



Challenge

Analysis of elemental impurities in organic matrices with high robustness and high resolution

Solution

High-resolution ICP-OES for the interference-free and accurate analysis of elemental parameters, which are relevant to composition and quality of biodiesel, after dilution in an organic solvent

Intended audience

biodiesel producers, process engineers, and analytical chemists working in quality control laboratories who monitor elemental impurities in FAME

Elemental analysis of biodiesel (FAME) according to EN and ASTM standard methods with HR array ICP-OES

Introduction

Biodiesel is the name given to fatty acid methyl esters (FAME), which are produced by the chemical process of transesterification of mostly vegetable oils and used as a substitute or blend component for fossil-based diesel fuels. In the European Union (EU), mainly used cooking oils (UCO), such as rapeseed oil, palm oil, sunflower oil and soybean oil are used as raw materials. Depending on the type of raw material, a distinction is made between different FAMEs, for example rapeseed oil methyl ester (RME) or used cooking oil methyl ester (UCOME).

In transesterification, the high molecular weight triglycerides of oils are broken down with the aid of a catalyst and converted to lower molecular weight fatty acid methyl esters with the addition of methanol. This process produces glycerol as a by-product, which is used in many industries. Biodiesel can be produced on either a small or industrial scale. Commercial plants often have high production capacities of several 100,000 tons of biodiesel per year.

FAME, which is also referred to as B100 („B“ for biodiesel and „100“ for 100%), is suitable as a fuel substitute for conventional diesel engines. Mixed operation of FAME and diesel fuel is also generally possible without any problems. The quality requirements for FAMEs are regulated in the EN 14214 and ASTM D6751 (Table 1). Following these standards, biodiesel needs to be tested for certain elements to ensure the performance and quality of the fuel. The soap building (saponisation) elements calcium (Ca), potassium (K), magnesium (Mg), and sodium (Na) are especially monitored during FAME production, because they can clog the engine filter and can cause instability. Phosphorus (P, from phospholipids) and sulfur (S, from glucosinolates) are “artifacts” from vegetable oils and are known to potentially poison the catalyst. Additionally, sulfur (S) needs to be controlled to reduce the emission of harmful sulfur dioxide into the environment. The determination of sulfur and other elements is described in several ASTM and EN methods^[1-6],

which are listed in Table 1. Even though these two standard specifications do not include a method for the determination of sulfur in biodiesel that uses an inductively coupled plasma optical emission spectroscopy (ICP-OES), this analytical

technique is more than suitable for this purpose. This is supported by the fact that there is an international standard, namely ISO 20424^[7], using ICP-OES for the determination of sulfur content in FAME samples.

Table 1: Limit concentrations and standard methods for elemental impurities in biodiesel according to international standards^[1-6]

Element	ASTM D6751		EN 14214	
	Limit [mg/kg]	Methods	Limit [mg/kg]	Methods
Group I metals (Na + K)	5 (combined)	EN 14538 (ICP-OES)	5 (combined)	EN 14108 (AAS) EN 14109 (AAS) EN 14538 (ICP-OES)
Group II metals (Ca + Mg)	5 (combined)	EN 14538 (ICP-OES)	5 (combined)	EN 14538 (ICP-OES)
P	10	ASTM D4951 (ICP-OES)	4	EN 14107 (ICP-OES) EN 16294 (ICP-OES)
S	15	ASTM D5453 (UVFL)	10	EN ISO 20846 (UVFL) EN ISO 20884 (XRF) EN ISO 13032 (XRF)

UVFL: ultraviolet fluorescence, XRF: X-ray fluorescence spectrometry

Organic matrices are one of the most challenging sample matrices to be analyzed by ICP techniques. The high load and carbon content of the organic matrix requires a robust sample introduction and plasma system, which reliably excites the samples within the ICP and does not suffer from carbon build-up within the torch system. For this challenge, the vertical geometry of the V-Shuttle Torch and the powerful high-frequency generator of the PlasmaQuant 9200 have proven themselves. This is confirmed by the analysis of biodiesel samples. Spectral interferences originating from the unspecific carbon background of the sample matrix are a major challenge to reliably measure concentrations of elements like sodium (Na) and phosphorus (P). To account for these interferences, classical ICP-OES needs to employ

laborious calibration strategies such as standard addition calibration or to select alternative emission lines with less sensitivity, which compromises the achievable limits of detection (LOD). The high-resolution optical system of the PlasmaQuant 9200 Elite (2 pm @ 200 nm) in combination with the CSI software algorithm (correction of spectral interferences) avoid such compromises since the most sensitive emission lines remain interference-free and hence, available for measurement.

The presented methodology will demonstrate the capability of the ICP-OES to quantify sulfur and other elemental contents in biodiesel samples following ASTM D4951^[4], EN 14538^[3], and ISO 20424^[7] (for sulfur) methods. This allows for an economic analysis covering all critical elemental parameters in one run.

Materials and Methods

Samples and reagents

The following chemicals were employed for standards and sample preparation: CONOSTAN® Standard S21+K multi-element organometallic standard at 100 and 885 mg/kg (CONOSTAN®), 1,000 mg/kg sulfur oil-based standard (CONOSTAN®), 1,000 mg/kg yttrium oil-based standard (CONOSTAN®), biodiesel blank oil (B100, VHGT™), and kerosene, low odor (Fisher Scientific).

Elemental analysis was performed in the following four certified reference materials (CRM):

- CRM #1: Ca, K, Mg, Na, P in B100 biodiesel (5 ppm, VHGT™)
 - CRM #2: Ca, K, Mg, Na, P in biodiesel B100 (20 ppm, CONOSTAN®)
 - CRM #3: Sulfur in B100 biodiesel (5 ppm, VHGT™)
 - CRM #4: Sulfur in biodiesel B100 (30 ppm, CONOSTAN®)
- Additionally, one representative FAME sample was spiked with a multi-element standard at 100 and 500 µg/kg and analyzed afterwards.

Sample preparation

Sample preparation was created to be straightforward, creating a consistency of analytes, lowering sample viscosity, and reducing possible interferences. Yttrium was employed as the internal standard. The yttrium standard was diluted with kerosene to achieve a final concentration of 2 mg/kg. This yttrium solution was used as a diluent for each sample and standard. To reduce the viscosity disparity between samples and standards, biodiesel blank oil was included if necessary, resulting in the final solution comprising of 25% oil by weight.

Calibration blank was made by diluting the biodiesel blank oil in the yttrium solution. Each standard was prepared by diluting the stock standard by weight to offer the necessary concentration. The multielement organometallic standard is made from metal sulfonates and therefore separate calibration standards were prepared from the 1000 mg/kg sulfur oil-based standard.

Calibration

EN 14538 (Ca, K, Mg, Na), EN 16294 (P) and ISO 20424 (S) recommend a five-point calibration with concentrations in the range given in Table 2. Since the other analytes generally have expected concentrations below 1 mg/kg, the calibration range was adjusted accordingly.

All before mentioned standard methods require for quality control (QC) samples to be measured after the calibration. These samples should be prepared from different stock solutions. The spiked levels of the QC samples need to be set in accordance with the working range and are also shown in Table 2.

Table 2: Concentration (mg/kg) of calibration and quality control (QC) standards

Element	Cr, Cu, Fe, Mn, Ni, Si, V, Zn	Ca, K, Mg, Na	P	S
Blank	0	0	0	0
Std. 1	0.045	-	-	-
Std. 2	0.254	-	0.254	-
Std. 3	0.522	0.522	0.522	-
Std. 4	1.06	1.06	1.062	-
Std. 5	-	-	2.08	-
Std. 6	-	5.03	-	-
Std. 7	-	10.0	-	-
Std. 8	-	-	-	0.981
Std. 9	-	-	-	2.48
Std. 10	-	-	-	5.13
Std. 11	-	-	-	10.07
QC Std. 1	0.251	1.01	0.510	1.02
QC Std. 2	0.515	5.06	1.003	5.09

Instrument settings

The PlasmaQuant 9200 Elite OES, equipped with the organic sample introduction kit, was employed for this analysis. Just 10 minutes of warm up time was necessary prior to the sample measurement. No oxygen was inserted into the plasma. A Teledyne CETAC Oils 7400 Homogenizing Dual Matrix Autosampler was employed to ensure good homogeneity of the samples. The instrument parameters can be seen in Table 3.

Table 3: Instrument settings

Parameter	Settings 9100 Elite	Settings 9200 Elite
RF power	1350 W	1450 W
Plasma gas flow	14 L/min	10 L/min
Auxiliary gas flow	1.5 L/min	1.75 L/min
Nebulizer gas flow	0.35 L/min	0.45 L/min
Nebulizer	Borosilicate concentric nebulizer, 1 mL/min	
Spray chamber	Borosilicate cyclonic spray chamber with dip tube, 50 mL	
Outer tube/inner tube	Quartz/quartz	
Injector	Quartz, inner diameter 1 mm	
Pump tubing	PU (black, black)	viton (black, black)
Sample pump rate	0.5 mL/min	
Fast mode	1 mL/min	
Read delay	90 s	
Rinse time	60 s	
Torch position*	-3 mm	-2 mm

* Spacing between injector and coil further suppresses carbon deposits on the injector tip

Method and evaluation parameters

In the EN 14538 and 162947 methods, analysis wavelengths are recommended. With the outstanding spectral resolution of the Analytik Jena PlasmaQuant 9200 Elite, each line can be chosen with no issue of interference. In the Analytik Jena ASpect PQ software, the automatic background correction (ABC) was utilized for data evaluation. The ABC function automatically sits in a global baseline to the whole spectral background concurrently throughout the sample analysis. Additionally, the CSI software tool was employed for certain elemental lines to remove background signals originating from the organic matrix. The evaluation parameters can be seen in Table 4.

Table 4: Method parameters

Element	Line [nm]	Plasma view	Integration mode	Replicates	Read time [s]	Evaluation		
						No. of pixel	Baseline fit	Correction
Ca	315.887	axial	peak	3	1	3	ABC ¹	-
Cr	267.716	axial	peak	3	1	3	ABC	-
Cu	324.754	axial	peak	3	1	3	ABC	-
Fe	259.940	axial	peak	3	1	3	ABC	-
K	766.491	axial	peak	3	1	3	static	CSI ²

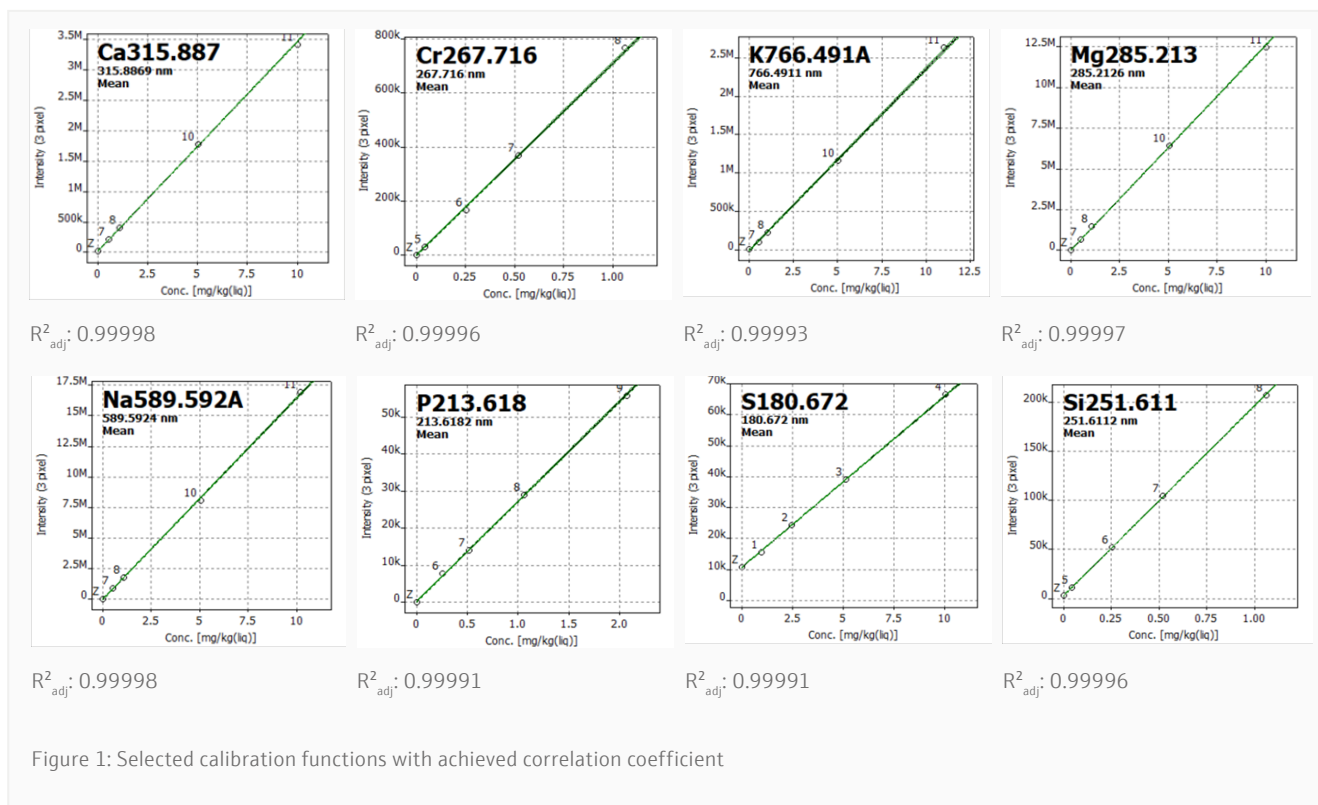
Table 4 (continued): Method parameters

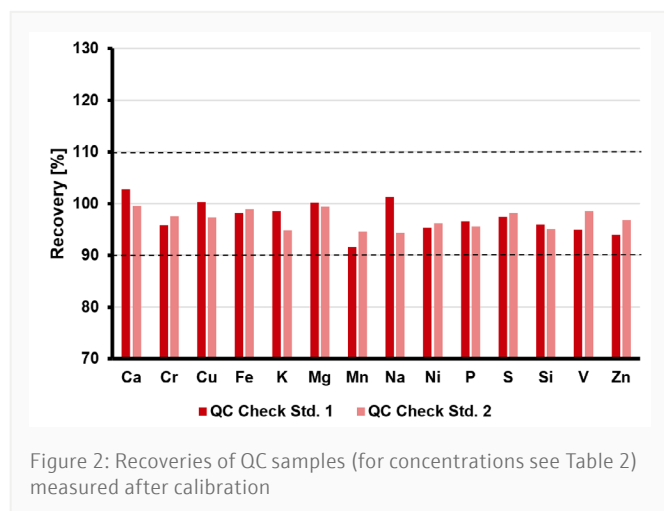
Element	Line [nm]	Plasma view	Integration mode	Replicates	Read time [s]	Evaluation		
						No. of pixel	Baseline fit	Correction
Mg	285.213	axial	peak	3	1	3	ABC	-
Mn	257.610	axial	peak	3	1	3	ABC	-
Na	589.592	axial	peak	3	1	3	ABC	CSI
Ni	221.648	axial	peak	3	1	3	ABC	-
P	213.618	axial	peak	3	1	3	ABC	CSI
S	180.672	axial	peak	3	1	3	ABC	-
Si	251.611	axial	peak	3	1	3	ABC	-
V	309.311	axial	peak	3	1	3	ABC	-
Zn	213.856	axial	peak	3	1	3	ABC	-

¹ Automated baseline correction² Mathematical correction of spectral interferences originating from organics

Results and Discussion

Linear calibrations were obtained with correlation coefficients greater than 0.999 for all elements indicating excellent linearity across the calibrated range. Selected calibration curves for the method are shown in Figure 1 together with the adjusted coefficient of correlation (R^2_{adj}).





Additionally, four reference materials were analyzed to demonstrate the validity of a method. Table 5 shows the certified values and recovery rates for the tested reference materials. All recoveries were within $\pm 8\%$ of the certified value.

Table 5: Quantitative results for several certified reference materials (CRMs)

Element	CRM #1		CRM #2		CRM #3		CRM #4	
	Certified [mg/kg]	Recovery [%]	Certified [mg/kg]	Recovery [%]	Certified [mg/kg]	Recovery [%]	Certified [mg/kg]	Recovery [%]
Ca	5	101.4	20	101.9	-	-	-	-
K	5	107.5	20	95.1	-	-	-	-
Mg	5	103.2	20	101.1	-	-	-	-
Na	5	100.6	20	104.0	-	-	-	-
P	5	100.2	20	101.8	-	-	-	-
S	-	-	-	-	5	99.3	30	103.3

To also demonstrate the applicability of the method for low-concentrated trace elements (e.g., Cu, and Ni), one FAME sample was spiked with a multi-element standard at 100 and 500 $\mu\text{g}/\text{kg}$ level. Achieved spike recoveries are shown in Figure 3.

The excellent recoveries of the 100 $\mu\text{g}/\text{kg}$ spike level are remarkable. The high-resolution optics in combination with the CSI software tool allows for an interference-free analysis of all investigated elements resulting in lowest limits of detection (LOD). Table 6 shows all used analytical wavelengths and the achieved method detection limits (MDL). Instrument detection limits (IDL) were determined using three times standard deviation from eleven measurements of the calibration blank. The method detection limits, comprising the instrument detection limits and the sample preparation, were in the lower $\mu\text{g}/\text{kg}$ range for most of the analytes.

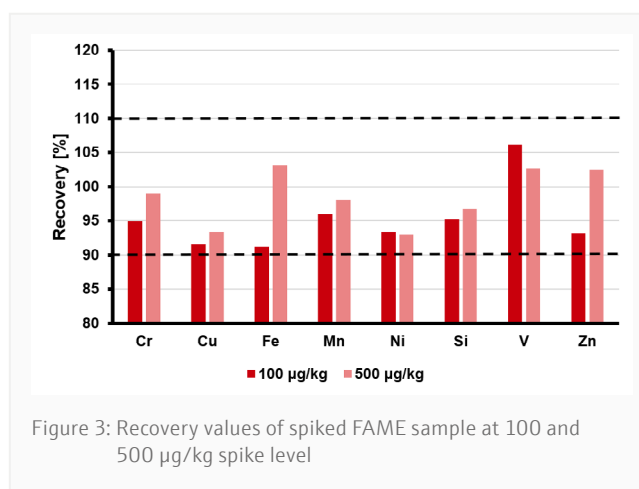


Table 6: Instrumental (IDL) and method detection limits (MDL) for elemental lines

Element	Line [nm]	Observational view	IDL [$\mu\text{g}/\text{kg}$]	MDL [$\mu\text{g}/\text{kg}$]
Ca	315.887	axial	1.4	5.6
Cr	267.716	axial	0.3	1.2
Cu	324.754	axial	0.6	2.4
Fe	259.940	axial	0.7	2.8
K	766.491	axial	7.5	30
Mg	285.213	axial	0.2	0.8
Mn	257.610	axial	0.6	2.4
Na	589.592	axial	9.1	36.4
Ni	221.648	axial	0.4	1.6
P	213.618	axial	5.7	22.8
S	180.672	axial	18.5	74.0
Si	251.611	axial	0.6	2.4
V	309.311	axial	0.6	2.4
Zn	213.856	axial	0.5	2.0

The CSI tool precisely removes background signals from the recorded sample spectrum resulting in a clean and simple-to-evaluate peak, which typically improves the signal-to-noise ratio and, consequently, accuracy and precision. Figure 4 shows the effectiveness of the CSI correction tool on the example of sodium (Na). On the left-hand side, as-recorded spectrum with significant contribution of background signals is displayed. Evaluating such a peak with a low-resolution instrument will result in a false quantification of the respective analyte. The corrected spectrum, as displayed on the right-hand side of Figure 4, shows an analyte peak that can be easily and reliably evaluated resulting in better signal-to-noise ratio and consequently to an improved accuracy and precision of the obtained results.

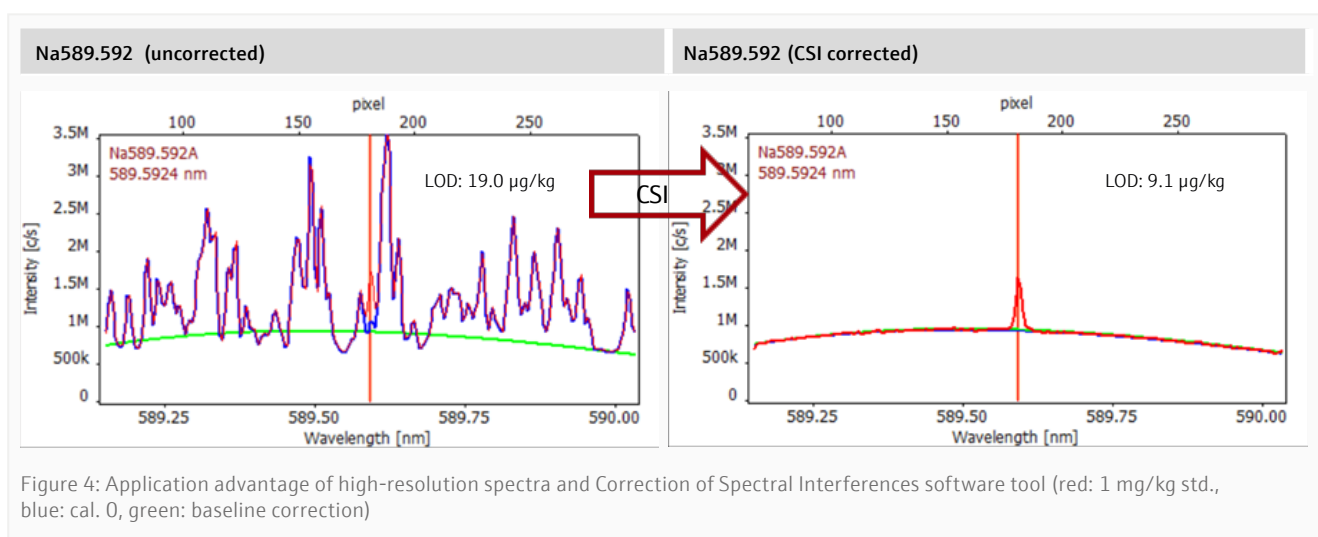
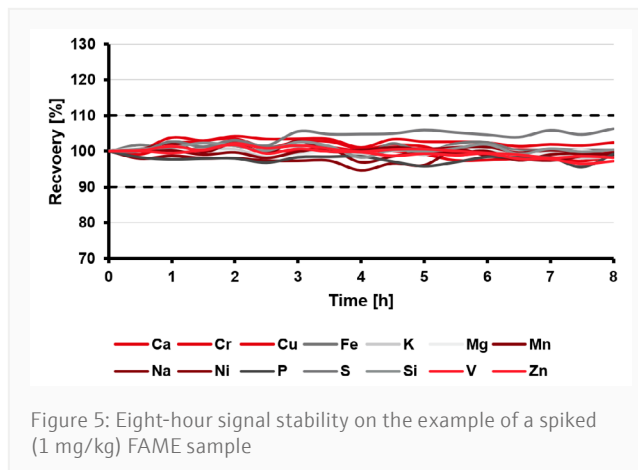


Figure 4: Application advantage of high-resolution spectra and Correction of Spectral Interferences software tool (red: 1 mg/kg std., blue: cal. 0, green: baseline correction)

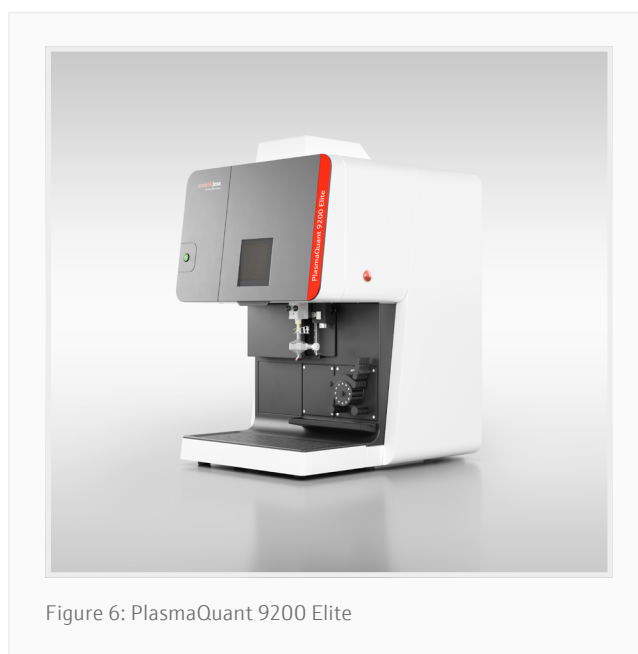
A good long-term stability of the ICP-OES system is indispensable for consistent and precise results while reducing the need for recalibration or remeasurement of samples. The investigation of the long-term stability via an uninterrupted measurement of a spiked (1 mg/kg) FAME sample revealed an excellent stability with an observed drift of less than 7% over an eight-hour run (Figure 5).



Summary

The presented methodology allows for a simple routine analysis of trace impurities in biodiesel samples by means of ICP-OES according to ASTM D6751 and EN 14214. Typical challenges when analyzing organic samples such as FAME are plasma instability, signal fluctuation due to carbon deposition, and matrix-based spectral interferences. High-accuracy and high-precision results are achieved by a uniform excitation of the organic samples using the high-frequency RF generator of the PlasmaQuant 9200 Elite. Carbon deposits on the glassware can be suppressed by using a vertical torch design, such as the unique V Shuttle Torch. Furthermore, an optimized torch position guarantees minimal soot formation and therefore, excellent long-term stability of the measurements.

The high spectral resolution of the PlasmaQuant 9200 Elite of 2 pm @ 200 nm in combination with the CSI software tool ensure a sufficient separation of analyte and background signals. Hence, the unspecific background resulting from the high carbon content in biodiesel is efficiently separated from analyte emission lines and spectral interferences are eliminated. It allows for the use of most sensitive emission lines and therefore guarantees highest sensitivity for all investigated elements. Additionally, data evaluation is easily performed by automatically executed baseline and spectral corrections with the help of software tools like ABC



and CSI. As a result, limits of detection in the lower $\mu\text{g}/\text{kg}$ range are achieved, which ensures the precise and accurate determination of the required analytes. It also allows biodiesel manufacturers to push their specification limits to a new level, proving the superiority of their FAME products.

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9200 Elite	818-09201-2	High resolution ICP-OES
ORGANIC KIT for PlasmaQuant 9200	810-88562-0	Sample introduction kit for organic samples
Teledyne Cetac Oils 7400	810-88122-0	Autosampler for oil samples with stirring functionality, dual port rinse station and drip capture

References

- [1] ASTM D6751 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels
- [2] EN 14214 Liquid petroleum products – Fatty acid methyl esters (FAME) for use in diesel engines and heating applications – Requirements and test methods
- [3] EN 14538 Fat and oil derivatives - Fatty acid methyl ester (FAME) - Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES)
- [4] ASTM D4951 Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry
- [5] EN 14107 Fat and oil derivatives - Fatty acid methylesters (FAME) - Determination of phosphorus content by inductively coupled plasma (ICP) emission spectrometry
- [6] EN 16294 Petroleum products and fat and oil derivatives - Determination of phosphorus content in fatty acid methyl esters (FAME) - Optical emission spectral analysis with inductively coupled plasma (ICP OES)
- [7] ISO 20424 Fatty acid methyl esters (FAME) – Determination of sulfur content – Inductively coupled plasma optical emission spectrometry (ICP-OES) method

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Headquarters

Analytik Jena GmbH+Co. KG
 Konrad-Zuse-Strasse 1
 07745 Jena · Germany

Phone +49 3641 77 70
 Fax +49 3641 77 9279

info@analytik-jena.com
 www.analytik-jena.com

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