Article

Determination of Trace Elements in B5-diesel Oil by HR-CS ET AAS Using a Simple Dilute-and-Shoot Approach

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Este trabalho descreve um procedimento simples, rápido e sensível para a determinação de Al, Cd, Cu, Fe, Pb e Mn em amostras comerciais de óleo diesel B5, utilizando espectrometria de absorção atômica de alta resolução com fonte contínua e atomização eletrotérmica (HR-CS ET AAS). O procedimento consiste na simples diluição das amostras utilizando *n*-propanol, com posterior acidificação com HNO_3. A calibração com padrões aquosos pôde ser empregada para a determinação de Cu, Fe, Pb e Mn, ao passo que soluções de calibração preparadas em *n*-propanol foram necessárias para a determinação de Al e Cd. Curvas de pirólise e atomização foram investigadas para os analitos preparados em soluções aquosas e para amostras de óleo diesel B5. Um estudo envolvendo o uso de modificadores foi conduzido. 480 µg de Zr para a determinação de Al, Mn e Pb e 500 µg de Ir para a determinação de Cd foram empregados como modificadores químicos permanentes. Temperaturas de pirólise de 700 °C para Cd, 800 °C para Pb e 1000 °C para os demais elementos foram utilizadas. As temperaturas de atomização foram otimizadas em 1500 °C para Cd, 1900 °C para Pb, 2300 °C para Cu, Fe e Mn e 2500 °C para Al. Os limites de quantificação foram determinados como 0,001 µg g^{-1} para Cd e Mn, 0,002 µg g^{-1} para Pb, 0,006 µg g^{-1} para Fe e 0,01 µg g^{-1} para Al e Cu. Testes de recuperação resultaram em valores recuperados entre 89 e 120% para amostras de óleo diesel B5. O método provou ser rápido, preciso e exato para estas amostras.

This work describes a simple, fast and sensitive procedure for the determination of Al, Cd, Cu, Fe, Pb and Mn in commercial B5-diesel oil samples using high-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS ET AAS). The procedure consists on simple dilution of the samples using *n*-propanol, with further acidification with HNO_3. Calibration against aqueous standards could be employed for the determination of Cu, Fe, Pb and Mn, whereas calibration solutions prepared in *n*-propanol were required for the determination of Al and Cd. The pyrolysis and atomization curves were investigated for the analytes prepared in aqueous solutions and for the B5-diesel oil samples. A study involving the use of modifiers was carried out. 480 µg of Zr for Al, Mn and Pb determination and 500 µg of Ir for Cd determination were employed as permanent chemical modifiers. Pyrolysis temperatures of 700 °C for Cd, 800 °C for Pb and 1000 °C for the other elements were adopted. The atomization temperatures were optimized as 1500 °C for Cd, 1900 °C for Pb, 2300 °C for Cu, Fe and Mn and 2500 °C for Al. The limits of quantification were determined as 0.001 µg g^{-1} for Cd and Mn, 0.002 µg g^{-1} for Pb, 0.006 µg g^{-1} for Fe and 0.01 µg g^{-1} for Al and Cu. Recovery tests resulted in recovery values between 89 and 120% for diesel oil samples. The method has proved to be fast, precise and accurate.

Keywords: B5-diesel oil analysis, trace elements, HR-CS ET AAS

Introduction

Most of the energy consumed in the world is generated from crude oil and coal. Diesel oil is a fossil fuel obtained

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from the process of fractional distillation of petroleum. Its physicochemical properties and structure are dependent on the procedures used to obtain the oil, as well as on its origin.[1] The combustion of diesel oil results in the release of large quantities of polluting gases to the atmosphere, especially when the engine does not receive a sufficient

amount of air to achieve complete combustion. The main pollutants are carbon dioxide, nitrogen oxides, alcohols, aldehydes, ketones, sulfur compounds and hydrocarbons,[2] as well as various inorganic compounds. Thus, the search for biofuels as alternatives to minimize the environmental impact caused by emissions from the combustion of diesel oil is an important and current topic of research. An interesting alternative resides on the use of fuels obtained from vegetable oils, which are already used in diesel engines at low concentrations without the need for substantial modifications in the engine. Biodiesel has no sulfur and aromatics at appreciable concentrations in its composition, being produced from renewable energy sources and regarded as non-toxic and biodegradable.[2,3]

Diesel oil is completely miscible with biodiesel, and the mixture of the two fuels in any proportion is possible. However, conventional engines that operate based on Diesel cycle can only work properly without the need for modifications with a maximum of 20% (v/v) of biodiesel in diesel oil.[1,3,4] In Brazil, it is currently mandatory to add biodiesel to any diesel oil commercially available in the country up to a final concentration of 5%, i.e., the so-called B5-diesel.[5] In addition to the environmental aspects, the addition of biodiesel improves the lubricating properties of the fuel compared to pure diesel oil.

The trace elemental content of B5-diesel, similarly to pure diesel oil, should be closely monitored in order to attest the quality of the fuel and the potential harmful effects originating from the release of trace elements to the environment. In addition, elements such as Cu, Pb and Zn can catalyze oxidation reactions when in contact with biodiesel, reducing significantly the lifetime of the final product.[6,7]

Manganese appears naturally in a wide concentration range in fuels, but it is also intentionally added as an antiknock agent in gasoline.[8] Copper and nickel are known to promote auto-oxidative reactions, especially concerning carbon-carbon unsaturated bonds, deteriorating the fuel efficiency due to the formation of "gums".[9] Moreover, these elements reduce the efficiency of automotive catalysts, which results in an increase in emission of the carbon monoxide and oxides of sulfur and nitrogen.[9] Iron, Cu, Al and Cr from storage tanks and from the distillation process are also known to corrode engines and boilers.[10,11]

Various techniques are currently employed for the determination of trace metals in diesel oil and biodiesel samples, such as molecular absorption spectrometry,[12-14] electroanalytical techniques[15-17] and chromatography.[18] However, although good results can be, in general, obtained using these techniques, atomic absorption and emission spectrometry appear to be the techniques of choice to perform this task.[19-23]

Chaves *et al.*[20] used emulsion sample preparation to determine Co, Cu, Fe, Mn, Ni and V in diesel oil and biodiesel samples by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS).[20] Reyes *et al.*[24] carried out the determination of Ni and Pb in diesel oil and gasoline samples by electrotermal atomic absorption spectrometry (ET AAS), adopting microemulsion sample preparation and the use of permanent chemical modifiers.[24] Ghisi *et al.*[25] used tetramethylammonium hydroxide (TMAH) to allow solubilization of biodiesel in water for the determination of Cu and Fe by ET AAS. This procedure allowed the reduction of the organic content of the samples, although it involved several preparation steps, including sample heating and sonication. Calibration was carried out using TMAH in the calibration solutions.[25] Overall, although analytical procedures involving the preparation of fuel samples as emulsions and microemulsions have been proven efficient for trace element determination in these samples, these procedures are often characterized by the addition of several reagents and the need for temperature control, sonication and homogenization, leading to a somewhat lower analytical frequency when compared to a typical dilute-and-shoot process.

In this work, high-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS ET AAS) was used to carry out the determination of six elements (Al, Cd, Cu, Fe, Pb and Mn) in B5-diesel oil samples. The main goal is to have a very simple and fast dilute-and-shoot approach that can be readily applied for the analysis of diesel oil, which is an interesting alternative to the most frequently used procedures that include emulsion or microemulsion formation[21,24-27] or acid digestion.[28,29]

Experimental

Instrumentation

All measurements were carried out using a ContrAA 700 high-resolution continuum source electrothermal atomic absorption spectrometer (Analytik Jena AG, Jena, Germany). The analytical lines for Al, Cd, Cu, Fe, Pb and Mn at 309.271, 228.8018, 324.754, 248.330, 283.306 and 279.482 nm, respectively, were used. The spectral bandwidth is approximately 1.6 pm *per* pixel, and the assessment of all 200 pixels of the detector corresponds to the evaluation of a spectral region of approximately ± 0.16 nm on both sides of the analytical wavelength. The integrated absorbance for all elements was measured over three pixels (center pixel ± 1), i.e., integrating over a spectral range of approximately 5 pm.

All the experiments were performed using pyrolytically-coated transversely heated graphite furnaces with pyrolytically-coated PIN-integrated graphite platforms (Analytik Jena). Sample introduction was carried out using a MPE-5 furnace autosampler (Analytik Jena).

Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as purge and protective gas. The temperature program of the graphite furnace used for the determination of Al, Cd, Cu, Fe, Pb and Mn is shown in Table 1.

Table 1. Temperature program for the determination of Al, Cd, Cu, Fe, Pb and Mn in B5-diesel oil samples using HR-CS ET AAS

Step	Temperature / °C	Ramp / (°C s⁻¹)	Hold / s	Ar flow rate / (L min⁻¹)
Drying	90	5	20	2.0
Drying	150	10	20	2.0
Drying	300	10	10	2.0
Pyrolysis	1000[a,b]/800[c]/ 700[d]	500	20	2.0
Atomization	2500[a]/2300[b]/ 1900[c]/1500[d]	1500	6	0
Cleanout	2550	500	4	2.0

[a]Temperatures for Al; [b]temperatures for Cu, Fe and Mn; [c]temperatures for Pb; [d]temperatures for Cd.

Reagents and samples

All reagents used were at least of analytical grade. Water with a resistivity of 18.2 MΩ cm was deionized in a Milli-Q system (Millipore, Bedford, MA, USA). Nitric acid was purified by double sub-boiling distillation in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). Aqueous 1000 mg L⁻¹ stock standard solutions of Al, Cd, Cu, Fe, Pb and Mn (Merck, Darmstadt, Germany) were used. *N*-propanol (Vetec, Rio de Janeiro, Brazil) was used for dilution of B5-diesel oil samples without additional purification. Thermally deposited Zr or Ir were used as permanent chemical modifiers. In order to perform the deposition of the permanent chemical modifiers, the temperature program shown in Table 2 was applied.

Table 2. Temperature program for the deposition of 480 μg Zr or 500 μg Ir as permanent chemical modifiers onto graphite platforms using HR-CS ET AAS

Step	Temperature / °C	Ramp / (°C s⁻¹)	Hold / s	Ar flow rate / (L min⁻¹)
Drying	130	5	30	2.0
Pyrolysis	300	30	20	2.0
Atomization	1000	50	10	0
Cleanout	2000	1000	3	2.0

Polypropylene flasks (BD, Franklin Lakes, NJ, USA) were used to prepare all solutions and samples.

A total of 12 B5-diesel oil samples, purchased at local gas stations located in the state of Santa Catarina, Brazil, were analyzed. The samples were collected and stored for short periods in polypropylene bottles. For simplification, the B5-diesel oil samples will be referred to as D1-D12 from this point on.

Sample preparation

Approximately 0.5 g of each B5-diesel oil sample was accurately weighed on polypropylene flasks and mixed with 1.0 mL of *n*-propanol and 25 μL of concentrated HNO_3. The final volume was made up to 2.5 mL using *n*-propanol. Prior to the determination of Cu and Fe in some of the samples, further dilutions between 2 to 10 times were carried out, due to the naturally higher concentrations of these elements.

All samples were prepared at least in triplicate. Calibration against aqueous standards was used for Cu, Fe, Mn and Pb determination, whereas Al and Cd required calibration solutions to be prepared in *n*-propanol.

In order to carry out the determination of Cd, Pb and Mn in some samples, multiple injections of the sample in the graphite furnace were necessary as a means to improve the detection capacity. Total volumes ranging between 60 μL and 120 μL were inserted into the graphite furnace in successive 20 or 30 μL injections. In these cases, after each injection, the temperature program was applied and interrupted at the end of the pyrolysis stage, except after the last injection, when the temperature program was applied until its completeness.

Results and Discussion

Sample preparation

Method development initiated with the choice of an adequate solvent to dilute the B5-diesel oil samples. Aiming at the use of a low-toxicity compound, ethanol and *n*-propanol were both evaluated. Preliminary tests indicated no significant differences in the magnitude of the analytical signals obtained in either of the solvents, but direct dilution of the diesel oil samples in ethanol lead to phase separation within a few seconds after mixing. This was, to some extent, expected given the natural composition of diesel oil, which is mostly paraffins, olefins and aromatics, with lower solubility in polar media. Fortunately, phase separation was absent when *n*-propanol was used as the solvent for dilution of B5-diesel oil, and simple dilution with *n*-propanol was finally chosen as the sample preparation step prior to analysis using HR-CS ET AAS.

Temperature program optimization

Considering the high organic content of the samples, it became necessary to introduce three drying steps prior to pyrolysis. These steps involve a relatively mild heating in order to avoid that the sample is projected on the walls of the graphite tube or even the quartz windows. This could result in analyte loss and negatively influence the accuracy and precision of the procedure. Pyrolysis and atomization curves for the analytes are presented in Figure 1.
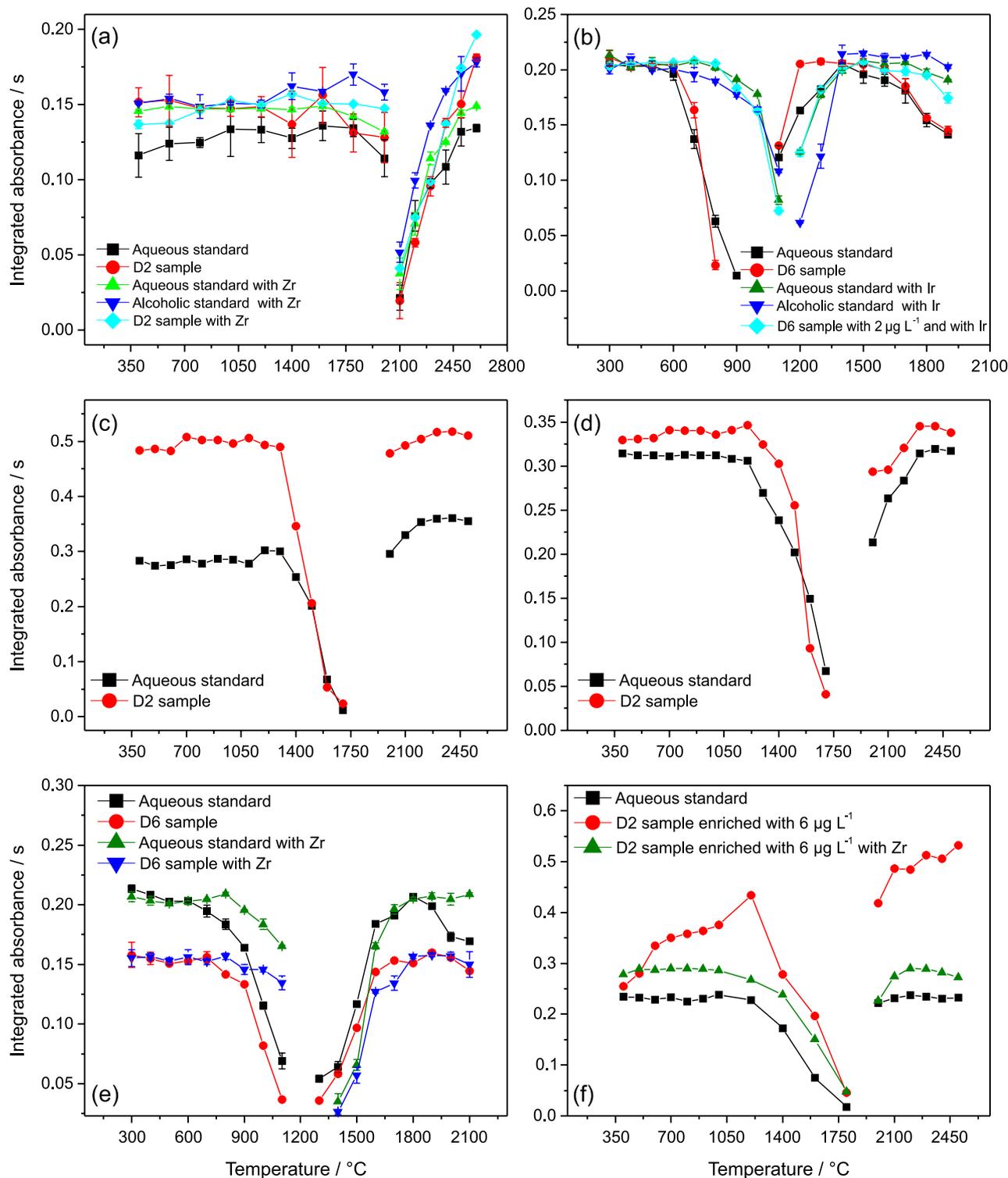
Figure 1. Pyrolysis and atomization curves for: (a) Al, (b) Cd, (c) Cu, (d) Fe, (e) Pb and (f) Mn in standard aqueous solutions and in a B5-diesel oil sample diluted with *n*-propanol. Refer to the text for information on individual conditions.

Aluminum

The optimization of pyrolysis and atomization temperatures was performed using a 20 µg L^{-1} Al aqueous standard, a 20 µg L^{-1} solution of Al prepared in *n*-propanol and the sample D2. The results are shown in Figure 1a.

The curves show that although thermal stability for Al is high, as expected, the precision obtained in the absence of a chemical modifier was seriously compromised, leading to typical relative standard deviation (RSD) values around 10-15% due to memory effect. This effect was already reported in a previous work[30] and it can be at least partially explained considering the atomization mechanism for Al, which involves the formation of carbides, suggesting significant interaction of the analyte with the graphite surface of the platform. Regarding the D2 B5-diesel oil sample, it is assumed that despite the decomposition that occurs during the pyrolysis step, a relatively large amount of carbon is available to interact with Al. However, the direct interaction of Al with the graphite platform may result in the formation of intercalation compounds, with additional influence on the atomization efficiency and on the precision of successive measurements.[30] As an attempt to overcome this effect, pyrolysis and atomization curves were also conducted using a graphite platform containing 480 µg Zr as a permanent chemical modifier, which could inhibit the interaction of aluminum with the structure of the graphite platform. As expected, the precision was significantly improved upon the use of Zr modifier, and this condition was considered as optimum for all further experiments.

Figure 1a shows that Al was stable up to temperatures as high as 1800 °C, with or without a chemical modifier. However, the use of pyrolysis temperatures higher than 1000 °C resulted in no evident benefits, since the organic content of the B5-diesel oil matrix is likely to be completely decomposed and volatilized at temperatures below 1000 °C. The use of excessively high temperatures could also shorten the lifetime of the graphite tube. Considering these aspects, a pyrolysis temperature of 1000 °C was adopted. Pyrolysis and atomization curves were also carried out using a 20 µg L^{-1} Al solution prepared in *n*-propanol, and no significant differences in the thermal behavior of the analyte were noticed, when compared to the D2 sample or with an aqueous standard.

The atomization curves show an approximate linear increase in signal with an increase in the temperature, which is expected, considering the refractory nature of Al. As a compromise between sensitivity and longer tube lifetime, atomization was maintained at 2500 °C.

Cadmium and lead

Pyrolysis and atomization temperatures for Cd and Pb were established considering 2 and 30 µg L^{-1} aqueous standards, respectively, in addition to a 2 µg L^{-1} Cd standard prepared in *n*-propanol and the sample D6 for both analytes. The referred sample was enriched with 2 µg L^{-1} Cd only for the purpose of this study. The results are shown in Figures 1b and 1e for Cd and Pb, respectively.

Due to the high volatility of these analytes and considering the need to adopt relatively high pyrolysis temperatures due to the highly concentrated matrix, the use of a permanent chemical modifier was proven necessary. Several studies in the literature report on the use of chemical modifiers for the determination of Cd and Pb in different samples.[31] The performance of two permanent modifiers was evaluated: 500 µg Ir for Cd and 480 µg Zr for Pb determination, thermally deposited onto the graphite platform surface.

As the most volatile element amongst the group of analytes in this study, Cd has shown to be more sensitive to the use of a chemical modifier. Figure 1b shows that without the use of a modifier, the signal was maintained stable up to 600 °C pyrolysis, whereas the use of thermally-deposited Ir provided thermal stability up to 700 °C, allowing more efficient elimination of the matrix and reduced background levels to be obtained. Under these conditions, the optimum atomization temperature was chosen as 1500 °C. Similarly to the procedure adopted for Al, the pyrolysis and atomization curves for Cd were also carried out for a standard solution prepared in *n*-propanol. As shown in Figure 1b, the observed thermal behavior of the analyte in the organic solvent is very similar to that observed for an aqueous standard and for the D6 diesel oil sample.

In Figure 1b, it can be noted that Cd showed good thermal stability (up to 700 °C pyrolysis) and the integrated absorbance increased up to an atomization temperature of 1500 °C using 500 µg Ir as a permanent chemical modifier. For Pb determination, the use of 480 µg Zr as a permanent modifier allowed a pyrolysis temperature of up to 800 °C and atomization at 1900 °C to be used.

Copper and iron

Figures 1c and 1d show the pyrolysis and atomization curves obtained for Cu and Fe, respectively, in aqueous standards prepared to contain 15 µg L^{-1} of each analyte and in the sample D2. It is possible to observe that pyrolysis temperatures of up to 1300 °C for Cu and 1200 °C for Fe can be used without any appreciable loss in sensitivity and without the need for a chemical modifier. Good precision

was obtained for both elements (RSD < 5%). A pyrolysis temperature of 1000 °C was selected for both elements, for the same reasons provided on the discussion regarding the pyrolysis temperature chosen for Al.

The atomization curves show that the integrated absorbance for both analytes remained approximately constant at temperatures higher than 2300 ºC, and this temperature was selected as optimum for the determination of both elements.

Manganese

The pyrolysis and atomization curves for a 6 µg L^{-1} Mn aqueous standard and for the D2 sample, which was enriched with 6 µg L^{-1} Mn, are shown in Figure 1f. The pyrolysis curve obtained for an aqueous solution of Mn shows that the element is thermally stable up to approximately 1000 °C. However, when the same study was conducted using the D2 diesel oil sample, an intriguing phenomenon was observed. As shown by the ball-labeled curve in Figure 1f, an increase in the pyrolysis temperature led to an increase in the integrated absorbance. This phenomenon was also observed during the optimization of the atomization temperature.

This behavior is highly suggestive of a memory effect, wherein the analyte is accumulated within the graphite structure after the execution of the temperature program and is gradually released into the gas phase in subsequent analytical cycles, resulting in erroneously high signals. In order to check and confirm this hypothesis, the integrated absorbance was measured using only *n*-propanol immediately after completing an analytical cycle with the D2 sample, and signals as high as 1.6 s could be detected in the absence of the analyte. It is believed that *n*-propanol is capable of infiltrating the pores of the graphite platform, resulting in a carry-over effect of Mn into the interstice of graphite, causing the accumulation of the metal. The ability of Mn to form carbides certainly contributes to this assumption.

In order to reduce memory effects, the use of a carbide-forming chemical modifier was proven successful. Pyrolysis and atomization curves were carried out using 480 µg Zr thermally deposited as a permanent modifier, and RSD values lower than 5% were obtained. Optimum conditions for Mn determination include pyrolysis and atomization temperatures of 1000 and 2300 °C, respectively, using 480 µg Zr as a permanent chemical modifier.

Analytical figures of merit

Prior to the analytical determination of the analytes, three different calibration approaches were evaluated regarding the

sensitivity: calibration against aqueous standards, against standards prepared in *n*-propanol and analyte addition calibration. The relative sensitivities obtained from the various calibration approaches are comparatively shown in Figure 2. For reference, the sensitivity obtained with analyte addition calibration was taken as 100%, and it is marked as the dotted horizontal line in Figure 2.
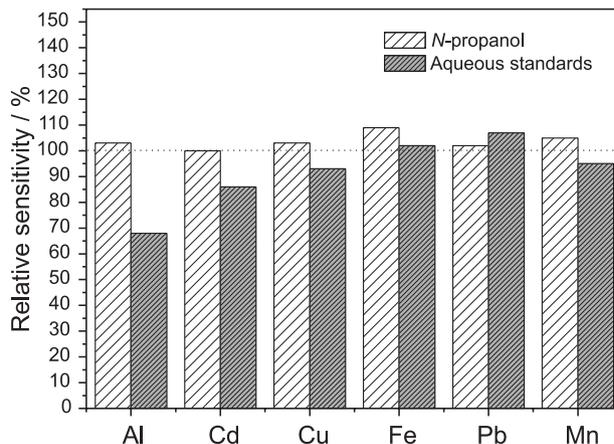
Figure 2. Relative sensitivities obtained under different calibration approaches for the determination of Al, Cd, Cu, Fe, Pb and Mn in diesel oil samples by HR-CS ET AAS. The dotted horizontal line represents the sensitivity obtained using analyte addition calibration, which was taken as the baseline for comparison.

Calibration curves were all conducted on the same day and under the same analytical conditions for each analyte. The results indicate that the differences in sensitivity obtained using calibration standards prepared with *n*-propanol or with deionized water are less than 10% compared to analyte addition calibration for Cu, Fe, Mn and Pb. Due to this negligible difference in sensitivity, calibration against aqueous standards could be employed to carry out interference-free determination of this group of elements.

The slopes of the calibration curves were significantly different from each other in the case of Al and Cd. For Al, a difference in sensitivity of over 32% comparing calibration against aqueous standards to analyte addition calibration was obtained, whereas for Cd the difference was 14%. However, the sensitivities were roughly the same when calibration was carried out using inorganic standards prepared in *n*-propanol and with analyte addition calibration, suggesting that simple dilution using *n*-propanol would be sufficient to provide good accuracy for Al and Cd determination.

Following the definition of the calibration procedures for all elements, the figures of merit of the method were determined and are presented in Table 3.

The limit of detection (LOD) was calculated as three times the standard deviation obtained from ten consecutive

Table 3. Analytical figures of merit obtained for the determination of Al, Cd, Cu, Fe, Pb and Mn in B5-diesel oil samples by HR-CS ET AAS

	Al	Cd	Cu	Fe	Pb	Mn
Wavelength / nm	309.271	228.802	324.754	248.327	217.000	279.482
Working range / ng	0.1-1.0	0.010-0.1	0.1-1.0	0.1-1.0	0.1-1.0	0.04-0.2
Slope / $(s\ pg^{-1})$	0.0004	0.005	0.001	0.0008	0.0005	0.002
R^2	0.9991	0,9999	0.9993	0.9998	0.9993	0.9992
LOQ / $(\mu g\ g^{-1})$	0.01	0.001	0.01	0.006	0.002	0.001
RSD / %	1-5	1-5	1-5	2-6	2-6	1-6
m_0 / pg	11	1	4	5	9	2

LOQ: limit of quantification; R^2: linear correlation coefficient.

readings of the blank divided by the slope of the calibration curve, and the limit of quantification (LOQ) as 3.3 times the calculated LOD. Both methods showed good linearity (R > 0.999), LOQ lower than 0.01 ng g^{-1} and a good precision with RSD values better than 7%, suitable for the proposed determinations in B5-diesel oil samples. The calculated characteristic masses (m_0) were all within 10% of the variation range concerning the values informed by the manufacturer, which attests the adequate operating conditions of the instrument.

Analytical application

Initially, the accuracy and precision of the proposed method for all analytes was investigated by means of recovery tests in commercial B5-diesel oil samples. Enrichment of the samples was accomplished by the addition of known amounts of inorganic standards, after dilution with *n*-propanol. The results are shown in Table 4.

The recovery values obtained for Al, Cd, Cu, Fe, Mn and Pb in B5-diesel samples were all within 89-120% range, which is considered adequate for the purpose of recovery experiments.

The proposed method was applied to the analysis of twelve B5-diesel oil samples from different regions of the state of Santa Catarina, Brazil, using the conditions previously described. The values determined for Al, Cd, Cu, Fe, Mn and Pb are shown in Table 5.

As shown in Table 5, the overall concentrations are relatively low, which justify the need for highly sensitive quantification approaches. The majority of the concentration values are around a few tens of ng g^{-1}.

Conclusions

The sample preparation procedure proposed proved to be very fast and extremely simple, avoiding complicated procedures, such as digestion, which often requires strong

Table 4. Results from recovery tests for the determination of Al, Cd, Pb, Cu, Fe and Mn in B5-diesel oil samples ($n = 3$)

Al			Cd			Cu		
Added / $(\mu g\ g^{-1})$	Determined / $(\mu g\ g^{-1})$	Range / %	Added / $(\mu g\ g^{-1})$	Determined / $(\mu g\ g^{-1})$	Range / %	Added / $(\mu g\ g^{-1})$	Determined / $(\mu g\ g^{-1})$	Range / %
0	0.116 ± 0.014	–	0	0.001 ± 0.0001	–	0	0.109 ± 0.001	–
0.050	0.163 ± 0.011	98	0.002	0.003 ± 0.0002	100	0.050	0.169 ± 0.006	106
0.100	0.219 ± 0.037	101	0.004	0.006 ± 0.0003	120	0.100	0.212 ± 0.023	101
0.200	0.337 ± 0.064	107	0.008	0.008 ± 0.0013	89	0.150	0.246 ± 0.022	95
Fe			Pb			Mn		
Added / $(\mu g\ g^{-1})$	Determined / $(\mu g\ g^{-1})$	Range / %	Added / $(\mu g\ g^{-1})$	Determined / $(\mu g\ g^{-1})$	Range / %	Added / $(\mu g\ g^{-1})$	Determined / $(\mu g\ g^{-1})$	Range / %
0	0.147 ± 0.020	–	0	0.002 ± 0.0001	–	0	< 0.002	–
0.050	0.222 ± 0.013	112	0.050	0.054 ± 0.001	96	0.020	0.020 ± 0.002	100
0.100	0.272 ± 0.014	110	0.100	0.097 ± 0.001	95	0.040	0.037 ± 0.005	108
0.150	0.305 ± 0.029	103	0.150	0.160 ± 0.001	105	0.060	0.055 ± 0.005	109

Table 5. Concentrations obtained for Al, Cd, Cu, Fe, Pb and Mn in B5-diesel oil samples by HR-CS ET AAS (average ± confidence interval at a 95% statistical level; $n = 3$)

Region	Sample	Al / (µg g⁻¹)	Cd / (µg g⁻¹)	Cu / (µg g⁻¹)	Fe / (µg g⁻¹)	Pb / (µg g⁻¹)	Mn / (µg g⁻¹)
Capital	D1	0.169 ± 0.014	< 0.001	0.097 ± 0.003	1.403 ± 0.052	0.004 ± 0.002	0.012 ± 0.0002
	D2	0.116 ± 0.014	< 0.001	0.337 ± 0.021	0.271 ± 0.024	< 0.002	0.001 ± 0.0001
	D3	< 0.01	< 0.001	0.448 ± 0.010	4.192 ± 0.126	0.005 ± 0.001	0.014 ± 0.002
	D4	0.032 ± 0.003	0.001 ± 0.0003	0.110 ± 0.001	0.147 ± 0.020	0.006 ± 0.001	< 0.001
SE	D5	0.033 ± 0.001	0.001 ± 0.0002	0.036 ± 0.003	0.171 ± 0.001	0.002 ± 0.00002	0.002 ± 0.0007
	D6	0.048 ± 0.007	0.008 ± 0.002	0.041 ± 0.005	0.295 ± 0.030	0.014 ± 0.003	0.003 ± 0.0001
West	D7	0.046 ± 0.015	0.003 ± 0.0001	0.402 ± 0.065	0.217 ± 0.063	0.044 ± 0.008	0.007 ± 0.0006
	D8	0.067 ± 0.011	0.012 ± 0.003	0.116 ± 0.009	0.021 ± 0.002	0.142 ± 0.016	0.003 ± 0.0008
North	D9	0.028 ± 0.006	0.016 ± 0.003	0.046 ± 0.006	0.091 ± 0.012	0.007 ± 0.0003	< 0.001
	D10	0.025 ± 0.008	0.035 ± 0.001	0.066 ± 0.004	0.106 ± 0.011	0.234 ± 0.014	0.008 ± 0.001
South	D11	0.030 ± 0.006	0.032 ± 0.005	0.061 ± 0.005	0.240 ± 0.042	0.030 ± 0.006	0.002 ± 0.0005
	D12	0.190 ± 0.003	0.047 ± 0.006	0.062 ± 0.004	0.092 ± 0.006	0.280 ± 0.016	0.005 ± 0.001

acids and heating. Dilution of samples with *n*-propanol is less prone to contamination, and if necessary, organic solvents can be fairly easily purified and dilution can be easily adjusted to the expected concentration of the elements of interest. Moreover, the procedure adopted for the pre-concentration of analytes such as Cd, Pb and Mn in the graphite furnace through multiple injections of the sample is a simple and elegant alternative to allow quantification of these elements, which are typically found at very low concentrations in diesel oil samples. The analytical method was proven to be precise, accurate and allowed the determination of trace elements in most of the analyzed B5-diesel oil samples. The use of Zr and Ir permanent modifiers has shown to be required for the determination of Al, Cd, Pb and Mn, allowing better repeatability, thermal stability and reducing memory effects. The other elements do not require the use of a chemical modifier, which further simplifies the procedure. Calibration can be performed using aqueous standards for Cu, Fe, Mn and Pb, whereas calibration solutions in *n*-propanol are required for the determination of Al and Cd. In all cases, inorganic standards were found to be suitable for calibration. Low limits of quantification and good recovery values proved that the method is suitable for the determination of Al, Cd, Cu, Fe, Mn and Pb in B5-diesel oil samples.

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