

Petrochemical Series – Analysis of Biodiesel using the iCAP 6000 series ICP

Matthew Cassap, ICP Applications Specialist, Thermo Fisher Scientific, Scientific Instruments, Cambridge, UK

Key Words

- iCAP Radial
- Organics
- Biodiesel



Benefits in Brief:

- Dedicated radial view plasma configuration provides enhanced analytical capabilities for important elements such as sulfur and phosphorus
- Swing frequency RF generator easily handles organic matrix samples and provides enhanced stability

Introduction

There is an ever increasing demand on fossil fuel resources due the rapid growth in energy consumption by industrializing nations and the already huge demand within developed ones. This is one reason why there has been a sharp increase in the cost of these commodities. Cost increases and environmental concerns about the burning of huge quantities of fossil fuels have lead many governments, companies, and increasingly, consumers, to invest in renewable sources of energy such as biofuels. Plant based biofuels have environmental benefits in that they approach carbon neutrality. This means that the absorption of carbon dioxide from the atmosphere by the plants during growth for the production of such fuels effectively balances the emission of carbon dioxide produced when the fuels are burned. One of the most common biofuels is biodiesel. Biodiesel is a fatty acid methyl ester (FAME) which can be derived from a number of sources such as plant oils, for example canola oil.

Biodiesel can also be blended with petroleum diesel to reduce the carbon footprint of a vehicle. This can also reduce other potentially environmentally harmful emissions, such as sulfur dioxide as biofuels are lower in sulfur than their fossil fuel counterparts.

The vast majority of biodiesel production plants currently use plant oils as a starting material for production. However, there is a drawback with this as plants tend to have relatively high phosphorous content. Phosphorous is undesirable in fuels as it can lead to the corrosion of mechanical components of engines. This is especially true in the case of jet fuels - one of the predicted growth areas of biodiesel, and the first commercial airline flight using biodiesel fuel is noted to have taken place in February 2008.

Sulfur is also an element of interest as its content in fuels is tightly controlled by fuel quality and environmental legislation (Table 1). 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. These constraints create a need to monitor the concentration of elemental contaminants in biofuels and this note discusses the the use of both duo view and dedicated radial view ICPs for this purpose.

	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.

Instrumentation

The Thermo Scientific iCAP 6000 Series ICP 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. Both the radial and duo view configurations of the iCAP 6000 can be used for this analysis, although the radial plasma view would be the configuration of choice due to the robust nature of the plasma and freedom from carbon-based emission interferences. When compared to the radial view configuration, the axial view of the duo configuration offers a longer viewing path-length which increases carbon-based interferences, effectively cancelling out any expected increase in sensitivity due to an increase in the background signal. Due to disadvantages found in many radial ICPs on the market there is a perception that axially viewed plasmas will produce superior performance for this application when in fact the radially viewed iCAP 6000 is

more than capable of meeting the requirements of the analysis. In this work, otherwise identical methodologies were compared using a dedicated radial view instrument and the axial view of a duo instrument.

The standard organics sample introduction kit was used for the analysis (Duo part number 8423 120 51801, radial part number 8423 120 51701), but Solvent Flex pump tubing (sample tubing part number 8423 120 51621, drain tubing part number 8423 120 51631) was used in place of the Viton pump tubing as it more resistant to biodiesel (biodiesel attacks rubber, which is why it is unsuitable for use in vehicles that contain rubber hoses and seals).

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 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 supplied by Conostan, Baie D'Urfé, QC, Canada. 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 (0.025 mg/kg to 1 mg/kg).

Method development

A method was created containing the wavelengths of interest (see Table 3). The auxiliary and nebulizer gas flow were adjusted to ensure that the base of the plasma was approximately 1 mm to the right of the load coil on the duo and 1 mm below the coil on the radial. 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 (see Table 2).

Parameter	Duo	Radial
Pump tubing	Sample Solvent Flex Orange/white Drain Solvent Flex White/white	Sample Solvent Flex Orange/white Drain Solvent Flex 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 High 5 seconds	Low 10 seconds 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 analyzed 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 set-up 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 shown below 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 recoveries obtained for both the iCAP 6000 duo and iCAP 6000 radial are comparable. The sample results show that the biodiesel meets the requirements of both the ASTM and EU standard, with only slightly elevated levels of sulfur at around 5.5 mg/kg. Other elements with elevated results are 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 come 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 are comparable and are 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 is 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 analyzed 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 value of the spike is also close to the detection limit of the method so the data has been omitted from Table 3.

The detection limits (Table 3, Figure 1) obtained for the majority of elements are similar with less than a factor of 2 difference between the radial and axial view. However, there is 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 higher. 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 is not a realistic option in this 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.

Conclusion

The analysis of biodiesel can be performed with either a radial or axial view ICP but due to background elevation from molecular emissions observed in the axial view, the expected analytical benefit in detection capability with axial compared to radial is not observed in this matrix. A radial ICP is therefore the preferred choice for this type of analysis as the detection limits observed in this study were comparable for both views for all elements except the important elements phosphorus, sulfur and lead, for which radial view showed a markedly improved detection limit. This comparison is indicated graphically in Figures 1a and 1b.

The radial view iCAP 6000 exhibited good detection limits and these were significantly lower than the maximum limits of elements permissible by the relevant legislation. The accuracy in the spike recovery was also within acceptable limits. This shows that the iCAP 6000 is an ideal ICP for this type of analysis.

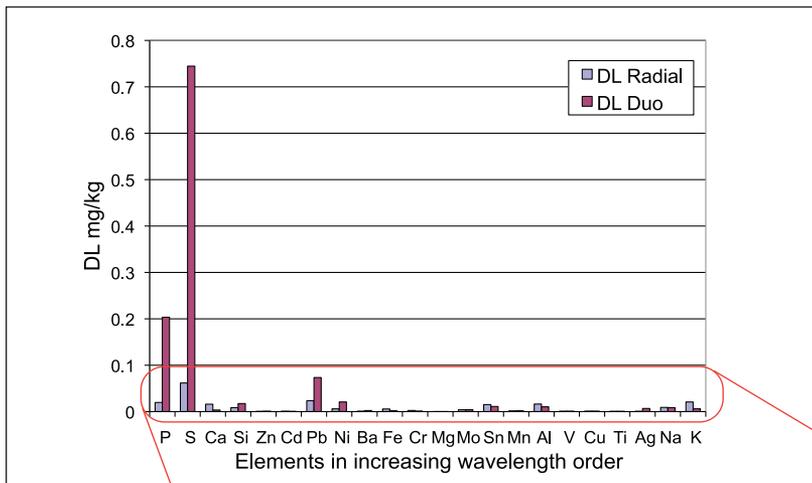


Figure 1a: Graphical comparison of detection limits produced by axial and radial view plasmas in a biodiesel matrix (expanded concentration scale)

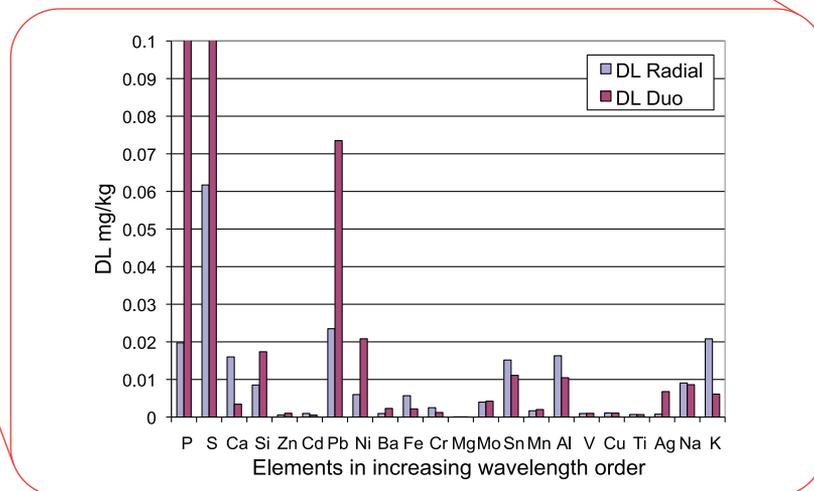


Figure 1b: Graphical comparison of detection limits produced by axial and radial view plasmas in a biodiesel matrix (zoomed concentration scale)

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Africa
+43 1 333 5034 127

Australia
+61 2 8844 9500

Austria
+43 1 333 50340

Belgium
+32 2 482 30 30

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