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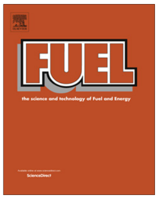

Assessment of the equivalence and correlation between total sulfur determination methods in biodiesel: An use of isotope dilution inductively coupled plasma mass spectrometry

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ABSTRACT

This paper describes an evaluation of current test methods for total sulfur determination in biodiesel, according to international specifications requirements, which was carried out using isotope dilution and inductively coupled plasma mass spectrometry (ID-ICP-MS) as a metrological tool. Closed vessel microwave-assisted digestion was employed using nitric acid and hydrogen peroxide as the decomposition medium, followed by isotope spike with ^{34}S dissolved in n-propanol. In order to overcome the spectral interference due to the presence of diatomic oxygen molecules in the ion beam, a reaction cell was used. Under optimized operating conditions, the determination of sulfur could be carried out at m/z +16, *i.e.*, monitoring SO^+ signal for both sulfur isotopes. The ID-ICP-MS method was able to provide reference values for a series of commercial samples, which resulted in the evaluation of an extended concentration range. Sample sets including commercial biodiesel and inorganic sulfur-enriched biodiesel were employed as a means to evaluate the accuracy of routine methods for possible different sulfur species. No statistically significant difference was observed among the values measured with the proposed method and with the standard methods by UV fluorescence spectrometry and inductively coupled plasma optical emission spectrometry.

1. Introduction

Biodiesel has been used worldwide and produced in large commercial scale. One advantage inherent to the usage of this biofuel is the significant decrease in the emission of sulfur compounds to the atmosphere, when compared to the combustion of fossil fuels. In Brazil, the maximum allowed concentration is 10 mg S per kg of biodiesel, whereas from 10 up to 500 mg kg^{-1} S is tolerable for fossil diesel fuel [1–2]. The most widely employed test method to determine the sulfur content in biodiesel consists on the use of UV fluorescence spectrometry (UVF), in which all the sulfur in the sample is converted to sulfur dioxide [3]. However, some doubts have been brought about the effectiveness of this reaction when inorganic sulfur species (such as sulfate) are present in the test samples [4]. In this scene, the standard test method recommended temperature to convert sulfate to sulfur dioxide (the fluorescence-active species) is 1075 °C under a constant oxygen flow, which may not be sufficient for analytical purposes. These conditions are suitable essentially for the organic forms of sulfur, which are predominant in fuels [5].

In Brazil, there are a few biodiesel manufacturers who use esterification process (EP) as a complementary route, whilst the main route is the transesterification process (TEP); the catalyst in EP is concentrated sulfuric acid, a potential sulfate source for biodiesel [6]. Hence, there is a need for a test method to determine total sulfur, even in inorganic form, without any doubt about the quantitative effectiveness of the analysis.

Ethanol is a biofuel with similar issues – its sulfur content is largely in the form of sulfate. Therefore, the European Commission for Standardization (CEN) has adopted an inductively coupled plasma optical emission spectrometry (ICP OES) test method as an alterna-

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tive for sulfur determination in ethanol fuel [7], predominantly due to the presence of sulfur in its inorganic form. Considering these aspects, the Brazilian Association for Technical Standards (ABNT) has standardized an ICP OES method for sulfur determination in biodiesel, which is similar to the CEN method for ethanol fuel analysis. Nowadays, both techniques (UVF and ICP OES) are present in Brazilian specification requirements for sulfur determination in biodiesel. This fact has demanded some studies to clarify the equivalence and correlation between these techniques [8,9].

This work has as a main goal to verify the statistical equivalence between UVF and ICP OES techniques, by comparing the results with an isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) method, which has been used to determine total sulfur in biodiesel samples in a reliable way [10–13]. In addition, ID-ICP-MS is a primary metrological technique, which provides lower uncertainty values [14]. Therefore, ID-ICP-MS is a suitable option to obtain reference values, which may be useful to evaluate the performance of routine techniques, highlighting the inorganic sulfur presence and a concentration range larger than the specification. When ID-ICP-MS was not useful, other statistical tools were used, such as Pearson's correlation and *t*-test.

2. Materials and methods

2.1. UVF and ICP OES materials and instrumentation

The UVF analyses were carried out in accordance with ASTM D5453-12 test method. The used UVF analyzers were a Multitek Model and a 9000S (used in sample sets 2 and 1, respectively, both PAC-ANTEK, USA), using for both 15 μL as sample volume, 1075 °C as the furnace temperature and 1–10 mg kg^{-1} as the calibration range. Calibration was carried out using dibenzothiofene (Aldrich, USA) solutions in toluene (Vetec, Brazil).

The ICP OES analyses were carried out in accordance with ABNT NBR 15867 [18] test method parameters. Two ICP OES spectrometers were used: a Varian 715-ES (Varian, USA), with a cooled spray chamber at 4 °C (for sample set 2) and an Optima 7300 DV (PerkinElmer, USA – for sample set 1). Calibration solutions were prepared in kerosene from serial dilutions of a 1000 mg kg^{-1} commercial sulfur standard in mineral oil (Conostan, USA), with concentrations ranging from 1 to 10 mg kg^{-1}.

2.2. ID-ICP-MS materials and instrumentation

A selection of chemicals were tested for sample preparation prior to ID-ICP-MS analysis. Firstly, ^{34}S standard powder (99.91%, Cambridge Isotope Laboratories, USA) was diluted in xylene (mixture of isomers, Sigma-Aldrich, USA) at 65 °C, to prepare a 10 mg kg^{-1} stock solution. In addition, the same solution was prepared with n-propanol (Vetec, Brazil) at the same temperature. These ^{34}S stock solutions were used to spike the samples before (solution in xylene) or after (with n-propanol) digestion of the samples. Microwave-assisted digestion was used to decompose the samples (Milestone Ethos Plus System, Italy). The procedure involved 0.25 g aliquots of the samples and 0.25 g of the 10 mg kg^{-1} ^{34}S stock solution (in xylene). Aqueous solutions were prepared using deionized water (18.2 MΩ cm minimum resistivity) produced by a Milli-Q system (Millipore, Bedford, USA). Nitric acid was purified by double sub-boiling distillation in a quartz still (Kürner Analysentechnik, Germany). Each sample aliquot was mixed with 2.5 mL HNO_3, 2.5 mL deionized water and 3.0 mL high purity hydrogen peroxide. The microwave heating program was set as follows: 2 min hold at 250 W, 2 min hold at 0 W, 6 min hold at 250 W, 5 min at 400 W and 5 min at 650 W. Since the digestion of sample pre-spiked with a xylene solution was inefficient, the samples were spiked after the digestion using the ^{34}S stock solution prepared in n-propanol. A 50 μL of 10 mg kg^{-1} ^{34}S solution in n-propanol was used to spike each sample solution after the digestion, due its solubility in aqueous medium. The final dilution to 50 mL was made with deionized water, and the resulting ^{34}S concentration was near 50 μg kg^{-1}. The ID-ICP-MS measurements were carried out using a NexIon 300D spectrometer (PerkinElmer, USA), using the parameters presented in Table 1. The use of a reaction cell has been described previously to carry out sulfur determination in fuels by ICP-MS [12,13], and oxygen is a suitable alternative to react with sulfur to bring the analyte to an interference-free *m*/*z* range, with the detection of SO^+ (*m*/*z* 48 and 50).

2.3. Samples

A preliminary study was carried out by analyzing five samples by UVF and ICP OES: A NIST2773 biodiesel certified reference material (CRM), a Spex biodiesel CRM, and three commercial biodiesel samples, which were one EP sample (mostly inorganic sulfur), one TEP sample (common sample), and a combined TEP/EP sample were analyzed. A second sample set had fifteen samples, which were analyzed by UVF, ICP OES and ID-ICP-MS. This set was composed by the same NIST2773, three Conostan biodiesel CRMs (with different S concentrations) and nine commercial biodiesel samples. Details of the sample sets are presented in Table 2.

2.4. Statistical methodology

Pearson's correlation coefficient (the classic linearity coefficient, *r*) was determined in order to verify the preliminary correlation between the results obtained using UVF and ICP OES. No equivalence tests were performed for the preliminary set, due to the limited set of data. The second data set has allowed the correlation analysis to be performed, as well as an equivalence paired *t* test. In addition, to test the accuracy of the routine methods, the ID-ICP-MS data were used as reference values, using the normalized error test (NET) for evaluation. In this methodology, the equation for NET is described as follows [15].

$$NE = \frac{(x - \bar{x})}{\sqrt{(u_a^2 + u_R^2)}} \tag{1}$$

where

NE is the normalized error;
x is the analysis result;
$\bar{x}$ is the reference value;
u_a^2 is the analysis uncertainty of measurement;
u_R^2 is the uncertainty of the reference value.

2.5. Measurement uncertainty and equations

The measurement uncertainties of the three methods for the second sample set were determined following ISO GUM and QUAM CITAC recommendation [16,17]. These included calculation of all applied sensitivity coefficients. The ID-ICP-MS measurement uncertainty was obtained as a necessary variable to use NET [18]. The equations adopted to determine all the ID-ICP-MS analysis sensitivity coefficients were derived from the ID equation (Eq. (1)), as follows:

$$C_x = C_S\left(\frac{W_S}{W_x}\right)\frac{M_{nat}}{M_{ref}}\left(\frac{R_{exp}fA_S - B_S}{B_x - R_{exp}fA_x}\right) \tag{2}$$

where:

C_x is the sulfur content in the sample, in mg kg^{-1};
C_S is the ^{34}S content in the sample in mg kg^{-1};