Feasibility of sulfur determination in diesel oil by inductively coupled plasma optical emission spectrometry after microwave-induced combustion using flame retardant

Sandra M. Cruz a, Paul Tirk b, Flavia M. Dalla Nora a, Lucas Schmidt a, Helmar Wiltsche b, Cezar A. Bizzi a, Guenter Knapp b, Erico M.M. Flores a,*

* Corresponding author. Tel./fax: +55 55 3220 9445.
E-mail address: ericommf@gmail.com (E.M.M. Flores).

HIGHLIGHTS
• Use of glass wool as flame retardant for digesting diesel oil by microwave-induced combustion.
• Use of flame retardant for controlling the kinetics of combustion reaction.
• Possibility of using diluted absorbing solution (2 mol L⁻¹ HNO₃) for sulfur determination.
• Digestion efficiency was higher than 99% (RCC lower than 1%).
• Suitability of sulfur determination by using ICP-OES.

ABSTRACT
Diesel oil sample preparation for further sulfur determination in fuels is considered a critical step during the analytical sequence mainly due to the high volatility of this sample. Combustion systems have been a suitable alternative to conventional digestion methods but its applicability for highly volatile matrices like diesel oil is restrict to low sample masses due to the high pressure generated during combustion. In order to overcome this limitation, the possibility of employing glass wool as a flame retardant for microwave induced combustion (MIC) method was investigated in the present work for further sulfur determination by inductively coupled plasma optical emission spectrometry. Using flame retardant it was possible to burn up to 400 mg of diesel oil without increasing the pressure in dangerous levels. Nitric acid (2, 4, 7 or 14.4 mol L⁻¹ HNO₃) was evaluated as absorbing solution and no significant difference was observed in sulfur recoveries for solutions. Digestion efficiency was evaluated by means of residual carbon content determination, which presented values always lower than 1% showing the high digestion efficiency. For comparison of results, S was also determined by the ASTM D 5453-12 method and an agreement better than 95% was obtained. The accuracy was better than 97% (analysis of certified reference material), blanks were negligible and the limit of detection was considered as suitable for quality control (2 µg g⁻¹).

© 2015 Elsevier Ltd. All rights reserved.
1. Introduction

Diesel oil belongs to a class of products obtained by crude oil processing and generally covers the range of boiling temperatures between 175 and 375 °C mainly presenting compounds with about eight to twenty-four carbon atoms (C₈ to C₂₄) [1,2]. Sulfur is an ubiquitous element in crude oil and the presence of sulfur compounds in diesel oil or in the middle distillate crude oil fraction can cause corrosion leading to damage of metallic parts of refineries as well as of combustion engines of automobiles [1,3,4]. Other implications include changes in color, odor and instability of the final product. Remaining sulfur also contributes to the release of sulfur oxides into the atmosphere causing environmental pollution like acid rain [3,5,6]. Furthermore, it can poison the catalysts used in emission control systems, consequently, reducing the oxidation effectiveness of carbon monoxide, hydrocarbons and volatile organic compounds [1,3,4]. Sulfur compounds are distributed in several crude oil distillation fractions and may also be present in the final products [7]. Depending on the origin of formation and maturation conditions of the preceding crude oil, a variety of sulfur compounds can be found [7] and their presence, especially in low and ultralow sulfur content diesel oil, is generally belonging to the group of benzothiophenes (BT) and dibenzothiophenes (DBT) as well as derivatives of these compounds containing alkyln substituents, such as 4,6-dimethyl-dibenzo-thiophene (4,6-DMDDBT) [3,8].

Refineries and manufacturers are subject to meet the requirements set by governmental organizations. The Environmental Protection Agency (EPA, United States) limits the allowed sulfur concentration for ultra low sulfur diesel to 15 mg kg⁻¹ [9]. Similar restrictions also exist in European Union as the directive 98/70/EC which sets a limit even lower (10 mg kg⁻¹) [10]. In order to comply with these regulations the continuous monitoring of sulfur is of high importance in the production and quality control of diesel oil.

For sulfur determination in diesel oil, sample preparation can be considered as a critical step and several methods have been applied in last years [11]. Direct injection of diesel oil for further inductively coupled plasma based analysis has been currently used for routine analysis. However, some drawbacks still remain as the need for high dilution factors to maintain a stable plasma [12], oxygen addition to nebulization gas and also the use of reference solutions especially prepared in organic medium [13]. Even using matrix-matched reference samples, changes in plasma can occur making direct injection of organic substances prone to some inconveniences for trace S determination [14–16]. Additionally, sulfur determination in crude oil and its fractions has been carried out by X-ray fluorescence (XRF) and also by sample combustion with further titration or infrared detection [17–21]. Despite some automatic sulfur analyzers allow the direct analysis of diesel oil, common procedures for S determination by other techniques involve a previous step of sample preparation [22]. However, acid digestion procedures can present limitations due to the relatively long time required [23] and low digestion efficiency [24]. As an example, Ulrich et al. [14] proposed a procedure involving a 12 h pre-digestion on a hot plate before applying microwave radiation for 30 min.

On the other hand, combustion systems provide some advantages over closed vessel wet digestion when dealing with organic samples. Due to the high temperature during combustion (>1000 °C) complete oxidation of sample matrix can be achieved, resulting also in low residual carbon content (RCC) [25]. Classical combustion is normally performed in bombs or oxygen flasks [25,26]. Both systems present some advantages mainly related to sample ignition and low risk of contamination, respectively [25,27]. However, for combustion bombs, the use of acid solutions must be avoided to prevent damage to the metallic vessel walls and low analytical frequency may be considered as one of the main limitations for this system [25]. The oxygen flask method presents restriction to the maximum sample mass and consequently poor limit of detection (LOD). In addition, both systems need continuous attention by the analyst, only one sample is processed in each run and digestion time is relatively long (up to 3 h considering the cooling step in case of combustion bombs) that decreases the throughput [25]. Normally, for the oxygen flask system, samples of 10–50 mg are burnt in vessels with a volume of 250–500 mL [28]. Table 1 summarizes some selected applications using combustion bombs and oxygen flask, for the subsequent determination of sulfur in oils, fuels, lubricants oil and crude oil products [25,26,29–31].

Alternatively, microwave-induced combustion (MIC) can overcome some of the mentioned difficulties and often provides an easy and rapid way for decomposing organic samples [24,32,33]. Essentially, solid samples are pressed as pellets and ignited using microwave radiation with a suitable igniter solution [34]. Analytes are retained in a convenient absorbing solution [28] and it should be noticed that the acid concentration can be much lower using MIC method when compared to conventional closed vessel wet digestion because the oxidation of organic matter is mainly promoted by the oxygen present in the gas phase [35]. As a result, interferences during measurement step by inductively coupled plasma based techniques are minimized and the use of hazardous substances are reduced thus leading to a greener procedure [16,36,37]. Furthermore, microwave heating can be used for a reflux step without opening the combustion vessel in order to improve analyte recovery [34].

However, problems are observed when working with viscous or liquid samples because they cannot be prepared as pellets and keeping sample on the sample holder is crucial to ensure complete combustion. In case of combustion of crude oil, a method using polyethylene film to wrap the samples was developed in a previous study for S determination in extra heavy crude oil after MIC by inductively coupled plasma optical emission spectrometry (ICP-OES) [34]. However, taking into account the presence of highly flammable organic substances, a rapid pressure increase could occur resulting in risks of explosion.

Taking into account the combustion reaction of highly flammable matrices such as diesel oil and the possibility of using a solid flame retardant, it is expected to achieve a safe combustion procedure without decreasing the sample mass [38]. Flame retardants are known to act chemically and/or physically in solid, liquid or gas phase [39]. By employing this kind of material it is possible
to decrease the combustion rate, making the oxidation reaction safer when it is applied to highly flammable or volatile samples.

In this sense, the present work aims to evaluate the use of glass wool as a flame retardant for digesting a relatively high mass of diesel oil by MIC method. Final digests were analyzed by ICP-OES for sulfur determination. The absorbing solution was optimized in order to obtain quantitative analyte recoveries. The maximum sample mass allowing a safe and complete combustion was evaluated by considering the efficiency of sample decomposition (assessed by RCC determination). In addition, a certified reference material (NIST SRM 1084a, wear metals in lubricating oil) and a method recommended by ASTM D 5453-12 were used in order to check the accuracy of the proposed method.

2. Materials and methods

2.1. Instrumentation

A microwave oven (Synthos 3000, Anton Paar, Austria) equipped with high-pressure quartz vessels (80 mL, maximum pressure and temperature of 80 bar and 280 °C, respectively) was used for digestions using MIC method. In this system, the sample is placed on a quartz holder, which is introduced into the vessel. For visualization of combustion a polycarbonate protection wall (45 × 60 cm, 10 mm thickness) was used in front of the microwave oven as a shield to assure safe conditions during these experiments. However, it was not necessary for normal application of combustion system as vessels are equipped with vent valves and rotor is covered with a polypropylene shield.

An inductively coupled plasma optical emission spectrometer (Optima 4300 DV, Perkin Elmer, United States) was used for the determination of S (and also C for digestion efficiency evaluation). Sulfur determination was also performed using a sulfur analyzer (Antek 9000NS). For the optimization of MIC method, diesel oil samples purchased from local market were used (samples 1, 2 and 3; total organic carbon of 85%). A standard reference material (NIST SRM 1084a, wear metals in lubricating oil, National Institute of Standards and Technology, United States) with informed value of sulfur content was used to evaluate the accuracy of the proposed procedure.

Glass wool (Pyrex, United States, diameter 0.08 mm) made in borosilicate glass, was used for holding oil samples on the quartz holder (100 ± 5 mg). Glass wool was previously cleaned with 2.8 mol L⁻¹ HNO₃ during 20 min in an ultrasonic bath (TI-H-5, 750 W, 35 kHz, Elmasonic, Germany), rinsed with water and dried in a class 100 laminar flow bench before use.

For the optimization of MIC method, diesel oil samples purchased from local market were used (samples 1, 2 and 3; total organic carbon of 85%). A standard reference material (NIST SRM 1084a, wear metals in lubricating oil, National Institute of Standards and Technology, United States) with informed value of sulfur content was used to evaluate the accuracy of the proposed procedure.

Glass wool (Pyrex, United States, diameter 0.08 mm) made in borosilicate glass, was used for holding oil samples on the quartz holder (100 ± 5 mg). Glass wool was previously cleaned with 2.8 mol L⁻¹ HNO₃ during 20 min in an ultrasonic bath (TI-H-5, 750 W, 35 kHz, Elmasonic, Germany), rinsed with water and dried in a class 100 laminar flow bench before use.

2.2. Samples, reagents and standards

High purity water (18.2 MΩ cm) was used for preparing all reagents and standard solutions. Nitric acid (65%, Merck, Germany) was previously purified in a sub-boiling system (Duopur, Milestone, Italy). Reference solutions for the calibration of ICP-OES were prepared by dilution of a multielement stock solution (10 mg L⁻¹ SCP33MS, SCP Science, Canada) in HNO₃ (0.7 mol L⁻¹). Absorbing solutions (2, 4, 7 and 14.4 mol L⁻¹ HNO₃) for MIC digestion were prepared by dilution of concentrated acid with water. A solution of 6 mol L⁻¹ NH₄NO₃ (Merck) was used as igniter solution for the MIC method [28].

Filter paper (15 mm of diameter, 12 mg, Black Ribbon Ashless, Schleicher and Schuell, Germany) was previously cleaned with 2.8 mol L⁻¹ HNO₃ during 20 min in an ultrasonic bath (TI-H-5, 750 W, 35 kHz, Elmasonic, Germany), rinsed with water and dried in a class 100 laminar flow bench before use.

2.3. Sample digestion by the proposed MIC method

Diesel oil samples were carefully dropped onto glass wool (around 100 mg) using a syringe (glass wool was wetted with diesel oil). In order to assure a suitable adsorption of the samples, the glass wool was prepared in a spherical shape. Subsequently, glass wool with adsorbed diesel oil was kept in a laminar flow bench before combustion (this time was optimized in order to achieve a reproducible combustion). In this work two filter papers were used, contrarily to conventional application of MIC for solid samples where only one filter paper is needed. It allowed a more reproducible combustion that was sometimes incomplete when using only one filter paper. The glass wool containing the adsorbed diesel was placed on the top of filter papers wetted with NH₄NO₃ solution, previously positioned in the quartz holder, which was further inserted into the quartz vessel already filled with 6 mL of the absorbing solution (2, 4, 7 or 14.4 mol L⁻¹ HNO₃). Each vessel was pressurized with 20 bar oxygen and microwaves were irradiated during 5 min (1400 W, combustion and reflux step) followed by a cooling step (0 W, 20 min). Final digestes were made up with water to 25 mL for further sulfur determination by ICP-OES.

It is important to consider that the allowed pressure rate used in the digestion system had to be adjusted from 0.8 bar s⁻¹ to 3 bar s⁻¹ because of the rapid increase in pressure occurring during combustion. Between each combustion run the quartz holders and vessels were cleaned with 6 mL of 20% HNO₃ during 10 min at 1400 W and 20 min of cooling step.
2.4. Evaluation of MIC digestion efficiency using a flame retardant

In order to evaluate the digestion efficiency of the proposed MIC method, C determination was performed in final digests using ICP-OES as previously described [41]. For external calibration, carbon reference solutions were prepared by dissolution of citric acid (Merck) in water (concentration ranging from 5 up to 500 mg L\(^{-1}\) of carbon), and all samples, blanks and reference solutions were prepared with yttrium as internal standard (1 mg L\(^{-1}\), SpexCertiprep, United States) [35]. The volatile carbon present in all samples and standards was removed before determination by purging all solutions with argon (0.1 L min\(^{-1}\), 2 min) [35]. The RCC was expressed as the percentage of C that remained in the final digests in relation to the C originally present in the sample.

2.5. Evaluation of the proposed procedure accuracy

Accuracy of the proposed procedure was evaluated by using a standard reference material (NIST SRM 1084a, wear metals in lubricating oil), which was performed using the optimized conditions of MIC method using glass wool. The determination of sulfur was also performed by the direct injection of sample in an automated analyzer equipment for sulfur determination by ultraviolet fluorescence according to ASTM D 5453-12 method [40] and the obtained results were used as reference values.

3. Results and discussion

3.1. Initial experiments without using flame retardant

Initially, the evaluation of the maximum sample mass to be combusted was performed by conventional MIC approach using 50 mg of diesel oil (without the use of glass wool). In this case the diesel oil sample was involved in a small polyethylene (PE) film which was then placed on the quartz holder. The preparation of PE film, successfully applied to crude oil samples, was described elsewhere [42]. For these tests, using diesel oil combustion was not reproducible, being incomplete in some cases and resulting in final digests presenting suspended black particles. However, using two disks of filter paper, a reproducible combustion was obtained without solid residues in the final digests. Taking into account highly flammable organic substances, the digestion in closed systems presents a risk of rapid pressure increase and therefore, the digestion of higher diesel oil masses by using MIC was carefully performed.

Using sample masses up to 100 mg of diesel the maximum pressure in the system was around 30 bar, which is related to a fast increase of pressure of about 10 bar during combustion (Fig. 1). However, when the sample mass was increased to 200 mg, the maximum pressure was 45 bar corresponding to an increase of 25 bar compared to the initial pressure of oxygen (20 bar). Based on these results, the evaluation of diesel oil masses higher than 200 mg was considered dangerous and no further experiments were performed using PE film or without flame retardant.

3.2. Use of glass wool as a flame retardant

Glass wool was used to reduce the kinetics of the combustion reaction, which was performed by increasing the sample mass step by step while monitoring the maximum pressure in quartz vessels during combustion. Glass wool masses between 75 and 200 mg were evaluated as flame retardants. By using glass wool mass of 100 ± 5 mg or higher (with adsorption time of 120 min) the diesel oil combustion was always complete. Under this condition, the combustion of diesel oil was stable without spillage, and a peak of pressure increase was not observed as before when using PE films. Then, a mass of 100 mg of glass wool was selected for further experiments. In order to obtain reproducible conditions, the time necessary for the adsorption of diesel oil on the glass wool was also evaluated (Fig. 2).

The evaluation of the adsorption time was performed using 200 mg of sample adsorbed on 100 ± 5 mg of glass wool. After diesel oil adsorption, the digestion vessel was pressurized with oxygen and microwave heating program started. When diesel oil was added on the glass wool and vessels were immediately pressurized with oxygen for further microwave heating (considered 0 min of sample adsorption), the sample combustion was not complete. In this case, the peak of maximum pressure during combustion was higher than 45 bar (Fig. 2). This result was similar to those results previously obtained using PE films (without using glass wool). It was observed for sample adsorption times ranging from 15 to 90 min (pressure peaks of 44 and 38 bar, respectively). Even for the last condition (90 min) presenting a relatively lower increase of pressure, the sample combustion was not reproducible. On the other hand, using higher adsorption time (ranging from 120 up to 180 min), it was observed a practically constant peak pressure (which was always lower than 36 bar). After 120 min of diesel oil adsorption, it presented a stable aspect in glass wool allowing a convenient manipulation (transportation, positioning on quartz holder, etc.). As a result, a more strong and stable interaction of glass wool surface with diesel oil was observed, which contributed for decreasing the kinetics of combustion reaction and then reducing the peak pressure. An important aspect to be observed refers to the relatively high amount of oxygen available inside the digestion...
was selected as absorbing solution for MIC method is important to achieve quantitative recoveries and analytes stability in solution [42]. The absorbing solution must be suitable to the kind of analyte and determination technique. In order to evaluate the influence of the absorbing solution on the analytes recovery, nitric acid solutions ranging from 2 to 14.4 mol L\(^{-1}\) were evaluated (Table 4).

It was observed that all the evaluated solutions allowed sulfur recoveries higher than 95%. Although no statistical difference (ANOVA, \(P > 0.05\)) was obtained between all the solutions, the results presented in Table 4 shows that in case of using diluted acids the relative standard deviation (RSD) was slightly lower. Therefore, a 2 mol L\(^{-1}\) HNO\(_3\) was selected as absorbing solution for further studies. Finally, the possibility of minimizing the acid consumption and consequently reducing the risk of interferences in the determination step by ICP-OES can be pointed out as additional benefits of the proposed method.

### 3.5. Sulfur determination in diesel oil samples after the MIC method

The MIC method was also applied to the digestion of a certified reference material with a similar composition to diesel oil (NIST SRM 1084a, wear metals in lubricating oil), which presents informed values of sulfur concentration. No statistical difference between results obtained by MIC (1714 ± 67 \(\mu\)g \(g^{-1}\), \(P > 0.05\)) and the informed value (1700 \(\mu\)g \(g^{-1}\)) was observed. For comparative purposes diesel oil samples (identified as 1, 2 and 3) were also analyzed according to the ASTM D 5453-12 using an automatic sulfur analyzer for direct analysis of diesel oil. The results were in good agreement with results obtained by the MIC method using diluted HNO\(_3\) (2 mol L\(^{-1}\)) and 400 mg of diesel oil (Table 5).

Using the proposed method, blanks were always negligible and up to eight samples can be processed by each run in 25 min. Limit of detection and limit of quantification (LOQ) were calculated based on three and ten times, respectively, the standard deviation of sulfur determination in blanks \((n = 10)\). Using the selected conditions the LOQ was considered suitable for S determination in commercial diesel oil samples (6.9 \(\mu\)g \(g^{-1}\)) and in agreement with the established limits for S in diesel oil [9,10].

### 4. Conclusions

In this work, the MIC method was modified in order to circumvent the limitations for combusting highly flammable liquid fuels for further sulfur determination by ICP-OES. By employing glass wool as flame retardant the method was found to be suitable for a safe combustion of diesel oil. Using the optimized MIC conditions, quantitative recoveries of sulfur were obtained after 5 min (combustion and reflux step) using a diluted nitric acid solution (2 mol L\(^{-1}\) HNO\(_3\)) as absorption medium. The use of glass wool allowed to burn up to 400 mg of diesel oil sample with very low RCC values. Additionally, a high digestion efficiency (>99%) was obtained for relatively high sample mass, also avoiding the use of concentrated reagents, and significantly reducing possible interferences in analysis by ICP-OES. Due to the use of relatively high sample mass and diluted absorbing solutions, the LOD was significantly lower (2 \(\mu\)g \(g^{-1}\)). Finally, the proposed procedure is in agreement with green chemistry recommendations because it allows the use of diluted solutions, which minimize the generation of residues.

### Acknowledgments

The authors are grateful to CNPq, CAPES and FAPERGS for grants and fellowships.

### References

for the multielement determination of whole milk powder

Allain P, Jaunault L, Mauras Y, Mermet JM, Delaporte T. Signal enhancement of

Matusiewicz H, Sturgeon R. Comparison of the efficiencies of on-line and high-

Fessayre S, Bacaud R, Geantet C, Vrinat M. Deep hydrodesulfurization of diesel

Botto RI. Sample preparation for crude oil, petroleum products and polymers.

Annual Book of ASTM Standards, ASTM D 1552-95. Standard test method for


