



Determination of Trace elements in Biodiesel Fuel using Inductively Coupled Plasma Optical Emission Spectrometry

Introduction

It is generally accepted that the world's fossil fuel supplies have a finite lifetime and that at some point it will be necessary to transition from the use of fossil fuels to other sources of energy. One approach to this transition that is gaining acceptance involves the use of biorenewable fuels where the feedstock is typically simple vegetation. In addition to being viable supplemental energy sources, biorenewable fuels carry with them some environmentally important advantages such as the feedstock regenerating themselves annually and consuming carbon dioxide from the atmosphere as it grows.

Biodiesel is a renewable fuel produced from feedstocks such as soy, canola, mustard, sunflower, coconut, palm and cottonseed oil as well as beef tallow, fish oils and waste vegetable oils. One example of a common biodiesel product is "B20" which is a blend of a blend of 20% biodiesel and 80% petroleum diesel.

In addition to the environmental benefits mentioned above, biodiesel carries with it a number of secondary advantages, such as:

- Reduction of toxic exhaust emissions – lower hydrocarbon (HC), carbon monoxide (CO) and particulate emission (PM)
- Lower toxicity than petroleum diesel
- Faster biodegradability – approximately 4 - 5 times faster than petroleum diesel
- Higher flashpoint than petroleum diesel – 150°C vs. 70°C
- Can be used in diesel engines with little or no modification

Biodiesel is manufactured by reacting the oil or fat under heat with an alcohol in the presence of a catalyst to give the mono-alkylesters, which is the biodiesel, and glycerol. The process is called "transesterification". Typically, methanol is used as the alcohol and sodium or potassium hydroxide as the catalyst.

Since the presence of contaminants in fuel can lead to operational problems (see **Table 1**), the American Society for Testing and Material (ASTM) has developed a standard to which pure biodiesel (B100) can be tested. The ASTM Standard is D-6751, which is shown in **Table 2**.

Element	Issue
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; and as a result, very low levels of contamination may lead to unexpected deterioration over time.
Alkali and Alkaline Metals	Sodium and potassium hydroxides are utilized as catalysts and magnesium and calcium as absorbents in the production of biodiesel and must be removed from the final product. 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 governmental agencies to assure compatibility with emission standards. In the U.S. there are three primary sulfur grades: S5000, S500, and S15, for both D1 and D2 (cold and warm weather diesel fuels) petroleum diesel fuel. Biodiesel blends may not exceed the applicable maximum sulfur levels as defined for petroleum diesel.

Table 1. Elemental contamination in diesel fuel.

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 -391	5	ppm
Total Combined Ca + Mg		5	ppm

Table 2. ASTM D-6751

A combination of physical, chromatographic and spectroscopic methods are used to apply the ASTM standard. As is often the case, trace metal analysis is an important part of quality control process for biodiesel. Accurate elemental analysis of biodiesel requires analytical methodology that is both sensitive and selective. ICP-OES meets these requirements and has the capability of determining up to 70 elements in a sample all in less than 30 seconds. ICP-OES permits close monitoring of elemental content throughout the manufacturing cycle from the raw material to the finished product. This application note will demonstrate that the Teledyne Leeman Labs Prodigy ICP can easily measure the elemental parameters specified in the D-6751 standards. Specifically, it will focus on use of the Prodigy ICP to apply the standard for measurement of P, S, Na, K, Ca and Mg in B100.

Instrument

A Prodigy High Dispersion Inductively Coupled Plasma (ICP) Spectrometer equipped with a radial view torch and an 88-position autosampler was used to generate the data for this application note.

The Prodigy is a compact bench-top simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a mega-pixel Large Format Programmable Array Detector (L-PAD). At 28 x 28 mm, the active area of the L-PAD is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows Prodigy to achieve significantly 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 6 orders of magnitude. For applications which require the measurement of chlorine, bromine or iodine an optional halogen detection system is available.



The Prodigy uses a 40.68 MHz free running, water-cooled oscillator, allowing it to handle even the most difficult sample matrices. A high sensitivity sample introduction system ensures that sufficient and steady emission signals are transmitted to the spectrometer. The torch and sample introduction system are uniquely integrated into the optical system through Prodigy's innovative Image Stabilization system, which treats the torch as an optical component by rigidly attaching it to Prodigy's optical spectrometer.

The sample introduction system consists of a four-channel peristaltic pump, cyclonic spray chamber with a knockout tube, single piece quartz torch and a Ryton™ V-groove nebulizer.

Method

To prevent matrix effects in the sample introduction system, the viscosities of samples and standards were matched as closely as possible. The viscosities of all oils tested were approximately the same. Under these conditions, an internal standard to correct for differences in aerosol transport efficiencies is unnecessary. Conostan PremiSol 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 calibration standards were prepared by diluting Plasma-Pure standards. For matrix-matching purposes, the calibration standards were prepared by diluting Conostan® base oil 75 in a 1:10 ratio. Standards

were prepared at the 0.00 ppm, 10.0 ppm and 20.00 ppm for all elements. Instrument operating parameters are shown in **Table 3**, below.

RF	1.2kW
Coolant	16 l/m
Aux	1 l/m
Neb	30 psi
Sample Uptake	1.0 ml/min
Optical Purge	low
Integration Time	30 sec

Table 3. Instrument Operation Parameters

For each wavelength, the *Prodigy* uses a 3 x 15 pixel subarray, which is centered on the wavelength of interest. Background correction points and the analytical peak have both position and width values within the subarray. In **Table 4**, the position value is designated by “x” in the column header, while “w” indicates the width. The default position for the analytical peak is 7 with a width of 3. All data in the subarrays are collected simultaneously. In addition, all pixel data are saved, permitting recalculation of results at a later time.

	Left Background Correction Position	Left Background Correction Width	Peak Position	Peak Width	Right Background Correction Position	Right Background Correction Width
P 213.618 r	1	1	7	3	12	2
Ca 317.933 r	3	2	7	3	12	2
Ca 315.887 r	1	1	7	3	12	2
Mg 285.213 r	2	3	7	3	12	3
Mg 280.271 r	2	2	7	3	13	3
S 180.731 r	1	3	7	3	12	3
K 766.491 r	5	2	7	3	10	1
Na 589.592 r	5	2	7	3	14	1

Table 4. Element Parameters

As an example, **Figure 1** illustrates the individual pixel data for the Mg 285.213 nm line. In the figure, the left and right background regions begin at pixel positions 2 and 12, respectively, with widths of 3 pixels. The analytical region of interest, where the Mg peak is found, begins at pixel position 7 and has a width of 3 pixels.

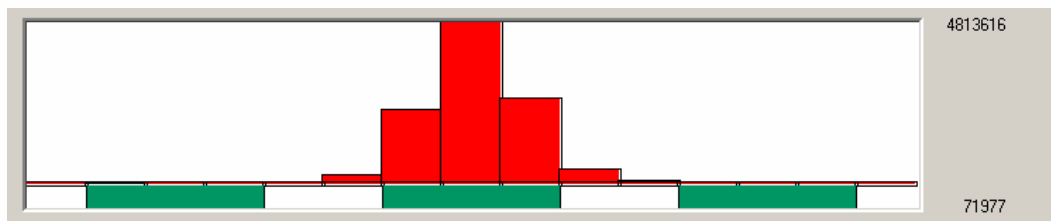


Figure 1. Mg 285.213 nm Element Parameter Example

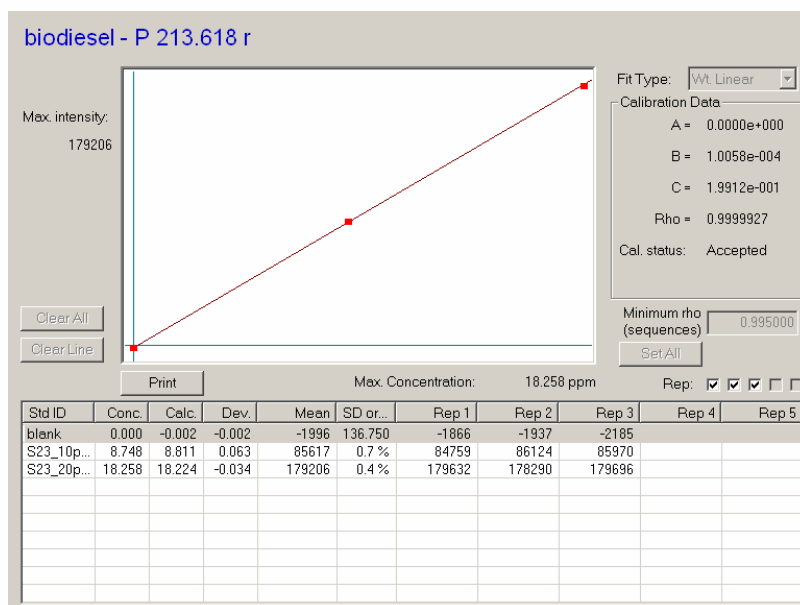


Figure 2. Typical Calibration Curve

Results

The results obtained from the analysis of a B100 biodiesel sample are shown in **Table 5**. All concentrations are displayed in ppm. The column labeled "Conc" contains the concentration of the analytes uncorrected for the 1:10 dilution. The concentrations in the original sample are listed in the column "Corrected Conc". ("ND" indicates that the analyte was not detected.)

The corrected results indicate this biodiesel sample passes the ASTM D-6751 standard. The results for sulfur also indicate it successfully passes the S-15 low sulfur designation that all highway diesel fuels will have to meet by the end of 2006.

The column labeled "% Recovery" contained the spike recovery data for a 3 ppm spike of all the analyte elements. (A separate sample was spiked with approximately 9 ppm Sulfur to determine its recovery since the multi-element stock standard contains Sulfur as a matrix element.) The spike data show excellent recoveries, indicating the 1:10 dilution is sufficient to eliminate any viscosity effects that may affect accuracy.

	Conc	SD	%recovery	Corrected Conc
P 213.618 r	0.0162	0.0101	99.1	0.1542
Ca 317.933 r	0.0022	0.0003	101.6	0.0209
Ca 315.887 r	0.0054	0.0017	99.3	0.0514
Mg 285.213 r	0.0017	0.0003	99.1	0.0162
Mg 280.271 r	0.0022	0.0001	106.8	0.0209
S 180.731 r	0.967	0.015	97.1	9.2073
K 766.491 r	0.0508	0.0269	101.1	0.4837
Na 589.592 r	ND	-	100.9	ND

Table 5. Analysis Results

Table 6 contains typical detection limits (DLs) obtained in the oil matrix. The DLs were determined by taking 3 replicate measurements in blank oil and multiplying the standard deviation by three. The detection limits indicate that the Prodigy can easily measure the analyte levels required for ASTM D-6751.

Element	DL, ppb
P 213.618 r	7.2
Ca 317.933 r	1.4
Ca 315.887 r	2.6
Mg 285.213 r	0.7
Mg 280.271 r	0.8
S 180.731 r	65
K 766.491 r	35
Na 589.592 r	20

Table 6. Detection Limits

Conclusion

Biodiesel fuel is easily analyzed using the Prodigy High Dispersion ICP. The detection limit capability of the instrument readily exceeds the requirements of the ASTM standard against which biodiesel must be measured.

Samples are easily prepared by dilution with a suitable solvent. Excellent recoveries were obtained from spiked biodiesel samples. This indicated that the method is suitable for the analysis of biodiesel fuels and that matrix interferences are not a problem.