



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,*}

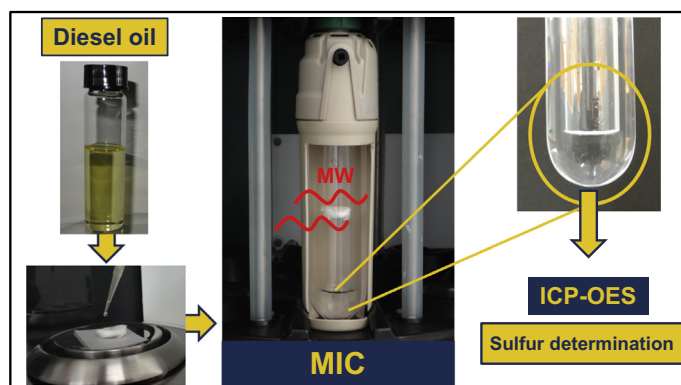
^a Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil

^b Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Graz, Austria

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 ($2 \text{ mol L}^{-1} \text{ HNO}_3$) for sulfur determination.
- Digestion efficiency was higher than 99% (RCC lower than 1%).
- Suitability of sulfur determination by using ICP-OES.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 June 2015

Received in revised form 7 July 2015

Accepted 20 July 2015

Available online 29 July 2015

Keywords:

Sample preparation

Diesel oil analysis

Sulfur determination

Diluted acid

Microwave induced combustion

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 restricted 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 $14.4 \text{ mol L}^{-1} \text{ HNO}_3$) 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 ($2 \mu\text{g g}^{-1}$).

© 2015 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel./fax: +55 55 3220 9445.

E-mail address: ericommf@gmail.com (E.M.M. Flores).

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 alkyl substituents, such as 4,6-dimethyl-dibenzo-thiophene (4,6-DMDBT) [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]. Alternatively, 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

Table 1

Analysis of lubricating oil, diesel oil and crude oil products using oxygen flask and combustion bomb for further S determination.

Sample	Digestion method	Technique of determination	LOD	Reference
Lubricating oil	Combustion bomb	IC	1.62%	[21]
Diesel oil	Combustion bomb	ICP-OES	*	[22]
Fuel	Combustion bomb	IC	0.07 µg mL ⁻¹	[25]
Crude oil products	Combustion bomb	Titration	0.01%	[26]
Fuel oils	Oxygen flask	IC	0.007%	[27]

* Not informed. IC: ion chromatography; ICP-OES: inductively coupled plasma optical emission spectrometry.

[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

Download English Version:

<https://daneshyari.com/en/article/205532>

Download Persian Version:

<https://daneshyari.com/article/205532>

[Daneshyari.com](https://daneshyari.com)