SHIMADZU APPLICATION NEWS

LAAN-A-AA-E017

● SPECTROPHOTOMETRIC ANALYSIS

No.A397

Analysis of Sodium & Potassium in Fatty Acid Methyl Esters (FAME)

Fatty acid methyl esters (hereafter, FAME) standardized as biodiesel fuel would contain Na and K due to the catalyst, etc. used during production. When these are present in excess, problems occur because they help form solids and metallic soaps, which adhere to the engine fuel injector interior and valves, and block the fuel filter[1]. Therefore, there is a standard for the total content of Na and K in FAME that is used in biodiesel fuel, specifying that the concentration must not exceed 5 mg/kg (European Standard EN14214[4], etc.).

One of the methods specified in EN14214 for the analysis of Na and K is the flame atomic absorption method. The test methods actually used are EN14108[2] and EN14109[3].

This Application News introduces an example of determination of Na and K in FAME produced from palm oil and coconut oil, using the flame atomic absorption method.

■ Reagents and Methods

A standard oil mixture (S-21) containing multiple organic metals (100 ppm each) and blank oil-75, both produced by ConocoPhillips Company (USA), was used for preparation of the standard solutions and xylene, produced by J.T.Baker (USA), was used for dilution. FAME produced from palm oil and coconut oil was used for the analysis sample.

The standard solutions and analysis sample solutions for determination of Na and K were prepared as xylene dilutions according to EN14108 and EN14109, respectively. (In the case of Na, 2 g of sample were diluted to 50 mL with xylene.) Analysis was conducted using the AA-6300, with the analytical conditions shown in Table 1.

Table 1 Analytical Conditions for Na and K by Flame AA

	Na	K
Analysis Wavelength	589.0 nm	766.5 nm
Slit Width	0.2 nm	0.7 nm
Current	12 mA	10 mA
Ignition Mode	Non-BGC	Non-BGC
Flame Type	Air: 17.0 L/min Acetylene: 1.4 L/min	Air: 17.0 L/min Acetylene: 1.5 L/min
Burner Height	8 mm	7 mm

The limit of detection (LOD) was obtained according to the equation below[5]. Specifically, we calculated the standard deviation of absorbance values obtained from 20 repetitions of blank sample measurement, multiplied this by 3 to obtain the corresponding absorbance value, and divided this by the slope of the calibration curve to obtain a concentration, which was then converted to the concentration in the undiluted solution.

$$LOD = \frac{3 \times \text{SD of 20 repetitions of blank measurement}}{\text{slope of calibration curve}} \times \frac{VF}{WF}$$

Where:

SD: Standard deviation

VF: Sample volume after dilution

WF: beginning sample weight

■ Results

The calibration curves for Na and K are shown in Figs.1 and 2, respectively. Excellent linearity is shown in both calibration curve, with correlation coefficients of 0.999 or greater. The calibration curves concentrations are those that were used for sample measurement after dilution. The limits of detection converted for the undiluted solution were 0.02 mg/kg for Na and 0.03 mg/kg for K.

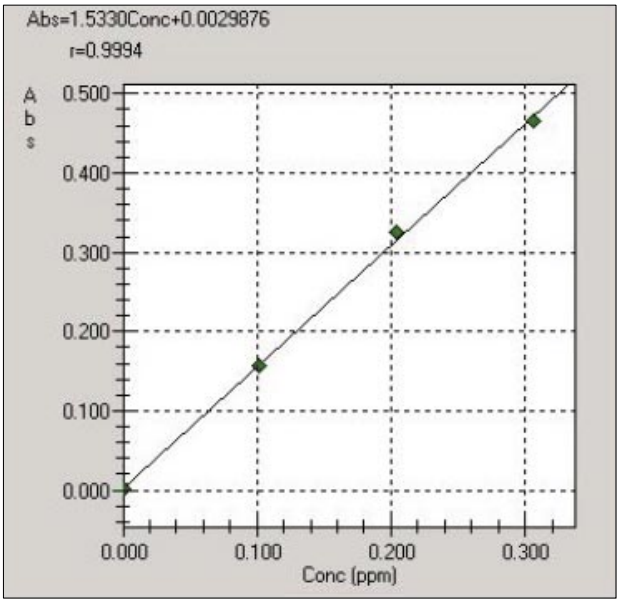

Fig.1 Calibration Curve for Sodium

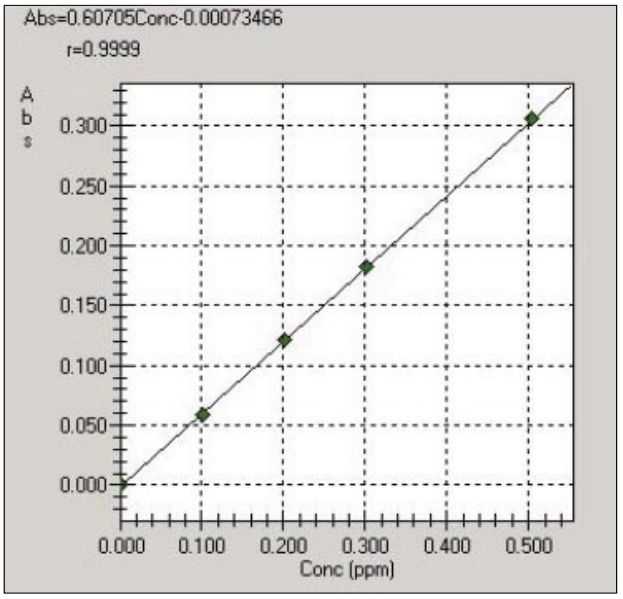

Fig.2 Calibration Curve for Potassium

Table 2 shows the concentrations of Na and K in the two types of FAME samples measured.

Table 2 Na and K Content in FAME Samples

(1) FAME from Palm Oil Stock	
Na Content	K Content
0.04 mg/kg	Less that limit of detection
Total 0.04 mg/kg	
(2) FAME from Coconut Oil Stock	
Na Content	K Content
0.07 mg/kg	0.07 mg/kg
Total 0.14 mg/kg	

The total content of Na and K in the two samples measured was less than 5 mg/kg, satisfying the specification indicated in EN14214. To reduce the effects of the viscosity of the stock oil samples, they were diluted with xylene. However, just in case, we checked whether or not there was any interference from the matrix affecting the analytical accuracy. The method consisted of adding a known quantity of standard solution to the diluted samples. This was used to obtain the recovery rate. The recovery rate (%R), which was calculated using the following equation[6].

%R = [(SSR-SR)/SA] 100 %

Where:

SSR: Measurement result of spiked sample

SR: Measurement result of un-spiked sample

SA: Spike concentration

As is evident from the results in Table 3, the recovery rate was 90% or better for both samples. Consequently, it can be judged that the level of interference from the matrix in this analysis was unremarkable and the values obtained using the calibration curve method are sufficiently reliable.

Table 3 Matrix Interference Test

Sample	Measurement Result
Palm oil stock FAME	0.001 ppm
Palm oil stock FAME spiked with 0.102 ppm Na	0.098 ppm
Recovery rate (%R) = 95.1%	
Coconut oil stock FAME	0.003 ppm
Coconut oil stock FAME spiked with 0.102 ppm Na	0.099 ppm
Recovery rate (%R) = 94.1%	

■ Conclusion

This experiment confirmed that the atomic absorption flame method is a convenient and accurate method for determining the Na and K content in FAME produced from palm oil and coconut oil.

■ References

(1) A Biodiesel Primer (www.methanol.org)

(2) BS EN 14108: 2003 Fat and Oil Derivatives – Fatty Acid Methyl Esters (FAME) – Determination of Sodium Content by Atomic Absorption Spectrophotometry

(3) BS EN 14109: 2003 Fat and Oil Derivatives – Fatty Acid Methyl Esters (FAME) – Determination of Potassium Content by Atomic Absorption Spectrophotometry

(4) BS EN 14214: 2003 Automotive fuels – Fatty Acid Methyl Esters (FAME) for Diesel Engines – Requirements and Test Methods

(5) SAP/CSC/CAM/AAS-031 – How to Determine LOD in AAS

(6) USEPA Contract Laboratory Program – Statement of Work for Inorganic Analysis

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