APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Biodiesel Analysis for Inorganic Contaminants Using the Optima 8000 ICP-OES with Flat Plate Plasma Technology

Introduction

In the Unites States, the production of biofuels is primarily driven by the use of corn for ethanol and soy beans for biodiesel. Unfortunately, the competition for these raw materials has had an adverse effect on the price of food stuffs produced from these crops. The search for alternative and more efficient sources of raw materials for biodiesel production is ongoing. Biodiesel can be made from any plant or vegetable material that contains oils as well as from animal fat. Common sources include soybeans, palm, rapeseed, and tallow. However, many other sources have been used, such as peanuts, coconuts, corn, switchgrass, and algae.

ASTM® International publishes both standard test methods and specifications for pure, neat biodiesel which is also known as B100. The European Union is also involved with publishing standards for biodiesel.[1] ASTM® D6751 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels describes the requirements for the use of biodiesel as a blend component with middle distillate fuels (e.g., diesel fuel).[2] The specification contains detailed requirements for biodiesel properties, chemical constituents, and contaminants. Biodiesel must meet these specifications prior to being blended with petroleum diesel fuel or being used directly in combustion engines. There are specific maximum limits for certain elemental contaminants which may be present as a result of the biodiesel reaction catalysts (sodium and potassium), constituents

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in the raw, non-catalyzed products (phosphorus and sulfur from vegetable oils), and other contaminant sources. The presence of these elements in biodiesel and biodiesel blends is problematic for combustion engines as they may adversely affect the quality of the fuel, engine wear, or emissions. The elements calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) may form hard salts and contribute to engine wear, filter plugging, and are also known to be soap-forming elements. The elements phosphorus (P) and sulfur (S) are potential catalyst poisons for emission control systems utilizing catalytic converters. The maximum permissible limits for these elements per ASTM® D6751 are listed in Table 1.

***Table 1.* ASTM® 6751 maximum permissible limits for biodiesel properties.**

Analyte	**Maximum Limits**
Ca and Mg, combined	5 ppm (µg/g)
Na and K, combined	5 ppm (µg/g)
P	0.0010 %mass (10 ppm)
S*	0.0015 %mass (15 ppm)

* Sulfur limits may vary by region and local regulations

Currently, analysis for sulfur in biodiesel specified in D6751-11b does not include ICP-OES methods. Thus, laboratories that are specifically required to adhere to D6751 may not use this instrumentation for demonstrating biodiesel product compliance to this sulfur specification. However, ICP-OES is a very effective technique for quantification of sulfur in biodiesel[3,4] which has been demonstrated in this work and may be used for the analysis of sulfur for non-regulatory purposes.

Biodiesel that has met the specifications in D6751 may then be blended with petroleum diesel or used directly as fuel. Diesel fuel found at the pump may contain up to 5% biodiesel without labeling according to ASTM® D975 Standard Specification for Diesel Fuel Oils,[5] and biodiesel blends in the range of 6-20% (i.e., B6 – B20) must meet D7467-10 Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20).[6] Demand for use of B100 as fuel is generally limited to agricultural and non-over-the-road applications.

Within D6751 are references to specific analytical methods for the analysis of the contaminant elements. Unfortunately, there is currently no one referenced method for the analysis of all six elements even though all of them can be analyzed by ICP-OES, and in fact, all but sulfur are referenced to ICP-OES methods. As of the publication of D6751-11b, the combined elements (Ca, Mg, Na, and K) are only approved by EN 14538 Fat and Oil Derivatives – Fatty Acid Methyl Ester (FAME) – Determination of Ca, K, Mg, and Na Content by Optical Emission Spectral Analysis with Inductively Coupled Plasma (ICP-OES).[1] Phosphorus content is only approved by ASTM® D4951 Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry.[7] Sulfur content is only approved by ASTM® D5453 Standard Test Method Standard for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence[8] and some other alternate ASTM® methods, none of which are based on ICP-OES.

One of the problems with having multiple method references for what ultimately is one instrumental technique is that there are discrepancies and inconsistencies between the methods. For example, EN 14538 contains a calibration check requirement based on concentration. At the D6751 specification limit of 5 ppm, the Ca and Mg QC criterion is ± 7.8% and the Na and K criterion is ± 5.8%. It is unclear why the limits for Na and K are tighter than those for Ca and Mg as it is well known that in the analysis of organic matrices, the spectral interferences and backgrounds for Na and K are more significant than for either Ca or Mg and therefore affect both bias and precision more profoundly. Many ASTM® test methods for elements, including D4951, cite a fixed calibration check criterion of ± 5%. In addition, D4951 has not been validated by ASTM® for the analysis of biodiesel or for the concentration limit of P found in D6751. Therefore, the required calibration check criteria for the elements is either dubious or not validated, leaving the laboratory in a difficult situation as these limits are difficult to achieve at such low concentrations.

Several earlier papers were prepared by PerkinElmer for the analysis of biodiesel by ICP-OES,[3,4,9] and this work draws on aspects of those previous papers but specifically addresses the application using the new Optima™ 8000 ICP-OES. Many improvements to ICP-OES technology have taken place over the years with the most recent being the replacement of the helical load coil used to generate the plasma. The Optima 8x00 ICP-OES series utilizes the new Flat Plate™ plasma technology that replaces the traditional helical coil design used since the inception of inductively coupled plasma. Flat Plate plasma technology utilizes two flat induction plates to produce a plasma that is compact, dense and robust. This plasma utilizes about half the argon required by previous helical coil designs while still delivering exceptional analytical performance. The Flat Plate system produces a flat-bottom plasma that minimizes the escape of sample and vapors around the outside of the plasma, making organic sample analysis easier. Plasma argon flow has been reduced to 10 L/min versus the typical 15-18 L/min used by helical systems for this application, which helps to reduce the cost of analysis.

Experimental Conditions

Instrumental Parameters

All data were generated using a PerkinElmer® Optima 8000 ICP-OES with an S10 autosampler. The sample introduction system was as follows:

- Low–flow GemCone™ nebulizer (Part No. N0770358)
- 4 mm baffled cyclonic spray chamber (Part No. N0776090)
- 1.2 mm I.D. straight bore quartz injector (Part No. N0781019)
- 1.2 mm injector adapter (Part No. N0776091)

All other sample-introduction hardware was default for the Optima 8000 including the single-slot torch. A 3-slot torch (Part No. N0780132) is often used for the analysis of oils and biodiesels to minimize soot formation on the torch. With the Flat Plate technology, soot formation in general is far less of a concern, and no appreciable differences have been noticed between the single and 3-slot torches.[10]

The plasma conditions used for the analysis of biodiesel are listed in Table 2 and the analytical wavelengths for the elements are listed in Table 3.

***Table 2.* Instrumental parameters for the analysis of biodiesel using the PerkinElmer Optima 8000.**

Parameter	Setting
Ignition mode	Organics
RF power (Watts)	1500
Plasma gas (L/min)	10
Auxiliary gas (L/min)	0.8
Nebulizer gas (L/min)	0.35
Plasma view	Radial
Viewing distance (mm)	15.0
Sample pump rate (mL/min)	2
Auto integration	0.5 s min – 5.0 s max Ca, K, Mg, and Na 0.5 s min – 10.0 s max P and S
Replicates	3
Background correction	2-point
Internal standard	Cobalt
Calibration model	Linear through zero, Linear calc intercept for S

***Table 3.* Analytical wavelengths for the analysis of biodiesel using the PerkinElmer Optima 8000.**

Analyte	Wavelength (nm)
Ca	317.933
Co (Int. Std.)	228.616
Mg	279.077
P	213.617
K	766.490
Na	588.995
S	180.669

Standard and Sample Preparation

One common approach to calibrating the instrument for analysis of biodiesel is to dilute organometallic standards in a solvent such as kerosene. The standards are commercially available as organometallics in petroleum base oil. While not a major issue, these diluted oil standards do not have the same physical properties as biodiesel. The use of an internal standard can generally compensate for the physical differences but since biodiesel standards are now available (VHG Labs, Inc.), matrix matching is now much easier and the preparation of calibration standards is much simpler. The samples and calibration standards are simply diluted in the solvent prior to analysis and there are minimal corrections required of the internal standard.

For this work, all samples and standards were diluted 1:4 using V-Solv™, a refined kerosene-like solvent (Part No. N9308265). This dilution is advantageous as it helps to homogenize any potential physical differences that might exist between samples, such as viscosity, and also allows the addition of the internal standard during the dilution step. The dilution factor is minimized to maintain the needed detection limits to comply with the specifications listed in D6751. Approximately 2.5 g of a 6% cobalt (Co) stock standard (Part No. N0776107) is added to one gallon of V-Solv™, and this solution is used as the diluent for both samples and standards. If sulfur is to be included as an analyte, a sulfur-free version of the stock Co standard is available. The calibration curves were generated using the standards 0, 1, 5, 10, 20 µg/g (ppm) for Ca, Mg, Na, K, P; and using 0, 5, 10, 20 µg/g for S. The calibration blank was neat biodiesel (Part No. N9308287) also diluted 1:4 in the diluent. Mixed element standards (including Ca, Mg, Na, K, and P) in the biodiesel matrix are available in varying concentrations and can be directly diluted into the solvent or a high concentration standard can be diluted in the biodiesel blank to create lower concentration standards that are in turn diluted 1:4 with the diluent. The sulfur standards are available as single element standards, also available in various concentrations. Because all samples and standards are diluted by the same ratio, preparation can be easily automated by many simple autodilutors, and dilution factors do not need to be entered into the software unless desired for tracking purposes. If oil-based standards are used and sulfur is to be analyzed, be careful to monitor sulfur concentrations in these standards as many contain sulfonates, resulting in high sulfur background levels.

To demonstrate the efficacy of this method, in particular the calibration, secondary check standards were prepared at or below the D6751 specification limits. A mixed-element oil standard, V23 (Part No. N9308249), containing 500 µg/g of 23 elements including Ca, Mg, Na, K, and P, was diluted in V-Solv™ to create an intermediate standard. Likewise, a single-element sulfur in oil standard (VHG Labs, Inc.), containing 1000 µg/g, was diluted in V-Solv™ to create a separate intermediate standard for sulfur. These intermediates were then diluted in the biodiesel blank to yield approximately 5 µg/g for all elements, except sulfur which was diluted to 15 µg/g. These standards were then diluted 1:4 in diluent just like all the other samples and standards. This process of iterative dilutions of highly concentrated oil standards helps to produce working standards that have physical properties as close as possible to biodiesel. As previously mentioned, these standards generally need to be kept separate due to the presence of sulfonates in many of the mixed-element organometallic standards. In addition to the secondary check standards, matrix spikes were also prepared to ensure that the elements could be recovered from the biodiesel matrix. An aliquot each of two separate samples, one of palm and one of soy-based biodiesel, were spiked with the intermediate standards. The intermediate standard was concentrated enough to minimize any dilution effects from the spike, but nevertheless was accounted for in the calculations. As with the check standard, the two biodiesel samples were spiked with 5 µg/g for all elements, except sulfur which was spiked at 15 µg/g.

Results and Discussion

In this work, the actual method conditions used to analyze the biodiesel samples were also used to analyze the low-level calibration standard (1 µg/g) in replicate to determine the method detection limits (MDLs). The standard deviation of the seven replicates was then multiplied by the student's t value (3.143) for six degrees of freedom (i.e., a population of 7 replicates). These MDLs are an appropriate and realistic representation of detection limits for this work with biodiesel and are presented in Table 4.

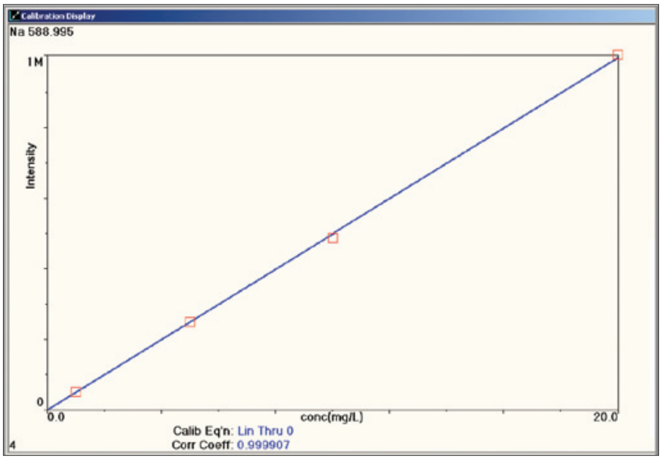
***Table 4.* Method detection limits (MDLs) for the analysis of biodiesel using a low-level standard (µg/g or ppm).**

Analyte	Standard Deviation	MDL
Ca	0.0041	0.013
K	0.022	0.070
Mg	0.0041	0.013
Na	0.025	0.079
P	0.0058	0.018
S	0.12	0.37

*These MDLs take into account the 4-fold dilution of all standards and samples. The 1 µg/g standard was diluted 4X resulting in an actual tested concentration of 0.25 µg/g.

While cobalt (Co) was the internal standard used and reported in this work, yttrium (Y) and scandium (Sc) were also evaluated. Rare earth elements, such as Y and Sc, may be affected by additives found in formulated oil lubricants and tend to be avoided for analysis of oils and fuels and Co has been found to work quite well as an internal standard. However, given that biodiesel contains no additives, the choice of internal standards is not limited. All three internal standard elements responded similarly in all of the biodiesel samples and the intensities for all three were typically within 4% of the intensity of the calibration blank.

The calibration curves were very linear with correlation coefficients (r^2) exceeding 0.999 for all elements except sulfur (Figures 1 and 2). Many of the calibration standards and reagents contain trace levels of sulfur which impact the low range of the calibration curve. Despite this low-level background contamination, the calibration curve for S yielded a very linear curve with a correlation coefficient of > 0.998.



Calib Eq'n: Lin Thru 0
Corr Coeff: 0.999907

Figure 1. Calibration curve for Na, CC=0.9999

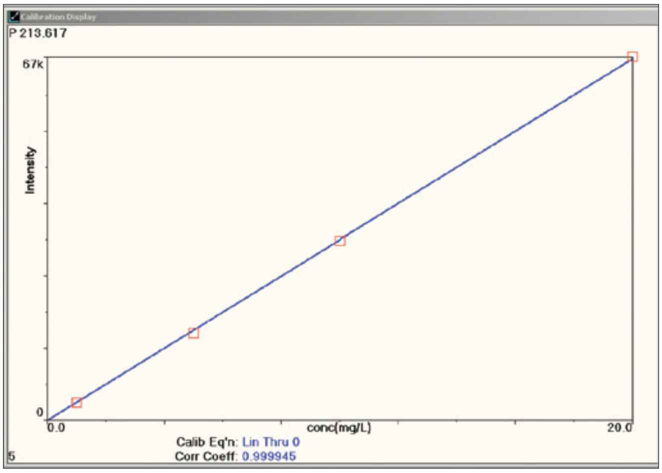


Figure 2. Calibration curve for P, CC=0.9999

A variety of biodiesel samples were analyzed from a variety of source raw materials including soy, palm, safflower, sunflower, grape seed, coconut, corn, peanut, rapeseed, and olive oils. Many of the samples contained detectable concentrations of some elements, but most of those were below the 1 ppm reporting limit. There were only two samples that did not meet the D6751 specification. Results for the analysis of all 13 samples are presented in Table 5.

Unfortunately, there are no known useful certified reference materials with which to validate this method. Both ASTM® (Crosscheck samples) and NIST® (SRM 2772) have reference materials but each represents actual biodiesel that meets the ASTM® D6751 specification for contaminant elements, and hence there are little to no detectable elements. In lieu of certified reference materials, the quality control (QC) sample and spiked samples were used to demonstrate the effectiveness of the method (Table 6).

***Table 5.* Results of the analysis of biodiesel samples according to ASTM® method D6751 using the Optima 8000 ICP-OES (µg/g)*.**

Sample	Ca	K	Mg	Na	P	S
Palm	<1	2.2	<1	<1	<1	<5
Rapeseed	<1	<1	<1	<1	<1	<5
Corn	<1	<1	<1	<1	<1	<5
Sunflower	<1	1.4	<1	<1	1.0	<5
Olive	<1	<1	<1	<1	<1	<5
Grape seed	<1	<1	<1	<1	<1	5.9
Safflower	<1	<1	<1	<1	<1	<5
Peanut	<1	<1	<1	<1	<1	<5
Coconut	<1	<1	<1	1.5	<1	<5
Palm (K)	<1	<1	<1	1.3	<1	<5
Soy (I)	<1	<1	<1	<1	<1	<5
Soy (A)	<1	<1	<1	5.9	<1	<5
Soy (B)	7.7	<1	3.2	3.2	6.4	<5

*For this work 1 µg/g or 5 µg/g for S was the lowest standard used and is considered the reporting limit for this work.

***Table 6.* Results for the analysis of a quality control and spiked biodiesel samples.**

Sample ID		Ca	K	Mg	Na	P	S
Blank	Sample	<MDL	<MDL	<MDL	<MDL	<MDL	N/A
	Spiked Sample	5.05	5.31	5.13	5.51	5.25	N/A
	Spike Level	5.00	5.00	5.00	5.00	5.00	N/A
	%Recovery	101	106	103	110	105	N/A
Soy (I)	Sample *	<MDL	0.339	<MDL	<MDL	0.147	N/A
	Spiked Sample	4.95	4.78	5.11	4.38	5.52	N/A
	Spike Level	4.96	4.96	4.96	4.96	4.96	N/A
	%Recovery	99.7	89.4	103	88.3	108	N/A
Palm	Sample *	0.200	2.08	0.167	0.905	0.142	2.93
	Spiked Sample	5.50	6.30	5.09	6.29	5.15	17.3
	Spike Level	5.01	5.01	5.01	5.01	5.01	15.0
	%Recovery	106	84.2	98.4	107	99.8	95.2

* Sample results have been corrected for the 5% dilution factor from the spike solution.

Conclusions

ICP-OES is a proven and effective technique for the analysis of biodiesel fuels and is the required technique for meeting ASTM® D6751 specifications for Ca, Mg, Na, K, and P contamination. While not approved in D6751, ICP-OES is also an effective technique for the analysis of S in biodiesel. The PerkinElmer Optima 8000 with Flat Plate plasma technology is particularly well suited for the analysis of organic samples such as biodiesel, demonstrating excellent accuracy, precision, and detection limits, even at the challenging specification limits of D6751. Even with sample dilutions, the detection limits are well below the D6751 specification limits, demonstrating more than the needed sensitivity. The stability of the Flat Plate plasma, combined with the sample introduction hardware, provides a very robust platform for the analysis of fuels and oils, including biodiesel, with no evidence of problematic soot deposits, minimizing signal drift and maintenance.

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