AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

ICP-122, REV. 0

SPECTROGREEN

Analysis of Biodiesel (FAME)

Introduction

The limited resources of fossil fuels and the negative climate impact of greenhouse gases released from their combustion, desire for alternative, renewable and CO_2-neutral fuels. Petroleum fuels can also be blended with biofuels to reduce the carbon footprint of a vehicle.

One of the most common biofuels is biodiesel (Fatty Acid Methyl Ester) which is produced by the triglyceride transesterification from vegetable, animal or waste oil. Due to the variety of sources of raw materials used and natural variations of the content of the individual ingredients in raw materials, the optimum performance and emissions of diesel engine operation is a particular challenge. Especially the ash building elements Na, K, Ca, Mg and P have to be analyzed during the production of FAME. Sulfur must be analyzed to control the environmental harmful emission of sulfur dioxide.

In the U.S. and Europe, standards have been established defining acceptable concentrations of these elements in FAME and are shown in Table 1.

	Europe	USA
Specification	EN 14214 [1]	ASTM D6751 [2]
Group I metals (Na + K)	< 5 mg/kg (combined)	< 5 mg/kg (combined)
Group II metals (Ca + Mg)	< 5 mg/kg (combined)	< 5 mg/kg (combined)
Phosphorus	< 4 mg/kg	< 10 mg/kg
Sulfur	< 10 mg/kg	< 15 mg/kg

Table 1: European and USA FAME specifications.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) can be used perfectly for the analysis of FAME, due to its multi-element determination capability, large linear dynamic range and high sensitivity. The application is described in the standard test methods EN14538 [3], EN 16294 [4], EN14107 [5], ISO 20424 [6] and ASTM D4951 [7].
This report describes the principle methodology for the analysis of FAME. It presents typical detection limits for a selection of elements as well as studies on precision, accuracy and stability.

Experimental

Instrumentation

All measurements were performed with the SPECTROGREEN ICP optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) with dual side-on plasma observation (DSOI). It enables an average factor 2 enhanced sensitivity compared to single radial plasma observation and a comparable sensitivity to later vertical torch dual view systems, while eliminating typical axial view interferences. In addition, it offers a high matrix compatibility, excellent linear dynamic range and precision without the need to change the plasma observation mode during analysis.

The SPECTROGREEN features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique. Consisting of two hollow section cast shells, optimized small volume and 15 linear CMOS detectors, the wavelength range between 163 and 770nm can be analyzed, allowing complete spectrum capture. Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later point in time.

The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the UV is achieved, allowing the determination of non-metals as well as the use of prominent and interference free lines in this region.

Utilizing SPECTRO's "Intelligent Calibration Logic" (iCAL), which normalizes the wavelength scale, the state of the optical system is automatically monitored.

An air-cooled, 27.12 MHz, free running type LDMOS ICP-generator is installed, which ensures excellent stability of the forward power even in the case of rapidly changing sample loads. All relevant ICP operating parameters are software controlled, allowing easy selection of the optimum operating conditions.

ICP operating conditions	
Plasma Power	1250
Observation Mode	Dual-Side-On
Coolant flow	15.0 L/min
Auxiliary flow	2.0 L/min
Nebulizer flow	0.75 L/min
Plasma Torch	Quartz, fixed, 1.8 mm injector tube
Spray Chamber	Cyclonic
Nebulizer	Noordermeer V-Groove
Sample aspiration rate	2 mL/min
Replicate read time	32 sec

Table 2: Typical ICP operating conditions

For sample introduction, a Noordermeer nebulizer and a cyclonic spray chamber were used. The ICP operating conditions are given in Table 2.

Calibration

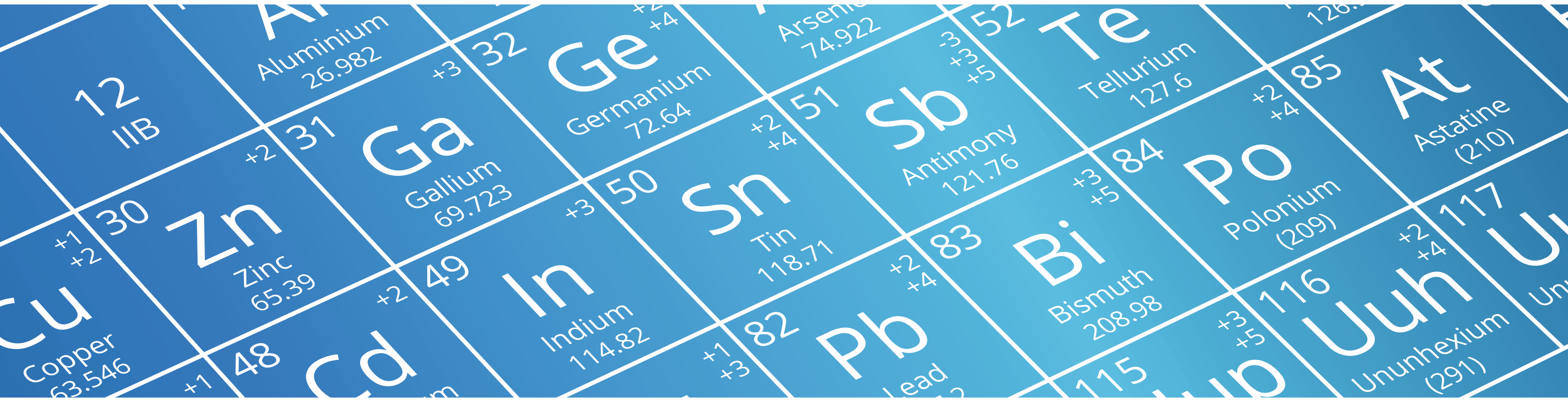
A commercially available multi-element standard [8], single element standards [9] and base oil [10] were used to prepare stock standards. Calibration standards and the quality control (QC) standard were prepared by diluting the stock standards 1:4 (w/w) with a dilution solution, which contained 2 mg/kg Y [11] as an internal standard. All dilutions were performed by weight. The analyte concentrations of all calibration standards are listed in Table 3.

Element	Std. 1 [mg/kg]	Std. 2 [mg/kg]	Std. 3 [mg/kg]	Std. 4 [mg/kg]	Std. 5 [mg/kg]	Std. 6 [mg/kg]	Std. 7 [mg/kg]	Std. 8 [mg/kg]
Ca, Mg, Na, K	0	0.05	0.1	1	2.5			
Cr, Cu, Fe, Mn, Zn	0	0.05	0.1	1	2.5			
P	0	0.05	0.1	1	2.5			
S	0					1	2.5	5

Table 3: Calibration standards

Sample Preparation

5g FAME sample was diluted using the diluent solution to 20g, in the same way as the standards. Additionally, the sample was spiked with a multi-element standard to test the accuracy of the method by spike recovery measurements.



Results and Discussion

Table 4 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [12]:

$$\mathrm{LOD} = 3\ \mathrm{RSD_b}\ c/100{*}\mathrm{SBR}$$

Where:

$\mathrm{RSD_b}$ – relative standard deviation of 10 replicates of the blank

c – concentration of the standard

SBR – signal to background ratio

The LODs were calculated considering the dilution factor of 4 and are expressed in µg/kg. referring to the original, undiluted FAME sample.

Element	λ [nm]	LOD (3σ) [µg/kg]
Ca	393.366	0.4
K	766.491	90
Mg	279.533	0.1
Na	589.592	65
P	177.495	15
S	180.731	46
Cr	267.716	3.4
Cu	327.396	9
Fe	259.941	2.4
Ni	221.648	5.5
Zn	213.856	1.4
Mn	257.611	0.5

Table 4: Typical Limits of Detection (LOD) in the original FAME sample

Accuracy and precision

Accuracy and precision of this method were investigated by analyzing a QC standard as a control sample as well as a spiked FAME sample.
Table 5 shows the concentrations of the prepared QC standard, the measured concentrations and the recovery of the given concentrations, along with the relative standard deviation (RSD) of this measurement with three replicate readings. Excellent recoveries, as well as high precision with a mean RSD value below 0.7% was achieved.

Element/Line	QC Standard Concentration [µg/kg]	Measured Concentration [µg/kg]	Recovery [%]	RSD [%]
Ca 393.366	202	207	103	0.8
Mg 279.553	202	206	102	0.2
Na 589.592	202	208	103	0.9
K 766.491	202	201	99.5	1.2
P 177.495	202	200	99	0.3
Cr 267.716	202	201	99.5	0.6
Cu 327.396	202	205	102	0.4
Fe 259.941	202	202	99.8	0.8
Mn 257.611	202	201	99.4	0.8
Ni 221.648	202	201	99.4	0.9
Zn 213.856	202	201	99.7	0.5

Table 5: Recovery values for the QC standard

The recovery measurements of a spiked FAME sample are displayed in table 6. As shown, the recovery of the spiked concentrations are in perfect agreement with the given values.

Element/Line	Measured Unspiked Sample Concentrations [µg/kg]	Given Sample Spike [µg/kg]	Measured Spiked Sample Concentrations [µg/kg]	Measured Sample Spike [µg/kg]	Spike Recovery [%]
Ca 393.366	6.2	502.6	511	505	100.4%
Mg 279.553	1.7	502.6	506	504	100.3%
Na 589.592	135	502.6	655	520	103.5%
K 766.491	0.0	502.6	496	496	98.7%
P 177.495	33.4	502.6	537	504	100.2%
Cr 267.716	0.19	502.6	501	501	99.6%
Cu 327.396	1.3	502.6	508	507	100.8%
Fe 259.941	2.1	502.6	504	502	99.9%
Mn 257.611	0.4	502.6	501	501	99.6%
Ni 221.648	0.0	502.6	501	501	99.7%
S 180.731	334	1002	1305	971	96.9%
Zn 213.856	2.9	502.6	507	504	100.3%

Table 6: Recovery of a spiked FAME sample

Conclusion

The SPECTROGREEN with DSOI offers a simple, fast, accurate, precise and cost-efficient method for the analysis of biodiesel. Excellent precision and recoveries were determined for a QC and a spiked FAME sample. In conjunction with an autosampler, the SPECTROGREEN can be easily automated. Independent from the number of lines and elements, an analysis (including three replicates and pre-flush) can be performed in less than two minutes.

References

[1] EN DIN 14214:2014-06; Liquid petroleum products - Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - Requirements and test methods

[2] ASTM D6751 (2015); SPECIFICATION FOR BIODIESEL FUEL BLEND STOCK (B100) FOR MIDDLE DISTILLATE FUELS

[3] EN DIN 14538:2006-09; 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] EN DIN 16294:2013-02; 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)

[5] EN DIN 14107:2003-10; Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of phosphorus content by inductively coupled plasma (ICP) emission spectrometry

[6] ISO/DIS 20424:2018-07; Fatty Acid Methyl Esters (FAME). Determination of sulfur content. Inductively coupled plasma optical emission spectrometry (ICP-OES) method

[7] ASTM D4951 (2014); TEST METHOD FOR DETERMINATION OF ADDITIVE ELEMENTS IN LUBRICATING OILS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

[8] Multi element Standard in Hydrocarbon oil, 100 mg/kg, VHG Labs, USA

[9] Single element Standard in Hydrocarbon oil, 1000 mg/kg, VHG Labs, USA

[10] Blank Oil, 75 cSt, VHG Labs, USA

[11] Sulfur-free Yttrium Standard in Hydrocarbon oil, 5000 mg/kg, VHG Labs, USA

[12] P. W. J. M. Boumans, Spectrochim. Acta 46B, 431 (1991)

www.spectro.com

GERMANY
SPECTRO Analytical Instruments GmbH
Boschstrasse 10
D-47533 Kleve
Tel. +49.2821.892.0
spectro.sales@ametek.com

U.S.A.
SPECTRO Analytical Instruments Inc.
50 Fordham Rd
Wilmington 01887, MA
Tel. +1 800 548 5809
+1 201 642 3000
spectro-usa.sales@ametek.com

CHINA
AMETEK Commercial
Enterprise (Shanghai) CO., LTD.
Part A1, A4 2nd Floor Building No. 1 Plot Section
No. 526 Fute 3rd Road East; Pilot Free Trade Zone
200131 Shanghai
Tel. +86.400.022.7699
spectro-china.sales@ametek.com

Subsidiaries:
▶**FRANCE:** Tel. +33.1.3068.8970, spectro-france.sales@ametek.com ▶**GREAT BRITAIN:** Tel. +44.1162.462.950, spectro-uk.sales@ametek.com
▶**INDIA:** Tel. +91.22.6196.8200, sales.spectroindia@ametek.com ▶**ITALY:** Tel. +39.02.94693.1, spectro-italy.sales@ametek.com
▶**JAPAN:** Tel. +81.3.6809.2405, spectro-japan.info@ametek.co.jp ▶**SOUTH AFRICA:** Tel. +27.11.979.4241, spectro-za.sales@ametek.com

SPECTRO operates worldwide and is present in more than 50 countries. For SPECTRO near you, please visit www.spectro.com/worldwide