Talanta 98 (2012) 118–122

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Photometric determination of phosphorus in mineralized biodiesel using a micro-flow-batch analyzer with solenoid micro-pumps

Marcelo B. Lima, Inakã S. Barreto, Stéfani Iury E. Andrade, Maria S.S. Neta, Luciano F. Almeida, Mário C.U. Araújo*

Universidade Federal da Paraíba, Departamento de Química, João Pessoa, PB, Brazil

ARTICLE INFO

Article history:
Received 21 May 2012
Received in revised form
21 June 2012
Accepted 21 June 2012
Available online 29 June 2012

Keywords:
Micro-flow-batch analyzer
Urethane-acrylate resin
Biodiesel
Molybdenum blue method
Phosphorus determination

ABSTRACT

A method for the determination of phosphorus in mineralized biodiesel using a micro-flow-batch analyzer (μFBA) with solenoid micro-pumps was proposed. The samples were mineralized using an ashing procedure at 550 °C followed by dissolution of the residue. The determination of phosphorus was performed by employing the well-known molybdenum blue method. The measures of the absorbance were performed at 850 nm using an InfraRed LED integrated into the μFBA. Comparing with the reference method, no statistically significant differences were observed when applying the paired t-test at a 95% confidence level. Recovery study shows results between 97.9% and 105.8%. The proposed microsystem using solenoid micro-pumps presented satisfactory robustness and high sampling rate (190 h^{-1}), with satisfactory reproducibility (relative standard deviation $<4.5\%$, $n=3$), low reagents consumption (32 μL per analysis) and cost to build the device. Moreover, μFBA presents limit of detection (0.014 mg Kg^{-1}), precision and accuracy compatible with the biodiesel regulations that establish a maximum concentration of 10 mg Kg^{-1} (Brazil, USA, EU), suggesting that it is a good alternative for the determination of phosphorus in biodiesel.

1. Introduction

Biodiesel is defined as the monoalkyl esters derived from vegetable oils or animal fats. It is produced by transesterification reaction with short-chain alcohols in the presence of catalysts, such as sodium hydroxide or potassium [1]. Quality control of biodiesel is greatly important to the successful commercialization of this fuel and its blends [2]. In Brazil, the National Petroleum, Natural Gas and Biofuel Agency (ANP) is responsible for the quality control of biodiesel [3]. Standards ASTM D6751 [4] and EN 14214 [5] also specify the limits and methods to be used.

An important monitoring parameter of quality control of biodiesel is phosphorus level. Although being present in low concentrations, phosphorus affects the catalytic conversion in the exhaust system of diesel engines and increases the generation of pollutant gases, such as carbon monoxide and carbon dioxide, sulfur dioxide, hydrocarbons, and particulate materials [6].

The determination of phosphorus in biodiesel is usually performed by inductively coupled plasma optical emission spectrometry (ICP OES), as recommended by the standards ANP resolution 07/08 [3], ASTM D6751 [4] and EN 14214 [5] using the procedure described in standards ASTM 4951 [7] and EN 14107 [8]. However, the ICP OES technique involves some disadvantages, such as dissolution of the sample in toxic organic solvents, difficulty in transport of the sample to the plasma and high cost of the analysis [6].

Alternatively, spectrophotometric methods have been developed, enabling easier analysis with good precision and low-cost. Recently, Silveira et al. [9] described a procedure based on the reaction of phosphorus with molybdenum blue, using 1-amino-2–naphthol-4-sulfonic acid as the reducing agent. A similar method was proposed by Lira et al. [6] using the flow injection analysis (FIA).

The FIA, being an automatic system, presents several advantages as, for example, reduction of the human effort, more precise analysis and an increase of the sample rate. Nevertheless, this type of system presents disadvantages, such as need for frequent recalibration and manual adjustment of the system, low sensitivity due to the sample dispersion and inefficient homogenization in the system, besides the necessity of carrier fluid which generates a high volume of residues [10].

These inconveniences can be overcome by using the flow-batch analysis (FBA) [11]. The FBA is an automated system that uses an instantaneous stop chamber and integrates batch and flow methods by using programmed multi-commutation [12].

---

* Correspondence to: Department of Chemistry, CCEN, Federal University of Paraiba, Caixa Postal 5093, CEP 58051-970, Joao Pessoa, Brazil.
Tel.: +55 83 3216 7438; fax: +55 83 3216 7437.
E-mail address: laqa@quimica.ufpb.br (M.C.U. Araújo).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.06.056

The main component is the mixing chamber where the whole analytical process, including fluids addition, sample pretreatment, homogenization, precipitation, extraction, preparation of calibration solutions, and detection, takes place under the total control of the software [10,13,14]. The sample is processed seamlessly with less: manipulation, consumption of reagents and samples, waste and chance for human error [15].

Recently, the flow-batch analyzer was miniaturized (μFBA) and applied for the determination of the Fe (II) in iron-based supplements (oral solutions) using the 1,10-phenanthroline method [16] and tannin determinations in green and black tea using the photometric (ferrous tartrate) and turbidimetric (copper (II) in acetate medium) methods [17]. The microfabrication used deep ultraviolet lithography and photopolymerizable urethane-acrylate photoresist. It contained an integrated photometer based light emitting diode (LED) and phototransistor for detection, and a nylon wire homogenizing system.

As the conventional flow-batch [12], the micro-flow-batch also combines favorable characteristics of both flow and batch analysis. As in the flow analyzers, the transportation of reagents, samples or other solutions into the micro-chamber (μCH) are carried out in a flow mode, and, as in the batch analyzers, the sample processing is carried out into μCH ("micro-beaker"). In these systems as described in previous studies, the following steps are performed: addition of the fluids; mixture/homogenization/reaction to generate colorful product into μCH and, absorbance measurement. Then the μCH is emptied through waste. Before processing a new sample, the cleaning step is carried out. Thus, micro-flow-batch systems do not use the carrier fluid. A cleaning solution is only used to clean the micro-chamber.

In previous applications, the μFBA used peristaltic pump and solenoid valves, respectively for the propulsion and commutation of the fluid [16,17]. However, these components can elevate the analyzer costs and may make its miniaturization unfeasible. These drawbacks can be circumvented by using solenoid micro-pumps [13].

In the present work, the characteristics of the μFBA with solenoid micro-pumps are explored in the determination of phosphorus in mineralized biodiesel using photometric detection. The microsystem was built in the urethane-acrylate resin, with InfraRed LED 850 nm and phototransistor integrated into the micro-chamber. The pretreatment of the biodiesel was performed as Silveira et al. [9], using the well-known molybdenum blue method [6].

2. Experimental

2.1. Instrumentation

To fabricate the micro-chamber (μCH) in urethane-acrylate resin, we used a commercial UV light source (Fotolight-MD2-A4, Carimbos Medeiros Ltda, Brazil), with two sets of mercury lamps (BLB-15 W-T8, SCT black light).

For layout design of the μCH, the CorelDraw® X5 program was used. The layout printing was on polyester transparency films for laser printing using an HP LaserJet P2014. After UV exposure, channels on the substrate were revealed by the removal of the non-exposed resin with an ultrasonic bath (model UltraCleaner 800, Unique, Brazil).

A spectrophotometer model 8453 Hewlett-Packard diode array UV–vis, equipped with cuvette (with an inner volume of about 4 mL, and an optical path of 1.0 cm), was used for absorbance measurements when employing the reference method.

2.2. Reagents and solutions

All reagents were of analytical grade and freshly distilled and deionized water ($>18\ \mathrm{M\Omega\,cm^{-1}}$) was used to prepare all solutions.

The stock phosphorus solution of 100 $\mathrm{mg\,L^{-1}}$ was prepared by appropriate dilution of potassium dihydrogen phosphate (KDP). The standard solutions (ranging from 0.10 to 10.0 $\mathrm{mg\,L^{-1}}$ of phosphorus) were prepared by mixing the stock solution with the acids solutions (H_2SO_4 1%, HNO_3 1%, and H_2O_2 1%) and were used for plotting the analytical curve in the μFBA.

A 340 $\mathrm{mmol\,L^{-1}}$ solution of ascorbic acid ($C_6H_8O_6$) was prepared by weighing 6 g of ascorbic acid and dissolving it in 100 mL of distilled water. A 5.4 $\mathrm{mol\,L^{-1}}$ sulfuric acid solution was prepared by transferring an aliquot of 30 mL of concentrated H_2SO_4 in 100 mL of water.

For the preparation of the stock solution of 32 $\mathrm{mmol\,L^{-1}}$ ammonium molybdate (QM), 20 g of salt were weighed and dissolved in 400 mL of water. After 4 h agitation, the solution was transferred to a 500 mL volumetric flask and the volume was completed with water.

The stock solution of 9 $\mathrm{mmol\,L^{-1}}$ potassium tartrate and antimony was prepared by weighing 3.0 g of potassium tartrate and antimony and dissolving them in distilled water. The solution was then transferred to a volumetric flask of 1000 mL and the volume completed with distilled water. This solution was stored in amber glass bottles under refrigeration.

The reagent solution was prepared by mixing 35 mL of concentrated sulfuric acid in 500 mL of water, then adding 215 mL of stock solution of 0.032 $\mathrm{mol\,L^{-1}}$ ammonium molybdate and 72 mL of 9 $\mathrm{mmol\,L^{-1}}$ potassium tartrate and antimony. The mixture was transferred to a 1000 mL flask and the volume completed with water. A solution of nitric acid (10%) was used to clean the microsystem fabricated.

The commercial urethane-acrylate photoresist, used for the fabrication of the μFBA, was acquired at Carimbos Medeiros Ltda, Brazil (MacDermid, flex-light trademark M050).

2.3. Sample preparation

Biodiesel originated from oils of soybeans, sunflower, and bovine fat were used. The samples were mineralized at 550 °C as indicated by Tubino et al. [9,18]. 10 g of biodiesel were weighed directly into quartz crucibles. In sequence 0.5 g of magnesium oxide was added. The mixture was calcinated at a temperature gradually to 550 °C. (1 h at 100 °C, 1 h at 180 °C, 5 h at 250 °C, 1 h at 300 °C and 2 h at 550 °C) in order to avoid loss of sample.

After cooling down carefully to the room temperature, the ashes were dissolved directly in the crucible with small portions of an aqueous 1.0 $\mathrm{mol\,L^{-1}}$ H_2SO_4 solution (total volume 25 mL) and gradually transferred to a 50.0 mL volumetric flask.

2.4. Fabrication process and assembly of the μFBA

The micro-chamber (μCH) was fabricated based on the methodology described in the literature [16,17]. Fig. 1 shows a photo of the microsystem and its dimensions. The detail of the attachment and sealing of the tubes can be seen in this photography. The homemade μCH about 100 μL of total volume was built in urethane-acrylate photoresist. A 48 μL volume with an optical path of about 5.0 mm was used for each determination. This microsystem is mounted onto a suitable support in a black (darkroom) box (10.0 cm × 8.0 cm × 4.0 cm), to preserve the system from the effects of spurious environmental radiation while in operation.

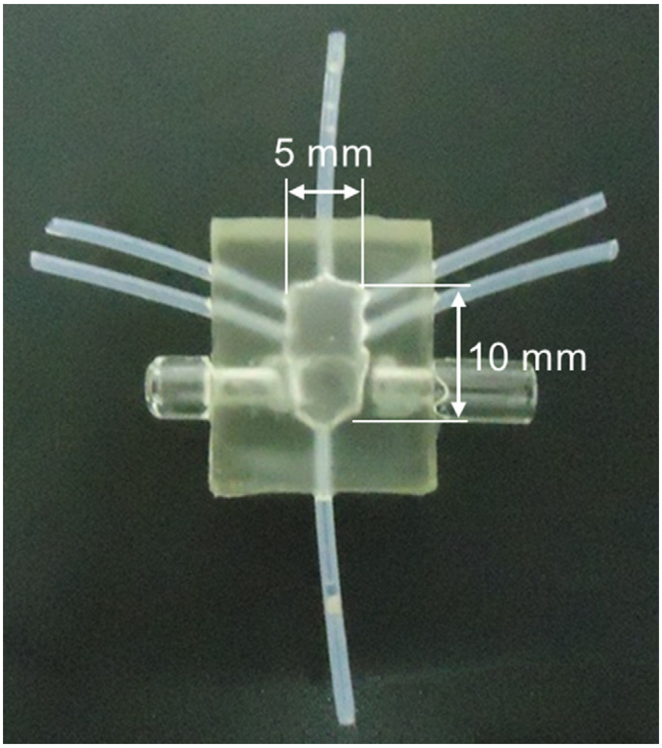

Fig. 1. Photograph of the microfabricated μFBA with its dimensions (mm).

The fluids are added with solenoid micro-pumps of 8 μL (μP_1–μP_4) and 20 μL (μP_5) per pulse (Biochem Valve Inc., Boonton, NJ, USA). Teflon® tubes with 0.5 mm internal diameter were used for fluids transport. A 0.4 mm nylon wire was used within the micro-chamber to ensure an efficient homogenization. The nylon wire was coupled to a CD/DVD-ROM motor drive (model MDN3GT3CPAC, 2000 rpm, 5 V dc).

The detection system integrated into the μCH was composed of an InfraRed LED 850 nm (L850-40K42) as source of radiation, and a phototransistor (PT333-3C) for detection. These devices, both LED and phototransistor having 5 mm of diameter, were mounted firmly outside the μCH against the glass tube openings which have an internal diameter of 2 mm. The 2 mm diameter was chosen for the glass tubes to minimize the resulting micro-chamber volume [17].

All tasks, such as data acquisition, solenoid micro-pumps, and drive motor activation, were done using a USB interface (USB6009, National Instruments®), which activated a lab made controller module. The software was developed in LabVIEW® 7.1 (National Instruments®).

2.5. Analytical procedure

The μFBA for the determination of phosphorus in biodiesel is shown in Fig. 2. The analyzer was operated as described in Table 1. The solenoid micro-pumps were actuated at 5 Hz, yielding flow rates ranging from 1.2 to 9.0 mL min^{-1}.

The reagents ammonium molybdate with antimony and potassium tartrate (2 pulses, μP_1) and ascorbic acid (2 pulses, μP_2) were added simultaneously. The homogenization was performed by the drive motor (DM) coupled to the nylon wire (NW) by 2 s. In the sequence was added the sample or standard solutions aliquot (2 pulses, μP_3) and again homogenized by DM for 2 s. After these steps, the absorbance is measured and the μCH is emptied (3 pulses, μP_5).

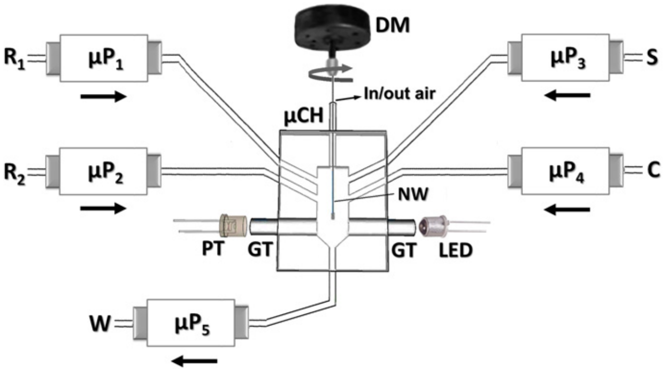

Fig. 2. The μFBA diagram. μP_1–μP_5: solenoid micro-pumps; R_1: ammonium molybdate with antimony and potassium tartrate; R_2: ascorbic acid; S: sample or standard solutions; C: cleaning solution (10% HNO_3); W: waste; μCH: micro-chamber (fabricated with urethane acrylate resin [17]); DM: drive motor; NW: nylon wire; GT: glass tube, LED: light emitting diode; PT: phototransistor.

Afterwards, the μCH is cleaned by activation of μP_4 (6 pulses), adding cleaning solution (10% HNO_3) while activated, and the DM is activated for 2 s performing the agitation. Then, μP_5 is activated (3 pulses) to discard the contents of the μCH. This cleaning and discard procedure must be done twice to effectively clean the μCH.

The procedure for in-line blank preparation is similar to described for the sample analysis. The difference is that 0.1 mol L^{-1} H_2SO_4 solution is used instead of the sample or standard solutions.

The problems with formation of air bubbles were not observed with the proposed automatic system. The solutions are introduced or removed from the μCH, the inner air escapes by this air passage (in/out).

2.6. Reference method

For comparison, the proposed μFBA performance was evaluated against a molybdenum blue method (reference method). Standard solutions were prepared from 1.0 to 10.0 mg L^{-1} [6]. The analytical signals (absorbance) were measured at a maximum absorbance of around 882 nm. The analysis of each sample was performed in triplicate and the concentrations were calculated from the analytical curve.

3. Results and discussion

3.1. μFBA parameters

Lima et al. [17] describe the μFBA using glass tubes attached to the μCH, facilitating the detection. Thus, we employed the same microsystem with solenoid micro-pumps for the determination of phosphorus in biodiesel. The InfraRed LED 850 nm was used for measuring absorbance. In the μFBA, the μCH contains a nylon wire with a shovel tip that allows fluids agitation. Complete mixing of the solutions in the micro-chamber was obtained in less than 2 s, due to the high speed of drive motor (2000 rpm).

For the method, the concentration and volume of both reagents and samples were evaluated in order to improve the sensitivity and reproducibility of the analytical signal. The system values selection (univariate method) was carried out in conformance with studied by Lira et al. [6]. All the optimization studies were performed automatically in the proposed μFBA. The range evaluated, and the values selected for each parameter are shown in Table 2.

Table 1
Switching course of the solenoid micro-pumps for the determination of phosphorus in the μFBA[a].

Step	Description	μP_1	μP_2	μP_3	μP_4	μP_5	Pulses	Time (s)
1	Addition of the reagents (R_1 and R_2)[b]	1/0	1/0	0	0	0	2	0.8
2	Homogenization using the drive motor (DM)	0	0	0	0	0	0	2.0
3	Addition of the sample (S)	0	0	1/0	0	0	2	0.8
4	Homogenization using the drive motor (DM)	0	0	0	0	0	0	2.0
5	Reading the analytical signal	0	0	0	0	0	0	1.0
6	Waste (W)	0	0	0	0	1/0	3	1.2
7	Cleaning with HNO_3 10% solution (C)[c]	0	0	0	1/0	0	6	2.4
8	Homogenization using the drive motor (DM)[c]	0	0	0	0	0	0	2.0
9	Waste of cleaning[c]	0	0	0	0	1/0	3	1.2

[a] Codes 1/0 and 0 indicate actuation of the solenoid micro-pumps and that the devices remain inactive, respectively.
[b] 2 pulses for each actuation of the micro-pump.
[c] The step 7, 8 and 9 are repeated twice for every sample.

Table 2
Selected parameters of the μFBA procedure for the determination of phosphorus in biodiesel.

Parameter	Evaluated range	Selected value
Ammonium molybdate (mmol L^{-1})	10–50	32
Antimony and potassium tartrate (mmol L^{-1})	1–50	9
Ascorbic acid (mmol L^{-1})	100–500	340
Sample volume (μL)	8–40	16
Reagent 1 volume (μL)[a]	8–40	16
Reagent 2 volume (μL)[b]	8–40	16
Total volume (μL)	32–80	48

[a] Ammonium molybdate with antimony and potassium tartrate.
[b] Ascorbic acid.

Table 3
Results for the determination of phosphorus in biodiesel using the proposed μFBA and the spectrophotometric reference method (mg Kg^{-1}). Mean values and uncertainties are based on three analytical determinations.

Samples	μFBA		Reference	
	Concentration $\pm t_{n-1} S/\sqrt{n}$[a]	RSD %[b]	Concentration $\pm t_{n-1} S/\sqrt{n}$[a]	RSD %[b]
Soybean	2.14 ± 0.16	4.43	2.31 ± 0.12	3.08
	7.28 ± 0.21	1.72	6.94 ± 0.18	1.54
	3.31 ± 0.14	2.51	3.19 ± 0.15	2.79
	5.62 ± 0.19	2.01	5.34 ± 0.11	1.22
Sunflower	8.08 ± 0.56	4.11	7.86 ± 0.31	2.34
	5.19 ± 0.27	3.09	5.11 ± 0.29	3.37
	3.07 ± 0.13	2.51	3.49 ± 0.11	1.87
Bovine fat	4.86 ± 0.20	2.44	5.03 ± 0.17	2.01
	6.75 ± 0.13	1.14	6.36 ± 0.13	1.03
	5.98 ± 0.22	2.18	6.08 ± 0.14	1.37

[a] Where n is the number of replicate measurements, t_{n-1} is the statistic parameter often called Student's t (with $n=3$, at 95% level of confidence) and S is the standard deviation.
[b] RSD: relative standard deviation.

3.2. *Analytical features and application*

The molybdenum blue method obtained a satisfactory analytical curve for the phosphorus determination in mineralized biodiesel with the regression equation $A=0.0313+0.4463C$; where A is the absorbance (analytical response) and C is the concentration of the analyte in mg Kg^{-1} of phosphorus in biodiesel. The linear correlation coefficient, r^2, was 0.9996 ($n=3$) in the range between 0.1 and 10.0 mg L^{-1}. Its analytical curve was statistically validated by the analysis of variance showing no lack of fit at a 95% confidence level.

Table 4
Recoveries of phosphorus in biodiesel.

Samples	Recovery %		
	0.5 (mg Kg^{-1})	2.5 (mg Kg^{-1})	5.0 (mg Kg^{-1})
Soybean	101.9 ± 2.1	97.9 ± 2.3	103.5 ± 2.8
Sunflower	105.8 ± 2.9	98.4 ± 2.5	102.3 ± 1.9
Bovine fat	99.4 ± 1.9	101.8 ± 2.7	101.6 ± 2.4

The limit of detection (LOD) and the limit of quantification (LOQ), for the proposed method were defined in 0.014 and 0.047 mg Kg^{-1}, respectively. The LOD and LOQ for both methods were calculated based on the criteria established by IUPAC [19]. The LOD and LOQ were evaluated as 3 S_b/S and 10 S_b/S, respectively, where S_b is the standard deviation for 10 measurements of the blank and S is the slope of analytical curve.

Table 3 presents the results obtained for the proposed μFBA for analysis, and those obtained for the reference spectrophotometric method. No statistically significant differences at a confidence level of 95% were observed between the results when applying the paired t-test. We can also showed satisfactory repeatability of the proposed method with a relative standard deviation (RSD %), less than 4.5% ($n=3$).

Recovery tests were also performed and, in this case, three samples (biodiesel from soybean, sunflower, bovine fat) were used. The volume of 1.0 mL standard solution with known phosphorus concentrations of 0.5, 2.5 and 5.0 mg Kg^{-1} was added to 9.0 mL of the biodiesel samples (2.3, 7.8 and 5.0 mg Kg^{-1} of phosphorus), for measurement using the proposed μFBA. The recovery values obtained are shown in Table 4. As can be seen, the recoveries obtained for each of the samples were within the 97.9–105.8% range, which is considered acceptable for this type of sample [6,9].

The μFBA presented an analytical frequency of about 190 samples per hour for the molybdenum blue method, with a waste generation of 144 μL per analysis.

Table 5 presents selected analytical features of the proposed μFBA, batch [9], and FIA [6] procedures for the determination of phosphorus in biodiesel. In general, the μFBA (compared to other procedures) presents satisfactory parameters, such as detection limit, relative standard deviation (RSD %), working range, sampling rate, elimination of the carrier fluid, and no associated fluid dispersion problems, such as loss of sensitivity.

4. Conclusion

The use of micro-pumps allowed the building of a portable and low cost analyzer when compared with others μFBA [16,17].

Table 5
Analytical characteristics of the proposed μFBA and other methods from the determination of phosphorus in biodiesel.

Parameter	μFBA	Batch [9]	FIA [6]
Analytical curve[a]	$A=0.0313+0.4463C$	$A=0.0019+0.145C$	$A=-0.018+0.002C$
Detection limit (mg Kg^{-1})	0.014	0.57	1.4
Working range (mg L^{-1})	0.1–10.0	0.5–2.5	1–10
Relative standard deviation (%)	<4.5	<4.1	<5.0
Sampling rate (h^{-1})	189	–	100
Sample consumption (μL)	16[b]	18000[b]	50[c]
Reagent consumption (μL)	32	7000	1000
Waste volume (μL)	144	25000	2200
Method	Molybdenum blue	Molybdenum blue[d]	Molybdenum blue
Integrated detection	Present	Absent	Absent
Carrier fluid	Absent	Present	Present

[a] Where *A* is the absorbance and *C* is the concentration of the analyte in mg Kg^{-1} of phosphorus.
[b] Volume of the sample after mineralization.
[c] Volume of the sample after digestion in the microwave.
[d] Using 1-amino-2-naphthol-4-sulfonic acid as the reducing agent.

The characteristics of the μFBA with solenoid micro-pumps and integrated detection are explored for the determination of phosphorus in mineralized biodiesel. This method is advantageous when compared to the flow injection analysis [6] because it is more sensitive and faster, it uses small quantities of samples and it does not utilize carrier fluid, generating less waste therefore.

According to the experimental results, the proposed μFBA presents limits of detection and quantification, precision and accuracy compatible with the biodiesel regulations that establish a maximum concentration of 10 mg Kg^{-1} (Brazil, USA, EU) [3–5]. The method is easy to perform and offers results at a relatively low-cost and uses no organic solvents.

It is worth noting that a disadvantage of the proposed method is that it does not include the pretreatment step of the sample in the automatic procedure as in previous paper [15,20,21].

Acknowledgments

The authors would like to thank the Brazilian agencies (CNPq and CAPES) for the research fellowships and scholarships.

References

[1] S.K. Hoekman, A. Broch, C. Robbins, E. Ceniceros, M. Natarajan, Renew. Sustain. Energy Rev. 16 (2012) 143.
[2] M.R. Monteiro, A.R.P. Ambrozin, L.M. Lião, A.G. Ferreira, Talanta 77 (2008) 593–605.
[3] Agência nacional do petróleo, gás natural e biocombustíveis. Resolução n.07, 19 de março de 2008. Regulamento técnico, n.07/2008. Brasília: Diário oficial da união.
[4] ASTM D6751, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, West Conshohocken, PA, 2009.
[5] BSI BS EN 14214, Automotive Fuels—Fatty Acid Methyl Esters (FAME) for Diesel Engines—Requirements and Test Methods, 2008.
[6] L.F.B. Lira, D.C.M.B. Santos, M.A.B. Guida, L. Stragevitch, M.G.A. Korn, M.F. Pimentel, A.P.S. Paim, Fuel 90 (2011) 3254–3258.
[7] ASTM D 4951, Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry, ASTM International, West Conshohocken, PA, 2009.
[8] BS EN 14107, Fat and Oil Derivatives—Fatty Acid Methyl Esters (FAME), Fat and Oil Derivatives. Determination of Phosphorous Content by Inductively Coupled Plasma (ICP) Emission Spectrometry, 2003.
[9] E.L.C. Silveira, L.B. Caland, M. Tubino, Fuel 90 (2011) 3485–3488.
[10] M. Trojanowicz, Advances in Flow Analysis, 1st edition, Wiley-VCH, Weinheim, 2008.
[11] R.S. Honorato, M.C.U. Araújo, R.A.C. Lima, E.A.C. Zagatto, R.A.S. Lapa, J.L.F.C. Lima, Anal. Chim. Acta 396 (1999) 91–97.
[12] P.H.G.D. Diniz, L.F. Almeida, D.P. Harding, M.C.U. Araújo, Trends Anal. Chem. 35 (2012) 39–49.
[13] S.D. Kolev, I.D. Mckelvie, Advances in Flow Injection Analysis and Related Techniques, 5th edition, Elsevier, Hungary, 2008.
[14] I.S. Barreto, S.I.E. Andrade, M.B. Lima, E.C. Silva, M.C.U. Araújo, L.F. Almeida, Talanta 94 (2012) 111–115.
[15] M.B. Lima, M. Insausti, C.E. Domini, M.F. Pistonesi, M.C.U. Araújo, B.S.F. Band, Talanta 89 (2012) 21–26.
[16] S.S. Monte-Filho, M.B. Lima, S.I.E. Andrade, D.P. Harding, Y.N.M. Fagundes, S.R.B. Santos, S.G. Lemos, M.C.U. Araújo, Talanta 86 (2011) 208–213.
[17] M.B. Lima, S.I.E. Andrade, D.P. Harding, M.F. Pistonesi, B.S.F. Band, M.C.U. Araújo, Talanta 88 (2012) 717–723.
[18] M. Tubino, J.R.O. Torres, Anal. Lett. 12 (1990) 2339–2349.
[19] A.D. McNaught, W. Andrew, IUPAC Compendium of Chemical Terminology, 2nd edition, Royal Society of Chemistry, Cambridge, 1997.
[20] J.A. Belloni, M.S. Di Nezio, M.F. Pistonesi, M.E. Centurión, Talanta 89 (2012) 526–530.
[21] M.A. Domínguez, M. Grünhut, M.F. Pistonesi, M.S. Di Nezio, M.E. Centurión, J. Agric. Food Chem. 60 (2012) 4812–4817.