Analysis of biodiesel oil (as per ASTM D6751 & EN 14214) using the Agilent 5100 SVDV ICP-OES

Application note

Petrochemical

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Introduction

The use of renewable fuels based on alkyl esters derived from "bio" sources such as vegetable or animal-derived oils has increased steadily since the 1990s. Biodiesel is rated using a "B" rating scale. B100 refers to 100% pure biodiesel and B20 represents 20% biodiesel blended with 80% petro-diesel. Typically, blended fuel with a B20 or below rating can be used in diesel-powered equipment, including automotive engines, with no, or minimal modification. Metal contaminants in biofuels are carefully controlled as part of the quality assurance testing of the final product and biofuel producers are required to adhere to various specifications including the maximum levels of Na & K, Ca & Mg, S and P content in fuels. Regulated levels specified in US ASTM standard D6751 (for the biodiesel component of a blended fuel) and European Union EN standard 14214 (for B100 or blended biofuels) are given in Table 1.

The determination of metals in biodiesel by ICP-OES with either a radially- or axially-viewed plasma is a well-established and regularly-used technique within the industry.

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This application note examines the use of the Agilent 5100 Synchronous Vertical Dual View (SVDV) ICP-OES for biodiesel analysis.

With the Agilent 5100 Synchronous Vertical Dual View (SVDV) ICP-OES, the operator has the flexibility to select the plasma view (radial or axial), based on the elements they need to measure and the detection limits they need to achieve.

The 5100 SVDV ICP-OES also offers a high level of plasma robustness, delivering long term analytical stability. Its fast sample analysis reduces argon gas consumption and associated running costs, and the instrument achieves excellent overall analytical performance.

Table 1. US and EU specifications for elemental contaminants in biodiesel.

Metal	ASTM D6751 mg/kg	EN 14214 – 2012 mg/kg
Group I metals: Na & K	5 (combined)	5 (combined)
Group II metals: Ca & Mg	5 (combined)	5 (combined)
Phosphorus	10	4
Sulfur	15	10

Experimental

Instrumentation
The Agilent 5100 SVDV ICP-OES was equipped with a glass concentric nebulizer and the Agilent organics kit that comprises a torch with a 1.4 mm i.d. injector, solvent resistant tubing, and a double pass cyclonic spray chamber. The instrument uses a solid-state RF (SSRF) system operating at 27 MHz to deliver a stable, robust plasma with excellent long term analytical stability, even for the analysis of organic samples. As the RF system is able to rapidly adjust to changes in plasma conditions, the 5100 SVDV ICP-OES can easily analyze a wide range of organic samples, from volatile organics such as methanol and gasoline to semi-volatiles like kerosene and other solvents, using low gas flow plasma conditions similar to those used to analyze aqueous solutions. All measurements were performed with axial plasma viewing. An Agilent SPS 3 Sample Preparation System was used for automatic sample delivery.

The 5100 SVDV ICP-OES features a three port gas module allowing an Ar/O_2 gas mix to be routed automatically through the auxiliary gas line. The addition of oxygen to the plasma is sometimes necessary to eliminate carbon build up in the torch. However, when using kerosene as the primary solvent, oxygen addition wasn't necessary because of the vertically-oriented plasma.

Fast Automated Curve-Fitting Technique (FACT)
When analyzing samples diluted in an organic solvent, spectral interferences originating from carbon are known to interfere with certain elements. In this analysis of biodiesel, FACT correction was applied to the K and Na lines to improve detection limits. Traditional off-peak background correction cannot effectively determine the background signal under the analyte peak with adequate accuracy or precision. Agilent's patented FACT background correction simplifies method development by eliminating the need to manually determine correction points for all elements. A more accurate measurement of the analyte signal is possible using FACT to model the complex background structure due to C-emissions. FACT models are easily created, based on the spectrum of a blank and analyte. For the determination of a low level of Na in a biodiesel matrix dissolved in a kerosene-based solvent, FACT can lower the quantitation limit by an order of magnitude, with no increase in analysis time. The MDLs for Na and K, using first FACT background correction and then Fitted background correction are given in Table 3, showing the lower quantitation possible with FACT background correction.

Method and instrument operating conditions used are listed in Table 2. Wavelengths and calibration parameters selected for the analysis are given in Table 3.

Table 2. Agilent 5100 SVDV ICP-OES method and instrument operating parameters.

Parameters	Setting
Ar/O$_2$ addition	Not required
Sample tubes	Black/black Solva Flex
Drain tubes	Blue/blue Solva Flex
SPS 3 rinse	Kerosene
Background correction	Fitted and FACT
Read time (s)	10
Replicates	3
Sample uptake delay (s)	20
Stabilization time (s)	10
Rinse time (s)	20 (fast pumping: On)
Pump speed (rpm)	10
RF power (kW)	1.40
Aux flow (L/min)	1.0
Plasma flow (L/min)	12.0
Nebulizer flow (L/min)	0.55

Standard and sample preparation

Working standards were prepared at 0.5 ppm, 1 ppm and 2 ppm from a Conostan Custom Blend Multi-element biodiesel standard, containing 20 ppm of Ca, Mg, Na, K and P (Conostan Division, Conoco Specialty Products Inc., Ponca City, OK, USA). Solutions were shaken before measurement to ensure proper mixing of P in solutions.

The standard blank was prepared by diluting the Metal Biodiesel Blank with the diluent 1:10.

The sulfur standards were prepared separately from a single element standard containing 20 ppm sulfur (Conostan). Kerosene (D60 Recosol) was used as the diluent. All solutions were viscosity-matched on a weight-to-weight basis using a Conostan Biodiesel Blank to give a total oil concentration of 10 % (w/w) in each solution. The B100 biodiesel sample was obtained from a local biodiesel distributor. To measure the recovery of the elements at the 0.5 ppm level, the B100 sample (0.75 g) was spiked with 0.25 g biodiesel standards (20 ppm) and diluted 1:10 with kerosene (10 g). The B100 sample was prepared the same way, but using a biodiesel blank instead of the biodiesel standard.

Results and discussion

The Method Detection Limits (MDLs) given in Table 3 are based on three sigma of ten replicate measurements of the standard blank solution during the analytical run. The results show that the method has the sensitivity required to exceed the US and EU specifications for the determination of Ca, K, Mg, Na, P and S in biodiesel.

Table 3. Agilent 5100 ICP-OES wavelengths and calibration parameters used throughout the analysis. Method Detection Limits (MDLs) are also shown. All results are shown in solutions.

Elements	λ (nm)	Background correction used	Calibration range (mg/kg)	Correlation coefficient	MDL (ppm)
Ca	422.673	Fitted	0-2	0.99995	0.004
K	766.491	FACT	0-2	0.99996	0.008
K	766.491	Fitted	0-2	0.99935	0.048
Mg	279.553	Fitted	0-2	0.99994	0.0004
Na	588.995	FACT	0-2	0.99991	0.002
Na	588.995	Fitted	0-2	0.99996	0.048
P	213.618	Fitted	0-2	0.99986	0.013
S	181.972	Fitted	0-2	0.99967	0.031

Calibration linearity
Figures 1 and 2 show calibration curves for Na and P, and Table 3 summarizes the calibration standard concentration range and correlation coefficients for all 6 elements. Correlation coefficients were greater than 0.999 with less than 10% calibration error on each calibration point.
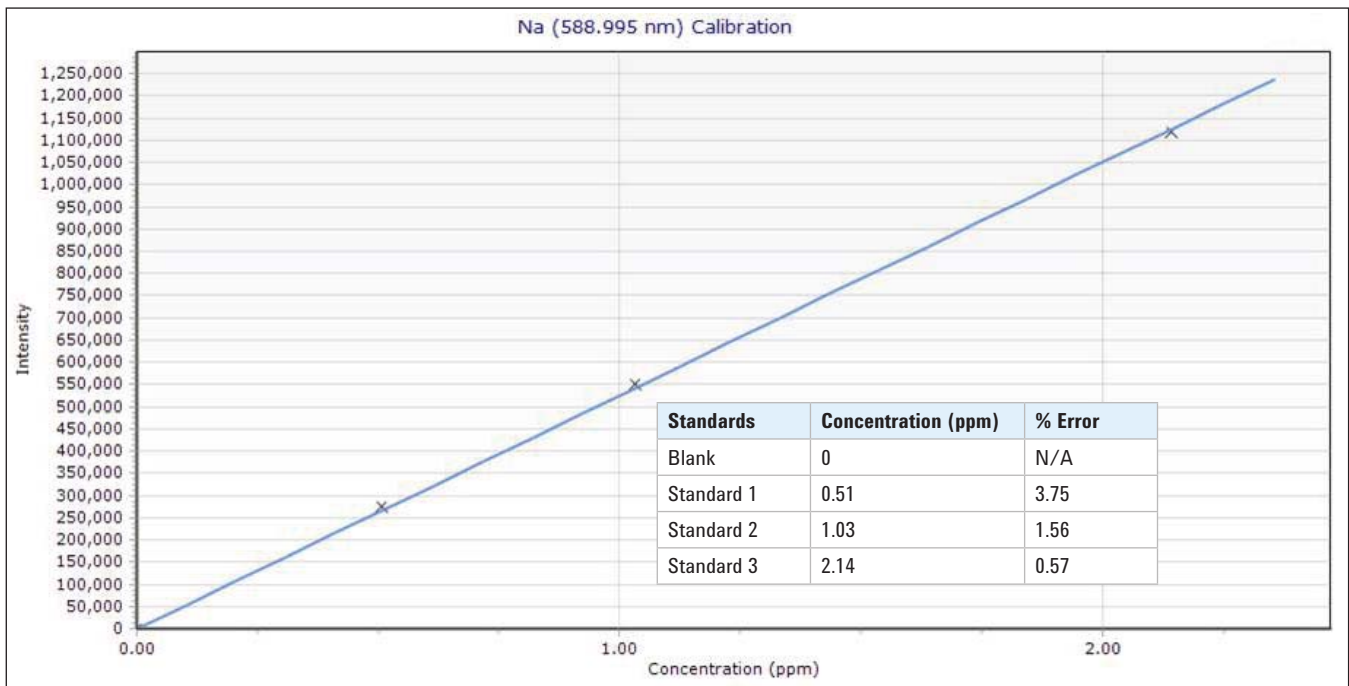
Figure 1. Calibration curve for Na 588.995 nm line, using FACT background correction, shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99991.
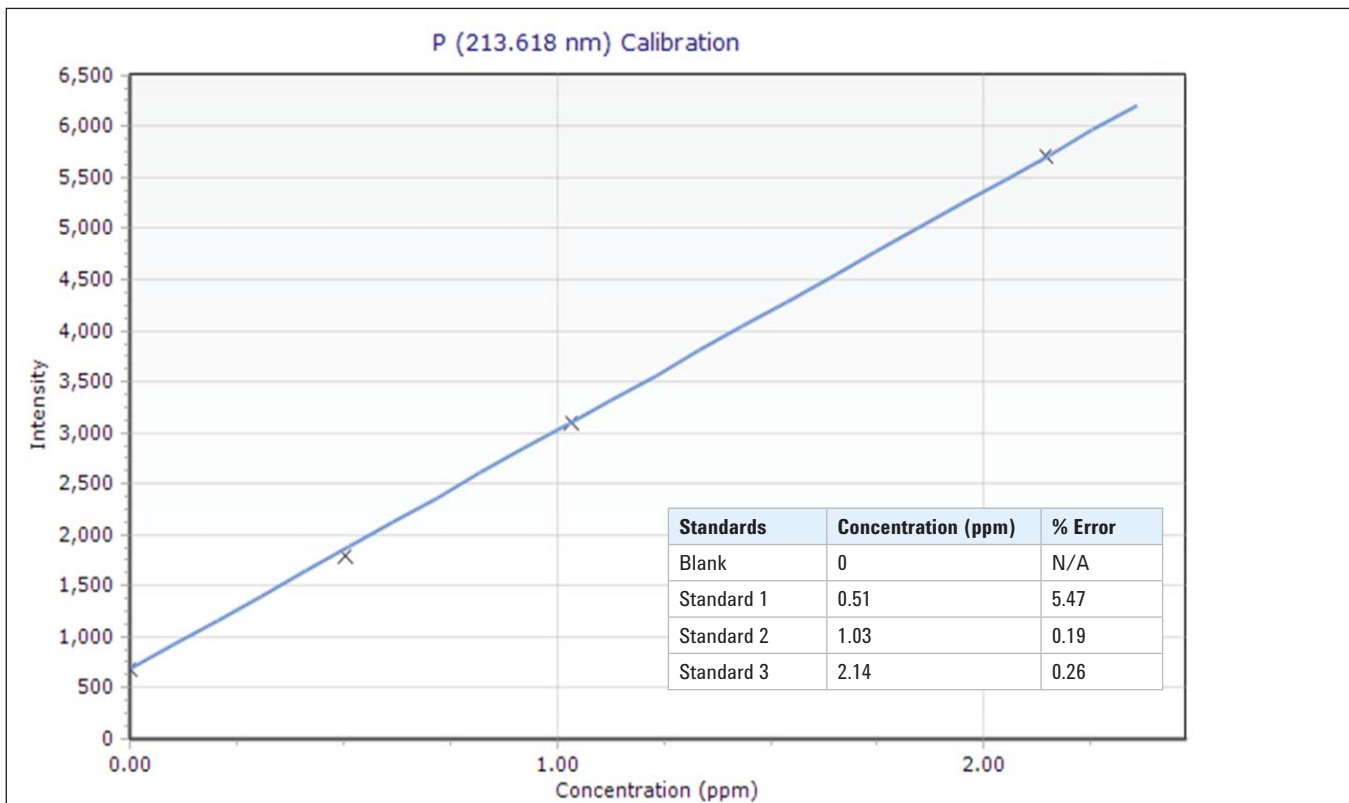
Standards	Concentration (ppm)	% Error
Blank	0	N/A
Standard 1	0.51	3.75
Standard 2	1.03	1.56
Standard 3	2.14	0.57

Figure 2. Calibration curve for P 213.618 nm line, using FBC background correction, shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99986.

Standards	Concentration (ppm)	% Error
Blank	0	N/A
Standard 1	0.51	5.47
Standard 2	1.03	0.19
Standard 3	2.14	0.26

Spike recoveries

The spike concentration of each of the 6 elements of interest in the B100 sample was approximately 0.5 ppm and all recoveries were within ±5% of the target value (Table 4). The excellent recoveries demonstrate the ability of the ICP-OES to accurately determine Ca, K, Mg, Na, P and S at the required levels in the biodiesel fuel samples. The measured values for Ca, K, Mg, Na, P and S in the B100 sample were all below the regulated limits specified in ASTM D6751 and EN 14214 standards.

Table 4. Measured values and spike recoveries (0.5 ppm) for 6 elements in B100 biodiesel sample, all results measured are in solutions.

Elements	λ (nm)	B100 Sample (ppm)	Spiked Solution (ppm)	Spike % Recovery
Ca	422.673	0.005	0.52	105
K	766.491	<MDL	0.49	97
Mg	279.553	<MDL	0.50	100
Na	588.995	0.005	0.49	97
P	213.618	0.39	0.90	102
S	181.972	0.26	0.79	103

Rapid sample throughput and low argon consumption

The 5100 SVDV ICP-OES achieved a sample-to-sample cycle time of 80 seconds, equivalent to 45 samples per hour, using only 27 litres of argon per sample. This was possible with use of an Agilent SPS 3 autosampler, combined with the fast Vista Chip 2 detector in the 5100 SVDV ICP-OES that reads all wavelengths in a single measurement.

Conclusions

Agilent's 5100 SVDV ICP-OES with a vertical torch operating in axial-view mode meets the challenges of routine biodiesel analysis with excellent method detection limits and spike recoveries for all selected wavelengths.

The vertical-orientation of the torch meant the addition of oxygen to the gas mix was not required.

The method is highly cost-effective with sample throughput of 80 seconds per sample and low argon consumption of 27 L/sample.

The availability of FACT background correction on the 5100 SVDV ICP-OES allows correction for any spectral interferences that cannot otherwise be resolved. This can lower the method detection limits in biodiesel samples, with this study demonstrating almost an order of magnitude difference in MDLs for both Na and K when FACT background correction was applied.

The B100 biodiesel sample analyzed in this study met the requirements of both the EU and ASTM standards.

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