ICP-Optical Emission
Spectroscopy

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Quality Control of Biofuels using an Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) for Metals Determination

Introduction

Fossil fuels (oil, natural gas and coal) contribute ~80% of the total world energy supply. Depending on the production and consumption rates, the presently known reserves of fossil fuels are estimated to last anywhere from 41 to ~700 years[1,2]. The limited supply of fossil fuels, concerns for energy security and the need to respond to climate change have led to growing worldwide interests in renewable energy sources such as biofuels[3]. Many observers consider biofuels to be the only feasible option for the substitution of fossil fuels in the transport sector. Currently, the most important biofuels are biodiesel and bioethanol, commonly referred to as first-generation biofuels[4]. Biofuels are renewable fuels derived from biological feedstocks, and include both liquid forms such as bioethanol (gasoline equivalent) and biodiesel (diesel equivalent), and gaseous forms such as biogas (e.g., methane). Biodiesel, especially those derived from vegetable oils, have been highlighted as an alternative for diesel engines due to their similar physical-chemical properties to petroleum diesel and also because they decrease pollutant emissions compared with fossil fuels[5].

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Biodiesel is a collection of alkyl esters derived from renewable biosources and in its purest form it is known as fatty acid methyl ester (FAME). Biodiesel can be produced from vegetable oil (e.g., palm oil), used frying oil, or animal fat through a transesterification process in which oil molecules (triglycerides) react with an alcohol (e.g., methanol) and a catalyst (e.g., potassium hydroxide) to form FAME and glycerol (by-product)[6]. For commercial purposes, FAME is generally blended with petrochemical diesel. Blends with up to 20% biodiesel (B20) offer lubricity and can be used in diesel engines without modification. Blends can improve combustion processes, yielding reductions in particulate matter, oxides of nitrogen, sulfur and hydrocarbons. In its simplest analysis, biofuels are considered to be carbon neutral because all CO_2 released during biofuel combustion is offset by carbon fixation during plant growth[6]. Studies over the past 15 years show that the displacement of gasoline or diesel by biofuels can result in average net reductions in green house gas emissions of 31% for bioethanol, 54% for biodiesel and 71% for cellulosic ethanol[7,8].

The quality of biodiesel is critical in providing good combustion and in preserving engine integrity[9]. The raw oil is generally low in inorganic contaminants, but the final material needs to be analyzed to ensure catalyst traces are low (Na and K) or that no other inorganic contaminant has been introduced during manufacturing. Phosphorus, if present can damage the catalytic converter systems used in modern vehicles and Ca, Mg, Na, K etc. can contribute to injector, fuel pump, piston and ring wear as well as to engine deposits. Presence of metals can also degrade the oxidational stability of biofuels thereby decreasing the shelf life[10].

Regulatory aspects

The U.S. and Europe have put specifications in place to define biodiesel that is of good quality and will perform well in a combustion engine. ASTM has published specification D6751-07 for FAME and B 99.9%[11]. ASTM D975 is the specification for different diesel compositions and other blends[12]. CEN has published specification EN 14214 for the same purpose[13]. Testing is important for all manufacturers to demonstrate that their product meets quality standards. Testing may be required whenever there is a change in raw material, equipment, catalyst or even material supplier[14].

Atomic spectroscopy techniques such as atomic absorption (flame and furnace), inductively coupled plasma – optical emission (ICP-OES), and inductively coupled plasma – mass spectrometry (ICP-MS) have been used for the determination of trace elements in oils. In some cases the capabilities of the techniques overlap and several are suitable for a particular analytical scenario. This study examines the suitability of ICP-OES for the determination of trace elements in biodiesel samples. ICP-OES is a promising tool for the analyst to ensure quality of biodiesel because of its multi-element nature, wide linear range, high degree of sensitivity and high sample throughput. The present study describes the method development for the analysis of biodiesel samples obtained from different feedstocks, using an ICP-OES to demonstrate compliance with ASTM D6751 and EU EN 14214 specifications (See Table 1 for specifications). Detection limits and possible interferences were evaluated and are reported.

Table 1. **U.S. and EU specifications for elemental content in biodiesel (mg/kg).**

Metal	ASTM D6751	EN 14214
Phosphorus	10	10
Calcium Magnesium	5 (combined)	5 (combined)
Sodium Potassium	5 (combined)	5 (combined)

Sulfur limits are also specified and can be met using the ICP-OES. However, ASTM specifies different methods for this analysis, so it was not included here.

Experimental

Instrumentation and operating conditions

The measurements were performed using the PerkinElmer® Optima™ 7300 DV ICP-OES instrument (PerkinElmer, Inc., Shelton, CT, USA) equipped with WinLab32™ for ICP, Version 4.0 software for simultaneous measurement of all analyte wavelengths of interest (See Figure 1). The 7300 DV instrument accomplishes this through use of a unique echelle spectrometer and segmented-array charge coupled device detector (CCD). The plasma source is generated with a 40 MHz free running generator. The free-running nature of the generator makes it ideal for difficult matrices such as organic solvents or oil.

A PerkinElmer S10 autosampler was used for high throughput automated analysis. The optimized operating parameters for the instrument are given in Table 2. The baffled cyclonic spray chamber and alumina injector (1.2 mm internal diameter) were used to reduce the sample load into the plasma. The low-flow GemCone™ nebulizer was chosen for its ability to deliver good detection limits as well as deliver complex samples without clogging.
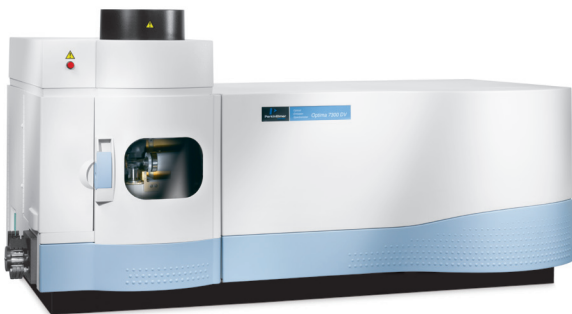

Figure 1. The Optima 7300 DV ICP-OES.

Table 2. Optima 7300 Operating Conditions.

Parameter	
Plasma gas flow	18 L/min
Auxiliary gas flow	1.6 L/min
Nebulizer gas flow	0.5 L/min
RF power	1450 watts
Viewing height	15 mm
Plasma view	Radial
Read delay	90 seconds
Read parameters	Min 0.5 and max 2.0 s
Peristaltic pump flow rate	1.0 mL/min
Processing	Peak area
Calibration	2-point, linear w/calculated intercept
Standards	1 and 10 ppm
Spray Chamber	Baffled cyclonic
Nebulizer	Low flow GemCone
Injector	Alumina 1.2 mm i.d.
Sample tubing	Solvent flex (0.76 mm)
Drain tubing	Solvent flex (1.14 mm)
Quartz torch	3-slot
Sample capillary	PTFE (1 mm)
Sample vials	Polypropylene

Standards, chemicals and equipment

A 23-element oil standard in base oil 75 (V23, PerkinElmer, Shelton, CT, USA) (500 μg/g) for ICP was used as the stock solution for preparing working standards. All standards (1 ppm and 10 ppm) were prepared in high purity kerosene procured from Spex (Spex Certiprep®, Metuchen, NJ, USA). Blank oil for analysis was prepared from PerkinElmer base oil 75 with high purity kerosene. Cobalt, used as internal standard, was also from PerkinElmer. For quality control, a multielement metallo-organic oil standard from Spex Certiprep® was used. Working standards were prepared daily in polypropylene vials from Sarstedt® and were prepared by weight-to-weight dilution. A Sartorius® analytical balance was used for all weight measurements. Eppendorf® micropipettes were used for pipetting solutions.

Sample preparation

Two B100 samples from two different feedstocks (Jatropha and palm oil) were obtained from commercial sources and used without further purification. Samples were prepared by a 10-fold weight dilution with high purity kerosene and were prepared in duplicate. Before adding to samples and standards, Co internal standard was added to the diluent (10 ppm) in order to compensate for viscosity and matrix-related interferences. One sample from each feedstock was spiked with the quality control standard for which concentration was selected to fall at the ASTM-specified value. A working blank was prepared by diluting the base oil 75 with diluent.

Results and discussion

Detection limits were determined using an integration time of 2 seconds and were the results of multiplying the standard deviation of the blank (ten replicates) by three. The detection limits are shown in Table 3 for both the solution introduced into the instrument and in terms of the original biodiesel sample taken for dilution. The table shows that the detection limits obtained are far below the ASTM specified limits for compliance.

Table 3. Estimated Detection Limits.

Element	Wavelength (nm)	Instrument DL (mg/kg)	Biodiesel DL (mg/kg)
Phosphorus	213.620	0.04	0.4
Sodium	588.993	0.02	0.2
Potassium	766.485	0.08	0.8
Calcium	422.673	0.004	0.04
Magnesium	285.213	0.002	0.02

The accuracy of the calibration curve was confirmed by calibrating with a 1 mg/g and 10 mg/g solution of V23 and then analyzing a QC standard of 5 mg/g from a different source (See Figure 2). The calibration curve was linear across the entire range with a correlation coefficient of at least 0.999 for all elements. The analysis showed agreement between the samples prepared in duplicate with good %RSD (See Table 4). Further, spike analysis studies showed good recovery ranging between 90-110%.

The goal of ICP-OES method development was to generate a method which would be most useful for routine quality control of biodiesel samples from different feedstocks. The wavelengths and background correction points were chosen based on their freedom from spectral interferences.

Quality control sample recovery values obtained show the stability (See Table 5) in instrument performance with respect to time. In optimization of the speed of analysis, the integration time used

Table 4. Analysis of Biodiesel Sample Duplicates.

Sample	Element	Wavelength (nm)	Replicate 1 (mg/kg) (%RSD)	Replicate 2 (mg/kg) (%RSD)
B100 Jatropha	Phosphorus	213.617 214.914	23.8 (0.4) 25.0 (0.8)	23.9 (2.3) 26.3 (1.6)
	Sodium	588.995 589.592	12.2 (5.2) 13.0 (2.8)	13.0 (1.6) 13.8 (0.8)
	Potassium	766.485	<DL	<DL
	Calcium	393.366 422.673	35.1 (1.4) 33.4 (1.9)	36.3 (1.1) 34.8 (0.3)
	Magnesium	279.077 285.213	22.1 (1.3) 21.1 (1.4)	22.1 (1.7) 21.7 (0.23)
B100 Palm Oil	Phosphorus	213.617 214.914	0.6 (34) <DL	0.07 <DL
	Sodium	588.995 589.592	0.51 (37) 0.23 (19)	0.82 (2.8) 1.6 (19)
	Potassium	766.485	<DL	<DL
	Calcium	393.366 422.673	0.24 (2.2) 0.50 (5.6)	0.17 (2.5) 0.44 (8.7)
	Magnesium	279.077 285.213	<DL 0.12 (4.1)	<DL 0.10 (8.5)

Table 5. Results of Spike Recovery and QC Analysis.

Sample	Analyte	Wavelength	% Spike Recovery	QC Recovery % (Start)	QC Recovery % (End)
B100 Jatropha	Phosphorus	213.617 214.914	108 110	89.1 90.0	89.2 90.2
	Sodium	588.995 589.592	107 108	91.8 91.2	90.1 90.7
	Potassium	766.49	103	92.7	88.4
	Calcium	393.366 422.673	107 109	91.3 88.0	91.3 90.0
	Magnesium	279.077 285.213	110 109	92.3 93.4	92.8 93.2
B100 Palm Oil	Phosphorus	213.617 214.914	96.4 79.9	89.1 90.0	89.2 90.2
	Sodium	588.995 589.592	92.8 101	91.8 91.2	90.1 90.7
	Potassium	766.49	99.2	92.7	88.4
	Calcium	393.366 422.673	102 94.8	91.3 88.0	91.3 90.0
	Magnesium	279.077 285.213	86.6 103	92.3 93.4	92.8 93.2

was two seconds (max). The total time from sample to sample including wash-in and wash-out of the sample was 130 seconds. Since wash-out or rinse time significantly contributes to the speed of analysis, the wash time could be reduced by using the flush option of the instrument. During oil sample analysis, it is very important to check for carbon deposits in the ICP torch and injector regularly. If excess carbon deposition is found, it should be cleaned by burning off the carbon in a muffle furnace set at 550 ˚C.
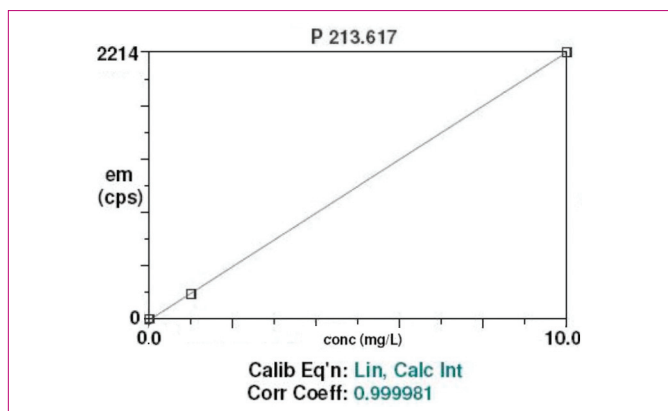

Figure 2. Calibration curve for phosphorus.

Two wavelengths were included for several elements as a quick check for unexpected interferences. When good agreement is seen in values obtained at the two wavelengths specified, it provides additional confidence in the values reported. Once a variety of samples have been tested and the wavelengths fully characterized with the matrix, the list can be reduced to one wavelength per element to reduce the analysis time. If a small sacrifice in productivity can be tolerated, this additional wavelength information would increase analysis confidence.

Conclusion

The two biodiesel samples measured from Jatropha and palm oil provide a good test of the method because they have different compositions and possible interferences. They also come from different points in the refinement process and therefore have differing levels of residual contamination. Limit of quantitation for any analysis is usually determined to be at least 10 times the method detection limit. This is the reason for poor precision in the case of palm oil-based B100, since the concentration values are close to the quantitation limit. The palm oil-based B100 showed results for all the metals falling below the ASTM specified limits and thereby passing the U.S. and EU specifications. But the Jatropha-based B100 does not pass the limits specified in the ASTM and EU standards, indicating further refinement is necessary before the product is used in a combustion engine.

The Optima 7300 DV simultaneous ICP-OES can be utilized successfully for routine quality control of biodiesel samples, as it offers excellent detection limits, exceptional accuracy and good %RSD at regulatory levels. It provides for very fast analysis with a sample (3 replicates) taking approximately 130 seconds to run. For higher productivity, optimization of the sample wash-in and wash-out may provide further improvements.

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