

Títol del treball: Possibilities of energy dispersive X-ray fluorescence techniques (EDXRF) for the determination of trace amounts of sulfur in biodiesel samples

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RESUM

El sofre és un element químic poc tòxic en la seva forma elemental, però quan es converteix en diòxid de sofre al combustionar amb l'aire és un compost irritant i tòxic. Aquest compost és alliberat en molts processos de combustió ja que, combustibles com el carbó, el petroli, el dièsel o el gas natural contenen certes quantitats de sofre. Per tant, en l'actualitat hi ha una clara necessitat de disposar de metodologies analítiques que permetin la determinació de sofre a nivells traça (<100 ppm) en mostres de combustible.

Si ve existeixen mètodes estandarditzats per a la determinació de sofre en aquest tipus de mostres, aquests mètodes consumeixen una quantitat de mostra rellevant i generen una quantitat de residus considerable. Altres mètodes publicats en la bibliografia científica per a determinar sofre en mostres de combustible, basats en la utilització de tècniques basades en plasma, inclouen un tractament important de la mostra com la combustió induïda per microones.

L'objectiu d'aquest estudi és desenvolupar un mètode ràpid, eficaç, fiable i respectuós amb el medi ambient per a la determinació de continguts traça de sofre en mostres de biodièsel. Per aquest motiu s'han avaluat les possibilitats analítiques de la tècnica de fluorescència de raigs X per dispersió d'energia (EDXRF) i la tècnica de fluorescència de raigs X per reflexió total (TXRF) per a tal propòsit.

En el mètode de EDXRF desenvolupat, el tractament de mostra es basa en una simple deposició d'uns pocs microlitres de mostra líquida (50 μL) damunt un suport orgànic comercial (Ultra-Carry[®]) i el seu posterior assecatge al aire. Seguidament, el suport pot ésser analitzat de forma directa. Amb aquesta metodologia s'ha obtingut un límit de detecció pel sofre de 9 ppm i una exactitud i precisió dels resultats acceptables tenint en compte els nivells de concentració de treball.

En canvi, els resultats pel que fa la determinació de sofre mitjançant TXRF no han estat tan prometedors. S'ha demostrat que el límit de detecció d'aquesta tècnica no permet la determinació de concentracions traça de sofre (límit de detecció ~ 1000 ppm). Aquest fet es pot explicar tenint en compte el poc volum de mostra ($\sim 1\mu\text{L}$) que es pot depositar sobre el suport reflector necessari per a dur a terme l'anàlisi mitjançant TXRF i també a la impossibilitat de treballar en condicions de buit al fer la mesura, fet que és especialment crític en la determinació d'elements lleugers com el sofre.

RESUMEN

El azufre es un elemento químico de baja toxicidad en su forma elemental, pero éste, al combustionar con el aire forma dióxido de azufre, un compuesto irritante i tóxico. Éste, es liberado en muchos procesos de combustión debido al hecho que, combustibles como el carbón, el petróleo, el diésel o el gas natural contienen ciertas cantidades de azufre. Por lo tanto, en la actualidad hay una clara necesidad de desarrollar metodologías analíticas que nos permitan determinar niveles traza de azufre (<100 ppm) en muestras de combustible.

Si bien existen métodos estandarizados para la determinación de azufre en este tipo de muestras, estos métodos consumen una cantidad de muestra relevante y generan una cantidad de residuos considerable. Otros métodos publicados en la bibliografía científica para determinar azufre en muestras de combustible, basados en la utilización de técnicas basadas en plasma, incluyen un tratamiento importante de la muestra como por ejemplo la combustión inducida por microondas.

El objetivo del estudio es desarrollar un método rápido, eficaz, fiable y respetuoso con el medio ambiente para la determinación de contenidos traza de azufre en muestras de biodiesel. Por este motivo, se han avaluado las posibilidades analíticas de la técnica de fluorescencia de rayos X por energía dispersiva (EDXRF) y la técnica de fluorescencia de rayos X por reflexión total (TXRF) para este propósito.

En el método EDXRF desarrollado, el tratamiento de la muestra está basado en una simple deposición de unos pocos microlitros de muestra líquida (50 μL) encima de un soporte orgánico comercial (Ultra-Carry[®]) y su posterior secado al aire. Seguidamente, el soporte puede ser analizado de forma directa. Con esta metodología, hemos obtenido límites de detección para el azufre de 9 ppm y una exactitud y precisión de los resultados aceptables al considerar los niveles de concentración con los que hemos trabajado.

Por otro lado, los resultados referentes a la determinación de azufre mediante TXRF no han sido tan prometedores. Se ha demostrado que el límite de detección de la técnica no permite la determinación de concentraciones traza de azufre (LOD \sim 1000 ppm). Este hecho puede explicarse debido al poco volumen de muestra (\sim 1 μL) que puede ser depositado encima del soporte reflector necesario para el análisis utilizando TXRF y también a la desventaja de no poder trabajar en condiciones de vacío al realizar el análisis, hecho que es especialmente crítico para la determinación de elementos ligeros como el azufre.

ABSTRACT

Sulfur is a low-toxicity element in its elemental form, but when combusts with air becomes sulfur dioxide, an irritating and toxic compound. This compound is released from many combustion processes because of the fact that different fuels such as coal, petroleum, diesel or natural gas contain certain amounts of sulfur. Therefore, nowadays there is a clear need to develop analytical methodologies that allow the determination of trace amounts of sulfur (<100 ppm) in fuel samples.

Even though there are some standardized methods for the determination of sulfur in these types of samples, these methods consume noticeable amounts of sample and generate high amounts of waste. Alternative methods published in the scientific literature for the determination of sulfur in fuel samples, based on the utilization of plasma based techniques, include a laborious treatment of the sample such as microwave-induced combustion.

The aim of the study is to develop a fast, accurate, trustworthy and environmentally friendly method for the determination of trace amounts of sulfur in biodiesel samples. For this reason, the analytical possibilities of energy-dispersive X-ray fluorescence (EDXRF) as well as the total-reflection X-ray fluorescence (TXRF) have been tested for this purpose.

In the EDXRF developed methodology, the treatment of the sample is based on a simple deposition of few microliters of the liquid sample (50 μL) onto a commercially organic holder (Ultra-Carry[®]) and a later dryness step. Then, the sample holder can be directly analyzed. Using this methodology, we have achieved a limit of detection of 9 ppm for sulfur as well as acceptable accuracy and precision of the results if taking into account the working concentration range.

Besides, the results regarding to the determination of sulfur by means TXRF have not been as promising as the ones obtained by EDXRF. It has been demonstrated that the limit of detection of the technique do not permit the determination of trace amounts of sulfur (LOD \sim 1000 ppm). This fact can be explained due to the low amount of sample (\sim 1 μL) that can be poured onto the reflector holder needed for performing the analysis using TXRF and due to the handicap of not being able to work under vacuum conditions during the analysis, a particularly critical fact when determining light elements like sulfur.

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1. INTRODUCTION

1.1-BIO-BASED FUELS (BIODIESEL)

The negative environmental consequences of fossil fuels such as environmental pollution, acid rain or aquatic oil spill as well as the concerns associated with the petroleum supplies have spurred the search for renewable transportation bio-based fuels. To be a viable alternative, a biofuel should provide a net energy gain, have environmental benefits and be economically competitive without reducing food supplies. By the moment, bioethanol and biodiesel are, the more promising alternatives, being the biodiesel the most advantageous one¹.

Biodiesel is diesel fuel made from vegetable oils, animal fats or recycled restaurant greases. It is safe, carbon neutral, biodegradable, with a low-sulfur content and it releases a 93% more of energy than the energy invested in its production. Moreover, relative to the fossil fuels, it reduces a 41% the greenhouse gas emissions and it decreases the air pollutants per net energy gain released to the atmosphere. Biodiesel is almost never used in its pure form (B100), and is usually blended with petroleum diesel. The most common blends are B2 (2% biodiesel), B5 and B10. The most automakers approve blends up to B5 because high-level biodiesel blends can damage the engine of the cars as well as for avoiding the problems associated with diminution of the energy content per liter of fuel².

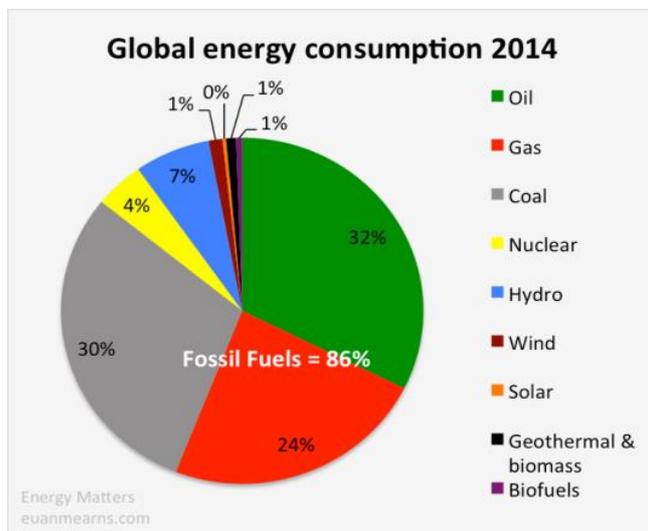


Figure 1: Pie chart of the global energy consumption, 2014^[3]

It is remarkable the fact that neither biofuel can totally replace petroleum without impacting food supplies because, for example, even dedicating all U.S. corn and soybean production to biofuels, they would meet just the 12% and the 6% of gasoline and diesel demand respectively. Thus, by the moment, the production costs are too high for converting biodiesel into a profitable energy source without blending it and without the governmental subsidies.

Figure 1 show that the use of biofuels during 2014 is positioned at the same level than other alternative energies representing a tiny percentage of the global energy consumption. It is important to highlight that the sum of oil, gas and coal (fossil fuels) still represent the 86% of the total energy used. Thus, further improvements in economic and energy costs have to be done for acquiring the energy from these resources.

1.2- DRAWBACKS OF SULFUR CONTENT IN FUEL

The air pollutants of major concern include SO_x , CO, NO_x , particulates, trace elements, olefins and aromatic hydrocarbons. These compounds are released from the exhaust gases after its combustion, and are converted into precursors to acid rain and atmospheric particulates.

Sulfur in the liquid fuel oil leads directly to the emission of SO_2 and sulfate particulate matter (SPM), endangers public health, reduces the life of the engine and can significantly impair the emission control technology designed to meet the NO_x and SPM emission standards. Additionally, it also contributes to a decrease of the efficiency of the catalysts used in some industrial processes.

Sulfur compounds represent one of the most common impurities present in the crude oil, and therefore, desulfurization methods have recently become an important subject of research. Sulfur is present in petroleum mostly as thiophenes, as sulfhydic acid and even in its elemental form. The research efforts have been focused on the development of methods based on the selective adsorption, biodesulfurizations and oxidative desulfurization in order to find a feasible solution to reduce sulfur to a concentration of less than 10 ppm⁴.

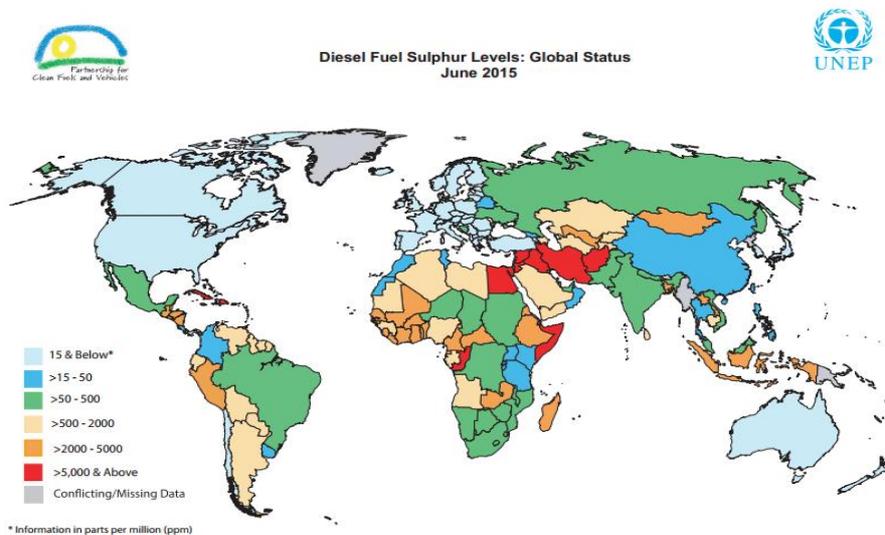


Figure 2: Diesel fuel global sulfur content status (2014)^[5]

In Figure 2 it is possible to observe the nationwide fuel sulfur levels for diesel and gasoline around the world (2014). This map only shows the national regulations and none the sub-national ones. Many countries around the world such as Brazil, China and India have some internal regulations that require higher quality fuels in key cities and regions. For example the capital city of China, Beijing, demands 10 ppm maximum sulfur content whereas in other regions of the country the permitted range increases up to 50 ppm. Hence, methods capable to detect low sulfur amounts in an accurate and trustworthy way are one of the challenges in the current chemical research.

1.3- ANALYTICAL TOOLS USED TO DETERMINE SULFUR IN FUEL

For sulfur determination in petroleum products, some standard test methods validated by the American Society of Testing Materials (ASTM) and the International Organization for Standardization (ISO) have been commonly used. ASTM and ISO are international standards organizations that develop technical standards for a wide range of materials, products, systems and services and the ones used for sulfur determination in fuels are ASTM D2622, ASTM D4294 and ISO 14596:2007.

ASTM D2622 and ISO 14596:2007 standard methods are based on the use of wavelength-dispersive X-ray fluorescence (WDXRF) while ASTM D4294 relies on the use of energy-dispersive X-ray fluorescence (EDXRF) (see section 1.4 for WDXRF and EDXRF basic principles details). ISO 14596:2007 indicates that the use of Zr as an internal standard for S in petroleum products improves the accuracy of the determination. The method is applicable to ranges from 0.001 % (m/m) to 2.50 % (m/m); higher contents can be determined by appropriate dilution⁶.

ASTM methods are based on the direct analysis of the liquid petroleum products by depositing 5 mL of sample in a disposable cell. Therefore, although the studies have shown the possibility to detect low concentrations of sulfur (<0.0001% (m/m) and 0.0017 % (m/m) for ASTM D2622 and ASTM D4294, respectively), the residues produced are noticeable^{7,8}.

In order to deal with this issue, a recent study published in the scientific literature shows the advantages of spotting a smaller amount of the sample (2x10 µL) onto a solid paper filter and analyzing it after a drying procedure⁹. However, this analytical approach has been only applied for the determination of sulfur in fuel and crude oils at considerable high concentration levels (0.2-2.9 %).

Alternatively to all those methods, sulfur in fuel samples has been also determined by XRF technique or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES) after using a more exhaustive sample treatment procedure¹⁰. For instance, Barker et al proposes the use of WDXRF spectrometry using the gravimetric standard addition method and Pereira et al. developed an analytical methodology based on the use of ICP-OES after a microwave-induced combustion (MIC). In both cases limits of detection around 3 ppm of sulfur have been obtained^{11,12}.

All methods described above present some limitations either for waste production, sample treatment or non-accurate results if working at trace concentration levels. Thus, the lack of accurate, fast, environmentally friendly and trustworthy methodologies for determining trace amounts of sulfur in fuel samples such as biodiesel justifies the development and the study of novel methodologies.

1.4- BASIC PRINCIPLES OF XRF TECHNIQUES

XRF is based on the use of an excitation radiation (usually an X-ray beam) to ionize the inner shells of the atoms present in the sample. This ionization brings the atoms to an excited state and produces an electron rearrangement that is translated into a characteristic energy releasement. These energies or wavelengths are then used to identify and quantify the elements present in the sample¹³.

XRF spectrometers are divided into two main categories depending on the fundamentals of the detection system. In wavelength-dispersive systems (WDXRF) the photons are separated by diffraction before being detected. WDXRF configuration relies on the use of an X-ray source that irradiates the sample and then a portion of the characteristic fluorescent irradiation is passed through the surface of the diffraction device, where the individual wavelengths are then diffracted to the detector according to Bragg's Law (Figure 3A). A simplest system consisting of two basic units, an excitation source and a detection system (EDXRF) can be used (Figure 3B). In this case, the resolution of the system is proportional to the resolution of the detector, and therefore a semiconductor of high resolution is typically employed. When the use of this detector is combined with a multichannel analyzer, the determination of all the X-rays emitted by the sample is allowable. Due to the count rate limitations of the semiconductor detector, source modifiers as well as filters, are commonly used to reduce the saturation of the detector and consequently the dead time of the analysis.

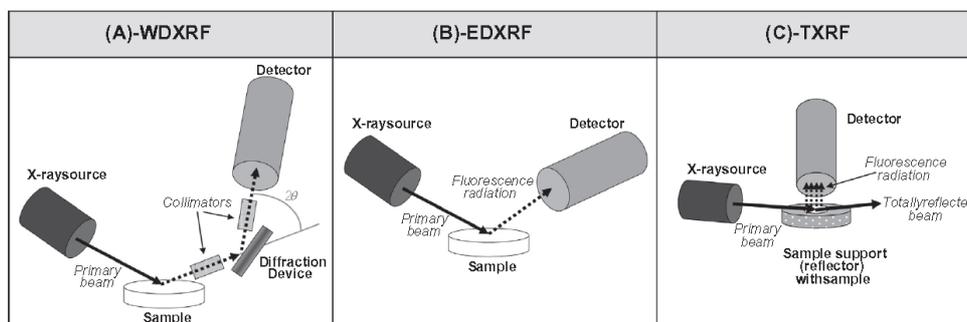


Figure 3: Basic designs for (A) WDXRF (B) EDXRF (C) TXRF systems^[13]

A variation of EDXRF is Total Reflection X-ray Fluorescence (TXRF) spectrometry. In this configuration, the primary beam impacts the sample at an angle of less than 0.1° instead of an angle of about 40° like in EDXRF (figure 3C, 3B). Moreover, the detector is placed very close to the sample. These facts contribute to an improvement of the sensitivity of TXRF systems compared to conventional EDXRF spectrometers.

EDXRF systems are usually preferred if multi-elemental information is needed and WDXRF is usually selected if a fast and accurate determination of only a few elements is required but flexibility is of little importance. Arising out from these statements, it appears more logical to use WDXRF when analyzing a single element as sulfur at low concentration levels, but it is important to take into account there are few commercially available benchtop WDXRF systems and therefore WDXRF analysis is usually performed by high-power systems which require higher investment costs and consumables¹⁴

2· OBJECTIVES

The goal of the study is to evaluate the possibilities of two low-power systems (EDXRF and TXRF) as analytical techniques for the determination of trace amounts (<100 ppm) of sulfur in biodiesel samples.

The concrete objectives of the project are:

- Evaluation of sample preparation and measuring conditions to carry out EDXRF and TXRF analysis of biodiesel samples.
- Evaluation of analytical capabilities (Limit of detection, linearity, accuracy and precision) of the proposed methodologies.
- Evaluation of the possibilities and drawbacks in comparison with other analytical methodologies.

3. METHODOLOGY

3.1- SOLUTIONS AND MATERIALS

- Standard solutions: CONOSTAN® Sulfur Standards in Biodiesel: 5, 10, 15, 30, 50, 100 ppm S (B100) blend.
- Certified Reference Material, National Institute of Standards and Technology: NIST 2773, Commercial 100% biodiesel CRM (7.39 ± 0.39 ppm S).
- Standard Reference Material, National Institute of Standards and Technology: SRM 1848, Lubricating oil for gasoline engines (2.327 ± 0.043 % S).
- Base oil 75 Standard: SPEX base oil for dilution of calibration standards.
- Thin films used for small size filters in EDXRF analysis

Table 1: Information referred to the thin films used in EDXRF analysis

Supplier	Tradename	Thickness (µm)	Material
Chemplex	Prolene	4	Polypropylene
Chemplex	Mylar	5	Polyester
Breitländer	BR-Polycarb-3	5	Polycarbonate

- Sample holders for EDXRF analysis

Table 2: Information referred to the different sample holders used in EDXRF analysis

Supplier	Tradename	Material
Rigaku	Micro-Carry®	Proprietary
Rigaku	Ultra-Carry®	Proprietary
Whatman	GF	Glass-fiber
Whatman	W n°1	Cellulose
Whatman	W n°42	Cotton
Whatman	W n°542	Cotton
Whatman	7402-004	Nylon
Whatman	7184-004	Cellulose Nitrate
Whatman	“Filter paper”	Cellulose derivatives

- Sample holders for TXRF analysis: Quartz glass discs with a diameter of 30 mm and thickness of 3 mm ± 0.1 mm (Bruker AXS, Spain)

3.2- INSTRUMENTATION

Recent technological advantages have led to the availability of benchtop low-power instrumentation. These smaller and more affordable instruments, present comparable LODs with large-scale system ones and therefore, great interest in its possibilities has recently risen up. In Table 3 instrumental characteristics and analytical conditions for the EDXRF and TXRF systems used in the present study are displayed. Moreover, in Figure 4, images of both systems are shown. Additional information about the selection of measuring conditions is displayed in sections 4.1.2 and 4.2.2

Table 3: Characteristics and analytical conditions for the EDXRF, TXRF systems (in parenthesis are shown the selected analytical conditions).

Equipment	EDXRF benchtop system (S2 Ranger, Bruker AXS)	TXRF benchtop (S2 Picofox, Bruker AXS)
Anode X-Ray tube	Pd	W
kV Range	10-50 (20)	(50)
µA	1-1000 (1000)	(1000)
Filters	5µm Ag, 200µm Al, 500µm Al, 100µm Cu, 200µm Cu (None)	None
Measuring mode	Air, vacuum, He (Vacuum)	(Air)
Measuring time (s)	(300)	(2000)
Detector	XFLASH™ Silicon Drift Detector (SDD) <129 eV at Mn-K _α	Peltier-cooled XFLASH™ Silicon Drift Detector (SDD) <150 eV at Mn-K _α



Figure 4: S2 Ranger (left) and S2 Picofox (right) benchtop systems, Bruker AXS

3.3- SAMPLE PREPARATION

3.3.1- EDXRF ANALYSIS

Figure 5 show an overview of the steps that were followed during the sample preparation for EDXRF analysis. First of all the sample is homogenized and after that, 50 μL of the sample are poured onto the commercially sample holders (Ultra-carry®). After two hours, the sample is dried and it can be placed into the sample holder. On top of the filter, a piece of teflon is placed in order to correct the background interferences. Detailed information about the conditions used for sample preparation and EDXRF measurement is displayed in sections 4.1.1 and 4.1.2.

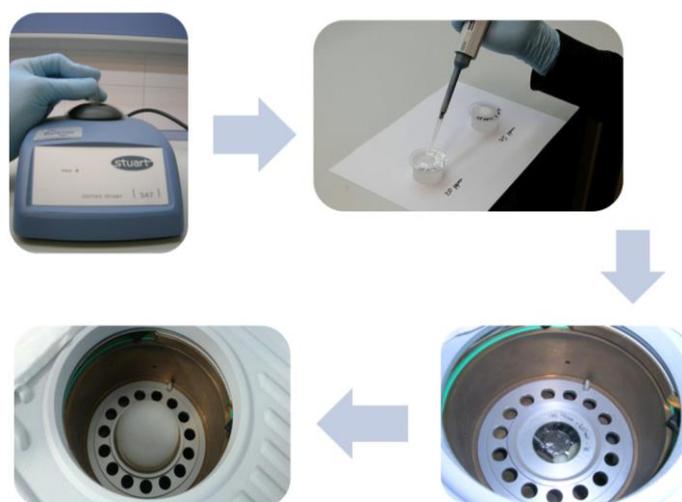


Figure 5: Sample preparation steps for EDXRF analysis of biodiesel samples

3.3.1- TXRF ANALYSIS

When TXRF analysis is performed, vortex and pouring steps are also followed but in TXRF, 2 μL are poured onto a reflective carrier. In addition, the dryness step is helped by applying heat with a hot plate set at 95°C. When the sample is dried, it is placed in the sample carrier and the sample cassette placed into the analyzer. Detailed information about the conditions used for sample preparation and EDXRF measurement is displayed in sections 4.2.1 and 4.2.2.



Figure 6: Sample preparation steps for TXRF analysis of biodiesel samples

4. RESULTS AND DISCUSSION

4.1- EDXRF ANALYSIS OF BIODIESEL SAMPLES

4.1.1- EVALUATION OF SAMPLE PREPARATION STRATEGY

There are several parameters related to the sample preparation that must be previously tested to obtain a high-quality data from the analysis performed. In the case of EDXRF, the following assays have been performed:

4.1.1.1- Type of sample holder

The first step of the study was to determine the proper sample holder to deposit the samples for the later EDXRF analysis. This fact is very important in order to determine low amounts of S in the target biodiesel samples. The analyses of the blanks of these different substrates proportionate a first overview of the possibilities of each support for the intended purpose.

Table 4: Data obtained from the analysis of the different sample holders when using EDXRF analyzer

Sample holder	Peak (Cps)	Background (Cps)	Net peak (Cps)
Micro-Carry	221,67	51,61	170,06
Ultra-Carry	67,64	30,17	37,47
Glass-fiber	26,88	21,54	5,34
Whatman 1	206,81	34,77	172,04
Whatman 42	270,01	56,32	213,69
Whatman 542	259,47	38,65	220,81
Nylon	189,23	28,57	160,66
Cellulose nitrate	548,00	29,13	518,87
Filter paper	303,03	38,25	264,75

*Cps: Counts per second

Observing the results obtained in Table 4 it can be concluded that almost all the materials contain trace amounts of sulfur and therefore, the majority of the sample holders are not appropriate for its intended use.

The spectrums deriving from the blank tests are shown in Figure 7. It is possible to observe a general view of the spectrum obtained as well as a zoom view of the region where the K lines from sulfur compounds appear (≈ 2.3 kV).

Analyzing the results, Ultra-Carry® and GF (glass-fiber) sample holders were chosen as the most promising ones for further studies. If looking to the zoom of both sample holders, it is possible to observe that little sulfur amounts are present and that the only drawbacks that can arise are related to the interferences of neighboring elements.

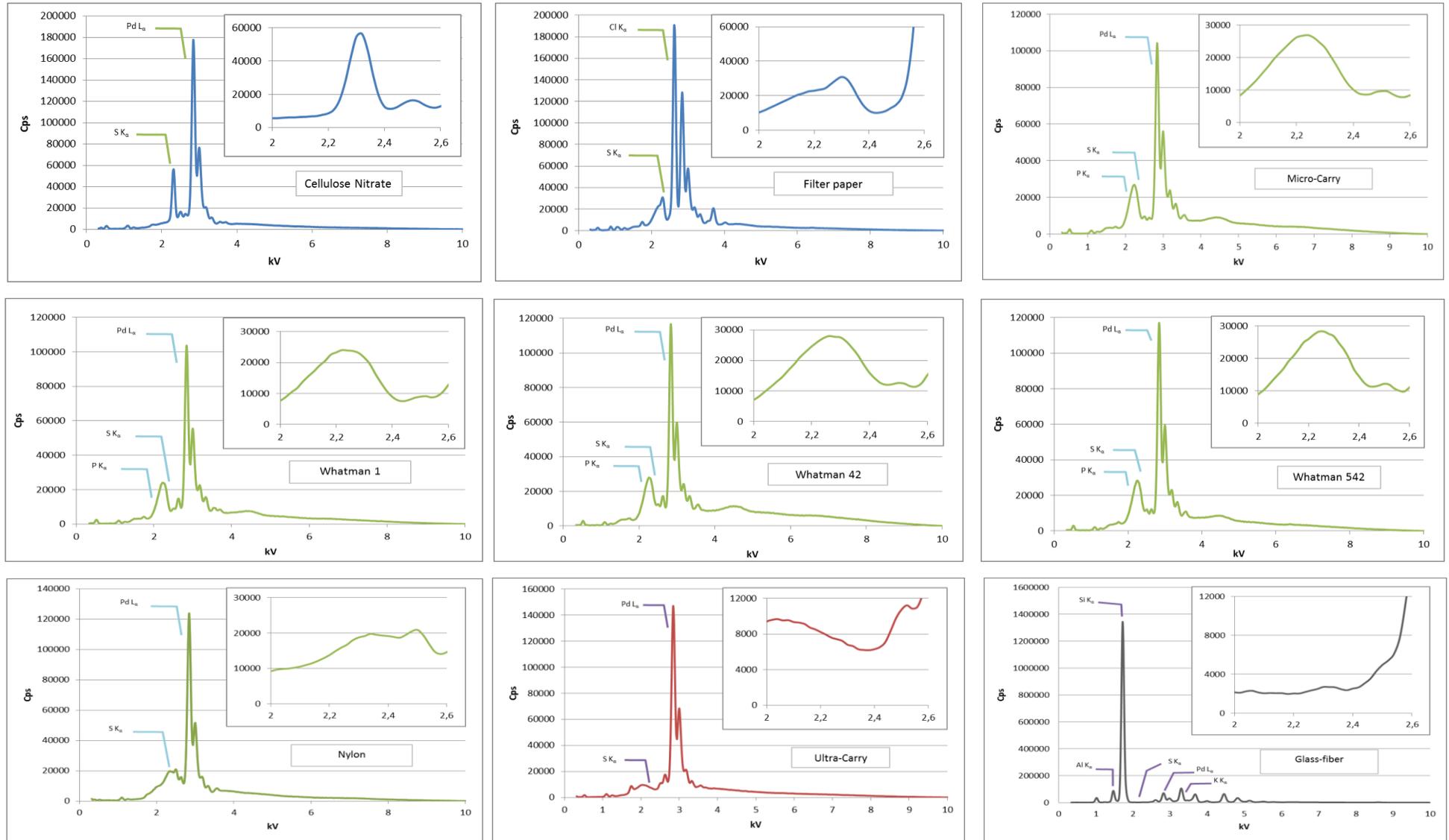


Figure 7: Spectrums obtained from the blank analysis of the sample holders. The Pd L is present in all the spectrums because of the material of the X-ray tube anode

4.1.1.2- Sample holder size

In order to determine if the filter size is a parameter that affects to the signal obtained, two different diameter sizes (2cm and 4.2 cm) of the GF (glass-fiber) sample holders were studied. In the case of the Ultra-Carry® support it is not possible to study the support size effect and experiments were performed using the commercially available sample deposition area (\varnothing : 1.8 cm). Due to the diameter of the EDXRF sampler, the use of smaller sizes hampers the possibility to directly analyze the sample and it has to be mounted in an adequate plastic cell using adequate thin films to fix it (see Figure 8). Special attention during the cell preparation has to be taken because of the fact that the wrinkles in the film will affect the number of transmitted X-rays.

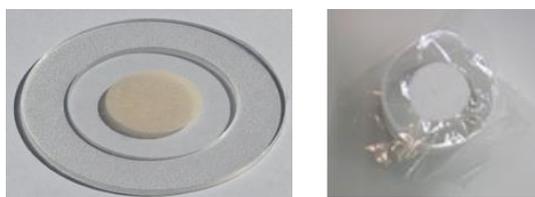


Figure 8: Images of the Ultra-Carry® and GF (glass-fiber) sample holders used in this study

The common film types can include polyester, polypropylene, polycarbonate and polyimide⁷. However, polycarbonate is usually preferred because of its high transmissivity of sulfur X-rays. Figure 9 shows the transmittance of some commonly used films in function of the energy applied and the thickness of the materials. The transmittance is defined as the fraction of energy that once entered into a layer of absorbing matter is able to reach the detector. In conclusion, when the transmittance is increased the energy detected and the sensitivity of the method will be usually increased as well. Regarding to these considerations is understandable that the transmittance of the materials increases when the film is thinner and the energy is higher.

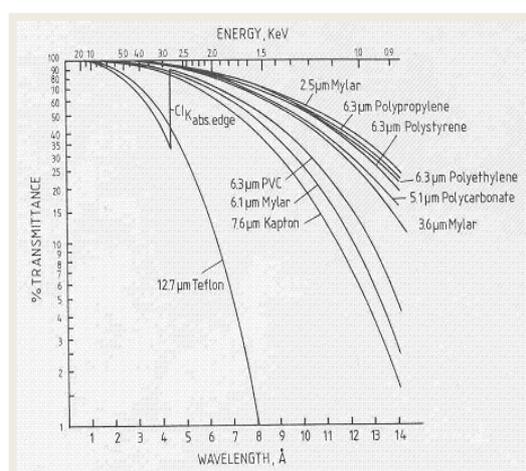


Figure 9: Percentage of transmittance of different materials in function of the energy applied

In our case, films available were from polyester, polypropylene, and polyethylene. With the purpose of finding out impurities which may affect the measurement of the method, blank analyses of those materials were performed.

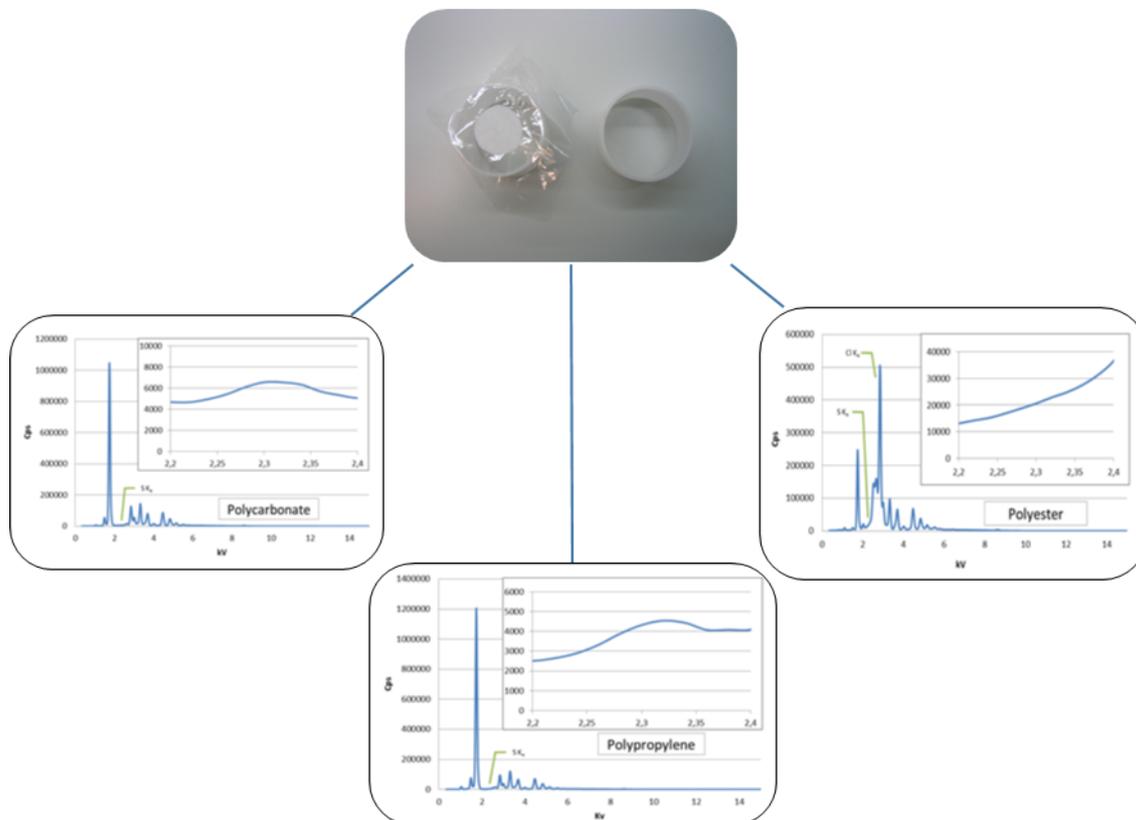


Figure 10: Sample preparation when using thin film materials and related TXRF spectra

If looking to the spectrums from Figure 10, on the one hand it can be concluded that the use of polycarbonate and polyester films is impaired due to the presence of a high amount of sulfur in polycarbonate film and to the presence of chloride interferences in polyester film. On the other hand, polypropylene film contains sulfur but in a lower amount, and therefore the studies were focused on the use of this thin film material.

4.1.1.3- Sample deposition volume

As stated in the previous section, a careful evaluation of the sample support size (in the case of the GF filters) and also the sample deposition volume was carried out in order to improve the sensitivity for sulfur determination.

Due to the size of the substrates, and in order to probe all the material deposited onto the sample holders, three aliquots of 30 μL of the biodiesel standard containing 100 ppm were poured. The results were compared with those obtained using a single deposition of 50 μL of the same standard (this is the maximum volume that can be used when using the commercial sample holders, Ultra-Carry®, without damaging its surface). Figure 11 depicts the ratio between the response given by the analyzer (Cps) and the amount of compound poured onto the substrate (μL). As bigger is the ratio bigger is the response and, in consequence, the quality of the data obtained from the analysis. Thus, the influence of different parameters such as the type and diameter of the sample holder, the use of thin films or the volume poured onto the substrate are evaluated in the bar chart.

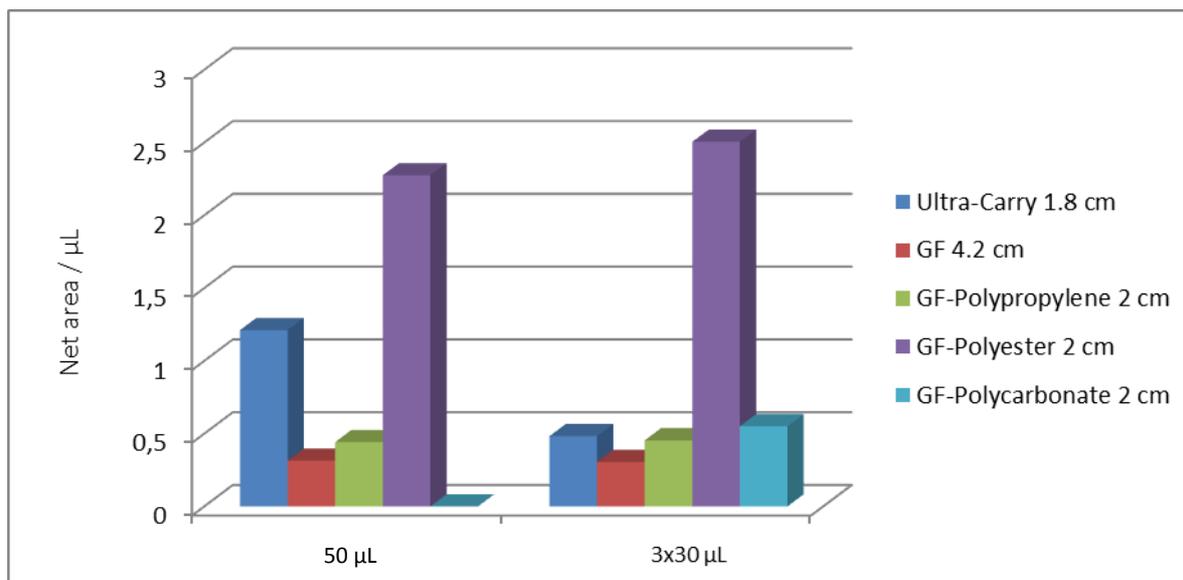


Figure 11: Bar graph representing the ratio (area/ μL) in function of the volume poured

Having a look at the aforementioned data, there are many remarkable facts to comment. The use of glass-fiber sampler holders with a polyester thin film seems to be the best option. Unfortunately, observing the spectrum of the blank (Figure 10) it is clear that the response obtained it is misrepresented by the interference of the chlorine that contains the film. Actually, it was foreseeable because the polyester used is the polyethylene terephthalate (PET) that usually contains impurities of polyvinyl chloride (PVC) due to the difficulties that presents the separation of these compounds¹⁵.

Therefore, taking into account the results reported in Figure 11, it seems that the best option for S determination at low levels is the use of a single deposition of 50 μL of the biodiesel sample onto commercially available Ultra-Carry® sample holders. Therefore, further studies will be focused on the use of this sample carrier. It is important to highlight that the use of a single deposition step improves the quality of the method because, among other things, long drying times after each deposition are avoided.

4.1.2- EVALUATION OF MEASUREMENT CONDITIONS

4.1.2.1- Measuring time

In XRF, the RSD values for replicate measurements of a single sample are supposed to reflect the uncertainty due to the instrument and counting statistics (repeatability). Usually, RSD values decrease when increasing the measuring time and therefore, statistical errors can be reduced to a minimum by selecting appropriate counting times¹³.

According to the ASTM D4294 standard method, the recommended counting time for sulfur determination at low levels (0.0000 to 0.1000%) is between 200 and 300 seconds⁷. In order to evaluate RSD values applying our method, one replicate of the 100 ppm biodiesel standard was analyzed four times at different measurement times. Results obtained are shown in Figure 12.

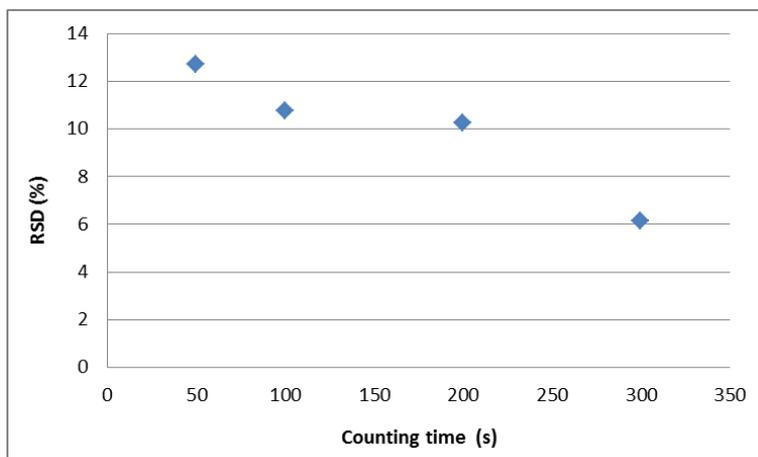


Figure 12: Percentage of relative standard deviation vs time of analysis

The results obtained show how there is a clear diminution of the deviation of the results when the counting time is increased and therefore, the measurement conditions were set to 300 seconds.

4.1.2.1- X-ray tube conditions

Another instrumental condition that is directly related with the spectrum shape and the sensitivity of the method are the X-ray tube conditions (kV/mA). The flow of electrons between the cathode and the anode is dependent on the current applied to the X-ray tube (expressed in mA) while the speed at which the electrons travel and strike the anode depends on the applied voltage (expressed in kilovolts). Therefore, both parameters influence the intensity of the X-ray radiation emerging from the tube. Taking this into account, the power of the X-ray tube, which is expressed as the product of the current and the high voltage, will be one of the most important parameters related to the sensitivity of XRF systems¹³.

In Figure 13 obtained EDXRF spectra for the analysis of a biodiesel standard containing 100ppm of sulfur using different excitation conditions are shown.

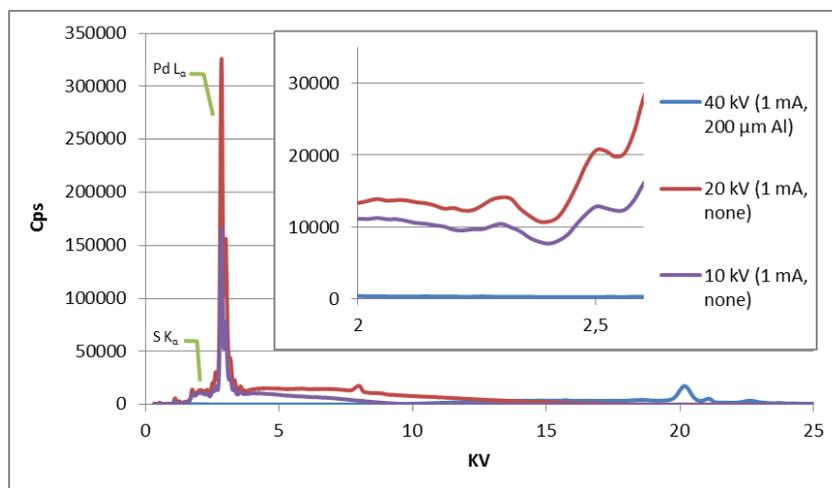


Figure 13: Spectrum shape in function of the X-ray power settings

When the power is set to 20 kV the counts per second (Cps) are higher than when the power is set to 10 kV. This fact is usually translated into higher sensitivities. On the other hand, when the power is set to 40 kV the use of primary filters to reduce spectral background is highly recommended. Filters are usually made from thin metal layers (10-500 μm) and act as absorbers for reducing the interfering lines. However, under these conditions sulfur was not possible to be detected. Taking into account the obtained results, the X-ray tube was set at 20 kV and the use of primary filters was avoided.

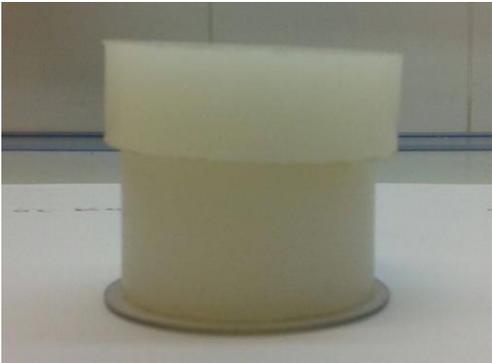
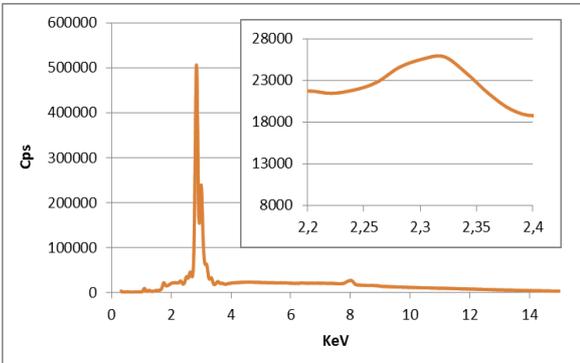
4.1.2.3- Sample measurement mode

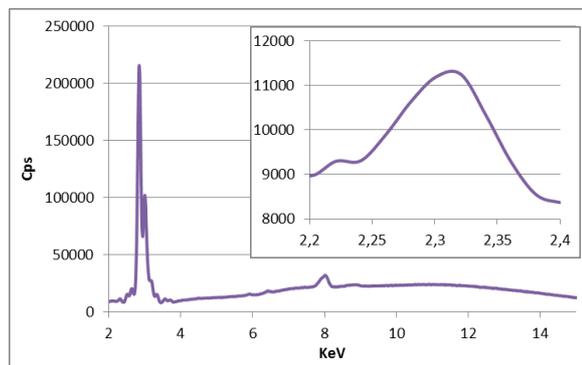
In XRF analyzers, the sample is usually placed into a metal holder cup (see Figure 5). Hence, radiation coming from these materials can interfere to the spectrum shape and the results of the determination. This fact is particularly relevant when thin layers (such as organic thin films) are analyzed.

In order to correct these interferences, a material (mask) with a low percentage of transmittance under the measurement conditions is used. As shown in Figure 9, Teflon has got a low transmittance at 20 kV that makes it a proper mask material for our determination. Two different Teflon configurations were evaluated to be placed on the loaded Ultra-Carry[®] holder back (100ppm sulfur standard) for such purpose.

As it can be observed in Table 5, when using a double-Teflon piece configuration the signal obtained is much higher than when using a single-piece configuration but the signal-to-noise ratio for sulfur peak is not significantly different. Taking into account that the dead time (amount of time that the spectrometer electronics are not allowable to process another analysis) is longer when more counts per second (Cps) arrive to the detector, a single-piece configuration was chosen.

Table 5: EDXRF spectrum obtained in function of the Teflon configuration used

Mask configuration	Spectrum
	



4.1.3- ANALYTICAL PARAMETERS

4.1.3.1- Evaluation of the detection limit

One of the most important parameters to evaluate is the limit of detection (LOD). This parameter, which is usually defined as the smallest amount of the compound that can be detected in a reliable way, in XRF spectrometry, it is usually calculated using the following formula:

$$LOD = \frac{3 \cdot [Concentration] \cdot \sqrt{Background}}{Net\ area} \quad (Equation - 1)$$

By using the aforementioned formula (using the results obtained in the analysis of a biodiesel standard solution of 15 ppm) a limit of detection of 9.6 ppm of sulfur was calculated. Taking into account that the official Standard Test Method (D-4294) reaches a LOD of 17.0 ppm using 5 mL of sample instead of 50 μ L, it is reasonable to conclude that the method developed has reached surprising efficient results.

4.1.3.2- Calibration

When determining trace concentrations, it is really important the proper estimation of the peak signal and the background in order to obtain a linear response between XRF net signal and analyte concentration. 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 estimation based on a mathematical algorithm given by the software (see blue lines in Figure 14), (2) selecting a region of interest for the sulfur peak and two background regions placed on both sides of the sulfur peak (see Figure 14 A) and (3) selecting a region of interest for the sulfur peak and one background region placed on the right side of the sulfur peak (see Figure 14 B).

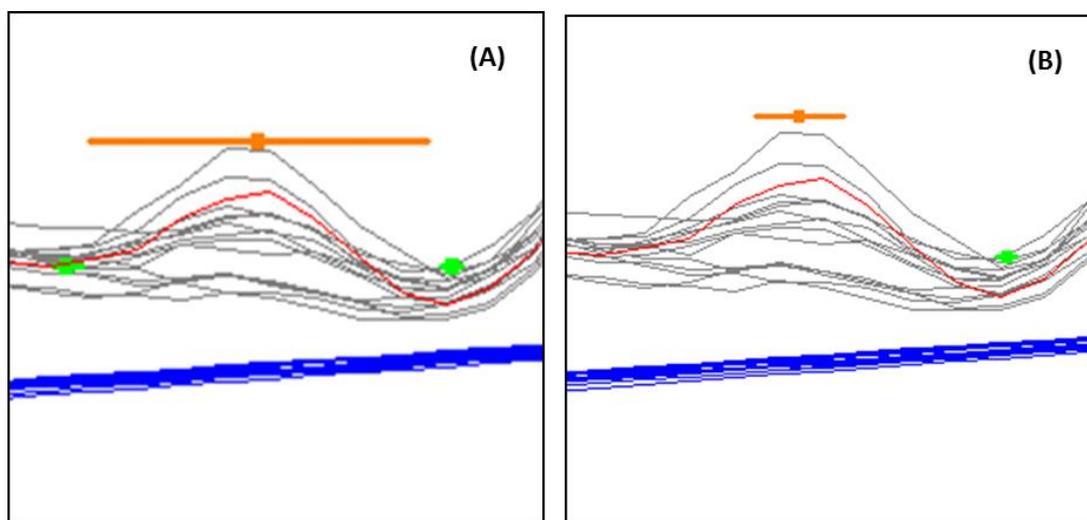


Figure 14: Comparison between using a double integration range (A) or a single integration range (B) for background estimation (green lines: background regions, orange line: sulfur peak region, blue line: background estimated by the software based on a mathematical algorithm).

Results obtained in the analysis of a set of biodiesel standards containing S concentration in the range of 10 to 100 ppm, 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 (Figure 14B). 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. 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 calibration curve by using CONOSTAN B100 standards from 10 to 100 ppm of S (see 3.1) was performed and the data obtained is shown below in Figure 15.

As it is shown, an acceptable linearity was obtained over the studied concentration range. It is remarkable the fact that higher concentrations than 100 ppm of sulfur were not evaluated because the method goal was to determine trace amounts of S (<100 ppm) in biodiesel samples.

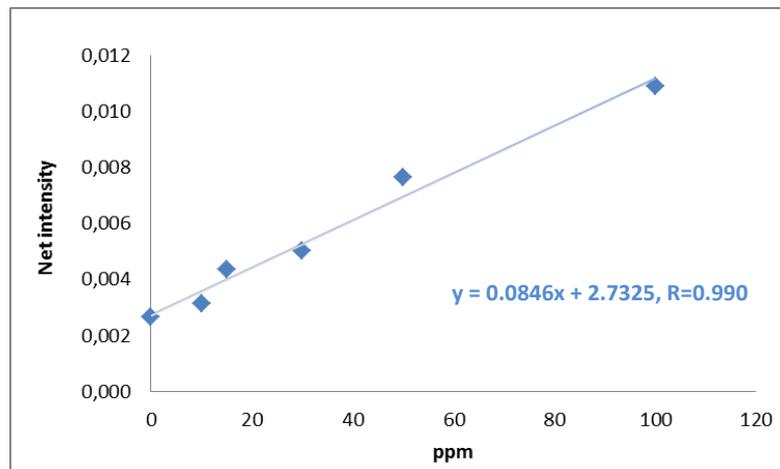


Figure 15: Linearity of the proposed methodology using CONOSTAN Standards (B100 matrix)

4.1.3.3- Evaluation of precision

As mentioned in section 4.1.2.1, the analysis of an individual replicate sample several times under the same conditions gave information about the instrumental standard deviation associated to the method. Moreover, by analyzing several different sample replicates, the global standard deviation (sum of instrumental and sample preparation error) can be estimated. Then, using equation-2, based on the propagation of aleatory errors, uncertainties arising from the sample treatment can be evaluated.

$$(RSD)_{Total}^2 = (RSD)_{Instrumental}^2 + (RSD)_{Sample\ preparation}^2 \quad (\text{Equation} - 2)$$

In the present study, an experimental test was performed in order to evaluate the global precision of the method and also the contribution of instrumental and sample preparation uncertainties. For that, four independent replicates of a biodiesel sulfur standard of 100ppm were measured once (global precision) and then one of this replicates was measured four times (instrumental uncertainty). These tests reported a percentage of RSD of 9.74 % and 4.65% for instrumental and global precision respectively. Then, using Equation-2, it can be deduced that the major contribution on the global precision is due to inaccuracies during the sample preparation step.

If comparing the percentage of relative standard deviation recommended by the ASTM D4294 standard method (repeatability values) at the level of 100 ppm of sulfur (8.5%)⁷ with the values obtained (9.74%), we can conclude that the precision of the results from the developed methodology is acceptable.

4.1.3.4- Evaluation of the accuracy

In order to evaluate the reliability of the method, usually a certified reference material is used. For the determination of low level of sulfur in biodiesel there is a commercially available certified reference material (NIST 2773). However, the certified sulfur concentration is as low as 7.39 ± 0.39 ppm and this concentration is around the limit of detection of the method. Therefore, it was not possible to use it to evaluate the accuracy of the developed methodology.

In order to cope with this problem, ASTM recommends the use of calibration check samples. In consequence, calibration check samples by making dilutions of 20, 40 and 75 ppm from the 100 ppm standard and the blank were prepared. The results from these analyses are shown below:

Table 6: Results and statistics derived from the analysis of the check samples (n=3)

Calibration check samples	Real concentration (ppm) ^a	XRF concentration (ppm)	SD (ppm)	RSD (%) ^b	Recovery (%)
20 ppm	21.340	23.807	3.787	15.9 (16)	111.6
40 ppm	39.153	38.750	7.518	19.4 (13.6)	99.0
75 ppm	75.331	71.028	2.312	3.3 (10.8)	94.3

^a Calculated by weight, ^b In parenthesis are displayed RSD (%) values reported in the ASTM Method D4294 for similar concentration levels

Analyzing the results from Table 6 we can conclude that the method reports quite good results in terms of accuracy and precision at the reported concentration levels with recovery values in the range of 94.3-111.6% and relative standard deviations between 3.3 and 15.9%. In spite of the relatively high RSD estimated for triplicate analysis of the calibration check sample containing 40 ppm of sulfur, the obtained value is not significantly different from the one reported in the ASTM Method D4294 for a similar concentration level (RSD=13.6%)⁷.

4.2- TXRF ANALYSIS OF BIODIESEL SAMPLES

The analytical capabilities of a low-power total X-ray fluorescence system were also evaluated for detecting trace amounts of sulfur in biodiesel samples. The main problem of the technique is the fact that is not possible to work under vacuum conditions and, therefore, absorption issues of the sulfur x-ray radiation arising from the sample by air are present. Consequently, higher limits of detection are expectable in comparison with the EDXRF method aforementioned.

4.2.1- EVALUATION OF SAMPLE PREPARATION STRATEGY

4.2.1.1- Biodiesel sample preparation

Usually, in TXRF analysis, in order to work under conditions of total reflection, a small amount of liquid sample is deposited on a reflective sample carrier. In the present work, we tested the possibility to deposit 10 µL of a 100ppm biodiesel standard on a quartz reflector and drying it before TXRF analysis. The drying step was performed by using two different conditions: under an IR lamp and on a hot plate set at 95°C. Using the IR lamp, the sample was not possible to bring to a complete dryness. In consequence, the following assays were performed using the heater module at a temperature of 95°C.

However, sulfur peak was not detected in the obtained TXRF spectrum. In order to try to improve the method sensitivity, three depositions of 10 μL of the 100 ppm biodiesel standard were carried out before the TXRF analysis. The use of a higher number of depositions was discarded since this analytical approach was pointed to be a practical and straightforward method in the end. However, the results from the performed analysis (3x10 μL depositions, dryness at 95°C) brought to a non-detectable sulfur peak (see Figure 16A). Since it was not possible to detect sulfur concentrations at the level of 100ppm and with the aim to estimate the limits of detection for sulfur determination by TXRF, a lubricating oil certified reference material (SRM 1848) with a concentration of sulfur of $2.327 \pm 0.043\%$ was considered.

Although the same deposition and dryness basis was carried out, a previous heating of the sample (85°C in a thermal block) was necessary in order to perform in a reliable way the aspiration and deposition of the sample on the quartz reflector using a micropipette. Moreover, to avoid inaccuracies due to sample deposition, sulfur concentrations were corrected by the exact weight of the standard deposited on the reflective carrier. It is interesting to remark that due to the nature of the sample matrix only a very small volume of the sample (1-2 μL) was used to carry out TXRF analysis. In Figure 16B it can be seen that at this concentration level the sulfur peak can be detected. It is also interesting to note that, from the TXRF analysis, information of other elements present in the sample can be obtained. For instance, the SRM 1848 sample contains an appreciable amount of Zn as it is shown in Figure 16B.

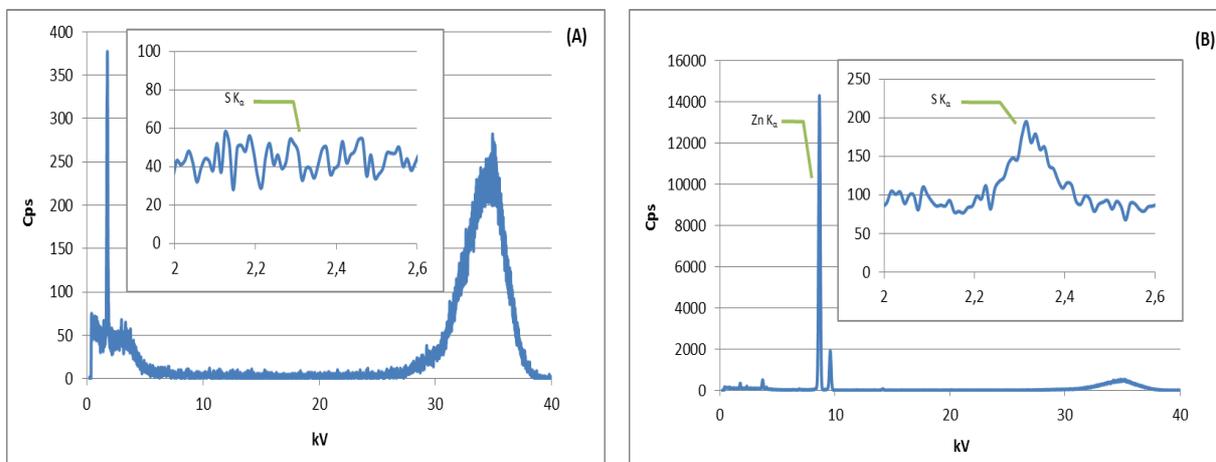


Figure 16: TXRF spectra of a biodiesel standard containing 100ppm of S (a) and a certified reference material (SRM 1848) lubrication oil containing 2.327% of sulfur (b)

4.2.2- EVALUATION OF MEASUREMENT CONDITIONS

Measurement conditions were selected in order to work under conditions of maximum sensitivity. For that, the conditions of the X-ray tube were set at 50 kV and 1000 μA . Regarding the measuring time it was set at 2000 seconds as compromise between an acceptable instrumental uncertainty and the total measuring time.

4.2.3- ANALYTICAL PARAMETERS

Limit of detection was estimated using the results obtained from the analysis of the lubricating oil certified reference material (SRM 1848) and it was determined to be around 1100 ppm. This value indicates the limitations of this method when compared with EDXRF for determining trace amounts of sulfur in combustible liquid samples.

In order to check if there was a linear trend between the sulfur content and the TXRF sulfur peak area, further studies were performed diluting the standard oil lubricating sample with base oil. The different dilutions were prepared by weight and the results of the analysis are presented in Figure 17.

The data obtained from the diluted samples is presented as a bar chart instead of with a regression line because of the fact that only three dilutions were performed. Otherwise, when representing these points in a regression line, a correlation coefficient of 0.996 is obtained. Therefore, it seems that a promising method can be obtained for sulfur determination at higher concentration sulfur levels by TXRF in a simple and economic way. Nevertheless additional tests have to be performed in order to check the real analytical capability in terms of accuracy and precision of this method.

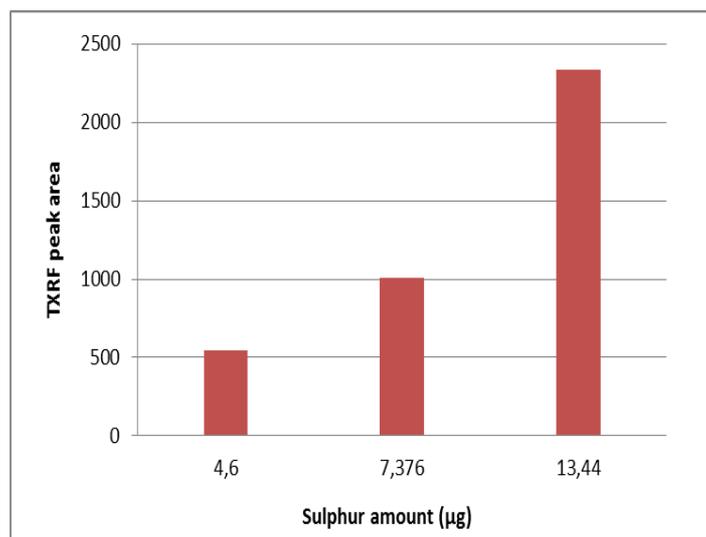


Figure 17: Relationship between TXRF peak area and sulfur amount

4.4- ETHICAL AND SUSTAINABILITY

Traditionally, ethics and chemistry do not run in the same circles, but the need to perform sustainable analysis for not jeopardizing future generations has led us to an irremediable need to join them. In consequence, green chemistry principles are a must for the modern chemical methodologies¹⁶.

In this study, the purpose of meeting together such kind of methodologies with the analysis of a green chemistry fuel (biodiesel) has been established. As explained in point 1.1, biodiesel it is not a profitable energy source by the moment but it is one of the most promising alternatives for replacing fossil fuels. Therefore, the main purpose of this study has been to develop an environmentally friendly methodology for analyzing an environmentally friendly fuel.

Regarding to some of the green chemistry principles, the EDXRF method developed has the aim to prevent waste instead of treat it after its creation. If comparing the developed methodology with the commonly used methods, this objective has been efficiently accomplished by:

- Using a volume of sample of 50 μL instead of 5mL.
- Utilizing thin sample holders to carry out EDXRF analysis instead of disposable cups
- Perform analysis using benchtop equipment in which no gas or cooling media is needed

Furthermore, the use of innocuous and safer solvents as well as the development of an inherently safe process has been one of the goals of the methodology. By last, we encourage the use of the green chemistry principles for the forthcoming methodologies development regarding to an undeniable fact:

“Nobody can go back and start a new beginning, but anyone can start today and make a new ending”

-Maria Robinson

5. CONCLUSIONS

We have developed an advantageously EDXRF analytical method for the determination of trace amounts of sulfur (<100ppm) in biodiesel samples as well as we have studied the possibilities of TXRF for the detection of sulfur at higher concentration levels (>1000ppm) in an oil lubricating matrix.

Regarding to EDXRF analysis:

The best strategy for the analysis of sulfur in biodiesel samples employing EDXRF implies the deposition of 50 μL of the sample onto a commercially available organic support (Ultra-Carrier[®]), an air drying process, the use of a measuring time of 300 s and setting up the X-ray tube conditions to 20 kV. Furthermore, the use of a Teflon mask has efficiently reduced the interferences produced by the inner parts of the equipment. Using such conditions a limit of detection of 9 ppm of sulfur has been estimated that is lower in comparison with other analytical methodologies based on EDXRF spectrometry. Moreover, accuracy and precision of the obtained results have proven to be adequate for the intended purpose.

Additionally, the production of waste and the use of consumables have been minimized if comparing them with recent methodologies for similar determinations. The use of benchtop equipment, Ultra-Carrier[®] sample holders and low amounts of sample (biofuel) allows the creation of this reduced volume of hazardous or misuse material.

Regarding to TXRF analysis:

A new analytical methodology based on the deposition of 2 μL of the sample onto a quartz reflector, drying the drop by means of hotplate and using a measuring time of 2000 s has been established. The main drawback of this methodology is the high detection limit for sulfur determination (>1000ppm) which hamper the determination of sulfur at trace levels. Therefore, despite the fact that additional tests have to be performed in order to check the real analytical capability in terms of accuracy and precision of this method, promising results have been obtained for determination of sulfur concentrations in the low percentage range (0.1-2%) by TXRF.

6· REFERENCES

- [1] J.Hill, E.Nelson, D.Tilman, S.Polasky, D.Tiffany, Environmental economic and energetic costs and benefits of biodiesel and ethanol biofuels, National Academy of Sciences of the United States of America 103 (2006) 11206-11210
- [2] http://www.afdc.energy.gov/fuels/biodiesel_blends.html (4/2016)
- [3] http://transportpolicy.net/index.php?title=Global_Comparison:_Fuels (5/2016)
- [4] V.C.Srivastava, An evaluation of desulfurization technologies for sulfur removal from liquid fuels, RSC Advances 2 (2012) 759-783
- [5] <http://euanmearns.com/global-energy-trends-bp-statistical-review-2015/> (4/2016)
- [6] ISO 14596. Petroleum products – determination of sulfur content –wavelength-dispersive X-ray fluorescence spectrometry. International Organization for Standardization (2007)
- [7] ASTM D 4294-16. Standard Test Method for sulfur in petroleum products by energy dispersive X-ray fluorescence spectrometry. ASTM Int (2016)
- [8] ASTM D 2622-16. Standard Test Method for sulfur in petroleum products by wavelength dispersive X-ray fluorescence spectrometry. ASTM Int (2016)
- [9] A.Doyle, A.Saavedra, M.L.B. Tristão, 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) 39-46.
- [10] P.A.Mello, J.S.F.Pereira, M.F.Mesko, J.S.Barin, E.M.M.Flores, Sample preparation methods for subsequent determination of metals and non-metals in crude oil-A review, Analytical Chimica Acta 746 (2012) 15-36
- [11] L.R.Barker, W.R.Kelley, W.F.Guthrie, Determination of sulfur in biodiesel and petroleum diesel by X-ray fluorescence using the gravimetric standard addition method, Energy & Fuels 22 (2008) 2488-2490
- [12] Leticia S. F. Pereira, Angelica C. Frohlich, Fabio A. Duarte, Robert A. Burrow, Edson I. Muller Erico M. M. Flores, Determination of halogens and sulfur in pitch from crude oil by plasma-based techniques after microwave-induced combustion, Journal of Analytical Atomic Spectrometry, 30 (2015) 1822-1827
- [13] E. Margui, R. V. Grieken, X-Ray Fluorescence Spectrometry and Related Techniques: An Introduction, first ed., Momentum Press, New York (2013) 1-6
- [14] E.Marguí, B.Zawisa, R.Sitko, Trace and ultratrace analysis of líquid samples by X-ray fluorescence spectrometry, Trends in Analytical Chemistry 53 (2014) 73-83.
- [15] http://www.grafixplastics.com/mylar_what.asp (4/2016)
- [16] http://igs.chem.cmu.edu/index.php?option=com_content&view=article&id=372&Itemid=516 (5/2016)