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# An air carrier flow system for the spectrophotometric determination of water in biodiesel exploiting bleaching of the cobalt chloride complex



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## ABSTRACT

Water content is an important parameter in biodiesel quality control, as excess of this substance may lead to biofuel hydrolysis, microorganism proliferation, and alterations in the oxidative stability of the biofuel. The threshold limit is established as  $200 \text{ mg kg}^{-1}$  and the determination is usually based on Karl Fischer titration. In this work, a simple, reliable and environmentally friendly procedure is proposed for water determination in biodiesel by exploiting a multicommutated flow system with air carrier stream. The method relies on the color fading of the cobalt chlorocomplex in the presence of the analyte, which is monitored by spectrophotometry. A linear response was observed from  $100$  to  $5000 \text{ mg kg}^{-1}$  water, with detection limit, coefficient of variation ( $n=20$ ) and sampling rate estimated as  $25 \text{ mg kg}^{-1}$ ,  $0.7\%$  and  $30 \text{ h}^{-1}$ , respectively. The procedure consumes only  $3.5 \text{ }\mu\text{g}$  of  $\text{CoCl}_2$  and generates  $750 \text{ }\mu\text{L}$  of waste per determination. Results obtained by using the standard additions method agreed with those attained by the Karl Fischer titration at the  $95\%$  confidence level.

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## 1. Introduction

Use of biodiesel fuel has increased worldwide due to its low impact on the environment and as a source of renewable energy to replace diesel and other petroleum derivatives. As such, this biofuel should meet the recommended parameters to ensure its quality for both use and storage [1] as well as to avoid emission of toxic substances.

Water determination is important for the quality control of biodiesel. The biofuel contains water as a result of the production process (washing to remove excess of alcohol and glycerol byproducts) and the absorption of atmospheric humidity. Excess of water may cause biodiesel hydrolysis yielding free fatty acids, which increases acidity and favors proliferation of microorganisms and corrosion of storage tanks [2]. Moreover, water may increase the formation of oxidation products during storage of the biofuel, which can damage the vehicle injection system and engine. In view of these aspects, water content in biodiesel is limited to  $200 \text{ mg kg}^{-1}$  [3,4] and this parameter should be monitored in the final product and during storage, which requires a fast and reliable procedure.

Water has been determined in different sample matrices by chromatography [5,6], spectrophotometry [7], fluorimetry [8], and mainly electroanalysis [9,10]. The Karl Fischer (KF) titration, the

most widespread method, has also been recommended for biodiesel analysis [11,12]. However, it presents some drawbacks such as the need for specialized equipment, rigorous sample manipulation, and the use of toxic reagents. Furthermore, biodiesel often contains additives and impurities that may favor side reactions during the coulometric KF titration [13].

Batch spectrophotometric procedures using alternative reagents, such as cobalt chloride [14], potassium dichromate [15], dithizone [16], and acridine orange [17] have been proposed for determination of water in various organic solvents. These procedures are time-consuming and involve several steps, thus impairing sample throughput and increasing the risks of systematic errors. Moreover, they are highly susceptible to sample contamination due to absorption of atmospheric humidity. Flow-based analytical procedures exploiting the KF reagent have been proposed to circumvent some disadvantages of the batch analogues [18–24]. In this sense, side reactions were minimized and sample throughput was increased by reducing the reaction time, while contamination from atmospheric humidity and contact of the analyst with the toxic reagents were diminished by sample processing in a closed system. On the other hand, sensitivity is usually worse than that achieved in the batch procedure and some interferences were not circumvented. The performance of flow injection spectrophotometric procedures for water determination in acetone exploiting different reagents was also evaluated [7].

In spite of the availability of some alternatives and the previously mentioned drawbacks, the KF method prevails in the analysis of biodiesel. This emphasizes the need for the

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development of rapid, reliable, and environmentally friendly procedures for biofuel analysis. The goal of the present work was therefore to develop a flow system with air carrier stream for the spectrophotometric determination of water in biodiesel based on discoloration of the cobalt chloride complex in ethanolic medium.

## 2. Materials and methods

### 2.1. Reagents and solutions

All solutions were prepared daily with anhydrous ethanol (99.9%, Merck, Germany) and analytical grade chemicals. The working standards were prepared within 100–5000 mg kg<sup>-1</sup> water, and a 5.25 × 10<sup>-3</sup> mol L<sup>-1</sup> cobalt chloride solution was used as reagent. Air was used as a carrier to minimize the ethanol consumption and to avoid dispersion of the sample zone. Anhydrous ethanol was also used in the washing step.

Biodiesel samples were analyzed by the standard additions method. Solutions were prepared from 3.75 mL of biodiesel with the addition of 10–50 μL of water (two spikes per sample). Volumes were made up to 5.00 mL with anhydrous ethanol, which is miscible with both water and biodiesel. Samples with the same dilution in ethanol, but without water addition, were taken as reference.

### 2.2. Apparatus

The flow system was built up with four three-way solenoid valves (NResearch, USA), a Teflon<sup>®</sup> confluence connector, and 0.8-mm i.d. polyethylene tubes. A peristaltic pump (model CP 78017-10, Ismatec IPC, Switzerland) was equipped with Tygon<sup>®</sup> and Viton<sup>®</sup> tubes for propelling aqueous and ethanolic solutions, respectively. The solenoid valves were computer-controlled through a parallel interface coupled to a current drive based on the ULN2803 integrated circuit [25]. The detection system consisted of a multi-channel CCD spectrophotometer (USB 2000, Ocean Optics, Dunedin, FL) with a tungsten-halogen light source and optical fibers for radiation transport. A lab-made glass flow-cell (30-cm optical path and 1.7 mm i.d.) with glass waveguides [26] was used for the spectrophotometric measurements. The control software was developed in Visual Basic 6.0 (Microsoft, USA), and data acquisition was performed with the software supplied by the spectrophotometer manufacturer.

### 2.3. Flow system

The flow diagram showed in Fig. 1 was operated according to the switching course in Table 1. The multicommutation approach was exploited for solutions management by binary sampling [27] and air was used as the carrier stream [28]. The fluids were propelled at 0.6 mL min<sup>-1</sup> (S, R and E) and 1.0 mL min<sup>-1</sup> (air). In the position showed in Fig. 1, all liquids are recycled to the corresponding vessels and only air is flowing to the system. Each solution is sampled by switching the corresponding valve simultaneously to V<sub>4</sub>, aiming to interrupt the air flow through the manifold and avoid segmentation of the sample zone. Volumes are defined by the flow rate and the switching times (see Table 1). The analytical cycle started (steps 1 and 2) by inserting 10 sample and reagent aliquots alternately (i.e. 10 sampling cycles). This corresponds to total sample and reagent volumes of 600 and 100 μL, respectively. The sample zone was transported by air through to reaction coil toward the detection cell (step 3). The analytical path was washed with ethanol by the actuation of valve V<sub>3</sub> before sample replacement (step 4).

The coiled reactor and the reagent solution were maintained inside a water bath with temperature controlled at 25.0 ± 0.1 °C

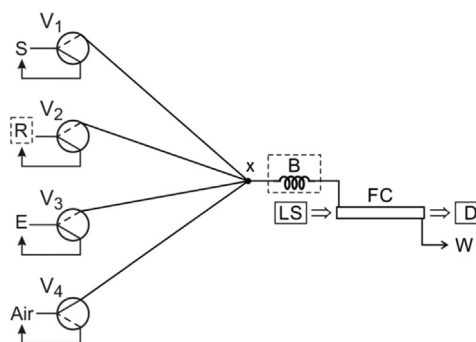


Fig. 1. Flow diagram of the proposed procedure. S=sample; R=reagent (5.25 × 10<sup>-3</sup> mol L<sup>-1</sup> CoCl<sub>2</sub> in anhydrous ethanol); E=anhydrous ethanol; Air=carrier stream; V<sub>1</sub>–V<sub>4</sub>: three-way solenoid valves; x=Teflon<sup>®</sup> joint point; B=50-cm coiled reactor; LS=tungsten-halogen light source; FC=30-cm long flow cell (1.7 mm i.d.); D=detector; W=waste. Dashed lines indicate components inserted in a temperature-controlled water bath (25.0 ± 0.1 °C).

Table 1  
Valve switching course for water determination in biodiesel.

Step	Description	Valves	Time (s)	Volume (μL)
1 <sup>a</sup>	Sample insertion	V <sub>1</sub> , V <sub>4</sub>	6.0	60
2 <sup>a</sup>	Reagent insertion	V <sub>2</sub> , V <sub>4</sub>	1.0	10
3	Measurement	0	10	–
4 <sup>b</sup>	Washing	V <sub>3</sub> , V <sub>4</sub>	5.0	50

<sup>a</sup> Ten sampling cycles.

<sup>b</sup> Step required only for sample replacement.

due to the thermochromic properties of the reagent [29]. Off-set adjustment of the detection system was performed with ethanol inside the flow cell. Absorbance values were measured as peak height at 650 nm; all measurements were carried out in triplicate. The analytical signal was based on the difference between reference and sample signals, measured in the absence and presence of water, respectively.

### 2.4. Reference procedure

Coulometric KF titration for determining the water content in engine fuels, as recommended by ASTM [3], was employed as the reference procedure for accuracy assessment. A biodiesel aliquot was injected into the titration vessel of a KF apparatus in which iodine was coulometrically generated at the anode for the KF reaction. After titration of the water content, excess of iodine indicated the end point.

## 3. Results and discussion

The proposed procedure was based on discoloration of the CoCl<sub>2</sub> complex, which shows thermochromic and solvatochromic properties [29], i.e., the solution color is affected by the temperature and solvent nature. The aqueous solution of cobalt chloride is pink due to the formation of the octahedral hexa-aquacobaltate complex, [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. On the other hand, anhydrous CoCl<sub>2</sub> is a blue solid and its solutions in different organic solvents (e.g. ethanol) are also blue due to the formation of chlorocomplexes. The reversible changes in color of this system caused by temperature are also known [29]. Despite being widely investigated, bleaching of the cobalt chloride complex was not still exploited for water determination.

The addition of low amounts of water into a CoCl<sub>2</sub> ethanolic solution causes fading of the blue color, simultaneously with the formation of the pink aquocomplexes. Thus, the hexa-aquacobaltate

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