



Simultaneous quantitative analysis of the acetate, formate, chloride, phosphate and sulfate anions in biodiesel by ion chromatography



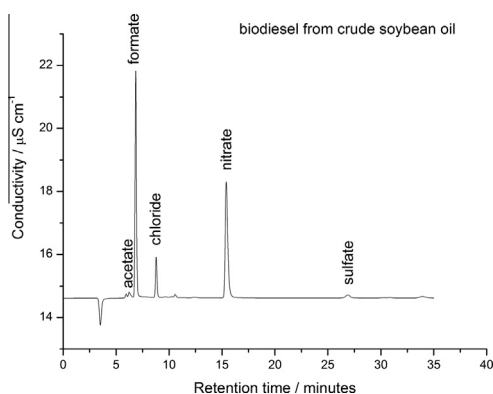
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HIGHLIGHTS

- Simultaneous quantitative analysis of anions in biodiesel by ion chromatography.
- The extraction of the anions from the matrixes is performed using water.
- The procedure is green and small volumes of water are used.
- It is simple and can be performed rapidly.
- Acetate, formate, chloride, phosphate and sulfate anions were analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

A quantitative ion chromatographic analytical method for the simultaneous determination of the acetate, formate, chloride, phosphate, and sulfate anions in biodiesel is proposed. Samples of biodiesels prepared from soy, canola and sunflower vegetable oils, from crude soy oil, and from bovine fat were analyzed. The extraction of the anions from the matrixes was performed using water with the assistance of ultrasound. The observed limits of detection and of quantitation in mg kg^{-1} and the mean relative standard deviation in percent were, respectively: acetate, 0.32, 0.97 and 4.4; formate, 1.36, 4.12 and 6.2; chloride, 0.098, 0.30 and 6.5; phosphate, 0.81, 2.47 and 7.1; and sulfate, 0.087, 0.264 and 7.8. The procedure can be considered to be green because it uses small volumes of water, is simple, and can be performed rapidly.

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1. Introduction

Biodiesel is a mixture of linear chain alkyl esters obtained through the transesterification of triacylglycerides of oils and fats with short chain alcohols. This reaction yields glycerol as a side product [1].

For commercialized biodiesel to be adequate for use in motors, it must present a series of properties that are normalized according to resolutions, such as, ASTM D 6751 norm in the United States, EN 14214 in Europe and to the resolution ANP 14/2012 [2] in Brazil.

According to the established norms, K^+ , Na^+ , Ca^{2+} , and Mg^{2+} cations as well as the phosphorus and sulfur contents must be quantified in biodiesel. The quantity of chloride admissible is not regulated, but the determination of this anion is important, as it is present in the raw material and can also be introduced by the rinsing of the crude biodiesel with a hydrochloric acid solution

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[3]. Recently, Martiniano et al. [4] quantified the Fe(II) and Cu(II) in biodiesel employing anodic stripping voltammetry.

The content of phosphorus in biodiesel comes from the raw materials used in the production, such as from the phospholipids present in vegetable oils and animal fats. The maximum phosphorus concentration allowed according to the Brazilian norms is 10 mg kg^{-1} [2]. Usually, before the transesterification reaction oils and fats undergo a pretreatment with hot water where the main parts of the phospholipids are removed together with other impurities, including waxes, metallic ions, and colloidal substances [5]. If the biodiesel synthesis is performed with crude oils or fats, the yield of the reaction is significantly lowered [6] and the obtained product can present a significant amount of phosphorus. Such types of biodiesel form great quantities of particulates in the exhaust gases from combustion motors. The phosphorus compounds that are formed can inactivate the catalytic convertors of vehicles, increasing the ambient problem [7]. The Brazilian norm RANP 14/2012 [2] establishes the ICP OES (EN ISO 14107 method), the ICP OES (NBR 15553) [8] and the ICP OES (ASTM D 4951) [9] for the quantification of phosphorus in biodiesel.

Like phosphorus, sulfur is also a typical poison for catalysts and therefore can affect catalytic convertors. However, biodiesel presents low levels of sulfur. Under Brazilian law, the maximum sulfur concentration allowed is 10 mg kg^{-1} . The regulated analytical methods are molecular fluorescence (methods EN ISO 20846 and ASTM D 5453) or dispersive X-ray fluorescence (method ISO 20884).

Ion chromatography has been applied to a variety of matrixes, including water [10–12], environmental [13], petroleum coke [14], food [15–18], and bioethanol fuel [19]. However, despite its versatility, this technique is rarely used for the analysis of biodiesel [20–22].

For a variety of matrixes, the pretreatment procedures for the quantitation of inorganic anions through ion chromatography only employ simple operations such as filtration, dilution and pH adjustment. However, for complex matrixes such as biodiesel, these types of procedures, even with online dialysis, are not enough for the elimination of the organic matter that interferes in the analysis. Therefore, other pretreatments techniques are desirable.

Liquid–liquid extraction has presented good efficiency for the treatment of several types of samples for the analysis of ions by ion chromatography. Dugo et al. [17] developed a procedure for the determination of fluoride, chloride, bromide, nitrite, nitrate, phosphate, sulfate and iodide ions in vegetable oils using this technique. Piovezan et al. [23] determined the sodium, potassium, calcium and magnesium contents in biodiesel using capillary electrophoresis after liquid–liquid extraction with water. Nogueira and Lago [24] reported that water extraction is an efficient process for extracting phosphate, sulfate, formate, acetate and glycerol from biodiesel. Caland et al. [20] used an acidic aqueous solution extraction assisted by heating and ultrasound for the simultaneous quantitation of sodium, potassium, calcium and magnesium in biodiesel using ion chromatography.

Considering that the liquid–liquid extraction is an efficient and simple procedure for the preparation of samples for ion chromatographic analysis, the aim of the present work was the simultaneous quantitation of anions in biodiesel using this procedure and technique.

2. Experimental

2.1. Instruments

A Metrohm 882 Compact IC chromatograph equipped with an isocratic pump and a dialysis system was used to perform the

experiments. A Na_2CO_3 (3.2 mmol L^{-1}) and NaHCO_3 (1.0 mmol L^{-1}) aqueous solution was used as the eluent. It was degased using ultrasound for 15 min. The injection volume was $20 \mu\text{L}$, and a Metrosep A Supp 5 ($4 \times 250 \text{ mm}$) column based on a polymeric substrate functionalized with quaternary ammonium groups was used. The conductivity of the eluent was suppressed with an anionic suppressor in the regeneration mode with a 100 mmol L^{-1} H_2SO_4 solution. The acquisition and treatment of the data were performed using the MagicNet 2.0 (Metrohm) software.

2.2. Reagents, solutions and samples

All of the reagents were of analytical grade, and the aqueous solutions were prepared using deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$ at 25°C) obtained from a Milli-Q device (Millipore Bedford, MA, USA).

Standard stock solutions of the acetate, formate and chloride anions (1000 mg L^{-1}) were prepared by weighing adequate masses of each salt and dissolving them in water in a volumetric flask.

The salts employed were sodium acetate (Synth, Brazil), sodium formate (Quimis, Brazil) and sodium chloride (Synth, Brazil). Standard solutions (1000 mg L^{-1}) of the phosphate and sulfate ions were acquired from Sigma–Aldrich (St. Louis, MO, USA). Standard solutions containing all of these anions were prepared by mixing adequate volumes of the individual solutions and diluting them with water to reach a final volume: acetate (1.00; 2.00; 3.00; 4.00; and 5.00 mg L^{-1}); formate (2.0; 4.0; 6.0; 8.0; and 10.0 mg L^{-1}); chloride (0.3; 0.6; 0.9; 1.2; and 1.5 mg L^{-1}); phosphate (1.0; 2.0; 3.0; 4.0; and 5.0 mg L^{-1}); and sulfate (0.5; 1.0; 1.5; 2.0; and 2.5 mg L^{-1}). All of the standard solutions were stored in polyethylene flasks.

The biodiesel samples from the soy, sunflower and canola oils as well as from the bovine fat were synthesized in our laboratory [25]. The biodiesel sample prepared from crude soy oil was furnished by industry.

2.3. Analytical procedures

2.3.1. Ultrasound assisted liquid–liquid extraction

Approximately 10 g (weighed to an accuracy of at least $\pm 0.01 \text{ g}$) were weighed directly into a 150 mL beaker. Twenty milliliters of water (the extractor) were added, and the system was stirred for 20 min. The obtained mixture was placed in a thermostatic bath at 85°C for 30 min and was then submitted to ultrasound for 15 min. Then, the solution was filtered through quantitative filter paper, and the aqueous phase was collected in a 25 mL volumetric flask. The solution was diluted to the mark with water. This solution was filtered through a $0.45 \mu\text{m}$ chromatographic filter and was then introduced into the chromatograph.

2.3.2. Assays for the recovery of the analytes

The biodiesel samples were spiked in order to evaluate the accuracy of the method by determining the quantities of the spiked analytes recovered. The fortification of the samples was performed, according the anion, using the following substances: acetate, acetic acid (Synth, Brazil); formate, formic acid (Synth, Brazil); chloride, 2-chloro-2-methylpropane (Sigma–Aldrich, St. Louis, MO, USA); phosphate, phosphoric acid (CHEMCO, Campinas, SP, Brazil); and sulfate, sulfuric acid (Synth, SP, Brazil). Standard stock solutions (1000 mg L^{-1}) of these substances were prepared in ethanol, and adequate volumes were added to the biodiesel samples. Homogenization was achieved by mechanical stirring for 10 min.

The extraction procedure was performed as described above in Section 2.3.1.

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