Accurate Characterization of Sulfur in Biodiesel Fuel Certified Reference Material

Yuko Kitamaki*, Yanbei Zhu, and Masahiko Numata

National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, JAPAN

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A certified reference material (CRM), NMIJ CRM 8302-a, for the quality control of biodiesel fuel analysis has been issued by the National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (NMIJ, AIST). This CRM is based on 100 % fatty acid methyl esters (palm oil-based, B100 Biodiesel). The certified parameters are content of water and 6 elements (S, Na, K, Mg, Ca and P); density and kinematic viscosity. The methods for the accurate characterization of sulfur in biodiesel fuel certified reference material are described. The concentration (mass fraction) of sulfur was determined by three inductively coupled plasma tandem quadrupole mass spectrometer (ICP-MS/MS) methods and a combustion ion chromatography (CIC) method. The CIC result was validated by determining sulfur content in three certified reference materials (NIST SRM 2773, NIST SRM 2298 and NIST SRM 2299). The certified value of sulfur in the CRM 8302-a was determined as the weighted mean of the results of the above four methods.

Keywords
Biodiesel fuel, Sulfur content, Certified reference material, Quality control

1. Introduction

Sulfur oxides in the atmosphere originating from the combustion of fuels cause acid rain and air pollution worldwide. Therefore, the sulfur content in liquid fuel, for example gasoline and diesel fuel, is regulated to 10 mg kg$^{-1}$ or less$^{1,2}$. Recently, biofuels have extensively investigated as an alternative to fossil fuel and to reduce the risks of global warming. As with fossil fuel, the sulfur content in bioethanol and biodiesel fuel is required to be 10 mg kg$^{-1}$ or less by the Japanese Industrial Standards (JIS)$^{2,3}$. Therefore, a certified reference material (CRM) for bioethanol, NMIJ CRM 8301-a, has been developed and issued by the National Metrology Institute of Japan (NMIJ)$^{5}$. On the other hand, only two biodiesel fuel CRMs for quality control, NIST SRM 2772 (Biodiesel (Soy-Based)) and NIST SRM 2773 (Biodiesel (Animal-Based)) are available$^{5,6}$. Therefore, a CRM for measurement of biodiesel fuel, NMIJ CRM 8302-a, has been developed by the NMIJ. This CRM is based on fatty acid methyl esters (FAMEs) produced from palm oil, because such biofuel is popular in Asian countries. The certified parameters of this CRM are contents of water and 6 elements (S, Na, K, Mg, Ca and P); density and kinematic viscosity. The certified values are traceable to the International System of Units (SI) or based on internationally-accepted values. In addition, the concentration of methanol is given as an indicative value.

Determination of sulfur in the candidate reference material used an inductively coupled plasma tandem quadrupole mass spectrometer (ICP-MS/MS). For measurements with the ICP-MS/MS, three kinds of combinations of pre-treatment and quantification procedures were applied. One of them is combination of microwave-assisted acid digestion and the isotope dilution mass spectrometry (IDMS) which is a primary method for accurate elemental analysis. In the first procedure, isotope enriched sulfur was added to the sample as an internal standard before microwave-assisted acid digestion. In the second procedure, the isotope enriched sulfur was added after ethanol dilution. In the third procedure, sulfate ion standard solution was added after microwave-assisted acid digestion.

Combustion ion chromatography (CIC) was also used to increase the reliability of measurement by an independent approach. CIC is not a primary method is one of common techniques employed for the determination of sulfur in fuels. In the case of CIC, sulfur content was evaluated by a standard addition method. The CIC measurement was validated by the determination of sulfur in three CRMs: NIST SRM 2773, NIST SRM 2298 (Sulfur in Gasoline (High Octane)) and NIST SRM 2299 (Sulfur in Gasoline (Reformulated)).
All standard solutions used for reverse IDMS and for the standard addition methods were prepared from traceable standard solutions by gravimetric blending. Therefore, the sulfur certified value in the NMIJ CRM 8302-a is traceable to the International System of Units (SI).

2. Experimental Methods

2.1. Instrumentation

An ICP-MS/MS, Agilent 8800 s (Agilent Technologies, Santa Clara, CA, USA) was used for the determination of sulfur. A microwave digestion apparatus, ETHOS 1 (Milestone General K.K., Kawasaki, Japan) and TFM® digestion vessels were utilized for the digestion of the biodiesel samples.

For CIC analysis, an ion chromatography pretreatment unit, AQF-2100H (Mitsubishi Chemical Analytech Co., Ltd., Chigasaki, Japan) was used to convert sulfur in the sample to sulfur oxides (SO\textsubscript{x}) by combustion. SO\textsubscript{x} was absorbed and oxidized to sulfate ion (SO\textsubscript{4}\textsuperscript{2–}) in absorbing solution containing hydrogen peroxide. Sulfate ion in the absorbing solution was measured with an ion chromatograph, DX-320 (Dionex, Sunnyvale, CA, USA).

Gravimetric blending used a balance XS 205DU (METTLER TOLEDO, Greifensee, Switzerland) calibrated by the Japan Calibration Service System to maintain traceability to SI.

2.2. Chemicals

For the ICP-MS/MS analysis, standard sulfate ion solution (JCSS, Kanto Chemical Co., Inc., Tokyo, Japan) was used to prepare the standard addition solutions. Isotope enriched sulfur (Oak Ridge National Laboratory, Oak Ridge, Tennessee. $^{34}$S = 94.27 %) was used to prepare the internal standard solution. Nitric acid and perchloric acid (Ultrapur® grade, Kanto Chemical) were used for digestion of the samples. Ethanol (infinity pure grade, Wako Pure Chemical Industries Ltd., Osaka, Japan) was used to dilute the sample for measurements with the ICP-MS/MS. Xylene (for RoHS, Wako Pure Chemical Industries) was used to prepare sample solutions for homogeneity assessment.

Thiophene (benzene-free (99.5 %), Acros Organics, Geel, Belgium) and toluene (infinity pure grade, Wako Pure Chemical Industries) were used to prepare standard addition solutions for the CIC analysis. The purity of thiophene was determined by the freezing point depression method and the subtraction method. Sulfur content in this thiophene was calculated using the atomic weight at NMIJ\textsuperscript{7}. Hydrogen peroxide (atomic absorption spectrometry grade, Wako Pure Chemical Industries) solution was used as the absorbing solution. Standard phosphate ion solution (JCSS, Kanto Chemical) was added to the absorbing solution as an internal standard. Sodium carbonate and sodium hydrogen carbonate (reagent grade, Wako Pure Chemical Industries) were used as the eluent for ion chromatography.

Pure water was prepared using a Millipore purification system (Element, Nihon Millipore Kogyo, Tokyo, Japan).

CONOSTAN Custom Blend Multi-Element Standard (5 element blend), (Matrix: Biodiesel, Conostan, Québec, Canada) containing 200μg g\textsuperscript{-1} of Na, K, Mg and Ca as alkyl aryl sulfonate salts, and 400μg g\textsuperscript{-1} of P as alkyl phosphate, was used for the preparation of the candidate reference material.

2.3. Preparation of the Candidate Reference Material

The raw material of the candidate reference material for CRM 8302-a was biodiesel fuel made from palm oil by ester exchange. According to the preliminary analysis, the contents of target elements (S, Na, K, Mg, Ca and P) in this candidate reference material were much lower than the respective regulation limits. Therefore, a custom standard solution for the determination of elements in biodiesel was added to adjust the element contents to approximately 2 mg kg\textsuperscript{-1} for P and 1 mg kg\textsuperscript{-1} for others. The sulfur content in the raw material was approximately 1 mg kg\textsuperscript{-1}, most of sulfur in the candidate reference material comes from alkyl aryl sulfonate in the spiked multi-element solution.

Approximately 5.6 L of the candidate reference material was subdivided into 353 ampoules containing approximately 15.5 mL each at the NMIJ\textsuperscript{9}.

2.4. Procedures for Sulfur Measurement

Sulfur in the candidate reference material was measured by four different methods.

(A) ID-ICP-MS/MS (pretreatment, acid digestion)

Acid digestion was carried out using 50 mL quartz digestion vessels. At least three subsamples were obtained for each ampoule, in which 0.5 g of the candidate reference material was taken and digested with nitric acid (3 mL) and perchloric acid (2 mL). The solution of isotope enriched sulfur was added to each subsample immediately after adding the mixed acid for acid digestion. The final volume of each subsample was adjusted to 50 mL by adding pure water.

The isotope enriched sulfur was transferred to the solution by acid digestion. The accurate concentration of the enriched isotope was determined by reverse ID-ICP-MS/MS with a JCSS standard solution.

(B) ID-ICP-MS/MS (pretreatment, ethanol dilution)

Approximately 5 g of the candidate reference material was diluted in about 45 g of ethanol. At least three subsamples were taken from each diluted sample. The subsamples were mixed with the solution of isotope enriched sulfur and measured by ID-ICP-MS/MS.

(C) ICP-MS/MS (pretreatment, acid digestion)

Acid digestion was carried out as for method (A), without addition of the solution of isotope enriched sulfur. A Co standard solution was added to the digested

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sample and $^{59}$Co was measured as the internal standard element to correct the signal drift of the instrument. The JCSS standard solution was added to the digested sample (with Co) to make subsamples for standard addition analysis.

(D) Combustion ion chromatography

Sulfur was measured by the standard addition method. All solutions for the CIC analysis were prepared by the gravimetric blending method using a 10 mL vial sealed with the Mininert Valve (GL Sciences Inc., Tokyo, Japan). Five concentrations (0 to 20 mg kg$^{-1}$) of sulfur solutions were prepared from thiophene and toluene as described in section 2.2. The sulfur solutions were mixed with the candidate reference material at a mass ratio of about 1 : 1 (2 mL each), and the sulfur content in the mixed solution was measured with the CIC analysis.

3. Results and Discussion

3.1. Validity of the CIC Analysis

The validity of the CIC analysis was established by measurement of the sulfur contents in three certified reference materials (NIST SRM 2773, NIST SRM 2298 and NIST SRM 2299). Two ampoules of each SRM were measured independently twice on separate days.

The values obtained by CIC analysis and certified values of the SRMs are shown in Table 1. The certified values of the SRMs were accurately determined by isotope dilution thermal ionization mass spectrometry. Each analytical result of sulfur by CIC analysis agreed with each certified value within the uncertainties. Therefore, the CIC analysis is valid for determination of sulfur in fuels at the range of 4 to 14 mg kg$^{-1}$.

3.2. Quantitation of Sulfur in NMIJ CRM 8302-a

Sulfur in the candidate reference material was measured by four different methods. Three ampoules of the candidate reference material were measured independently three times on separate days. Obtained results were comparable within the uncertainties as shown in Table 2. Thus, the certified value of sulfur content ($C_s$) in the CRM 8302-a was determined from the results (3.4).

3.3. Homogeneity Assessment and Stability Assessment

The between-ampoule inhomogeneity of the candidate reference material was assessed by measuring 3 subsamples taken from each of 10 ampoules randomly selected from the 353 ampoules. The candidate reference material was diluted by a factor of 10 with xylene and directly measured with ICP-MS/MS. Sulfur contents were measured by an external standard method. The uncertainty associated with sample inhomogeneity was estimated by the method described in ISO Guide 35.8. The between-ampoule inhomogeneity standard deviation ($s_{bb}$) was 0.6 %.

The long-term stability of the candidate reference material at room temperature was assessed for about 20 months before certification. The evaluation of sulfur stability was performed by method (C) shown in section 2.4. Sulfur was measured by the standard addition method. The results of the stability assessment are summarized in Table 3. The linear regression model was used to check for any trend in the data on the samples. The slope obtained by the linear regression was not statistically significant for a 95 % confidence level. Therefore, the uncertainty associated with sample instability ($u_{inst}$) was estimated by the method.

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Table 1 Sulfur Contents in NIST SRMs Obtained by CIC and Certified Values

| NIST SRM | Certified value | CIC result |
|----------|----------------|------------|
| SRM 2773 B100 Biodiesel (animal-based) | (7.39 ± 0.39) mg kg$^{-1}$ | (7.35 ± 0.26) mg kg$^{-1}$ |
| SRM 2298 Sulfur in gasoline (high octane) | (4.7 ± 1.3) mg kg$^{-1}$ | (4.5 ± 0.3) mg kg$^{-1}$ |
| SRM 2299 Sulfur in gasoline (reformulated) | (13.6 ± 1.5) mg kg$^{-1}$ | (13.4 ± 0.5) mg kg$^{-1}$ |

Values after plus or minus are the expanded uncertainties.

Table 2 Measurements of Sulfur Contents in NMIJ CRM 8302-a

| Method | Sulfur content |
|--------|----------------|
| (A) ID-ICP-QMS/QMS (pretreatment, acid digestion) | (7.24 ± 0.08) mg kg$^{-1}$ |
| (B) ID-ICP-QMS/QMS (pretreatment, ethanol dilution) | (7.15 ± 0.09) mg kg$^{-1}$ |
| (C) ICP-QMS/QMS (pretreatment, acid digestion) | (7.11 ± 0.16) mg kg$^{-1}$ |
| (D) CIC | (7.15 ± 0.11) mg kg$^{-1}$ |

Values after plus or minus are the standard uncertainties due to measurement.
described in ISO Guide 35\(^{9}\). That is, \(t \times s(b_1)\) was evaluated as

\[
\mu_{u} = t \times s(b_1)
\]

(1)

where \(s(b_1)\) is the standard deviation of the slope of the regression, and \(t\) is the period until the expiration date of certification. The expiration of the candidate reference material was set at 4 years from the homogeneity assessment, and the \(t\) value was \((4 \times 365)\) days. Based on this analysis of the stability test, the value of \(s(b_1)\) was \(1.67 \times 10^{-3}\) mg kg\(^{-1}\). The value of \(\mu_{u}\) was evaluated as \(0.24\) mg kg\(^{-1}\) (3.4 % as relative value).

### 3.4. Calculation of Certified Value and Uncertainty

The certified value of the sulfur content \((C_s)\) in CRM 8302-a was determined as the weighted mean of the results of the four analyses (Table 2). The weights, proportional to the inverse of uncertainty due to measurement by each analytical method, were used for the calculation. Based on the results in Table 2, the value of \(C_s\) and the standard uncertainty due to measurement \((u(C_s))\) were 7.17 mg kg\(^{-1}\) and 0.05 mg kg\(^{-1}\), respectively. The standard uncertainty of the certified value was evaluated using the uncertainties due to measurement \((u(C_s))\), between-ampoule inhomogeneity \((s_{bb})\) and long-term instability \((u_{ults})\) according to ISO Guide 35\(^{9}\). The uncertainty of the certified value is summarized in Table 4. The expanded uncertainty of 0.51 mg kg\(^{-1}\) was decided from the standard combined uncertainty of 0.253 mg kg\(^{-1}\) and the coverage factor \((k)\) of 2.

### 4. Conclusions

The NMIJ CRM 8302-a (Biodiesel Fuel (Palm Oil-Based)) was issued by NMIJ, AIST in March 2016. The certified sulfur content is \((7.17 \pm 0.51)\) mg kg\(^{-1}\). To determine the sulfur certified value, four analytical methods were used to ensure the reliability of the certified value. This CRM can be used for the calibration of instruments and for the confirmation of the validity of analytical methods or instruments during analysis of biodiesel fuel samples and similar materials.

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| Test day          | Sulfur content [mg kg\(^{-1}\)] |
|-------------------|---------------------------------|
| 0 (Homogeneity assessment) | 7.25                            |
| 15 (0.5 months)   | 7.36                            |
| 37 (1 month)      | 7.43                            |
| 242 (8 months)    | 7.28                            |
| 575 (20 months)   | 7.15                            |

Table 4 Uncertainty Budget of CRM 8302-a

| Source of uncertainty | Value | Standard uncertainty | Unit | Relative standard uncertainty |
|-----------------------|-------|----------------------|------|------------------------------|
| Measurement, \(u(C_s)\) | 7.17  | 0.050                | mg kg\(^{-1}\) | 0.007                        |
| Homogeneity, \(s_{bb}\) |       |                      | mg kg\(^{-1}\) | 0.006                        |
| Stability, \(u_{ults}\) |       |                      | mg kg\(^{-1}\) | 0.034                        |
| Combined standard uncertainty | 7.17  | 0.253                | mg kg\(^{-1}\) | 0.035                        |
要 旨
バイオディーゼル燃料認証標準物質中の硫黄の精確な値付け

北牧 祐子, 朱 彦北, 沼田 雅彦
(国研)産業技術総合研究所 計量標準総合センター 物質計測標準研究部門,
305-8563 茨城県つくば市梅園1-1-1つくば中央第3事業所

産業技術総合研究所 計量標準総合センター（NMIJ, AIST）では、バイオディーゼル燃料（B100）中成分分析などの精度
管理用認証標準物質、NMIJ CRM 8302-aの開発を行った。本
認証標準物質は、バーム油由来の脂肪酸メチルエステルであ
り、認証項目は水、6種類の元素（S, Na, K, Mg, Ca, P）,
密度および動粘度である。本論文では、バイオディーゼル燃料
認証標準物質中の硫黄の精確な値付けについて述べる。硫黄の
値付けには、誘導結合プラズマ質量分析法と燃焼-イオンクロ
マトグラフィーを用いた。誘導結合プラズマ質量分析法では、
試料の前処理に3種類の方法を採用した。燃焼-イオンクロマ
トグラフィーによる硫黄定量法の妥当性確認は、硫黄の認証値
が付与されている3種類の認証標準物質（NIST SRM 2773,
NIST SRM 2298, NIST SRM 229）を用いて行った。硫黄の認
証値は、4種類の手法で得られた測定値を重み付けして平均す
ることで決定した。