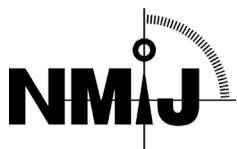


National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan



Reference Material Certificate

NMIJ CRM 4601-c
No. +++3,5-Bis(trifluoromethyl)benzoic Acid for Quantitative NMR (^1H , ^{19}F)

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 ^1H and ^{19}F signal areas in nuclear magnetic resonance (NMR) spectroscopy. It is also intended for use in controlling the precision of analysis and confirming the validity of the analytical methods.

Certified Value

The certified value of this CRM is given in the table below. The uncertainty of the certified value is the expanded uncertainty obtained by multiplying the combined standard uncertainty by a coverage factor (k) of 2, and it is the half-width of an interval estimated to have a level of confidence of approximately 95 %.

Substance	CAS No.	Certified value, Mass fraction (kg/kg)	Expanded uncertainty, Mass fraction (kg/kg)
3,5-Bis(trifluoromethyl)benzoic acid	725-89-3	0.9993	0.0005

Analysis

The certified value of this CRM is the arithmetic mean of purities determined by the mass balance approach and freezing point depression method. In the mass balance approach, impurities were analyzed using a high-performance liquid chromatograph with an ultraviolet detector (HPLC-UV), a gas chromatograph / flame ionization detector (GC-FID), a Karl-Fischer titrator (KF) and a Thermogravimeter (TG). For the freezing point depression method in a stepwise scan method, a differential scanning calorimeter (DSC) was used. The standard uncertainty was estimated by combining uncertainties due to each analytical method, difference between two methods, homogeneity and stability.

Metrological Traceability

The certified value of this CRM was determined by the mass balance approach, and by the freezing point depression method which is the primary method. Organic impurities were determined with the HPLC-UV and GC-FID by using standard solutions prepared by gravimetric mixing from 3,5-bis(trifluoromethyl)benzoic acid (NMIJ CRM 4601-b). Water content was determined by coulometry with the Karl-Fischer titrator which was validated. Ignition residue was determined with the TG calibrated with a JCSS-calibrated weight. The calibration of temperature and enthalpy were performed with NMIJ CRM 5401-a (cyclohexane) and NIST SRM 2232 (indium) for the freezing point depression method with the DSC. The certified value, therefore, is traceable to the International System of Units (SI).

Expiration of Certification

This certificate is valid for one year from the date of shipment, provided that this CRM is stored in accordance with the instructions given in this certificate.

Description of the material

This CRM is in the form of a white powder. This CRM of ca. 200 mg in net volume is kept in an amber glass vial. The vial is sealed in an aluminum-laminated bag.

Instructions for Storage

This CRM should be kept at a temperature between 15 °C and 25 °C, and shielded from light in a clean desiccator.

Instruction for Use

From the viewpoint of homogeneity, 5 mg or more of this CRM should be used for each analysis. The CRM is for laboratory use only. The CRM should be used promptly once a vial is opened, and kept in a clean desiccator.

As molar mass, (258.119 ± 0.011) g/mol ($k=2$) (IUPAC 2022) or (258.1165 ± 0.0062) g/mol ($k=2$) (IUPAC 2016) is recommended to use for 3,5-bis(trifluoromethyl)benzoic acid.

Precautions for Handling

Refer to the safety data sheet (SDS) on this CRM before use, and wear a protective mask and protective gloves when using this CRM.

Preparation

This CRM was purified by recrystallization and subdivided by Wako Pure Chemical Industries, Ltd. This CRM was bottled into amber glass vials and sealed in an aluminum-laminated bag under dry air atmosphere.

Technical Information

The solubility and chemical shifts in the NMR spectra of the CRM in widely used deuterated solvents are shown below. The following solubility and chemical shifts can be changed by temperature or coexisting solutes. ^1H NMR spectra of the CRM in some solvents are available from the Spectral Database for Organic Compounds, SDBS (https://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi) by National Institute of Advanced Industrial Science and Technology. See SDBS No. 15118. Possible overlap between signals originated from the calibrant (this CRM) and measurands shall be checked. The CRM is insoluble in D_2O , benzen- d_6 or toluene- d_8 practically (less than 0.5 mg/mL). The density of this CRM was 1.71 g/cm³ at 25 °C.

Solvent	Solubility (mg/mL) (25 °C)	Chemical shift (ppm)	
		^1H NMR (δ : 0 ppm(TMS), 25 °C)	^{19}F NMR (δ : -164 ppm(C_6F_6), 25 °C)
Dimethylsulfoxide- d_6	≥ 20	8.42(1H), 8.44(2H)	-62.8
Methanol- d_4	≥ 20	8.21(1H), 8.51(2H)	-66.0
Acetonitrile- d_3	≥ 20	8.23(1H), 8.49(2H)	-64.0
Chloroform- d	0.5	8.12(1H), 8.54(2H)	-60.8
Dichloromethane- d_2	1	8.15(1H), 8.55(2H)	-62.1
Acetone- d_6	≥ 20	8.34(1H), 8.55(2H)	-64.2
0.1 M NaOD/ D_2O	10	7.97(1H), 8.14(2H)	-62.9

TMS in the table shows the abbreviation for tetramethylsilane.

NMIJ Analysts

The technical manager for this CRM is ITOH N. and the production manager is YAMAZAKI T. The analysts are YAMAZAKI T., SHIMIZU Y., KITAMAKI Y., NAKAMURA S., BAO X. and YAMANAKA N.

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.

Note

Some parts of analytical methods were developed with support of a competitive grant (2013) by Chemicals Evaluation and Research Institute (CERI).

November 24, 2022

ISHIMURA Kazuhiko
President

National Institute of Advanced Industrial Science and Technology

If you have any questions about this CRM, please contact:

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Sample