

Optimization of an open-focused microwave oven digestion procedure for determination of metals in diesel oil by inductively coupled plasma optical emission spectrometry

Flavio W. Sant'Ana^{a,d}, Ricardo E. Santelli^a, Alessandra R. Cassella^b, Ricardo J. Cassella^{c,*}

^a Programa de Pós Graduação em Geoquímica, Universidade Federal Fluminense, Outeiro de São João Batista s/n, Centro, Niterói, RJ 24020-150, Brazil

^b PETROBRAS, CENPES, PDEDS/QM, Rio de Janeiro, Brazil

^c Departamento de Química Analítica, Universidade Federal Fluminense, Outeiro de São João Batista s/n, Centro, Niterói, RJ 24020-150, Brazil

^d Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, INMETRO, Rio de Janeiro, Brazil

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Abstract

This work reports the optimization of a focused microwave assisted procedure for the wet acid dissolution of diesel oil in order to allow the determination of metals in the samples by inductively coupled plasma optical emission spectrometry (ICP-OES). The dissolution process was monitored by measuring residual carbon content (RCC), also by ICP-OES, in the final solutions obtained after application of digestion program. All experimental work was performed using a commercial sample of diesel oil containing $85.74 \pm 0.13\%$ of carbon. The initial dissolution program comprised three steps: (i) carbonization with H_2SO_4 ; (ii) oxidation with HNO_3 and (iii) final oxidation with H_2O_2 . During work it was verified that the first step played an important role on the dissolution process of this kind of sample. It is therefore, necessary to give a detailed optimization of such step. Employing the optimized conditions it was possible to digest 2.5 g of diesel oil with a 40 min-heating program. At these conditions, residual carbon content was always lower than 5%. Optimized methodology was applied in the determination of metals in three diesel oil samples by ICP-OES. Recovery tests were also performed by adding 10 μg of metals, as organic standards, to the samples before digestion. Recovery percentages always higher than 90% were obtained for the metals of interest (Al, Cu, Fe and Ni), except for Zn, which presented recoveries between 70 and 78%.

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1. Introduction

Diesel oil is a mixture of hydrocarbons with boiling points that vary between 170 and 370 °C, which corresponds to the intermediary distillate fraction from petroleum. Hydrocarbons present in diesel oil contain from 9 to 20 carbon atoms, corresponding to a fraction lighter than fuel oil and heavier than kerosene. The mechanisms of degradation of diesel oil are very complex and they were not totally elucidated, but it is evident that the stability of the oil depends on its chemical composition. The presence of some metals like copper, iron and zinc, at trace level, can affect the stability of the oil, accelerating its

oxidation ($\text{Cu} > \text{Fe} > \text{Zn}$). In this context, the contact of diesel oil with metallic components of the storage system can result in contamination of the product with metals as organometallic compounds [1]. This way, the development of reliable methods for the determination of metals in diesel oil is a very important issue.

Determination of metals in organic liquids like oils by plasma-based techniques can be performed utilizing three approaches: (1) dilution of sample in a convenient organic solvent and introduction of the solution obtained into the instrument [2–4]; (2) preparation of an emulsion with the sample and its introduction into the spectrometer [5–7] and (3) digestion of the sample before injection using microwave radiation, hot plate or dry ashing [8–18]. The use of the first two approaches is suitable when a low manipulation of the samples is required, but it is limited by the small number of

* Corresponding author. Tel.: +55 21 2629 2222; fax: +55 21 2629 2143.
E-mail address: cassella@vm.uff.br (R.J. Cassella).

metallic standard solutions prepared in oil available in the market [19,20]. In the other hand, the third approach is slower and requires a tedious digestion work, but aqueous standard solutions can be used in the calibration strategy.

Digestion procedures are regularly carried out on hot plates with open vessels using acid or basic reagents, which, in most cases, require several hours of heating to achieve total dissolution of sample [21]. Employment of microwave radiation for heating in the preparation of organic or inorganic samples accelerates this step, providing results comparable to those obtained after heating on hot plates. Additionally, the development of dissolution procedures based on the use of microwave radiation presents other advantages over classical methods such as simplicity and the possibility of digestion of difficult matrices [22]. The high cost of instrumentation can be considered as disadvantage. Some review papers were published in the specialized literature, reporting the developments achieved in microwave sample preparation [23–25].

The use of open-focused microwave ovens has increased since 1990s. In this kind of equipment, the sample is put into the flask located through the microwave radiation guide and it is directly irradiated by all microwave energy generated in the magnetron. This approach allows the use of microwave ovens with low power without losing efficiency. Also, in contrast with closed-vessel microwave ovens, open-focused ones operate under atmospheric pressure, lowering the risk to the operator. Other advantages such as low cooling time, possible introduction of reagents during procedure and the possibility to digest larger quantities of sample are relevant [26].

Although open- and closed-vessel microwave ovens are now widespread in analytical laboratories, their application for the digestion of different kinds of petroleum derived oils is still scarce. A restricted number of papers report the use of closed-vessel microwave ovens for this task [9–14], while very few papers describe the utilization of open-focused microwave ovens for the same purpose [15–18]. It is important to remark that only three papers were found in the current literature reporting the microwave-assisted digestion of diesel oil. These papers just relate the application of methods with closed-vessel microwave ovens.

Ulrich and Wichser [27] promoted a previous digestion of 200 mg of diesel oil for 12 h on a hot plate with 3 ml of ultra pure HNO_3 . After elapsed this time, 1 ml of H_2O_2 was added and the vessel was closed and adjusted in the microwave cavity where it was irradiated for 33 min at 1000 W. After cooling, which took 30 min the flask was opened and the volume was completed to 10 ml with water. Metals of interest were determined in this final solution by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) techniques.

Hearn et al. [28] used a closed-vessel microwave procedure for the digestion of diesel oil in order to determine sulfur by ICP-MS. A reagent mixture of HNO_3 and H_2O_2 was employed and the heating program lasted 45 min (ramp from 500 to 1000 W in 15 min + 1000 W for 30 min). The greatest limitation of this procedure was the low sample mass (100 mg) permitted for the digestion.

In turn, Heilmann et al. [29] compared different sample preparation methods for the determination of sulfur in gasoline and other fuel samples by isotope dilution ICP-MS. One of the methods tested was the digestion of samples with a closed-vessel microwave oven previously to injection into the spectrometer. A four-step-heating program was designed, which took around 40 min to be completed using a mixture containing 5 ml of concentrated HNO_3 with 2 ml of H_2O_2 and 200 mg of sample. A maximum power of 1000 W was set leading the system to achieve a maximum temperature of 220 °C.

The goal of this work was to optimize a digestion procedure of diesel oil samples for the determination of some metals of interest (Al, Cu, Fe, Ni and Zn) by ICP-OES. The digestion was performed using an open-focused microwave oven as energy source and the residual carbon content (RCC) was used as variable to control the efficiency of the process [17]. Also, it is important to remark that this paper is the first report about the dissolution of diesel using an open-focused microwave oven device.

2. Experimental

2.1. Instrumentation

A Jobin Yvon (Longjumeau Cedex, France) Ultima 2 sequential ICP-OES was used throughout the experimental work. It was equipped with a Meinhard nebulizer and a cyclonic chamber to introduce samples and standards. The operational conditions employed are summarized in Table 1.

The digestion procedure was conducted in a focused microwave oven with three cavities from Prolabo (Fontenay-sous-Boi, France), model Microdigest 3.6. Throughout whole experimental work only one cavity was used in order to guarantee the repeatability of the microwave irradiation. Acid vapors generated during experiments were aspirated and bubbled into 10% (m/v) KOH solution using a suitable pumping system also provided by Prolabo.

Table 1
Operational parameters of the ICP-OES for the measurement of metals and residual carbon content in the digested samples

Parameter	Metals	Residual carbon
RF generator power (kW)	1.20	1.15
Plasma gas flow rate (l min^{-1})	12	12
Nebulizer gas flow rate (l min^{-1})	0.45	0.45
Nebulizer pressure (bar)	2.30	2.30
Nebulizer	Meinhard	Meinhard
Spectral line (nm)		
C		193.026
Al	394.401	
Fe	259.940	
Cu	324.754	
V	311.838	
Zn	213.856	
Ni	221.647	
Y (internal standard)	224.306	

A Perkin Elmer (Norwalk, CT, USA) 2400 series II elemental analyzer coupled with a Perkin Elmer AD-4 microbalance was employed for the determination of the percentage of organic carbon in the sample taken as reference. The system was equipped with a conductivity detector.

2.2. Reagents

All water (18 M Ω cm resistivity) used throughout experimental work was obtained in a Simplicity Milli-Q Water System (Millipore, Milford, MA, USA). The reagents (concentrated H₂SO₄, HNO₃ and H₂O₂, all from Merck, Darmstadt, Germany) were of analytical grade and used as received.

Aqueous stock standard solutions with 1000 mg l⁻¹ concentration of all metallic elements studied were purchased from SPEX (Metuchen, NJ, USA). Oil stock standard solutions with 1000 μ g g⁻¹ concentration of all elements were provided by Conostan (Houston, TX, USA).

Urea reference solutions (0.02–1%, w/v, in carbon) employed in the determination of RCC were prepared from a 10% (w/v) in carbon urea stock solution. All reference solutions were prepared in 10% (v/v) HNO₃ medium and contained 1 mg l⁻¹ Y as internal standard.

Three samples of diesel oil were purchased from three local gas stations of different distributors.

2.3. Optimization strategy

Optimization strategy was based on the obtaining maximum mineralization employing maximum amount of sample and minimum amounts of reagents in a shortest time. As mentioned before, the efficiency of the mineralization was monitored by measuring the RCC by ICP-OES employing the emission line of carbon at 193.026 nm [17] and operational conditions shown in Table 1.

The parameters to be optimized (volume of concentrated H₂SO₄ and HNO₃; irradiation power and time in carbonization step; volume of H₂O₂ added in last step and mass of sample) were chosen taking into account that diesel oil digestion follow three steps: (i) carbonization, with concentrated H₂SO₄, in which the oil is dehydrated and a first break of carbon chains

is performed; (ii) partial oxidation with concentrated HNO₃, in which less resistant organic matter is mineralized and (iii) total oxidation with H₂O₂, in which more resistant organic matter is destroyed. The initial program tested is shown in Table 2.

Internal standardization with 1 μ g ml⁻¹ Y was used as quantification strategy for RCC in order to eliminate transport interferences due to the presence of viscous H₂SO₄ in the solutions obtained. Optimization was performed by univariate approach (varying each parameter at a time), except for the last step of the program. Sample A, containing 85.74 \pm 0.13% carbon ($n = 3$), was used in all optimization experiments.

2.4. Determination of metals in diesel oil samples

A mass of 2.5 g of diesel oil was accurately weighted in the borosilicate vessel of the open-focused microwave oven, 5 ml of concentrated H₂SO₄ were added and a power of 60 W was applied for 5 min. After elapsed this time, more 5 ml of concentrated H₂SO₄ were added to the mixture and an increasing power was applied in two stages: (a) 120 W for 10 min and (b) 150 W for 10 min. Then, 4 ml of concentrated HNO₃ were added and the solution was irradiated for 10 min at 210 W power. In order to complete the digestion cycle, 10 ml of H₂O₂ were added and the mixture was irradiated for more 5 min. The obtained solution was left to stand until achieve room temperature and quantitatively transferred to a 50-ml-volumetric flask. Then, 250 μ l of a 200 mg l⁻¹ Y (internal standard, 1 μ g ml⁻¹ final concentration) solution were added and the volume was made up to the mark with water. Metals of interest (Al, Cu, Fe, Ni and Zn) were determined by ICP-OES in this final solution employing internal standardization approach due to the presence of viscous H₂SO₄. Analytical blanks were prepared by employing the same procedure without sample. ICP-OES operational conditions for the determination of each metal are also expressed in Table 1.

3. Results and discussion

Releasing of metals from organic structure of the diesel oil is a fundamental condition for their accurate and sensitive measurements by ICP-OES. This releasing can be attained by the evaluation of RCC in the digestates obtained after digestion of oil, which must be lower than 10% [30]. This way, all optimization was performed searching for experimental conditions that resulted in lowest RCC in final solutions. RCC was calculated taking into account the amount of carbon remained in the solution after digestion, which was determined by ICP-OES. This amount was then related to the initial amount of carbon added for digestion according to the following expressions:

$$RCC(\%) = \frac{C_{\text{solution}}(\%) \times \frac{V_{\text{final}}(\text{ml})}{100}}{M_{\text{sample}}(\text{g}) \times C_{\text{sample}}(\%)} \times 100$$

which results in

$$RCC(\%) = \frac{C_{\text{solution}}(\%) \times V_{\text{final}}(\text{ml})}{M_{\text{sample}}(\text{g}) \times C_{\text{sample}}(\%)}$$

where $C_{\text{solution}}(\%)$ and $V_{\text{final}}(\text{ml})$ are the concentration of carbon found by ICP-OES and the volume of the final solution,

Table 2
Initial heating program tested for the digestion of diesel oil for metals determination by ICP-OES

Step	Acid	Volume (ml)	Power (W)	Time (min)
1 (carbonization)	H ₂ SO ₄	10	60	3
2 (partial oxidation)	HNO ₃	5	90	5
			120	5
			150	10
3 (partial oxidation)	HNO ₃	5	210	10
4 (final oxidation)	H ₂ O ₂	10	210	5

Mass of sample taken was 1 g.

respectively; M_{sample} (g) is the mass of sample digested and C_{sample} (%) is the percentage of carbon in the sample previously determined by elemental analysis (in the whole optimization it was 85.74%).

3.1. Optimization of carbonization step

In the carbonization step, the influences of H_2SO_4 volume, irradiation power and time were studied. The possible inclusion of a second carbonization in the program was also evaluated.

3.1.1. Influence of H_2SO_4 volume

In this experiment, the irradiation power and time were maintained at initial values, 60 W and 3 min, respectively. The influence of the volume of concentrated H_2SO_4 added was investigated in the range 2–10 ml, always with 1 g of sample. All digestions were carried out in triplicate. The obtained results are shown in Fig. 1.

As can be seen, the volume of concentrated H_2SO_4 employed in the carbonization presented remarkable effect on the RCC obtained at the end of digestion. In a general way, for highest volumes of concentrated H_2SO_4 lowest RCC was verified, indicating that, in these conditions, more efficient breaking of long organic chains was attained. When 2 ml of concentrated H_2SO_4 were added a large amount of solid carbon deposit was observed in the vessel at the end of heating program, leading to the measurement, in solution, of a RCC lower than actual. Volumes of concentrated H_2SO_4 higher than 10 ml were not tested in order to avoid excessive acidity and viscosity in the final solution, which could disturb the measurement of metals (and RCC) by ICP-OES. Therefore, a volume of 10 ml concentrated H_2SO_4 was employed for further experiments.

3.1.2. Influence of irradiation power

Once the volume of concentrated H_2SO_4 to be employed was established, the irradiation power was varied in order to verify its

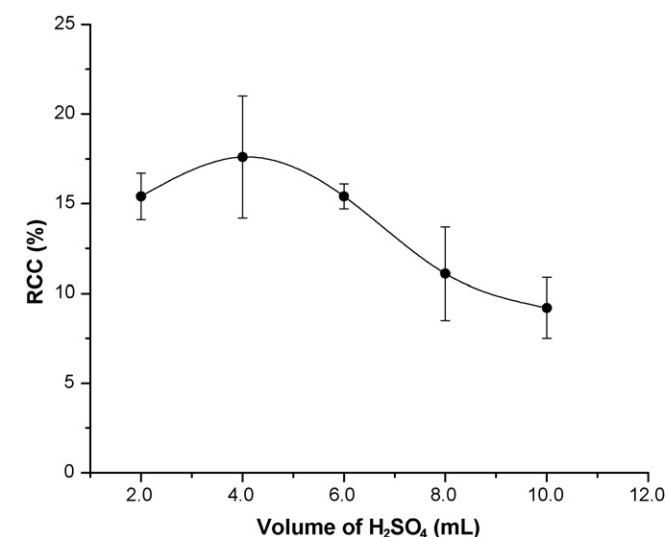


Fig. 1. Influence of the volume of concentrated H_2SO_4 on the mineralization efficiency of diesel oil by focused microwave oven procedure. Sample mass = 1 g.

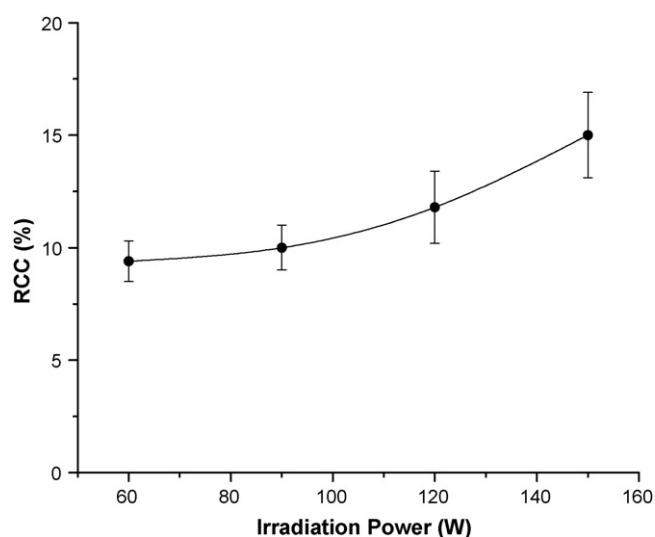


Fig. 2. Influence of irradiation power on the mineralization efficiency of diesel oil by focused microwave oven procedure. Sample mass = 1 g.

effect on diesel oil mineralization. The influence of irradiation power was examined between 60 and 150 W, also for 1 g of sample. The results obtained in this experiment are shown in Fig. 2.

The irradiation power showed noticeable influence on oil mineralization. In opposition to the expected behavior, the RCC increased from 9.5 to 15% with the increase of irradiation power from 60 to 150 W. Also, the formation of black solid deposits on vessel walls was observed when an irradiation power of 120 W or 150 W was used. This may be due to fast dehydration of the organic chains of the oil with consequent formation of carbon residues. Such carbon agglomerates were more resistant to mineralization with HNO_3 and H_2O_2 resulting in higher values of RCC in final solution. This way, an irradiation power of 60 W was chosen for the methodology.

3.1.3. Influence of irradiation time

In order to complete the evaluation of carbonization step, the influence of irradiation time was studied in the range 3–10 min, also employing sample masses of around 1 g. The behavior of RCC through irradiation time variation is shown in Fig. 3.

As the same way that for irradiation power, it would be expected that increasing irradiation time the RCC would decrease due to higher energy transferred to the system, leading to more efficient carbonization of diesel oil, preparing it for later oxidation with HNO_3 and H_2O_2 . Again, this behavior was not observed for the range tested. Although small variations of RCC along the range, it was virtually the same if the precision is taken into account. This way, an irradiation time of 5 min was selected for the heating program in order to make it faster and robust.

The results obtained along the execution of the optimization experiments pointed out to a noticeable importance of the carbonization step with concentrated H_2SO_4 , especially regarding to the volume of acid employed for this purpose. In face of such results, a modification of the carbonization step was tested, in order to obtain lower RCC values in the final solutions and

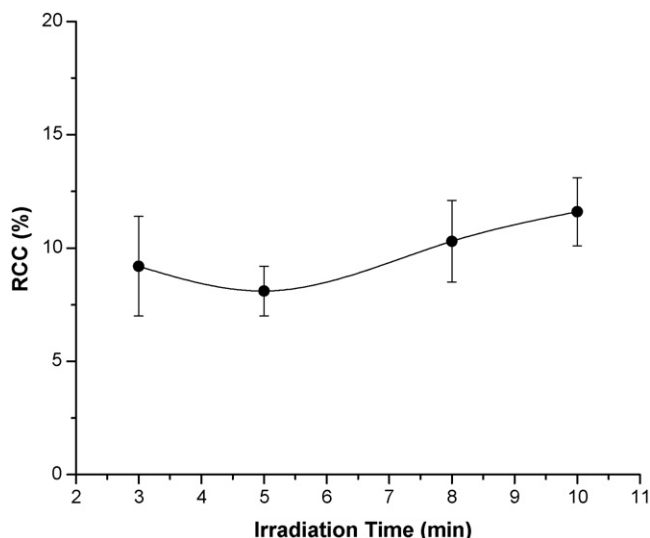


Fig. 3. Influence of irradiation time of the carbonization step on the mineralization efficiency of the diesel oil. Sample masses = 1 g.

thus achieve quantitative determination of metals. According to Perez [31], replacing step 2 (partial oxidation with concentrated HNO_3 , see Table 3) by a second carbonization step yields a procedure more efficient for the dissolution of diesel oil and enhances dehydration of organic chains, which facilitates the posterior oxidation with concentrated HNO_3 . To test this, a second carbonization step was added to the heating program. In this new condition, the total volume of concentrated H_2SO_4 (10 ml) was equally divided between the two carbonization steps, being added in two portions of 5 ml. In turn, the applied power was increased slowly starting at 60 W (as optimized) and finishing at 150 W. These modifications were done to create a program with slower increase of temperature in order to avoid the formation of great amounts of polymerized black carbon, which showed to be very difficult to oxidize by subsequent steps of the heating program with concentrated HNO_3 and H_2O_2 . The intermediate program comprising the new strategy for the carbonization step is shown in Table 3.

Results obtained by application of this new program for different sample masses are shown in Fig. 4. As can be seen in the figure, even for sample masses as high as 3.5 g, a remarkable

Table 3
Intermediate heating program established after optimization of the carbonization step

Step	Acid	Volume (ml)	Power (W)	Time (min)
1 (carbonization)	H_2SO_4	5	60	5
2 (carbonization)	H_2SO_4	5	120	10
			150	10
3 (partial oxidation)	HNO_3	5	210	10
4 (final oxidation)	H_2O_2	10	210	5

Mass of sample taken was 1 g.

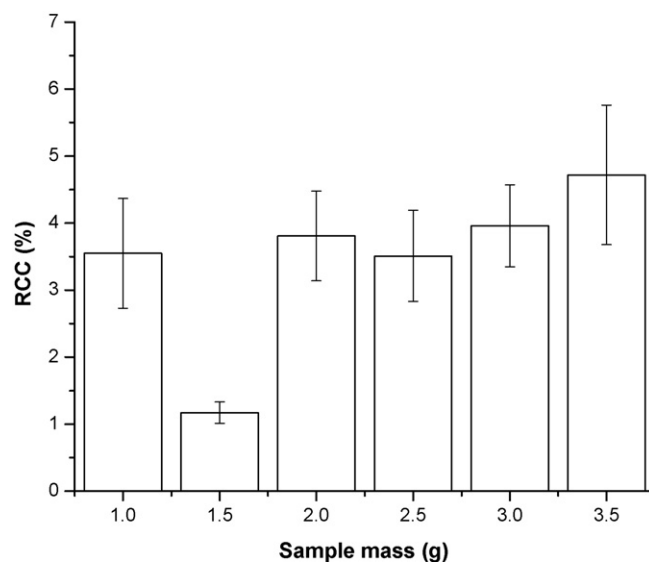


Fig. 4. Influence of the mass of sample on the RCC obtained after addition of a second carbonization step to the heating program.

reduction in the RCC was observed, indicating that there was a sensitive improvement in the digestion procedure under study. A mean value of 3.45% of RCC was observed which was much lower than those obtained when only one carbonization step was included in the program (8.1% RCC).

3.2. Optimization of oxidation steps with concentrated HNO_3 and H_2O_2

Following the optimization of heating program, the oxidation step with concentrated HNO_3 was evaluated only regarding to the volume of acid used for digestion of diesel oil. The volume of concentrated HNO_3 added was studied in the range of 2–8 ml for a sample mass of 2 g. No remarkable effect was noted varying this parameter since the RCC values just varied from 2.04 to 2.74% with an average value of 2.51%. Further experiments were performed with 4 ml of concentrated HNO_3 in order to ensure efficient mineralization with lower amount of acid. Once this step showed to have minor importance on the digestion efficiency and the values of RCC obtained were lower enough for injection of samples into the spectrometer, the other variables (irradiation power and time) were not studied.

The evaluation of the influence of final oxidation step with H_2O_2 was performed together with the capacity of the procedure to digest increased sample masses. For this purpose a multivariate experiment based on a Doehlert matrix [32–37] was planned by varying the mass of diesel oil between 1.5 and 3.5 g and the volume of H_2O_2 between 10 and 20 ml. A summary of the experiment and the results obtained for RCC are shown in Table 4.

Treating the data obtained in the multivariate experiment with Statistica for Windows (Version 6) software it was possible to generate the equation of the response surface of the model:

$$\text{MC} = 81.95 + 9.5M + 1.38V - 2.0M^2 - 0.03MV - 0.063V^2$$

Table 4
Doehlert design experiments for the optimization of mass of sample and H₂O₂ volume

Step	Mass of sample (g)	H ₂ O ₂ volume (ml)	RCC (%)	Mineralized carbon ^a (%)
1	2.5	15	1.4	98.6
2	3.0	10	0.3	99.7
3	3.5	15	5.0	95.0
4	3.0	20	6.3	93.7
5	2.0	20	6.5	93.5
6	1.5	15	1.8	98.2
7	2.0	10	0.8	99.2

^a Mineralized carbon = 100% – RCC.

where *MC*, *M*, and *V* represent the mineralized carbon, mass of sample and volume of H₂O₂ added, respectively. The surface can also be graphically represented, as shown in Fig. 5. The critical point of the surface, which represents the point (conditions) where maximum mineralization of carbon present is observed, can be obtained by deriving the mineralized carbon in terms of mass of sample and volume of H₂O₂ and making the obtained equations equal to zero

$$\frac{\delta MC}{\delta M} = 0 \quad \text{and} \quad \frac{\delta MC}{\delta V} = 0$$

This way, a system with two linear equations and two variables is obtained. Solving such system is possible to find the critical point of the surface, which denotes the conditions for obtaining maximum mineralization (minimum RCC) after digestion. In the present case, the critical point of the surface was obtained for 10.4-ml volume of H₂O₂ and 2.3 g sample mass. Therefore, for the methodology, a hydrogen peroxide vol-

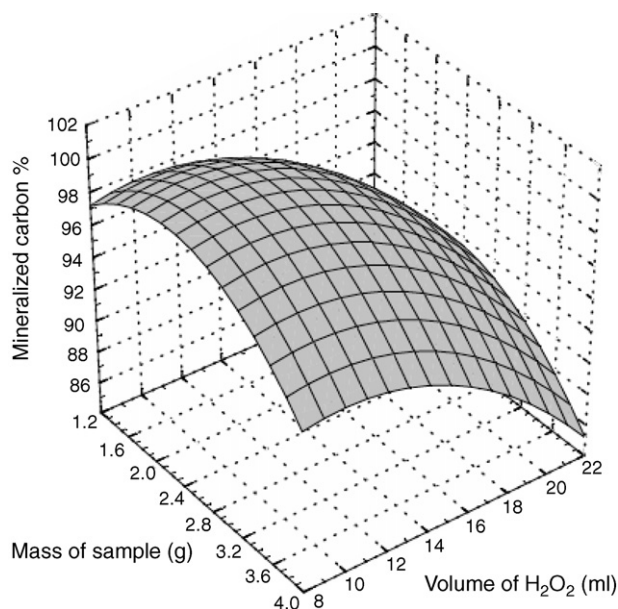


Fig. 5. Response surface obtained from the results of the Doehlert design experiments. Critical point was identified as: mass of sample = 2.3 g and volume of H₂O₂ = 10.4 ml.

Table 5
Final heating program established for the digestion of diesel oil aiming the determination of metals by ICP-OES

Step	Acid	Volume (ml)	Power (W)	Time (min)
1 (carbonization)	H ₂ SO ₄	5	60	5
2 (carbonization)	H ₂ SO ₄	5	120 150	10 10
3 (partial oxidation)	HNO ₃	4	210	10
4 (final oxidation)	H ₂ O ₂	10	210	5

Mass of sample = 2.5 g.

ume of 10 ml and a sample mass of 2.5 g were established in order to obtain maximum sensitivity besides more efficient mineralization of samples. The final heating program developed is presented in Table 5.

4. Analytical features and application

The digestion procedure was developed to fractionate and oxidize the hydrocarbons chains present in the diesel oil and thus release metals retained in the organic matrix, in order to allow their determination by ICP-OES. For evaluating the efficiency of the dissolution procedure developed, samples purchased in local gas stations from three different suppliers were analyzed in terms of the concentration of the metals of interest (Al, Cu, Fe, Ni and Zn). In order to estimate the accuracy of the procedure, the percent recoveries for the studied metals were also determined by adding a known amount (10 μg) of each metal (as oil standard) to a sample that had been analyzed previously. Recoveries of the spiked metals ranged from 70 to 106% for three independent measurements. Table 6 shows the results obtained for each sample and the recoveries obtained in each case.

According to the results, the recovery of the metals in the three samples tested were quantitative, presenting values always better than 90%, except for Zn. Such values denote that the digestion procedure proposed in this work is efficient to destroy the resistant organic matrix, allowing the releasing of metals for the solution. Only Zn provided recoveries below 90% in the three samples analyzed. This result indicates that this metal is volatilized and lost during intense heating promoted by the digestion program. This phenomenon for Zn was already reported by Bressani [16] in the digestion of lubricating oil with an open-focused microwave oven.

The detection limits of the method showed to be sufficient for the analysis. The values for Al, Cu, Fe, Ni and Zn were 0.12, 0.089, 0.14, 0.052 and 0.11 μg g⁻¹, respectively, taking into consideration the digestion of 2.5 g of sample. The R.S.D verified for three independent determinations of each analyte (except Cu) varied between 8.0 and 24%. For the case of Cu, the R.S.D was around 70%, but it is important to remark that all concentrations determined were near to the detection limit.

Table 6

Results obtained in the analysis of samples of diesel oil (expressed as $\mu\text{g g}^{-1}$; mean \pm standard for three independent determinations) and recovery test

Sample	C content (%)	Al	Cu	Fe	Ni	Zn
A	85.74 \pm 0.13	1.00 \pm 0.13	0.11 \pm 0.07	0.35 \pm 0.06	<LOD	0.57 \pm 0.04
A + addition		93 \pm 10%	98 \pm 8%	99 \pm 6%	94 \pm 1%	75 \pm 8%
B	85.55 \pm 0.15	0.87 \pm 0.07	0.10 \pm 0.07	0.41 \pm 0.10	<LOD	0.50 \pm 0.09
B + addition		106 \pm 8%	94 \pm 8%	101 \pm 5%	106 \pm 8%	78 \pm 8%
C	85.92 \pm 0.20	0.70 \pm 0.06	0.10 \pm 0.06	0.36 \pm 0.06	<LOD	0.36 \pm 0.06
C + addition		99 \pm 6%	95 \pm 8%	90 \pm 6%	90 \pm 2%	70 \pm 7%

Mass of sample was 2.5 g and the amount of each metal added in the recovery experiment was 10 μg .

5. Conclusions

The results obtained in this work showed that the focused microwave assisted procedure is a good alternative for the digestion of diesel oil samples aiming metals determination by ICP-OES, since the whole digestion was carried out in less than 1 h. According to Archanjo et al. [1], the total time spent for mineralization of this kind of sample by wet acid method using hot plate was estimated in 16 h.

During optimization of the methodology it was possible to verify that the carbonization step with concentrated H_2SO_4 is the critical part of the whole procedure. Splitting of this step in two sub-steps improved the efficiency of the digestion, allowing the application of the heating program to largest masses of sample, which permitted that lower detection limits could be achieved.

The final program developed in this work spent only 40 min, being possible to digest up to 2.5 g of sample with mineralization efficiency better than 95%. It was also demonstrated that the use of increased amounts of reagents, higher irradiation power and longer irradiation time was not necessary to improve the mineralization efficiency.

In terms of metals determination by ICP-OES, the use of internal standard (in the case, Y) was essential for quantification of the analytes. This occurred due to the high proportion of H_2SO_4 remained in the final solution, which affected the transport of sample solutions to the plasma. For the most of analytes tested (Al, Cu, Fe, Ni and Zn), recoveries better than 90% were observed by employing the developed digestion method. The unique exception was Zn, which presented recoveries between 70 and 78% due to volatilization after heating by the open-focused microwave oven.

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