



Direct determination of sodium, potassium, chromium and vanadium in biodiesel fuel by tungsten coil atomic emission spectrometry



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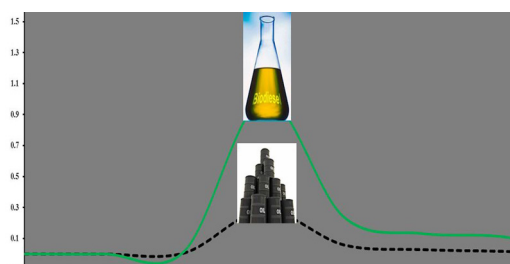
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HIGHLIGHTS

- Direct analysis of biodiesel on a tungsten coil atomizer.
- Determination of Na, K, Cr and V by tungsten coil atomic emission spectrometry.
- Sample dilution with methanol or ethanol.
- Ten-microliter sample aliquots and limits of detection between 20 and 90 $\mu\text{g kg}^{-1}$.
- Low consumption of reagents, samples and gases in a 140 s per run procedure.

GRAPHICAL ABSTRACT



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ABSTRACT

High levels of sodium and potassium can be present in biodiesel fuel and contribute to corrosion, reduced performance and shorter engine lifetime. On the other hand, trace amounts of chromium and vanadium can increase the emission of pollutants during biodiesel combustion. Sample viscosity, immiscibility with aqueous solutions and high carbon content can compromise biodiesel analyzes. In this work, tungsten filaments extracted from microscope light bulbs are used to successively decompose biodiesel's organic matrix, and atomize and excite the analytes to determine sodium, potassium, chromium and vanadium by tungsten coil atomic emission spectrometry (WCAES). No sample preparation other than simple dilution in methanol or ethanol is required. Direct analysis of 10- μL sample aliquots using heating cycles with less than 150 s results in limits of detection (LOD) as low as 20, 70, 70 and 90 $\mu\text{g kg}^{-1}$ for Na, K, Cr and V, respectively. The procedure's accuracy is checked by determining Na and K in a biodiesel reference sample and carrying out spike experiments for Cr and V. No statistically significant differences were observed between reference and determined values for all analytes at a 95% confidence level. The procedure was applied to three different biodiesel samples and concentrations between 6.08 and 95.6 mg kg^{-1} for Na and K, and between 0.22 and 0.43 mg kg^{-1} for V were obtained. The procedure is simple, fast and environmentally friendly. Small volumes of reagents, samples and gases are used and no residues are generated. Powers of detection are comparable to other traditional methods.

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1. Introduction

The rapid economic development of several countries and a growing world population have resulted in a steady increase of energy demand in the last decades. Data published by the Energy Information Administration in its 2011 International Energy

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Outlook [1] show that the world energy consumption in 2008 was 5.05×10^{17} Btu (British thermal units), and that this number will grow to 6.19×10^{17} , and 7.70×10^{17} Btu in 2020 and 2035, respectively. Considering aspects such as sustainability, environmental impacts and energy independence, several alternative renewable sources of energy have been introduced. One of the most popular ones is biodiesel fuel, which is produced from materials such as soybeans, peanuts, sunflower, palm oil, cotton seed, animal fat, etc. Biodiesel is obtained by the transesterification reaction between esters of fatty acids and short chain alcohols such as methanol and ethanol. Among other obvious advantages, this mixture of alkyl esters can be used to fuel common diesel engines with little to no modifications [2].

High levels of Na and K are usually present in biodiesel because NaOH and/or KOH are used as catalysts in the transesterification process. On the other hand, trace levels of other metals may also be found in this fuel due to their presence in the original fatty acid source, or to their incorporation during the purification, refining, storage and transportation stages [3]. These metals can compromise the biodiesel stability and increase the production of pollutants. Sodium and K, for example, are related to ash build-up in the engine which results in corrosion, reduced performance and shorter engine lifetime. Vanadium is an active poison even at low concentrations, which can compromise the efficiency of the catalyst material in the engine exhaust system. In addition, elements such as Cr, V, Ni, Pb, etc. are released in the environment during fuel combustion and can significantly increase air pollution and the incidence of respiratory diseases [4]. Thus, several pieces of legislation have been established to limit the maximum levels of metals allowed in biodiesel fuel. For Na and K, for example, the maximum combined concentration (Na + K) is 5 mg kg^{-1} , as established by North American (ASTM D6751), European (EN 14214) and Brazilian (ANP 07/2008) legislations [5–7].

Biodiesel analysis is not trivial. Characteristics such as viscosity, immiscibility with aqueous solutions and high carbon content can affect sensitivity, accuracy and precision. Different sample preparation procedures (dilution with kerosene, ethanol or 1-propanol; ashing in muffle furnace; solid sampling; emulsion and micro-emulsion preparation; acid digestion; among others) and determination with flame or graphite furnace atomic absorption spectrometry (FAAS or GFAAS); inductively coupled plasma optical emission or mass spectrometry (ICP OES or ICP-MS), and microwave-induced plasma optical emission spectrometry (MIP OES) have been proposed to determine major and trace elements in biodiesel [3,8–11]. An interesting and fast alternative is to decompose the biodiesel organic matrix directly on an electrothermal vaporizer (ETV) and introduce the analyte vapors into an ICP-MS [12,13]. Despite the effectiveness of all these procedures, elements such as Na, K, Cr and V remain a challenge because of FAAS and ICP OES relatively low sensitivities and GFAAS and ICP-MS interferences.

In this work, tungsten filaments extracted from commercially available microscope light bulbs are used to successively decompose biodiesel's organic matrix, and atomize and excite the analytes to determine Na, K, Cr and V by tungsten coil atomic emission spectrometry (WCAES). This method, first described in 2005 [14], has been successfully applied to different analytes and samples, with performances comparable to other traditional analytical methods [15–17]. It is especially sensitive for Groups 1 and 2 elements [17–19], and instrumentation improvements have allowed effective determinations of more refractory elements such as Cr and V [20–22]. In the work described here, 10- μL sample aliquots were used and no sample preparation other than simple dilution in methanol or ethanol was required. The tungsten coil atomizers last for up to 50 runs, which is adequate to analyze several samples with no residues produced and low consumption of reagents and gases.

Table 1

Heating cycle used with 150 W, 15 V coils to determine Na and K in methanol-diluted biodiesel samples by WCAES.

Step	Applied current (A)	Atomizer surface temperature (K) ^a	Time (s)	Step
1	1.7	850	25	Vaporization
2	2.0	940	30	Vaporization and pyrolysis
3	2.5	1100	25	Pyrolysis
4	2.8	1190	30	Pyrolysis
5	0	298	10	Cooling
6	7.0	2490	20	Atomization
7	10.0	3420	3	Cleaning

^a Estimated from $T(K) = 309I(A) + 325$ [24].

2. Experimental

2.1. Instrumentation

For Na and K, the tungsten coil atomizer was extracted from 150 W, 15 V microscope light bulbs (Osram Xenophot HLX 64633, Augsburg, Germany). The bulb's fused silica envelope was removed leaving its base intact. A 200 W constant-current power supply (Vicor, VI-LU1-EU-BM, Andover, MA, USA) were used to resistively heat the atomizer, and the heating cycle presented in Table 1 was employed for biodiesel analysis. The analytical signals were collected by a 25 mm diameter, 75 mm focal length fused silica lens, and the 1:1 coil image was projected onto the 25 μm entrance slit of a handheld charge coupled device-based (CCD) spectrograph (USB4000, Ocean Optics, Dunedin, FL, USA). A pinhole (c.a. 0.5 mm) was drilled on an aluminum cap, which was then placed on the spectrograph entrance slit to minimize the background signal from the atomizer [22]. To ensure the best signal-to-background ratios, the coil image was positioned adjacent, but not overlapping the pinhole aperture. The heating program was written in Visual Basic, and power supply and spectrograph were controlled by a desktop computer using an USB 2.0 port. An integration time of 0.8 s, with 25 spectra collected totalizing 20 s, were adopted for all determinations. The atomizer was housed in a borosilicate glass cell (Ace Glass, product No. D131703, Vineland, NJ, USA) and a protecting gas mixture of 10% H_2 /90% Ar flowed at 1.0 L min^{-1} during all steps of the heating cycle. More details on the atomization cell can be found in the literature [17].

Due to Cr and V refractory characteristics, the previously described atomizer was replaced by a 250 W, 24 V tungsten filament (Platinum EVC/FGX, Long Island City, NY, USA). In addition to the possibility of reaching higher atomization temperatures, this larger atomizer minimizes sample losses caused by splashing [13]. The heating cycle presented in Table 2 and a 400 W constant-current power supply (Vicor, VI-MU3-CQ-BM) were also employed in all Cr and V determinations. To improve sensitivity, the handheld spectrograph was replaced by a crossed Czerny-Turner monochromator (MonSpec 18, Scientific Measurement Systems, Grand Junction, CO, USA) and a thermoelectrically cooled

Table 2

Heating cycle used with 250 W, 24 V coils to determine Cr and V in ethanol-diluted biodiesel samples by WCAES.

Step	Applied current (A)	Atomizer surface temperature (K) ^a	Time (s)	Step
1	0.5	450	50	Vaporization and pyrolysis
2	3.9	1300	10	Pyrolysis
3	0	298	10	Cooling
4	13	3580	4	Atomization

^a Estimated from $T(K) = 250I(A) + 325$ [17,22].

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