Date of Shipment: ***** xx, 20xx

National Institute of Advanced Industrial Science and Technology
National Metrology Institute of Japan

Reference Material Certificate
NMIJ CRM 8302-a
No. +++
Biodiesel Fuel (Palm Oil-Based)

This certified reference material (CRM) was produced in accordance with the NMIJ’s management system and in compliance with ISO GUIDE 34:2009 and ISO/IEC 17025:2005. This CRM is intended for use in the calibration of instruments, and confirming the validity of methods and instruments, during analysis of the following components in biodiesel fuel (fatty acid methyl esters) samples and similar materials; and during measurement of density.

Certified Values
The certified values of this CRM are given in the tables below. The uncertainty of the certified value is the half-width of the expanded uncertainty interval calculated using a coverage factor \((k)\) of 2, which gives a level of confidence of approximately 95%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CAS No.</th>
<th>Certified value</th>
<th>Expanded uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mass fraction (mg/kg)</td>
<td>Mass fraction (mg/kg)</td>
</tr>
<tr>
<td>Water</td>
<td>7732-18-5</td>
<td>393</td>
<td>25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Certified value</th>
<th>Expanded uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass fraction (mg/kg)</td>
<td>Mass fraction (mg/kg)</td>
</tr>
<tr>
<td>Na</td>
<td>1.26</td>
<td>0.22</td>
</tr>
<tr>
<td>Mg</td>
<td>0.83</td>
<td>0.11</td>
</tr>
<tr>
<td>K</td>
<td>0.72</td>
<td>0.15</td>
</tr>
<tr>
<td>Ca</td>
<td>1.01</td>
<td>0.16</td>
</tr>
<tr>
<td>P</td>
<td>2.09</td>
<td>0.35</td>
</tr>
<tr>
<td>S</td>
<td>7.17</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Analysis
The certified values of this CRM are the weighted means of the results obtained from the following methods:

1. Water:
   - Coulometric and volumetric Karl Fischer (KF) titration.

2. Na:
   - Inductively coupled plasma tandem quadrupole mass spectrometry (ICP-MS/MS); pretreatment: acid digestion; quantification: standard addition.
   - High resolution inductively coupled plasma mass spectrometry (HR-ICP-MS); pretreatment: acid digestion; quantification: standard addition.
   - Flame atomic absorption spectrometry (FL-AAS); pretreatment: xylene dilution; quantification: absolute calibration curve

(3) Mg, K and Ca:
   - Isotope dilution (ID-) ICP-MS/MS; pretreatment: acid digestion.
   - ICP-MS/MS; pretreatment: acid digestion; quantification: standard addition.

(4) P:
   - ICP-MS/MS; pretreatment: acid digestion; quantification: standard addition.
Date of Shipment: ***** xx, 20xx

- Flow injection-inductively coupled plasma mass spectrometry (ICP-MS); pretreatment: xylene dilution; quantification: standard addition.
- Inductively coupled plasma optical emission spectrometry (ICP-OES); pretreatment: xylene dilution; quantification: standard addition.

(5) S:
- ID-ICP-MS/MS; pretreatment: acid digestion.
- ICP-MS/MS; pretreatment: acid digestion; quantification: standard addition.
- ID-ICP-MS/MS; pretreatment: ethanol dilution.
- Combustion ion chromatography; quantification: standard addition.

Metrological Traceability

(1) Water: The certified value was determined by two validated methods. Because the calibration solutions for the measurements were prepared from ultrapure water, the purity of which was evaluated by the freezing point depression method (primary method of measurement) in NMIJ, and prepared gravimetrically using a JCSS (Japan Calibration Service System)-calibrated balance, the certified value is traceable to the International System of Units (SI).

(2) Na, Mg, K, Ca, and P: Each certified value was determined by isotope dilution-mass spectrometry as the primary method of measurement and by other validated analytical methods. Their calibration standards were prepared from JCSS standard solutions by a gravimetric method using a JCSS calibrated electronic balance. Therefore, the certified values are traceable to SI.

(3) S: The certified value was determined by isotope dilution-mass spectrometry as the primary method of measurement and by other validated analytical methods. For the ICP-MS/MS measurements, calibration standards were prepared from a JCSS standard solution by a gravimetric method using a JCSS calibrated electronic balance. For the combustion ion chromatography, the calibration standards were prepared gravimetrically by diluting thiophene with a JCSS-calibrated balance. The purity of the thiophene was determined by the differential scanning calorimetry (DSC) and impurity analysis in NMIJ. Therefore, the certified value is traceable to SI.

Indicative Value

The indicative value of this CRM is given in the table below. The uncertainty of the indicative value is the half-width of the expanded uncertainty interval calculated using a coverage factor (k) of 2, which gives a level of confidence of approximately 95%.

<table>
<thead>
<tr>
<th>CAS No.</th>
<th>Indicative value</th>
<th>Expanded uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>67-56-1</td>
<td>564</td>
</tr>
</tbody>
</table>

Methanol was analyzed by isotope dilution mass spectrometry using a headspace-gas chromatograph/mass spectrometer equipped with a DB-624 column. Methanol-d3 was used as the internal standard. The homogeneity and stability of the methanol concentration are reflected in the uncertainty of the indicative value.

Mutual Recognition Arrangement under Meter Convention

The certified values of the mass fraction of water, Na, Mg, K, Ca, and P in this certificate are consistent with the calibration and measurement capabilities (CMCs) that are included in Appendix C of the Mutual Recognition Arrangement (MRA) drawn up by the International Committee for Weights and Measures (CIPM). Under the MRA, all participating institutes recognize the validity of each other’s calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (as for Appendix C of MRA, see http://kcdb.bipm.org/AppendixC/default.asp).

Expiration of Certification

This certificate is valid for six months from the date of shipment, provided that the CRM is stored in accordance with the instructions given in this certificate.
Date of Shipment: ***** xx, 20xx

Sample Form
This CRM is in the form of yellow viscous liquid at room temperature. This CRM of ca. 15 mL in net volume is kept in an amber glass ampoule with argon gas.

Homogeneity
The homogeneity of this CRM was evaluated by measuring 9 or more ampoules randomly selected from a group of 326 ampoules. The uncertainties due to inhomogeneity are reflected in the uncertainties of the certified values. The measurements were performed by one of the methods for each item represented in “Analysis”.

Instructions for Storage
This CRM should be stored at a temperature of 15°C to 30°C and shielded from light.

Instructions for Use
This CRM is for laboratory use only. Prior to use, the ampoule should be shaken gently and opened after several minutes. To avoid sample evaporation and moisture absorption, the CRM should be used promptly once the ampoule is opened.

Precautions for Handling
Wear a mask, gloves, and other personal protective equipment during handling. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation
The raw material of this CRM is biodiesel fuel (fatty acid methyl esters) that was made from palm oil. Commercial methanol and an element standard solution in biodiesel fuel, “Custom blend multi-element Standard (Na, K, Mg, Ca: 200 µg/g and P: 400 µg/g, containing Na, K, Mg, Ca-alkylbenzene sulfate and alkyl phosphate)”, were added to the material at NMIJ. The spiked biodiesel fuel was homogenized by mechanical mixing and 15 mL of the mixture was sealed in an amber ampoule under argon gas.

Technical Information
For the measurement of water content, a plastic paraffin film was attached to the ampoule just after breaking it open at 35 % relative humidity (25 °C). The sample was taken from the bottom of the ampoule using a gas-tight syringe. When comparing the water content measured immediately after opening and after 30 min, the increase was ca. 15 mg/kg and the obtained results remained within the uncertainty limit of the certified value.

The density of this CRM measured using a vibrating U-tube densimeter at the time of the certification was 0.875 g/cm³ (15 °C).

NMIJ Analysts
The technical manager and production manager for this CRM are M. Numata and Y. Kitamaki, respectively. The analysts are M. Numata, Y. Kitamaki, Y. Zhu, T. Narukawa, S. Inagaki, N. Hanari, Y. Fujita, Y. Kano, S. Nakamura, N. Morii, S. Taniguchi, M. Matsuo, R. Iwasawa, and I. Kudo.

Information
If substantive technical changes occur that affect the certification before the expiration of this certificate, NMIJ will notify the registered customers. Customer registration on the NMIJ Website (given below) will facilitate notification. Technical reports regarding this CRM can be obtained from the contact details given below.

Reproduction of Certificate
In reproducing this certificate, it should be clearly indicated that the document is a copy.
Note
This CRM was developed in collaboration with National Institute of Standards and Technology (NIST) with support of a grant from Japan-U.S. Cooperative Project of on Energy and Environmental Technology Research/Standardization (Japan-U.S. Environmental Technology Research Cooperation, 2013-2014) by the Ministry of Economy, Trade and Industry.

March 9, 2016
Ryoji Chubachi
President
National Institute of Advanced Industrial Science and Technology

If you have any questions about this CRM, please contact:
National Institute of Advanced Industrial Science and Technology,
National Metrology Institute of Japan,
Center for Quality Management of Metrology, Reference Materials Office,
1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan
Phone: +81-29-861-4059; Fax: +81-29-861-4009, https://www.nmij.jp/english/service/C/

Revision history
May 30, 2018: Certified value of kinetic viscosity was eliminated based on long-term stability monitoring.
The description on Mutual Recognition Arrangement under Meter Convention was added.
April 24, 2019: Certified value of density was eliminated based on long-term stability monitoring. The density at the time of the certification was added in “Technical Information.”