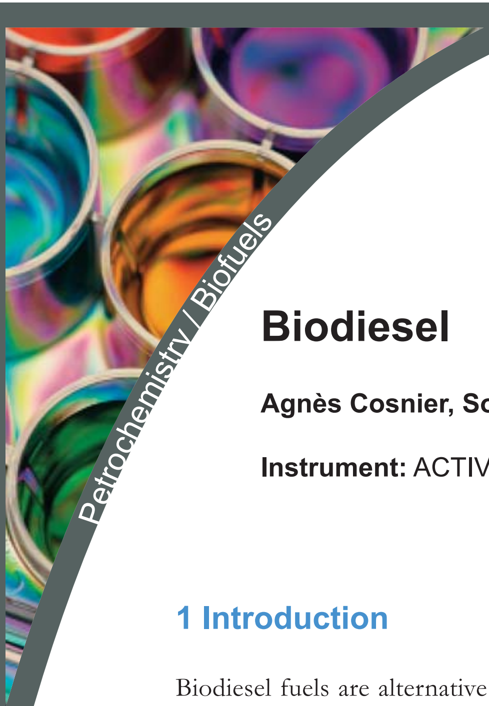

Petrochemistry / Biofuels

Biodiesel

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Instrument: ACTIVA-S

1 Introduction

Biodiesel fuels are alternative fuels used to contribute to CO_2 emission reduction from cars, improving operation of diesel equipment in the mean time. Ethanol-based gasoline is also part of these renewable sources.
Biodiesel is constituted of alkyl esters made from the transesterification of vegetable oils (soybean, rapeseed, canola, and palm oils are commonly used) and animal and vegetable fats (tallow, yellow grease, stearic acid are examples). The reaction of oil or fatty acid with methanol is catalysed with reagents such as NaOH. Beside biodiesel, a by-product is obtained, Glycerol (glycerine), which is re-usable in the chemistry industry.

This application flash describes the analytical procedure for all products from raw materials to biodiesel, following the international norms. Another application flash deals with bio-ethanol (1).

2 Operating conditions

Depending on the product, the sample preparation may vary, in terms of solvent choice. However, the sample introduction system and parameters are the same, and analyses can be performed in a routine way. The ACTIVA-S is the ideal ICP-AES instrument for this application, thanks to its Simplicity and Stability criteria.

• Sample description
Among the key tests to perform on biodiesel for follows characterisation are the analysis of non-metal elements:
– P can poison catalytic converters and can create hard deposits affecting engine performance,
– Na & K may form abrasive solids or metallic soaps which may cause abrasion and filter plugging,
– Ca & Mg metals clog particulate trap.

The USA and European specifications for biodiesel are listed in Table 1 (in % mass / ppm units).

Table 1: USA and European Biodiesel norms for P, S, Na, K, Ca and Mg

	ASTM D-6751	pr EN 14214	E DIN 51606
P	0.001 / 10	0.001 / 10	0.001 / 10
S	0.05 / 500	0.001 / 10	0.01 / 100
Na + K	0.0005/5	0.0005 / 5	0.0005 / 5
Ca + Mg	0.0005 / 5	0.0005 / 5	0.0005 / 5

• Sample preparation
The solvent used is Kerosene or a mixture of Heptane and Kerosene (10/90). Oil and biodiesel are diluted 1:10 in Kerosene, and animal fat 1:10 in Heptane/Kerosene (fatty acids would necessitate a dilution 1:20).
This dilution factor allows the operator to run all types of samples with the same analytical method, and does not require the use of internal standard correction thus, simplifying the operations. The robust conditions of the Total Plasma View based on a vertical torch contribute to this simplification of the operating conditions.
The standard solutions are prepared from Spex Certiprep organo-metallic standards (multi-element at 900 ppm and single-element (K and S) at 1000 ppm) and Base Oil 75, diluted in Kerosene or Heptane/Kerosene.
Tables 2 and 3 gives plasma and instrument parameters.

Table 2: Plasma parameters

Parameter	Specification
Power	1200 W
Plasma gas	14 L/min
Auxiliary gas	0.5 L/min
Sheath gas	0.2 L/min
Nebuliser gas	2 bar
Sample uptake	1 mL/min (20 rpm)
Plasma view	Radial*

* Total Plasma View (observation of the complete NAZ, Normal Analytical Zone), for minimised matrix effects and optimum sensitivity.

Table 3: Specifications of the ACTIVA-S ICP spectrometer

Parameter	Specification
Generator	40.68 MHz, solid state, water-cooled
Optical System	Czerny-Turner (0.64 m Focal)
Gratings	4343 / 2400 g/mm
Spectral range	160 - 800 nm
Resolution	12 pm in 160 - 430 nm range 22 in 430-800 nm range
Sample introduction	JY nebuliser (Pt sample needle 0.7 mm i.d) / Scott spray chamber (glass)
Pump tubing	Black/black SolvFlex (sample) Grey/grey SolvFlex (drain)
Torch design	Vertical demountable 3 mm i.d injector

3 Analytical Results

• Limits of quantification

The limits of detection are estimated from a calibration in 10 % Base Oil in Kerosene, with the formula LOD = 3 x SD. SD is the Standard Deviation of the blank concentration from an analysis with 10 replicates.

The limit of quantification is then LOQ = 3.3 x LOD.

Table 4 gives the LOQs of the elements of interest in biodiesel application samples, corrected by the dilution factor (unit is ppm). We notice that sensitivity of Na and K can be easily improved (if it is required for another application), by automatic addition of oxygen: LOQ(Na) = 0.1 ppm and LOQ(K) = 0,15 ppm in the sample.

Table 4: LOQs (ppm)

		LOQ			LOQ
P	178.229 nm	0.3	Ca	422.673 nm	0.15
S	180.676 nm	0.6	Ca	393.366 nm	0.01
Na	588.995 nm	0.8	Mg	279.806 nm	0.25
K	766.490 nm	2	Mg	279.553 nm	0.02

Using simple operating conditions, all samples from biodiesel application can be analysed on a routine basis, according to the norms.

• Sample analysis

Table 5 gives examples of biodiesel application analysis, with analysis of rapeseed oil, stearic oil (saturated fatty acid from animal or vegetable fat) and biodiesel. Simple calibration is made with standards of 10 % Base Oil in Kerosene only. Rapeseed oil and biodiesel are prepared in Kerosene (10 times diluted) and stearic acid in Heptane/Kerosene with exact dilution factor of 17.07 (+ heating at 40 °C). Spikes of P and S were added to the stearic acid (main element of interest in this type of sample) to validate the methodology, and illustrate the minimised matrix effects thanks to the superior plasma configuration.

Table 5: Results in raw samples (corrected by the dilution factor), in ppm unit

	Rapeseed oil		Stearic acid		Stearic Acid + 5 ppm spike (in solution)			Biodiesel "A"		Biodiesel "B"	
Element (Wavelength)	Conc. (ppm)	SD (ppm)	Conc. (ppm)	SD (ppm)	Conc. (ppm)	SD (ppm)	Recovery (%)	Conc.	SD (ppm)	Conc. (ppm)	SD (ppm)
Ca 422.673	124.22	2.16	<0.15					<0.15		<0.15	
Ca 393.366	120.04	0.66	0.14	0.01				<0.01		<0.01	
K 766.490	39.21	0.28	2.0	0.17				<2		<2	
Mg 279.553	20.30	0.07	0.13	0.01				<0.02		<0.02	
Mg 279.906	21.45	0.23	<0.25					<0.25		<0.25	
Na 588.995	84.95	0.38	<0.8					7.98	0.09	1.2	0.13
P 178.229	215.63	1.80	15.94	0.54	93.98	2.65	92.8	<0.3		<0.3	
S 180.676	14.68	0.07	1.80	0.07	69.08	2.13	98.5	<0.6		<0.6	

Reference: (1) Application Flash, PETRO 02, "Bio-ethanol", Agnès Cosnier, Sophie Lebouil, Sébastien Vélasquez, HORIBA Jobin Yvon, Longjumeau, France