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Vapor permeation-stepwise injection simultaneous determination of methanol and ethanol in biodiesel with voltammetric detection

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ABSTRACT

A novel vapor permeation-stepwise injection (VP-SWI) method for the determination of methanol and ethanol in biodiesel samples is discussed. In the current study, stepwise injection analysis was successfully combined with voltammetric detection and vapor permeation. This method is based on the separation of methanol and ethanol from a sample using a vapor permeation module (VPM) with a selective polymer membrane based on poly(phenylene isophtalamide) (PA) containing high amounts of a residual solvent. After the evaporation into the headspace of the VPM, methanol and ethanol were transported, by gas bubbling, through a PA membrane to a mixing chamber equipped with a voltammetric detector. Ethanol was selectively detected at +0.19 V, and both compounds were detected at +1.20 V. Current subtractions (using a correction factor) were used for the selective determination of methanol. A linear range between 0.05 and 0.5% (m/m) was established for each analyte. The limits of detection were estimated at 0.02% (m/m) for ethanol and methanol. The sample throughput was 5 samples h^{-1}. The method was successfully applied to the analysis of biodiesel samples.

1. Introduction

Biodiesel occupies a prominent position among alternatives to conventional petrodiesel fuel due to various technical, economic and ecological factors. The technology of biodiesel production includes the transesterification process of vegetable oil (e.g., soy oil) or animal fats (e.g., swine lard) with methanol or ethanol in the presence of a catalyst (alkali, acid or an enzyme) [1–3]. After the transesterification reaction, excess alcohol is removed from the biodiesel by extraction and distillation. The amount of alcohols in biodiesel is regulated by American (ASTM D 6751) and European (EN 14110) biodiesel standards and the permitted maximum level of alcohols in biodiesel samples is 0.2% (m/m). Excess alcohols cause metal corrosion, particularly aluminum corrosion; decrease diesel fuel flash point; and degrade rubber and polymer parts of engines.

Various analytical methods have been developed (Table 1) for the determination of alcohols in biodiesel. They are based on gas chromatography (GC) [4–6], near infrared (NIR) [7–11] and UV–vis [10] spectroscopy. GC is the most used technique due to its high accuracy in the quantification of minor components. However, baseline drift and overlapping signals can have a detrimental effect on GC accuracy [12]. The GC accuracy can be improved by using a headspace solid-phase microextraction [6]. This technique is characterized by high sensitivity, good reproducibility and recovery. The application of chemometric tools in the NIR spectroscopy allows the determination of methanol and water in biodiesel [8]. NIR and visible spectroscopy are able to predict methanol and glycerol traces in biodiesel samples [10]. Moreover, the technique for the determination of residual alcohol content in biodiesel through determination of its flash point was proposed [13], but this method does not allow the simultaneous determination of methanol and ethanol. In the present research [14], a cyclic voltammetry method was developed for the simultaneous determination of analytes in fuel ethanol.

Automation of analysis is an important and rapidly growing trend in modern analytical chemistry. Recently, the automation of analytical procedures based on flow analysis has been developed. Therefore, labor costs for the analysis are decreased, and the volume of sample solutions and reagents are reduced.

Currently only one flow method for the determination of methanol in biodiesel samples is described [15]. The proposed method is based on the liquid–liquid extraction of methanol from a sample solution to a phosphate buffer using a membrane unit with a polyvinylidene fluoride membrane. The determination of

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Table 1
Comparison of the suggested method with previously reported for the determination of methanol and ethanol in biodiesel.

Detection technique	Analyte	Sample preparation	Sample amount	On-line analysis	Linear range	LOD	Ref.
GC	MeOH	Dilution	100 μL	No	–	0.001% (m/m)	4
GC	MeOH	Headspace solid phase microextraction	1 mL	No	0.005–0.05% (m/m)	–	6
NIR	MeOH	–	–	No	–	51 ppm	9
VIS and NIR	MeOH	–	10 μL	No	0.003–0.433% (m/m)	–	10
FP	EtOH, MeOH	–	65 mL	No	to 1% (v/v)	0.1% (v/v)	13
CV	EtOH, MeOH	Dilution	–	No	0.1–0.5% (v/v)	0.028 and 0.045% (v/v) for EtOH, MeOH	14
VIS	MeOH	Membrane extraction	200 μL	Yes	0.001–0.200% (m/m)	0.0002% (m/m)	15
CV	EtOH, MeOH	Vapor permeation	1 mL	Yes	0.05–0.5% (m/m)	0.02% (m/m)	This work

GC – gas chromatography, NIR – near infrared spectroscopy, VIS – visible spectroscopy, FP – flash point determination, CV – cyclic voltammetry.

methanol was then achieved in aqueous solution by converting it to hydrogen peroxide through the use of alcohol oxidase, followed by the use of 2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) as an electron donor for horseradish peroxidase, giving the colored ABTS radical cation.

In this work, a new flow method for the simultaneous determination of methanol and ethanol in different types of biodiesel with analytes vapor permeation through the PA membrane and cyclic voltammetry detection has been developed. Vapor permeation (VP) is frequently used for the separation of volatile analytes in complex samples [16] and can be coupled with flow methods. The PA was chosen as the membrane material because of its good physico-chemical properties and high selectivity with respect to methanol in pervaporation of tert-butyl methyl ether/methanol and cyclohexane/methanol mixtures, as seen in previous work [17,18]. It should be noted that the PA membrane studied in this work is different from the PA membrane described in previous works [17–19]. The studied membrane has higher free volume, which significantly effects the transport of low molecular substances through it. The stepwise injection analysis [20–22] was chosen for the automation of methanol and ethanol determination in biodiesel because its manifold allows to mix solutions by a gas flow. This feature can be used to increase the efficiency of methanol and ethanol penetration during vapor permeation.

2. Experimental

2.1. Manifold and apparatus

A stepwise injection manifold (Fig. 1) includes a syringe pump (Sciware systems, Spain), a reversible peristaltic pump MasterFlex L/S (Cole-Parmer, USA) with modified PVC pumping tube (Watson-Marlow, Russia), two six-way solenoid valves (Cole-Parmer Inc., USA), a homemade mixing chamber (MC) (a cylindrical-shaped PTFE tube (20 mm in height and 15 mm in i.d.) equipped with a magnetic stirrer and integrated with the miniaturized home-made Ag/AgCl reference, platinum auxiliary and gold working (Ø=3 mm) electrodes), 797 VA Computrace Analizer (Metrohm, Switzerland), communication tubes (PTFE, 0.5 mm i.d.) and a laboratory-made vapor permeation module. The vapor permeation module (Fig. 1) was constructed from two titanium discs (i.d. 50 mm), held together by four stainless steel bolts. The depths of the chambers, separated by the PA membrane (35 mm diameter

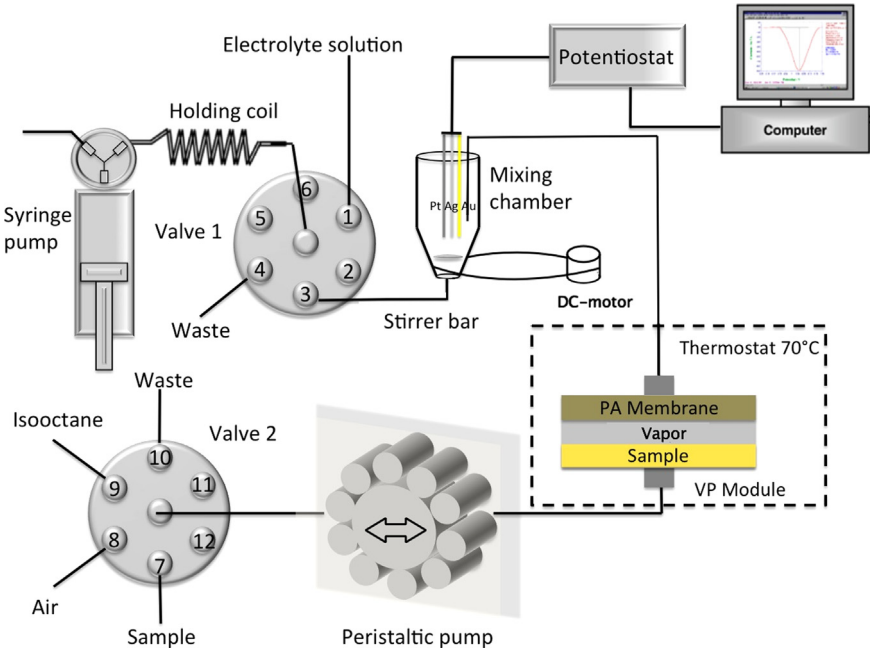

Fig. 1. The VP-SWI manifold for the simultaneous determination of methanol and ethanol in biodiesel samples.