



Determination of trace sulfur in biodiesel and diesel standard reference materials by isotope dilution sector field inductively coupled plasma mass spectrometry



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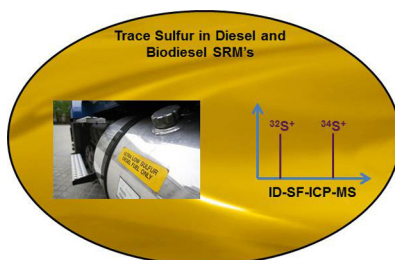
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HIGHLIGHTS

- Sulfur mass fractions are measured below 10 mg kg^{-1} in diesel fuel materials.
- SF-ICP-MS resolves molecular interferences, including oxygen and sulfur hydrides.
- A detection limit of 0.7 mg kg^{-1} (in the fuel sample) was obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

A method is described for quantification of sulfur at low concentrations on the order of mg kg^{-1} in biodiesel and diesel fuels using isotope dilution and sector field inductively coupled plasma mass spectrometry (ID-SF-ICP-MS). Closed vessel microwave-assisted digestion was employed using a diluted nitric acid and hydrogen peroxide decomposition medium to reduce sample dilution volumes. Medium resolution mode was employed to eliminate isobaric interferences at ^{32}S and ^{34}S related to polyatomic phosphorus and oxygen species, and sulfur hydride species. The method outlined yielded respective limits of detection (LOD) and limits of quantification (LOQ) of 0.7 mg kg^{-1} S and 2.5 mg kg^{-1} S (in the sample). The LOD was constrained by instrument background counts at ^{32}S but was sufficient to facilitate value assignment of total S mass fraction in NIST SRM 2723b Sulfur in Diesel Fuel Oil at $9.06 \pm 0.13 \text{ mg kg}^{-1}$. No statistically significant difference at a 95% confidence level was observed between the measured and certified values for certified reference materials NIST SRM 2773 B100 Biodiesel (Animal-Based), CENAM DRM 272b and NIST SRM 2723a Sulfur in Diesel Fuel Oil, validating method accuracy.

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1. Introduction

The emission of sulfur compounds from the combustion of fossil fuels has been related to the formation of acid rain and atmospheric pollution. During fuel combustion, sulfur compounds can be oxidized to sulfur dioxide or trioxide and then react with water,

generating sulfuric acid and sulfates, which contribute to acid rain and particulate formation and deposition, respectively [1,2].

In order to address environmental contamination concerns, different governmental agencies around the world have promulgated rules regulating and reducing the maximum sulfur content allowed in fuels. Prior to year 2010, the Environmental Protection Agency (EPA) defined low sulfur diesel as diesel with a sulfur content less than 500 mg kg^{-1} and in 2010, mandated the use of ultra low sulfur diesel (ULSD) which must have less than 15 mg kg^{-1} sulfur [3]. This standard is now very similar to the European Union (EU) Euro V standard, which is set at 10 mg kg^{-1} sulfur [4]. Biodiesel has been

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added to diesel as an alternative to reduce S and other pollutant emissions, and maximum sulfur content allowed in biodiesel varies from 10 to 500 mg kg⁻¹ depending on the regulatory agency [5]. Therefore, it is important to develop high accuracy, sensitive methods to monitor sulfur in fuels and keep pace with the requirement to measure sulfur at ultra-trace levels. Accurate sulfur determination in fuels is still a challenge for analytical chemistry, especially at low concentrations.

The sample preparation step for elemental analysis plays an important role in analytical method development and is the first issue that usually needs to be addressed. Microwave-assisted radiation digestion has been used for this purpose since 1975 and has been widely applied in different fields such as environmental, geochemistry and energy [6]. According to Costa et al., oil samples subjected to microwave-assisted acid digestion yield low residual carbon content (RCC) digests and, in the case of using closed vessels, low procedure blanks are also obtained [7]. Sample digests with low residual carbon content can also be generated via Carius tube digestion, wherein the sample is decomposed in a completely sealed system, often at pressures and temperatures that far exceed those achievable with microwave-assisted digestion. Carius tube digestion in combination with isotope dilution mass spectrometry for quantification of sulfur was pioneered by Kelly and coworkers at NIST for the determination of S in fossil fuel SRMs [8]. These ID-MS methodologies have been adapted to high pressure asher, which have also been used for the value assignment of sulfur content to fuel oil certified reference materials [9]. Korn et al. proposed a procedure for biodiesel digestion using HNO₃ and H₂O₂ in a microwave oven with closed vessels, which is safer, faster and requires lower acid volumes compared to open systems with conventional heating [10]. Alternatively, using diluted nitric acid (2.0–7 mol L⁻¹) in closed microwave systems has been shown to achieve the same temperatures and pressures that can be reached using concentrated 14 mol L⁻¹ HNO₃ [11]. Castro et al. proposed a four reaction mechanism to explain the digestion process inside the microwave vessel and, according to the authors, the HNO₃ can be regenerated since there is oxygen and water present in the system. In addition, the residual acid remaining in the digests depends on the initial acid concentration [12]. The advantages detailed above ascribed to employment of closed digestion systems cannot be achieved for open system digestions, which are unsuitable for metrology of sulfur in liquid fossil fuel matrices, due to loss of analyte, through volatilization of the sample or decomposition media.

Considering the low sulfur content in biodiesel and some diesel samples, it is undesirable to use concentrated nitric acid in sample preparation. This requires high dilution factors since high acid concentrations will affect the nebulization process [13] and promote signal suppression in inductively coupled plasma mass spectrometry (ICP-MS), due to the impact on the ionization temperature of the plasma discharge [14]. In addition, sulfur has a relatively high ionization potential (10.36 eV) [15], and accuracy can be affected by small changes in plasma temperature, especially if non matrix-matched calibrants and samples are measured separately in time. The use of matrix matching calibration strategies such as the method of standard additions or isotope dilution can mitigate these effects to some extent, but measurement precisions can be improved if samples require less dilution due to high acid content.

ICP-MS is a versatile tool with a multielemental capability and often, low limits of detection are observed since interference free simple spectra are obtained [16]. However, in ICP-MS based on quadrupole mass analyzers, sulfur isotopes (*m/z* 32, 33 and 34) suffer intense spectral interferences from oxygen and phosphorous polyatomic species such as ¹⁶O₂⁺, ³¹PH⁺, ¹⁶O₂H⁺, ¹⁶O¹⁸O⁺, and sulfur hydride species, which hamper the accuracy and sensitivity of the method [15]. The reduction of background signal by introduction of He, H₂ and Xe into a hexapole cell was investigated

by Mason et al. and at least a 10-fold improvement was observed for S⁺/O₂⁺ ratio by charge transfer reaction. In addition, a further improvement was observed for H₂ gas introduction [17]. The dynamic reaction cell[®] has been used to promote SO⁺ formation by introducing O₂ into the quadrupole cell, and then performing the sulfur determination by monitoring *m/z* 48, which has less interference [18]. On the other hand, high resolution and medium resolution sector field mass analyzers provide adequate resolution to accurately measure S isotopes without additional gases or ion molecule-reaction and collision cell modules. Double focusing mass analyzers (magnet and electrostatic) provide resolutions of the order of 10 000 and >4000 in high and medium resolution modes, respectively, which successfully mitigates all the oxygen and phosphorus based interferences, in addition to sulfur hydride species at ³³S⁺, from ³²S¹H⁺ and ³⁴S⁺, from ³³S¹H⁺ or ³²S¹H₂⁺ molecular species [19,20].

Using the isotope dilution mass spectrometry (IDMS) method, high accuracy and precision are obtained through the measurement of elemental isotope ratios. The approach is based on addition of an enriched isotopic spike to an unknown amount of the analyte to be determined in the sample [20–22]. Thermal ionization mass spectrometry (TIMS) and ICP-MS has been used in conjunction with IDMS for quantification of S in fuel-based certified reference materials [8,23,24]. In this work, a closed vessel microwave-assisted digestion method based on employing a diluted nitric acid and hydrogen peroxide decomposition medium, and sector field ID-ICP-MS has been evaluated for sulfur mass fraction determinations in biodiesel and diesel samples. In addition, the total sulfur mass fraction in candidate SRM 2723b Sulfur in Diesel Fuel Oil has been value assigned using the new method. This data set will be combined with results from other NIST methods to assign a certified S mass fraction value to this material.

2. Experimental

2.1. Description of materials

Several fuel oil Certified Reference Materials were used to validate the accuracy of the new method: Standard Reference Material 2773 B100 Biodiesel (Animal Based), a commercial 100% biodiesel produced from animal feedstocks, SRM 2723a Sulfur in Diesel Fuel Oil, a commercial “No. 2-D” distillate fuel oil, and DRM 272b (CENAM, Centro Nacional de Metrología, El Marqués, México), a Mexican commercial diesel fuel. A renewal material, SRM 2723b Sulfur in Diesel Fuel Oil was also obtained from NIST for value assignment of sulfur mass fraction.

2.2. Sample preparation

The specific sample preparation and calibrant spiking procedures applied for determination of sulfur in SRM 2723a and SRM 2723b are described in detail here. Similar concepts and optimization methodologies were applied to the other materials studied; CENAM DRM 272b and SRM 2773, but this required utilization of different concentration ³⁴S spike solutions, and different sample or spike masses, due to the sulfur mass fraction content. Samples were kept at room temperature and homogenized by simple hand inversion. Microwave-assisted digestion was used to decompose the samples. The procedure applied for SRM 2723b involved pre-digestion spiking of approximately 0.25 g aliquots of the samples and the SRM 2723a controls with ³⁴S (approximately 0.25 g of a nominal 10 μg g⁻¹ ³⁴S solution) for isotope dilution quantification. The sample to spike mass ratios were programmed to yield ³²S/³⁴S ratios near unity, with an error magnification factor of approximately 1. All samples and spikes were weighed by difference into

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