



Determination of Ca, K, Mg, Na, sulfate, phosphate, formate, acetate, propionate, and glycerol in biodiesel by capillary electrophoresis with capacitively coupled contactless conductivity detection

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ABSTRACT

In this work, a new method employing capillary electrophoresis (CE) for the determination of several species in biodiesel is introduced. The concentrations of inorganic species (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , and PO_4^{3-}) and glycerol are of interest to the regulatory authorities due to their ability to form undesirable compounds in engines. Additionally, other species of low molecular weight (e.g., acetate, formate, and propionate) are of interest because they contribute towards increasing the acidity. These species are formed by the degradation of biodiesel and cause damage to engines and the environment. The cation separation was performed in background electrolyte (BGE) composed of 30 mmol L^{-1} of 2-(*N*-morpholino)ethanesulfonic acid (MES)/*L*-histidine (His), pH 6. The separation of anionic species was carried out in similar BGE with 0.2 mmol L^{-1} cetyltrimethylammonium bromide (CTAB) added. For glycerol, a neutral species, its oxidation with periodate was employed. This well-known reaction is specific to polyols and generates iodate. The amount of iodate produced by the reaction was determined by CE. The separation was carried out in approximately 1 min using BGE composed of 30 mmol L^{-1} acetic acid, pH 3. The analytical parameters evaluated were: linearity ($r > 0.99$), the RSD values for area and migration time were $< 3.4\%$ and 0.9% , respectively, and recovery was in the range of 89 to 107%.

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1. Introduction

The field of research on alternative fuels developed in order to reduce the dependence on petroleum derivatives and to improve air quality. Biodiesel has shown potential for reducing the problem of carbon monoxide (CO), carbon dioxide (CO_2) and sulfur dioxide (SO_2). Additionally, the use of biodiesel eliminates black smoke and reduces particulate matter [1].

The term biodiesel is generally used to define a mixture of simple alkyl esters of long-chain fatty acids derived from vegetable oil or animal fats for use in compression ignition engines [2]. It is typically

produced by the transesterification of triglycerides in vegetable oils with an alcohol in the presence of a catalyst, usually alkaline. This process has been widely used to reduce the high viscosity of triglycerides [3].

The determination of Na and K in biodiesel samples is important since alkaline hydroxides are used as catalysts in the transesterification step and they can form undesirable compounds in the engines [4]. The presence of Ca and Mg in biodiesel is due to the utilization of hard water during the purification step. Other species such as sulfur and phosphorus compounds are present in organic and inorganic forms. The main anthropogenic source of this inorganic species comes from neutralization and desiccation steps. Additionally, the determination of glycerol is relevant because high concentrations of this species were a major cause in the past of the clogging of filters and general faults in diesel engines [5].

The metal concentration in biodiesel is generally low and requires the use of highly sensitive analytical techniques for detection. The development of strategies for the determination of metals has several problems due to the high complexity and organic nature of metal matrices. Nowadays, these determinations are mainly accomplished by atomic absorption (AAS) and emission spectrometry (AES), and various pre-treatment strategies employ direct analysis, dilution with organic solvents, emulsion, extraction and complete digestion [6–13].

Abbreviations: BGE, background electrolyte; C^4D , capacitively coupled contactless conductivity detection; CE, capillary electrophoresis; CTAB, cetyltrimethylammonium bromide; EOF, electroosmotic flow; His, (*L*) histidine; I.S., internal standard; LOD, limit of detection; LOQ, limit of quantification; MES, 2-(*N*-morpholino)ethanesulfonic acid; RSD, relative standard deviation.

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In addition, inductively coupled plasma optical emission spectrometry (ICP-OES) has demonstrated the potential to determine total phosphorus in biodiesel. Total sulphur determination is carried out by UV-fluorescence spectroscopy.

The Brazilian norm (RANP 07/08) [14], as well as other standard methods (EN 14214, ASTM D 6751), has established the concentrations of Na plus K as being below 5 mg kg^{-1} , and Ca plus Mg as being 5 mg kg^{-1} . These methods recommend the use of AAS for the determination of Na and K and/or ICP-OES for Ca, Mg, Na, K and P. The ICP-OES method has the advantage of being multi-elemental.

Edlund et al. [4] described the application of ICP-OES for the simultaneous determination of K, Na, Ca, Mg, Cl and P in biodiesel by dissolving samples and organometallic standards in kerosene. However, this method showed some disadvantages, such as the low stability of the analyte in the organically diluted standard solutions, the need for organometallic standards for calibration and the use of dangerous organic solvents that require special conditions for their handling. In order to avoid having to use dangerous organic solvents, dos Santos et al. [10] employed ethanol as the solvent for diluting the biodiesel and the standard solutions. To compensate for transport interference, yttrium was used as the internal standard (I.S.). Other methods based on water-in-oil microemulsions as the sample preparation are reported in the literature; these methods are accomplished by FAAS [7,12] and ICP-OES [13]. On the other hand, electrochemical methods have been proposed as an alternative. Castilho and Stradiotto [15] described an alternative potentiometric method. In this work, a nickel hexacyanoferrate-modified electrode was developed to determine the concentration of potassium ions in biodiesel. Determination of copper with minimum pre-treatment was reported by employing stripping chronopotentiometry using a gold working electrode [16]. Other techniques used for the determination of biodiesel quality were reviewed by Monteiro et al. [17].

The determination of glycerol in biodiesel is accomplished by separation techniques, such as gas chromatography (GC) and high performance liquid chromatography (HPLC). Gas chromatography has the advantage of the possible simultaneous separation of glycerol and mono-, di- and tri-glycerides [14].

Recently, a method using capillary electrophoresis (CE) technique was reported for the determination of cationic species in biodiesel, which used indirect UV detection (214 nm), because this species did not show good absorption [18]. Another application of this technique is the determination of glycerol in biodiesel. A reaction with periodate was employed for indirect determination, because glycerol is a neutral species [19]. Since this reaction is specific to polyalcohol, to avoid interferences of other compounds which have vicinal hydroxyls (e.g., mono- and di-glycerides) the extraction of glycerol to aqueous phase was performed before the oxidation reaction.

Capacitively coupled contactless conductivity detection (C^4D) can be considered as a universal detection technique for CE that shows a good sensitivity for all ionic species. The basic principle of conductivity detection – the measurement of a difference in conductivity between migration analyte zones and the background electrolyte (BGE) – has favored the application of C^4D for the determination of non-absorbing species [20]. Several methods employing $CE-C^4D$ can be found in the literature, and show its application on several samples [21,22]. An introduction to the fundamentals can be found in References [23,24].

The present work shows an alternative method for the analysis of biodiesel samples by employing $CE-C^4D$ to achieve the detection limits established by regulatory authorities. In addition, other species that contribute to the biodiesel acidity – formate, acetate, and propionate – are also attended by one of the developed methods. The work also aimed to demonstrate the versatility of $CE-C^4D$; applications are illustrated for different classes of compounds using a single technique, where in some cases small changes to the separation conditions were required.

2. Experimental

2.1. Reagents

All reagents and solvents were of analytical grade. Cetyltrimethylammonium bromide (CTAB), L-histidine (His), 2-(*N*-morpholino)ethanesulfonic acid (MES), KCl, NaCl, CaCl_2 , MgCl_2 , and LiCl were purchased from Sigma (St. Louis, MO). Acetic acid, chloroacetic acid, formic acid, propionic acid, glycerol, periodic acid, sodium iodate, and sodium thiocyanate were purchased from Merck (Darmstadt, Germany). All of the BGE and standard solutions were prepared by dissolving the reagents or diluting the stock solutions in deionized water (Barnstead, Dubuque, IA, USA).

2.2. Equipment

All of the analyses were performed using home-made $CE-C^4D$ equipment [25]. The detector was operated at 600 kHz and $2 V_{pp}$. A $75\text{-}\mu\text{m}$ i.d. \times $375\text{-}\mu\text{m}$ o.d. fused silica capillary (J&W Scientific, Folsom, CA, USA) with 50 cm in length was used. The effective length was 40 cm for all experiments but that one for glycerol determination, which were carried out with 10 cm. The samples were hydrodynamically introduced, elevating the anodic reservoir at 10 cm for 30 s. A constant voltage of 25 kV was used for all experiments.

2.3. Samples

The biodiesel samples were acquired directly from different manufacturers. The extraction of polar species was carried out by weighing 10–880 mg of a sample into a vial (2 mL) and adding 200–1000 mg of deionized water or BGE diluted tenfold. The extraction was performed by shaking the vial in a vortex mixer (Q220, Quimis, Diadema, Brazil) and then centrifuging it (Force 7 Microcentrifuge, Denver Instrument, Arvada, USA) at 10,000 rpm for 8 min. After centrifugation, the aqueous phase was removed and kept for analysis.

3. Results and discussion

3.1. Optimization of separation conditions

3.1.1. Separation of K^+ , Na^+ , Ca^{2+} and Mg^{2+}

The BGE employing MES/His has commonly been used as a running buffer for the separation of small ions in $CE-C^4D$ due to its low conductivity and buffering capacity. Since the injection of untreated samples directly into the capillary is not possible due to the hydrophobic characteristic of biodiesel, the extraction of the aqueous phase was studied for this sample.

The extraction was performed using two different solutions: deionized water and BGE diluted tenfold. In both cases, $200 \mu\text{mol L}^{-1}$ LiCl was added as an I.S. The extraction process was carried out with 880 mg of the biodiesel sample and 200 mg of extraction solution, which provided an enhancement factor of 4.4 times. Fig. 1 presents the relative area of inorganic cations by using these two procedures. The extraction was performed in duplicate and analyzed in triplicate injections. The results show that the extraction time did not have a significant influence on the extraction. On the other hand, the differences in composition of the extraction solutions caused differences in the extraction results: the solution containing diluted BGE showed better extraction efficiency. This was possibly due to ionic exchange between the electrolyte cations (histidine) and the inorganic cations of the sample. Thus, the condition of extraction employed was diluted BGE and 30 s of extraction time. Fig. 2 shows the electropherograms of a standard solution of K^+ , Na^+ , Ca^{2+} and Mg^{2+} , blank extractor and biodiesel samples after extraction.

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