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Novel extraction induced by emulsion breaking as a tool for the determination of trace concentrations of Cu, Mn and Ni in biodiesel by electrothermal atomic absorption spectrometry

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ABSTRACT

This work proposes a novel method for the determination of trace concentrations of Cu, Mn and Ni in biodiesel samples by electrothermal atomic absorption spectrometry. In order to overcome problems related to the organic matrix in the direct introduction of the samples, a new extraction approach was investigated. The method was based on the extraction induced by emulsion breaking, in which metals were transferred from the biodiesel to an acid aqueous phase after formation and breaking of a water-in-oil emulsion prepared by mixing the biodiesel sample with an aqueous solution containing surfactant and nitric acid. Several parameters that could influence the performance of the system were evaluated. Quantitative extractions of the analytes were obtained when the extraction was performed using an emulsifier solution containing 2.1 mol L^{-1} of HNO_3 and 7% m/v of Triton X-100. The extraction time had remarkable influence on the efficiency of the process, being necessary an agitation time of 60 min to achieve maximum extraction. The limits of quantification were below 1 μg L^{-1} for the three analytes under study. The accuracy of the method was tested by application of a recovery test (recovery percentages between 89% and 109% were observed) and by comparison with a well-established method, taken as reference.

1. Introduction

Nowadays, the discovery and development of renewable sources of energy has great interest worldwide, since there is an increasing concern about the shortage of fossil fuels. One of the most promising alternatives to fossil fuels is the biodiesel, defined as the alkyl ester of fatty acids, obtained from transesterification of oils and/or fats with short chains alcohols like methanol or ethanol [1,2]. In several countries, the use of biodiesel is widespread, being added to the mineral diesel in different proportions [3]. The use of biodiesel as energy source brings some advantages over the use of petroleum-derived diesel such as the lower emission of carbon monoxide, nitrous oxide, sulfur compounds, hydrocarbons and particulate matter [4]. The presence of metals in biodiesel is also an environmental problem, since they can be released to the atmosphere during biodiesel combustion, impairing the quality of the air. Other problem is related to the deleterious effect of metals on the quality of the product, since they act as catalysts in several oxidation reactions of organic molecules [5]. Data provided by Sarin et al. [6] showed that the presence of metals caused a remarkable depression of the oxidation stability of biodiesel, probably because of the acceleration of free radical oxidation due to a metal-mediated initiation reaction. According to the authors, Cu, Mn and Ni had negative influence on oxidation stability of biodiesel, mainly Cu, that had the most prominent effect on this parameter even at low concentrations.

Incorporation of metals to biodiesel can occur through different pathways. They can be transferred to biodiesel in the production process as result of the contact of the oil with equipments employed in reactors and distillation units and also due to the contact of biodiesel with metallic parts of the tanks used for its storage. Another aspect to be considered is the natural occurrence of metals in the vegetable oils utilized as feedstock in the biodiesel production, because of their absorption from soils during plant growth [7].

The determination of metals in biodiesel is a subject relatively popular in the current literature. Several analytical methods have been reported for this task, and most of them are related to the application of atomic spectrometric techniques. In general, these works are focused on the determination of Na, K, Ca and Mg, which are the elements usually controlled in this kind of sample, especially because they are largely transferred to biodiesel in the transesterification reaction, due to the large use of sodium and potassium hydroxides as catalysts, and washing of the final product. Amais et al. [8] used microemulsions for the determination of Ca, Mg and

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Zn in biodiesel by flame atomic absorption spectrometry (FAAS). The microemulsions were prepared with biodiesel, n-propanol, Triton X-100 and nitric acid and external calibration was used as quantification approach. Very similar strategy was used by Lyra et al. [9], but in this case, for the determination of Na, K, Ca and Mg. Jesus et al. [10] also developed a method for FAAS determination of Na and K in biodiesel by aspirating the samples in the form of microemulsions. Unlike Amais et al. [8] and Lyra et al. [9], Jesus et al. used n-pentanol as co-solvent.

Oliveira et al. [11] proposed a method for Na determination based on the dry decomposition of biodiesel at 600 °C and posterior dissolution of the residue with a 1% v/v nitric acid solution. The main advantage of this procedure was the possibility to realize the calibration with aqueous standard solutions of the analyte. However, the intense manipulation can lead to losses and contamination of the samples. On the other hand, minimum sample handling can be achieved by simple dissolution of biodiesel in a convenient solvent before quantification of metals. Ethanol has been used for this purpose and could be employed when FAAS [12] or ICP OES [13] were utilized for quantification. The disadvantage of this kind of procedure is the high dilution factor imposed to the samples, which degrade the detection and quantification limits.

The determination of Na, K, Ca and Mg in biodiesel, in general, is not an analytical challenge, since they can be found in the samples at relatively high concentrations. In opposition to this situation, some transition metals are found at very low concentrations, being necessary the development of alternative strategies to achieve suitable limits of quantification, especially because the complex nature of the matrix that contains very high carbon content. In this context, some methods were already reported.

Woods and Fryer [14] reported the use of an ICP-MS fitted with an octopole reaction system for direct determination of 30 elements in biodiesel. The samples were diluted with kerosene in order to decrease their viscosity before introduction into the spectrometer. The limits of detection were in the μg kg^{-1} range, except for sulfur that was in the mg kg^{-1} level. Pillay et al. [15] also performed the determination of metals in biodiesel by ICP-MS. However, in this case, the samples were digested in a microwave-oven with nitric acid solution before determination of the metals of interest. Souza et al. [16] quantified 7 elements in biodiesel by ICP OES. The samples were introduced in the form of surfactant emulsions prepared with Triton X-100.

It has also been demonstrated that the use of ETAAS is adequate for direct determination of metals in biodiesel. Lobo et al. [17,18] tested different strategies for the determination of metals in biodiesel by GFAAS, and furthermore, they employed univariate and multivariate approaches for optimization of the parameters of the methodologies. Ghisi et al. [5] also employed GFAAS as detection technique for Cu and Fe determination in biodiesel, after treatment of the samples with tetramethyammonium hydroxide (TMAH).

The main goal of this work is to propose a novel method for the determination of Cu, Mn and Ni in biodiesel employing a recently-developed methodology [19–23] based on the extraction induced by emulsion breaking. The proposed method provided the pre-concentration of the analytes in the extracts, which improved significantly the limits of detection and allowed their quantification at trace concentrations in the samples.

2. Experimental

2.1. Apparatus

The determination of the analytes (Cu, Mn and Ni) in the extracts and standard solutions was performed with a Varian (Mulgrave, Australia) graphite furnace atomic absorption spectrometer, model AA240Z, equipped with a Varian GTA 120 atomizer unit and a Varian PSD 120 auto sampler. Individual hollow cathode lamps for Cu, Mn and Ni, also supplied by Varian, were utilized as radiation sources. All measurements were carried out with graphite tubes equipped with L'vov platform made of pyrolytic graphite (Varian part no. 63-100026-00). Background correction was performed with a Zemman-effect based corrector, which was operated with a constant magnetic field intensity of 0.8 T.

Argon with 99.99% (Linde Gases, Macaé, Brazil) of purity was employed as protective gas for the graphite tube. The instrumental conditions (lamp currents, wavelengths and slit widths) for each analyte are shown in Table 1.

The emulsions were broken by heat, employing a water bath with a temperature control (±0.1 °C), model NT 247, supplied by Nova Técnica (São Paulo, Brazil).

2.2. Reagents and solutions

Purified water employed for the preparation of all aqueous solutions was obtained in a Direct-Q 3 System (Millipore, Milford, MA, USA), with resistivity not lower than 18.2 MΩ cm.

Aqueous stock standard solutions of the elements of interest with 1000 μg mL^{-1} concentration were supplied by Tedia (Fairfield, OH, USA). Diluted standard solutions employed in this work were prepared by dilution of the stock solutions with water.

Oil-based stock solutions of Cu, Mn and Ni with 1000 μg g^{-1} concentration were supplied by Conostan (Houston, TX, USA). The oil-based standard solutions of the selected metals were prepared by suitable dilution of the stock solution with HPLC grade hexane, which was supplied by Tedia.

Solutions of Triton X-100, employed for the emulsification of biodiesel, were prepared by dissolving a convenient mass of the surfactant in exactly 100 mL of HNO_3 solution. The concentration of the HNO_3 solution was established according to the experiment. The concentrated nitric acid used to prepare such solutions had trace metal grade and was supplied by Tedia (Fairfield, OH, USA).

A blended biodiesel sample was employed in the experiments of optimization. All samples of biodiesel analyzed by the proposed method were donated by Petrobras and prepared from soybean oil. They were stored in a low-density polyethylene flask and kept in a light-free place at laboratory ambient temperature (23 ± 1 °C).

2.3. Extraction procedure

The analytes of interest were extracted from the samples by the extraction induced by emulsion breaking technique, employing the conditions optimized in the present work. The extraction induced by emulsion breaking was performed through four steps. Firstly, the emulsions were formed by vigorous mixing of 5 mL of biodiesel with 1 mL of surfactant solution (Triton X-100 and Triton X-114), in a 13 mL capped polyethylene tube. After that, the flasks containing the emulsions were put on a horizontal roller mixer, where they were agitated for 60 min, a time enough to complete the extraction of the analytes of interest. Then, the flasks were transferred to the water bath, at 90 ± 1 °C, where they were kept until the breaking of the emulsions, which was indicated by the formation of two phases: (i) the upper phase, containing the

Table 1
Operational conditions employed in the determination of Cu, Mn and Ni by ETAAS.

Parameter	Cu	Mn	Ni
Wavelength (nm)	324.8	279.5	232.0
Lamp current (mA)	7.0	5.0	4.0
Nominal spectral resolution (nm)	0.2	0.2	0.2

Table 2
Temperature program employed in the determination of Cu, Mn and Ni in the extracts obtained from application of extraction induced by emulsion breaking to biodiesel.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (mL min^{-1})
Drying	85	15	0	300
	95	60	0	300
	120	10	0	300
Pyrolysis	1000 (Cu)	6	3	300
	1300 (Mn)	4	3	
	1400 (Ni)	6	3	
Atomization	2300 (Cu, Mn) 2500 (Ni)	1	3	0
Cleaning	2400 (Cu, Mn) 2600 (Ni)	2	0	300

biodiesel and (ii) the lower phase, which was the aqueous acid solution containing the extracted analytes. Breaking of the emulsions occurred after approximately 7 min of heating. The fourth step of the procedure was the collection of the lower aqueous phase, which was performed with the aid of a micropipette. The aqueous phase was directly transferred to the vials of the ETAAS or diluted with water, when necessary, for the quantification of the analytes in the extracts.

2.4. *Determination of metals in the extracts by ETAAS*

The determination of the concentrations of Cu, Mn and Ni in the extracts and in the standard solutions was performed using the same temperature program, however, using different pyrolysis and atomization temperatures (Table 2), which were set according to the metal under study. The addition of chemical modifiers was avoided in order to minimize the contamination and keep the blank signals low. In all cases, the measurements were performed by introducing 20 μL of solution (extract or standard solution) into the graphite tube and running the temperature program. The peaks related to atomic absorption were measured in integrated absorbance mode. The operational conditions used in the measurement of each element are listed in Table 1.

3. Results and discussion

The proposed methodology was optimized taking into account two aspects: (i) the extraction efficiency, which was evaluated by measuring the analytical signals for the metals in the extracts and (ii) the time needed to break the emulsions, which had high influence on the time taken to complete the treatment of the biodiesel samples. Some parameters that could affect the performance of the system were studied such as: the concentration of HNO_3 in the extractant solution, the concentration of the surfactant (Triton X-100) used in the emulsification process and the extraction time. Also, the temperature program was evaluated for the measurement of the metals in the extract.

3.1. *Influence of the HNO_3 concentration*

In organic matrices (as biodiesel), metallic cations can be found in different forms, like free ions or bonded to organic molecules. The addition of acid to the emulsions is important to enhance the displacement of the metallic cations from organic molecular structures, enhancing their transference to the aqueous phase. It is important to notice that the affinity of the free metal ions by the aqueous phase is much higher than their affinity by the organic phase. In this sense, a study was performed to investigate the influence of the acid concentration in the solution used for emulsification of biodiesel. The concentration of HNO_3 in the solution was changed from 0 (no addition of acid) to 2.1 mol L^{-1}. The concentration of Triton X-110 was constant and equal to 4% m/v.

As it can be seen in Fig. 1, for Cu and Mn, there was no significant variation of the signals with the variation of the concentration of HNO_3 in the solution used for emulsification. This result can indicate that these metals could be in the free form or bonded through weak interactions with the organic molecules present in the biodiesel. Nevertheless, for Ni, the results were different. The maximum extraction of Ni was only achieved when an acid concentration of at least 2.1 mol L^{-1} was employed, indicating that part of this metal can be strongly bonded to the matrix of biodiesel. In order to apply only one condition for the extraction of all analytes, a concentration of 2.1 mol L^{-1} was established for the method.

The concentration of HNO_3 also had influence on the time needed to break the emulsions, heated at 90 °C. The influence of this parameter was also tested in the range of 0–2.1 mol L^{-1}. Although some variation of the time required for breaking the emulsions was observed, they were always very low, varying from 2 to 7 min. In the experiments using 2.1 mol L^{-1} of HNO_3 (chosen for the method), the time of heating needed to induce the breaking of the emulsions was 5 min, which was considered satisfactory because it did not affect the total time taken to complete the procedure.

3.2. *Influence of Triton X-100 concentration*

The use of surfactants to help the formation of emulsions is widespread. According to Isaacs and Chow [24], the presence of surfactants decreases the interfacial tension between the two liquids (aqueous and oil phases), lowering the energy required for emulsification. In general, the higher is the concentration of surfactant, the higher is the stability of the emulsion, because the droplets formed in the system are smaller. Smaller droplets increase the contact between the two phases, which can improve the extraction efficiency occurring at interfacial region. In this sense, the effect of the Triton X-100 concentration was evaluated. For this purpose, the concentration of HNO_3 was fixed at 15% v/v and the concentration of Triton X-100 was varied from 1% m/v to 10% m/v.

The concentration of surfactant did not affect significantly the extraction induced by emulsion breaking of Mn and Ni in the

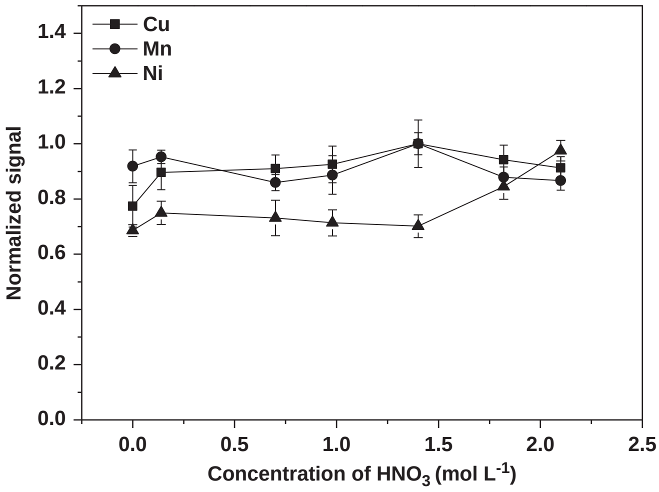

Fig. 1. Effect of the concentration of the HNO_3 in the solution employed for emulsification on the extraction of Cu, Mn and Ni from biodiesel by the proposed method. Concentration of Triton X-100 = 4% m/v and extraction time = 60 min.

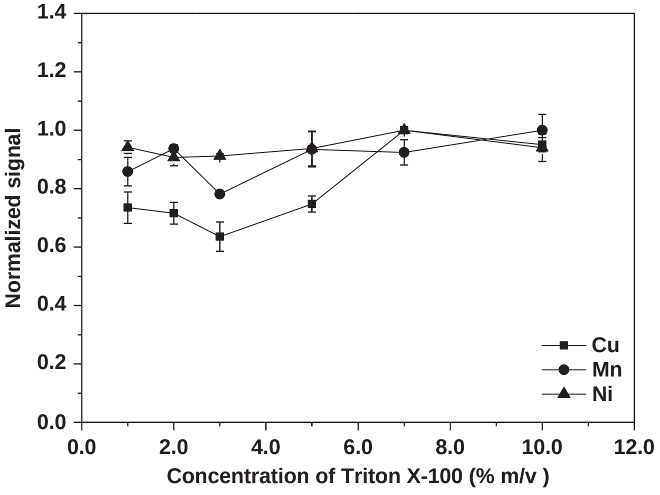

Fig. 2. Effect of the concentration of Triton X-100 in the solution employed for emulsification on the extraction of Cu, Mn and Ni from biodiesel by the proposed method. HNO_3 concentration=2.1 mol L^{-1} and extraction time=60 min.

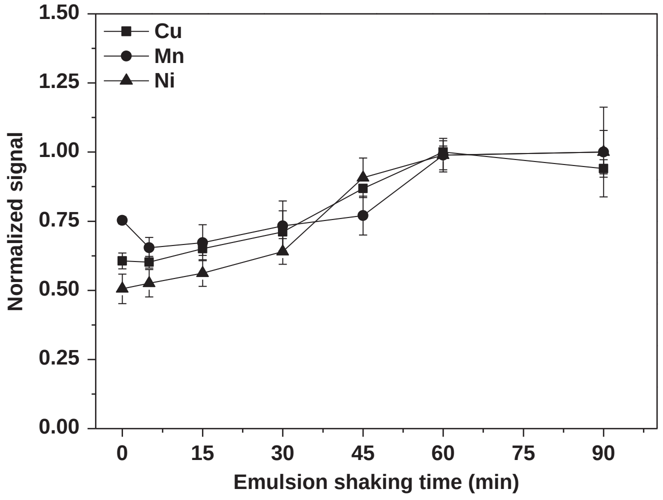

Fig. 3. Effect of the extraction time on the extraction of Cu, Mn and Ni from biodiesel by the proposed method. HNO_3 concentration=2.1 mol L^{-1} and Triton X-100 concentration=7% m/v.

range of concentration studied. For Cu (Fig. 2), the increase of the Triton X-100 concentration resulted in the increase of the relative analytical signal, evidencing that more Cu was transferred from oil to the aqueous phase in the extraction process. Maximum Cu signals were observed in the range of 7–10% m/v Triton X-100.

The influence of Triton X-100 concentration on the time needed to break the emulsions, at 90 °C, was more pronounced than the influence of the HNO_3 concentration. The use of high concentrations of Triton X-100 resulted in the formation of very stable emulsions, which took long time to be broken. So, a concentration of Triton X-100 of 7% m/v was selected for the method, in accordance with the highest extraction efficiency for the three metals and the lowest time to prepare the samples.

3.3. *Influence of the extraction time*

Sometimes, the process of transference of metals from oil to aqueous phase demands time, since the kinetics of extraction can be slow. In order to test the effect of the extraction time (time elapsed between emulsion formation and breaking), this variable was varied in the range of 0–120 min. During the extraction time, the emulsions were kept under continuous agitation (on a roller mixer) in order to avoid any separation of the phases. The concentrations of HNO_3 and Triton X-100 in the emulsifier solutions were those optimized in the previous experiments.

As it can be seen in Fig. 3, the extraction time had remarkable influence on the extraction of the three metals under study. Quantitative recovery of the metals could only be achieved when the emulsions were agitated for at least 60 min. These results can indicate that the metals, in biodiesel, are bonded to organic molecules through strong interactions, which take a relatively long time to be cleaved and yield inorganic species with high affinity by the water phase. Also, it seems that metals present stronger affinity by the oil phase in the biodiesel than by the oil phase of diesel oil [21], since the extraction time required for achieving maximum extraction was higher. So, an extraction time of 60 min was established for the method to ensure maximum transference of Cu, Mn and Ni to the aqueous phase in the extraction process.

3.4. *Thermal behavior of Cu, Mn and Ni in the extracts—pyrolysis and atomization curves*

After establishing the extraction conditions, new experiments were performed to evaluate the difference between the extracts and standard solutions when the measurements of the metals of interest are carried out by ETAAS. In this experiment, pyrolysis and atomization curves were built up in order to compare the thermal behavior of each analyte in the presence and absence of the matrix (of the extract). The temperature program utilized for this purpose (Table 1) had a drying step with maximum temperature of 120 °C, which was enough to provide total volatilization of the water present in the aqueous extracts. The pyrolysis time was constant in all measurements and no chemical modifier was employed to avoid increasing of the blank signals.

Pyrolysis and atomization curves were constructed with standard solutions of Cu, Mn and Ni at concentrations of 10, 3.0 and 20 μg L^{-1}, respectively. Extracts obtained from the extraction of sample B_2 in the optimized conditions were employed for comparison. The results are shown in Fig. 4. As it can be seen, no remarkable differences were noted among the profiles of the pyrolysis and atomization curves for the three analytes in the two media (standard solution and extract). This result evidenced that the thermal behavior of Cu, Mn and Ni in the extract is practically the same of that observed in aqueous solution, giving a reasonable indication that no matrix interferences are present when the analytes are measured in the extract using the temperature program initially established. From the respective temperature curves, it was possible to establish the best pyrolysis and atomization temperatures for the determination of Cu, Mn and Ni in the extracts by ETAAS. The pyrolysis and atomization temperatures were set at 1000 and 2300 °C for Cu, 1300 and 2300 °C for Mn and 1400 and 2500 °C for Ni, respectively.

3.5. *Evaluation of the calibration strategy*

The presence of surfactants and some organic matter extracted from biodiesel along with the analytes could cause some nonspecific interferences on the measurements of the metals in the extracts by ETAAS. The results obtained in the investigation of the thermal behavior of metals during the ETAAS measurements indicated that no matrix interferences were present, but in spite of that, a test was performed to confirm this statement. For this purpose, analyte addition curves were constructed by adding known concentrations of the analytes to the extracts and compared to analytical curves built up with standard solutions prepared in aqueous medium. The results obtained are showed in Table 3.

There were no differences among the slopes of the analyte addition and analytical curves, confirming that there were no

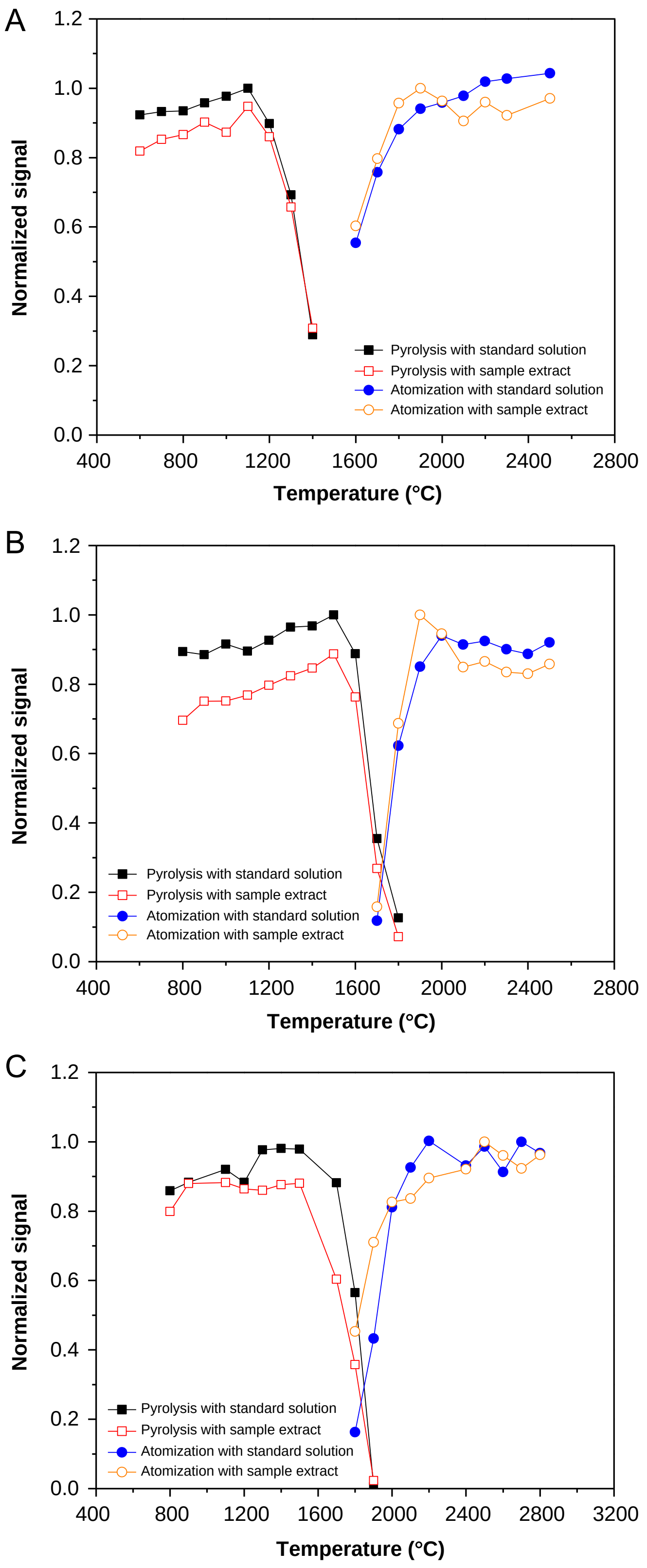

Fig. 4. Pyrolysis and atomization curves for (A) Cu, (B) Mn and (C) Ni in the aqueous standard medium and in the extract from biodiesel obtained by the proposed method (see text for experimental details).

matrix interferences in the determination of the metals in the extracts by ETAAS. So, it was possible to employ the method of external calibration for the quantification of the analytes in the samples treated by the proposed methodology.

Table 3
Comparison between the slopes (L μg^{-1}) obtained in the analyte addition and analytical curves for the measurement of Cu, Mn and Ni in the aqueous extracts obtained from extraction induced by emulsion breaking of biodiesel.

Analyte	Analyte addition curves	Analytical curves
Copper	0.0102 ± 0.0004	0.0098 ± 0.0002
Manganese	0.0344 ± 0.0014	0.0345 ± 0.0012
Nickel	0.0113 ± 0.0004	0.0115 ± 0.0004

Table 4
Figures of merit of the proposed methodology.

Parameter	Analyte		
	Cu	Mn	Ni
Limit of detection (μg L^{-1})^{b}	0.053	0.18	0.30
Limit of quantification (μg L^{-1})^{b}	0.18	0.60	0.99
Repeatability (%) (n=3, sample B$_1$)	1.3	5.6	2.7
Reproducibility (%) (n=3, sample B$_1$)	5.4	6.7	5.4

4. Figures of merit of the proposed methodology

The limits of detection and quantification of the proposed methodology were derived from repetitive analysis of the samples and using analytical curves constructed with standard solutions prepared in water, which was the same medium of the standard solutions employed in the external calibration procedure employed for quantification of Cu, Mn and Ni in the aqueous extracts. The methodological limits of detection and quantification were estimated from the analysis of three independent aliquots of the sample B_1, in the same moment, and taking into account the preconcentration factor (5 times) achieved when applying the developed procedure. The same experiment served to estimate the repeatability (within-run) of the procedure, also taking into account the variability of the whole procedure. Reproducibility (between-run) was tested by analyzing independent aliquots of same sample B$_1$ in three consecutive days. In both cases (repeatability and reproducibility) the precision was expressed as the coefficient of variation of the mean obtained in the analysis of the independent aliquots. Such data are presented in Table 4. As it can be noted, the proposed methodology was able to determine very low concentrations of metals in the samples, since the methodological limits of quantification were always lower than 1 μg L^{-1}. The precision was satisfactory for this kind of procedure, being situated in the range of 1.3–5.6% for within-run analysis and 5.4–6.7 % for between-run analysis.

5. Application of the developed method in the determination of metals in biodiesel samples

Five samples of biodiesel were analyzed in relation to the content of Cu, Mn and Ni, using the extraction method developed in this work and ETAAS as analytical technique. As there are no certified materials of biodiesel with certified concentrations of the metals under study, two different strategies were employed to test the accuracy of the method. In the first case, the results obtained by the proposed method were compared with those obtained when the samples were analyzed using the direct introduction of emulsions into the ETAAS, taken as reference method [25]. Secondly, a recovery test was carried out, by spiking the samples with known amounts of each analyte, which were added to the samples in the form of organometallic standards diluted in hexane.

Table 5
Results obtained in the determination of Cu, Mn and Ni in the biodiesel samples by the proposed and reference methods. Results are expressed as mean ± standard deviation ($n=3$).

Analyte	Method	Samples				
		B_1	B_2	B_3	B_4	B_5
Cu ($\mu g\ L^{-1}$)	Proposed	15.6 ± 0.2	26.4 ± 1.6	11.3 ± 0.7	5.4 ± 0.4	17.7 ± 0.6
	Reference[a]	17.8 ± 0.7	32.7 ± 4.7	13.2 ± 0.5	6.7 ± 1.0	20.9 ± 0.6
Mn ($\mu g\ L^{-1}$)	Proposed	3.6 ± 0.2	3.8 ± 0.5	< LOQ	3.6 ± 0.3	10.4 ± 0.3
	Reference[a]	3.8 ± 0.2	4.2 ± 0.4	< LOQ	3.9 ± 0.5	9.1 ± 0.4
Ni ($\mu g\ L^{-1}$)	Proposed	40.8 ± 1.1	37.8 ± 1.3	< LOQ	7.7 ± 0.2	55.9 ± 5.5
	Reference[a]	45.7 ± 4.7	42.3 ± 6.3	< LOQ	7.9 ± 1.1	65.7 ± 2.9

[a] The limits of quantification for the determination of Cu, Mn and Ni when the reference method was employed were 3.7, 0.96 and 2.7 $\mu g\ L^{-1}$, respectively.

Table 6
Recovery percentages obtained in the analysis of spiked samples.

Sample	Cu (12 $\mu g\ L^{-1}$)[a,b]	Mn (8 $\mu g\ L^{-1}$)[a,b]	Ni (22 $\mu g\ L^{-1}$)[a,b]
B_1 (%)	102 ± 2	98 ± 4	89 ± 3
B_2 (%)	109 ± 1	91 ± 6	106 ± 2
B_3 (%)	106 ± 2	109 ± 1	91 ± 1
B_4 (%)	103 ± 3	103 ± 4	97 ± 1
B_5 (%)	95 ± 3	99 ± 2	91 ± 1

[a] Between parentheses is the concentration of each analyte added to the samples.

[b] Results are expressed as mean ± standard deviation ($n=3$).

Table 5 shows the concentrations of Cu, Mn and Ni determined by the two methods (proposed and reference). The concentrations of the three metals determined in the samples were not statistically different (at 95% confidence level) when a Student test was employed to compare the results for each sample by the two methods, confirming that the proposed method is really accurate for the determination of trace concentrations of Cu, Mn and Ni in biodiesel. Also, the recovery percentages observed in the recovery test were in the range of 95–109% for Cu, 91–109% for Mn and 89–106% for Ni (Table 6). The recovery percentages showed that these metals were quantitatively extracted from biodiesel using the extraction induced by emulsion breaking and confirmed that no matrix interferences are present in the measurement of the metals in the aqueous extracts by ETAAS.

6. Conclusions

The developed method, based on the extraction induced by emulsion breaking, was efficient for the determination of Cu, Mn and Ni in biodiesel samples by ETAAS. It was simple and sensitive enough to quantify trace concentrations of the analytes in the samples without matrix interferences, since the analytes were transferred to an aqueous phase, where they were easily measured by ETAAS. Besides, the transference of the analytes to the water extract allowed the use of aqueous standards solutions for external calibration, which simplified the whole procedure and avoided interferences due to the high content of carbon in the samples. Another aspect to be highlighted was the preconcentration of the analytes in the extract (5 times), which improved the limits of detection and quantification.

The concentration of HNO_3 in the solution used in the emulsification had not strong influence on the extraction efficiency of Cu and Mn but had a decisive role in the quantitative extraction of Ni, which was only achieved when the HNO_3 concentration was 2.1 mol L^{-1}. The concentration of Triton X-100 influenced only the extraction of Cu, which was quantitative in concentrations higher than 7% m/v. On the other hand, the extraction time presented remarkable effect on the transference of the three metals from biodiesel to the aqueous phase. Only after 60 min of shaking it was possible to reach quantitative extractions of Cu, Mn and Ni.

The developed methodology was successfully applied in the analysis of real samples of biodiesel. The obtained results were not different from those obtained by a reference method, based on the introduction of the samples as detergent emulsions into the ETAAS instrument. Also, recovery percentages in the range of 89–109% were observed when the analytes were added to the samples as organometallic standards.

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References

[1] A.C. Pinto, L.L.N. Guarieiro, M.J.C. Rezende, N.M. Ribeiro, E.A. Torres, W.A. Lopes, P.A.P. Pereira, J.B. Andrade, J. Braz. Chem. Soc. 16 (2005) 1313–1330.

[2] U. Schuchardt, R. Sercheli, R.M. Vargas, J. Braz. Chem. Soc. 9 (1998) 199–210.

[3] K.R. Jegannathan, E-S. Chan, D. Ravindra, Renew. Sustain. Energy Rev. 13 (2009) 2163–2168.

[4] M. Ghisi, E.S. Chaves, D.P.C. Quadros, E.P. Marques, A.J. Curtius, A.L.B. Marques, Microchem. J. 98 (2011) 62–65.

[5] S. Jain, M.P. Sharma, Renew. Sustain. Energy Rev. 14 (2010) 667–678.

[6] A. Sarin, R. Arora, N.P. Singh, M. Sharma, R.K. Malhotra, Energy 34 (2009) 1271–1275.

[7] E.S. Chaves, E.J. Santos, R.G.O. Araujo, J.V. Oliveira, V.L.A. Frescura, A.J. Curtius, Microchem. J. 96 (2010) 71–76.

[8] R.S. Amais, E.E. Garcia, M.R. Monteiro, J.A. Nóbrega, Fuel 93 (2012) 167–171.

[9] F.H. Lyra, M.T.W.D. Carneiro, G.P. Brandão, H.M. Pessoa, E.V. Castro, Microchem. J. 96 (2010) 180–185.

[10] A. Jesus, M.M. Silva, M.G.R. Vale, Talanta 74 (2008) 1378–1384.

[11] A.P. Oliveira, R.D. Villa, K.C.P. Antunes, A. Magalhães, E.C. Silva, Fuel 88 (2009) 764–766.

[12] A.I. Barros, A.P. Oliveira, M.R.L. Magalhães, R.D. Villa, Fuel 93 (2012) 381–384.

[13] E.S. Chaves, M.T.C. Loos-Vollebregt, A.J. Curtius, F. Vanhaecke, Spectrochim. Acta B 66 (2011) 733–739.

[14] G.D. Woods, F.I. Fryer, Anal. Bioanal. Chem. 389 (2007) 753–761.

[15] A.E. Pillay, M. Elkadi, S.C. Fok, S. Stephen, J. Manuel, M.Z. Khan, S. Unnithan, Fuel 97 (2012) 385–389.

[16] R.M. Souza, L.G. Leocádio, C.L.P. Silveira, ICP OES, Anal. Lett. 41 (2008) 1615–1622.

[17] F.A. Lobo, D. Goveia, A.P. Oliveira, E.R. Pereira-Filho, L.F. Fraceto, N.L. Dias-Filho, A.H. Rosa, Fuel 88 (2009) 1907–1914.

[18] F.A. Lobo, D. Goveia, A.P. Oliveira, L.P.C. Romão, L.F. Fraceto, N.L. Dias-Filho, A.H. Rosa, Fuel 90 (2011) 142–146.

[19] R.J. Cassella, D.M. Brum, C.E.R. de Paula, C.F. Lima, J. Anal. At. Spectrom. 25 (2010) 1704–1711.

[20] R.J. Cassella, D.M. Brum, L.F.S. Caldas, C.E.R. de Paula, C.F. Lima, Anal. Chim. Acta 690 (2011) 79–85.

[21] R.J. Cassella, D.M. Brum, N.F. Robaina, A.A. Rocha, C.F. Lima, J. Anal. At. Spectrom. 27 (2012) 364–370.

[22] N.F. Robaina, D.M. Brum, R.J. Cassella, Talanta 99 (2012) 104–112.

[23] L.F.S. Caldas, D.M. Brum, C.E.R. de Paula, R.J. Cassella, Talanta 110 (2013) 21–27.

[24] E.E. Isaacs, R.S. Chow, Practical aspects of emulsion stability, in: L.L. Schramm (Ed.), Emulsions: Fundamentals and Applications in the Petroleum Industry, American Chemical Society, Washington D.C., 1992, pp. 51–77.

[25] R.J. Cassella, D.M. Brum, C.F. Lima, T.C.O. Fonseca, Fuel 90 (2011) 1215–1220.