Revista Virtual de Química
ISSN 1984-6835

Artigo

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Rev. Virtual Quim., **2018**, *10* (3), 542-550. Data de publicação na Web: 30 de maio de 2018

http://rvq.sbq.org.br

Determinação de Ca, Mg, Na e K em Biodiesel de Oleaginosas do Norte do Brasil

Resumo: Neste estudo, a espectrometria de absorção atômica com chamas (FAAS) foi utilizada para determinar os teores de cálcio (Ca), magnésio (Mg), sódio (Na) e potássio (K) em biodiesel produzido com diferentes oleaginosas (bacaba, bacuri, castanha-do-brasil e palma). As amostras foram digeridas com ácido nítrico, ácido sulfúrico e peróxido de hidrogênio usando sistema aberto com aquecimento convencional. As recuperações obtidas pelo método de adição e recuperação para Ca, Mg, Na e K foram de 86 - 113%, 81 - 101%, 96 - 118% e 89 - 119%, respectivamente. Os resultados mostraram níveis de Ca e Na variando entre 58,56 - 126,6 mg kg^{-1} e 3,06 - 4,61 mg kg^{-1} nas amostras. Os níveis de Mg nas amostras estavam abaixo do limite de detecção. Teores de K foram encontrados apenas nas amostras B2 e B4. Este estudo mostrou que tanto a oleaginosa quanto o catalisador utilizado na produção do biodiesel durante o processo de síntese podem influenciar as concentrações finais dos metais nas amostras de biodiesel.

Palavras-chave: metais; biodiesel; Amazônia; FAAS.

Abstract

In this study, flame atomic absorption spectrometry (FAAS) was used to determine calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) contents in biodiesel produced with different oilseeds (bacaba, bacuri, Brazil nut, and palm). The samples were digested with nitric acid, sulfuric acid, and hydrogen peroxide using an open system with conventional heating. The recoveries obtained by the addition and recovery method for Ca, Mg, Na, and K were 86 - 113%, 81 - 101%, 96 - 118%, and 89 - 119%, respectively. The results showed that levels of Ca and Na ranged from 58.56 - 126.6 mg kg^{-1} and 3.06 - 4.61 mg kg^{-1} in the samples. The Mg levels in samples were below the limit of detection. Contents of K were found only in samples B2 and B4. This study showed that both the oleaginous and the catalyst used in biodiesel production during the synthesis process can influence the final concentrations of the metals in the biodiesel samples.

Keywords: metals; biodiesel; Amazon; FAAS.

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DOI: 10.21577/1984-6835.20180041

Volume 10, Número 3 Maio-Junho 2018

Revista Virtual de Química
ISSN 1984-6835

Determination of Ca, Mg, Na, and K in Biodiesel of Oilseed from Northern Brazil

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Recebido em 15 de março de 2018. Aceito para publicação em 12 de maio de 2018

1. Introduction

Biodiesel is described as an alternative fuel chemically composed by mono-alkyl esters of fatty acids derived from lipids of natural occurrence, and it can be produced, along with glycerin, through the reaction of triacylglycerols (or triglycerides) with ethanol or methanol, in the presence of an acid or basic catalyst. The catalysts are produced from renewable and biodegradable sources, such as vegetable oils, animal fat, and oils used for cooking food (frying), used in internal combustion engines with ignition by compression. [1-2]

Due to the great biodiversity, extensive areas of agriculture, favorable climate, and soil conditions, Brazil has different sources of vegetable oils, such as sunflower, soybean, castor plant, babassu, jatropha, pupunha palm, coconut, cotton, palm, and others. [3] Besides vegetable oils, several other oilseeds, which are still under evaluation and development of their supply chains, can be used for biodiesel production. [4] The Northern region of Brazil has potential for use of palm,

babassu, and soybean oils; however, due to the wide variety of native species in the Amazon, there could still be several other raw materials (palm trees) that have not yet been investigated. Amais *et al*. [5] evaluated metal concentrations in five types of biodiesel (African oil palm, castor beans, mineral oil, palm, and soybeans) using microemulsions and flame atomic absorption spectrometry (FAAS). Lin *et al.* [6] studied the transesterification process of Jatropha oil.

Inorganic contaminants present in biodiesel, such as Ca, Mg, Na, and K affect the engine performance and may cause corrosion and clogging of some components. These elements form deposits and promote side reactions that contribute to biodiesel decomposition. Na and K are introduced with the addition of Na and K hydroxide in the catalytic process as homogeneous basic catalysts because of their high conversion levels achieved and low costs in the transesterification and esterification processes. There are several limitations of the biodiesel purification steps, which hinder the recovery and reuse of the catalyst due to the dissolution of ionic bases with consequent biodiesel contamination, where the metal ions are solubilized in the medium. Other contaminants, such as Ca and Mg, are also present in vegetable oils used for biodiesel production. The Brazilian legislation has determined values for the control of Na, K, Ca, and Mg levels. [7] The investigation of other elements may become important due to several factors, including the following: 1-sulfur, which can cause acid rain and 2-silicon, which is added as an antifoam agent in petroleum-derived products, particularly diesel, causing decreased engine performance, corrosion, and increased emissions of particulate material. [8]

Several analytical techniques have been used to control the presence of metals in biodiesel, such as flame atomic emission spectrometry (FAES), flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF AAS), inductively coupled plasma optical emission spectrometry (ICP OES), and inductively coupled plasma mass spectrometry (ICP-MS) [1,9-12].

European norms recommend the dilution of the biodiesel sample with xylene, calibration with organic standards and direct determination of Ca, Mg, K, and Na by ICP OES and determination of K and Na only by FAAS. [13-14] On the other hand, Brazilian norms propose the determination of Ca, Mg, K, and Na by FAAS. [13]

Jesus, Zmozinski, Barbara, Vale, and Silva (2010) determined Ca and Mg levels in biodiesel by FAAS using samples prepared as water-in-oil microemulsions.[15] Lyra, Carneiro, Brandão, Pessoa and Castro (2010) quantified Na, K, Ca and Mg in biodiesel samples by FAAS using samples prepared as microemulsions without a surfactant. [10] Amais, Garcia, Monteiro and Nóbrega (2012) determined Ca, Mg, and Zn in biodiesel microemulsions by FAAS using discrete aspiration for sample introduction. [5] Magalhães, Barros, Oliveira, Silva, and Villa (2014) proposed a sample preparation procedure using ethanol for determination of Ca, Mg, Na, and K in biodiesel by FAAS. [1]

Regarding the wide range of biodiesel produced with oilseeds from Northern Brazil, this study aimed to develop an analytical method for determining Ca, Mg, Na, and K in biodiesel produced with bacaba (*Oenocarpus bacaba*), Brazil nut (*Bertholletia excelsa*), bacuri (*Platonia insignis*), and palm (*Elaeis guineensis*) by FAAS using a conventional open system.

2. Materials and methods

2.1. Samples

The following biodiesel samples were obtained from different plant sources and provided by the Grupo de Catálise e Oleo Química of the Instituto de Ciências Exatas e Naturais from Universidade Federal do Pará (UFPA): B1 (bacaba), B2 (bacuri), B3 (Brazil nut), and B4 (palm). On the other hand, the

palm biodiesel (B5) was provided by a local biodiesel industry. The biodiesel characteristics are shown in Table 1.

Table 1. Characteristics of the biodiesel samples

Sample	Oil	Process	Catalyst	Alcohol
B1	Bacaba	Transesterification	Methanesulfonic	Ethanol
B2	Bacuri	Transesterification	Methanesulfonic	Ethanol
B3	Brazil nut	Transesterification	Methanesulfonic	Ethanol
B4	Palm	Transesterification	KOH	Methanol
B5	Palm (Industry)	Esterification	KOH	Methanol

2.2. Sample preparation

The biodiesel samples were digested in a conventional open system (Tecnal block digester, Model TE-040/25-1). The volume of acid and heating temperature of the conventional open system were studied. A mass of about 0.5 g of each biodiesel sample (n = 3) was weighed, and 2 mL of 18 mol L^{-1} H_2SO_4 and 2 mL of 14 mol L^{-1} HNO_3 were added. The samples were left to rest for 12 hours. After this time, a volume of 1 mL of 14 mol L^{-1} HNO_3 was added to the samples, and then the digestion tubes were placed in the conventional open system at a temperature of 100 °C. One hour after the beginning of the digestion process, the temperature was raised to 150 °C. Once a decrease in gas formation was verified, the temperature was once again raised to 180 °C. The digestion tubes were removed from the conventional open system and cooled down at room temperature, followed by the addition of 3 mL of 30% (w/w) H_2O_2. Again, the digestion tubes were placed in the conventional open system until bleaching of the sample was obtained along with the disappearance of foams. After digestion, the digested samples were transferred to volumetric tubes and diluted to 20 mL with deionized water. The final acidity of all digested samples was determined by acid-base titration using a NaOH standardized solution.

2.3. Determination of Ca, Mg, Na, and K in biodiesel by FAAS

For analysis of Ca and Mg, an aliquot of the digest was diluted with 1% (w/v) lanthanum chloride solution. For the determination of K, a volume of the digest was diluted with 1% (w/v) cesium chloride solution. For quantification of Na, an aliquot of digest was diluted with 1% (w/v) potassium chloride solution. The solutions obtained were analyzed for the determination of Ca, K, Mg, and Na by FAAS (AA 220, Varian, Mulgrave, Australia). The instrumental parameters used are shown in (Table 2).

The analytical blanks were prepared by the same procedure, but without the addition of sample. The accuracy of the proposed method was assessed by the method of addition and recovery.

Table 2. Instrumental parameters used for determination of Ca, Mg, Na, and K in biodiesel samples by FAAS

Elements	λ (nm)	Current (mA)	Spectral resolution (nm)	Gas
Ca	423.0	10	0.5	C_2H_2/Ar
Mg	285.2	4	0.5	C_2H_2/Ar
Na	589.6	10	1.0	C_2H_2/Ar
K	766.5	5	1.0	C_2H_2/Ar

3. Results and discussion

3.1. Figures of merit

The limit of detection (LOD) and limit of quantification (LOQ) by FAAS were calculated from measurements of the analytical blank. LOD and LOQ values were defined as 3s/b and 10s/b, where *s* is the standard deviation of the blank (*n* = 10) measurements and *b* is the slope of the calibration curve.[21] The figures of merit obtained for the determination of Ca, Mg, Na, and K in the biodiesel samples by FAAS are summarized in Table 3.

Table 3. Figures of merit obtained for FAAS

Parameters	Ca	Mg	Na	K
Slope	0.024	0.618	0.619	0.739
R^2	0.999	0.997	0.967	0.999
LOD (mg kg^{-1})	0.3	0.02	0.15	0.03
LOQ (mg kg^{-1})	1.0	0.06	0.50	0.09
C_o*	183	7	7	6

*Characteristic concentration; LOD: limit of detection; LOQ: limit of quantification; R2: correlation coefficient.

The LOD and LOQ obtained show that the calibration used was able to reproduce results in low concentrations at levels that have reliable precision and accuracy. The values of the linear coefficients (R^2) show a good linearity in relation to the analytical response *versus* concentration with values between 0.967 - 0.999.

3.2. Method validation

The accuracy of the measurements by FAAS were also verified by the addition and recovery method. The digest samples were spiked with three different concentrations of the analytes and resulting solutions were analyzed by FAAS, as shown in Table 4.

Table 4. Recoveries obtained for Ca, K, Mg, and Na for the method of addition and recovery in digests samples by FAAS

	Spiked (mg L^{-1})	Found (mg L^{-1})	Recovery (%)
	2.0	2.32	110
Ca	2.5	2.96	113
	3.0	3.13	86
	0.1	0.29	101
K	0.2	0.21	84
	0.3	0.30	81
	0.25	0.25	96
Mg	0.30	0.37	118
	0.35	0.38	105
	1.0	1.80	119
Na	1.5	2.00	89
	2.0	2.35	109

Recoveries obtained for Ca, Mg, K, and Na in digest samples ranged from 86.0 - 113.0%, 96.0 - 118.0%, 81.0 – 101.0%, and 89.0 - 119.0%, respectively. It could be concluded that the amounts recovered are acceptable and allow inferring that the measurement accuracy by FAAS is suitably considering the levels of analyte added.

3.3. Concentrations of elements in biodiesel samples

The concentrations of the elements determined in the biodiesel samples produced with bacaba (B1), bacuri (B2), Brazil nut (B3), palm (B4) and palm obtained in industry (B5) by FAAS are presented in Table 5.

Table 5. Concentration of Ca, Mg, K, and Na (mg kg^{-1}) in biodiesel samples by FAAS (mean ± S.D., *n* = 3)

Elements	B_1	B_2	B_3	B_4	B_5
Ca	91.2 ± 1.5	99.48 ± 18.38	126.6 ± 5,6	58.56 ± 4.75	106.4 ± 3.2
Mg	< 0.06*	< 0.06*	< 0.06*	< 0.06*	< 0.06*
Na	3.86 ± 0,01	4.27 ± 0,01	3.06 ± 0.02	4.45 ± 0.01	4.61 ± 0.01
K	< 0.09*	15.87 ± 0,02	< 0.09*	15.34 ± 0.04	< 0.09*

* Limit of quantification (LOQ).

The high concentrations of Ca, Na and K were found in samples B2 and B4. This could be due to the composition of the oleaginous plant in which the biodiesel was obtained. [18] These high values of Ca could have also been introduced into biodiesel during the

purification process or could have come from the washing water, since Ca is insoluble in soap.[15, 18]

The Ca contents obtained in this study were higher when compared with the values found for biodiesel samples studied by other authors. [15, 19] The Mg levels in samples were below the LOD. Jesus *et al.* (2010) and Edlund*et al.* (2002) found Mg content in biodiesel samples. [15, 19] The Na concentration obtained in samples were lower than the values found in biodiesel samples studied by Korn *et al.* (2010). [20] The B2 and B4 samples presented high values of K. The value found in B2 could be due to bacuri oil used in the process of obtaining biodiesel. According to Soares (2010), the seed of bacuri has a high level of this element (3567 mg kg^{-1}). [21] On the other hand, this one high value of K found in B4 was due to the use of KOH as the catalyst during the biodiesel synthesis and the incomplete purification of the product. [18, 19] Chaves *et. al.* [22] and Jesus *et al.* [23] found high contents of K in some biodiesel samples they studied.

All biodiesel samples studied showed contents above the limit specified by the ANP (National Agency for Petroleum, Natural Gas and Biofuels) resolution Nº 51/2015 for the sum of Ca + Mg and Na + K (5.0 mg kg^{-1}). The Na + K levels for B1, B3 and B5 samples were below the limit established by ANP (5.0 mg kg^{-1}). [13] This could be due to the fact that these samples were produced with no metal in their catalytic and purification process. Thus, the low Na and K concentrations found could be attributed to the oilseeds themselves (bacaba, bacuri and Brazil nut). Moreover, the results obtained for Ca + Mg in the samples were above the maximum levels established, mainly due to the contribution of a high level of Ca present in samples, showing that the purification process of vegetable oils was not efficient to remove this metal. The K concentrations present in B2 and B4 samples were higher than the values obtained for B1, B3, and B5 samples.

4. Conclusions

The analytical procedure developed with the use of acid digestion in a conventional open system and the reduction of the volume of acids was effective and feasible, generating appropriate limits of detection and quantification (1.0 mg kg^{-1}) for the elements studied. Biodiesel samples produced with bacaba (B1), Brazil nut (B3), and industrial palm (B5) showed levels of Na + K within limits established by ANP resolution No. 51/2015. On the other hand, the samples obtained with bacuri (B2) and palm (B4) exceeded the levels of Na + K allowed by the ANP. All studied samples presented levels of Ca + Mg above limits established by the ANP. This study showed that the metal contents in the samples can be due to both oleaginous reasons and due to the catalyst used in biodiesel production.

Acknowledgments

The authors are grateful to the National Council for Scientific and Technological Development (CNPq) for scholarships granted to Alves, B. S. F. and Cruz, A. S. and also to Leivyson Rafael Vieira da Conceição for providing some samples.

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