



Development of a method to determine Ni and Cd in biodiesel by graphite furnace atomic absorption spectrometry

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ABSTRACT

This paper proposes a low cost, simple, fast method for determining Ni and Cd in biodiesel samples by graphite furnace atomic absorption spectrometry (GFAAS). The method was evaluated in biodiesel from different sources. Tungsten was used as a permanent modifier and the samples were prepared in the form of microemulsions, by mixing about 0.5 g of biodiesel with 5 g of surfactant (Triton X-100) in volumetric flasks and completing the volume with HNO₃ 1% (v/v). The detection limits obtained for Ni and Cd in microemulsions were ≤ 0.9 and $0.1 \mu\text{g L}^{-1}$, respectively. The relative standard deviation (% R.S.D., $n = 12$) was $\leq 8.20\%$ for Ni (washed animal fat sample) and $\leq 4.71\%$ for Cd (sunflower oil sample). Accuracy was checked based on addition and recovery experiments, which yielded recovery rates varying from 93% to 108% for Ni and from 98% to 116% for Cd. Sample preparation is rapid and easy, and the use of an inorganic standard for calibration makes this sample preparation procedure suitable for routine applications.

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1. Introduction

Biodiesel appears to be a promising substitute for fossil fuel, since it allows for the qualitative and quantitative reduction of several species that contaminate the environment (CO₂, SO_x, aromatic compounds) [1–4], and is also a renewable source of energy, unlike diesel oil and other petroleum derivatives [5–7]. Its perfect miscibility and physicochemical similarity to mineral diesel oil means that biodiesel can be used pure or mixed in any proportions with other solvents to run diesel cycle engines without requiring substantial or expensive adaptations [2,7]. Chemically, biodiesel is defined as a mono-alkyl ester of long-chain fatty acids with physicochemical characteristics similar to those of mineral diesel, which is produced through chemical processes such as transesterification or thermal cracking [8,9]. Most of these processes involve the transesterification of oils or fats (from plants or animals) with short chain alcohols (methanol or ethanol), using sodium or potassium hydroxide as a catalyst [10,11].

Hardly any chemical reaction, including transesterification, is ever complete, so the reaction products (alkyl esters) are usually contaminated with other compounds. The presence of potassium

or sodium in the end product leads to the formation of insoluble soap, which forms deposits in the filters of vehicles [5,12,13]. Sodium and potassium in fatty acid methyl ester are determined by diluting a sample in organic solvent (xylene, cyclohexane or petroleum ether) and examining it by flame atomic absorption spectrometry (FAAS) [14–16]. However, biodiesel may contain other inorganic contaminants (e.g., Cu, Pb, Cd, Ni, etc.) because the plant itself (raw material) absorbs metals from the soil, and/or because it may be incorporated into the product during transportation, production or storage [1,17,18]. Although metal concentrations in biofuels are usually low, their determination requires adequate sample preparation procedures and sensitive analytical techniques [19,20]. The techniques for determining trace elements must be chosen with clear knowledge about their capabilities and limitations [21].

Today, these determinations are done mainly by graphite furnace atomic absorption spectrometry (GFAAS) [19,22] and inductively coupled plasma mass spectrometry (ICP-MS) [23]. Techniques such as X-ray fluorescence spectrometry, spectrophotometry, polarography, titrimetry and anodic stripping voltammetry are used less frequently [20].

Sample pretreatment, which is probably the most critical stage of fuel analysis, consists of submitting the sample to a procedure that renders it more appropriate for analysis [16]. This is the stage

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of an analysis in which most errors occur. It is most time-consuming and increases the cost of the analysis; therefore, all the stages of a pretreatment procedure must be considered carefully [20,23].

The literature offers few examples of fuel analysis without previous treatment. The use of untreated fuel samples for the determination of trace metals usually leads to general problems such as volatility, flammability and immiscibility with water, and a number of specific problems depending on the analytical technique employed [1]. Widely used traditional methods such as wet digestion and microwaves have advantages and limitations [20]. However, despite some inconveniences, they are highly effective in eliminating organic matter using acids and oxidants. An alternative currently employed for analyzing samples without the previous destruction of organic matter is the emulsion or microemulsion system, which allows for efficient stabilization of trace metals in organic solutions [5,16,24]. A macroemulsion is obtained, either oil-in-water (O/W, droplets of oil-in-water) or water-in-oil (W/O, droplets of water-in-oil), depending on the dispersal phase. In emulsions and microemulsions, the fuel is dispersed in the aqueous phase as microdroplets stabilized by micelles or vesicles generated by the addition of a detergent. Besides their physicochemical characteristics, the size of the resulting droplets is a differential between emulsion and microemulsion [25–27].

In Brazil, the obligatory percentage of biodiesel mixed in diesel oil sold throughout the country was increased from 2% to 3% on July 1, 2008. This decision was taken by the National Council of Energy Policy (CNPE). Although biodiesel of different origins is already in use in automotive vehicles because it is produced from renewable sources, the literature still contains very few papers on the subject. Moreover, Brazilian legislation still lacks an adequate standard for controlling biodiesel quality with respect to metals such as Cu, Pb, Ni and Cd. It is therefore essential to develop analytical procedures for preparing samples and for determining these metals in biodiesel samples. Thus, the objective of this study was the development of an analytical method for the determination of Ni and Cd concentrations in biodiesel samples by GFAAS, using microemulsions and W as a permanent chemical modifier.

2. Experimental

2.1. Instruments and accessories

All the experiments were carried out using a Varian Model Spectra AA240Z electrothermal atomic absorption spectrometer with Zeeman-effect background correction, equipped with a PSD 120 autosampler. The spectrometer's longitudinally heated graphite tubes were designed with an integrated platform. Varian hollow cathode $\lambda = 228.8$ nm lamps with a spectral bandwidth of 0.5 nm were used for Cd, and $\lambda = 232.0$ nm lamps with a spectral bandwidth of 0.2 nm were used for Ni. The instruments and accessories included a Milli-Q Plus water deionizer system, (Millipore®), automatic micropipettes of different volumes (fixed and variable), a Sartorius 2432 analytical balance with a maximum capacity of 200 g, a heated magnetic shaker (Nova Técnica), polyethylene disposable tubes (Corning), focused microwaves – Rapid Digestion system (SPEX), ZetaPlus – Brookhaven Instr. Corp. at a fixed angle of 90° at 25 °C, and 99.9% argon (White Martins, Brazil) as the purge gas.

2.2. Reagents, solutions and samples

All the solutions were prepared with high purity deionized water (18.2 M Ω cm⁻¹) obtained from a deionizer system (Milli-Q

Plus, Millipore®). Nitric acid (Synth-65%, v/v) was used after sub-boiling the reference analytical solutions and samples. The analytical solutions of the analytes were prepared daily using 1000 mg L⁻¹ of stock solutions (Normex®, Carlo Erba) in 1.0% (v/v) distilled HNO₃; Triton X-100 (Tedia). The biodiesel samples were obtained by transesterification prepared via the ethanol route, using NaOH as the catalyst. These samples were supplied by Brazilian biodiesel research laboratories in Curitiba, PR and Cuiabá, MT. A sample, named B10 (10% (v/v) biodiesel in diesel), which was supplied by a filling station in Sorocaba, SP, was also analyzed, but additional information was unfortunately not provided.

2.3. Preparation of the chemical modifier

As shown in an earlier work [2], the best results were obtained using W as a chemical modifier, demonstrating that in this case W offers several advantages [27,28]. A solution of 1.0 g L⁻¹ of W was prepared by dissolving 0.1794 g of NaWO₄·2H₂O (Merck) in 100 mL of deionized water. The atomizer was coated with the W permanent modifier in two steps: (i) tungsten deposition; and (ii) thermal treatment of the tungsten deposited in the tube. The heating schedule applied in this procedure was performed as described by Lima et al. (1998, 1999) [29,30].

2.4. Study of the electrothermal behavior

It is important to optimize the heating schedule in GFAAS in order to establish the initial working conditions [31,32]. In previous studies, experimental design was used as a tool to determine the optimal temperature of pyrolysis (Tp) and temperature of atomization (Ta), which were 800 and 2300 °C for Ni and Tp-500 °C and Ta-1400 °C for Cd [2]. Table 1 indicates the heating schedule employed in the present study.

2.5. Preparation of samples and optimization of the procedure

An analysis was made of the biodiesel samples obtained from different sources, as indicated in Table 2.

The sample preparation procedure consisted of mixing about 0.5 g of biodiesel with 5 g of surfactant (Triton X-100) and completing the volume with HNO₃ 1% (v/v) in plastic volumetric flasks of 50.0 mL under mechanical shaking for 20 min.

An evaluation was made of the influence of Triton X-100 masses of 1.0, 3.0, 5.0 and 10 g on the values of samples containing a concentration of 25.0 μ g Cd L⁻¹ (within the linear value for Cd) in HNO₃ 1.0% (v/v) [33].

The mean diameter (evaluated based on the volume distribution) of microemulsions in the dispersion was determined by photon correlation spectroscopy (PCS), using a laser light-scattering instrument (ZetaPlus, Brookhaven) at a fixed angle of 90° at

Table 1
Heating schedule used in the experiments.

Steps	Cycle	Temperature (°C)	Time (s)	Gas flow (mL min ⁻¹)
1	Drying	85	5.0	300 (Ar)
2		95	40.0	300 (Ar)
3		120	10.0	300 (Ar)
4	Pyrolysis	^a	5.0	300 (Ar)
5		^a	20.0	300 (Ar)
6		^a	2.0	0 (read)
7	Atomization	^b	0.8	0 (read)
8		^b	2.0	0 (read)
9	Cleaning	2900	2.0	300 (Ar)

^a Pyrolysis temperature (Tp).

^b Atomization temperature (Ta).

Table 2
Origin of biodiesel samples.

Samples	Origin
S1	Soybeans
S2	Soybeans
S3	Puréed animal fat
S4	Washed animal fat
S5	Non-washed animal fat
S6	Sunflower
S7	Cotton
S8	10% (v/v) of biodiesel in diesel (B10)

25 °C. The zeta potential was analyzed with the same equipment. This evaluation was carried out using different types of microemulsions prepared in 50.0 mL plastic flasks by mixing 0.5 g of biodiesel with four different masses of Triton X-100 (1.0, 3.0, 5.0 and 10 g), completing the volume with HNO₃ 1% (v/v), and shaking the mixtures in a magnetic shaker for 20 min.

An evaluation was made of the influence of sample volumes of 10, 20, 30 and 40 µL on the absorbance patterns of 10.0 µg Ni L⁻¹ in HNO₃ 1.0% (v/v) and 1.0 µg Cd L⁻¹ in HNO₃ 1.0% (v/v).

Since certified biodiesel material is not yet available, addition and recovery tests were performed in order to ascertain the precision and accuracy of the method using the microemulsion sample of 10.0 µg Ni L⁻¹ and 1.0 µg Cd L⁻¹ in HNO₃ 1.0% (v/v).

3. Results and discussion

3.1. Preparation of the samples

The analysis of the influence of Triton X-100 on the absorbance signals of the 25.0 µg L⁻¹ Cd standard in HNO₃ in 1.0% (v/v) indicated that the greatest absorbance occurred with 1.0 g of Triton X-100. The use of both 1.0 and 3.0 g of Triton X-100 caused the formation of large volumes of foam, extending the time required for the microemulsion to stabilize, while the formation of microemulsion with 10 g of Triton X-100 took a long time, probably due to

difficulties for the reagent to homogenize. Thus, since greater stabilization was achieved with 5.0 g of Triton X-100 and little foam was formed, this mass was considered adequate for the preparation of microemulsions. This method is relatively low-cost, since it uses Triton X-100 as surfactant and consumes little electricity, simple – requiring only mechanical agitation, and very fast – approximately 20 min of preparation.

3.2. Physicochemical characterization of the microemulsion

Most of the studies on microemulsions published in the literature state that the analyses were done in the form of microemulsions [5,24,26], but no mention is made of the particle size to indicate that these were actually microemulsions. To indicate some of the physicochemical parameters of the microemulsions prepared in this work and evaluate the choice of reagents, Table 3 lists some of the analyzed characteristics.

Table 3 shows that the mean particle size in the samples ranged from 310 to 560 nm. In the literature, microemulsions (ME) are usually described as spherical aggregates with diameters of less than 1400 Å, typically in the order of 100 Å [22,23,34]. The suffix “micro” is misleading, for the system involves droplets with sizes so small that they are optically transparent [35]. Another interesting parameter is the polydispersion (particle size distribution), which ideally should be very low. As can be seen in Table 3, the values were low, with the lowest polydispersion of 0.01 obtained with 5.0 g of Triton X100. The zeta potential reflects the particle surface load, and this parameter may be influenced by particle composition and by poor dispersion. The spheres should present a relatively zeta potential (±) 30 to ensure physicochemical stability, since strong repulsive forces tend to prevent aggregation due to occasional collisions of adjacent spheres [36]. The Zeta (Z) values listed in Table 3 (+7 < Z < +11) lie within the interval considered good. Thus, the microemulsions may be considered stable, presenting low values of polydispersion and a high zeta potential value, confirming their satisfactory preparation.

3.3. Optimization of the method

Fig. 1 shows the influence of the volume of the sample on the absorbance signals of the 10.0 µg Ni L⁻¹ and 1.0 µg Cd L⁻¹ in HNO₃ 1.0% (v/v) pattern.

In Fig. 1a, note that the sample volume of 10 µL presents a low Ni absorbance value. Higher sensitivity was recorded in sample volumes of 30 and 40 µL (Fig. 1a), but the replicates were not satisfactory, showing high estimated standard deviations. The volume of the 20 µL sample was adequate, since it presented a significant absorbance for the 10.0 µg Ni L⁻¹ standard and a low estimated

Table 3
Physicochemical parameters of the microemulsions.

Amount of Triton X-100 (g)	Particle size (nm)	Polydispersion	Zeta potential (mV)
1	311.4	0.03	+6.53
3	450.3	0.02	+8.70
5	550.2	0.01	+9.31
10	556.8	0.12	+10.01

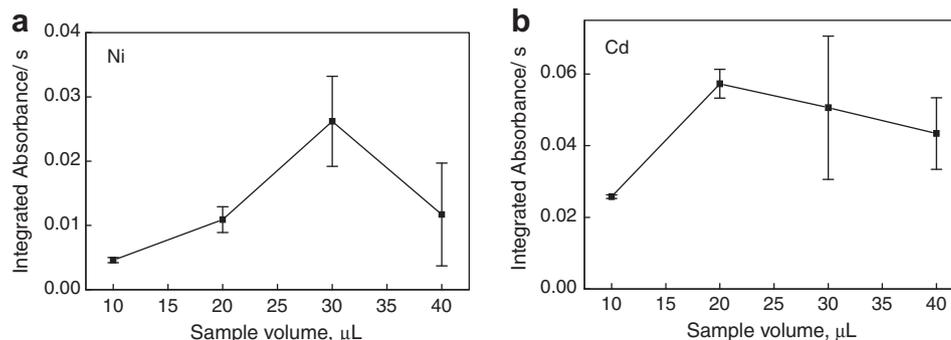


Fig. 1. Influence of the sample's volume on the absorbance signals (corrected from the blank signal) of the solutions: (a) 10.0 µg Ni L⁻¹ in HNO₃ 1.0% (v/v); (b) 1.0 µg Cd L⁻¹ in HNO₃ 1.0% (v/v).

Table 4
Concentration (in $\mu\text{g g}^{-1}$) of Ni and Cd in the samples.

Samples	[C] ($\mu\text{g g}^{-1}$)	
	Ni	Cd
S1	$\leq\text{LQ}$	0.7
S2	$\leq\text{LQ}$	0.6
S3	$\leq\text{LQ}$	0.2
S4	$\leq\text{LQ}$	0.3
S5	$\leq\text{LQ}$	$\leq\text{LQ}$
S6	$\leq\text{LQ}$	0.2
S7	$\leq\text{LQ}$	0.2
S8	$\leq\text{LQ}$	2.4

standard deviation, and this volume was therefore chosen for the subsequent analyses.

An analysis of Fig. 1b indicates that the sample volume of 10 μL presented low absorbance content, while 20 μL of sample showed a significant increase in the intensity of the absorbance signal due to the increased population of atoms generated in the atomizer. In addition to the introduction of 10 and 20 μL of sample, the estimated standard deviation was relatively low, showing good repeatability in the experimental measurements for Cd. However, for 30 and 40 μL of sample, due to the larger volume of sample in the atomizer, the sample projected out of the atomizer, as recorded by the webcam of the apparatus, leading to a high estimated standard deviation. Therefore, a volume of 20 μL was used for the subsequent analyses.

Table 4 shows the results of the analysis of eight biodiesel samples evaluated under the conditions adopted in this study.

Low detection limits were obtained for Ni ($\text{LD} \leq 0.9 \mu\text{g L}^{-1}$). However, as indicated in Table 4 for Ni, the concentration of Ni in all the samples studied here was lower than this value. Therefore, Ni was not detectable in the samples using the method employed here. From the environmental standpoint, this can be considered a positive outcome for the use of biodiesel, since Ni is a natural constituent of petroleum and is generally present in its derivatives. Lower limits of detection were obtained for Cd ($\text{LD} \leq 0.1 \mu\text{g L}^{-1}$). The concentrations in the samples were low, but lay within the limits of detection.

Still with respect to Table 4, note that the concentration of Cd in sample S5 fell below the detection limit. This was probably the result of washing during the biodiesel preparation process, when the metal was eliminated.

In addition, the values of Cd found in animal fat samples were consistently lower than those obtained from vegetable biodiesel samples. This is probably due to the fact that vegetables can absorb metals, which is not the case with samples of animal origin. The presence of Cd in the biodiesel samples was attributed to the great-

er mobility of this element in soil than Ni [37,38]. It is also worth noting that Cd has been used in the form of CdCl_2 as a fungicide, and as such, may constitute another source of soil contamination [39,40].

Table 5 shows the results of the addition and recovery tests for each sample. These results reveal recovery values of 93–108% for Ni and of 98–116% for Cd, indicating that the method used here is suitable for determining nickel and cadmium in biodiesel matrices from different sources and origins. Moreover, low values of relative standard deviations (R.S.D. %) were obtained, i.e., $\leq 9.0\%$ for $10.0 \mu\text{g Ni L}^{-1}$ and $\leq 5.0\%$ for $1.0 \mu\text{g Cd L}^{-1}$, respectively.

4. Conclusion

The analytical method developed with microemulsions and GFAAS can be considered efficient in determining Ni and Cd in biodiesel samples, since it presented relatively low standard deviations and good recovery values. The preparation of samples in the form of microemulsions was satisfactory and may constitute a useful alternative, since it does not require previous distribution of organic matter, is inexpensive, simple, and fast, and poses less risk of contamination than traditional methods, as well as higher stability, without the need for organometallic standards and carcinogenic solvents. This work contributes by proposing an alternative analytical method to control the quality of biodiesel by determining and quantifying the presence of metals such as Ni and Cd, which are not yet controlled by Brazilian standards.

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Table 5
Recovery rates ($n = 3$) and relative standard deviations (% R.S.D.) of biodiesel samples using W as the modifier, prepared with $10 \mu\text{g L}^{-1}$ of Ni and $1.0 \mu\text{g L}^{-1}$ of Cd.

Samples	Recovery, % \pm R.S.D.	
	Ni	Cd
S1	108 \pm 2.0	100 \pm 4.0
S2	105 \pm 1.0	104 \pm 3.0
S3	103 \pm 3.0	108 \pm 1.0
S4	102 \pm 2.0	99 \pm 4.0
S5	101 \pm 3.0	116 \pm 4.0
S6	93 \pm 9.0	98 \pm 5.0
S7	97 \pm 3.0	102 \pm 4.0
S8	93 \pm 1.0	95 \pm 2.0

(% R.S.D.) relative standard deviations.

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