

National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan



Reference Material Certificate

NMIJ CRM 4604-a
No. +++Phenylphosphonic Acid for Quantitative NMR (^1H , ^{31}P)

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 ^{31}P signal areas for quantitative nuclear magnetic resonance (qNMR) spectroscopy, and validation of 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)
Phenylphosphonic Acid	1571-33-1	0.9983	0.0015

Analysis

The certified value of this CRM was the weighted mean of purities determined by the mass balance approach, neutralization titration method and ^1H qNMR. For the mass balance approach, impurities were evaluated by using a high performance liquid chromatograph with an ultraviolet detector (HPLC-UV), a headspace gas chromatograph with mass spectrometer (HS-GC/MS), a Karl-Fischer titrator (KF) and a thermogravimeter (TG). For the neutralization titration method, an automatic potentiometric titrator was used. For ^1H qNMR, NMR spectrometer with ^1H resonance frequency of 600 MHz was used. The standard uncertainty was estimated by combining uncertainties due to each analytical method, difference among the three methods, sample homogeneity and stability.

Metrological Traceability

The certified value of this CRM was determined by the mass balance approach, neutralization titration method and ^1H qNMR. Water content was evaluated by coulometry with the KF validated with NMIJ CRM 4222-e (Water in Mesitylene(0.1 mg/g)). Ignition residue was evaluated with the TG calibrated with a JCSS-calibrated weight. NMIJ CRM 3001-c (Potassium Hydrogen Phthalate) was used as the calibrant of titrant concentration for purity evaluation by neutralization titration method. NMIJ CRM 4603-a (Potassium Hydrogen Phthalate for Quantitative NMR (^1H)) was used as the reference material for purity evaluation by ^1H qNMR. 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 the material 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 of phenylphosphonic acid at ordinary temperature. This CRM of ca. 200 mg in net mass is kept in an amber glass vial. The vial is sealed in an aluminum-laminated plastic bag.

Instructions for Storage

This CRM should be stored in a refrigerator at temperatures of 2 °C to 10 °C and protected from light.

Instruction for Use

The CRM should be allowed to warm to room temperature before opening and stored in the refrigerator after opening. Considering the homogeneity, a minimum sample size of 5 mg should be used to ensure valid results. The CRM is for laboratory use only. (158.093 ± 0.006) g/mol ($k = 2$) (IUPAC 2022) can be used for the molar mass of phenylphosphonic acid.

Precautions for Handling

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

Preparation

This CRM was purified by recrystallization and subdivided by FUJIFILM Wako Pure Chemicals Co. This CRM was bottled into amber glass vials and sealed in an aluminum-laminated bag under argon atmosphere.

Technical Information

The solubility and chemical shifts in the NMR spectra of this CRM in widely used deuterated solvents are shown below. The following solubility and chemical shifts will be changed by temperature or coexisting solutes. Therefore, possible overlap between signals originated from the calibrant (this CRM) and measurands has to be checked. This CRM is insoluble in chloroform-*d*, dichloromethane-*d*₂, benzene-*d*₆ or toluene-*d*₈ practically (less than 0.5 mg/mL).

Solvent	Solubility (mg/mL) (25 °C)	Chemical shift (ppm)	
		¹ H NMR (δ:0 ppm(TMS), 25 °C)	³¹ P NMR (δ:0 ppm(H ₃ PO ₄), 25 °C)
Dimethylsulfoxide- <i>d</i> ₆	≥ 20	7.45(2H), 7.50(1H), 7.67(2H)	13.1
Methanol- <i>d</i> ₄	≥ 20	7.48(2H), 7.56(1H), 7.81(2H)	15.2
Acetonitrile- <i>d</i> ₃	2	7.48(2H), 7.58(1H), 7.75(2H)	17.4
Tetrahydrofuran- <i>d</i> ₈	≥ 20	7.39(2H), 7.46(1H), 7.77(2H)	14.9
Pyridine- <i>d</i> ₈	≥ 20	7.43(3H), 8.42(2H)	10.2
D ₂ O	≥ 20	7.54(2H), 7.60(1H), 7.78(2H)	15.1
0.1 mol/L NaOD/D ₂ O	10	7.40(3H), 7.71(2H)	11.2
0.1 mol/L DCl/D ₂ O	≥ 20	7.53(2H), 7.62(1H), 7.77(2H)	17.3
Acetic acid- <i>d</i> ₄	≥ 20	7.49(2H), 7.58(1H), 7.86(2H)	18.4
Acetone- <i>d</i> ₆	≥ 20	7.48(2H), 7.57(1H), 7.80(2H)	16.1

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., and the analysts are YAMAZAKI T., SHIMIZU Y., KITAMAKI Y., KUROE M., OKAMOTO C., 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 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

This reference material was developed based on the results of joint research with FUJIFILM Wako Pure Chemicals Co.

February 21, 2025

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, <https://unit.aist.go.jp/nmij/english/refmate/>