



Analysis of Biodiesel and Determination of Traces in New Oil by ICP-AES

Jean-Michel Mermet¹, Sébastien Velasquez², Sophie Lebouil²

¹Spectroscopy Forever, Tramoyes, France, ²Horiba Jobin Yvon, 16 rue du Canal, 91160 Longjumeau, France, e-mail: info@jobinyvon.fr

Biodiesel refers to a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, made by transesterification of vegetable oils or animal fats, which can be used (alone, or blended with conventional petrodiesel) in unmodified diesel-engine vehicles.

Biodiesel

Among the key tests to perform on biodiesel samples, there is the control of P, S, Na + K, Ca and Mg (Table 1) as P can poison catalytic converters and can create hard deposits affecting engine performance, Na and K may form abrasive solids or metallic soaps, which may cause abrasion and filter plugging, and Ca and Mg metals may clog the particulate trap.

	ASTM D-6751	pr EN 14214
P	10	10
S	500	10
Na + K	5	5
Ca + Mg	5	5

Table 1. U.S. and European biodiesel specifications (ppm)

Instrumentation

A Horiba Jobin-Yvon ACTIVA-M ICP-AES instrument was used with the following characteristics (Figs 1 et 2):



Figure 1. Photograph of the ACTIVA-M

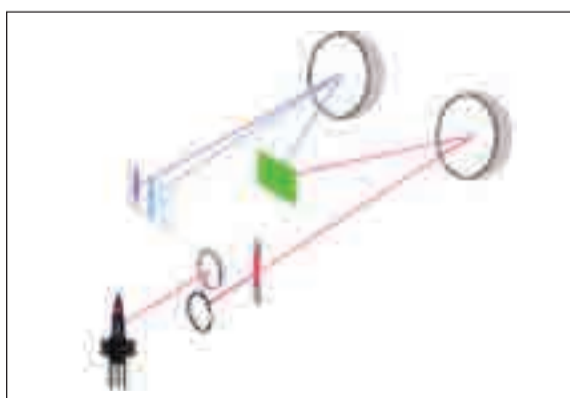


Figure 2: Schematic drawing of an ACTIVA instrument

- Back-thinned illuminated, low noise CCD detector
- Constant resolution: <10 pm in the range 120-430 nm and 18 pm in the range 430-800 nm
- Dual back-to-back gratings (4343 g/mm and 2400 g/mm)
- Spectral windows in the range 4-8 nm
- Simultaneous measurements of peak and background

- Practical dynamic range of 10⁷, with a linear response over 5 orders of magnitude
- Dedicated tools for multi-line analysis (SMARTVIEW for semi-quantitative analysis, S3-base and MASTER for multi-line selection, SOS for outliers).
- RF 40.68 MHz water-cooled generator
- Fully demountable torch with 3-mm injector i.d., with radial viewing providing excellent LODs along with reduced matrix effects).

The calibration procedure was based on the use of Spex Certiprep organometallic standards (multi-elements at 900 ppm and single-element (K and S) at 1000 ppm) and Spex Certiprep Base Oil 75 with kerosene as the solvent. The concentration was in the range 0 - 1 ppm for all elements, excepted 0 - 50 ppm for S. The sample preparation was simply a 1:10 dilution with kerosene.

The limits of detection (LOD, ppm, corrected by the dilution factor) are given in Table 2

	LOD
P 178.229 nm	0.7
S 180.676 nm	0.7
Na 588.995 nm	0.6
K 766.490 nm	1.1
Ca 393.366 nm	0.02
Mg 279.553 nm	0.02

Table 2. Limits of detection (LOD) in biodiesels

Biodiesel precursor (colza oil)

The SMARTVIEW tool for semi-quantitative analysis makes it possible to obtain a reliable estimation of the concentrations through the use of several lines per element and previously stored calibrations. The tool includes reprocessing with the possibility of adding lines/elements/standards. The results are exported in an Excel format and treated with a macro to calculate the median for each element. A comparison between semi-quantitative and quantitative analysis is given in Figure 3.

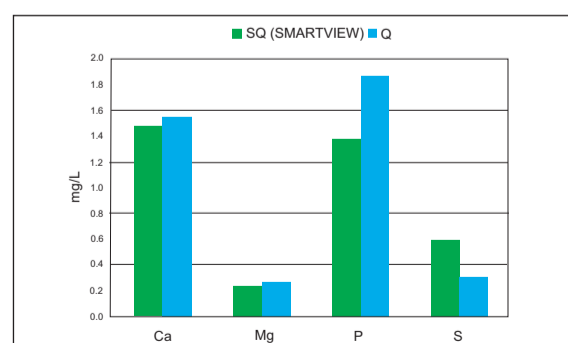


Figure 3: Semi-quantitative analysis of colza using the SMARTVIEW tool (SQ) and comparison with quantitative analysis (Q). It may be seen the good agreement.

Residual fuel

There is an interest of low-level determination capability for sodium in residual fuel for example due to the influence of sea water presence. The requirements are a LOQ of 20 ppb in the sample along with easy methodology and good reproducibility. To achieve the LOQ with simplicity, besides the characteristics mentioned above, the ACTIVA-M provides the following benefits:

- Low noise detector, adapted to the full normal analytical zone (NAZ) height, for both sensitivity and linear dynamic range optimisation.
- Automatic O₂ addition in the plasma to prevent overlap of the green C₂ Swan bands on the alkali lines.
- Use of a sheath gas flow rate (Figure 4), leading to reduced sample deposit and memory effects, and to optimisation of alkaline sensitivity.



Figure 4: Photograph and schematic drawing of the sheathing gas system

An addition of a sheathing gas at 1000 W, leads to a decrease in the plasma temperature (measured with Fe lines) from 5700 K down to 3900 K. As a result, a 'cold' plasma is obtained, and atomic alkali lines are enhanced (Figure 5).

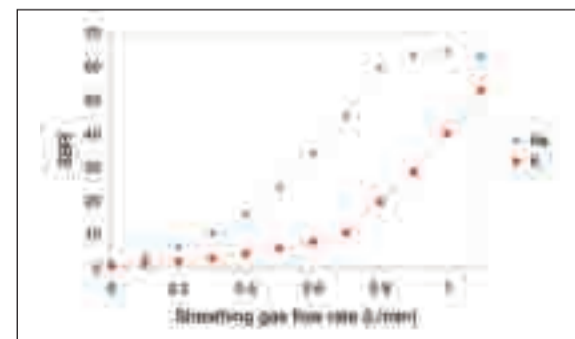


Figure 5: Influence of the sheathing gas flow rate on the Na and K SBRs.

A JY pneumatic nebuliser (0.7 mm Ø) associated to a Scott double-pass spray chamber was selected. The operating conditions were a power of 1200 W with a 14 L/min plasma gas, a 0.2 L/min auxiliary gas flow rate, a 0.9 L/min sheath gas flow rate, and a 0.070 L/min O₂ gas (introduced via the nebulisation, using a mass flow controller)

The sample preparation consisted of a 1:2 dilution of sample with xylene, and the standards were prepared with 50% Base Oil (Spex Certiprep) / 50 % xylene

Acquisition was based on an integration time of 5 seconds (with background and peak being measured simultaneously), and with an optimisation of the pixels zone read-out with maximum of light (from vertical pixel # 200 to 400, over 512 pixels), i.e. ca 3 mm high along the plasma axis (Figure 6).

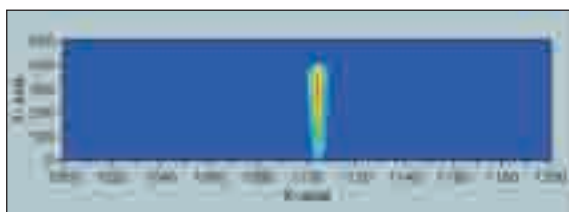


Figure 6: Imaging on the plasma zone onto the detector, with an optimum between vertical pixel 200 and pixel 400.

The effect of O₂ addition may be seen in Figure 7, with the suppression of the spectral interferences due to C₂ molecular bands.

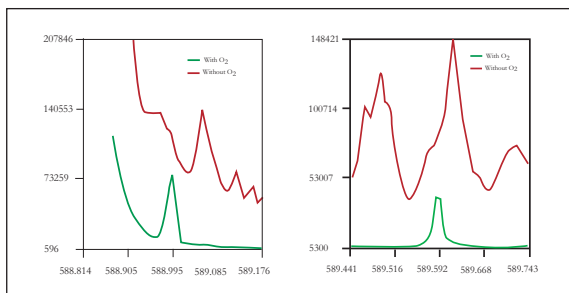


Figure 7: Effect of the addition of O₂ on the suppression of the Swan C₂ bands on the Na 588.9 and 589.592 nm lines (sample diluted 1:2 in xylene, Na ~ 0.28 ppm).

The following limits of detection and quantitation were obtained using a calibration with 0 and 100 ppb: for Na 588 nm, a LOD of 0.45 ppb in solution, 0.90 ppb in the sample (LOQ: 2.7 ppb), and for Na 589 nm a LOD of 0.75 ppb in solution, 1.50 ppb in the sample (LOQ: 4.5 ppb). To study the long-term stability and the recovery, all elements were determined with similar conditions, excepted for the sheath gas, 0.9 L/min for Na, and 0.2 for the others, and O₂ addition only for Na (automatic addition when Na was determined). Calibration was in the range 0 - 100 ppm. Results are summarised in table 3.

Ethanol

Ethanol fuel is used as a biofuel alternative to gasoline (as a side benefit improving engine performance), when it is obtained from the conversion of carbon-based renewable feedstock. Currently, it is produced by fermentation of starch or sugar from a wide variety of

Element	Concentration (ppm)	Mean of in-runprecision (%)	RSD over 1hour (%)	%Recovery (5ppm standard)
Al 167.02	5.15	1.1	0.61	103.0
Al 396.152	5.12	0.72	0.53	102.4
Fe 259.94	4.95	0.45	0.62	99.0
Na 588.995	5.17	0.55	0.99	103.4
Na 589.592	5.14	0.58	0.6	102.8
Ni 221.647	5.01	0.45	0.58	100.2
Si 251.611	4.97	0.7	0.66	99.4
V 292.402	4.95	0.6	0.71	99.0
V 311.071	4.89	0.56	0.93	97.8

Table 3: Concentration, precision, %RSD over 1 h and %recovery in residual fuel.

Element	LOD(ppb)	Element	LOD(ppb)	Element	LOD(ppb)
Ag 328.028	0.5	Fe 259.940	0.5	Pb 220.353	1.7
Al 167.020	0.15	Hg 194.163	1.8	S 180.676	5.1
Al 396.152	2.7	K 766.490	30	Sb 206.833	2.3
As 189.042	2.2	Li 670.784	0.6	Se 196.026	40
B 249.773	1.4	Mg 279.806	4.0	Si 251.611	2
Ba 455.403	0.04	Mo 202.030	0.4	Sr 407.771	0.01
Ca 317.933	1.6	Na589.592	5	Ti 337.280	0.3
Cd 228.802	0.2	Ni 221.647	0.3	Tl 190.864	2.7
Co 228.616	0.3	P 177.440	5	V 292.402	4
Cr 267.716	0.35	P178;229	4.3	Zn 206.200	0.5
Cu 324.754	0.3	P 213.618	3	Zn 213.856	0.6

Table 4: LODs in pure ethanol (in ppb unit)

agricultural feedstocks (e.g. sugar cane, corn and switchgrass).

Ethanol is a highly volatile solvent and needs special operating conditions for ICP-AES analysis. The best alternative is to use a cooled spray chamber to minimise solvent loading in the plasma and maintain robust conditions. This procedure has also the advantage of improving the limits of detection. A power of 1200W, a carrier flow gas of 0.35 L/min and a sheathing gas flow rate of 0.35 L/min were used. For this experiment, a Horiba Jobin Yvon ULTIMA 2 ICP-AES instrument was selected.

A new approach consists of using a cyclonic spray chamber cooled by Peltier effect. Such a system (Glass Expansion IsoMist) incorporates a cyclonic spray chamber featuring a central transfer tube, which is encapsulated in a conductive resin for intimate contact with the Peltier heat transfer block. The temperature can be set up in the range of - 10 to + 60 °C, in 1 degree increments. It is then possible to run pure ethanol solutions.

Calibration was performed with pure ethanol (analytical grade, Merck) as the blank. Standards were prepared in ethanol from Precis single element stock solutions (Horiba Jobin Yvon).

Limits of detection obtained in pure ethanol are given in Table 4.

A spike of 10 ppb in the blank has been performed for some elements (from Precis mono-element solutions) to show the efficiency of the methodology in terms of long-term sensitivity and recovery (table 5).

Element	Conc (mg/L)	SD (mg/L)	RSD (%)	Recovery (%)
Ag 328.068	10.06	0.07	0.69	100.6
Al 167.020	10.91	0.20	1.85	109.1
As 189.042	10.76	0.22	1.87	107.6
Ba 455.403	10.11	0.06	0.58	101.1
Be 313.042	10.32	0.10	0.93	103.2
Cd 228.616	10.46	0.30	2.57	104.6
Cr 267.716	10.31	0.15	1.50	103.1
Cu 324.754	9.82	0.13	1.32	98.2
Fe 259.940	9.90	0.06	0.64	99.0
Li 670.784	10.13	0.18	1.79	101.3
Mn 257.610	9.86	0.09	0.88	98.6
Mo 202.030	10.27	0.14	1.36	102.7
Ni 221.647	10.23	0.28	2.72	102.3
Pb 220.353	9.31	0.80	9.21	93.1
Sr 407.771	10.08	0.02	0.21	100.8
Ti 337.280	9.88	0.03	0.27	98.8
Tl 190.864	10.47	1.19	11.38	104.7

Table 5: Long term stability and recovery in bioethanol

Conclusions

ICP-AES technique is fully appropriate for the determination of analytes in biofuels, bioethanol and related materials, in terms of accuracy (trueness of the results), precision, limits of detection, and long-term stability.