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A spot test for iodine value determination in biodiesel based on digital images exploiting a smartphone

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ABSTRACT

A spot test was developed for indirect determination of iodine value in biodiesel by using digital images taken by a smartphone. The procedure is based on the iodine consumption in the halogenation reaction of unsaturated compounds in biodiesel. The remaining reagent was determined after complex formation with starch, thus circumventing the background absorption inherent to biodiesel samples. The images were captured using the cell phone camera in a paper support and converted to RGB values using free application software (PhotoMetrix® 1.1.1). The reflectance values from the red channel were inversely proportional to the color intensity because of the complementary color of the iodine-starch complex. Hexane was used for diluting a biodiesel reference sample, whose iodine value was predetermined by the Friedman method for constructing the calibration curves. A linear response was observed in the range 10–106 g I_2/100 g of biodiesel, as described by the equation $S = 155 + 0.722C$ (g I_2/100 g), $r = 0.990$. Coefficient of variation and the detection limit were estimated as 4.9% ($n = 10$) and 8 g I_2/100 g, respectively. The spot test consumed only 49 μg of I_2 and generated 64 μL of effluent per determination. Analytical responses for biodiesel derived from different sources were in agreement, thus demonstrating the absence of matrix effects. These results agreed with those of the iodometric reference procedure at the 95% confidence level. The proposed procedure, which is the first application of a spot test for biodiesel analysis, is practical, inexpensive, and robust. Moreover, it uses less toxic chemicals and minimizes reagent amount and waste generation in relation to the usual methods for iodine value determination.

1. Introduction

Biofuels are sustainable alternatives to fossil fuels and their use can help to drastically reduce the emission of greenhouse gases [1]. Biodiesel is produced by transesterification of triglycerides of oils or fats with methanol or ethanol, usually under alkaline catalysis, resulting into a mixture of methyl or ethyl esters and glycerol as by-product [2]. The biofuel can be used directly or blended with diesel [3]. Because of the increasing demand (*e.g.* it is expected that by 2020, the demand for biodiesel only in Brazil will become 12.4 billion L/year [4]), various raw materials have been exploited for biodiesel production, which also increases the need for the development of more practical analytical procedures.

Quality parameters have been established to ensure the optimal performance of biodiesel, to prevent damages to the engines, and to minimize emissions of toxic substances [5]. Molecular structures of the formed esters, the amount of contaminants from raw materials, incomplete transesterification, and inadequate storage affect the biodiesel quality [2]. The iodine value, which indicates the unsaturation of the alkyl esters [6] and is related to the position of double bonds in the molecular structure, is one such quality parameter and can vary according to the raw material employed [6]. Vegetable oils have more unsaturated compounds than animal fats, which also reflect in the properties of the final product [7]. The iodine value also gives an estimative of the susceptibility of the biofuel to oxidation [8] and it is usually expressed as the number of grams of iodine consumed per 100 g of biodiesel [9].

The European EN14214 standard establishes a maximum of 120 g I_2/100 g biodiesel, whereas only measurement and registration of the iodine value are required in Brazil and United States. Both regulations adopt the procedure described in EN 14111 for determining the iodine value [10]. The official procedure is based on the Wijs method, which involves the use of toxic reagents and solvents, such as iodine chloride and carbon tetrachloride. In addition, a high reagent amount is required because of the low reactivity with the unsaturated compounds [11], which also increases the analysis time and waste volume. These drawbacks make the Wijs method infeasible for routine analysis. An additional hindrance is that the procedure cannot be applied to samples with iodine value below of 51.6 g/100 g biodiesel [12], such as some biodiesel from animal fats.

Some alternative volumetric procedures to the Wijs method have been described in the literature, such as the Friedman titration with

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visual [13] or potentiometric [14] end-point detection. These procedures use an iodine solution in ethanol instead of iodine chloride, but they also generate significant waste amounts. Other alternatives derive from procedures proposed for the determination of the iodine value in oils and fats, such as near infrared (NIR) spectroscopy [15], nuclear magnetic resonance (^{1}H NMR) [16], as well as prediction from theoretical modeling [17]. In spite of the suitable analytical performance, these methods involve laborious procedures and high cost instrumentation. A more recent proposal is based on liquid-liquid microextraction in a flow-based system, which exploits the fading of the color of a triiodide solution inserted within biodiesel aliquots [18]. Although this procedure is simpler than the previously reported ones, it also has limitations for monitoring the quality parameter in biodiesel production plants.

Spot tests are simple, fast, and inexpensive analytical tools, which require low volumes of sample and reagent. They were first used in 1834 to determine free chlorine by impregnating a filter paper with potassium iodide and then adding starch to it for indirect analyte detection [19]. Since then, this approach has been widely used for qualitative and quantitative analysis of both organic and inorganic compounds [20,21]. However, it has not been used for the quality control of biodiesel. Herein, we propose a spot test to simplify the determination of the iodine value of biodiesel, in order to directly monitor this quality parameter in production stations. This spot test is based on digital image colorimetry carried out with a smartphone camera and it drastically reduces both the amount of reagents and waste generation.

2. Experimental

2.1. Apparatus

Digital images were obtained using a smartphone (Moto X, 13 megapixel camera equipped with Android 6.0, Motorola) employing the PhotoMetrix® 1.1.1 software [22]. The images were acquired in the "univariate analysis" module and the region of interest was 32 × 32 pixels. Analyses were performed under controlled lighting provided by two tubular fluorescent lamps (Philips, 32 W); a paper piece was placed on a white sheet to minimize the background reflectance and the influence of external light. The smartphone was placed 5 cm above the paper support. Quantitative (hydrophilic) filter papers (Nalgon®) were cut in a circular form of 6 mm diameter and placed on a piece of a hydrophobic and inert white paper. The value of the R channel (RGB color system) was transferred to Microsoft Excel® 2013 for data treatment.

2.2. Reagents and solutions

All chemicals were of analytical-reagent grade. The solutions were freshly prepared using deionized water (resistivity > 18 MΩ cm) or anhydrous ethanol (Merck). Iodine solutions (8 mmol L^{-1}) were daily prepared by dissolving 22 mg I_2 (Merck, 99.5%) in ethanol. A 1% (m/v) starch solution was also daily prepared by dissolving solid starch in hot water. Biodiesel with iodine value of 106 g I_2/100 g (determined by the Friedman method [13]) was used as reference. Calibration curves were obtained using solutions prepared by diluting this reference biodiesel in n-hexane (Merck, >99%), obtaining solutions with concentrations ranging from 0 to 100% (v/v). Biodiesel samples from different raw materials (bovine fat, soybean oil, and cottonseed oil) were analyzed by the proposed procedure without any pretreatment.

2.3. Proposed procedure

Sample (40 μL) and the alcoholic iodine solution (24 μL) were transferred to a 1.5-mL Eppendorf® tube and mixed manually. After 5 min, 5 μL of the mixture was transferred to the paper piece, followed by 5 μL of the starch solution. The image of the iodine-starch complex was immediately captured with the smartphone camera under constant lightening (see Section 2.1) and the values of the R channel were measured (Fig. 1). The difference between the responses obtained without (*i.e.* by replacing biodiesel by hexane) and with biodiesel was taken as the analytical signal. All samples were diluted up to 50% (v/v) with hexane before measurements, which were carried out in triplicate.

2.4. Reference procedure

The reference procedure was based on the Friedman titration with visual end-point detection [13]. About 0.100–0.150 g of the sample was accurately weighted and transferred to 250 mL Erlenmeyer flasks, followed by the addition of 15 mL of ethanol and stirring for 5 min on a heater plate at 50 °C. Subsequently, 20 mL of the alcoholic 0.100 mol L^{-1} I_2 solution and 200 mL of deionized water were added. The titration was performed with a previously standardized 0.100 mol L^{-1} $Na_2S_2O_3$ solution until the aqueous phase becomes slightly yellow. After adding 3 mL starch 1% (m/v), the end-point was detected based on the color changing from blue to colorless. The iodine value was calculated by Eq. (1).

$$\text{Iodine value} = \frac{(B\text{-}A) \times C \times 12.69}{m} \quad (1)$$

where A and B are the volumes of $Na_2S_2O_3$ consumed in the titration of I_2 in the presence and absence of the sample, respectively, C is the $Na_2S_2O_3$ concentration, and m is the sample mass in grams.

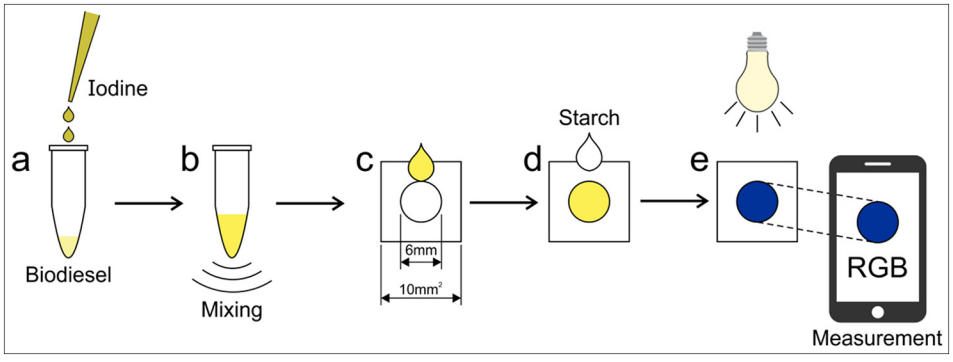

Fig. 1. Schematic diagram of the colorimetric spot test. (a) Reaction of biodiesel with iodine; (b) Mixing and subsequent reaction time; (c) Transfer of 5 μL of the mixture to the paper; (d) Addition of 5 μL of starch (1% m/v) and (e) acquisition of the RGB value by employing the software PhotoMetrix® 1.11.