.6
Zn 202.548 r	<DL	108.5	0.5

Conclusions

The analysis of petroleum samples was successfully performed using the Teledyne Leeman Labs Prodigy7 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 Prodigy7 can be used to provide accurate and reliable analysis of a variety of elements over a wide range of concentrations in viscous sample matrices. The use of an 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 Prodigy7 ICP-OES was well suited to the determination of elements in petroleum 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.