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Article

High Pressure Asher (HPA-S) Decomposition of Biodiesel Samples for Elemental Analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES)

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A presença de alguns elementos inorgânicos no biodiesel pode comprometer a qualidade do combustível e aumentar a emissão de poluentes. Neste contexto, este artigo descreve um procedimento para o preparo das amostras de biodiesel utilizando *high pressure asher* (HPA) para a determinação de Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Sr e Zn, em biodiesel de soja, girassol, sebo bovino, algodão e mamona, por espectrometria de emissao optica com plasma indutivamente acoplado (ICP OES). Os parâmetros de digestão do HPA foram otimizados para digerir 1,5 g de biodiesel, com HNO_3 e H_2O_2, a temperatura de 300 °C e pressão de 435 psi, considerando o fator de diluição da amostra, os sólidos dissolvidos e a acidez da amostra para as determinações por ICP OES. A concentração dos elementos determinados nos biodieseis acima listados foram calculados utilizando o método de adição de padrão. Os limites de detecção na faixa de 0,05-0,7 mg kg^{-1} foram adequados para atender os parâmetros de qualidade de biodiesel, seguindo a política de governo e legislações em todo o mundo. Portanto, o procedimento proposto mostrou-se eficiente para eliminar as principais interferências orgânicas presentes em amostras à base de óleo, permitindo uma condição analítica rápida, precisa, livre de interferências e robusta para a caracterização do biodiesel.

The presence of some inorganic elements in biodiesel can compromise the fuel quality and enhance the emission of pollutants. In this context, a new procedure for biodiesel sample preparation using a high pressure asher (HPA) is presented, aiming the determination of Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Sr, and Zn, in soybean, sunflower, animal fat, cotton and castor oil, by inductively coupled plasma optical emission spectrometry (ICP OES). The digestion conditions of the HPA were optimize to digest 1.5 g of biodiesel, with HNO_3 and H_2O_2, at a temperature of 300 °C and pressure of 435 psi, which considered the sample dilution factor, the total solids in solution and the acidity for ICP OES determinations. Analytes concentrations in these biodiesels were calculated using standard addition method. Detection limits from 0.05 to 0.7 mg kg^{-1} were suitable to attend biodiesel quality parameters, government policy and legislations worldwide. Therefore, the proposed procedure proved to be efficient to eliminate the major organic interferences typically present in oil based samples allowing a fast, precise, interference-free and robust analytical condition for biodiesel characterization.

Keywords: biodiesel samples, high pressure asher (HPA-S), elemental analysis, inductively coupled optical emission spectrometry (ICP OES)

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Introduction

The instability in the petroleum prices and the concern about environmental impacts due to intensive use of fossil fuel, has been leading the effort to improve alternative technologies using renewable energy.[1] Crop-based fuels denoted as biofuels, emerged as a real alternative to the use of gasoline and conventional diesel in transportation. Having the advantages of been easily available from common biomass sources, biodegradable, environmental friendly and renewable. Since it is made of renewable biological materials the balance of the carbon cycle could be maintained. Furthermore, there are other benefits in using biofuel, not only related to the environment, but also economic and social.[2,3] Due to all of the benefits, in the last few years, an exponential increase in the consumption of such biofuels has taken place.[4]

Biodiesel is an alternative to petroleum based fuels used in cars and other vehicles with diesel engine. Refers to vegetal oils, animal fats, algae, or even recycled cooking greases diesel fuel. Produced by the transesterification of triglycerides with alcohol,[5] predominantly from rapeseed in Europe, palm oil in Asia and soybeans in Brazil.[6] It is considered a clean fuel as it has almost no sulfur, no aromatics and has about 10% built-in oxygen, which helps it to burn completely and also gives it a high octane number.[7] Compared to the diesel originated from petroleum, biodiesel can reduce the emission of particulate matter (PM), carbon dioxide (CO_2), carbon monoxide (CO), sulfur dioxide (SO_2), unburnt hydrocarbon (UBHC) and metals.[8,9]

The presence of some inorganic elements in biodiesel, as in fossil fuels, has a direct bearing on the engine during combustion, emissions and ash chemistry. For diesel and biodiesel engine, Ca, K, Mg, Na and P are considered the most critical elements. Therefore, worldwide regulation agencies and organizations for standardization decided to harmonize the determination procedures for these elements. These chemical elements achieve the biodiesel through different pathways, which are related to the biomass origin, harvesting method and oil processing procedures.[10] Depending on their concentrations levels, it may influence the engine performance and fuel behavior. Specifically, the quantification of Ca, Mg, K, Na, and P in biodiesel becomes necessary to evaluate fuel quality and to control the emission of pollutants to the atmosphere.[11-15] The normative document issued by the European Committee for Standardization (CEN), for fat and oil derivatives, which also includes biodiesel, recommend the dissolution of the samples in xylene prior to the analysis by inductively coupled plasma optical emission spectrometry (ICP OES)[16,17] and flame atomic absorption spectrometry (F AAS).[18,19] Similarly, the Brazilian National Standards Organization (ABNT), established the dilution of biodiesel in either xylene or kerosene, with different dilution rates, depending on the element to be analyzed by ICP OES[20] and F AAS.[21]

Although sample preparation procedures, based on organic matter digestion for ICP OES elemental analysis, of oil and petroleum samples are well established in the literature,[22,23] few reports focus biodiesel analysis. Following the standard procedure, biodiesel was diluted in kerosene (1:4) for the determination of Ca, Cl, K, Mg, Na and P by ICP OES. In this procedure, the addition of oxygen to the Ar plasma was used to improve Na and K determination by depleting C residues in samples.[11] Likewise, sample dilution with ethanol was proposed for the simultaneous determination of Ca, P, Mg, K and Na by ICP OES. External calibration with standard solutions in ethanol, and the use of Y as internal standard achieved accurate and precise results.[11,24] The addition of oxygen to the auxiliary Ar was also required to decrease C background and avoid plasma extinction.[11] Another approach was based in the production of emulsions with biodiesel, using Triton X-100 and water for analysis by F AAS[25] and ICP OES.[26]

Despite the currently use of sample dilution with organic solvents, several disadvantaged of these sample pretreatment were peer reviewed by Korn *et al.*.[22] Among the difficulties described are the low stability of the analyte in the organic diluted standard solutions; the need of oil based organometallic calibration standards, which might also show a sensitivity different from the organometallic compounds present in the fuel; the complex handling of some organic solvents due to their high vapor pressure and/or low viscosity; and their toxicity which requires special care to avoid any health hazard for laboratory personnel. Further, the analysis of samples with organic solvents by atomic spectroscopy techniques is hampered by flame or plasma instabilities or extinction, contamination of the atomizer with carbon residues, and the undesirable matrix effects which depends on the composition of the fuel and diluents used.[22,23] For elemental analysis of biodiesel samples by spectrometric methods, the high pressure asher (HPA-S) system was a choice to attain complete digestion of the organic matter, overcoming digestion problems related to oil based sample preparation procedures, such as mineralization with sulfuric acid in an open system, mineralization of small sample amounts in a closed microwave system, dry ashing in open crucibles, matrix evaporation followed by acid dissolution, acidic extraction, and samples dilution in organic solvent.[22,23,27-30] In this work, a procedure for biodiesel sample preparation using a high pressure asher system is proposed for determination of Al,

Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Sr, and Zn by ICP OES. The complete decomposition of soybean, sunflower, cotton and castor oils, and animal fat biodiesels, were attained with HNO_3 and H_2O_2, in an ultrasonic bath followed by the total digestion in the HPA. Furthermore, the proposed procedure minimizes the risks of contamination and analyte losses, along with high sample throughput, easy handling and safety.

Experimental

Apparatus

The oily samples were digested in the high pressure asher HPA-S (Anton Paar® GmbH, Austria), equipped with 90 mL reaction vessels. The reaction vessels were place into a pressure vessel filled with nitrogen. Reaching up to 130 bar pressure and heating to a maximum of 320 °C.

Twelve analytes were simultaneously determined using an Optima™ 3000 DV ICP OES (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The ICP OES was operated using plasma Ar flow rate of 15.0 L min^{-1}; cross-flow nebulizer Ar flow rate of 0.75 L min^{-1}; auxiliary Ar flow rate of 1.2 L min^{-1}; rf power 1.4 kW, and reflected power < 3 W. The analytes and emission lines measured using radial view are listed in Table 1. Some elements were measured in different emission lines, although only one line was used to quantify the element concentration in each sample.

Table 1. Analytes and wavelengths used

Analyte	Wavelength / nm
Aluminum	Al I 308.215, Al I 396.152[a]
Calcium	Ca II 317.933, Ca II 396.847[a], Ca II 393.366
Copper	Cu I 324.754
Iron	Fe II 259.940
Potassium	K I 766.491
Magnesium	Mg II 279.079, Mg II 280.270[a]
Manganese	Mn II 257.610
Sodium	Na I 589.592[a], Na I 330.237
Nickel	Ni I 232.003
Phosphorus	P I 214.914
Strontium	Sr II 407.771
Zinc	Zn I 213.856[a], Zn II 202.548

[a]Used for quantification purposes.

Regent and solutions

Purified water (18.2 MΩ cm) produced by a Milli-Q system (Millipore, Bedford, MA) was used through-out. The samples were digested using sub boiled distilled nitric acid and analytical grade hydrogen peroxide from Merck (Darmstadt, Germany).

Stock solutions of Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Sr and Zn containing 1000 mg L^{-1} (Spex Ind., Edison, NJ, USA) were properly diluted to produce working multielement standard solutions for calibration purposes and to apply the standard addition method.

The limit of detection (LOD) was estimated using 3× the standard deviation of 10 blank measurements, expressed as concentration using calibration solutions ranging from 0.10 mg L^{-1} to 5.0 mg L^{-1}. To calculate the element concentration in the samples, the standard addition method was applied. A multielement solution containing 0.0, 5.0, 10.0 and 15.0 mg L^{-1} was added to each sample, in triplicate, before the digestion procedure.[31] To validate the proposed method, the recovery was calculated using the 10.0 mg L^{-1} addition, following the IUPAC recommendation for standard addition methods.[33]

Sample preparation

Five biodiesel samples produced from soybean, sunflower, cotton and castor oil and one sample from animal fat were digested and subsequently analyzed. Two decomposition methods where undertaken aiming the complete sample digestion, a direct digestion and a two steps procedure with an ultrasonic pre-treatment. In the pre-treatment step, the vessels were covered with a Parafilm® or Teflon Tape and placed in an ultrasonic bath during 30 min at 100 °C. After received another portion of the acid mixture, the reaction vessels were sealed and placed inside the HPA-S's pressure vessel for attain total sample mineralization. After the preliminary tests, the optimal digestion program selected for the biodiesel samples consisted in two steps temperature ramp to attain complete sample mineralization under safety conditions. First of all, the temperature was gradually increased along 20 min from 20 to 100 °C and holding it for 5 min. In the following 10 min, the temperature was increased up to 150 °C and holding it for more 10 min. Afterwards, the temperature was programmed to ramp during 20 min to attain 300 °C and hold that temperature for 40 min. After digestion, the samples were cooled down and diluted to a final volume of 15 mL in order to achieve concentrations in solution within the dynamic range of the instrument.

Results and Discussion

The harmonization of Na, K, Ca, Mg and P maximum concentration allowed in biodiesel samples is fundamental

to attend their commercialization worldwide, aligning the limits and methods used in Brazil.[31] The source of contaminants vary with the type of biodiesel and the production process. Alkali (Na and K) and alkaline earth (Ca and Mg) metals are introduced into the biodiesel fuel during the production process. Whereas alkali metals stem from catalyst residues, alkaline-earth metals may originate from hard washing water. Na and K are associated with the formation of ash within the engine. Calcium soaps are responsible for sticking the injection pump. Phosphorus has a strongly negative impact on the long term activity of exhaust emission catalytic systems and for this reason its presence in biodiesel is limited by specification. According to the Brazilian regulation, the maximum amount allowed for the sum (K + Na) and (Ca + Mg) should not exceed 5 mg kg^{-1}, aligning these parameters with the European Union (EU) and United States of America (USA).[32] For P, the maximum content allowed for the referred Standardization Organizations is 10 mg kg^{-1}.[32] Biodiesel are also contaminated with other metallic and semi-metallic elements. However there are no specific regulations or proposed rules for these elements.

For biodiesel analysis, the heating program of the high pressure asher (HPA-S) used had to be adjusted for amounts of sample considering the sample dilution factor, the total solids in solution and acidity for ICP OES determinations. Therefore, two decomposition procedures were carried out, a direct digestion and a two-step digestion with an ultrasonic pre-treatment. The direct digestion in the HPA-S allowed the use of up to 0.5 g of biodiesel sample, with HNO_3 plus H_2O_2. Attempt to digest 1.5 g of biodiesel in one-step, burn out the sample instead of digesting it, as shown in Figure 1A. Accordingly, the direct digestion procedure failed to eliminate the organic residues in solution which was attained by using an ultrasonic pre-treatment. In the two-step procedure, employing the pre-treatment followed by the digestion in the HPA-S, the digested solution looked as in Figure 1B and C. In this way, to achieve a complete digestion of 1.5 g biodiesel sample, 6 mL of HNO_3 plus 4 mL of H_2O_2 were used in the two steps allowing a sample dilution factor of 25, which is reasonable for ICP OES measurements. However, this digested samples remains colored, Figure 1B. This cloudy yellow-brown color indicates an incomplete digestion, however, addition of H_2O_2 during the pre-digestion step, resulted in a clear, transparent digested solution, as depicted in Figure 1C. As a result, the sample amount used in the digestion procedure point out a compromise among the acidity, concentration level of the element in the sample, and detection limit, which were suitable parameters for ICP OES determinations.

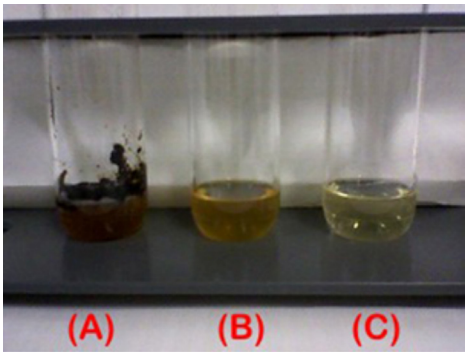

Figure 1. Biodiesel digested samples residues following different procedures. (A) direct digestion in the HPA-S; (B) two step digestion procedure, with 6 ml HNO_3 and the subsequently addition of 4.5 mL H_2O_2 and (C) two step digestion procedure, first the addition of 4 mL HNO_3 + 2.5 mL H_2O_2 followed by the addition of 2 mL HNO_3 + 2 mL H_2O_2.

Despite the investigation of several elements related to biodiesel quality, only Ca, Mg, Na, K, and P were regulated by Standards Organizations worldwide, through documents ruled by the Brazilian Association of Technical Regulations (ABNT 15553:2008), the European Standards (EN 14538:2007), and others. Therefore, the alignment of the maximum concentration for these elements and the use of standardized method in different countries, as Brazil, EU and USA became fundamental to attend their commercialization. The ABNT 15553, specify the determination of concentrations higher than 1 mg kg^{-1} for Ca, Mg, Na, and P, and 2 mg kg^{-1} for K by ICP OES. However, the analyses of other major elements can lead to a more complete overview of the biodiesel sample quality. In this way, the limit of detection (LOD) achieved by proposed method, considering the final sample dilutions, expressed in mg kg^{-1} and presented in Table 2, attested to be suitable for biodiesel analysis.

Table 2. Limits of detection (LOD), in mg of the analyte per kg of biodiesel

	LOD / (mg kg^{-1})
Al	0.32
Ca	0.25
Cu	0.02
Fe	0.36
K	0.28
Mg	0.02
Mo	0.01
Mn	0.09
Na	0.70
Ni	0.13
P	0.79
Sr	0.06
Zn	0.10

In this proposal, the standard addition method was used to calculate the concentrations of Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Sr, and Zn due to the absence in certified reference material for biodiesel and to overcome possible matrix interference during the analysis. As presented in Table 3 and Figure 2, the results obtained for soybean, castor oil, cotton, sunflower, and animal fat biodiesel samples employing the digestion procedure described were suitable for the determinations proposed, allowing for the limits specified by the standardization organizations. The results obtained presented correlation coefficients varying from 0.990 to 0.999 for Al, Cu, K, Mg, Mn, Ni and Zn, and 0.980 to 0.999 for Ca, Fe, Mo, Na, and Sr. For P, the correlation was reduced because of the relatively low sensitivity for this element by ICP OES determination (Table 3). Considering the maximum concentration regulations for Na, the results obtained for the presented biodiesel sample are higher than the maximum allowed, but

Table 3. Element concentration in soybean, castor oil, cotton, sunflower and animal fat biodiesel samples determined by ICP OES applying the standard addition method. The linear regression equation and the correlation coefficient for each standard addition are presented afterward

Element	Concentration / (mg kg^{-1})				
	Soybean	Castor oil	Cotton	Sunflower	Animal fat
Al	1.12 ± 0.25 $y = 664.03x + 743.28$ (0.9965)	0.458 ± 0.195 $y = 700.67x + 320.8$ (0.9997)	0.769 ± 0.163 $y = 635.45x + 448.41$ (0.9967)	< LOD $y = 738.12x + 50.854$ (0.9935)	< LOD $y = 672.74x + 101.75$ (0.9978)
Ca	2.19 ± 0.31 $y = 47663x + 104566$ (0.9898)	3.40 ± 1.24 $y = 45911x + 156298$ (0.9963)	2.72 ± 0.55 $y = 40773x + 111096$ (0.998)	2.69 ± 0.60 $y = 49368x + 132839$ (0.9969)	2.50 ± 0.32 $y = 42472x + 106313$ (0.9964)
Cu	0.660 ± 0.010 $y = 1289.8x + 851.52$ (0.9993)	0.743 ± 0.008 $y = 1316.1x + 977.42$ (0.998)	0.536 ± 0.054 $y = 1236.3x + 662.44$ (0.998)	0.327 ± 0.036 $y = 1415.3x + 462.36$ (0.9958)	0.463 ± 0.010 $y = 1275.3x + 590.86$ (0.9955)
Fe	2.34 ± 0.38 $y = 139.33x + 325.44$ (0.9963)	1.08 ± 0.27 $y = 158.77x + 170.83$ (0.9893)	0.578 ± 0.281 $y = 136.49x + 78.873$ (0.9962)	1.24 ± 0.19 $y = 122.6x + 151.83$ (0.9847)	0.937 ± 0.180 $y = 145.01x + 135.93$ (0.9946)
K	< LOD $y = 3762.5x + 1901.1$ (0.9975)	0.873 ± 0.025 $y = 3802.4x + 3320.5$ (0.9968)	5.32 ± 0.37 $y = 2807x + 14945$ (0.999)	0.454 ± 0.015 $y = 3528.7x + 1601.2$ (0.9945)	< LOD $y = 3638.8x + 550.27$ (0.9915)
Mg	0.577 ± 0.108 $y = 1882.8x + 1087.2$ (0.9974)	0.854 ± 0.043 $y = 1968.4x + 1681.3$ (0.9987)	0.413 ± 0.021 $y = 1440.8x + 595.74$ (0.9996)	0.311 ± 0.079 $y = 1591.9x + 494.74$ (0.9962)	0.142 ± 0.025 $y = 1550.7x + 220.34$ (0.9994)
Mn	0.481 ± 0.004 $y = 1030.6x + 496.11$ (0.9964)	0.138 ± 0.004 $y = 1102.3x + 152.3$ (0.9998)	< LOD $y = 896.12x + 59.374$ (1.0)	< LOD $y = 1024.2x + 29.31$ (0.9989)	< LOD $y = 966.92x + 48.322$ (0.9979)
Mo	0.599 ± 0.039 $y = 38.693x + 23.186$ (0.9969)	0.767 ± 0.052 $y = 34.26x + 26.28$ (0.9994)	1.26 ± 0.01 $y = 34.659x + 43.748$ (0.9803)	1.13 ± 0.11 $y = 31.526x + 35.749$ (0.9969)	0.691 ± 0.044 $y = 35.033x + 24.211$ (0.999)
Na	34.4 ± 0.88 $y = 4183.7x + 143915$ (1.0)	101 ± 1 $y = 4484.6x + 451839$ (0.9836)	29.4 ± 0.4 $y = 4172.3x + 122549$ (0.9909)	11.5 ± 0.7 $y = 8034.7x + 92537$ (0.9841)	13.5 ± 0.3 $y = 6855.8x + 92529$ (0.9846)
Ni	0.203 ± 0.004 $y = 31.024x + 6.3004$ (0.9955)	< LOD $y = 35.019x - 3.8375$ (0.9999)	< LOD $y = 31.216x - 3.4294$ (0.9978)	< LOD $y = 32.843x - 7.1401$ (0.9945)	< LOD $y = 31.35x + 3.6061$ (0.9991)
P	< LOD $y = 1.4484x + 0.3106$ (0.9999)	< LOD $y = 1.3552x - 0.3015$ (0.9697)	1.46 ± 0.32 $y = 1.1439x + 1.6649$ (0.9984)	< LOD $y = 1.455x + 0.2694$ (0.9852)	0.931 ± 0.153 $y = 1.1586x + 1.078$ (0.9934)
Sr	0.329 ± 0.007 $y = 155451x + 51120$ (0.998)	0.250 ± 0.004 $y = 162818x + 40751$ (0.9983)	0.127 ± 0.033 $y = 143762x + 18262$ (0.9826)	0.479 ± 0.021 $y = 137278x + 65736$ (0.9946)	< LOD $y = 149283x + 6121.6$ (0.9967)
Zn	8.33 ± 0.22 $y = 67.378x + 561.46$ (0.9902)	4.87 ± 0.76 $y = 82.421x + 401.8$ (0.9991)	4.39 ± 1.03 $y = 69.242x + 303.92$ (0.9958)	5.47 ± 0.30 $y = 60.611x + 331.68$ (0.9954)	3.74 ± 0.77 $y = 74.641x + 278.92$ (0.9984)

Number of replicates (n = 3).

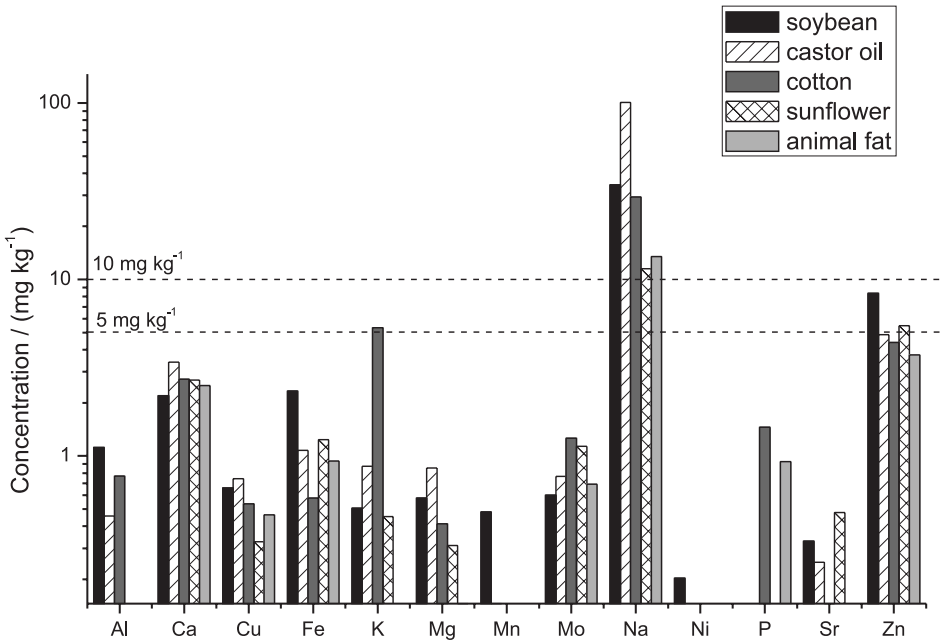

Figure 2. Elements concentration in soybean, castor oil, cotton, sunflower and animal fat biodiesel samples. The dashed lines, point out the 5 mg kg^{-1} concentrations, which are the maximum permissible levels, allowed for the sum Ca + Mg, Na + K and 10 mg kg^{-1} for P, following the Brazilian Standardization Organization.

for castor oil the concentration was four times higher than the upper limit value. For K, the cotton biodiesel sample result was slightly higher than the limit value proposed in the regulation. Despite the non-regulation for Zn, the concentration of this element in the samples was in the level of the maximum permissible for the regulated ones. The high concentration of Na and K in the five biodiesel analyzed is probably arising from the production process. During the transesterification process to produce biodiesel, sodium and potassium hydroxide are used as catalysts that can contaminate the final product.[34,35]

All recovery values calculated for the addition of 10 mg kg^{-1}, presented in Table 4, were adequate demonstrating the accuracy of the proposed procedure. Therefore, the presented results showed that the proposed method is adequate for biodiesel sample quality monitoring, considering that it attains the limit of detection (LOD) required in the legislation and is able to determine higher concentration of the listed elements.

Table 4. Recoveries (%) after analyte addition of 10.0 mg L^{-1}

	Soybean	Castor oil	Cotton	Sunflower	Animal fat
Al	97.6	100.3	99.2	103.1	99.4
Ca	98.3	97.4	100.9	100.6	98.2
Cu	99.3	99.1	98.8	102.0	98.3
Fe	99.4	95.8	101.9	99.2	101.4
K	98.1	97.9	101.0	97.0	97.1
Mg	98.6	101.0	99.6	101.5	99.5
Mn	97.9	99.5	100.0	100.6	98.8
Mo	101.2	99.3	94.5	98.9	100.3
Na	96.9	101.3	103.7	102.9	100.4
Ni	100.2	100.2	99.3	102.3	99.1
P	100.3	106.8	99.4	96.5	103.8
Sr	98.7	99.4	95.7	97.1	98.3
Zn	98.1	101.2	99.0	102.6	101.5

Number of replicated (n = 3).

Conclusions

The proposed HPA-S high pressure digestion procedure is a reliable alternative for biodiesel and oil based sample preparation aiming metals determination by ICP OES. The complete chemical decomposition of most oils based samples using HNO_3 and H_2O_2, was attained because the HPA-S reaches pressure up to 435 psi and temperature up to 300 °C.

The present proposal allows preparing larger sample volumes than in microwave digestions, using just nitric acid plus hydrogen peroxide, and no organic solvent to obtain extracts compatible with ICP OES.

The application of the standard addition method was effective to overcome possible non-spectral interference in the ICP OES analysis, caused by the different physical properties of the sample solution. The detection limits and results attained with the proposed sample preparation procedure were adequate to attend the worldwide biodiesel quality legislation.

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