

Biofuels

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The Analysis of Biodiesel for Inorganic Contaminants, including Sulfur, by ICP-OES

Introduction

The alternative fuels market has been growing over the past few years and is expected to continue. Biodiesel production increased from 9 million tons/year in 2007 to 11.1 million tons/year in 2008, an increase of almost 20%. Although the fluctuating price of conventional petroleum-based fuel influences the rate of development and acceptance, it is generally acknowledged that petroleum-based fuel will run out. Governments around the world, such as the U.S., Brazil, China, and India have set goals for increased biofuel use and research into processing of raw materials that minimize competition with food and water is continuing.

Table 1. European and U.S. Specifications for Metals in Biodiesel (1,2).

Element	EN14214		ASTM D6751		Comments
	Limit (mg/kg)	Methods	Limit (mg/kg)	Methods	
S	10.0	20846 (UVFL) 20884 (XRF)	15.0	D5453 (UVFL)	D1266 (lamp), D2622 (XRF), D3120 (microcoul), D4294 (XRF)
P	10.0	14107 (ICP-OES)	10.0	D4951 (ICP-OES)	
Na	sum 5.0	14108 (AA)	sum 5.0	UOP 391	
K		14109 (AA)			
Ca	sum 5.0	14538 (ICP-OES)	sum 5.0	UOP 389	
Mg		14538 (ICP-OES)			

Biodiesel is one example of an alternative fuel. It can be used in diesel engines in a 20% mix with conventional fuel without any modification to the engine. The emissions are lower and the fuel replaces some of the lubricity lost in removing sulfur to comply with new diesel fuel regulations. Sulfur limits in conventional diesel fuel have been lowered from 500 ppm to less than 15 ppm in the U.S. and less than 10 ppm in Germany and other EU countries. Measurements of sulfur and other metals in biodiesel are important to ensure adequate performance of the fuel.

- High Levels of Na and K can form a soap solution and are common catalysts of the biodiesel reaction. If not removed they can cause instability and filter clogging.
- Ca and Mg can also form soap and the creation of problems similar to those caused by Na and K.
- Sulfur and phosphorous are both considered “carryover elements” from vegetable oil
 - P from phospholipids
 - S from glucosinilates
- Sulfur and phosphorous are both potential catalyst poisons

In the U.S. and Europe, standards have been established proving acceptable concentrations of these elements in biodiesel and are shown in Table 1.

Although methodology for sulfur does not currently include inductively coupled plasma optical emission spectroscopy (ICP-OES), it is a modern technique analytically capable of this determination. There are several ASTM methods specifying ICP-OES for a variety of elements in similar matrices, such as D7151-05, D7111-05, D5185-05, and D4951-06.⁽³⁻⁶⁾ This paper will demonstrate the measurement of sulfur using ICP-OES for biodiesel.

Experimental

The Optima™ 7000 (PerkinElmer, Inc., Shelton, CT, USA) was used for all measurements. Samples were obtained from a biodiesel producer and run with the addition of yttrium (Conostan®, Ponca City, OK). “Sulfur in Diesel Fuel” series, blank, 5, 10, and 15 mg/kg calibration standards and multielement standards (Conostan®, Ponca City, OK) were combined to provide calibration standards. Instrument conditions are shown in Table 2.

Table 2. Instrumental ICP-OES Conditions for Biodiesel Analysis.

Instrument	Optima 7000 ICP-OES
RF Power	1500 W
Nebulizer Flow	0.50 L/min
Auxiliary Flow	0.8 L/min
Plasma Flow	16.0 L/min
Sample Pump Flow	0.5 mL/min
Plasma Viewing	Radial
Processing Mode	Area
Auto Integration	2 sec min-5 sec max
Read Delay	30 sec
Rinse	30 sec
Replicates	3
Background Correction	one or two points
Spray Chamber	Cyclonic
Nebulizer	MicroMist
Injector	Ceramic 1.2 mm id
Total Analysis Time per Sample	~2 minutes

The radial mode of viewing the plasma was used for all elements because of sufficient sensitivity. Because the sample is an organic liquid, little improvement in detection limit is seen using axial viewing because of the enhancement of the organic structure. Yttrium was chosen as an internal standard because it is not usually observed in biodiesel samples, has a clean spectrum with no interferences and does not interfere with the analytes of interest. Other elements, such as cobalt, may also be a suitable internal standard element. The MicroMist nebulizer (Glass Expansion®, USA) was chosen because of the low uptake rate and excellent precision.

Two wavelengths were evaluated for determination of sulfur in biodiesel. The wavelengths selected and the resulting profiles are shown in Figure 1 for the suite of blank and calibration standards in the radial mode.

Although both wavelengths demonstrate a baseline free from structure, the S 180.669 nm wavelength is more sensitive. This wavelength was further evaluated for issues arising from typical samples of diesel and biodiesel, shown in Figure 2.

No overlaps are observed on the wavelength of interest and a rugged location was identified for a background correction point as shown by the small cross on the baseline at a slightly higher wavelength.

Results and discussion

To ensure the accuracy of the method developed, NIST 2723 Sulfur in Diesel Oil, was prepared in duplicate. Table 3 shows the results for the analysis.

The standard deviation and relative standard deviation of the three replicate measurements was very good. The relative percent difference between the two duplicate preparations and measurements was 3.5% which is well below the 20% usually deemed acceptable for environmental programs. The reference value of the standard was recovered within the tolerance of the certified value.

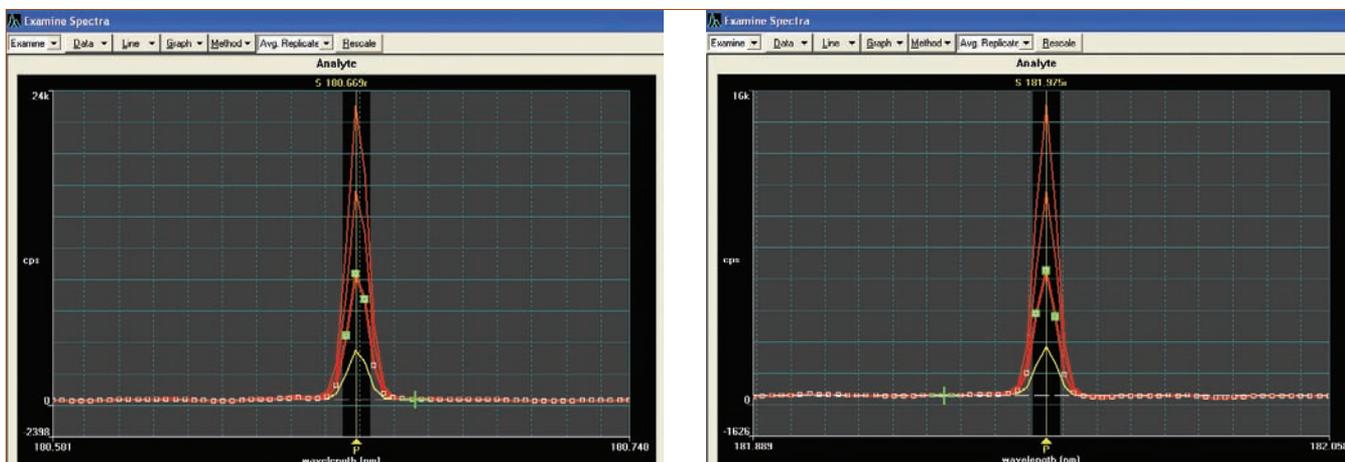


Figure 1. Evaluation of two wavelengths for sulfur determination, 180.669 nm and 181.975 nm.

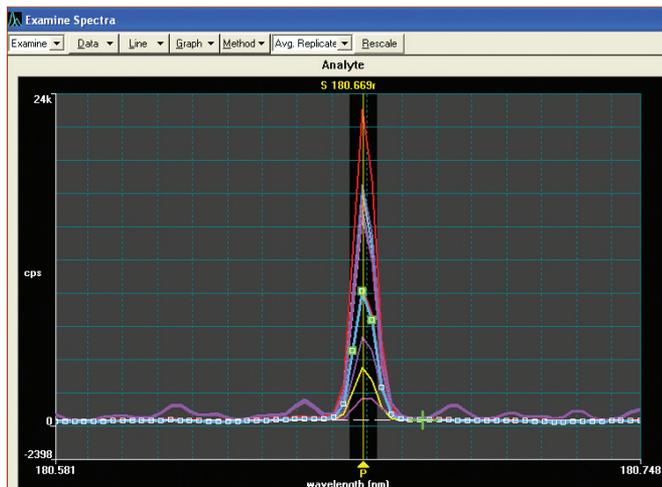


Figure 2. Calibration standards, NIST material and samples at 180.669 nm.

Table 3. Results for Sulfur (180.669 nm) from Measurement of a NIST Standard Reference Material.

Sample ID	Mean (mg/kg)	SD (mg/kg)	%RSD	RPD
NIST 2723 I	11.3	0.10	0.89	
NIST 2723 II	10.9	0.07	0.61	
Mean of Duplicates	11.1			3.5
NIST Certified Value	11.0 ± 1.1			

Several biodiesel samples from different batches were measured in the same fashion and the results are shown in Table 4. The starting material for the samples is most likely soybeans, but the sampling point in the manufacturing process (whether completely cleaned) is unknown.

Table 4. Biodiesel Sulfur Results.

Sample ID	Mean (mg/kg)	SD (mg/kg)	%RSD
B8-10-1	17.5	0.059	0.33
B8-10-2	1.56	0.11	7.13
Lot 95081	4.9	0.096	1.95

The results show measurements for a variety of concentrations, with good precision, even at the 1.5-mg/kg concentration level. The detection limit for sulfur was measured to be 0.01 mg/kg in the original fuel.

The most efficient analysis would be to measure all necessary elements in biodiesel samples at the same time. ICP-OES is a multielement technique, suited for this purpose and elements were added to the existing sulfur method. After optimization the detection limits were measured using blank oil and calculated for the original starting material (method detection limits). Detection limits are shown in Table 5 and show that we can detect far below the compliance limit, ensuring confidence at higher concentrations.

Table 5. Method Detection Limits for Biodiesel Analysis.

Element	Biodiesel Detection Limit (mg/kg)
S 180.669	0.01
P 178.221	0.09
Na 589.592	0.1
K 766.490	0.1
Ca 317.029	0.05
Mg 285.213	0.01

Table 6 shows the results for the entire suite of elements necessary to meet the U.S. and European requirements, measured in a single run for duplicate samples.

Table 6. Results for Duplicate ICP-OES Measurement of the Full Suite of Elements in Biodiesel.

Element	Sample 1 (mg/kg)	Sample 1 Dup (mg/kg)	Relative Percent Difference
S 180.669	0.64	0.60	9
P 178.221	6.9	6.8	1
Na 589.592	3.0	2.7	10
K 766.490	< DL	< DL	–
Ca 317.029	7.7	7.7	0.6
Mg 285.213	3.4	3.6	5

The agreement between two duplicate sample preparations is good, shown in the relative percent difference calculations in the last column. Values that differ by less than 20% are usually acceptable.

A variety of samples are shown in Table 7, showing biodiesel from two types of starting material, soybeans for the commercial biodiesel and used frying oil for the batch made at a nearby university. The blend combines commercial biodiesel with petroleum-based diesel fuel in a blend of 20% biodiesel.

Table 7. Analysis Results for Several Biodiesel Samples and a Blend.

Element	Commercial Biodiesel	Academic Batch	Academic Batch-washed	B20 Blend
S 180.669	0.8	0.9	0.9	4.44
P 178.221	7.6	1.5	1.2	1.6
Na 589.592	1.9	23.0	18.1	0.58
K 766.490	< DL	< DL	< DL	< DL
Ca 317.933	7.4	0.7	< DL	1.54
Mg 285.213	2.8	< DL	< DL	0.63

The values measured for Na and K would add up to 1.9 mg/kg for the commercial biodiesel, within the acceptable limit for the ASTM and EU standards. Sodium in the academic biodiesel exceeds the limit specified of a total of 5 mg/kg for Na + K. The washed version has lower sodium, but may require additional washing to reduce the sodium content below the value specified in the standard. The measurement of Ca + Mg in the commercial sample adds up to 10.2 mg/kg, exceeding the allowable limit of 5 mg/kg. This biodiesel may be a sample taken prior to washing the final product.

Table 8 shows the results for sample spikes to further ensure the method is operating properly. The samples were spiked at two levels, 5 mg/kg and 20 mg/kg. Recoveries are generally acceptable if they fall within 80-120% recovery. The results are excellent for both starting materials and the different spiking concentrations.

Table 8. Spike Recoveries at Two Concentrations.

	Commercial Biodiesel (5 ppm)	Commercial Biodiesel (20 ppm)	Academic Batch (20 ppm)
S 180.669	98	90.6	88.6
P 178.221	94.5	108	102
Na 589.592	111	107	104
K 766.490	–*	113	109
Ca 317.933	91.7	101	95.4
Mg 285.213	99.4	104	101

* K inadvertently omitted from the spiking standard.

Conclusion

ICP-OES is shown to measure sulfur in biodiesel fuel with good accuracy and precision in standard reference materials and in samples. ICP-OES is a multielement technique that can measure sulfur and other elements together in one run for an economical analysis, about 2 minutes per sample. The instrument detection capability is sufficient for the regulatory limits currently in place and lower limits that might be required in the future. The long linear range of the instrument allows for a wide range of concentrations to be measured, which may differ through out the process from raw material to finished product.

References

1. EN14214 Automotive Fuels – Fatty Acid Methyl Esters (FAME) for Diesel Engines – Requirements and Test Methods, available from www.bsi-global.com
2. ASTM 6751-07b Standard Specification for Biodiesel Fuel Blend Stock (B100 for Middle Distillate Fuels, available from www.ASTM.org

3. D7151-05 Standard Test Method for Determination of Elements in Insulating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), available from www.ASTM.org
4. D7111-05 Standard Test Method for Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), available from www.ASTM.org
5. D5185-05 Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), available from www.ASTM.org
6. D4951-06 Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry, available from www.ASTM.org

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