

National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan



Reference Material Certificate

NMIJ CRM 8301-a
No. +++

Bioethanol

This certified reference material (CRM) is produced in accordance with the NMIJ's management system and is in compliance with ISO 17034 and ISO/IEC 17025. This CRM is intended for use in the calibration of instruments, and for confirming the validity of analytical methods and instruments during analysis of water, methanol, sulfur, and copper in ethanol fuel samples and similar materials.

Certified Values

The certified values, expressed as mass fractions, 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 %.

	CAS No.	Certified value, Mass fraction (mg/kg)	Expanded uncertainty, Mass fraction (mg/kg)
Water	7732-18-5	1688	28
Methanol	67-56-1	482	23

	Certified value, Mass fraction (mg/kg)	Expanded uncertainty, Mass fraction (mg/kg)
S	2.43	0.23
Cu	0.0537	0.0041

Analysis

The certified values were based on the analytical results obtained using the methods described below:

- (1) Water: The certified value is the weighted mean of results obtained by coulometric and volumetric Karl Fischer (KF) titration.
- (2) Methanol: The certified value is the weighted mean of results obtained using a gas chromatograph/mass spectrometer (GC/MS: isotope dilution mass spectrometry [IDMS]) and using a gas chromatograph equipped with a flame ionization detector (GC-FID).
 - GC/MS: electron impact ionization; selected ion monitoring; internal standard, methanol- d_3
 - GC-FID: internal standard, 2,2,4-trimethylpentane
- (3) Sulfur: The certified value is the weighted mean of results obtained by a combustion-ultraviolet fluorescence method and combustion-ion chromatography.
- (4) Copper: The certified value was calculated as the weighted mean of results obtained by inductively coupled plasma mass spectrometry (ICP-MS), isotope-dilution (ID) ICP-MS, and graphite furnace atomic absorption spectrometry (GF-AAS) after 10-fold dilution into a 1 mol/L HNO₃ solution. The sampling bias in characterization analysis was also considered while calculating the certified value.

Metrological Traceability

- (1) Water: The certified value was determined by two validated methods. Because the calibration solutions used in the measurements were prepared from ultrapure water, the purity of which was evaluated by the freezing point depression method (primary method of measurement) at NMIJ and which was prepared gravimetrically using a JCSS (Japan Calibration

Service System)-calibrated balance, the certified value is traceable to the International System of Units (SI).

- (2) Methanol: The certified values were determined by IDMS as a primary method of measurement and by another validated method. Because the calibration solution used in the measurements was prepared from the reagent methanol, the purity of which was evaluated by the mass balance approach at NMIJ and which was prepared gravimetrically using a JCSS-calibrated balance, the certified values are traceable to the SI.
- (3) Sulfur: The certified value was determined by two validated methods. The calibration solutions used in the measurements were prepared gravimetrically using a JCSS-calibrated balance by diluting thiophene or NMIJ CRM 4217-a (sulfur in toluene) with a solvent. The purity of thiophene was determined by differential scanning calorimetry (DSC) and by impurity analysis at NMIJ. Therefore, the certified value is traceable to the SI.
- (4) Copper: The certified value was determined by multiple independent methods including a primary method, i.e., ID-ICP-MS. All the samples and standard solutions for Cu measurement were prepared on the basis of a gravimetric method carried out using a JCSS calibrated electronic balance. Calibration standards were prepared from a single element standard solution of Cu guaranteed by the JCSS, and the certified value is traceable to the SI.

Expiration of Certification

This certificate is valid for 6 months from the date of shipment, provided that the material is stored in accordance with the instructions given in this certificate.

Sample Form

This CRM is in the form of a clear liquid and it of ca. 8.5 mL in net volume is kept in an amber glass ampoule with argon gas.

Homogeneity

The homogeneity of the CRM was determined by analyzing 10 or more bottles randomly sampled from 440 bottles. The inhomogeneity of the analytes was evaluated by ANOVA and was reflected in the uncertainty of the certified values.

Instructions for Storage

This CRM should be stored at a temperature between 15 °C and 30 °C in a clean place 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.

This CRM is highly hygroscopic. For the measurement of water content, a gas-tight syringe should be used to take the sample; moreover, it is recommended that all the operation from ampoule opening to measuring be performed in a glove box purged with dry gas. However, as shown in Information, moisture absorption can be reduced by using the rubber cap accompanying this CRM, even in ambient air. Except for measurements of water, the rubber cap should not be used for material sampling to avoid the elution of ingredients from the cap.

A mask, gloves, and other protective gear should be worn during handling. This CRM should be handled, stored, and disposed of in accordance with relevant laws.

Precautions for Handling

This CRM should be kept away from heat and ignition sources. Further, protective equipment such as safety glasses, safety mask, and safety gloves should be worn during in the handling of this CRM. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

The raw material for this CRM is bioethanol fuel that was obtained from rice. Purified water, methanol, dimethylsulfide, and copper (II) acetate (ethanol solution with acetic acid) were added to the CRM gravimetrically at NMIJ. Spiked bioethanol was homogenized by mechanical mixing, and 8.5 mL of the mixture was sealed in an amber ampoule with argon gas.

Technical Information

The density of this CRM was 0.7942 g/mL (15 °C), 0.7900 g/mL (20 °C), or 0.7857 g/mL (25 °C). The measurement was

performed using an oscillational density meter. Acetic acid (approximately 50 mg/kg) was added to the CRM.

When the samples were taken and their water content was measured in ambient air, the increase in water concentration for 30 min was 8 mg/kg at 10 % relative humidity (23 °C) and 14 mg/kg at 45 % relative humidity (24 °C). The obtained results remained within the uncertainty limit of the certified value. For measurements, just after opening the ampoule, the rubber cap was attached on the ampoule. Samples for KF titration were taken every 10 min from the bottom of the ampoule by using a gas-tight syringe through the cap.

NMIJ Analysts

The technical manager and production manager for this CRM is KATO K. and NUMATA M., respectively, and the analysts are INAGAKI S., KITAMAKI Y., ZHU Y., NARUKAWA T., HANARI N., TANIGUCHI S., MATSUO M., IWASAWA R., and NARUSHIMAI.

Information

If substantive technical changes occur that affect the certification before the expiration of this certificate, NMIJ will notify the registered customer. 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.

April 1, 2020

ISHIMURA Kazuhiko
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://unit.aist.go.jp/nmij/english/refmate/>

Revision history

March 19, 2014:	The expiration of this certificate was changed to "March 31, 2018" from "March 31, 2015."
April 1, 2015:	"Metrology Management Center" was renamed to "Center for Quality Management of Metrology."
January 11, 2017:	The description in "Expiration of Certification" was changed to "6 months from the date of shipment."