Direct analysis of biodiesel microemulsions using an inductively coupled plasma mass spectrometry

Renata S. Amais, Edivaldo E. Garcia, Marcos R. Monteiro, Ana Rita A. Nogueira, Joaquim A. Nóbrega

Abstract

An analytical procedure for direct introduction of biodiesel samples into an inductively coupled plasma mass spectrometer (ICP-MS) by using microemulsion for sample preparation was developed here. Cadmium, Co, Cu, Mn, Ni, Pb, Ti, and Zn were determined in biodiesel microemulsified samples prepared from different oleaginous sources (African palm, castor beans, palm, soybeans and an unknown oleaginous). Microemulsions were prepared using 0.25 mL Triton X-100, 0.25 mL 20% v/v HNO3, 0.50 mL biodiesel sample and 4.0 mL n-propanol. Argon–oxygen mixture was added to the plasma as auxiliary gas for correcting matrix effects caused by the high carbon load due to biodiesel microemulsions. The oxygen gas flow rate was set in 37.5 mL min−1. The accuracy of the developed procedure was evaluated by applying addition-recovery experiments for biodiesel samples from different sources. Recoveries varied from 76.5 to 116.2% for all analytes but Zn in castor beans biodiesel sample (65.0 to 76.2%). Recoveries lower than 86.6% were obtained for palm biodiesel sample, probably due to matrix effects. Detection limits calculated by using oxygen in the composition of the auxiliary gas added to the plasma were higher than those calculated without using it, probably due to the highest formation of oxides. Despite oxides formation, best analytical performance was reached by using oxygen as auxiliary gas and by proper correction of transport interferences. The developed procedure based on microemulsion formation was suitable for direct introduction of biodiesel samples in ICP-MS.

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1. Introduction

Biodiesel is described as an alternative fuel composed by fatty acid alkyl esters, which is produced from renewable sources such as vegetable oils and animal fats [1]. The instability of the petroleum market and the constant exhaustion of the petroleum sources as well as the advantages of the use of renewable, biodegradable and non-toxic sources of energy have stimulated researches for substituting petroleum based fuels by focusing production processes and quality control for alternative fuels such as biodiesel [2,3]. From a technical viewpoint, vegetable sources employed to produce biodiesel are more adequate than animal sources, since the biodiesel produced from them does not demand any modification in the diesel engines and have a high energetic yield [4].

Due to its great biodiversity, large agriculture areas, and climate and soil conditions, Brazil provides different vegetable oil sources such as soybeans, castor seeds, coconut, cottonseeds, palm and others [5]. Global production of biodiesel is approximately 5 billion gallons and its volume is likely to increase due to the implementation of 10:90 v/v blend of biofuel and conventional diesel fuel in many countries [6]. Brazilian biodiesel production had an increase of 124% in the period from 2005 to 2008, and in Brazil the 4:96 v/v blend of biodiesel and diesel derived from petroleum was implemented in July 2009 [7].

Biodiesel contaminants such as Na, K, Ca and Mg may affect motor performance and corrode some motor components. These elements caused formation of deposits and may promote side reactions that contribute for decomposition of biodiesel. Sodium and K are introduced due to the use of sodium and potassium hydroxide as catalysts for transesterification process. Others, as Ca, Mg and P, are present in raw materials used for biodiesel production. Phosphorus indirectly increases the emission of pollutant gases because it negatively affects catalysts employed for exhaust gases [8]. Brazilian legislation establishes the control for levels of Na, K, Ca, Mg and P [9]. Other elements may become important due to different factors, for instance sulfur may cause acid rain [10], silicon added as antifoaming in petroleum-derived products may cause decrease of motor performance, corrosion, and increase the emission of particulate matter [11].

Keywords:
Biodiesel
Microemulsions
ICP-MS
Auxiliary gas
Oxygen
Sample preparation is one of the most important steps in any analytical procedure for metal determinations in complex samples. Several procedures for sample preparation of oils and fuels aiming metal determinations are described in the literature, either based on direct analysis or employing full mineralization of samples by using acid digestion procedures [12–16]. Metals and metalloids are frequently determined in biodiesel samples using spectrometric techniques [17]. Depending on the employed spectrometric technique, determinations are hampered due to several problems related with signal generation, aspiration rate, sample nebulization, residual carbon content and also due to the temperature of the atomization system. As a consequence, the analysis of oils, fuels and biofuels using direct procedures is difficult. Taking into account the complexity of the matrix, it may seem that the complete matrix elimination employing dry ashing is the most efficient procedure for sample preparation [18]. However, this procedure is too slow and needs careful temperature control for avoiding losses of volatile metals and contaminations. According to Costa et al. even microwave-assisted acid digestion procedures may require a relatively long time [19].

Graphite furnace atomic absorption spectrometry (GF-AAS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS) offer some advantages compared to other spectrometric techniques, since they make feasible the use of sample preparation procedures that do not require complete elimination of organic matrixes. A simple dilution using organic solvents can be employed for GF-AAS [20]. However, the use of dilution procedures generates severe problems associated with the stability of metals in sample and reference solutions [21]. Alternatively, oil, fuel and biofuel analysis may be performed by using procedures that involve the formation of emulsion and microemulsion for solving problems associated with relatively long time of analysis, contaminations, and losses of elements. The use of microemulsion offers some advantages over emulsion systems, since they are thermodynamically stable and allow the use of reference solutions prepared in aqueous medium for calibration instead of expensive and unstable organometallic standards [3]. However, it should be mentioned that the use of dilution, emulsion and microemulsion procedures may also be affected by problems [22,23].

Taking into account the determination of metals in biodiesel samples, the first work was published by Edlund et al. [1] and dealt with the simultaneous determination of Ca, Cl, K, Mg, Na and P by ICP OES by diluting samples with kerosene (1:4 m⁻¹). It was described that the difficulties normally found with sample dilution, as previously reported, were overcome by adding a mixture of gases (Ar/O₂) to the plasma, and the spectral interferences caused by carbon were minimized, mainly considering the analytical lines for Na and K. Santos et al. [24] also determined these elements by ICP OES using ethanol for sample dilution and yttrium as internal standard for correcting non-spectral interferences. In another work, Souza et al. [25] determined Ca, Cu, Fe, Mg, Mn, Na and P by ICP OES with axial and radial viewings by employing emulsion formation with Triton X-100, water, yttrium as internal standard and aqueous reference solutions, avoiding the use of organic solvents for preparing reference solutions.

Woods and Fryer determined 31 elements in biodiesel samples diluted with kerosene (1:3 m⁻¹) by ICP-MS with oxygen as auxiliary gas [26]. They observed a better performance for ICP-MS and a wider range of elements that could be determined compared to other methods such as ICP OES and flame atomic absorption spectrometry (FAAS), which are the most widely employed methods for the determination of a limited number of elements present in samples of biodiesel. De Jesus et al. [3] determined Na and K in biodiesel samples employing FAAS. Biodiesel samples were converted in microemulsions using n-pentanol 56.6% (m m⁻¹), sample or vegetable oil 20% (m m⁻¹), Triton X-100 14.4% (m m⁻¹) and water (aqueous solution of KCl or NaCl and/or diluted HNO₃), Chaves et al. [27] also determined Na and K by FAAS using microemulsions and obtained limits of detection comparable to those established by the Brazilian legislation for biodiesel.

Alternative procedures for sample preparation of biodiesel, such as the formation of emulsion and microemulsion as well as the use of a mixture of gases in ICP-MS, have not been described in the literature yet, or they have not been critically evaluated. The addition of oxygen to the plasma by an additional mass flow controller to remove the excess of carbon from the plasma and to prevent it from condensing on the interface and ion lenses is necessary. Considering that carbon contents in emulsions and microemulsions are too high, it is important to carry out a systematic evaluation about the use of these procedures associated with methods characterized by high sample throughput, low detection limits, and a wide elemental range of determination, such as ICP-MS. In this work, an analytical procedure for analysis of biodiesel samples with and without the use of oxygen as auxiliary gas in the ICP for evaluating the direct introduction of biodiesel samples as microemulsions was developed.

2. Experimental

2.1. Instrumentation and operating conditions

An inductively coupled plasma mass spectrometer (Varian 820-MS, Mulgrave, Australia) equipped with an automatic sampler SP3 and an additional gas flow controller (AGM-1, Varian) for adding oxygen (99.99%, White Martins, Sertãozinho, SP, Brazil) as auxiliary gas in the ICP was employed. Nebulizer and double path spray chamber (Scott type) were made using perfluorooctane (PFA) for allowing introduction of organic solvents without affecting the lifetime of the sample introduction system. Instrumental and operating conditions are summarized in Table 1.

2.2. Reagents, analytical solutions and samples

All solutions were prepared using analytical-grade reagents and distilled and deionized water obtained by using a Milli-Q® system (Millipore Corp., Bedford, MA, USA) to a resistivity of 18.2 MΩ cm. In order to avoid metal contamination, glasswares and polypropylene flasks were washed and soaked in 10% v⁻¹ HNO₃ solution and rinsed thoroughly with deionized water, prior to use.

For microemulsion preparation, HNO₃ (Merck, Darmstadt, Germany) previously purified by using a sub-boiling system (Milestone, Sorisole, Italy) was employed. Polyoxyethylene (10) octylphenyl ether (Triton X-100) (Acros Organics, Morris Plains, NJ, USA), n-propanol and a certified MR-1284 light mineral oil (Tedia, Rio de Janeiro, RJ, Brazil) were used without further purification. Inorganic reference solutions of Cd, Co, Cu, Mn, Ni, Pb, Ti and Zn were prepared by appropriated dilutions from stock solutions 1000 mg L⁻¹ (Tec-Lab, Hexis, São Paulo, SP, Brazil).

Biodiesel samples B100 produced from different vegetable sources (African palm, castor beans, palm and soybeans) were provided by the

### Table 1

ICP-MS operating conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generator frequency (MHz)</td>
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</tr>
<tr>
<td>Torch inner diameter (mm)</td>
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<tr>
<td>RF power (kW)</td>
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</tr>
<tr>
<td>Points per peak</td>
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</tr>
<tr>
<td>Replicates/samples</td>
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</tr>
<tr>
<td>Dwell time (ms)</td>
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</tr>
<tr>
<td>Gas flow rates</td>
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</tr>
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<td>Outer (L min⁻¹)</td>
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</tr>
<tr>
<td>Intermediate (L min⁻¹)</td>
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</tr>
<tr>
<td>Sheath gas (L min⁻¹)</td>
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<tr>
<td>Nebulizer flow (L min⁻¹)</td>
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<tr>
<td>Sampler and skimmer cones</td>
<td>Ni</td>
</tr>
</tbody>
</table>
Center for Characterization and Development of Materials (CCDM), UFSCar-UNESP, São Carlos SP, Brazil.

2.3. Preparation of microemulsion

The choice of the procedure for preparation of the microemulsions was based on simple manipulation and easily available reagents. In preliminary experiments, a suitable stability of the microemulsions for inorganic analysis by FAAS for at least 8 h and any phase separation was observed. Some experiments were performed with microemulsions prepared using ethanol as co-solvent. Considering the stability tests carried out in both media, it was observed that microemulsions prepared in ethanol were less stable than those prepared in n-propanol for reference solutions containing light mineral oil. This behavior was not observed for biodiesel samples. This effect may be explained based on differences between ethanol and n-propanol polarities. It means that n-propanol has a stronger interaction with the oil and aqueous phases of the microemulsions due to the lower polarity when compared to ethanol. Consequently, further measurements were made using microemulsions prepared with n-propanol. A homogeneous, transparent and stable microemulsion was obtained when a solution containing 0.25 mL of 20% v v⁻¹ HNO₃ plus 0.25 mL of Triton X-100 was added to 0.5 mL of biodiesel into graduated polyethylene flasks. The volume was made up to 5.0 mL using 4.0 mL n-propanol. Finally, the mixture was homogenized by using a vortex mixer for 2 min.

This same procedure was adopted for preparation of reference solutions. It used 0.1 mL of light mineral oil instead of biodiesel sample for simulating the sample matrix, and a volume of 4.4 mL n-propanol was added as an organic solvent. The volume of light mineral oil added was 5-fold lower than the volume of biodiesel oil because the goal was to adjust the viscosity of these solutions to avoid variations in aspiration rate and aerosol formation.

Small volumes of inorganic reference solutions of Cd, Co, Cu, Mn, Ni, Pb, Ti, and Zn were added for avoiding any instabilization of the microemulsion. The maximum concentrations of reference solutions employed to evaluate the dynamic linear range of calibration curves were 50 µg L⁻¹ for Cd, Co, Cu, Mn, Pb and Zn and 150 µg L⁻¹ for Ni and Ti in both media, with and without using oxygen gas. Finally, it must be emphasized that a 2% v v⁻¹ Triton X-100 solution was aspirated between samples for avoiding memory effects.

Limits of detection (LODs) were calculated according to the IUPAC recommendation and using the background equivalent concentration (BEC) concept. The BEC and LOD were calculated according to the following equations:

\[
\text{BEC} = \frac{C_{rs}}{\text{SBR}}
\]

\[
\text{SBR} = \frac{I_{rs} - I_{\text{blank}}}{I_{\text{blank}}}
\]

\[
\text{LOD} = \frac{3 \times \text{BEC} \times \text{R.S.D.}}{100}
\]

where, \(C_{rs}\) concentration of multielement reference solution (20 µg L⁻¹); SBR, signal-to-background ratio, \(I_{rs}\) and \(I_{\text{blank}}\) signal intensities for multielement reference and blank solutions, respectively, and R.S.D., relative standard deviation for 10 measurements of blank solution.

3. Results and discussion

3.1. Effect of oxygen gas flow rate introduced as auxiliary gas

The effect of the oxygen gas flow rate (12.5 to 162.5 mL min⁻¹) on the introduction of microemulsions in n-propanol medium is shown in Fig. 1. By monitoring the signal intensities of ¹¹⁴Cd⁺, ⁵⁹Co⁺, ⁶⁳Cu⁺, ⁵⁵Mn⁺, ⁶⁰Pb⁺ and ⁶⁵Zn⁺ isotopes by using 10 µg L⁻¹ of each reference solutions, an increment of signal intensities at 37.5 mL min⁻¹ oxygen flow rate was observed, except for Cd, Cu and Pb isotopes, with highest intensities reaching at 12.5 mL min⁻¹. However, considering that the highest intensity signals obtained for Cd, Cu and Pb at 12.5 mL min⁻¹ were only slightly higher than those observed at 37.5 mL min⁻¹, this latter oxygen gas flow rate was selected as a compromise condition for further experiments and also considering the highest SBR values observed for this condition. The SBR values obtained for Cd, Co, Cu, Mn, Pb and Zn at 37.5 mL min⁻¹ oxygen gas flow rate were 45, 16, 17, 50, 31 and 86% higher than those observed at 12.5 mL min⁻¹.

A severe decrease of signal intensities for all isotopes was observed when using oxygen gas flow rates higher than 37.5 mL min⁻¹ probably due to the favorable formation of oxides. The relatively high dissociation energy (D₀) for CO⁺ (D₀ = 8.33 eV) [28] together with the high carbon load introduced into the plasma when inserting biodiesel microemulsions favors its formation. However, excess of oxygen atoms will react with M to form MO⁺ (M = isotope elements), despite the comparatively low dissociation energies associated with MO⁺ species, for instance D₀ ZnO⁺ = 1.65 eV, D₀ MnO⁺ = 2.95 eV and D₀ CoO⁺ = 3.29 eV [29].

It must be pointed out that plasma remained stable in spite of the high carbon load even when oxygen was not added as auxiliary gas. The same behavior is not reported for ICP OES in the literature. However, the analytical performance of the ICP was deteriorated without using oxygen as auxiliary gas.

3.2. Analytical figures of merit

According to preliminary experiments, the use of reference solutions prepared in 1% v v⁻¹ HNO₃ was not feasible because their viscosities and physical properties are diverse from the biodiesel microemulsions and, consequently, aerosol formation is completely different for these solutions. These differences were even accentuated when oxygen was added because of preferential formation of oxides in solutions without high carbon loads. Limits of detection limit (LODs) and sensitivities, defined as the slope of the calibration curve, with 37.5 mL min⁻¹ O₂ and without this gas are shown in Table 2.

Introduction of biodiesel microemulsions without using oxygen gas flow rate led to higher intensity signals for the element isotopes evaluated. The increment of intensity signals for ⁵⁵Co⁺, ⁵⁵Mn⁺ and ⁶⁵Zn⁺ was about 50% (Table 2). However, according to Table 3, recoveries attained without using oxygen were always lower than 68%, except for biodiesel from African palm with recoveries around 88%. Best recoveries were reached when oxygen was used probably due to a better control of plasma environment under conditions of a high carbon load coming from biodiesel microemulsions. Consequently, the addition of oxygen to the plasma is essential for performing direct analysis of biodiesel samples introduced as microemulsions, and this condition was kept in all further experiments. Since there is no biodiesel certified reference material for the determined elements, addition-recovery tests were employed in order to evaluate the accuracy.
It could be emphasized that the blank values obtained when using oxygen in the composition of the auxiliary gas were higher in comparison with the referred values obtained without using it. This effect may be related to the formation of polyatomic interferences and to the introduction of contamination arising from the oxygen employed. In addition, it should be mentioned that when the peristaltic pump was operated in fast mode among the microemulsion introductions without using oxygen as auxiliary gas, an emission of the Swan bands that originated due to the inefficient degradation of carbon compounds introduced by biodiesel microemulsions was observed. However, even at these conditions clogging of the sampler and skimmer orifices caused by residual carbon deposition did not occur.

3.3. Metal determinations in biodiesel microemulsions

Biodiesel samples from different oleaginous sources such as African palm, castor beans, palm, and soybeans were introduced into the ICP-MS as microemulsions prepared with n-propanol, and the following elements were determined: Cd (m/z 114), Co (m/z 59), Cu (m/z 63), Mn (m/z 55), Ni (m/z 58), Pb (m/z 208), Ti (m/z 47), and Zn (m/z 64). Sample introduction was carried out either with (37.5 ml min⁻¹) or without using oxygen introduced as auxiliary gas into the ICP. Table 4 contains data obtained for biodiesel samples. All values determined for Cu and Ni were below the respective LODs.

It was observed that Ti and Zn were the elements present in the highest concentrations for different biodiesel samples, varying from 145.8 to 180.0 ng mL⁻¹ and from 64.7 to 184.3 ng mL⁻¹ for Ti and Zn, respectively. As it can be observed, the wide concentration range determined for Zn in different biodiesel samples may be due to the contamination processes due to its relatively high abundance in nature, as well as due to the higher variability of Zn concentration in the different oleaginous sources employed to produce the analyzed biodiesel samples. The relatively high concentration observed for Ti probably originated from the use of solid-based catalysts such as TiO₂ employed in the biodiesel production process [30]. For other analytes, all concentrations determined were lower than those found for Ti and Zn. The lowest concentrations in the different biodiesel samples were determined for Cd.

4. Conclusions

The developed procedure was effective for the direct introduction of biodiesel microemulsions prepared with n-propanol as organic solvent into the ICP-MS using oxygen as auxiliary gas in the composition of the plasma. The simple and fast procedure for sample preparation makes the proposed method an attractive alternative for routine analysis considering mainly the multielement capability for analyzing complex matrices with high carbon load.

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References


