National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan

Reference Material Certificate

NMIJ CRM 5008-a
No. +++

Polystyrene (Polydisperse)

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 verification of instruments and protocols determining molecular mass distribution of polymers.

Certified Values

The certified value of the mass-average molar mass M_w, number-average molar mass M_n, and polydispersity index M_w/M_n of the polystyrene 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 %.

	Certified Value (g/mol)	Expanded Uncertainty (g/mol)
Mass-average Molar Mass M_w	276 000	15 000
Number-average Molar Mass M_n	94 600	6 400

	Certified Value	Expanded uncertainty
Polydispersity Index M_w/M_n	2.92	0.17

Analysis

The certified value of the mass-average molar mass M_w of the polystyrene was determined by the weighted average of the value from static light scattering (SLS) method with toluene as a solvent and the value from size exclusion chromatography with multi-angle light scattering (SEC-MALS) method. The certified value of polydispersity index M_w/M_n was determined by SEC-MALS method. Two kinds of columns were used for SEC-MALS with a refractive index (RI) detector by using tetrahydrofuran as a solvent. The certified value of the number-average molar mass M_n of the polystyrene was calculated by the division of M_w by the value of M_w/M_n.

Metrological Traceability

The chloride ion standard solution distributed by JCSS and the table of refractive index increment of salty solution[1)] were used to change the output of RI detector into refractive index increment for determination of the certified value. The scattering light intensity of SLS and MALS was calibrated by Rayleigh ratio of toluene[2)], 1.406×10^{-5} cm^{-1}. This CRM is traceable to International System of Units (SI).

[1)] Kruis, A. *Z. Physik. Chem.* **1936**, *34*, 13. [2)] Kaye, W.: McDaniel *J. Appl. Opt.* **1974**, *13*, 1934-1937.

Indicative Values

The indicative values of differential molar-mass distribution dw/dLog$M$ of the polystyrene are given in the table below. The values of dw/dLog$M$ were determined at the same time of determination of the certified values.

Log*M*	d*w*/dLog*M*	Log*M*	d*w*/dLog*M*	Log*M*	d*w*/dLog*M*	Log*M*	d*w*/dLog*M*
6.7	2.48×10^{-4}	5.7	7.68×10^{-1}	4.7	2.19×10^{-1}	3.7	1.35×10^{-2}
6.6	-8.48×10^{-5}	5.6	9.52×10^{-1}	4.6	1.54×10^{-1}	3.6	1.11×10^{-2}
6.5	3.34×10^{-4}	5.5	1.08×10^{0}	4.5	1.11×10^{-1}	3.5	8.86×10^{-3}
6.4	1.81×10^{-4}	5.4	1.14×10^{0}	4.4	8.22×10^{-2}	3.4	7.13×10^{-3}
6.3	1.18×10^{-3}	5.3	1.10×10^{0}	4.3	6.13×10^{-2}	3.3	6.21×10^{-3}
6.2	6.51×10^{-3}	5.2	9.76×10^{-1}	4.2	4.52×10^{-2}	3.2	5.02×10^{-3}
6.1	3.36×10^{-2}	5.1	7.92×10^{-1}	4.1	3.42×10^{-2}	3.1	4.09×10^{-3}
6.0	1.21×10^{-1}	5.0	6.03×10^{-1}	4.0	2.66×10^{-2}	3.0	3.51×10^{-3}
5.9	3.02×10^{-1}	4.9	4.40×10^{-1}	3.9	2.09×10^{-2}	2.9	3.67×10^{-3}
5.8	5.40×10^{-1}	4.8	3.11×10^{-1}	3.8	1.68×10^{-2}		

Expiration of Certification

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

Sample Form

This CRM consists of 20 mg pellets which are clear at room temperature. This CRM of ca. 5 g in net volume is kept in a brown glass bottle.

Homogeneity

The homogeneity of this CRM was evaluated by Match Factor of chromatograms for 7 bottles picked up randomly from 500 bottles. The analysis of the variance reveals the homogeneity and no differences between bottles.

Instructions for Storage

This CRM should be stored at a temperature between 5 °C and 35 °C, and shielded from light with the cap tightly closed.

Instructions for Use

This CRM is for laboratory use only. The CRM should be used promptly once the bottle is opened. The minimum amount for the use of this CRM is 20 mg.

Precautions for Handling

Keep away from fire, heat and sparks and ventilate the air. Wear suitable protective clothing and gloves. Refer to the safety data sheet (SDS) on this CRM before use.

Preparation

The CRM was prepared from industrially produced polystyrene within a single production lot and subdivided into brown grass bottles with 5 g each.

Technical Information

The calibration curve of SEC-MALS for getting certificate values was determined by the relationship between elution time and molar mass at the peak top of chromatogram of SEC-MALS with RI detector by using the calibration data of this CRM 5008-a[3], several kinds of monodisperse polystyrenes with the average molar mass less than 20 000, three NMIJ Polystyrene CRMs (NMIJ CRM 5001-a, 5002-a, and 5004-a), and hexylbenzene as calibration standards. The concentration from RI chromatogram was corrected by the molar-mass dependence of refractive index increment[4], and the molar mass at the peak was corrected by the second virial coefficient for the concentration. This CRM contains a small amount of unknown low-molecular-weight component which appears at the end of elution time in SEC chromatogram, and it was neglected on the calculation of the certified values. The most significant contribution for the uncertainty of average molar mass was the Rayleigh

ratio of toluene, which corresponds to 3.8 % of the expanded uncertainty. The number-average molar mass M_n was 86 000 ± 5 300 g/mol (the value after "±" means the standard deviation of repeating measurements) which was determined by membrane osmotic pressure measurement with toluene as a solvent.

[3] The calibration data corresponds to the pairs of molar masses and elution times. [4] Itakura,M.: Sato, K.: Lusenkova, M.A.: Matsuyama, S.: Shimada, K.: Saito, T.: Kinugasa, S. *J. Appl. Polym. Sci.*, **2004**, *94*, 1101-1106.

NMIJ Analysts

The technical manager is KINUGASA S. The production manager is KINUGASA S. The analysts are KINUGASA S. and KISHINE K.

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
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Revision history
April 1, 2015: "Metrology Management Center" was renamed to "Center for Quality Management of Metrology."
February 10, 2016: The description in "Expiration of Certification" was changed to "one year from the date of shipment"