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

Renata S. Amais a, Stephen E. Long b, Joaquim A. Nóbrega a, Steven J. Christopher b,∗

a Group of Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, São Carlos, SP, Brazil
b Chemical Sciences Division, National Institute of Standards and Technology, Charleston, SC, United States

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.

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 32S and 34S 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 instrumental background counts at 32S but was sufficient to facilitate value assignment of total S mass fraction in NIST SRM 2723b Sulfur in Diesel Fuel Oil at 9.06 ± 0.13 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.

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
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 HNO\(_3\) and H\(_2\)O\(_2\) 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\(^{-1}\) HNO\(_3\) [11].

Castro et al. proposed a four reaction mechanism to explain the digestion process inside the microwave vessel and, according to the authors, the HNO\(_3\) 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 phosphorus polyatomic species such as \(^{16}\)O\(_2^+\), \(^{31}\)PH\(^+\), \(^{16}\)O\(_2^+\), \(^{16}\)O\(^{18}\)O\(^+\), and sulfur hydride species, which hamper the accuracy and sensitivity of the method [15]. The reduction of background signal by introduction of He, H\(_2\) and Xe into a hexapole cell was investigated by Mason et al. and at least a 10-fold improvement was observed for \(^{32}\)O/\(^{32}\)O\(^+\) ratio by charge transfer reaction. In addition, a further improvement was observed for H\(_2\) gas introduction [17]. The dynamic reaction cell [18] has been used to promote SO\(^+\) formation by introducing O\(_2\) into the quadrupole cell, and then performing the sulfur determination by monitoring \(m/2\) 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 10000 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 33\(^{33}\)S, from \(^{32}\)S\(^{1}\)H\(^+\) and \(^{34}\)S\(^{1}\)H\(^+\), from \(^{33}\)S\(^{1}\)H\(^+\) or \(^{32}\)S\(^{2}\)H\(^+\) molecule 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 \(^{34}\)S 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 \(^{34}\)S (approximately 0.25 g of a nominal 10 \(\mu\)g g\(^{-1}\) \(^{34}\)S solution) for isotope dilution quantification. The sample to spike mass ratios were programmed to yield \(^{32}\)S/\(^{34}\)S ratios near unity, with an error magnification factor of approximately 1. All samples and spikes were weighed by difference into.
quartz microwave vessels using a four place balance that had been internally calibrated and checked using external weights (1 g check weight) prior to use. The microwave method was performed as follows: (1) 0W–1400W ramp over 40 min, (2) 40 min hold at 1400 W. The slow 35 W min$^{-1}$ ramp rate was required to minimize pressure spikes in the sealed vessels. Maximum temperatures ranging from 205 to 220 °C were achieved during the hold period.

All solutions were prepared using deionized water (18.2 MΩ cm resistivity) produced by a Milli-Q Element system (Millipore, Billerica, MA, USA). High purity grade nitric acid 65–70% (v v$^{-1}$) and hydrogen peroxide 30% (m m$^{-1}$) (Optima, Fisher Scientific, Fairlawn, NJ, USA) were used for sample preparation. The acid decomposition medium consisted of 2.5 mL of high purity, concentrated nitric acid (14 mol L$^{-1}$ HNO$_3$) + 2.5 mL of high purity deionized water + 3 mL of high purity, concentrated hydrogen peroxide. After the heating program, no precipitates were observed in the resultant sample digests, and diluted samples were clear. The final volume was made up to 50 mL and samples presented sulfur in both the $^{32}$S and $^{34}$S isotopes at approximately 45 ng g$^{-1}$ prior to analysis.

### 2.3. Calibration

Standard Reference Material 3154 Sulfur (S) Standard Solution (Lot No. 892205, Certified S mass fraction 10.30 ± 0.03 mg g$^{-1}$) was used to calibrate isotopic spike solutions via reverse isotope dilution prior to use. Nominal 6.8 mg kg$^{-1}$ (diluted SRM 3154) natural and 10 mg kg$^{-1}$ 34S spike (99.999% certified 34S enrichment, Trace Sciences International Lot No. 12B) solutions were prepared. The isotopic abundances and atomic mass of S hailed from the spike were verified by measuring the $^{32}$S, $^{33}$S and $^{34}$S isotopes after microwave-assisted dissolution of the 34S spike powder into solution. The measured 34S abundance was 99.956% (compared to manufacturer value of 99.999%), with the combined mass contributions from the three S isotopes yielding an atomic mass of 33.967 g mol$^{-1}$, a value within 0.003% of the expected atomic mass of 33.968 g mol$^{-1}$. The 36S isotope was not measured and the abundance and corresponding mass contribution from this isotope was assumed to be negligible in the high purity 34S spike material. Four gravimetric blends of the natural S (approximately 0.37 g) and isotopic S (approximately 0.25 g) solutions were produced and measured (target 32S/34S ratios of 1, corresponding to an approximate error magnification factor of 1).

### 2.4. Instrumentation

All samples were measured in medium resolution mode on a sector-field ICP-MS (Element XR, Thermo Scientific, Waltham, MA, USA). Table 1 lists the instrumental settings for the study.

The sample introduction system comprised a concentric nebulizer and an ESI (Elemental Scientific, Omaha, NE, USA) stable sample introduction spray chamber which combines a cyclonic and double-pass Peltier-cooled spray chamber. Mass offset experiments utilizing a spike calibration blend solution were conducted prior to running the analytical samples, in order to establish method mass offsets for the 32S and 34S isotopes.

### 2.5. Equations

The following measurement function [25] was used to calculate the mass fraction of sulfur in the 34S spike solution calibrant:

$$C_{\text{spike}} = \frac{M_{\text{STD}} \bullet (BR - A)}{M_{\text{K}} \bullet (A_s - B_s R)}$$

and to calculate the mass fraction of sulfur in the analytical samples, the following equation was used:

$$C_{\text{sample}} = \left[ \frac{M_{\text{K}} \bullet (A_s - B_s R)}{(BR - A)} \right] S_b = \frac{1}{W}$$

where $C_{\text{spike}}$ is the concentration of sulfur in the isotopically enriched 34S spike solution in units of mass fraction (μg g$^{-1}$), $M_{\text{STD}}$ is the absolute mass of sulfur (μg) derived from a gravimetrically prepared SRM 3154 spike calibrant solution added to the reverse spike calibration blend, $B$ is the natural abundance of the 34S spike isotope in SRM 3154 (%), $R$ is the mass bias corrected $^{32}$S/$^{34}$S ratio in the reverse spike calibration blend (unitless quotient, related to mole fraction), $A$ is the natural abundance of the $^{32}$S reference isotope SRM 3154 (%), $M_s$ is the mass (g) of 34S spike aliquot added to the reverse calibration blend, $K$ is the natural to spike relative atomic mass ratio (unitless quotient), $A_s$ is the abundance of the $^{32}$S reference isotope in the isotopically enriched spike (%), $B_s$ is the abundance of the 34S spike isotope in the isotopically enriched spike (%), $C_{\text{sample}}$ is the concentration of sulfur in SRM 2773, SRM 2723a and SRM 2723b in units of mass fraction (μg g$^{-1}$), $S_b$ is the absolute mean measured blank (μg), and $W$ is the mass of test portion processed [24].

### 3. Results and discussion

#### 3.1. Figures of merit

The spectral resolution required to separate the pairs of ions $^{16}$O$^{18}$ and $^{32}$S$^+$, and $^{16}$O$^{18}$O$^+$ and $^{34}$S$^+$, are approximately 1800 and 1300, respectively. Before each measurement the experimental resolution was monitored using an instrument tuning solution containing $^{115}$In at a concentration of 1 μg L$^{-1}$. A resolution of 4500 or greater was typically observed in medium resolution mode, which was adequate to resolve the spectral interferences for the sulfur isotopes, including sulfur-hydrides, which could possibly affect either abundance measurements or isotope dilution measurements. Considering the nuclidic masses of hydrogen and the sulfur isotopes, of all possible S hydrides, the one requiring the most resolution (3908) is $^{33}$S$^+$H$^+$ on m/z 33. Resolutions of 2783 and 1645, respectively, are needed to measure 34S isotope free from the $^{33}$S$^+$H$^+$ and $^{32}$S$^+$H$^+$ molecular interferences. The mass spectral scan in Fig. 1 for NIST SRM 3154 clearly shows that the most
troublesome and abundant hydride at nominal m/z = 33 is fully resolved from the 33S peak. The production efficiency for 32S1H+ sulfur hydride is estimated to be 0.07% with the wet sample introduction setup applied in this work.

Isotope ratio data were corrected for mass discrimination/bias on the day of each experiment. Correction factors ranging between 1.032 and 1.060, or 1.6% per amu and 3% per amu were observed for 32S/34S isotope ratios in samples of SRM 3154 run in medium resolution mode, using a linear mass bias model [26] and a known 32S/34S ratio of 22.550. A spike calibration solution was interspersed between unknown samples and measured repeatedly over the course of each experiment to monitor isotope ratio drift. The standard deviation due to isotope ratio drift was minimal, ranging from approximately 0.07% RSD to 0.2% RSD for 3 repeated measures, so isotope ratio data were not corrected for drift. The repeatabilities were however used to assign uncertainties due to mass bias correction.

The 32S and 34S instrument background ion counts were monitored repeatedly during the analyses and intensity data for each analytical sample were corrected for background contributions for the respective isotopes. The instrument background subtraction for the blanks and samples was performed using the closest instrument blank to each sample in the run sequence. The instrument background at m/z 32 influenced the determination of procedural S blanks, which were corrected for instrument background, and in some cases produced negative sulfur blanks. The absolute S procedural blanks ranged from 0 ng (eight negative blanks) to 6 ng to 13.5 ng (two positive blanks), resulting in application of minor blank corrections to the sample data (approximately 0.0002% relative to 0.15% relative, depending on the S concentration in the samples). The background subtraction at m/z 32 is responsible for the low absolute sulfur blanks, indicating that the procedural blanks do not incorporate much additional sulfur compared to a 1% mass fraction nitric acid instrument blank.

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as three times and ten times the standard deviation of the mean concentration of S determined in 10 procedure blanks, respectively. The analytical method yielded LOD and LOQ values of 0.7 and 2.5 mg kg−1 (in the fuel sample), respectively, and instrumental LOD and LOQ values were 3.5 μg L−1 and 12.5 μg L−1, respectively. It is important to highlight that a limitation of the method was the instrument background signal at 32S which ranged from 6 × 104 counts per second to 1 × 105 counts per second. The source of this background was systematically investigated, with possible sources including reagent contamination, laboratory contamination, Ar supply gas contamination and a possible contamination of the ICP-MS extraction lens. High resolution scanning was also employed to verify that the background was not related to a spectrally unresolved interfering species, and a sulfur trapping system was also installed to try and reduce the sulfur background in the Ar supply gas, however, no definitive source could be identified. We speculate that the S contamination might originate from our source of high purity water or uptake tubing, but not reagents, because our instrument blanks (e.g. 1% mass fraction nitric acid) and our 34S-spiked reagent microwave process blanks tend to produce near identical 32S signals regardless of sample dilution volume. Higher limits of detection for sulfur determination in fuels by ID-SF-ICP-MS are found in the literature such as 18 and 4 mg kg−1 in gasoline microemulsions introduced by injection high-efficiency nebulizer (DIHEN) and microwave assisted digests introduced by micro-concentric nebulizer and Scott type spray chamber, respectively [27]. Instrumental LOD values as low as those presented in this work were recently obtained by Balcaen et al. via monitoring 32S16O+, 33S16O+ and 34S16O+ (4, 3 and 6 μg L−1, respectively) in organic solution by using isotope dilution and the new ICP-MS/MS instrumental technique [28].

3.2. Effect of acid concentration on sample decomposition

One of the goals for this work was to test the feasibility of using lower acid content microwave-assisted decomposition solutions as a means to adequately digest the diesel fuel samples, and avoid excessive dilution, such that the S mass fractions in the diluted samples were adequate to maintain measureable signals for samples of low total sulfur content. The use of higher concentration acids would dictate the use of larger dilution factors to achieve the same matrix conditions in the ICP source, and for ultra-low sulfur content fuel samples could compromise limits of detection. Fig. 2 presents the results obtained for SRM 2723a digested using 14 and 7 mol L−1 nitric acid. No statistically significant differences could be observed between the certified value and results obtained using either concentrated or diluted HNO3 decomposition solutions.

3.3. Method validation and candidate SRM 2723b value assignment

The S mass fraction results for three control materials decomposed in dilute nitric acid (7 mol L−1) are presented in Table 2. The expanded uncertainty for SRM 2773 is based solely on sample replication, however the CENAM and the SRM 2723a material expanded uncertainties (and those of candidate SRM 2723b), are based on determining individual components of uncertainty according to ISO
The largest sources of uncertainty for the CENAM and SRM 2723 materials tended to be sample replication, mass bias and instrument background subtraction, the latter which was estimated as a 0.5\% relative Type B uncertainty [29], based on the magnitude and fluctuations in 34S background signals observed over the course of several projects, relative to measured signals for the analytical samples. One possible way to reduce the contribution of instrument background subtraction uncertainty would be to dilute samples less and push the 32S and 34S signals up in to the analog detection regime, greater than 1 order of magnitude above the analog noise baseline. This strategy would help mitigate the need for instrument background subtraction, but could not be applied to very low S mass fraction diesel sample or blank measurements. Analog detection could potentially overcome the dynamic range constraints of pulse counting measurements occurring in the presence of high background signals, however, greater matrix effects could result and impact mass bias and other system and plasma source parameters. The ability to initially use dilute acid for the microwave digestions of diesel fuels presents an advantage for future testing of this strategy.

### 4. Conclusions

It was demonstrated in this work that it is feasible to use diluted nitric acid and microwave-assisted digestion, followed by ID-SF-ICP-MS for biodiesel and diesel fuel measurements of sulfur mass fraction. Accurate results were obtained for three diesel fuel SRM control materials, lending confidence to the measured sulfur mass fraction values for candidate SRM 2723b Sulfur in Diesel Fuel Oil (9.05 ± 0.13 mg kg⁻¹). The data described in this work for SRM 2723b will be combined with recent data from X-ray fluorescence spectrometry to assign a certified S mass fraction value to this material. Future work will involve application of the described methodologies to the value assignment of total sulfur in fuel oil SRMs at levels below 1 mg kg⁻¹. Despite the favorable accuracy and precision of the proposed method, it does not presently have a limit of detection and quantification adequate enough to conduct accurate measurements on SRM 2772 B100 Biodiesel (Soy-Based) which has an approximate S mass fraction lower than 0.6 mg kg⁻¹. This is currently limited by the magnitude of the instrument background and a thorough understanding of our procedural blanks, and thus more work will be directed towards lowering the limit of detection in order to certify reference materials with sub single mg kg⁻¹.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Certified value (mg kg⁻¹)</th>
<th>Found (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B100 Biodiesel Animal-Based (SRM 2773)</td>
<td>7.39 ± 0.39</td>
<td>7.42 ± 0.32(^a)</td>
</tr>
<tr>
<td>Sulfur in Diesel Fuel Oil (SRM 2723a)</td>
<td>10.90 ± 0.31</td>
<td>10.85 ± 0.30(^b)</td>
</tr>
<tr>
<td>Sulfur in Diesel Fuel Oil (DRM 272b)</td>
<td>409.2 ± 8.6</td>
<td>412.7 ± 4.1(^c)</td>
</tr>
</tbody>
</table>

\(^a\) n = 10. \(^b\) n = 6. \(^c\) n = 5.

### Table 3

Certification measurements of SRM 2723b.

<table>
<thead>
<tr>
<th>SRM 2723b – units</th>
<th>Mass fraction (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2723b – 1</td>
<td>9.214</td>
</tr>
<tr>
<td>2723b – 2</td>
<td>9.038</td>
</tr>
<tr>
<td>2723b – 3</td>
<td>9.072</td>
</tr>
<tr>
<td>2723b – 4</td>
<td>9.040</td>
</tr>
<tr>
<td>2723b – 5</td>
<td>9.104</td>
</tr>
<tr>
<td>2723b – 6</td>
<td>8.960</td>
</tr>
<tr>
<td>2723b – 7</td>
<td>8.916</td>
</tr>
<tr>
<td>2723b – 8</td>
<td>9.117</td>
</tr>
</tbody>
</table>

Mean (mg kg⁻¹) 9.058
Standard deviation (mg kg⁻¹) 0.093
RSD (\%) 1.03
U\(^t\) (mg kg⁻¹) 0.13

\(^t\) Expanded uncertainty (coverage factor k = 2.20).

The measured S mass fraction values for each of the three control materials agree with the corresponding certified values, demonstrating the application of lower acid content decomposition solutions to measurement of both low (≤ 10 mg kg⁻¹) and high (≥ 500 mg kg⁻¹) sulfur content diesel samples.

SRM 2723a was used as the control for the candidate SRM 2723b value assignment measurement process. Both the control and the candidate SRM were measured in the same analytical sequence using the same spike solution (9.911 ± 0.008 mg kg⁻¹ 34S, n = 4, mean ± standard deviation). The individual mass fraction data for each unit of SRM 2723b are presented in Table 3, and Table 4 presents an example uncertainty budget for the new candidate reference material (SRM 2723b), with an expanded uncertainty under 1.5\% relative.

### Table 4

<table>
<thead>
<tr>
<th>Source</th>
<th>(c_i)</th>
<th>(u_i)</th>
<th>Units</th>
<th>(c_iu_i)</th>
<th>DF(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replication</td>
<td>8</td>
<td>1</td>
<td>3.296E–02</td>
<td>mg kg⁻¹</td>
<td>3.30E–02</td>
</tr>
<tr>
<td>Blank correction</td>
<td>4</td>
<td>1</td>
<td>1.353E–02</td>
<td>mg kg⁻¹</td>
<td>1.35E–02</td>
</tr>
<tr>
<td>Spike calibration</td>
<td>4</td>
<td>1</td>
<td>3.478E–03</td>
<td>mg kg⁻¹</td>
<td>3.48E–03</td>
</tr>
<tr>
<td>Mass bias</td>
<td>3</td>
<td>1</td>
<td>3.700E–02</td>
<td>mg kg⁻¹</td>
<td>3.70E–02</td>
</tr>
<tr>
<td>Combined type A uncertainty ((u_a))</td>
<td></td>
<td></td>
<td></td>
<td>5.11E–02</td>
<td></td>
</tr>
</tbody>
</table>

Overall degrees of freedom 6

### Table 3

<table>
<thead>
<tr>
<th>Source</th>
<th>(c_i)</th>
<th>(u_i)</th>
<th>Units</th>
<th>(c_iu_i)</th>
<th>DF(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRM 3154 calibrant</td>
<td>1</td>
<td>1.319E–02</td>
<td>mg kg⁻¹</td>
<td>1.32E–02</td>
<td>(\infty)</td>
</tr>
<tr>
<td>Weighing uncertainty</td>
<td>1</td>
<td>5.229E–03</td>
<td>mg kg⁻¹</td>
<td>5.23E–03</td>
<td>(\infty)</td>
</tr>
<tr>
<td>Instrument background subtraction</td>
<td>1</td>
<td>2.615E–02</td>
<td>mg kg⁻¹</td>
<td>2.61E–02</td>
<td>(\infty)</td>
</tr>
<tr>
<td>Combined type B uncertainty ((u_b))</td>
<td></td>
<td></td>
<td></td>
<td>2.97E–02</td>
<td></td>
</tr>
<tr>
<td>Combined uncertainty ((u))</td>
<td></td>
<td></td>
<td></td>
<td>5.95E–02</td>
<td></td>
</tr>
<tr>
<td>Effective degrees of freedom</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.2</td>
</tr>
<tr>
<td>Coverage factor (k)</td>
<td></td>
<td></td>
<td></td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td>Expanded uncertainty (U)</td>
<td></td>
<td></td>
<td></td>
<td>1.31E–01</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Degrees of freedom.
mass fractions of sulfur. It should also be noted that the analytical methodology described might be impacted by the organosulfur speciation in any particular sample matrix, so should not be considered universally applicable to all fuel oil types without further testing.

**NIST disclaimer**

The commercial instruments and products utilized in this work are described only to communicate the details of the analytical procedures applied. These commercial items are not specifically endorsed by NIST. The procedures described exposed the analysts to corrosive acids, flammable materials and highly pressurized samples, which required the use of appropriate personal protective equipment.

**Acknowledgments**

The authors would like to thank grants 2010/17387-7 and 2012/00920-0, São Paulo Research Foundation (FAPESP). We also gratefully acknowledge our fellow co-workers Dr. W. Clay Davis and Dr. Y. Nuevo-Ordonez for instrument operations assistance for sulfur measurements via SF-ICP-MS, and Dr. John Molloy for coordination of S measurement efforts for the fuel oils SRM program.

**References**


