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Methyl oleate as matrix simulacrum for the simultaneous determination of metals in biodiesel samples by flame atomic emission spectroscopy

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ABSTRACT

A measurement procedure for direct and simultaneous quantification of Na, K and Ca in biodiesel by flame atomic emission spectroscopy (FAES) was developed. A lab-made device was constructed by coupling a nebulizer/combustion system from a commercial photometer to a continuous emission detector in a spectral range of 255 to 862 nm. Instrumental optimizations were carried out evaluating the most important variables, such as gas flow rates and sample introduction temperature, indicating that a temperature of 50 °C enhances the analytical signals and assures good precision. The direct analysis method was properly validated and presented limits of quantification of 0.09, 0.07 and 0.43 μg kg^{-1} for Na, K and Ca, respectively. Accuracy of the proposed procedure was checked by comparing the results with those obtained by the standard procedure described in ABNT NBR 15556 and the standard addition method.

1. Introduction

Biodiesel is a renewable fuel composed of alkyl esters composed of long-chain fatty acids, derived from vegetable oils or animal fat [1]. In Brazil, pure biodiesel is designated as B100 [2], and the mixtures of biodiesel with diesel are categorized as BX, where X represents the percentage of biodiesel added to mineral diesel [3]. A variety of routes for this biofuel synthesis have been developed, but the most commonly applied route is the methanolysis using sodium methoxide as catalyst.

Brazil's National Petroleum, Natural Gas and Biofuels Agency (ANP) regulates the fuels industry and establishes the criteria for quality control of biodiesel. The standard procedures established by the ANP are based on the classic route for biodiesel synthesis, reflecting characteristics such as kinematic viscosity, specific density, cold filter plugging point and stability to oxidation, which are dependent on the oleaginous properties. Other parameters such as copper corrosiveness, total contamination and water content are different modes to evaluate whether the transport and storage of biodiesel are adequate. Parameters such as ester, mono, di and triacylglycerol contents indicate if the reaction had an adequate yield. Finally, the concentrations of free glycerol, total glycerol and metals and metalloids are characteristics of the synthesis process that are related to the efficiency of the biofuel purification stage. However, besides being used to evaluate the production, transportation, storage, stability, gas emission control and environmental contamination aspects, these parameters are also used to control and prevent impairments to the vehicles that use the fuel.

The presence of metals can result in a series of issues such as the acceleration of biofuel decomposition, catalysis of oxidation reactions and reduction of thermal stability and efficiency, contributing to corrode the internal engine parts [4–6] besides compromising the catalyst system, thus increasing atmospheric pollution [7,8]. Trace elements can be incorporated in biodiesel during the oil extraction, synthesis, washing, refinement, transportation and storage [6]. They can also originate from the plants as a consequence of their growing area [9,10]. The monitoring of Na, K, Ca and Mg is necessary due to their capacity to form insoluble soaps and abrasive solids, resulting in deposits within vehicles' filters, which increases engine wear and corrosion [4–6]. Phosphorus promotes the poisoning of catalytic converters formation of gums [11,12].

The standard procedures to quantify metals established by Brazilian legislation are based on techniques such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectroscopy (ICP OES) as described in the NBR 15553 and 15556 standards, respectively [11,13]. For Na and K determination, the ANP establishes the use of alternative procedures such as those specified in NBR 15554 [14] and NBR 15555 [15], as well as European Standard Methods EN 14108 [16], 14109 [17] and 14538 [18]. All these procedures are based on direct dilution of biodiesel in different solvents, such as xylene or toluene, using an external calibration curve

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with organometallic standards, where the viscosity of the calibration solutions is adjusted with mineral oil.

A considerable number of procedures have been described in the literature. The techniques that involve atomic absorption spectrometry have been widely employed to measures the concentration of metals in biodiesel by applying electrothermal atomic absorption spectrometry (ET-AAS) [6–13,19], graphite furnace atomic absorption (GF-AAS) [8,20–23], and flame atomic absorption spectroscopy (FAAS) [24–27]. They are advantageous due to their low cost, sensitivity and simplicity [24,28]. Atomic emission techniques are also applied to metal determination using inductively coupled plasma optical emission spectroscopy (ICP OES) [29,30]. Inductively coupled plasma mass spectrometry (ICP–MS) [31,32] is also used due to its ability to detect multiple elements and high sensitivity. Finally, flame atomic emission spectroscopy has also been used for metal quantification in biodiesel samples [33–37].

The determination of metals in organic samples such as biodiesel can be a tedious analytical task when previous digestion procedure is required [38]. The advantage is related to the possibility of using aqueous standards for calibration [39,40]. On the other hand, direct dilution with organic solvents is simple and fast as well as compatible with sample introduction by pneumatic nebulization. This procedure overcomes problems associated with the high viscosity of the oil samples, but it has the disadvantage of the high toxicity of some of these solvents, which can lead to serious health risks [41]. Emulsions or micro emulsions can also be applied for biodiesel sample preparation [20,23–27,29,32,34,36]. The main advantages of using emulsions and micro emulsions in analytical chemistry are related to the modification of the sample matrix through the formation of an oil-in-water system. This procedure requires minimum sample manipulation, presents high stability and the possibility of using inorganic standards for calibration when the emulsion is acidified with mineral acid [42]. However, preparing micro emulsions requires an adequate combination of reagents and long sample preparation time. Furthermore, some of these emulsions quickly become unstable.

The direct analysis of metals in biodiesel is not a simple task due to the physical and chemical characteristics of the sample, such as high viscosity and matrix complexity. The main advantage of direct analysis is the minimal manipulation of the sample, reducing the risk of analyte loss and contamination. It is also fast, inexpensive and less subject to error in estimating the results. In the case of the spectrometric techniques that use nebulization, the disadvantages of direct analysis of biodiesel are the difficulties to introduce the samples due to their high viscosity and production of a rich fuel flame, which complicates the total burning of the organic matter and causes the possibility of interference due to the complexity of the matrix.

In this sense, the dilution of biodiesel in a solvent with similar physical–chemical characteristics can be advantageous. Methyl oleate is a commercial product that presents similar physical–chemical properties to biodiesel, such as viscosity, and it also is one of the major biodiesel compounds [43]. The viscosity of methyl esters decreases with increasing temperature [44], a factor that is crucial to the success of the procedure.

The goal of this work was to develop a direct and simultaneous procedure for quantification of Ca, K and Na in biodiesel samples using methyl oleate as matrix simulacrum by the flame atomic emission spectrometry technique in a lab-made device with a continuous emission detector.

2. Experimental

2.1. Instrumentation

The measurements were carried out in a lab-made device comprised of a combustor-nebulizer system from a flame photometer (Evans Electroslenium Ltd., Essex, England) combined with an EPP2000 StellarNet detector. The apparatus was connected to a computer running the SpectraWiz program using Windows. The instrumental parameters were obtained through the continuous spectra emission recorded by the detector with the assistance of an optical fiber. The measurements of the analytical signals were based on the height of the peak emission.

Table 1
Operational conditions of the flame atomic absorption spectrometer.

Parameter	Set value		
Flame air/acetylene	10.0–2.5 L min^{-1}		
Flame C_2H_2/N_2O	7.5–6.5 L min^{-1}		
Integration time	10 s		
Analyte	**Na**	**K**	**Ca**
Current lamp (mA)	12	12	15
Slit width (mm)	1.8	2.7	2.7
Wavelength (nm)	589.00	766.49	422.67

Synthetic medicinal air was used as oxidant and liquefied petroleum gas (LPG) was used as fuel. The quantification through the standard ABNT NBR 15556 procedure was carried out in a flame atomic absorption spectrometer (AAnalyst 400-PerkinElmer, USA), using a multielement Na and K lamp, multielement Ca and Mg lamp (PerkinElmer, USA) and deuterium lamp for background correction. The aspiration rate was set manually to obtain the largest instrumental signal. The operational conditions are shown in Table 1.

A vortex agitator was used for homogenization of the solutions, operating at 3400 rpm. Ultra purified water was used in all experimental work (Master System P&D produced by Gehaka, Brazil).

2.2. Reagents and solutions

In order to build the calibration curves for both the proposed procedure and the standard NBR 15556, a multi element organometallic standard was used, the 23-element oil standard in base oil 75, containing Al, Sb, Ba, B, Cd, Ca, Cr, Cu, Fe, Pb, K, Mg, Mn, Mo, Ni, P, Si, Ag, Na, Sn, Ti, V and Zn (SPEX CertiPrep., USA), in the concentration of 100 μg g^{-1} for each element. The Li organometallic standard (1000 μg g^{-1}) in base oil 75 (SPEX Certi Prep., USA) was also used.

A stock solution of Na, K and Ca (100 μg g^{-1}) was prepared for the analyte addition curves from Conostan (USA) organometallic standards, with concentrations of 500 ppm for Ca and Mg, and 5000 ppm for Na and K. In order to plot the calibration curves for the standard procedure NBR 15556, a highly pure mineral oil (Produtos Ideal, Brazil) was used, as well cyclohexane (Synth, Brazil).

Methyl oleate (Dhaymers Química Fina, Brazil) was chosen as solvent and matrix simulacrum for the proposed procedure. Methyl oleate is a long-chain ester (18 carbon atoms) that presents very similar physical–chemical to biodiesel. This compound is mentioned in the literature as reference substance for biodiesel due to its properties [45].

To clean the sample introduction system, a solution of 50% v/v ethanol:water was used.

2.3. Samples

Biodiesel samples were obtained through transesterification of different vegetable oils and animal fats by the methyl or ethyl route according to the description in Table 2. The samples were provided by different producers.

The kinematic viscosity at 40 °C was performed according to the ASTM D445 standard method [46], using oil standards (*IPT—Instituto de Pesquisas Tecnológicas*) and mineral oil OP10 for