



# Fully automated spectrophotometric procedure for simultaneous determination of calcium and magnesium in biodiesel



Andrey Y. Shishov\*, Larisa. S. Nikolaeva, Leonid N. Moskvina, Andrey V. Bulatov

Institute of Chemistry, Saint Petersburg State University, RU-198504 Saint Petersburg, Russia

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## ABSTRACT

An easily performed stepwise injection (SWIA) procedure based on on-line dilution of biodiesel samples and the formation of color-forming calcium (II) and magnesium (II) complexes with Eriochrome Black T (EBT) in an organic medium followed by spectrophotometric determination is presented. A sample of biodiesel was placed at the bottom of a mixing chamber connected to an automatic SWIA manifold. Isopropyl alcohol was used as the diluent under bubbling. The solution was submitted for on-line spectrophotometric simultaneous determination of calcium and magnesium based on the classic least-square method. The linear ranges were from 2 to 20  $\mu\text{g g}^{-1}$  and from 1.2 to 12  $\mu\text{g g}^{-1}$ , and the detection limits, calculated as 3 s for a blank test ( $n=5$ ), were found to be 0.6  $\mu\text{g g}^{-1}$  for calcium and 0.4  $\mu\text{g g}^{-1}$  for magnesium. The sample throughput was 30  $\text{h}^{-1}$ . The method was successfully applied to the analysis of biodiesel samples.

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## 1. Introduction

Biodiesel is a relatively new source of renewable energy, which has recently gained an increased attention worldwide [1]. Biodiesel is composed of a mixture of mono-alkyl esters of long chain fatty acids obtained through the transesterification of vegetable oils or animal fats with short-chain alcohols in the presence of a catalyst, such as compounds of calcium and magnesium [2–11]. Besides, magnesium sulfate and calcium oxide are also used as drying agents for biodiesel [12]. The presence of these metals in biodiesel may lead to the formation of solid deposits in engines [13,14]. Currently, European (EN 14214) legislation regulates Ca and Mg content in biodiesel, which cannot exceed higher than 5  $\mu\text{g g}^{-1}$ .

Highly sensitive analytical methods, such as atomic absorption (AAS) [12–15], atomic emission [16] and inductively coupled plasma optical emission spectrometry [17–21], are widely used to determine Ca and Mg content in biodiesel. To reduce the viscosity of biodiesel samples and matrix interferences, most of these methods require sample preparation by dilution in organic solvents such as n-propanol [13,14,17], o-xylene [18], aviation kerosene [20] and ethanol [21] or microemulsion formation [22]. These sample preparation procedures allow us to use aqueous standards for calibration. Other procedures for extraction of Ca and Mg from biodiesel in

an aqueous medium, such as capillary zone electrophoresis [23,24], ion chromatography [25] and electrochemical methods [26–29], are also employed for analytical determination. Comparisons of existing methods for determination of calcium and magnesium in biodiesel are summarized in Table 1. These methods are not automatic and thus require manual sample preparations.

An important and rapidly growing trend in modern analytical chemistry is the automation of analytical procedures. Nowadays, automation of analytical procedures based on flow analysis is continuously being developed. In this way, labor costs for the analyses decrease and the volumes of both samples and reagents as well as the waste generated substantially reduce. A large number of methods based on flow analysis have been proposed for the automated analysis of biodiesel [30–36]. To the best of our knowledge, there is no procedure for the determination of calcium and magnesium in biodiesel in a flow system. SWIA is a universal solution for the automation of analytical reactions, wherein dispersion of the reaction products is prevented [37–43]. In this case the analytical signal is at a maximum and similar to the signal obtained using a manual technique. The aim of this work was to develop a fully automated procedure for the simultaneous determination of calcium and magnesium in biodiesel in stepwise injection analysis. In our work, the selective color-forming reagent EBT was chosen for the spectrophotometric determination of calcium and magnesium in an organic medium. EBT is mainly used for spectrophotometric determination of calcium and magnesium in aqueous medium [44]. To eliminate the procedure of Ca and Mg extraction from biodiesel

\* Corresponding author.

E-mail address: [andrey.shishov.rus@gmail.com](mailto:andrey.shishov.rus@gmail.com) (A.Y. Shishov).

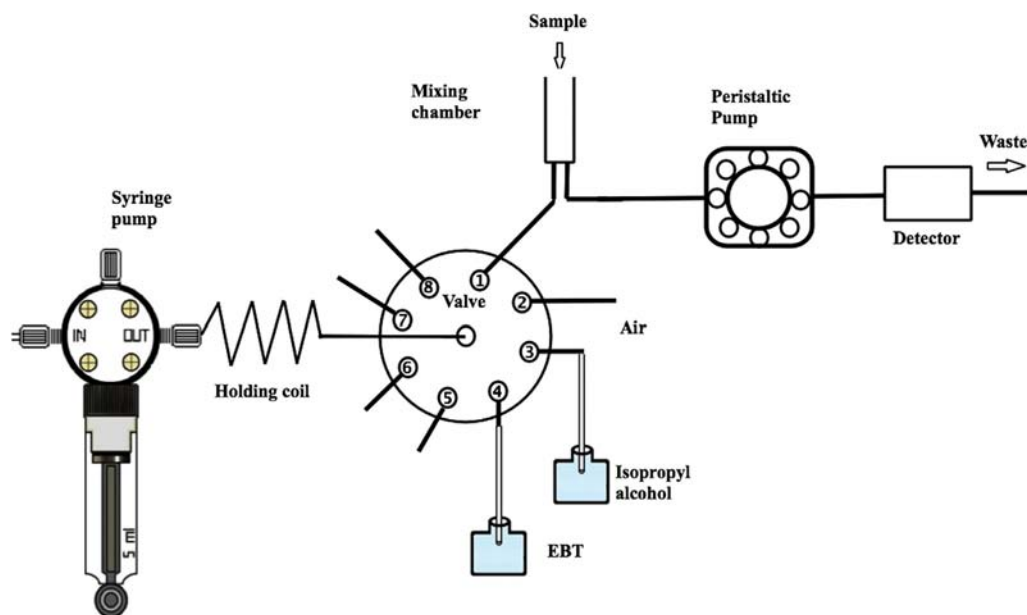


Fig. 1. SWIA manifold for determination of calcium and magnesium in biodiesel.

in aqueous medium, we carried out the reactions in isopropyl alcohol based medium followed by simultaneous spectrophotometric determination of analytes based on the classical least squares method.

## 2. Experiment

### 2.1. Reagents and solutions

Analytical grade chemicals were used throughout the work. The stock solutions ( $0.5 \mu\text{M g}^{-1}$ ) of calcium and magnesium were prepared by dissolving their 2-ethylhexanoates (ABCR, Germany) in biodiesel. The EBT solution ( $100 \mu\text{M}$ ) (Merck, Germany) was prepared by dissolving the reagent in 0.5 M solution of triethanolamine (TEA) in isopropyl alcohol.

### 2.2. Samples

Biofuel samples were obtained from the following feedstocks: sunflower, canola, corn and palm. These samples were previously prepared using sodium hydroxide as an alkaline catalyst [45] to avoid the ingress of calcium and magnesium at this stage. From GC–MS analysis [46], it was observed that the biofuel samples contained methyl esters of *n*-nonanoic, *n*-hexadecanoic, *n*-octadecanoic, 9-octadecenoic, and 9,12-octadecadienoic acids. The working samples of biodiesel (B20) were obtained by mixing biofuel and diesel in 1:4 (m/m) ratio.

### 2.3. Manifold and apparatus

The SWIA manifold (Fig. 1) included an eight-way valve (Sciware Systems, Spain), syringe pump (Sciware Systems, Spain), peristaltic pump MasterFlex L/S (Cole-Parmer, USA) (the flow rate was from  $0.5$  to  $5 \text{ mL min}^{-1}$ ), mixing chamber (a cylindrical-shaped PTFE tube with a funnel-shaped inlet at the bottom, 20 mm height and 10 mm i.d.), holding coil and communication tubes (PTFE, 0.5 mm i.d.). The manifold was equipped with a USB 4000 spectrophotometer (Ocean Optics Inc., USA) with a 50 mm path-length flow cell (FIALab<sup>®</sup> Instrument Systems Inc., Bellevue, USA), optical fibers QP400-2-UV-VIS (Ocean Optics Inc., USA) and

a Model D 1000 CE UV source (Analytical Instrument System Inc., USA). The analyzer was operated automatically using a computer.

An AA-7000 atomic absorption spectrometer (Shimadzu, Japan) was used for calcium and magnesium determination in the biodiesel samples. A GC–MS–QP2010 Ultra gas chromatograph mass spectrometer (Shimadzu, Japan) was applied to identify fatty acid methyl esters in the biofuel samples.

### 2.4. SWIA procedure

In the first step of the measurement, 0.01 g of the biodiesel sample was placed at the bottom part of the mixing chamber (Fig. 1). The syringe pump was then set to the “Out” position and 0.2 ml of isopropyl alcohol (3) was aspirated through the corresponding ports of the multiport valve into the holding coil by backward movement of the syringe pump plunger. The isopropyl alcohol was then transferred by forward movement of the syringe pump from the holding coil through the channel (1) into the mixing chamber. After the completion of this operation, 1 ml of air (2) was injected first into the holding coil and then passed through the mixing chamber at a rate of  $6 \text{ mL min}^{-1}$ .

In the second step, 0.2 ml of  $100 \mu\text{M}$  EBT (4) was delivered into the mixing chamber through the holding coil. To stir the reaction mixture and complete the color-forming reactions, 1 ml of air (2) was delivered into the mixing chamber through the holding coil at a rate of  $6 \text{ mL min}^{-1}$ . This resulted in the formation of complexes of Ca (II) and Mg (II) with EBT. The formed complexes were then transferred from the mixing chamber into the flow cell of the spectrophotometric detector using the peristaltic pump. The absorbance measurement was performed under stopped-flow conditions for 5 s and the solution was discharged as waste. In the next step, all the components of the manifold were washed with isopropyl alcohol. The measurement of the analytical signal for a blank solution was carried out using the above-mentioned algorithm, but in this case isopropyl alcohol was aspirated instead of the sample solution.

### 2.5. Multivariate calibration

For multivariate calibration [47], we prepared a set of 10 standards containing calcium and magnesium of known concentrations in the

**Table 1**  
Comparison of the suggested method with previously reported for determination of Ca and Mg in biodiesel.

Detection technique	Analyte	Sample preparation	Sample amount	Fully automated technique	Linear range	LOD	Reference
FAAS	Ca, Mg	Microemulsion	1 ml	No	–	0.04 $\mu\text{g g}^{-1}$ (Ca), 0.005 $\mu\text{g g}^{-1}$ (Mg)	12
FAAS	Ca, Mg	Microemulsion	1 ml	No	–	0.11 $\mu\text{g ml}^{-1}$ (Ca), 0.03 $\mu\text{g ml}^{-1}$ (Mg)	13
ICP-OES	Ca, Mg	Dilution in n-propanol	0.45 g	No	–	0.04 $\mu\text{g g}^{-1}$ (Ca), 0.001 $\mu\text{g g}^{-1}$ (Mg)	17
ICP-OES	Ca, Mg	Diluted in xylene	–	No	0.5–5.0 $\mu\text{g g}^{-1}$	6 $\mu\text{g g}^{-1}$ (Ca), 0.3 $\mu\text{g g}^{-1}$ (Mg)	18
AV-ICP-OES	Ca, Mg	Dilution in etanol	2.5 g	No	0.1–2.0 $\text{mg L}^{-1}$	0.03 $\mu\text{g g}^{-1}$ (Ca), 0.005 $\mu\text{g g}^{-1}$ (Mg)	21
CE	Ca, Mg	Liquid–liquid extraction	200 mg	No	0.5–20 $\mu\text{g g}^{-1}$	0.3 $\mu\text{g g}^{-1}$	23
IC	Ca, Mg	Ultrasound liquid–liquid extraction	10 g	No	–	0.23 $\mu\text{g g}^{-1}$ (Ca), 0.36 $\mu\text{g g}^{-1}$ (Mg)	24
AdsSV	Mg	Liquid–liquid extraction	12 ml	No	0.6–7 $\mu\text{M}$	$2.9 \times 10^{-7}$ $\text{mol L}^{-1}$	25
SWASV	Ca	Microwave assisted digestion	300 mg	No	–	$1.6 \times 10^{-3}$ $\mu\text{M}$	26
SWIA/UV–vis	Ca, Mg	Dilution in isopropyl alcohol	10 mg	Yes	2–20 $\mu\text{g g}^{-1}$ for Ca and 1.2– 12 $\mu\text{g g}^{-1}$ for Mg	0.6 $\mu\text{g g}^{-1}$ (Ca), 0.4 $\mu\text{g g}^{-1}$ (Mg)	This work

AV-ICP-OES – axial view inductively coupled plasma optical emission spectrometry; FAAS – atomic absorption spectrometry; ICP-OES – inductively coupled plasma optical emission spectrometry; IC – ion-chromatography; CE – capillary electrophoresis; SWASV – square-wave anodic stripping voltammetry; AdsSV – adsorptive stripping voltammetry.

range of 0.05–0.5  $\mu\text{M g}^{-1}$  in isopropyl alcohol. The number of calibration standards should not be less than the number of determined components. The calibration standards were analyzed according to SWIA procedure. For determination of Ca and Mg, following wavelengths were chosen for the working range: 520, 525, 530, 535, 540, 545, 550, 555, 560 and 565 nm. These wavelengths were selected according to the following criteria: the number of wavelengths must be more than the amount of the analytes; the value of the absorbance at the chosen wavelength should not be less than half the absorbance at the maximum of the absorption spectra; and with each selected wavelength linear dependence of the absorption on the concentration of the analytes must be observed [48].

The absorbance measured at the selected wavelengths was used to obtain matrix A. The matrix of proportionality was calculated according to the equation  $P = CA^T(AA^T)^{-1}$ . This matrix was used for the analysis of the biodiesel samples. Mathematical operations were performed in the Excel (Microsoft Office) program.

## 2.6. AAS procedure

The results of SWIA determination of Ca and Mg were compared with those obtained by means of AAS [13] on AA-7000 atomic absorption spectrometer (Shimadzu, Japan). Biodiesel samples were mixed with Triton X-100, 4 M  $\text{HNO}_3$  and n-propanol in 10:5:5:80 (v/v/v/v) ratio. The resonance lines at 422.7 nm and 285.2 nm for Ca and Mg, respectively, were used. Air/acetylene and nitrous oxide/acetylene flames were used for Mg and Ca determinations, respectively.

## 2.7. GC–MS procedure

Fatty acid methyl esters in the biofuel were estimated using gas-chromatograph mass spectrometry [46]. GC–MS was equipped with an SPB-624 MS capillary column (6% cyanopropyl phenyl and 94% dimethyl polysiloxane, 30 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  coating). The injector temperature was kept at 220  $^\circ\text{C}$ , while the interface temperature and the ion source were kept at 200  $^\circ\text{C}$ . Helium was used as a carrier gas at a flow rate of 2  $\text{ml min}^{-1}$ . A sample volume of 2  $\mu\text{l}$  was injected in splitless mode with 1 min purge time. The electron ionization source was run at 70 eV. For identification of the

esters, a library search was carried out using NIST, NBS and Wiley GC–MS libraries.

## 3. Results and discussion

### 3.1. Choice of solvent

The determination of Ca and Mg is based on the development of color by formation of Ca (II) and Mg (II) complexes with EBT in an alkaline medium. To eliminate the procedure of Ca and Mg extraction from biodiesel into an aqueous medium, we carried out the reactions in alcohol based media. Alcohols have been proposed as a medium for the formation of the colored complexes because biodiesel, EBT and the complexes formed are soluble in alcohols.

The ratio of biodiesel to solvent (ethyl and isopropyl alcohols) was varied in a range from 1:1 to 1:25 (v/v) in order to select the optimum condition. The criterion for the choice of the solvent and the ratio was its ability to be mixed well with biodiesel in order to provide high repeatability. The results showed (Fig. 2) that isopropyl alcohol is the most suitable solvent for on-line dilution of biodiesel samples. RSD for biodiesel and isopropyl alcohol in a ratio of 1:20 is minimal and does not depend on the type of biofuel. The isopropyl alcohol content lower than 1:20 (v/v) in the mixture had a negative effect on the reproducibility of the results due to emulsion formation. Therefore, this ratio was consistently used in all the measurements.

### 3.2. Optimization of chemical variables

In the present work TEA was proposed as the alkaline agent for the color development due to complex formation of calcium (II) and magnesium (II) with EBT. The complexes of magnesium (II) and calcium (II) with EBT showed absorbance maxima at 540 and 550 nm, respectively, in isopropyl alcohol solutions. The criterion for the choice of concentration of TEA was the bathochromic shift of the spectral maximum of EBT. The concentration of TEA was varied from  $10^{-4}$  to 1 M. The results showed (Fig. 3) that the optimal concentration of TEA was 0.5 M and that EBT absorbance maximum shifted from 510 nm to 600 nm.

To optimize the conditions of the SWIA spectrophotometric determination of Ca and Mg, the effect of concentration of the

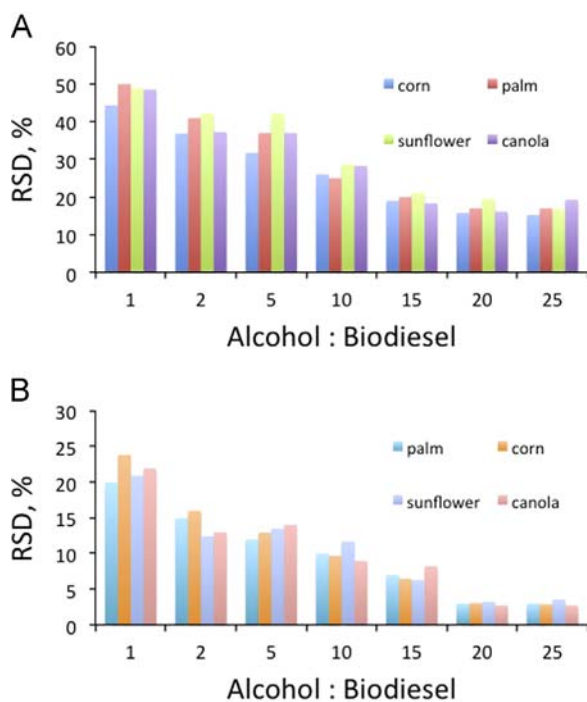


Fig. 2. Effect of the ratio biodiesel:solvent on the RSD (%): (A) ethyl alcohol and (B) isopropyl alcohol.

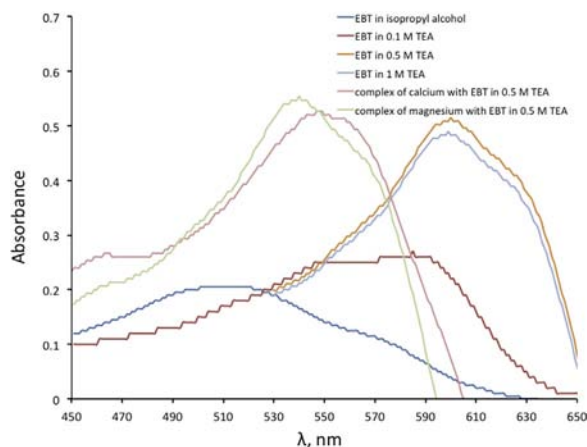


Fig. 3. Effect of the TEA concentration on the spectrum of EBT in isopropyl alcohol ( $C_{\text{EBT}}=50 \mu\text{M}$ ,  $C_{\text{Ca}}=25 \mu\text{M}$ , and  $C_{\text{Mg}}=25 \mu\text{M}$ ).

color-forming reagent was studied. For this purpose, 0.2 ml of  $50 \mu\text{M}$  calcium or magnesium in isopropyl alcohol was delivered through the valve into the mixing chamber by reversible movements of the syringe pump (Fig. 1). A portion of the color-forming reagent (0.2 ml) was also delivered into the mixing chamber. The concentration of color-forming reagent was varied from 10 to  $200 \mu\text{M}$ . The solution was stirred by the flow of air for 10 s. The optimal concentration of EBT that ensured formation of the complexes in a ratio of 2:1 (reagent:analyte) was  $100 \mu\text{M}$  (Fig. 4).

### 3.3. Optimization of mixing

To provide effective mixing of the solution in the mixing chamber, a cylindrical-shaped tube with a funnel-shaped inlet at the bottom was used. The effect of the time, during which the reaction components were mixed with air in the mixing chamber, on the efficiency of solution homogenization and completeness of

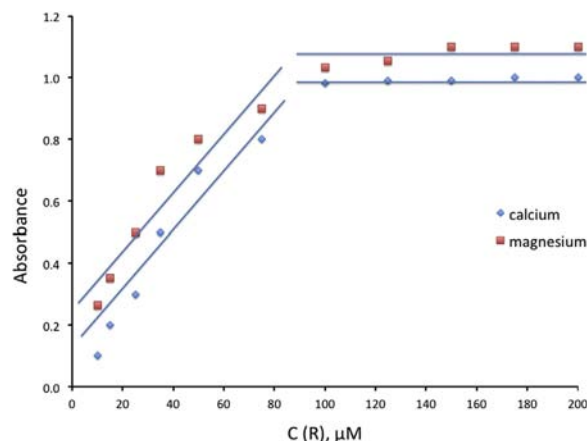


Fig. 4. Effect of EBT concentration on the absorption of complexes with calcium (II) and magnesium (II) in isopropyl alcohol ( $C_{\text{Ca}}=50 \mu\text{M}$ ,  $C_{\text{Mg}}=50 \mu\text{M}$ ).

the chemical reaction was investigated in an air volume range from 0.5 to 5 ml. An air volume of 1 ml was found to be optimal for the homogenization of the solution in the mixing chamber because in this case the maximum absorbance value was observed.

### 3.4. Interference effect

The effect of potentially interfering ions, especially heavy metals, on the determination of analytes was investigated. This was done by the addition of known concentrations of each ion to a fixed analyte concentration of  $25 \mu\text{M}$  in an isopropyl alcohol solution. The tolerable concentration of each foreign metal species studied was considered to be less than 5% of relative error in the signal. The results showed that the following substances did not interfere in the mentioned ranges:  $\text{Zn}^{2+}$  at up to 20-fold excess,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  at up to 100-fold excess.

### 3.5. Analytical performance

The limits of detection (LOD) calculated as three times the standard deviation ( $3s$ ) and limits of quantification (LOQ) calculated as 10 times the standard deviation ( $10s$ ) of the blank test ( $n=5$ ) were assessed as 0.6 (Ca), 0.4 (Mg)  $\mu\text{g g}^{-1}$  and 2.0 (Ca), 1.2 (Mg)  $\mu\text{g g}^{-1}$ , respectively. It should be pointed out that the LOD values found in this work were below the amount of Ca and Mg allowed in biodiesel by the legislation. The experimental calibration matrix for classical least-square method was designed with 10 samples of 2–20  $\mu\text{g g}^{-1}$  and 1.2–12  $\mu\text{g g}^{-1}$  for Ca and Mg, respectively. The suggested procedure proved satisfactory reproducibility of the analytical responses by evaluation of the relative standard deviation (RSD) from 10 replicated measurements of Ca and Mg contents in samples with value from 2.5% to 5%. The system throughput, assessed as the sampling frequency, was found to be  $30 \text{ h}^{-1}$ . The evaluated analytical parameters were also compared with those reported in the literature (Table 1).

### 3.6. Analytical application

The proposed procedure was applied to the analysis of four biodiesel samples made from different raw materials. The obtained results showed no significant differences in calcium and magnesium concentrations obtained by the suggested and the reference methods [13] (Table 2). The paired  $t$ -test showed that calcium and magnesium contents found using SWIA method were insignificantly different from those obtained by AAS method at a 95% confidence level.

**Table 2**The results of the determination of calcium and magnesium in biodiesel samples ( $n=5$ ,  $t=2.306$ ,  $P=0.95$ ).

Type of biodiesel	Added Ca ( $\mu\text{g g}^{-1}$ )	Found Ca ( $\mu\text{g g}^{-1}$ )		Added Mg ( $\mu\text{g g}^{-1}$ )	Found Mg ( $\mu\text{g g}^{-1}$ )		Recovery (%)		t-test	
		SWIA	AAS [13]		SWIA	AAS [13]	Ca	Mg	Ca	Mg
Palm	0	$3.1 \pm 0.1$	$3.0 \pm 0.1$	0	$6.8 \pm 0.1$	$7.0 \pm 0.2$	–	–	0.51	1.1
	5	$8.1 \pm 0.1$	$8.2 \pm 0.2$	5	$11.6 \pm 0.1$	$12.0 \pm 0.2$	101	97	1.1	1.5
	10	$13.1 \pm 0.1$	$13.3 \pm 0.1$	10	$17.4 \pm 0.1$	$17.1 \pm 0.2$	101	102	1.2	1.4
Canola	0	< LOD	< LOD	0	< LOD	< LOD	–	–	–	–
	5	$5.2 \pm 0.2$	$5.1 \pm 0.1$	5	$5.0 \pm 0.1$	$4.9 \pm 0.1$	104	100	1.1	1.1
	10	$10.1 \pm 0.1$	$10.3 \pm 0.2$	10	$10.2 \pm 0.2$	$10.3 \pm 0.1$	101	102	0.8	0.7
Corn	0	< LOD	$1.0 \pm 0.1$	0	$2.1 \pm 0.1$	$2.0 \pm 0.1$	–	–	–	0.9
	5	$5.2 \pm 0.1$	$5.5 \pm 0.1$	5	$7.1 \pm 0.1$	$7.2 \pm 0.2$	104	101	1.7	1
	10	$10.3 \pm 0.1$	$10.2 \pm 0.1$	10	$12.6 \pm 0.1$	$13.0 \pm 0.2$	94	105	1.1	2.1
Sunflower	0	$10.3 \pm 0.2$	$10.1 \pm 0.1$	0	< LOD	< LOD	–	–	0.9	–
	5	$15.3 \pm 0.1$	$15.1 \pm 0.1$	5	$5.2 \pm 0.1$	$5.1 \pm 0.1$	101	104	0.9	1.1
	10	$20.5 \pm 0.2$	$20.8 \pm 0.2$	10	$10.3 \pm 0.2$	$10.2 \pm 0.1$	102	103	1.2	1.3

#### 4. Conclusions

A novel SWIA procedure for simultaneous determination of calcium and magnesium in biodiesel samples has been developed. The procedure is based on the on-line dilution of a biodiesel sample in isopropyl alcohol and the formation of color-forming calcium (II) and magnesium (II) complexes with Eriochrome Black T in an organic medium, followed by subsequent spectrophotometric detection. The developed method is fully automated. A non-toxic solvent is used in the method to eliminate the procedure of Ca and Mg extraction from biodiesel into an aqueous medium to carry out the color-forming reactions. The applicability of the method was demonstrated in real sample analysis and the obtained results were compared with the reference method. The described method is advantageous when compared with the official EN 14214 method, because it is fast, uses small quantities of samples, thus generates less waste, and especially because it can be operated at a lower cost.

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