

Accepted Manuscript

A sustainable and simple energy dispersive X-ray fluorescence method for sulfur determination at trace levels in biodiesel samples via formation of biodiesel spots on a suitable solid support



Eva MarguÍ, Martín Resano, Ignasi Queralt

PII: S0584-8547(18)30556-1

DOI: <https://doi.org/10.1016/j.sab.2019.04.003>

Reference: SAB 5602

To appear in: *Spectrochimica Acta Part B: Atomic Spectroscopy*

Received date: 17 December 2018

Revised date: 30 March 2019

Accepted date: 1 April 2019

Please cite this article as: E. MarguÍ, M. Resano and I. Queralt, A sustainable and simple energy dispersive X-ray fluorescence method for sulfur determination at trace levels in biodiesel samples via formation of biodiesel spots on a suitable solid support, *Spectrochimica Acta Part B: Atomic Spectroscopy*, <https://doi.org/10.1016/j.sab.2019.04.003>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A sustainable and simple energy dispersive X-ray fluorescence method for sulfur determination at trace levels in biodiesel samples via formation of biodiesel spots on a suitable solid support

Eva Marguí^{a,*}, eva.margui@udg.edu, Martín Resano^b, mresano@unizar.es, Ignasi Queralt^c, ignasi.queralt@idaea.csic.es

^aDepartment of Chemistry, Faculty of Sciences, University of Girona. C/M. Aurèlia Campmany 61, 17003 Girona, Spain

^bDepartment of Analytical Chemistry, Aragón Institute of Engineering Research (I3A), University of Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

^cInstitute of Environmental Assessment and Water Research, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain

* Corresponding author.

Abstract

The aim of the present work is the development of a simple, sensitive and sustainable EDXRF method for the determination of trace amounts of sulfur in biodiesel samples. In this method, the deposition of several microliters of sample onto an organic thin layer and the analysis of the resulting adsorbed biodiesel spot by benchtop EDXRF is proposed.

A careful study was performed to select the volume and the best solid support to deposit biodiesel samples, including filters made of different materials (glass fiber, Nylon, cellulose, paper) and a commercial disposable absorbent pad (UltraCarry, Rigaku). A critical issue that limits the use of most of these solid supports was the relative high blank signals that hamper the determination of sulfur at trace levels. Finally, it was found that best strategy was the deposition of 50 μL of biodiesel on the UltraCarry sample retainer. Operating conditions for EDXRF measurements were also evaluated to obtain the best instrumental sensitivity for sulfur determination (Excitation: 20 kV, no primary filter, measurement time: 300s).

Using the best analytical conditions the quantification limit of the method was 7 mg kg^{-1} of sulfur. This value is even better than the one reported in the ASTM D4294 method (LOQ: 16.0 mg kg^{-1}) but using a sample amount 100 times smaller. The linearity was confirmed in the range of 10-100 mg kg^{-1} by analyzing a set of commercial biodiesel standards. Accuracy and precision of the results, evaluated by the analysis of samples prepared with the same matrix as the standards, with levels of 20, 40 and 75 mg kg^{-1} of sulfur, and processed as unknowns, proved acceptable (Recoveries: 94.3-110.6%, RSD: 10.8-13.6%, $n=3$) for the intended purpose.

Overall, the performance of the method developed is promising and it could be used to determine trace amounts of sulfur in biodiesel samples in a simple, sustainable and cost-effective way. Furthermore, since the original sample is adsorbed onto a solid support, repeat confirmatory analyses on the same specimen, if needed, can be carried out.

Keywords: sulfur; biodiesel; EDXRF; preconcentration

1. Introduction

Sulfur is present in petroleum products mostly as thiophenes, as sulfhydrylic acid and even in its elemental form and it represents one of the most common impurities found in crude oil. Compounds containing this element are among the most undesirable constituents of petroleum because they can lead to plant corrosion and atmospheric pollution [1]. For this reason, sulfur limits in conventional diesel have been significantly decreased from 500 mg kg⁻¹ to less than 15 mg kg⁻¹ in the US. In the EU the limit has been set to 10 mg kg⁻¹ since 2009 [2], and the same limit applies in Japan as well [3]. In view of that, research efforts have been focused on the development of methods based on bio/oxidative desulfurization of conventional fuels [4], or on the use of alternative fuels with lower sulfur content such as biodiesel, which is constituted of alkyl esters made from the transesterification of vegetable oils and animal/vegetable fats [5]. Additional advantages of biodiesel over other conventional petroleum products include a better efficiency and a reduction of greenhouse gas emissions and thus, its use has been growing over the past years and it is expected to continue [6]. Hence, the development of methods capable to detect low sulfur amounts (e.g., capable of establishing if a sample complies with the regulations) in biodiesel samples in an accurate, sustainable and trustworthy way is desirable.

For sulfur determination in petroleum products, X-ray fluorescence spectrometry (XRF) has been widely used, as it offers robustness and much lower running costs. This technique allows direct probing of few milliliters of the liquid sample in a cell without any additional sample treatment. Several scientific papers dealing with the use of both wavelength and energy dispersive XRF systems (WDXRF and EDXRF) have been published for the determination of sulfur in gasoline, diesel fuels and petroleum derivatives [1-2, 7-8]. Because the analysis relies on the X-ray radiation directly probing the liquid sample, important matrix effects are found since the penetration of the radiation in the internal layers of the sample results in the absorption of both excitation radiation and fluorescence from sulfur, to an extent that depends upon the composition of the matrix [7]. For example, it is known that variations in oxygen content and/or in the C/H mass ratio of the petroleum product under evaluation produce significant variations in the measured values [9]. Therefore, corrections for

matrix effects using Compton normalization, internal standardization or the use of empirical calibration using oil standards with a similar matrix to the samples are employed.

In addition to scientific research papers, American Society of Testing Materials (ASTM) methods based on the use of XRF spectrometry are also widely used and accepted worldwide for the analysis of petroleum products and derivatives. Among them it is interesting to highlight ASTM D2622 [10] and ASTM D7039 [11] methods, which makes use of WDXRF spectrometry, and the ASTM D4294 method [12], focused on the use of EDXRF. All of them are based on the direct analysis of few milliliters of petroleum sample with interference and matrix effect corrections from other elements present in the sample. Although these methods can be used for sulfur determination at low concentration levels (i.e., ASTM D2622 (WDXRF): 3 mg kg⁻¹ -4.6 wt% total sulfur, ASTM D4294 (EDXRF): 16 mg/ kg⁻¹ -4.6 wt% total sulfur) they were initially designed for the analysis of sulfur contents in the high mg kg⁻¹ range and, therefore, the applicability of this test methods at lower sulfur concentrations (i.e., below 20 mg kg⁻¹ of sulfur in the case of ASTM D4294 method) must be established on an individual basis. Taking into account the decrease of sulfur limits in conventional diesel and the introduction of other alternative fuels such as biodiesel, other ASTM methods for the specific determination of sulfur at trace and ultratrace levels have been developed (ASTM D7220-06 [13] and ASTM D7220-12 [14]). However, these methods are very specific in terms of the excitation technology for EDXRF, and a system enabling polarized excitation geometry is required instead of the most conventional EDXRF spectrometers.

In view of these premises, the main aim of this study was the development of a simple, sensitive and more sustainable EDXRF method for the determination of trace amounts of sulfur in biodiesel samples in comparison to the ASTM D4294 method. In the present contribution, the deposition of several microliters of biodiesel sample onto an organic thin layer and the analysis of the resulting adsorbed sample spot by benchtop EDXRF is proposed. With this simple sample treatment procedure, limits of quantification for sulfur can be improved even using an amount of sample significantly lower. In a recent review article, we highlighted the use of organic thin layers for preconcentration purposes when dealing with the analysis of aqueous samples by

conventional XRF [15]. The main reasons for that are the reduction of the absorption/enhancement effects and the low background of the exciting radiation scatter when analyzing this type of materials [16-17]. Moreover, a similar type of approach is gaining popularity in clinical analysis, due to practical and logistical reasons, as dried spots are stable and simple to store and keep or send [18]. However, the use of this analytical preconcentration approach for other type of liquid samples such as oil or petroleum has been limited and, according to the authors' knowledge, only one research paper has been published dealing with the determination of sulfur in fuel and crude oils but at high concentration levels (0.2-2.9 wt% of total sulfur) [7]. For the specific case of sulfur determination at trace levels, a limitation of this preconcentration approach is the potential high sulfur signal arising from the solid substrate where the liquid sample is deposited upon. Therefore, firstly, a careful evaluation of different solid substrates made of different materials was carried out. Sample preparation and measurement conditions were also evaluated so as to obtain the best sensitivity for sulfur determination at trace levels ($<100 \text{ mg kg}^{-1}$). Quantification was carried out by empirical calibration using commercial biodiesel standards, and the accuracy and precision of the results was studied by analysis of samples prepared with the same matrix as the standards, with levels of 20, 40 and 75 mg kg^{-1} of sulfur, which were processed as unknowns. The performance of the method developed is promising and it could be used to determine trace amounts of sulfur in biodiesel samples in a simple, sustainable and cost-effective way. Furthermore, since the original sample is adsorbed onto a solid support, repeat confirmatory analyses on the same specimen can be carried out, unlike what occurs with the ASTM D4294 method.

2. Material and Methods

2.1 Calibration standards and quality control samples

Commercially available biodiesel standards in 100% (B100) biodiesel blend containing different sulfur concentrations (blank matrix, 10, 15, 30, 50 and 100 mg kg^{-1}) were used for calibration purposes (CONOSTAN®, SCP Science). These standards are

manufactured in accordance with ASTM methods D7039, D6751, D5453 and EN14214 for ICP and XRF analysis.

In order to test the suitability of the developed EDXRF method for the determination of trace amounts of sulfur in biodiesel samples, quality control samples containing different sulfur concentrations (20, 40, 75 mg kg⁻¹) were prepared by dilution of the biodiesel standard containing 100 mg kg⁻¹ of sulfur using the blank standard with the same matrix (100% (B100) biodiesel blend), and processed as unknowns.

2.2 Sample preparation procedure

Calibration standards and quality control biodiesel samples were homogenized for 20 s by vortex mixing. Then, 50 µL of liquid sample were carefully deposited onto the surface of a suitable sample holder (thin layer). Several sample holders made of different materials were evaluated for such purpose (see section 3.1 for additional details). Then, standards and samples were left - at room temperature for 2 h and the loaded thin layers were directly sealed in the sample holder of the equipment for EDXRF analysis. In order to avoid instrumental blanks from the sample holder of the EDXRF system, a circular piece of Teflon with a thickness of 1.5 cm was used as a backstopper. Teflon possesses a low transmittance at 20 kV that makes it a proper mask material to be used for such a purpose [19].

2.3. EDXRF analysis

A commercially available benchtop EDXRF spectrometer (S2 Ranger, Bruker AXS, GmbH, Karlsruhe, Germany) was used in the present study. This instrument is equipped with a Pd target X-ray tube (max. power 50 W) and a XFLASH™ LE Silicon Drift Detector (SDD), ultra-thin beryllium window (0.3 µm thickness) with a resolution lower than 129 eV at Mn-Kα line for a count rate of 100000 counts-per-second. In this LE configuration of SDD detectors the intensities for Na K-alpha and Mg K-alpha are, respectively close to 8 and 4 times higher than the intensity recorded by conventional SDD detectors. The instrument is also equipped with nine primary filters that can be used in front of the tube before X-ray beam impinges the sample surface to improve measuring conditions for the elements of interest and it can operate under vacuum

conditions. More detailed information about the equipment and the measuring conditions used for sulfur determination can be found in Table 1.

The software used to control the equipment, to build the calibrations and to perform the data treatment was SPECTRA EDX (Bruker AXS, GmbH, Germany). This software can perform the full line profile fitting, deconvolutions when lines overlap, intensity corrections for inter-element effects and full-quantitative routines.

3. Results and Discussion

3.1 Selection of the sample support

As stated in the introduction section, preconcentration of aqueous samples onto solid substrates is an analytical strategy used in some applications dealing with the determination of metals at trace levels using XRF [16]. However, the use of this method for other type of liquid samples such as oil or petroleum has been limited mostly due to the sample viscosity and matrix effects arising from X-ray absorption of primary and secondary fluorescence radiation [7]. For the specific case of sulfur determination at trace levels, an additional limitation of this preconcentration approach is the potential high sulfur signal arising from the solid substrate where the liquid sample is deposited on. For this reason, a first experimental test was conducted to evaluate the presence of sulfur in several solid substrates made of different materials and available as thin layers. In Table 2, data obtained from the analysis of the different blank sample supports using EDXRF analysis are summarized. Solid substrates made of glass-fiber (GF), cellulose, cotton, nylon and cellulose nitrate were placed between two 4.0 μm -thick Prolene[®] (polypropylene) X-ray foils (supplied by Chemplex Industries, Inc., Palm City, FL, USA) mounted in special sample holders, which incorporates snap-on ring at the end of the cell for attachments of thin-film supports. In addition, two commercial sample supports purchased from Rigaku (Micro-Carry[®] and Ultra-Carry[®]) were also tested. These sample retainers are made of an external PET ring which holds a polyester film in where an adsorbent special cellulose filter is fixed. According to the supplier's specifications, Micro-Carry[®] sample retainers are recommended for the determination of elements with $Z > 20$ whereas Ultra-Carry[®] supports are best suited for the determination of light elements ($Z < 20$). In this latter case, the composition of the solid surface is slightly different to the ones designed for

measuring elements with higher Z values with the aim of reducing the signal contribution from light elements in the blank retainers, in order to improve in that way their detection and their subsequent quantification. In a recent contribution, both solid surfaces have been successfully used for the analysis of aqueous extracts related to cultural heritage samples [20].

As it can be seen in Table 2, almost all the solid sample supports considered give an appreciable sulfur signal in the resulting EDXRF spectrum and therefore are not suitable for the determination of trace amounts of this element in biodiesel samples. According to these results, Ultra-Carry[®] and glass fiber supports were selected as sample holder candidates for further studies, due to the low sulfur signal observed by EDXRF.

3.2 Sample volume deposited on the sample support

The sample volume deposited on the sample support can have a significant influence on the sulfur signal measured by EDXRF and therefore on the method sensitivity. For that, different volumes of a biodiesel standard containing 100 mg kg⁻¹ of sulfur were deposited on Ultra-Carry[®] and glass fiber supports, presented as circular pieces of 1.8 cm in diameter, and were analyzed by EDXRF. In the case of the glass fiber support, a higher size of the circle could be considered since the size is not limited as in the case of the Ultra-Carry[®] support (see images in Figure 1 for additional details). Nevertheless, for a better comparison, in both cases the same support size was considered. Moreover, in a previous publication it was demonstrated that if the dried residue is too large, only a small fraction of the analyte is excited and in consequence a low intensity of fluorescent radiation is observed [21].

As stated in the previous section, the Ultra-Carry[®] retainers are made of an external PET ring which holds a polyester film where the solid adsorbent is fixed. Therefore, this filter can be directly placed in the sample holder of the EDXRF system. In the case of the GF support, the circular piece of 1.8 cm in diameter has to be placed between two X-ray foils mounted in special sample holders to carry out the EDXRF analysis. Taking into account that the transmittance and potential impurities of the foil can affect the determination of sulfur at trace levels, a preliminary study using different X-ray foils made of polyester (Mylar[®], thickness: 5µm, Chemplex Industries, Inc), polypropylene

(Prolene[®], thickness: 4 μm , Chemplex Industries, Inc) and polycarbonate (BR-Polycarb-3, thickness: 5 μm , Breitländer, LGC Standards) was carried out. EDXRF spectra obtained from the analysis of the different foil materials showed that the use of polycarbonate and polyester foils is hampered by the presence of a high sulfur signal in the polycarbonate foil and the presence of high amounts of chlorine (arising from the impurities of polyvinyl chloride, PVC) in the polyester foil that hindered the fitting of the sulfur peak. In view of these results, experiments dealing with the use of GF as sample support were performed using X-ray foils made of polypropylene.

In Figure 1, the effect of sample volume deposited on Ultra-Carry[®] and GF supports on the relative sulfur EDXRF signal is displayed. Deposition volumes higher than 50 μL were not considered since it was the maximum volume that could be used in Ultra-Carry[®] sample holders without damaging its surface. In order to evaluate the effect of using higher sample volumes on sulfur response, three aliquots of 30 μL were subsequently deposited on the supports (total volume of 90 μL) and the results obtained were compared with those obtained using a single deposition of 50 μL . As it can be seen, the best option for sulfur determination at trace levels was the deposition of 50 μL of biodiesel onto the commercially available Ultra-Carry[®] sample holders. The use of a higher volume using successive deposition does not greatly improve the sulfur signal surely due to potential absorption issues when depositing larger sample volumes that weaken the sulfur analytical response. It is also important to highlight that the use of a single deposition step improve the method performance since the time used to prepare the sample is significantly reduced.

3.3 EDXRF measurement conditions

To obtain the best analytical signal for sulfur determination, an evaluation of the best EDXRF measuring conditions was performed. Tests were conducted by analysing 50 μL of a biodiesel standard containing 100 mg kg^{-1} of sulfur on the commercially available Ultra-Carry[®] sample holder.

Firstly, the influence of the high voltage of the X-ray tube on sulfur determination was evaluated. The aforementioned sample was measured at 10kV, 20 kV and 40 kV. In the latter case, a primary filter of 200 μm of Al was used to reduce the continuum of the X-ray tube. EDXRF spectra obtained using the different excitation conditions are

displayed in Figure 2. As expected, better excitation was obtained when setting the X-ray tube at low high voltages [15]. Finally, the X-ray tube was set at 20kV for further measurements since at such conditions a similar signal-to-noise ratio for sulfur determination was obtained in comparison with 10 kV but with a higher sulfur response.

In XRF, the relative standard deviation (RSD) for replicate measurements of a single sample is supposed to reflect the uncertainty due to the instrument and counting statistics. Usually, RSD values decrease when increasing the measurement time and therefore, statistical errors can be reduced to a minimum by selecting appropriate measurement times. In order to evaluate RSD values using the proposed EDXRF method, 50 μL of a biodiesel standard containing 100 mg kg^{-1} of sulfur were analysed in quadruplicate in the range of 50 to 300 s. Results obtained are summarized in Figure 3. As it is shown, RSD values are significantly decreased (from ~ 12 to ~ 6 %) when increasing the measurement time from 50 to 300s. According to these results, a measurement time of 300 s was selected for further experiments. Higher measurements times were not considered so as not to increase the total analysis time of the proposed EDXRF in comparison with the ASTM D4294 standard method which recommend a counting time for sulfur determination at low levels (0 to 0.1%) between 200 and 300 s [12].

3.4 Analytical performance of the developed EDXRF method

Accurate results in XRF analysis require strategies to compensate interferences imposed by the sample matrix. Some strategies used for such purpose include the use of internal standards, mathematical corrections or an element calibration using standards with a similar matrix to the target samples. For instance, Doyle et al [7] employed fundamental parameters method using ASTM proficiency test samples to perform mathematical adjustment of the analytical model to quantify the amounts of S, Ca, Fe, Ni and V in crude oil samples. Other authors used empirical calibration with available standard solutions in an oil matrix and matrix corrections such as Compton normalization or internal standardization as quantitative strategy for trace metal determination [2, 8, 22].

In the present contribution, empirical calibration was used as quantification approach. For such purpose a set of commercial biodiesel standards in the range of 10-100 mg kg⁻¹ of sulfur (plus a blank standard, also commercially available) were analyzed using the best analytical conditions aforementioned and the sulfur signal was plotted versus concentration. It should be noted that in order to obtain a good fit for the calibration at low concentration levels, a proper estimation of the peak signal and the background is needed. For this reason, a careful study of the background estimation for sulfur determination was carried out. Three different approaches were tested: (1) considering the background under the analyte peak by using a mathematical algorithm given by the software, (2) selecting a region of interest for the sulfur peak and two background regions placed on both sides of the sulfur peak and (3) selecting a region of interest for the sulfur peak and one background region placed on the right side of the sulfur peak.

Results obtained in the analysis of a set of biodiesel standards containing sulfur concentration in the range of 10 to 100 mg kg⁻¹, demonstrated that the best way to estimate the background, and thus the net sulfur signal, was selecting a region of interest for the sulfur peak and one background region placed on the right side of the peak. The other two approaches were discarded due to the inaccuracies in the background estimation.

In addition to a proper evaluation of the peak signal and the background, it is of significance the correction of analyte response from line overlapping and absorption issues arising from neighboring elements and sample matrix. In the case of sulfur determination, the analyte signal was corrected by the responses of Cl-K α , Si-K α and Pd-K α (arising from the X-ray tube anode) lines.

After checking the conditions that lead us to the best data quality, a good linearity (R^2 : 0.990) was obtained over the studied concentration range (10-100 mg kg⁻¹). Concentrations higher than 100 mg kg⁻¹ of sulfur were not evaluated because the method goal was to determine trace amounts of sulfur (<100 mg kg⁻¹) in biodiesel samples.

Limit of quantification (LOQ) for sulfur determination using the developed EDXRF method was also evaluated from the standard deviation of the calibration curve and it was found to be below 10 mg kg⁻¹. As it is shown in Table 3, this value is better than

that estimated by the ASTM D4294 method, even using a sample amount 100 times lower and a low-power EDXRF system with a maximum power of 50 W. An additional advantage of the proposed method in comparison with the ASTM D4294 method is the possibility of sample re-analysis. In the case of ASTM D4294 method, a few mL of petroleum product are directly placed in a plastic cup with a proper X-ray film. Using such approach, samples should be analyzed immediately after pouring into the sample cell to avoid sedimentation or change of concentration over the time. Another drawback is the formation of air bubbles inside the cell caused by mixing. For this reason, if the sample needs to be re-analyzed a freshly prepared sample cup with a fresh portion of sample shall be used. In this sense, the solid sample support used in the present study for biodiesel sample deposition can act not only as a suitable media for sulfur determination by XRF, but also as a suitable material to preserve the analyte until the appropriate analysis or re-analysis can be done. As it is shown in Figure 4, acceptable standard deviations between results obtained in the analysis of two biodiesel standards containing 50 and 100 mg kg⁻¹ of sulfur immediately after preparation or after two weeks were obtained. This finding shows that the amount of sulfur on the solid support does not change overtime and opens the possibility of biodiesel samples preservation and storage.

Another interesting aspect of the developed EDXRF method is the decrease of sample consumption and waste generation in comparison with the standard method. For example, for ultra-low (<50 mg kg⁻¹) sulfur levels the standard method recommends the use of disposable cells instead of the reusable ones which increase the amount of wastes generated and limit the method sustainability.

3.5 Application of the EDXRF method to quality control samples

As recommended by the ASTM D4294, precision and accuracy of the method should be evaluated by means of quality control samples. Given the fact that, to the best of the authors' knowledge there are no biodiesel certified reference materials with sulfur suitable contents (both NIST SRM 2773 and NMIJ CRM 8302-a show values that are very close to the LOQ of our method), three samples were prepared in our laboratory and processed as unknowns. These three quality control samples were prepared in-house by dilution of the biodiesel standard containing 100 mg kg⁻¹ of sulfur with the

blank standard (that has the same matrix), up to levels of approximately 20, 40 and 75 mg kg⁻¹. Results obtained for triplicate analysis using the developed EDXRF method are reported in Table 4. As it is shown, no statistically significant differences were obtained between expected sulfur concentration and those estimated using the EDXRF method with recovery values between 94-113% in the range of 20 to 75 mg kg⁻¹ of sulfur. This fact confirms that, if proper matrix-matching is done, the method can provide accurate results.

RSD values calculated at different sulfur concentrations are also reported and as it can be seen, they are similar to those obtained by the ASTM D4294 method for similar sulfur concentrations. However, it is interesting to have in mind that the amount of sample analyzed using the developed method is 100 times lower than the standard method.

Evaluation of the total repeatability of the proposed EDXRF method including the contributions arising from the EDXRF measurement and sample preparation was also carried out. Tests were performed analyzing four replicates of a biodiesel standard containing 100 mg kg⁻¹ of sulfur. Besides, one of the replicates was measured four times and the RSD associated was also calculated. This uncertainty is related to the instrument stability and counting statistics. Therefore, by means of error propagation, the uncertainty due to sample preparation (deposition of the biodiesel onto the solid support) can also be estimated. Results obtained are displayed in Table 5. As it is shown, global precision is acceptable according to the ASTM D4294 method for this sulfur concentration level. From Table 5 it can also be deduced that uncertainties in sample preparation have a significant contribution to the global precision of the obtained results for sulfur determination.

4. Conclusions

A simple and sustainable EDXRF method based on the deposition of several microliters of biodiesel onto an organic thin layer and the analysis of the resulting adsorbed sample spot has been developed and successfully applied to determine low amounts of sulfur in biodiesel samples. With this simple sample treatment procedure, limits of quantification for sulfur can be improved in comparison with the most commonly used

ASTM D4294 method, even using an amount of sample significantly lower. Moreover, the solid sample support used in the present study for biodiesel sample deposition can act not only as a suitable media for sulfur determination by XRF, but also as a suitable material to preserve the analyte until the appropriate analysis can be done. This fact opens the possibility of sample re-analysis overtime. Moreover, since disposable cells are not required for sample measurements, the production of laboratory residues is decreased which is in agreement with green chemistry statements. In this regard it is also interesting to highlight that the EDXRF system used is equipped with a low power X-ray tube and an SDD detector and thus, no gas or cooling media are needed for function.

The analytical performance of the method developed, in terms of accuracy and precision of the obtained results, is acceptable taking into account the low levels of sulfur, and the LOQ provided enables screening of biodiesel samples to determine compliance with the regulations in EU, EEUU or Japan. Despite the fact that the proposed EDXRF method has been developed for the specific determination of sulfur at low levels in biodiesel samples, the method can be extended to other petroleum products and other analytes although suitable calibration standards should be provided.

Acknowledgments

MR acknowledges the funding obtained *via* CTQ2015-64684P (MINECO/FEDER) and from the Aragón Government (Fondo Social Europeo).

Authors would like to acknowledge to Mr. Arnau Ortiz for his contribution on the performance of the experimental work.

References

- [1] M.F. Gazulla, M. Orduña, S. Vicente, M. Rodrigo, Development of a WD-XRF analysis method of minor and trace elements in liquid petroleum products. *Fuel* 108 (2013), pp. 247-253.
- [2] L.R. Barker, W. Robert Kelly, W.F. Guthrie, Determination of sulfur in biodiesel and petroleum diesel by X-ray fluorescence (XRF) using the gravimetric standard addition method-II. *Energy Fuels* 22 (2008), pp. 2488-2490.
- [3] Y. Kitamaki, Y. Zhu, M. Numata, Accurate characterization of sulfur in biodiesel fuel certified reference material. *J. Jpn. Petrol. Inst.*, 59 (2016), pp. 317-321.
- [4] V.C. Srivastava, An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Adv.* 2 (2012), pp. 759-783
- [5] A. Demirbas, Global biofuel strategies. *Energy Educ. Sci. Tech.*, 17 (2006), pp. 27-63.
- [6] A. Demirbas, Importance of biodiesel as transportation fuel. *Energy Policy*, 35 (2007) pp. 4661-4670.
- [7] A. Doyle, A. Saavedra, M.L.B. Tristao, R.Q. Aucelio, Determination of S, Ca, Fe, Ni and V in crude oil by energy dispersive X-ray fluorescence Spectrometry using direct sampling on paper substrate. *Fuel*, 162 (2015), pp. 39-46.
- [8] K. Zhang, J. Hu, S. Gao, Y. Liu, X. Huang, X. Bao, Sulfur content of gasoline and diesel fuels in northern China. *Energy Policy*, 38 (2010), pp. 2934-2940.
- [9] S. Pessayre, R. Bacaud, C. Geantet, M. Vrinat, Deep hydrodesulfurization of diesel oils. Matrix effects in the analysis of low sulfur diesel oils by energy dispersive X-ray fluorescence spectroscopy. *Fuel*, 78 (1999), pp. 857-860.
- [10] ASTM D 2622-16. Standard Test Method for sulfur in petroleum products by wavelength dispersive X-ray fluorescence spectrometry. (<https://www.astm.org/Standards/D2622.htm>).
- [11] ASTM D 7039-15a. Standard Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry (<https://www.astm.org/Standards/D7039.htm>)
- [12] ASTM D 4294.16. Standard Test Method for sulfur in petroleum and petroleum products by energy dispersive X-ray fluorescence spectrometry. (<https://pentasflora.com/wp-content/uploads/2014/02/D4294-Sulfur.pdf>)
- [13] ASTM D 7220-06. Standard Test Method for Sulfur in Automotive Fuels by Polarization X-ray Fluorescence Spectrometry. (<https://www.astm.org/DATABASE.CART/HISTORICAL/D7220-06.htm>)
- [14] ASTM D 7220-12. Standard Test Method for Sulfur in Automotive, Heating, and Jet Fuels by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry. (<https://www.astm.org/DATABASE.CART/HISTORICAL/D7220-12.htm>).
- [15] E. Marguí, R. Van Grieken, C. Fontàs, M. Hidalgo, I. Queralt. Preconcentration methods for the analysis of liquid samples by X-ray fluorescence techniques. *Appl. Spectrosc. Rev.*, 45 (2010), pp. 179-205.
- [16] E. Marguí, M. Hidalgo, I. Queralt, K. Van Meel, C. Fontàs, Analytical capabilities of laboratory, benchtop and handheld X-ray fluorescence systems for detection of metals in

aqueous samples pre-concentrated with solid-phase extraction disks. *Spectrochim. Acta Part B*, 67 (2012), pp. 17-23.

[17] G. Elias, E. Marguí, S. Díez, C. Fontàs, Polymer inclusion membrane as an effective sorbent to facilitate mercury storage and detection by X-ray fluorescence in natural waters. *Anal. Chem.*, 90 (2018), pp. 4756-4763.

[18] M. Resano, M.A. Belarra, E. García-Ruiz, M. Aramendía, L. Rello. Dried matrix spots and clinical elemental analysis. Current status, difficulties, and opportunities. *TRAC-Trend Anal. Chem.*, 99 (2018), pp. 75-87.

[19] E. Marguí, I. Queralt, E. García-Ruiz, E. García-González, L. Rello, M. Resano, Energy dispersive X-ray fluorescence spectrometry for the direct multi-element analysis of dried blood spots. *Spectrochim. Acta Part B*, 139 (2018), pp. 13-19.

[20] C. García-Florentino, M. Maguregui, E. Marguí, I. Queralt, J.A. Carrero, J.M. Madariaga, Development of X-ray fluorescence quantitative methodologies to analyze aqueous and acid extracts from building materials belonging to cultural heritage. *Anal. Chem.*, 89 (2017), pp. 4246-4254.

[21] R. Sitko, K. Kocot, B. Zawisza, B. Feist, K. Pytlakowska, Liquid-phase microextraction as an attractive tool for multielement trace analysis in combination with X-ray fluorescence spectrometry: an example of simultaneous determination of Fe, Co, Zn, Ga, Se and Pb in water samples. *J. Anal. At. Spectrom.*, 26 (2011), pp. 1979-1985.

[22] P.T. Palmer, D. Guinea, G. Chu, Rapid determination of trace metals in oil using handheld X-ray fluorescence spectroscopy, *Spectrosc.*, 29 (2014), pp. 38-45.

Table 1 Instrumental characteristics and measuring parameters used for EDXRF measurements

EDXRF benchtop system (S2 Ranger, Bruker AXS)	
Anode X-ray tube	Pd
kV/mA	20/0.284
Primary filter	None
Detector	XFLASH TM SDD, <129 eV at Mn-K _α
Measuring mode	Vacuum
Measuring time	300s
Absorption effect corrections	Variable alphas, Intensity model
Line overlap corrections by intensity	Cl-K _α , Si-K _α , Pd-K _α Compton
Analytical lines (keV)	S-K _α : 2.309

Table 2 Sulfur signal for different types of thin layers evaluated as sample supports for the analysis of biodiesel samples by EDXRF

Sample support		EDXRF analysis		
Tradename (supplier)	Material	sulfur peak (Cps)	Background (Cps)	sulfur net peak (Cps) ^b
Micro-Carry [®] (Rigaku) ^a	Proprietary	221.7	51.6	170.1
Ultra-Carry [®] (Rigaku) ^a	Proprietary	67.6	30.2	37.4
GF/F WHA1825047 (Whatman)	Glass-fiber	26.9	21.5	5.4
W n° 1 (Whatman)	Cellulose	206.8	34.8	172
W n° 42 (Whatman)	Cotton	270.0	56.3	213.7
W n° 542 (Whatman)	Cotton	259.5	38.7	220.8
7402-004 (Whatman)	Nylon	183.2	28.6	154.6
7184-004 (Whatman)	Cellulose	548.0	29.1	518.9
Filter paper (Whatman)	nitrate	603	38.3	564.7
	Cellulose derivative			

^a See section 2.1 for specific details, ^b Net peak: Peak-Background

Table 3 Comparison of analytical performance of the proposed EDXRF method and the reference method ASTM D4284 for the determination of sulfur in biodiesel samples

Characteristic	ASTM D4294	Developed EDXRF method
Type of XRF system	High-power	Low-power (50 W)
Sample volume (μL)	5000	50
Possibility of re-analysis	No	Yes
Limit of quantification (mg kg^{-1})	16 ^a	7

^a Estimated from the method's pooled limit of quantification (PLOQ) according to the ASTM D6259.

Table 4 Results obtained using the developed EDXRF method for the analysis of quality control samples prepared in-house containing different sulfur concentrations (n=3)

Quality control sample	EDXRF method		
	Determined sulfur (mg kg ⁻¹)	Recovery (%)	RSD (%)
21.3	24 ± 4	113	19 (16) ^a
39.1	39 ± 8	99	20 (14) ^a
75.3	71 ± 2	94	3 (11) ^a

^a In parenthesis RSD (%) values reported in the ASTM D4294 method for similar sulfur concentration levels

Table 5 Evaluation of the total repeatability of the proposed EDXRF method including the contributions arising from the EDXRF measurement and sample preparation. Tests were performed using a biodiesel standard containing 100 mg kg⁻¹ of sulfur

Uncertainty (RSD in %)		
Total (n=4, 1 measurement)	EDXRF measurement (n=1, 4 measurements)	Sample preparation ^b
9.7 ^a	4.7	8.5

^a RSD value recommended by the ASTM D4294 method at the level of 100 mg kg⁻¹ is 8.5%

^b Estimated by error propagation ($(RSD_{Total})^2 = (RSD_{EDXRF})^2 + (RSD_{Sample\ preparation})^2$)

Figure Captions

Figure 1. Relative sulfur signal obtained at different deposition volumes. (A) Ultra-Carry[®] ($\varnothing_{\text{effective}}$: 1.8cm), Glass fibre filter ($\varnothing_{\text{effective}}$: 1.8 cm). Tests were performed using a biodiesel standard containing 100 mg kg⁻¹ of sulfur.

Figure 2. Effect of the X-ray tube conditions and the use of primary filters on sulfur determination by EDXRF. Tests were performed using a biodiesel standard containing 100 mg kg⁻¹ of sulfur and a measurement time of 300s. Dashed line corresponds to the spectrum obtained for a blank sample carrier analysis.

Figure 3. Effect of measurement time on RSD values for the analysis of a biodiesel standard containing 100 mg kg⁻¹ of sulfur. Typical counting time for sulfur content determination according to the ASTM D4294 reference method is 200-300 s for sulfur concentrations up to 0.1%.

Figure 4. Variation of sulfur concentration determined in biodiesel standards overtime using the developed EDXRF method.

Figure 1.

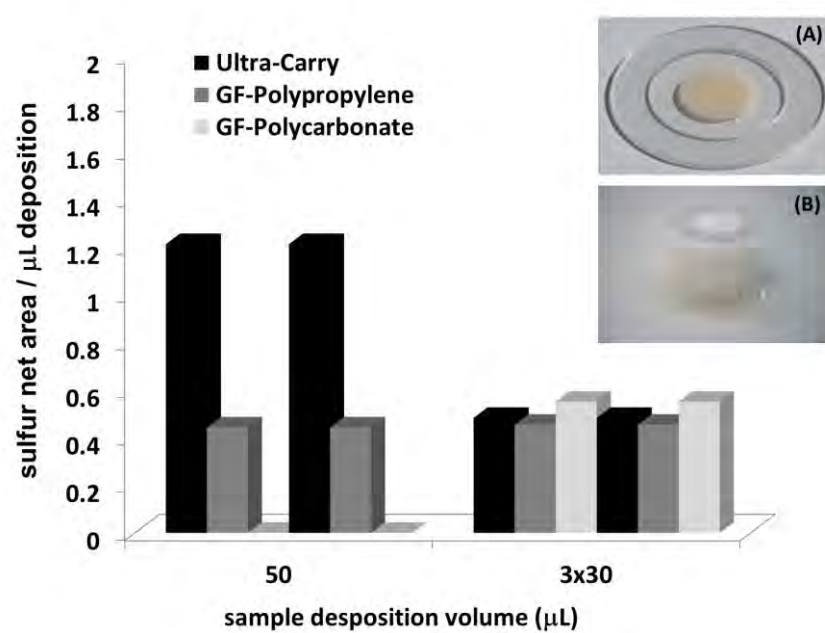


Figure 2.

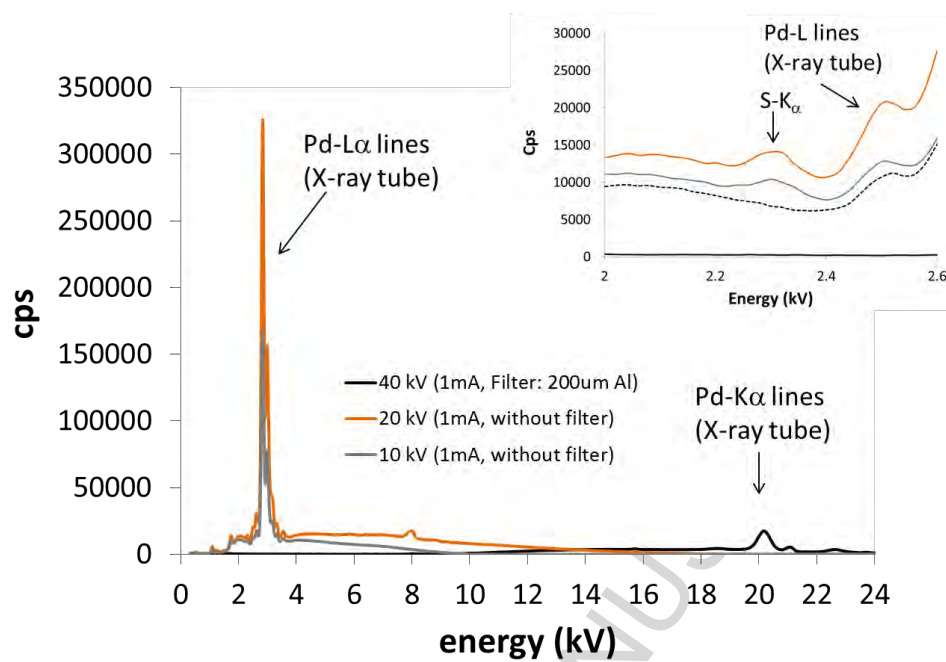


Figure 3.

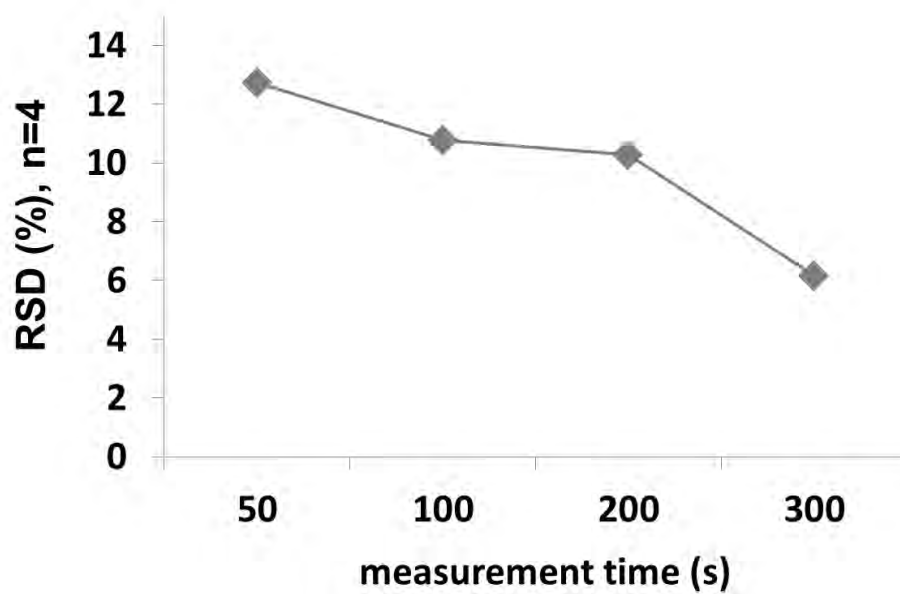
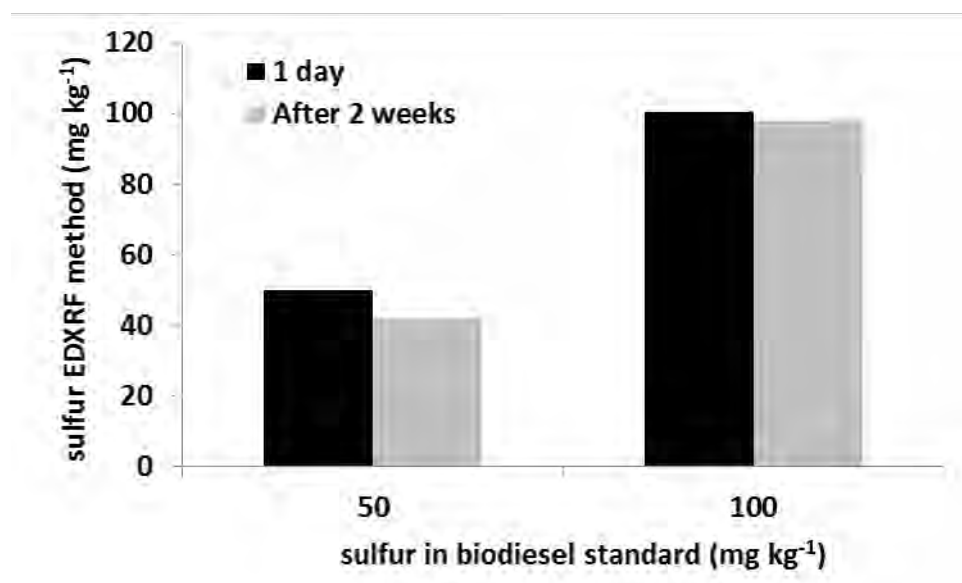


Figure 4.



HIGHLIGHTS

- A EDXRF method for S determination at trace levels in biodiesel samples is proposed
- Sample preparation entails formation of dried biodiesel spots
- Limit of quantification of sulfur in biodiesel is 7 mg kg⁻¹
- Quantification by biodiesel standards containing S in the range of 10-100 mg kg⁻¹
- Possibility of sample-reanalysis overtime.