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Elemental Analysis of Biodiesel

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Key Words

- iCAP 6300 Duo
- Biodiesel
- Organics

Benefits in Brief

- Simplified method development via software tools.
- Duo configuration allows optimum plasma view for different wavelengths.

Introduction

Many countries are looking to biofuels for greater energy security and as a long term solution to reducing carbon emissions. Brazil is one of the most successful countries so far at implementing national biofuel programs with 43.8 %[1] of energy being produced from renewable sources (of which biofuels are a large contribution). Bioethanol has been used for a number of decades with great success in the country as an alternative to mineral oil based petroleum. In 2004 The National Program for the Production and Use of Biodiesel (PNPB) was created by President Luiz Inácio Lula da Silva[2].

The main aims of PNPB are to introduce biodiesel in to the market as a blend with mineral oil based diesel, with the biodiesel component at 2 % (B2), which will negate the need to convert engines to be compatible with biodiesel. Over a defined period of time the concentration of biodiesel in the blends will be increased. As part of this policy all new diesel vehicles sold after a specified date must be compatible with biodiesel.

Biodiesel is produced by the transesterification of biological oils. This reaction occurs in the presence of a catalyst such as sodium or potassium hydroxide.

The quality of biodiesel in Brazil is controlled by specifications set by the National Petroleum Agency (ANP). For export reason the ANP also requires Brazilian biodiesel to meet the requirements of ASTM and European methods (Table 1 below).

	Units	Specification	Standard		
			ABNT NBR	ASTM	EN/ISO
Group I Na & K	mg/kg	5 max (combined)	15553 15554 15555 15556	-	EN 14108 EN 14109 EN 14538
Group II Ca & Mg	mg/kg	5 max (combined)	15553 15556	-	EN 14538
Phosphorus	mg/kg	10 max	15553	D6751	EN 14107
Sulfur	mg/kg	10 (EN) 15 (ASTM)	-	D6751	EN ISO 20846 EN ISO 20884

Table 1: Biodiesel specifications.

According to these standards the elements that can be determined by ICP-OES are sodium, potassium, calcium, magnesium and phosphorus. According to the regulations set out by ANP, sulfur should be determined by x-ray techniques. Due to the multi-element capabilities of ICP-OES sulfur can also be determined using this technique. ANP and ABNT (Brazilian Association of Technical Standards) have been working on the validation of this method.

The method described in this paper has been developed as part of a Brazilian national project to establish a network of biodiesel testing facilities in response to the PNPB.

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Method

Standard preparation

Standards were prepared from S21 (The S21 standard contained the following elements Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn) and potassium oil based standards. These were diluted by weight with blank kerosene to cover the expected concentration range and taking the maximum allowed values into account (Table 1). The organo-metalic compounds in the oil based standards are metal-alkylsulfonates, for this reason separate standards for sulfur were prepared from oil based sulfur standards.

Only six elements in the standards were required for analysis to meet the specifications in Table 1. Analysis of the additional elements in the S21 standard is not compulsory but can provide useful information relating to the biodiesel and quality issues that may affect the fuel's manufacture, storage or performance.

Sample preparation

Biodiesel samples can be analyzed directly without sample preparation. The viscosity of biodiesel samples can vary so a dilution may need to be performed to negate these effects. This prevents low recoveries on samples with higher than average viscosities. Typically a 10-fold dilution (on a weight basis) with a suitable solvent such as kerosene is carried out.

An alternative to dilution is the addition of an internal standard. Selection of the internal standard compound is critical to the analysis. A good choice of internal standard is a group of compounds known as Naphthenates (one such example is cobaltnaphthenate).

For the samples used in this case, the viscosity of the biodiesel was deemed not to be an issue and samples could be analyzed directly. If the analysis of raw materials such as plant oil is to be performed, a ten fold dilution is necessary.

Spikes of the samples were also prepared to check the recovery of the elements. An aliquot of the sample was weighed and a known amount of the oil-based standards was added to the sample. This was then made up to a known weight with a suitable solvent. This method was used for simplicity as opposed to preparing intermediate standards and spiking small volumes in to a known amount of sample.

Instrumentation

The Thermo Scientific iCAP 6300 Duo was used for the analysis. This has full wavelength coverage from 166 to 847 nm with Fullframe capability which offers full spectrum trend analysis and contamination identification between batches of biodiesel produced. The iCAP 6300 Duo has the ability to view the plasma both axially for low level elements and radially for elements at higher concentrations and to avoid interferences.

The non-volatile organics sample introduction kit was used for the analysis and the plasma and sample introduction parameters are shown in Table 2 below.

Parameter	Setting
Pump Tubing	Sample – Viton – Orange/White Drain – Viton – White/White
Pump Rate	25 rpm
Nebulizer	V-Groove
Nebulizer Gas Pressure	0.16 MPa
Spray Chamber	Glass Cyclonic Baffled
Center Tube	1 mm
RF Power	1250W
Coolant Gas Flow	12 L/min
Auxiliary Gas Flow	1.5 L/min
Integration Time	High Wavelengths 10s Low Wavelengths 5s

Table 2: Plasma and sample introduction parameters used for the analysis.

Method development

Wavelengths for the elements of interest were selected. The wavelengths selected were based on the relative sensitivity and possible interferences on the wavelength. The software associated with the iCAP 6000 Series contains an interference library holding this information. In addition to the wavelength selected, the decision to read the wavelength using the axial or radial view of the plasma had to be taken. This was based on the required sensitivity and also possible interferences resulting from the matrix present. In the case of biodiesel the main matrix element is carbon. Carbon-based emissions occur in the cooler regions of the plasma and generally emit light in the visible region of the spectrum; this would mainly affect group I and II elements. These elements were measured using both the axial and radial view of the plasma.

A Fullframe of the high standard and the blank was taken. This is a graphical depiction of the spectrum of the sample. This allows the identification of inferences and contamination of solvents and standards. This aids in the selection of wavelengths for analysis and can also be used to fingerprint batches of samples.

The standards and samples were then analyzed. The sub-array plots (spectral peaks) for each of the wavelengths of interest was examined. The background correction and the peak integration zones were adjusted to correct for any interferences.

The instrument was then calibrated with the prepared standards and the samples were analyzed. A detection limit study was also carried out by analyzing a blank solution with 10 replicates, then multiplying the SD (standard deviation) of the replicates by three. A single wavelength for each element was then selected based on the DL, spike recoveries and linearity of the calibration graphs (Table 3 below).

	Axial			Radial		
	DL mg/kg	QL mg/kg	Coefficient	DL mg/kg	QL mg/kg	Coefficient
Ca 184.006 nm	0.003	0.01	0.999999	0.0132	0.044	1.000000
K 769.896 nm	0.0264	0.088	0.999874	0.1353	0.4510	1.000000
Mg 279.553 nm	0.0003	0.001	0.999992	0.0006	0.0020	0.999986
Na 589.592 nm	0.0156	0.0520	0.999987	0.0177	0.0590	0.999992
P 178.866 nm	0.0147	0.0490	0.999994	0.1113	0.3710	0.999994
S 180.731 nm	0.0087	0.0290	0.999999	0.0444	0.1480	0.999979

Table 3: Results of the detection and quantification limit study with typical calibration correlation coefficients.

Results

In the absence of a certified reference material (CRM), spike recoveries were used to assess the performance of the method. The recoveries of the spiked samples are within acceptable limits (+ or – 5 % of the spiked value, see Table 4 below).

	Spikes					
	Blend PIB			Residual oil		
	Found mg/kg	Spike mg/kg	Recovery %	Found mg/kg	Spike mg/kg	Recovery %
Ca 184.006 nm Radial	0.7256	0.7958	91.1	0.7243	0.7526	96.2
K 769.896 nm Axial	1.0765	0.0513	100.8	1.1131	0.0958	100.5
Mg 279.553 nm Axial	0.8148	0.7958	102.3	0.0962	0.0958	99.2
Na 589.592 nm Radial	0.2180	0.0999	100.3	0.2181	0.0958	100.4
P 178.866 nm Axial	0.0755	0.0513	99.4	0.0984	0.0958	99.9
S 180.731 nm Radial	0.9429	0.0643	99.6	1.6306	0.0556	100.7

Table 4: Results of the spike analysis.

The standards were also analyzed as unknowns to determine the reproducibility of the instrument. The results are shown in Table 5 below and demonstrate that the concentrations found when the standards were analyzed as unknowns are in good agreement with the prepared values (+ or – 5 % of the prepared values).

	Prepared standard concentration mg/kg	Found standard concentration mg/kg
Ca 315.887 nm Radial	0.50873	0.5083
K 769.896 nm Axial	0.50873	0.5048
Mg 279.553 nm Axial	0.50873	0.4947
Na 589.592 nm Radial	0.50873	0.5039
P 178.766 nm Axial	0.50873	0.5088
S 180.731 nm Radial	0.50097	0.5197

Table 5: Results of analyzing the standards as unknowns.

The results of the sample analysis (Table 6 below) show that all of the samples submitted for analysis generally have low concentrations of the elements of interest with the exception of sulfur and sodium. The high concentration of sodium in the samples is an indication that residues from the catalysts are still present in the samples. The elevated concentration of sulfur in the samples is likely to have originated from the plant oils used to manufacture the biodiesel and selection of low sulfur oils could avoid these elevated concentrations. Not all of the samples analyzed meet the current specification for biodiesel with Bioamax and residual oil failing for sulfur.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Ca 315.887 nm Radial	0.5184	<DL	0.0059	0.0003	0.0002	0.0940
K 769.896 nm Axial	0.2942	0.0683	0.0984	0.3672	0.0951	0.3078
Mg 279.553 nm Axial	0.0386	0.0015	0.0005	0.0030	0.0009	0.4400
Na 589.592 nm Radial	0.8097	1.4000	0.8160	0.8568	0.8215	1.2540
P 178.766 nm Axial	0.5078	0.4592	0.3674	0.2980	0.3558	0.5147
S 180.731 nm Radial	18.02649	39.69855	1.8110	2.1210	0.5002	2.1660

Table 6: Results of the biodiesel analysis expressed in mg/kg.

Conclusions

The iCAP 6300 Duo is capable of analyzing biodiesel samples, producing low detection limits and accurate results, facilitating compliance measurements. The spike recoveries and values for standards analyzed as unknowns demonstrate the accuracy and reproducibility of the method.

The detection limits obtained are well below the maximum permitted levels set out in varying biodiesel quality standards and allow for future reductions in these levels.

The Fullframe capabilities of the iCAP 6300 allow non-method elements to be defined which is an essential tool for trouble shooting in manufacturing processes.

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