



Signal correction using molecular species to improve biodiesel analysis by microwave-induced plasma optical emission spectrometry



Kenneth L. Lowery^a, Tina McSweeney^b, Shiba P. Adhikari^a, Abdessadek Lachgar^a, George L. Donati^{a,*}

^a Department of Chemistry, Wake Forest University, Salem Hall Box 7486, Winston-Salem, NC 27109, USA

^b Agilent Technologies, 2500 Regency Parkway, Cary, NC 27518, USA

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ABSTRACT

Microwave-induced plasma optical emission spectrometry (MIP OES) and a simple dilute-and-shoot sample preparation procedure with 1-propanol are used to determine Ca, K, Mg and Na in biodiesel fuel. MIP naturally occurring molecular species are used to probe plasma condition variations during sample introduction, and then correct analytical signals to improve accuracies. The electronic transitions for N_2^+ ($0-0, B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) and OH ($0-0, A^2\Sigma^+ \rightarrow X^2\Pi$) are used as molecular probes. A biodiesel standard reference sample is analyzed and the results for the molecular probe signal correction method are compared with values obtained with a traditional external standard calibration (EC). Improved accuracies were observed for Ca using the N_2^+ probe, and for K, Mg and Na using OH. Recoveries were in the 82–104% range for all analytes (60–130% for EC). The limits of detection (LODs) for Ca, K, Mg and Na are 70, 7, 9 and 8 $\mu\text{g/L}$, respectively (2 mg/kg for Ca, and 0.2 mg/kg for all the other analytes). The method was applied to three biodiesel fuel samples and the concentrations ranges for Ca, K and Na were 9.0–16.0, 10.6–142.1, and 7.8–52.7 mg/kg, respectively. Magnesium values were lower than the LOD in all cases. Analytical signal correction using plasma naturally occurring molecular species has the potential to significantly improve accuracy and sample throughput. It allows for effective determinations without the need for time-consuming calibration methods such as standard additions.

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1. Introduction

Renewable fuels have become an important part of the energy portfolio in many countries. Among those, biodiesel is one of the most promising alternatives to petroleum-derived fuels, with worldwide production systematically increasing in the last decade. In Brazil, one of the largest producers and consumers of biodiesel fuel in the world, 2.7 billion liters were produced in 2011 [1], with an estimate 4.1 billion liters expected for 2016 [2]. In the United States, 4.9 billion liters were produced between February 2015 and January 2016 [3]. Biodiesel fuel production is simple and requires relatively low initial investment. It is most commonly obtained by the transesterification reaction between vegetable oils or animal fats and methanol. In addition to environmental and energy independence aspects, one of the main advantages of using this alternative fuel is its compatibility with common diesel engines, which require little to no modifications to run on pure biodiesel [4].

Many mineral contaminants can be incorporated into biodiesel during its production, transport and storage. However, four elements are a major cause of concern in the biodiesel production chain due to their potentially high concentrations in the final product: Ca, K, Mg

and Na. Sodium and potassium hydroxides are used as catalysts in the transesterification reaction. On the other hand, Ca and Mg are incorporated when successive washing and purification steps are employed to remove high concentrations of Na and K. Even at low concentrations, these elements form insoluble soaps that contribute to ash build-up in the engine, ultimately compromising its performance and increasing air pollution. They can reduce biodiesel's oxidative stability and significantly contribute to the corrosion of engine parts [5]. Thus, regulatory agencies in the United States, the European Union and Brazil have established that biodiesel fuel with a Na + K concentration higher than 5.0 mg/kg cannot be sold in their markets. The same value is applicable for Ca + Mg [6–8].

It is clear that a simple and efficient analytical procedure for the determination of Ca, K, Mg and Na in biodiesel is in high demand. However, issues associated with this fuel's high viscosity, incompatibility with aqueous solutions and complex matrix can make the development of a simple, fast and accurate procedure a challenging proposition. Several methods have been used to improve accuracy and sample throughput in biodiesel analysis, with inductively coupled plasma optical emission spectrometry (ICP OES) and flame methods (i.e. flame atomic absorption and atomic emission spectrometry, FAAS and FAES) being the most common approaches [9–12]. Extreme variations in the composition of an atomization environment (e.g. Ar plasma) usually are the

* Corresponding author.

E-mail address: donatig@wfu.edu (G.L. Donati).

main cause of poor accuracy in spectrochemical analysis [13,14]. This effect is especially severe when complex matrices and high carbon-content samples such as biodiesel fuel are analyzed. The main strategies to minimize matrix effects in ICP OES fuel analysis are the use of robust conditions [13], introduction of O₂ gas into the plasma to decompose carbon species [15], and standard additions calibration. On the other hand, complete sample digestion, the preparation of emulsions and microemulsions, and standard additions are the few available alternatives to ensure accuracy in FAAS and FAES determinations [10,11]. Most of these procedures are time-consuming, especially the ones requiring standard additions, which require the preparation of a calibration curve for each individual sample.

In this work, we use microwave-induced plasma optical emission spectrometry (MIP OES) and simple dilution in 1-propanol to determine Ca, K, Mg and K in biodiesel fuel. The N₂ plasma used in MIP OES is more tolerant to organic solvents and high carbon-content samples than an Ar ICP OES [16,17]. It is also less prone to matrix effects than FAAS and FAES because of its significantly higher temperatures when compared to a nitrous oxide flame [18,19]. On the other hand, the N₂ MIP is less robust and has a lower temperature than an Ar ICP [19,20]. We evaluate the use of naturally occurring molecular species in the N₂ MIP to correct for plasma composition changes during the introduction of biodiesel samples. The molecular electronic transitions for N₂⁺ (0–0, B²Σ⁺_u → X²Σ⁺_g) and OH (0–0, A²Σ⁺ → X²Π_i) are used as molecular probes for analytical signal correction [21–23].

2. Experimental

2.1. Instrumentation

Biodiesel analyses were carried out with a MIP OES (4200 MP-AES, Agilent Technologies, Santa Clara, CA, USA) equipped with a SPS 4 automatic sampler, solvent-resistant tubing, a double-pass cyclonic spray chamber and an inert Flow Blurring nebulizer (OneNeb). Nitrogen gas used to run the instrument was provided by a liquid N₂ Dewar. The instrument's external gas control module (EGCM) and default operating conditions were used in all determinations (Tables 1 and 2). With the EGCM, air is introduced through the MIP torch's auxiliary gas inlet to decompose carbon-containing species and prevent soot deposition on the torch and the optical system. Niobium and terbium emission lines at 391.470 and 308.958 nm were used to monitor the N₂⁺ and OH molecular species. The MIP OES software (MP Expert) allows the user to fine-tune the position on the emission profile from which the analytical signals are recorded by dragging the cursor to the desired location. This feature has ensured the accuracy of electronic transition measurements for both N₂⁺ and OH, with emission band heads at 391.4 and 309 nm, respectively (Fig. 1 and Table 2).

2.2. Reagents and standard reference solutions

Distilled-deionized water (18 MΩ cm, Milli-Q®, Millipore, Bedford, MA, USA) and trace metal grade nitric acid (Fisher, Pittsburgh, PA, USA) were used to prepare all aqueous solutions. Trace metal grade 1-propanol (TraceSELECT®, Fluka, Saint Louis, MO, USA) was used to prepare non-aqueous solutions and to dilute the biodiesel samples. Single-

Table 1
Operating conditions for the direct analysis of biodiesel fuel by MIP OES.

Instrumental parameter	Operating condition
Microwave frequency (MHz)	2450
Microwave power (kW)	1.0
Integration time (s)	3
Peristaltic pump speed (rpm)	15
Number of replicates	3
Stabilization time (s)	15
Background correction	Auto

Table 2

MIP OES instrumental default settings and analytical wavelengths used for biodiesel fuel analysis using aqueous or 1-propanol standard reference calibration solutions.

Element	Wavelength (nm)	Plasma viewing position ^a	Nebulization gas flow rate (L/min)	EGCM air flow rate
Ca	422.673	0	0.60	Medium
K	766.491	0	0.75	Medium
Mg	285.213	0	0.90	Medium
Na	588.995	0	0.95	Medium
Nb (N ₂ ⁺ ion)	391.470	0	0.75	Medium
Tb (OH radical)	308.958	0	0.75	Medium

^a It has no specific unit. Based on stepper motor positioning of a mirror. Position 0 approximately corresponds to the center of the plasma [19].

element aqueous stock solutions of Ca, K, Mg and K (1000 mg/L, SPEX CertPrep, Metuchen, NJ, USA) were used to prepare the standard reference solutions (aqueous and non-aqueous) used for calibration. The external standard calibration method was used in all determinations. Calibration curve solutions prepared in aqueous 1% v/v HNO₃ or 1-propanol were evaluated.

2.3. Samples and sample preparation

A reference sample of biodiesel (Metals in Biodiesel, B100M5–20, VHG Labs, Manchester, NH, USA) was used to check the method's accuracy. Three biodiesel samples produced in the Department of Chemistry of Wake Forest University were also analyzed. Approximately 0.25 g of the biodiesel reference sample (VHG Labs) was accurately weighed using a four decimal place electronic balance (Mettler AE 100, Hightstown, NJ, USA), and diluted to 5.00 mL with 1-propanol (Fluka). The mixture was then homogenized for 1 min with a vortex mixer (Scientific Industries Inc., Bohemia, NY, USA) before analysis by MIP OES. The same dilution procedure was applied to 0.10–0.20 g of the other three biodiesel samples.

3. Results and discussion

3.1. Signal correction using molecular species

The energy available in a MIP is sufficient to excite molecular species. Depending on the plasma gas, its impurities, and the constitution of the analytical solution, intense emission band heads can be observed for OH, NH, N₂, N₂⁺, CN, among other gas species [23–25]. As discussed before, the introduction of complex matrix samples into the plasma can significantly change its constitution, temperature, and/or electron number density, which results in poor accuracy [13,14,19]. In the present work, we hypothesize that some of MIP's naturally occurring molecular species could be used to probe plasma fluctuations and then correct analytical signals to improve accuracy. In this case, electronic transitions for N₂⁺ (0–0, B²Σ⁺_u → X²Σ⁺_g) and OH (0–0, A²Σ⁺ → X²Π_i), with emission band heads at 391.4 and 309 nm, were used as molecular probes [21–23]. Considering that plasma fluctuations may affect analytical (A) and molecular probe (P) signals differently, we have evaluated two signal correction treatments. Calibration curves were built using either A / P or A × P on the y-axis, and analyte concentration (C) on the x-axis. Calcium, K, Mg and Na were then determined in a biodiesel reference sample, and the results for the molecular probe signal correction method (A / P vs. C, or A × P vs. C) were compared with values obtained using the traditional A vs. C calibration. Standard reference solutions prepared in 1% v/v HNO₃ or 1-propanol were evaluated in this study. The most accurate results are presented in Table 3.

The results show the typical severe matrix effects in biodiesel analyses. Although Na requires no signal correction and no solvent matching (i.e., it may be determined using aqueous standard reference solutions), poor recoveries are observed for all the other analytes using the

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