Determinación de elementos traza en biodiesel según ASTM Standard D-6751 - Teledyne Leeman Lab's Prodigy 7 ICP-OES

Introduction

Biodiesel is a renewable fuel produced from vegetable oil, animal fats and waste cooking oil. Additionally, feed-stocks such as soy, canola, mustard, sunflower, coconut, palm and cottonseed oil, as well as beef tallow and fish oils, have also been used. As the world's energy demand increases, the use of biodiesel has rapidly escalated. By blending biodiesel with conventional petroleum diesel, an economical fuel with acceptable emissions, material compatibility, and cold-weather performance is produced. In the United States "B20" (blend of 20% biodiesel and 80% petroleum diesel) is recognized as an alternative diesel fuel. Some of the advantages of biodiesel include:

- Reduction of toxic exhaust emissions – lower amounts of hydrocarbon (HC), carbon monoxide (CO) and particulate emissions (PM)
- Greenhouse gas savings – carbon dioxide (CO_2) produced by burning biodiesel is used by the same crops that subsequently produce more fuel
- Fast biodegradability – approximately 4-5 times faster than petroleum diesel
- Lower toxicity than petroleum diesel
- Higher flashpoint than petroleum diesel - 150 °C vs. 70 °C
- Use in diesel engines with little or no modification

Because the presence of contaminants in biodiesel can lead to performance issues, the American Society for Testing and Material (ASTM) and European Standard (EN) have developed standards to which pure biodiesel (B100) can be tested. ASTM Standard D-6751 - "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels" is shown in Table I.

Table I ASTM D-6751			
Property	**ASTM Method**	**Biodiesel Specification (B100)**	
		Limits	**Units**
Flash Point	93	130 min	°C
Water and Sediment	2709	0.05 max	% volume
Kinematic Viscosity (40 °C)	445	1.9-6.0	mm^2/sec
Sulfated Ash	874	0.02 max	Max wt. %
Sulfur	5453	15 (S15) 500 (S500)	ppm
Copper Strip Corrosion	130	No. 3 max	
Cetane Number	613	47	min
Cloud Point	2500	Report	°C
Carbon Residue	4530	0.050 max	wt %
Acid Number	664	0.080 max	Mg KOH/g
Free Glycerol	6584	0.020	wt %
Total Glycerol	6584	0.240	wt %
Phosphorus	4951	10 max	ppm
Vacuum Distillation End Point	1160	360	°C
Total Combined Na + K	UOP-389	5	ppm
Total Combined Ca + Mg		5	ppm

Failure to meet the specifications in Table I is often related to the presence of the following contaminants:

- **Phosphorus** – Phosphorus has been shown to damage the ability of after-treatment systems to reduce exhaust emissions as intended. The influence of phosphorus is cumulative. As a result, very low levels of contamination may lead to unexpected deterioration of the treatment system, when significant quantities of fuel are consumed.
- **Alkali and Alkaline Metals** – Sodium and potassium hydroxides (catalysts), and magnesium and calcium (absorbents), are used in the production of biodiesel and then removed later in the refining process. These residual metals can form deposits in fuel injection system components and poison emission control after-treatment systems.
- **Sulfur** – Sulfur levels in fuel are regulated by various governmental agencies to assure compatibility with emission standard requirements. In the United States there are currently three sulfur grades: S5000, S500 and S15, for both D1 and D2 petroleum diesel fuel. Biodiesel blends may not exceed the applicable maximum sulfur levels, as defined for petroleum diesel.

This application note will demonstrate the ability of the Teledyne Leeman Lab's Prodigy7 Simultaneous ICP-OES to measure the elemental parameters specified in ASTM D-6751. Specifically, it will focus on use of the Prodigy7 to apply the standard for measurement of P, S, Na, K, Ca and Mg in B100 biodiesel fuel.

Instrument

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 antiblooming 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, freerunning RF Generator, allowing it to handle the most difficult sample matrices, as well as common organic solvents.

Sample Introduction

For this application note the sample introduction system consisted of the following components:

- 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 and allows 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.

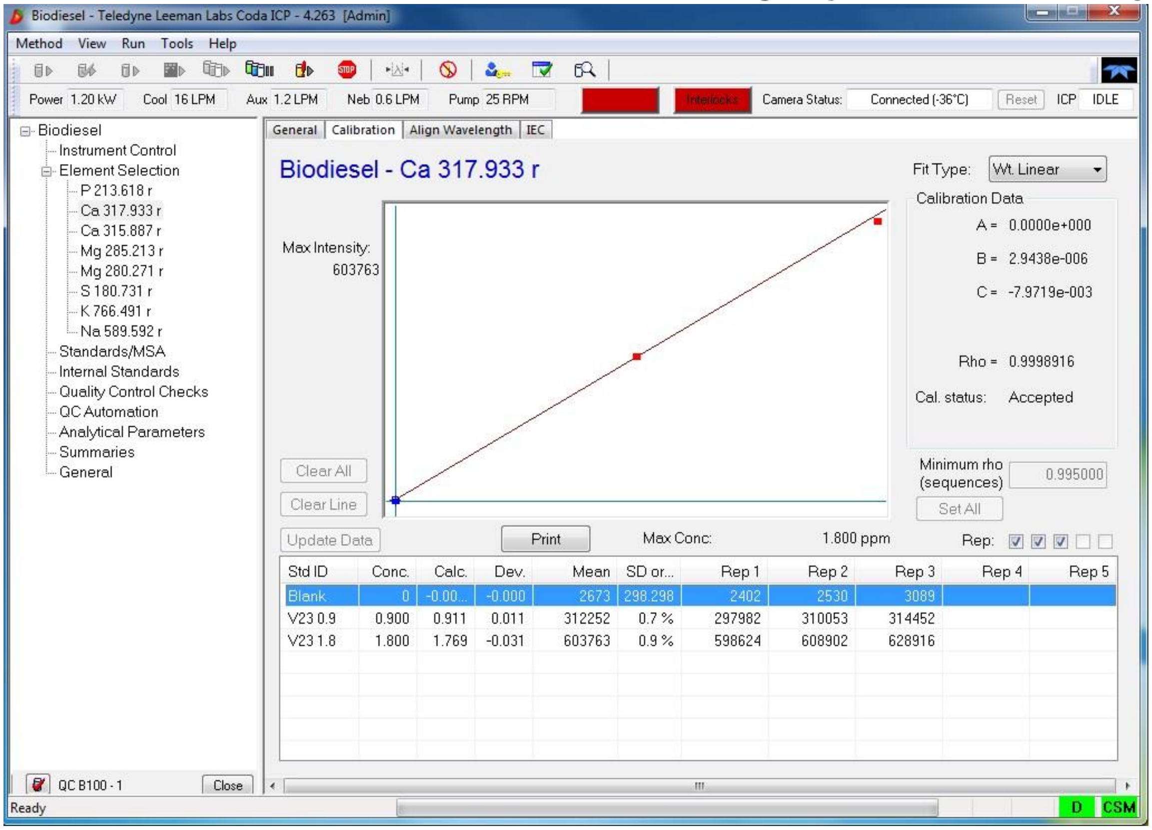
Method

To prevent matrix effects in the sample introduction system, the viscosities of samples and standards were matched as closely as possible. Under these conditions, an internal standard to correct for differences in aerosol transport efficiencies is unnecessary. VHG Labs V-Solv™ was used as a solvent for all samples and standards. All dilutions were performed on a weight-to-weight basis. The biodiesel sample was prepared by diluting 1:10. The reference standards Metals in Biodiesel 20 µg/g (P, Ca, Mg, K and Na) and Sulfur in Biodiesel 500 µg/g obtained from VHG Labs were diluted to final concentrations of 1.0 and 2.0 µg/g, respectively. The calibration standards were prepared by diluting VHG Labs 900 µg/g V23 and 5000 µg/g S standards. For matrix matching purposes, the calibration standards were prepared by diluting VHG Labs Base Oil 75 in a 1:10 ratio. The concentrations of calibration standards are listed in Table II and the calibration curve for Ca 317.933 is shown in Figure 1.

Table II Calibration Standards

Element	Blank (ppm)	STD 1 (ppm)	STD 2 (ppm)	STD 3 (ppm)	STD 4 (ppm)
P	0	0.9	1.8	-	-
Ca	0	0.9	1.8	-	-
Mg	0	0.9	1.8	-	-
S	0	-	-	2.5	5.0
K	0	0.9	1.8	-	-
Na	0	0.9	1.8	-	-

Figure 1 Ca 317.933 nm Calibration Curve



All samples were analyzed using a dual-view instrument, and all elements were measured in radial view. The operating conditions used for all data collection are listed in Table III.

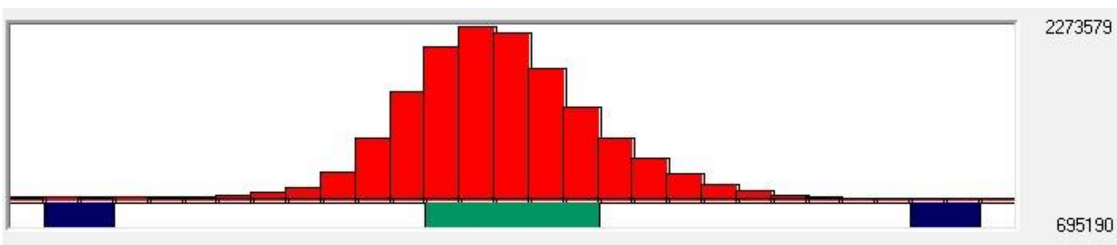
Table III Instrument Operating Parameters	
Instrument	
RF Power	1.20 kW
Coolant Flow	16 L/min
Auxiliary Flow	1.2 L/min
Nebulizer Pressure	0.6 L/min
Uptake Rate	25 rpm
Sample Introduction	
Torch	Quartz Demountable
Injector	1.0 mm bore
Sample	
Integration Time	30 seconds

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. Wavelength and background correction position data are listed in Table IV below. All data in the subarrays is collected simultaneously. Additionally, all pixel data are saved, permitting recalculation of results at a later time.

Table IV Wavelength Parameters					
Element	Wavelength, nm	Left Background Correction		Right Background Correction	
		Position	Width	Position	Width
P	213.618 r	-	-	27	2
Ca	317.933 r	2	2	27	2
Ca	315.887 r	-	-	27	2
Mg	285.213 r	2	2	27	2
Mg	280.271 r	2	2	27	2
S	180.731 r	2	2	27	2
K	766.491 r	-	-	27	2
Na	589.592 r	6	2	-	-

Figure 2 illustrates the element parameters for the Ca 317.933 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 317.933 nm Wavelength Parameter Example



Results

The results obtained from the analysis of a B100 biodiesel sample are shown in Table V. The column labeled "Final Conc., ppm" contains the concentration of the analytes after the dilution factor was applied, and "ND" indicates the analyte was not detected. The results indicate this biodiesel sample passes the ASTM D-6751 standard.

The column "Recovery, %" contains the spike recovery data for a 1 ppm spike of all the analyte elements. A separate sample was spiked with approximately 2 ppm sulfur to determine its recovery, since the multielement stock standard contains sulfur as a matrix element. The results obtained from the analysis of the reference standards, Metals in Biodiesel and Sulfur in Biodiesel, are presented in Table VI and Table VII.

Table V B100 Sample				
Element	Wavelength (nm)	Final Conc., ppm	Recovery, %	RSD, %
P	213.618 r	ND	106.6	0.9

Ca	317.933 r	0.192	102.7	0.3
Ca	315.887 r	0.179	103.7	0.6
Mg	285.213 r	0.036	95.4	0.1
Mg	280.271 r	0.052	99.1	0.1
S	180.731 r	2.315	94.4	4.4
K	766.491 r	0.401	98.1	2.1
Na	589.592 r	1.855	85.3	0.4

Table VI Metals in Biodiesel

Element	Wavelength (nm)	Conc., (ppm)	Recovery, %
P	213.618 r	1.0	85.5
Ca	317.933 r	1.0	94.5
Ca	315.887 r	1.0	95.1
Mg	285.213 r	1.0	94.6
Mg	280.271 r	1.0	92.1
K	766.491 r	1.0	85.7
Na	589.592 r	1.0	99.2

Table VII Sulfur in Biodiesel

Element	Wavelength (nm)	Conc., (ppm)	Recovery, %
S	180.731 r	2.0	94.5

Detection Limits

A study was performed to determine the Instrument 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 shown in Table VIII and are in units of parts per million (ppm).

Table VIII Detection Limits (DLs)

Element	Wavelength (nm)	DL (ppm)
P	213.618 r	0.028
Ca	317.933 r	0.003
Ca	315.887 r	0.006
Mg	285.213 r	0.0007
Mg	280.271 r	0.0001
S	180.731 r	0.307
K	766.491 r	0.029
Na	589.592 r	0.013

Conclusion

Biodiesel fuel is easily analyzed using the Prodigy7 ICP. The detection limit of the Prodigy7 readily exceeds the requirements of the ASTM D-6751 Standard against which biodiesel must be measured. Samples are easily prepared by dilution with a suitable solvent. Sample spike recoveries and reference standards results indicate that the method is suitable for the analysis of biodiesel fuels and that matrix interferences are not an issue.

References

1. ASTM D6751-15ce1, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, West Conshohocken, PA, 2015, www.astm.org