

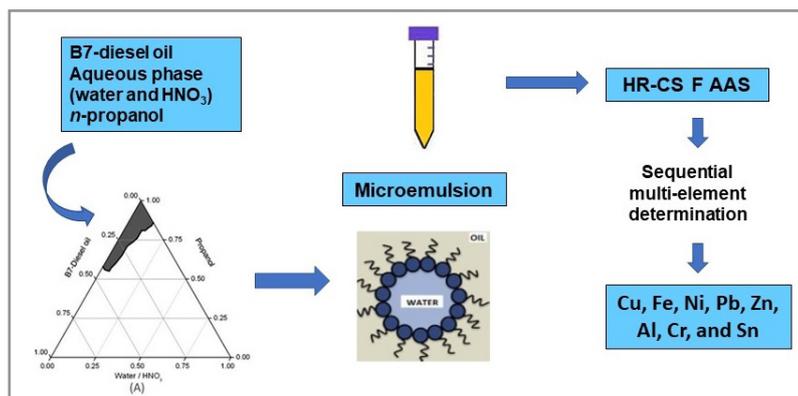
TECHNICAL NOTE

Multi-Element Determination of Trace Elements in B7-diesel Oil by High-Resolution Continuum Source Flame Atomic Absorption Spectrometry

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In this work, a method for sequential multi-element determination of Cu, Fe, Ni, Pb, Zn, Al, Cr and Sn in B7-diesel oil samples by high-resolution continuum source flame atomic absorption spectrometry (HR-CS F AAS) was proposed. The sample preparation was based on formation of microemulsion (ME), which was investigated through a three-phase diagram. The ME composition adopted was B7-diesel oil (3.3 g), aqueous phase containing nitric acid (1.4 mol L⁻¹, 300 μ L)

and *n*-propanol (up to 10 mL). The use of surfactant Triton X-100 in the formation of ME was also evaluated. Limits of detection in the range of 0.01 – 0.4 mg kg⁻¹ were obtained. Spike-recovery tests were accomplished and the results varied between 93 and 124%. The accuracy of the proposed method was confirmed by the analysis of certified reference material (CRM) NIST SRM 1084a (Wear-Metals in Lubricating Oil); there was no statistical difference between the obtained results and the certified values (at 95% confidence level). Twelve B7-diesel oil samples were analyzed and Cu, Fe and Cr were found in three samples. The proposed method was simple, fast and accurate. The sequential multi-element determination of trace elements presented advantages as low costs and reduction in analysis time, being appropriate for routine analysis.

Keywords: Diesel oil analysis, F AAS, high-resolution continuum source, microemulsion, sequential multi-element determination

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INTRODUCTION

Diesel oil is one of the most important derivatives from crude oil. It is a mixture of hydrocarbons which contains from 9 to 20 carbon atoms and with boiling point ranging between 170 and 370 °C [1]. Diesel engines present advantages in output power and fuel efficiency; due to this characteristic diesel engine became the choice for several kinds of transport such as passenger vehicles, heavy trucks, buses, trains, boats, ships and others [2]. In Brazil, it is mandatory to add biodiesel to diesel oil commercially available in the country [3]. In 2005, the percentage of biodiesel added was initially 2% (v/v). When the experimental part of this work was started the percentage of biodiesel was 7%, so-called B7-diesel oil. The amount of biodiesel should be increased gradually until a maximum concentration of 15% (v/v), and this percentage should be reached around of 2023, according to Brazilian government projections [3]. Quality control of fuels is important because the presence of some undesirable elements and compounds can lead to fuel degradation and / or instability [4]. Among these elements, metals have a remarkable negative role. The presence of metals (such as Cu, Fe, Ni, Pb, Zn, Al, Cr and Sn) in diesel oil may have several origins: from the raw material, corrosion processes in the storage tanks, leaching during the distillation and refining processes or even contamination from additives [5]. Copper and Ni can promote auto-oxidation reactions, decreasing fuel efficiency due to gum formation [6]. These elements also reduce the effectiveness of vehicles catalysts, increasing the emission of carbon monoxide, sulfur and nitrogen oxides. Iron, Cu, Al and Cr present in storage tank alloys and from the distillation process are known to damage engines and boilers [7]. Moreover, metals as Cr, Ni, Zn, Al and Sn are known by their toxic and / or carcinogenic potential [8,9]. Thus, the control of trace elements such as Cu, Fe, Ni, Pb, Zn, Al, Cr and Sn is essential in order to ensure the fuel quality and the potential harmful effects of releasing these elements to the environment. Even with all negative aspects presented, metals concentration is not controlled in diesel oil, according to American Standard Test Method (ASTM) D396 [10].

Usually, metals are present in fuels in trace levels, requiring sensitive and reliable techniques. Spectrometric techniques are highlighted in relation to accuracy among the techniques used for quantification of trace elements in fuels; some examples are flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF AAS), inductively coupled plasma-optical emission spectrometry (ICP OES) and inductively coupled plasma-mass spectrometry (ICP-MS) [11,12]. The use of a continuum source together with high-resolution monochromator (HR-CS) has brought many advantages for the AAS techniques. The use of high-intensity xenon short-arc lamp as a continuum source, a high-resolution double-echelle monochromator and a CCD array detector provides the possibility to determine many elements in a fast sequential mode when FAAS is used, with high precision, efficient background correction [13], higher tolerance for organic liquids analysis and lower costs than other multi-element techniques.

The direct analysis of fuels without any pre-treatment is limited due to their complex matrices, volatility and flammability. Thus, they must be properly converted in a format compatible with the instrumentation. Moreover, when methods based on nebulization are used, differences of viscosities and in other physical characteristics between samples and calibrations solutions must be carefully evaluated [14,15]. There are several methods for fuel samples preparation. Methods based on dilution, emulsion or microemulsion (ME) preparation and sample decomposition are among the most used [15]. The sample preparation can require excessive manipulation of samples resulting in loss of analytes and/or contamination of the sample with reagents used in the process.

Methods based on formation of ME are flexible and very attractive for complex matrices as petroleum derivatives [12,16], fuels [15,17], and biofuels [14,18,19]. These systems are compatible with external calibration using aqueous standards and the sample preparation time is reduced, when compared with digestion procedures. Moreover, higher stability of the analytes in the ME has been reported [18], especially when acidified solution is used, and no carcinogenic reagents are required, such as xylene (frequently used in the dilution methods) [16,17]. Amorin Filho et al. [20] evaluated different sample preparation methods for the determination of Cu, Cr, Fe, Ni, Pb, Sb and Zn in lubricating oil by HR-CS FAAS. The

compared procedures were microwave-assisted acid decomposition, direct dilution in kerosene, and oil-in-water emulsification. The authors reported that emulsified aqueous medium could be used for calibration and reduction in organic wastes and minimization of time and costs involved in the analysis was achieved.

Microemulsions are optically transparent and thermodynamically stable dispersion systems of at least three components: a polar and a non-polar liquid phase (water and oil respectively), and a suitable surfactant often in combination with a co-surfactant such as an aliphatic alcohol [21,22]. The use of microemulsified systems for diesel oil has been reported in the literature for different purposes [23,24]. Quadros et al. [7] reported the use of ME as sample preparation for the determination of trace elements in B5-diesel oil diluted with *n*-propanol and HNO₃ by high-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS ET AAS), using calibrations against aqueous standards for Cu, Fe, Mn and Pb, and standards prepared in *n*-propanol for Al and Cd. The authors highlighted the fast, precise and accurate results. A method based on extraction induced by emulsion breaking (EIEB) was proposed by Cassella et al. [1] for Zn determination in diesel oil by F AAS. This author also determined Al, Cu, Mn, Ni, Sn and V in diesel oil using the same sample preparation (EIEB) but by ICP-MS [25]. In both works, preconcentration factors of five times were obtained improving significantly the limits of detection obtained. It should be pointed out that the sequential multi-element determination of trace elements in diesel oil by HR-CS F AAS has not been reported yet, justifying the investigation of this technique for this application, associated with a very advantageous sample preparation method based on ME.

Thus, the goal of this work is to propose a simple, fast and accurate method for the sequential determination of Cu, Fe, Ni, Pb, Zn, Al, Cr and Sn in microemulsions of B7-diesel oil samples by HR-CS F AAS. The elements selected in this work have negative aspects to the quality of B7-diesel samples or have toxic potential when released into the environment. The ME formation with and without surfactant was investigated through a three-phase diagram. The accuracy of the method was investigated by analyzing a certified reference material (CRM) and by recovery tests.

MATERIALS AND METHODS

Instrumentation

The determinations of Cu, Fe, Ni, Pb, Zn, Al, Cr and Sn in B7-diesel oil were carried out with a ContrAA 300 high resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Germany) equipped with a xenon short-arc lamp (continuum spectrum emitted between 190 and 900 nm, operating in a hot-spot mode), a prism pre-monochromator, an echelle grating monochromator for high resolution (about 1.5 pm per pixel at 200 nm) and a charge-coupled device (CCD) array detector. This arrangement allows a fast sequential multi-element analysis in the flame mode. The determinations were performed with air - acetylene flame (for Cu, Fe, Ni, Pb and Zn) and nitrous oxide - acetylene flame (for Al, Cr and Sn). The aspiration rate of 2.8 mL min⁻¹ and a 50 mm burner were used for all elements. Nebulizer chamber with sealing rings resistant to organic solvents were used (Analytik Jena AG, Germany). The optimized instrumental parameters for each analyte are presented in Table I.

High-purity acetylene (99.0%, from White Martins, Brazil) was used as fuel. Compressed air provided by an air compressor (model FIAC CDS 8/50, Araraquara, São Paulo, Brazil) was used as oxidant for Cu, Fe, Ni, Pb and Zn, and nitrous oxide (99.0%, from White Martins, Brazil) was used for Al, Cr and Sn. A sub-boiling distiller (Kürner Analysentechnik, Rosenheim, Germany) was used for nitric acid distillation.

Table I. Instrumental Parameters for Determination of Cu, Fe, Ni, Pb, Zn, Al, Cr and Sn in B7-diesel Oil Samples by HR-CS F AAS

Analyte	Wavelength (nm)	Relative sensitivity (%)	Flame	C ₂ H ₂ flow rate (L h ⁻¹)	Reading Height (mm)	Pixels evaluated
Cu	324.754	100	C ₂ H ₂ - Air	40	5	CP ^a ± 1
Fe	248.327	100	C ₂ H ₂ - Air	60	6	CP ± 1
Ni	232.003	100	C ₂ H ₂ - Air	45	6	CP ± 1
Pb	217.000	100	C ₂ H ₂ - Air	65	6	CP ± 2
Zn	213.857	100	C ₂ H ₂ - Air	45	6	CP ± 1
Al	396.152	91	C ₂ H ₂ - N ₂ O	185	5	CP ± 1
Cr	357.868	100	C ₂ H ₂ - N ₂ O	180	4	CP ± 2
Sn	224.605	100	C ₂ H ₂ - N ₂ O	235	4	CP ± 2

^aCP: Center pixel.

Reagents, Solutions and Samples

Analytical grade reagents were used throughout. Solutions and ME were prepared with distilled and deionized water (DDW) from a Milli-Q water purification system (Millipore, Bedford, MA, USA) with 18.2 MΩ cm resistivity. All containers and glassware used were previously decontaminated with a 1.4 mol L⁻¹ nitric acid solution for at least one day and rinsed with DDW. A sub-boiling distilled nitric acid (Merck, Germany) was used for ME preparation. Other reagents used, *n*-propanol (Merck, Darmstadt, Germany), base mineral oil (0.87 g cm⁻³ Specsol, Quimlab, São Paulo, Brazil), oleic acid (Vetec, Rio de Janeiro, Brazil) and toluene (Synth, São Paulo, Brazil), Triton X-100 (Union Carbide, Danbury, Connecticut, USA), Cu, Fe, Ni, Pb, Zn, Al, Cr and Sn inorganic and organic standards (1000 mg L⁻¹ from Specsol (São Paulo, Brazil)). For accuracy evaluation of the proposed method, the certified reference material SRM 1084a (wear-metals in lubricating oil) from the National Institute of Standards & Technology (NIST Gaithersburg, MD, USA) was used. The B7-diesel oil samples (S10 and S500; this designation denotes the maximum sulfur content allowed in the commercialized fuel) analyzed in this work were supplied by the CECOM (Centro de Combustíveis, Biocombustíveis, Lubrificantes e Óleos, Universidade Federal do Rio Grande do Sul, RS, Brazil) from different regions of Rio Grande do Sul State, Brazil.

Microemulsion Preparation

For the ME preparation, B7-diesel oil, aqueous phase (1.4 mol L⁻¹ HNO₃) and *n*-propanol were mixed and shake manually for few seconds. The construction of two ternary diagram phases were accomplished by varying the proportions of B7-diesel oil, diluted nitric acid and *n*-propanol with and without surfactant (Triton X-100), respectively. The ME formation was evidenced through visual transparency. These procedures have been done at 25 °C, maintained by air conditioning of the laboratory. The ME composition adopted for analysis was 3.3 g of B7-diesel oil, 300 μL of water and the final volume of 10 mL filled with *n*-propanol (about 3.7 g). The nitric acid (1.4 mol L⁻¹) was used in ME composition (added within the water component) to increase analytes stability in the medium. The CRM analysis was carried out with 0.1 g of sample followed by the addition of 3.2 g of a previously analyzed B7-diesel oil sample whose concentration was below de LOD, i.e., free of analytes, (for the adjust of viscosity) and the final volume of 10 mL filled with *n*-propanol. The final volume was enough for the sequential multi-element determination of all analytes. A 0.74 g of mineral oil was used in the ME standards for calibration (replacing the B7-diesel oil), and metals

inorganic standards added into the aqueous phase. A blank solution was prepared with 0.74 g of mineral oil solution, aqueous phase ($1.4 \text{ mol L}^{-1} \text{ HNO}_3$) and *n*-propanol. Standards were prepared from aqueous stock solutions described above, pipetting the volume into the aqueous phase to give concentrations in the ranges of $0.5 - 2.0 \text{ mg L}^{-1}$ for Cu; $1.0 - 3.0 \text{ mg L}^{-1}$ for Fe; $0.5 - 2.0 \text{ mg L}^{-1}$ for Ni; $1.0 - 4.0 \text{ mg L}^{-1}$ for Pb; $1.0 - 3.0 \text{ mg L}^{-1}$ for Zn; $5.0 - 20.0 \text{ mg L}^{-1}$ for Al; $1.0 - 4.0 \text{ mg L}^{-1}$ for Cr and $2.0 - 10.0 \text{ mg L}^{-1}$ for Sn in 10 mL volumetric flasks.

Analytical Procedure

The sequential measurements of the eight elements in ME of blank, standards, and B7-diesel oil by HR-CS F AAS were carried out according to type of flame and wavelength. Thus, the sequence of measurement was: Cu, Fe, Ni, Pb, Zn (air-acetylene flame), Al, Cr and Sn (nitrous oxide-acetylene flame). The aspiration rate was manually optimized and a compromise condition based on the maximum absorbance for most of the elements was chosen. Experimental conditions as the acetylene flow rate and burner height were optimized automatically by the software, considering the maximum absorbance as criterion. The most sensitive absorbance lines were used for the measurements, the only exception was for Al, for what the absorbance line with 91% was used, which will be discussed in the results. The multi-element determinations were carried out with optimized conditions which were adjusted for each analyte, being the experimental conditions adjusted by the software before each analyte determination. In order to evaluate matrix effects, recovery experiments were performed with organic and inorganic standards. In the first experiment the sample were spiked with organic standards of each analyte to obtain the following final concentrations: 2.5 mg L^{-1} Cu and Fe; 2.6 mg L^{-1} Ni; 3.0 mg L^{-1} Pb and Cr; 4.0 mg L^{-1} Zn; 15.0 mg L^{-1} Al; and 10.0 mg L^{-1} Sn. A small volume of the organic standards diluted in mineral oil were added directly in the sample and the flask was closed and the mixture was homogenized under vigorous manual agitation for at least 15 min. The spike concentrations values were chosen to be within the linear range of the calibration curves of each analyte. The sample was left to rest and in the next day it was again agitated for 5 min before the ME preparation for analysis. In the spike with inorganic standards, the aqueous standards of each analyte were added to the aqueous phase during the ME preparation to obtain the following final concentrations: 1.5 mg L^{-1} Cu and Ni; 2.0 mg L^{-1} Fe and Zn; 2.6 mg L^{-1} Pb; 3.0 mg L^{-1} Cr; 15.0 mg L^{-1} Al; and 8.0 mg L^{-1} Sn. All measurements of standards, samples and spiked samples were carried out in triplicate ($n = 3$), according the parameters presented in Table I.

RESULTS AND DISCUSSION

Investigation of microemulsion composition

Based on our previous experience with ME of biodiesel [26-28], the composition of the ME investigated in this work was initially B7-diesel oil, water/nitric acid and *n*-propanol. The use of greater amount of water with nitric acid was attempted in order to facilitate the optimization of instrument after analysis of aqueous solutions. In order to obtain the region where a homogeneous and stable system could be achieved a ternary phase diagram was built (Figure 1-A) as described hereafter. The diagram has three components: B7-diesel oil, water (containing $1.4 \text{ mol L}^{-1} \text{ HNO}_3$) and *n*-propanol. The points inside the triangle were plotted fixing the quantity of one component and varying the others (the variations were 5% (w/w) for each). Each point represents a mixture and has its proper physical characteristics (emulsified or transparent mixture) visually identified. Several proportions were tested until the emulsion / microemulsion limits could be obtained and a diagram representing the limits was built. Figure 1-A shows two distinct regions: region in gray (where a homogeneous and transparent solution is found (ME)) and region in white (where mixtures form emulsions). As can be seen, with a fraction of water/ HNO_3 higher than 0.1 (10% w/w), the stabilization of the hydrophobic phase was not possible (favoring formation of an emulsion). Moreover, the maximum amount of water required a minimum amount of B7-diesel oil, reducing the sensitivity of the method. On the other hand, the minimum of water (about 5% w/w) allowed the use of a fraction of about 0.4 (40% w/w) of B7-diesel oil. In order to investigate if the use of surfactant (Triton X-100) would increase the ME area in

the phase diagram a second ternary phase diagram was built (Figure 1-B) with 13% (w/w) of Triton X-100, and volume completed to 10 mL with *n*-propanol. As can be seen, the use of the surfactant increased the ME region; higher amount of diesel (almost 70% w/w), could be stabilized considering the amount of water not exceeding 5% (w/w). Nevertheless, the amount of water allowed in the system to get the ME has reduced. The use of larger amount of sample increases the concentration of analytes in the in the ME, but also should increase the viscosity, reducing the nebulization efficiency and, thus, not resulting in the expected improvement in the limit of detection (LOD). Therefore, the use of surfactant as a constituent of the system was discarded, favoring the simpler method, avoiding a further preparation step and additional costs with the reagent. It should be pointed out that the homogenization of the ME containing 13% (w/w) Triton X-100 required a few minutes more for sample preparation, reducing the analyses throughput. Thus, the adopted composition was 3.3 g (about 40% w/w) of B7-diesel oil and 0.3 mL of H₂O/HNO₃, completed to 10 mL with *n*-propanol. It is important to emphasize that this composition is not in the border of the ME phase, shown in Figure 1-A. The adopted proportion was chosen because, even with small alterations in the proportion of the components of the system, e.g. the mass of sample or using samples with different characteristics (S10, S500 or different diesel/biodiesel mixtures), the formation of the ME is not affected. The ME developed in this work is water in oil (w/o) type, where the aqueous phase is dispersed in a continuous oil phase.

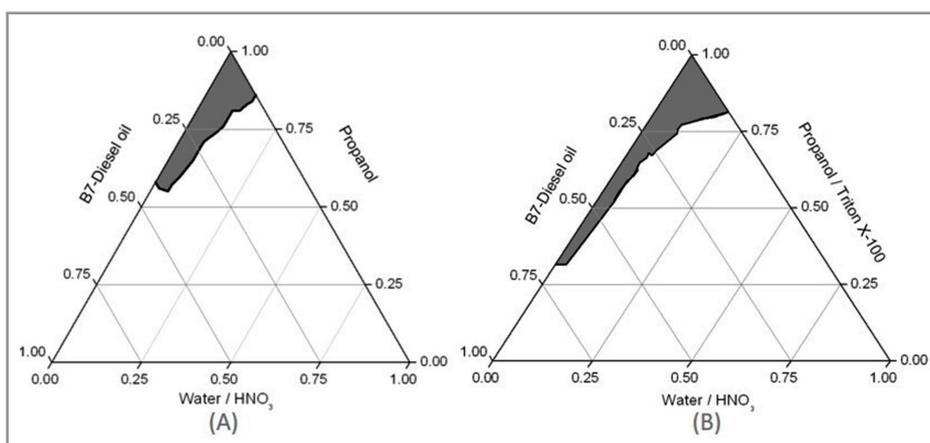


Figure 1. Ternary phase diagrams of B7-diesel oil, water/HNO₃ and *n*-propanol at 25 °C: (A) without Triton X-100 and (B) with 13% (w/w) Triton X-100. The component content in the system is in mass fraction. Microemulsion region is highlighted in gray.

Microemulsion for Calibration Curves

As pointed out by Sánchez et al. [14,15] the organic solvents can affect the nebulization process in many ways. Considering that the pneumatic aerosol is generated by interaction between the solution with the gas stream at high speed, the mean droplet size distribution in the aerosol depends on the physical properties of the solution, mainly the surface tension and viscosity. For organic solvents, surface tension is generally lower than for aqueous samples, while the viscosity shows a more variable behavior. The viscosity, e.g., affects both aspiration rate and nebulization, while density and volatility, plays important role in the transport of the aerosol [14,15]. All these events influence the amount of sample that reaches the atomizer. Thus, it is necessary that standards and samples have similar physical characteristics to prevent nebulization and transport interferences in F AAS analysis. In this work, oleic acid, toluene and mineral oil (in different proportions) were investigated as a substitute for the sample in the calibration standards. The results obtained by recovery tests with ME prepared with B7-diesel sample (free of analytes) were compared with those obtained with ME prepared with oleic acid, toluene or mineral oil (in different proportions). The best results were obtained when the sample was replaced by 0.74 g of mineral oil (about 9% w/w) as

shown by the results obtained for Cu (Figure 2). This study was carried out only for Cu considering that the physical interferences affect the transport of the solution, thus affecting all analytes in the same way. Consequently, the standards for calibration were prepared in the same way, replacing the sample by 0.74 g of mineral oil to simulate the diesel oil matrix in the ME and adding the inorganic standards into the aqueous phase. After the addition of all components, the system was manually shaken for a few seconds and the formation of a clear and stable solution was achieved. It should be emphasized that using DDW, sub-boiling distilled nitric acid and other analytical grade reagents, analytical signals measured in the ME blank were below de LOD for all analytes.

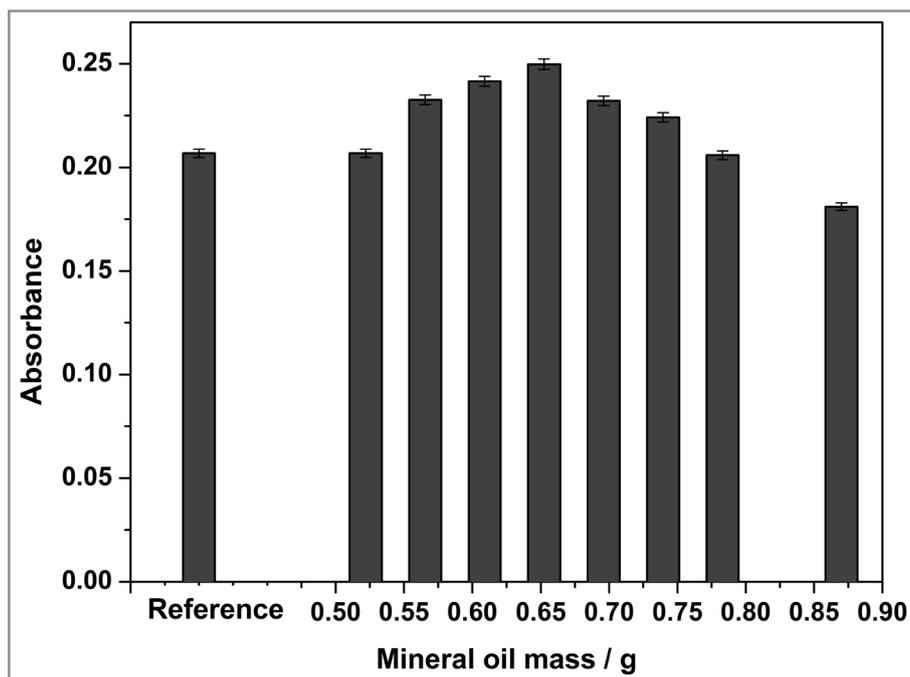


Figure 2. Evaluation of mineral oil mass added to the microemulsion for calibration. All systems contain 2 mg L^{-1} Cu, $300 \mu\text{L}$ of aqueous phase ($1.4 \text{ mol L}^{-1} \text{ HNO}_3$) and *n*-propanol (up to 10 mL). Reference: instead of mineral oil, this system contains 3.3 g of B7-diesel oil.

Optimization of the Spectral and Instrumental Parameters

The most sensitive analytical lines were used for all analytes, except for Al, for which the secondary line at 396.152 nm (91% relative sensitivity), was used. The main line for Al at 309.271 nm is within the range of strong OH absorption bands, which might cause some deterioration of the signal-to-noise ratio if not properly corrected [29]. The number of pixels used for measurements of the analytical signal was evaluated; for Pb, Cr and Sn an increase the sensitivity was obtained using 5 pixels for measurements (center and two lateral pixels; $\text{CP} \pm 2$). For the other elements, no significant increase in the signal was obtained, thus only 3 pixels (center and one lateral pixel; $\text{CP} \pm 1$) were used. These different behaviors are related with the peak profile of each element [29].

The optimization studies were performed for the following instrumental parameters: acetylene flow rate, burner height and aspiration rate. The adjustment of the aspiration rate was performed manually, observing the intensity of the analytical signal of each element, considering the maximum value of the analytical signal. With the aspiration rate near 2.8 mL min^{-1} , higher values of analytical signals were obtained for most of the analytes. Thus, the aspiration rate of 2.8 mL min^{-1} was adopted. The optimization of the other equipment conditions for analysis (burner height and acetylene flow rate) was automatically

carried out by the spectrometer software, taking the highest absorbance signal as parameter. Thus, the aspiration rate was the unique compromise condition, while the atomization and measurement conditions chose were the optimum for each element. Table II shows the selected conditions.

Figures of Merit

After the optimization procedures, calibration curves with inorganic standards added to ME were carried out for each analyte. The calibration parameters as linear regression equations, correlation coefficients as well as the figures of merit obtained for the method are presented in Table II. The characteristic concentration, (C_0), is defined as the analyte concentration that produces an absorbance signal of 0.0044 (1% absorption) with flame atomization [29]. The limit of detection (LOD) and limit of quantitation (LOQ) were calculated according to International Union of Pure and Applied Chemistry (IUPAC) recommendations, as 3 times and 10 times, respectively, the standard deviation of 10 measurements of a blank solution, divided by the sensitivity of calibration curve. The characteristic concentrations obtained by the proposed method, presented values slightly higher than those reported in the literature [29]. Correlation coefficients greater than 0.99 (except for Zn) were obtained for all investigated analytes.

Table II. Figures of Merit Obtained for the Determination of Trace Elements in B7-diesel Oil Microemulsion by HR-CS F AAS and Comparison with Data from the Literature

Analyte	Proposed method					Other methods		
	Sensitivity (L mg ⁻¹)	R ²	C ₀ ^a (mg L ⁻¹)	LOD ^b (mg kg ⁻¹)	LOQ ^b (mg kg ⁻¹)	LOD ^c (mg kg ⁻¹)	LOD ^d (mg kg ⁻¹)	LOD ^e (mg kg ⁻¹)
Cu	0.0960	0.9983	0.04	0.01	0.02	0.09	n.d	0.003
Fe	0.0403	0.9983	0.10	0.01	0.04	0.14	n.d	0.001
Ni	0.0380	0.9990	0.11	0.01	0.04	0.05	0.01	n.d
Pb	0.0247	0.9995	0.18	0.01	0.05	n.d ^f	0.01	0.0006
Zn	0.1316	0.9867	0.03	0.02	0.06	0.11	n.d	n.d
Al	0.0093	0.9995	0.47	0.07	0.3	0.12	n.d	0.003
Cr	0.0431	0.9943	0.08	0.4	1.4	n.d	n.d	n.d
Sn	0.0040	0.9998	1.00	0.3	1.1	n.d	n.d	n.d

^a C₀: Characteristic concentration.

^b The LOD and LOQ were calculated considering the mass of sample and final volume used in sample preparation (3.3 g and 10 mL, respectively).

^c LOD obtained by ICP OES.

^d LOD obtained by GF AAS.

^e LOD obtained by HR-CS ET AAS.

^f n.d: not determined.

Comparing the LODs obtained in this work with the values reported in the literature for fuel analysis such as diesel-oil, B5-diesel oil and gasoline, our results were similar to those obtained by other more sensitive techniques, such as ICP OES for Al, Cu, Fe, Ni and Zn [4] and GF AAS for Ni and Pb [30], and higher than the values obtained by F AAS for Zn with preconcentration (2.0 µg kg⁻¹) [1], and by HR-CS ET AAS for Al, Cu, Fe and Pb [7].

Analytical Results

To assure the accuracy of the proposed method the CRM NIST SRM 1084a (Wear-metals in lubricant oil) was analyzed. For this, the ME was prepared according to the procedure described in the Experimental

section (ME preparation). The results obtained (Table III) were not significantly different of the certified values at the 95% confidence level (Student's *t* test; the calculated *t*-values: Pb (1.083), Ni (3.897), Fe (2.853), Cu (2.665), Sn (1.915) and Cr (3.343) were lower than the *t*-critical = 4.303). Unfortunately, there are not certified values for Al and Zn in this material.

Table III. Analytical Results Obtained for NIST SRM 1084a by the Proposed Method (mean \pm sd; n=3)

Analyte	Certified value (mg kg ⁻¹)	Obtained value (mg kg ⁻¹)
Cu	100.0 \pm 1.9	102.0 \pm 1.3
Fe	98.9 \pm 1.4	104.5 \pm 3.4
Ni	99.7 \pm 1.6	101.5 \pm 0.8
Pb	101.1 \pm 1.3	103.6 \pm 4.0
Cr	98.3 \pm 0.8	106.6 \pm 4.3
Sn	97.2 \pm 2.6	91.2 \pm 5.4

In order to evaluate the matrix effect, recovery experiments were performed by spiking some selected samples of B7-diesel oil with inorganic aqueous standard and organic oily standard of all analytes as described in the Experimental (Analytical Procedure). The recovery values obtained were very satisfactory for most of elements, ranging from 93% to 110%, confirming the absence of the matrix effects; the exceptions were the results obtained with organic standard for Al (124%) and Sn (119%), as shown in Table IV. These relatively worse recovery values may have occurred because the mixture of samples and organic standards was not sufficiently homogeneous. However, the good results presented for most elements show also the similar behavior of organic and inorganic standard, corroborating the possibility of using inorganic aqueous standards for calibration.

Table IV. Recovery Tests Carried out with Inorganic and Organic Standards Added to B7-diesel Oil Prepared as Microemulsions (mean \pm sd; n=3)

Analyte	Inorganic standards		Organic standards	
	Spike (mg L ⁻¹)	Recovery (%)	Spike (mg L ⁻¹)	Recovery (%)
Cu	1.5	101.7 \pm 2.1	2.5	94.7 \pm 0.1
Fe	2.0	99.7 \pm 5.3	2.5	96.7 \pm 0.2
Ni	1.5	96.4 \pm 3.8	2.6	109.6 \pm 0.03
Pb	2.6	93.2 \pm 0.5	3.0	96.5 \pm 0.1
Zn	2.0	104.7 \pm 2.9	4.0	95.2 \pm 0.05
Al	15.0	99.8 \pm 4.5	15.0	124.2 \pm 0.3
Cr	3.0	103.7 \pm 2.1	3.0	102.9 \pm 0.1
Sn	8.0	96.0 \pm 1.8	10.0	118.8 \pm 0.4

Twelve B7-diesel oil samples were analyzed in this work (ten S10 and two S500). Low concentrations of Cu ($0.18 \pm 0.02 \text{ mg kg}^{-1}$) and of Fe ($0.05 \pm 0.02 \text{ mg kg}^{-1}$) in one S10 diesel oil sample and of Cr (0.9 ± 0.2 and $0.8 \pm 0.1 \text{ mg kg}^{-1}$) in two S500 diesel oil samples were found. The other samples did not present concentrations of the analytes above the LOD of the method, evidencing the good quality of the diesel oil samples. The results obtained in this work for Cu and Fe were similar to the concentrations range found in the literature using different sample preparations and techniques [4,7,31,32]. Some papers reported concentrations above the LOD for Ni, Pb, Zn and Al in diesel oil using more sensitive techniques [4,7,25,31,32] or preconcentration procedures [1,33,34]. It should be mentioned that in Brazil there is no legislation establishing maximum values for concentrations of any trace metal in diesel oil.

CONCLUSION

The method proposed in this work proved to be fast, simple and accurate for the multi-element sequential determination of Cu, Fe, Ni, Pb, Zn, Al, Cr, and Sn in B7-diesel oil samples by HR-CS F AAS. The sample preparation based on simple formation of ME of samples with *n*-propanol and water/nitric acid showed to be a fast approach for trace elements determination, when compared with digestion procedures. The construction of a phase diagram has provided the variations possibilities for sample preparation (composition, amount of sample, etc.). Moreover, the good results obtained in this work suggest that this procedure might be used with minor modification for analysis of other biodiesel/diesel mixtures or determinations of other elements in B7-diesel oil. It should be stressed that a minimum sample preparation, the use of aqueous standard in calibration and the sequential multi-element determination of analytes allowed a fast and low-cost analysis. The total time to determine eight analytes was around 5 min, due to the adjustment of wavelengths, flame parameters and composition. These features, together with LODs comparable to those of multi-elemental or more sensitive techniques, added to the robustness of flame for organic liquids analysis and the lower cost of implementation and operation, are the clear advantages of the proposed method. Moreover, it can be considered appropriate to the principles of Green Analytical Chemistry, as a small amount of a nontoxic solvent is used (5.7 mL of *n*-propanol/sample). Thus, the proposed method can be suggested as an alternative for routine analysis.

Conflict of interest

The authors declare no competing financial interest.

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