# Efficient Biodiesel Analysis Using ICP Emission Spectrometry

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Due to the increasing cost of petroleum, depleting reserves and the growing environmental concerns surrounding the use of petroleum, many governments, companies and increasingly consumers, are investing in renewable energy sources such as biodiesel. Biodiesel is a more environmentally friendly alternative to diesel fuel, commonly produced through the transesterification of vegetable oils or animal fats. Biodiesel can be used in its pure format (B100) or blended with petroleum diesel at varying concentrations. In order for biodiesel to be qualified for use, it needs to comply with a set of regulations specifying the maximum concentrations of certain elemental contaminants in the final blend.

This article will discuss the benefits deriving from the use of biodiesel, the fuel's varying applications and the regulations governing its production and use. An experiment will be described to demonstrate the suitability of radial view Inductively Coupled Plasma (ICP) emission spectrometry for effective biodiesel analysis.

## Benefits

One of the most important benefits driving the rising use of biodiesel is energy security and the reduction of fossil fuel-dependance.[1] In addition, biodiesel has better lubricating properties compared to contemporary lower viscosity diesel fuels. As a result, blending biodiesel with petroleum diesel reduces engine wear, thus increasing the life of fuel injection equipment such as high pressure injection pumps and fuel injectors.[2] Featuring greater lubricity and comprehensive combustion capabilities, biodiesel leads to an overall fuel efficiency improvement of about 2% when compared with petroleum diesel.[3]

A further significant benefit of plant-based biodiesel is that it is almost carbon neutral. Biodiesel is produced from plant cops which absorb carbon dioxide from the atmosphere during their growth. This effectively balances the emission of carbon dioxide resulting from burning the fuel. When blended with petroleum diesel, biodiesel can also reduce other potentially environmentally harmful emissions, such as sulfur dioxide, when compared with unblended petroleum diesel. This is because biodiesel fuels contain a lower concentration of sulfur than their fossil fuel counterparts.

## Applications

Currently, biodiesel can be used in a wide range of applications while new areas of applicability are continuously examined. The transportation industry presents many opportunities for biodiesel, which is already being used in vehicles and trains and has been tested for use in aircraft. However, aviation is a particularly challenging application area due to the inherent risks of air travel. Biodiesel can also be used as a heating fuel in both domestic and commercial boilers and can burn biodiesel without any conversion required. Furnaces become more efficient and according to a study conducted by Andrew J. Robertson and presented at the Biodiesel Expo 2006 in the UK, B20 biodiesel used as heating fuel could reduce household $CO_2$ emissions by 1.5 million tons per year.[4]

## Regulations

Currently, there are two main standards governing the production and use of biodiesel. Introduced in February 2003, EN 14214 is an international standard that describes the minimum requirements for biodiesel. EN 14214 specifies requirements and test methods for marketed and delivered fatty acid methyl esters (FAME) to be used either as automotive fuel for diesel engines at 100% concentration, or as an extender for automotive fuel for diesel engines.[5]

ASTM D6751 is the most common standard referenced in the United States and Canada, covering pure biodiesel grades S15 and S500 for use as a blend component with middle distillate fuels. The standard prescribes the required properties of biodiesel fuels at the time and place of delivery while the same requirements may also be applied at other points in the production and distribution process, provided that there is relevant agreement between the supplier and the purchaser.[6]

These regulations require that the concentration of elemental contaminants in biodiesel, as well as the biodiesel/diesel percentage are regularly monitored to ensure optimum engine performance and to avoid any potential failures. This is especially important in the aviation industry where the tendency of biodiesel to freeze in the frigid air at 35,000 feet poses serious risks.[7] Both of the standards ensure that important prerequisites in the fuel production process are satisfied, including acid value, complete reaction, the removal of glycerin, catalyst and alcohol, the absence of free fatty acids, low sulfur content, cold filter plugging point and cloud point.[8]

## The Need to Analyse Biodiesel

The majority of biodiesel production facilities currently use plant oils as a starting material for production. However, the presence of these plant oils poses a serious disadvantage since these plants contain a relatively high phosphorous content. Phosphorous is an undesirable element in fuels as it can lead to the corrosion of the mechanical components of engines, and this is especially true in the case of jet fuels. Sulfur is also an element of interest as it degrades engine wear if present in excess concentrations in the starting materials. As a consequence, the content of phosphorous and sulfur in biodiesel fuels is tightly controlled by fuel quality and environmental legislation (*Table 1*).

| | Europe | USA |
|---|---|---|
| Specification | EN 14214 | ASTM D6751 |
| Sulfur | 10 max | 15 max |
| Phosphorous | 10 max | 10 max |
| Group I metals (Na & K) | 5 max (combined) | |
| Group II metals (Ca & Mg) | 5 max | |

*Table 1: European and USA biodiesel specifications. All concentrations expressed as mg/kg.*

The amount of both phosphorous and sulfur in biodiesel is ultimately determined by the concentrations of these two elements in the starting materials. By carefully selecting plant oils which are low in these two elements, the concentration in the final product can be controlled. In response to these constraints, it is important to use a powerful method capable of providing accurate and reliable measurements of the concentration of elemental contaminants in biodiesel. An experiment was developed to test the suitability of both duo view and dedicated radial view ICP emission spectrometry for this type of analysis.

## Experimental

### Instrumentation

A Thermo Scientific iCAP 6000 Series ICP emission spectrometer was used to perform the analysis. A standard organics sample introduction kit was used for the analysis and Solvent Flex pump tubing was preferred over the traditional Viton pump tubing as the former is more resistant to biodiesel.

Both the radial and duo view configurations of the iCAP 6000 Series can be used for this analysis. Traditionally, the duo view has been the configuration of choice for ICP emission spectrometers used to perform biodiesel analyses, due to significant disadvantages encountered with many radial view ICP instruments and the perception that axially viewed plasmas can produce superior performance in biodiesel matrices. However, latest advancements in radial plasma view technology offer a more robust option and minimize the carbon-based emission interferences associated with the duo's axial view configuration. When compared to the radial view configuration, the axial view of the duo configuration offers a longer viewing path-length and an inability to select a viewing position which minimises the collection of molecular emissions. This increases carbon-based interferences, effectively cancelling out any expected increase in sensitivity due to an increase in the background signal.

### Sample preparation

A sample of biodiesel derived from used cooking oil (multi-source) was obtained from a local supplier. This sample was diluted by a factor of ten with kerosene on a weight-to-weight basis. An additional aliquot of the sample was diluted and a multi-element spike, from oil-based standards (Conostan S-21, Conostan, Baie D'Urfé, QC, Canada), was added.

### Standard preparation

Multi-element standards were prepared from Conostan S-21 300 mg/kg oil-based standards and a separate potassium Conostan 5000 mg/kg oil-based standard.

A single element standard for sulfur was prepared from Conostan 5000 mg/kg sulfur standards. All standards were diluted in kerosene and blank oil was added to match the diluted oil concentration of 10% by weight. The standards were prepared to cover the expected concentration range of the elements of interest, namely 0.025 mg/kg to 1 mg/kg.

### Method development

A method was developed containing the wavelengths of interest. The auxiliary and nebulizer gas flow were adjusted to ensure that the base of the plasma was approximately 1 mm from the load coil on the duo view configuration and 1 mm below the coil on the radial view configuration. The nebulizer gas flow was then adjusted to ensure that the sample channel extended approximately 3 mm from the load coil. The other sample introduction parameters such as pump speed and radial viewing height were adjusted to provide the best signal-to-background ratio (*Table 2*).

| Parameter | Duo | Radial |
|---|---|---|
| Pump tubing | Sample<br>Solvent Flex<br>Orange/white<br>Drain<br>Solvent Flex<br>White/white | Sample<br>Solvent Flex<br>Orange/white<br>Drain<br>Solvent Flex<br>White/white |
| Pump rate | 40 rpm | 40 rpm |
| Nebuliser | V-groove | V-groove |
| Nebuliser gas flow | 0.4 L/min or 0.14 MPa | 0.4 L/min or 0.14 MPa |
| Spray chamber | Glass cyclonic baffled | Glass cyclonic baffled |
| Centre tube | 2 mm | 1 mm |
| RF Power | 1250 W | 1150 W |
| Coolant gas flow | 12 L/min | 12 L/min |
| Auxiliary gas flow | 1.5 L/min | 1.5 L/min |
| Integration times | Low 10 seconds<br>High 5 seconds | Low 10 seconds<br>High 5 seconds |
| Radial viewing height | NA | 12 mm |

*Table 2: The parameters used for the analysis*

The instrument was then calibrated and the samples analysed in a single run. The sub-array plots for each of the wavelengths were examined and adjustments to the central integration region and background correction points were made, as necessary, to correct for interferences. This process would need to be performed only for method setup and is not a necessary step once the method is set. A detection limit study was performed by measuring ten replicate analyses of a matrix-matched blank. The standard deviation of the results of the ten replicate readings were multiplied by three to provide the detection limits.

## Results

The results of the sample analysis, spike recoveries and detection limits are demonstrated in *table 3*.

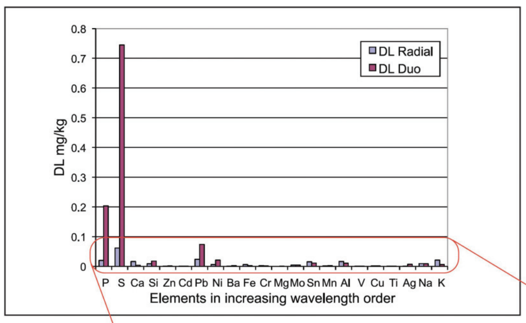
| | Radial mg/kg | | | | Duo mg/kg | | | |
|---|---|---|---|---|---|---|---|---|
| | B100 Dilution Corrected | Spike Found | Spike Recovery (%) | DL | B100 Dilution Corrected | Spike Found | Spike Recovery (%) | DL |
| Ag 338.289 nm | <DL | 0.58 | 99.4 | 0.0008 | 0.12 | 0.57 | 98.8 | 0.0068 |
| Al 308.215 nm | <DL | 0.56 | 96.2 | 0.0163 | <DL | 0.59 | 100.7 | 0.0105 |
| Ba 233.527 nm | <DL | 0.60 | 102.7 | 0.0010 | <DL | 0.59 | 101.5 | 0.0023 |
| Ca 184.006 nm | <DL | 0.65 | 111.0 | 0.0160 | 0.20 | 0.60 | 103.9 | 0.0034 |
| Cd 214.438 nm | 0.03 | 0.59 | 101.0 | 0.0010 | 0.04 | 0.57 | 98.4 | 0.0005 |
| Cr 267.716 nm | <DL | 0.59 | 102.0 | 0.0025 | 0.02 | 0.59 | 101.3 | 0.0012 |
| Cu 324.754 nm | 2.19 | 0.56 | 95.7 | 0.0011 | 2.22 | 0.58 | 99.6 | 0.0011 |
| Fe 238.204 nm | 4.07 | 0.62 | 107.3 | 0.0057 | 4.29 | 0.64 | 110.3 | 0.0022 |
| K 766.490 nm | <DL | 1.13 | 95.5 | 0.0208 | 0.25 | 1.11 | 93.7 | 0.0061 |
| Mg 279.553 nm | 0.03 | 0.59 | 102.2 | 0.00006 | 0.06 | 0.60 | 102.4 | 0.00007 |
| Mn 293.930 nm | 0.02 | 0.58 | 100.6 | 0.0017 | 0.04 | 0.58 | 99.7 | 0.0020 |
| Mo 281.615 nm | <DL | 0.59 | 101.2 | 0.0040 | <DL | 0.58 | 100.0 | 0.0042 |
| Na 589.592 nm | 0.15 | 0.62 | 107.4 | 0.0091 | 0.22 | 0.62 | 106.4 | 0.0086 |
| Ni 231.604 nm | <DL | 0.62 | 106.6 | 0.0060 | <DL | 0.58 | 99.7 | 0.0208 |
| P 178.284 nm | 0.72 | 0.61 | 105.1 | 0.0198 | <DL | N/A* | N/A* | 0.2034 |
| Pb 220.353 nm | <DL | 0.61 | 105.1 | 0.0235 | <DL | 0.60 | 102.4 | 0.0735 |
| S 182.034 nm | 5.54 | 0.93 | 103.1 | 0.0617 | <DL | 0.93 | 102.8 | 0.7446 |
| Si 212.412 nm | 13.42 | 0.57 | 97.4 | 0.0085 | 13.37 | 0.56 | 95.7 | 0.0174 |
| Sn 283.999 nm | <DL | 0.58 | 99.7 | 0.0152 | <DL | 0.59 | 100.6 | 0.0111 |
| Ti 334.941 nm | <DL | 0.58 | 99.4 | 0.0007 | 0.01 | 0.58 | 99.7 | 0.0007 |
| V 309.311 nm | <DL | 0.59 | 100.9 | 0.0010 | 0.03 | 0.59 | 101.2 | 0.0010 |
| Zn 213.856 nm | 0.19 | 0.60 | 103.3 | 0.0005 | 0.21 | 0.59 | 101.5 | 0.0010 |

*Table 3: The results of the biodiesel analysis on both radial and duo (axial view) iCAP 6000 instruments. * Results for the spike for phosphorus for this sample were close to the detection limit and are therefore omitted.*

The sample analysis results obtained for both the iCAP 6000 Series duo and iCAP 6000 Series radial view configurations were comparable. The results showed that the biodiesel sample analyzed meets the requirements of both the ASTM and EN standards, with only slightly elevated levels of sulfur at around 5.5 mg/kg. Other elements with elevated results were silicon, copper and iron. The elevated iron and copper results could be attributed to contamination from production and storage vessels. The silicon contamination is likely to have originated from a washing agent (magnesium silicate) that is used in the production of the biodiesel.

The spike recoveries of both the duo and radial instruments were comparable and within acceptable limits (<10% deviation from the expected concentration) with the exception of calcium on the radial and phosphorus on the axial view instrument. The calcium result was only slightly elevated and could be the result of contamination of the flask that the sample was prepared in. The phosphorus results for the sample analysed in the axial view were close to the detection limit of the instrument, leading to an inaccurate result when this was used to calculate the spike recovery. An incorrect value was therefore obtained for the spike recovery. The results for the spike for phosphorus were close to the detection limit in the duo configuration and were therefore omitted.

The detection limits (*Table 3, Figure 1*) obtained for the majority of elements were similar, with less than a factor of 2 difference between the radial and axial view configurations. However, there was a significant difference between the detection limits obtained for phosphorus and sulfur in the axial and radial views, with the detection limits for the axial view being poorer. This is due to the presence of molecular emission interferences in this region of the spectrum. The selection of an alternative wavelength to improve the detection limits was not a realistic option in that case, as both of these elements have their most intense emission lines in this region and higher wavelengths would lead to a large decrease in sensitivity.



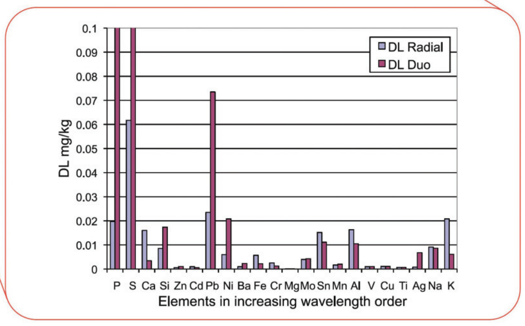


*Figure 1a: Graphical comparison of detection limits produced by axial and radial view plasmas in a biodiesel matrix (expanded concentration scale).*

*Figure 1b: Graphical comparison of detection limits produced by axial and radial view plasmas in a biodiesel matrix (zoomed concentration scale).*

## Conclusion

Biodiesel analysis can be performed using either a radial or axial view ICP emission spectrometer. However, due to background elevation from molecular emissions observed in the axial view, the expected analytical benefit in detection capability with axial compared to radial view cannot be observed. A dedicated radial view plasma configuration is therefore the preferred choice for this type of analysis as it achieves markedly superior detection limits for lower concentrations of samples, being capable of providing accurate, dependable analysis of the important elements of phosphorus, sulfur and lead. These detection limits are significantly lower than the maximum limits of elements permissible by the relevant legislation. This is a crucial benefit as, according to the regulations, detection limits must be ten times below the regulated concentration levels to provide sufficient margin to ensure a confident measurement. The accuracy in the spike recovery is also within acceptable limits.

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