Application Note
Energy and Chemicals

Agilent
Trusted Answers

ASTM D8351-22: Elemental Analysis of Biodiesel using MP-AES

Simple, accurate, and safe analysis of biodiesel samples using an Agilent 4210 MP-AES

Authors

Jenny Nelson and Neli Drvodelic, Agilent Technologies, Inc.

Introduction

The ASTM D8351-22 test method covers the determination of elements in biodiesel and biodiesel blends using microwave plasma atomic emission spectrometry (MP-AES) (*1*). The specific elements within the scope of the method are calcium (Ca), magnesium (Mg), phosphorus (P), potassium (K), and sodium (Na). The analysis is important because the presence of metals and metalloids in engine fuels can adversely affect the performance of engines and shorten the lifetime of equipment. Also, some elements act as catalyst poisons, affecting the amount of unwanted gases and particulate matter that are emitted from engines.

Since Agilent introduced the first commercial MP-AES instrument in 2011, many petrochemical laboratories have adopted the technique as a safer and more sensitive alternative to traditional Flame Atomic Absorption Spectroscopy (FAAS) (*2, 3*). MP-AES uses a nitrogen-based plasma as an atomization source rather than acetylene required by FAAS. The N_2 can be produced from air using the Agilent 4107 nitrogen generator, significantly reducing the costs and time associated with the supply and handling of gas bottles. MP-AES is often preferred over FAAS where lab-safety is important because it does not require flammable gases and can be used without close supervision, including for overnight runs. MP-AES with a N_2 generator can also be used in the field or remote areas where the petroleum industry operates.

The Agilent 4210 MP-AES is fully controlled using MP Expert software that guides operators through typical workflows using application-specific preset methods (*4*), facilitating its ease of use. The 4210 is quick to start, and the plug-and-play torch ensures reproducible performance, even between different operators. The instrument also includes smart diagnostic software so that analysts can check for any problems quickly, maximizing instrument uptime.

In this study, we report the average results obtained by five laboratories using MP-AES for the analysis of biodiesel samples measured in accordance with the ASTM D8351-22 method (*1*).

Experimental

Instrumentation

All measurements were performed using five 4210 MP-AES instruments in five different laboratories. Depending on each lab's set up, the N_2 was supplied from an Agilent 4107 Nitrogen Generator, an in-house gas supply, or a combination of the two methods. Each MP-AES instrument was set up with an organics kit comprising an External Gas Control Module (EGCM), inert OneNeb Series 2 nebulizer, and a double-pass glass cyclonic spray chamber. The OneNeb nebulizer offers increased nebulization efficiency and a narrow distribution of small droplets. These performance characteristics allow the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, while maintaining excellent sensitivity. The EGCM injects air into the plasma preventing the build-up of carbon in the torch. The samples were introduced to the MP-AES using an Agilent SPS 4 autosampler. Instrument operating conditions are given in Table 1.

Table 1. MP-AES operating conditions.

Parameter	Setting
Read Time (s)	3 to 10
Number of Replicate	3
Sample Uptake Delay (s)	60
Stabilization (s)	30
Rinse Time (s)	Approximately 60 s (depends on lab)
Pump Speed (rpm)	5
Sample Pump Tubing	*Orange/green (0.38 mm ID)
Internal Standard Tubing	*Orange/green (0.38 mm ID)
Waste Pump Tubing	*Blue/blue (1.65 mm ID)
Internal Standard	Yttrium
Background Correction	Auto
Air Injection Required	Yes

**Solvent-resistant tubing made from a fluoropolymer elastomer and synthetic rubber compound.*

ASTM D8351-22 method

All five laboratories used an Agilent MP Expert software method "Applet" for ASTM D8351-22 that was provided by the authors. MP Expert Applet is a browser-based software interface that is suitable for routine operation of the 4210 MP-AES by users of all skill levels (*4*). Once an Applet has been created, it simplifies method setup by loading predefined analytical parameters such as analytes, wavelengths, background correction technique, and EGCM mode. It also ensures that operating conditions are quick to apply and are consistent from analyst-to-analyst. To ensure the accuracy and precision of the analysis of biodiesel, the setting of the analyte nebulizer flow rate and EGCM are critical. Auto background correction was used for the application to resolve element emission lines from the organic matrix. The acquisition parameters used for the ASTM D8351-22 method are given in Table 2.

Table 2. MP-AES method acquisition parameters for the ASTM D8351-22 method.

Element	Wavelength (nm)	Nebulizer Flow Rate (L/min)	EGCM Air Injection Flow Rate	Background Correction
Calcium	396.847	0.5	High	Auto
Magnesium	285.213	0.5	Medium	Auto
Phosphorus	213.618	0.5	Medium	Auto
Potassium	766.491	0.5	High	Auto
Sodium	588.995	0.5	High	Auto
Yttrium*	371.029	0.5	High	Auto

** Internal standard.*

Reference materials and samples

An in-house biodiesel reference material and a certified reference material (CRM) National Metrology Institute of Japan (NMIJ) 8302-a Biodiesel Fuel (Palm Oil-Based) were used to verify the method.

Biodiesel samples were collected by ASI Standards (Spring, Texas, USA) from various companies that were participating in the ASTM interlaboratory study (ILS).

Standards and sample preparation

All calibration standards were prepared from Agilent biodiesel organometallic standards (5). Working standards for Ca, Mg, P, K, and Na at 0.1, 1, 5, 10, 20 mg/kg. The 0.1 and 1 mg/kg standards were prepared by diluting the 20 mg/kg standard with Agilent A-Solv ICP Solvent and the other standards were poured directly from the bottle.

A blank calibration standard was used as the initial and continuing calibration blank (ICB and CCB). An Agilent 10 mg/kg multi-element standard was used as a Continuing Calibration Verification (CCV) solution for all elements. Yttrium, which was used as an internal standard (IS) at 20 mg/kg, was added to the sample line before the nebulizer using a mixing tee-connector. Standards, blanks, quality control (QC) samples, and IS were diluted with A-Solv ICP solvent.

Results and discussion

Calibration

Figure 1 shows representative calibration curves for Ca, Mg, P, K, and Na obtained from the analysis of the standard solutions using MP-AES under optimized conditions. Linear calibration curves were obtained for all elements.

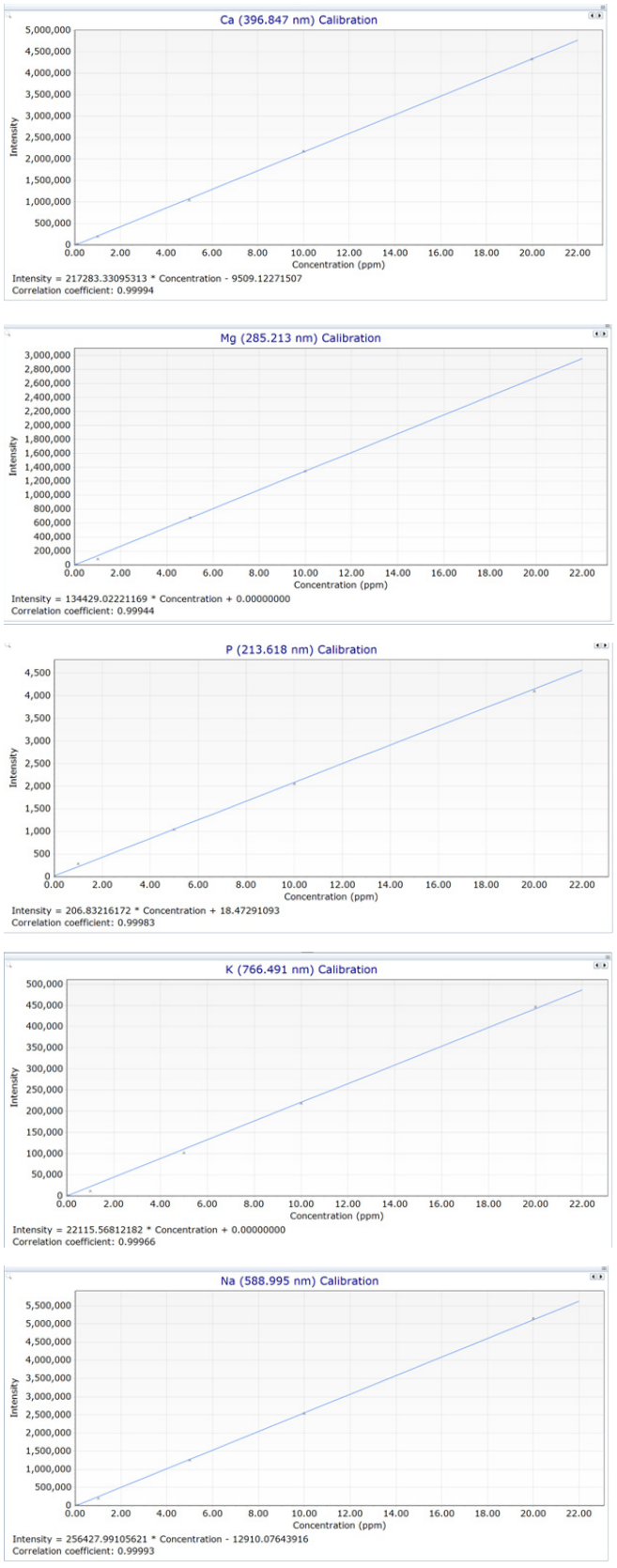

Figure 1. Typical MP-AES calibration curves for Ca, Mg, P, K, and Na.

Method Detection Limits

Method detection limits (MDLs) (3σ) were calculated by measuring 10 consecutive blank readings. The MDLs (Table 3) show the suitability of the 4210 MP-AES method for the multi-element determination of Ca, Mg, P, K, and Na in biodiesel.

Table 3. Method detection limits (ppm) for Ca, Mg, P, K, and Na.

Element	Wavelength (nm)	MDL (ppm)
Calcium	396.847	0.01
Magnesium	285.213	0.02
Phosphorus	213.618	0.19
Potassium	766.491	0.04
Sodium	588.995	0.02

Quality control

To check the ongoing validity of the calibration during the analysis of biodiesel samples over three days, CCV standards were analyzed after every 10 samples. In accordance with the ASTM ILS guidance, the MP-AES was calibrated at the beginning of every day. Acceptance criteria for the recovery of elements in the QC samples are not specified in ASTM D8351-22, allowing labs to set their own limits. In this study, the QC stability plot in Figure 2 shows the recovery of all elements to be within ±10%. The results demonstrate the excellent robustness, stability, and precision of the 4210 MP-AES over three days.

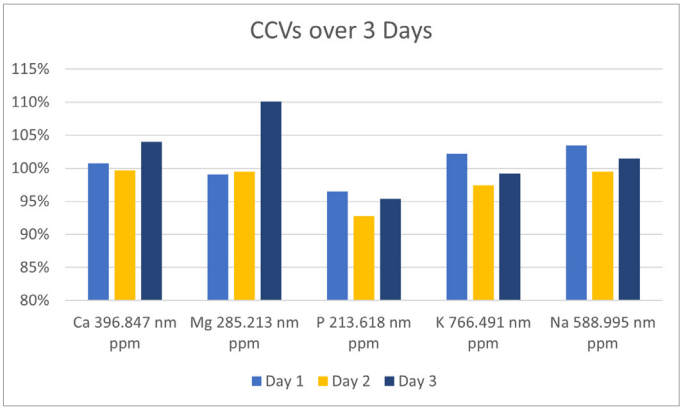

Figure 2. Recovery data for QC samples was measured every 10 samples over three days.

Recoveries of certified elements in biodiesel

The results in Table 4 show excellent recoveries within ±20% of the certified values or information values for all elements in the two biodiesel reference materials. The data demonstrates the accuracy, reproducibility, and reliability of the method for the analysis of biodiesel.

Table 4. Average recoveries for results of multiple elements in two biodiesel RMs. All recoveries are within the reproducibility test criteria described in ASTM D8351.

	Third-Party Biodiesel RM (n=10)			NMJ CRM 8302-a (n=9)		
Element and Wavelength (nm)	Measured Value (mg/kg)	Target Value (mg/kg)	Recovery (%)	Measured Value (mg/kg)	Target Value (mg/kg)	Recovery (%)
Ca 396.847	5.15 ± 0.2	5	103	0.98 ± 0.02	1.01 ± 0.16	97
Mg 285.213	5.54 ± 0.3	5	111	0.84 ± 0.01	0.83 ± 0.11	101
P 213.618	5.05 ± 0.4	5	101	1.88 ± 0.34	2.09 ± 0.35	90
K 766.491	4.96 ± 0.4	5	99	0.69 ± 0.01	0.72 ± 0.15	95
Na 588.995	5.62 ± 0.2	5	112	1.04 ± 0.02	1.26 ± 0.22	83

Quantitative results

Quantitative results for Ca, Mg, P, K, and Na in representative biodiesel samples measured over four days by MP-AES are shown in Table 5. All measured values have been corrected for the weight/weight dilution factors to obtain the concentration in the original sample. All elements were present at low concentrations in all samples. Table 6 also shows good reproducibility of the data obtained for three aliquots of the B100 biodiesel sample.

Table 5. Average quantitative results for Ca, Mg, P, K, and Na in biodiesel samples measured using MP-AES in five labs. All data mg/kg.

	B5	B40	B100 - Sample 1	B100 - Sample 2	B100 - Sample 3
Ca	11.66 ± 0.5	0.77 ± 0.1	0.35 ± 0.1	0.54 ± 0.1	0.89 ± 0.1
Mg	0.56 ± 0.1	1.09 ± 0.2	<MDL	<MDL	3.54 ± 0.8
P	6.25 ± 0.8	1.46 ± 0.4	0.54 ± 0.1	<MDL	3.03 ± 0.5
K	0.68 ± 0.2	<MDL	0.33 ± 0.1	<MDL	2.31 ± 0.4
Na	6.43 ± 0.3	1.27 ± 0.1	1.86 ± 0.4	3.57 ± 0.3	1.36 ± 0.3

Conclusion

The publication of ASTM D8351-22-20 method for MP-AES provides the petroleum industry with a viable technique for the direct analysis of biodiesel. D8351-22-20 relates to the quantification of Ca, Mg, P, K, and Na in biodiesel and biodiesel blends.

Excellent accuracy was demonstrated with good recoveries for certified elements in two biodiesel reference materials. A QC stability test over the three days showed the excellent robustness, stability, and precision of the 4210 MP-AES over long periods, with no need to recalibrate.

The simplicity, accuracy, and reproducibility of the method, plus the low running costs, ease-of-use, and safety of MP-AES make it suitable for routine use in the petroleum industry.

References

1. ASTM D8351-22: Standard Test Method for Determination of Trace Elements in Biodiesel and Biodiesel Blends by Microwave Plasma Atomic Emission Spectrometry (MP-AES), ASTM International, West Conshohocken, PA, 2022, https://www.astm.org/d8351-22.html
2. S. Rand and A. Verstuyft, eds., Significance of Tests for Petroleum Products: 9th ed. J. Nelson, Chapter 23, Analytical Methods for Determination of Inorganic Species in Petroleum Products and Lubricants: A Focus on New Technologies and Techniques in the Petroleum Industry, West Conshohocken, PA: ASTM International, 2018, https://www.astm.org/DIGITAL_LIBRARY/MNL/SOURCE_PAGES/MNL1-9TH.htm
3. ASTM D8322: Elemental Analysis of Crude Oil and Residual Fuels using MP-AES, Agilent publication, 5994-3230EN
4. Agilent MP Expert Software, Agilent publication, 5990-8975EN
5. Petrochemical Reference Materials, Metals in Biodiesel, Agilent website, accessed September 2022, https://www.agilent.com/en/product/chemical-standards/petrochemical/metals-in-biodiesel

Consumables and chemical standards list

Consumable Description	Part Number
Easy-fit MP-AES torch	G8003-70000
OneNeb 2 inert concentric nebulizer	G8010-60293
Double-pass glass cyclonic spray chamber	G8000-70007
Pump tubing, FPM orange/green for sample and internal standard	3710068700
Pump tubing, FPM blue/blue for sample waste	3710043900
Y-piece connector for internal standard	1610132400
Chemical Standards Description	**Part Number**
A-Solv ICP Solvent	5190-8717
B100 biodiesel blank, 100 mL	5190-8718
Metals in Biodiesel Standard 5 mg/kg: Ca, K, Mg, Na, and P	5190-8721
Metals in Biodiesel Standard 10 mg/kg: Ca, K, Mg, Na, and P	5190-8722
Metals in Biodiesel Standard 20 mg/kg: Ca, K, Mg, Na, and P	5190-8723
Yttrium (Y) standard, 1,000 mg/kg in 75 cSt hydrocarbon oil	5190-8795
A21+K multi element standard, 100 mg/kg in 75 cSt hydrocarbon oil	5190-8710

For more information on biodiesel standards, volumes, and mixes, go to www.agilent.com/chem/standards

www.agilent.com/chem/4210mp-aes

DE45128088

Printed in the USA, October 28, 2022
5994-5332EN