

National Institute of Advanced Industrial Science and Technology

## National Metrology Institute of Japan



## Reference Material Certificate

NMIJ CRM 4602-a  
No. +++1,4-Bis(trimethylsilyl)-2,3,5,6-tetrafluorobenzene for Quantitative NMR ( $^1\text{H}$ ,  $^{19}\text{F}$ )

This certified reference material (CRM), 1,4-bis(trimethylsilyl)-2,3,5,6-tetrafluorobenzene, is produced in accordance with the NMIJ's management system and in compliance with ISO 17034 and ISO/IEC 17025. This CRM is intended for use in the calibration of  $^1\text{H}$  and  $^{19}\text{F}$  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 analytical methods.

**Certified Value**

The certified value of this CRM is the purity (mass fraction) 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)
1,4-Bis(trimethylsilyl)-2,3,5,6-tetrafluorobenzene	16956-91-5	0.9998	0.0003

**Analysis**

The certified value of this CRM is the weighted 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 with flame ionization detector (GC-FID) and a Karl-Fischer titrator (KF). In the freezing point depression method, an adiabatic calorimeter was used. The standard uncertainty was evaluated by combining uncertainties from each analytical method, sample homogeneity, stability and difference between the methods.

**Metrological Traceability**

The certified value of this CRM was determined by the mass balance approach and the freezing point depression method which is the primary method. Water content was determined by a KF validated with NMIJ CRM 4222-a. An adiabatic calorimeter, in which the temperature, heating time, standard resistance, and voltage were calibrated, was used in the freezing point depression method. Therefore, the certified value 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 the material remains unopened and is stored in accordance with the instructions given in this certificate.

**Description of the material**

This CRM is 1,4-Bis(trimethylsilyl)-2,3,5,6-tetrafluorobenzene in the form of a white powder at room temperature. This CRM (100 mg) was bottled into a brown glass vial and stored in an aluminum-laminated bag.

**Instructions for Storage**

This CRM should be stored at a temperature between 2 °C and 10 °C and shielded from light in a clean area.

**Instructions for Use**

To ensure homogeneity, a minimum sample mass of 2 mg should be used. This CRM is for laboratory use only. This CRM should be allowed to warm to room temperature before opening, and used promptly owing to its slight volatility.

A molar mass of  $(294.434 \pm 0.007)$  g/mol ( $k=2$ ) (IUPAC 2016) can be used for this CRM. As this CRM may become unstable in some solutions, it is recommended that the stability is checked before use by monitoring changes in the sample solution over time.

**Precautions for Handling**

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

**Preparation**

The raw material of this CRM was synthesized by the Heteroatom Chemistry Team at the Interdisciplinary Research Center for Catalytic Chemistry in the National Institute of Advanced Industrial Science and Technology. After purification by recrystallization and sublimation, this CRM was subdivided by Wako Pure Chemical Industries, Ltd. This CRM was bottled in a brown vial and sealed in an aluminum-laminated bag under a dry argon atmosphere.

**Technical Information**

The solubility and chemical shifts in the NMR spectra of this CRM in widely used solvents are shown below (next page). The following solubility and chemical shifts will be changed by temperature or coexisting solutes. Therefore, the overlap between signals originating from the calibrant (this CRM) and measurands must be checked. This CRM is insoluble in D<sub>2</sub>O (less than 0.5 mg/mL). The density of this CRM was 1.25 g/cm<sup>3</sup> at 25 °C.

Solvent	Solubility (mg/mL) (25 °C)	Chemical shift (ppm)	
		<sup>1</sup> H NMR ( $\delta$ :0 ppm(TMS), 25 °C)	<sup>19</sup> F NMR ( $\delta$ :−164 ppm(C <sub>6</sub> F <sub>6</sub> ),25 °C)
Dimethylsulfoxide- <i>d</i> <sub>6</sub>	5	0.35	−128.6
Methanol- <i>d</i> <sub>4</sub>	≥ 20	0.38	−130.4
Acetonitrile- <i>d</i> <sub>3</sub>	≥ 20	0.40	−130.0
Chloroform- <i>d</i>	≥ 20	0.38	−128.8
Dichloromethane- <i>d</i> <sub>2</sub>	≥ 20	0.39	−129.4
Acetone- <i>d</i> <sub>6</sub>	≥ 20	0.40	−129.8
Toluene- <i>d</i> <sub>8</sub>	≥ 20	0.30	−128.4
Tetrahydrofuran- <i>d</i> <sub>8</sub>	≥ 20	0.39	−129.5
Benzene- <i>d</i> <sub>6</sub>	≥ 20	0.24	−128.4

TMS in the table shows the abbreviation for tetramethylsilane.

**NMIJ Analysts**

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

**Information**

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

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

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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/>

Sample