National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2493

Bingham Mortar Mixture for Rheological Measurements

This Standard Reference Material (SRM) is intended for use in calibrating rheometers for measuring the rheological properties of cement paste and mortar. A unit of SRM 2493 consists of four containers, one glass bottle of corn syrup (500 g), two plastic jars of limestone powder (600 g each) and one plastic jar of 1 mm glass beads (1500 g).

Certified Values: A NIST certified value is a value for which NIST has the highest confidence in its accuracy and that all known or suspected sources of bias have been investigated or taken into account [1]. The certified Bingham yield stress and plastic viscosity values are given in Tables 1 through 3 and are based on measurements from analyses made using a parallel serrated plate rheometer performed at NIST by a single operator and on a model developed at NIST. The fit curve for viscosity vs. shear rate, shown in Figure 1, is provided as a reference. The expanded uncertainties of the certified values are consistent with the NIST uncertainty policy described in the NIST Technical Note 1297 [2], and are computed using a random coefficient regression model evaluated by Monte Carlo methods.

Expiration of Certification: The certification of **SRM 2493** is valid, within the measurement uncertainty specified, until **31 December 2022**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and Use"). This certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive changes occur that affect the certification before the expiration of the certification, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Preparation of the material and coordination of the technical measurements leading to certification were performed by Chiara F. Ferraris of the NIST Materials and Structural Systems Division. The development of the computation model used to provide certified values was performed by Nicos S. Martys of the NIST Materials and Structural Systems Division, and William L. George of the NIST Applied and Computational Mathematics Division.

Statistical consultation on measurement design and analysis of the certification data was performed by Blaza Toman of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Jason Averill, Division Chief
Materials and Structural Systems Division

Gaithersburg, MD 20899
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Steven J. Choquette., Director
Office of Reference Materials

Certified Values: The certified values presented in this certificate were generated using a parallel plate rheometer for paste and a computational model [3]. To calibrate a rheometer [4,5] using the data provided in this certificate, two methods are suggested: A) a method using the approximation of the Bingham equation and B) a method based on the viscosity vs. shear rate curves. In Section "Instructions for Storage and Use", a methodology is described for both methods. Method A is an easier method to use and would provide both the yield stress and the plastic viscosity as per Bingham model, but it uses only the linear portion of the stress-rate curve. On the other hand, Method B utilizes the entire stress-rate curve and is not model dependent.

Method A: Based on Bingham parameters

The measurands are the parameters listed and the certified values are metrologically traceable to the indicated coherent SI units. In Tables 1, 2 and 3, the values of the Bingham parameters are provided both by a parallel plate rheometer [6] and the computational model.

Table l. Certified Yield Stress and Plastic Viscosity Values for 0 % Concentration

Parameter	Type of geometry	Certified Value[(a)] (Pa)	Standard Uncertainty (Pa)	Expanded Uncertainty (Pa)
Yield Stress	Parallel plate	24.7	0.5	1.0
	Model	23.1	1.8	3.6
Plastic Viscosity	Type of geometry	Certified Value (Pa·s)	Standard Uncertainty (Pa·s)	Expanded Uncertainty (Pa·s)
	Parallel plate	7.9	0.2	0.5
	Model	8.1	0.8	1.6

(a) based on parallel plate measurement and the computational model

Table 2. Certified Yield Stress and Plastic Viscosity Values for 20 % Concentration

Parameter	Certified Value[(a)] (Pa)	Standard Uncertainty (Pa)	Expanded Uncertainty (Pa)
Yield Stress	31.0	3.6	5.2
Plastic Viscosity	Certified Value (Pa·s)	Standard Uncertainty (Pa·s)	Expanded Uncertainty (Pa·s)
	14.9	2.3	3.0

(a) Based on the computational model

Table 3. Certified Yield Stress and Plastic Viscosity Values for 40 % Concentration

Parameter	Certified Value[(a)] (Pa)	Standard Uncertainty (Pa)	Expanded Uncertainty (Pa)
Yield Stress	38.8	5.2	6.2
Plastic Viscosity	Certified Value (Pa·s)	Standard Uncertainty (Pa·s)	Expanded Uncertainty (Pa·s)
	57.9	8.7	11.8

(a) Based on the computational model

Method B: Based on the Viscosity vs. shear rate curve

Measurements for this method were made using paste made from SRM 2492 to serve as the matrix fluid of a suspension composed of mono-sized glass bead inclusions. SRM 2492 paste is identical to SRM 2493 paste measured by parallel plate. Due to different scaling behavior of the experimental data in high and low shear rate regimes, the data were divided into two regions, above and below the shear rate equal to 1 s^{-1}. The data in each region was fitted to functions f_1 and f_2 (see equation 1 and 2 respectively). To represent the full data set with a single function, equation 3 was developed, which seamlessly combines the two functions without any significant deviations from f_1 and f_2.

$$f_1(\dot{\gamma}) = \frac{A_1}{\dot{\gamma}^{B_1}} + C_1 \qquad \textit{[Eq. 1]}$$

$$f_2(\dot{\gamma}) = \frac{A_2}{\dot{\gamma}^{B_2}} + C_2 \qquad \textit{[Eq. 2]}$$

$$\mu = \frac{\left(C_2 + \frac{A_2}{\dot{\gamma}^{B_2}}\right) + \left(C_1 + \frac{A_1}{\dot{\gamma}^{B_1}}\right) e^{2\,a(\dot{\gamma}-1)}}{1 + e^{2\,a(\dot{\gamma}-1)}} \qquad \textit{[Eq. 3]}$$

where

$\dot{\gamma}$ = Shear rate
μ = Viscosity
A_i, B_i, *and* C_i $(i = 1,2)$ = coefficients to fit the curve
a = fitting parameter to smoothly combine curves f_1 and f_2.

<u>Paste</u>*:* The coefficients were estimated by a non-linear least square regression fit to the paste SRM 2492 data (identical to SRM 2493 paste), obtained with the parallel plate geometry. The maximum difference was 3 % or less of the experimental values. The standard uncertainty of the estimates of the coefficients was calculated [4] and is given in parentheses. The fitting parameter was set as $a = 4$ and not estimated, therefore it has no uncertainty. The viscosity (μ) can be calculated at any given shear rate with equation 3, and the factors below:

A_1=16.411 (0.64) ; B_1=0.988 (0.02); C_1=9.641(0.98)
A_2=19.178 (0.61) ; B_2=0.727 (0.09); C_2=7.116 (0.78)
a=4

<u>*Mortar:*</u> To obtain the viscosity vs. the shear rate with inclusions of 20 % or 40 % by volume of 1-mm glass beads, the shear rate and the viscosity in equation 3 need to be scaled by the factors shown in Table 4. These values are used to multiply the paste shear rate and the viscosity respectively to obtain the value of bead concentrations at 20 % or 40 %.

Table 4. Scaling Parameters to Factor the SRM 2492 Curve to a Mortar Curve with Known Concentrations.

Concentration [%]	**μ_{sc} factor**	**$\dot{\gamma}_{sc}$ factor**
20	1.85	0.66
40	7.20	0.23

Note: *The uncertainty in scaling parameters, based on a least square regression fit of simulation data to equation 3 is 10 % or less*

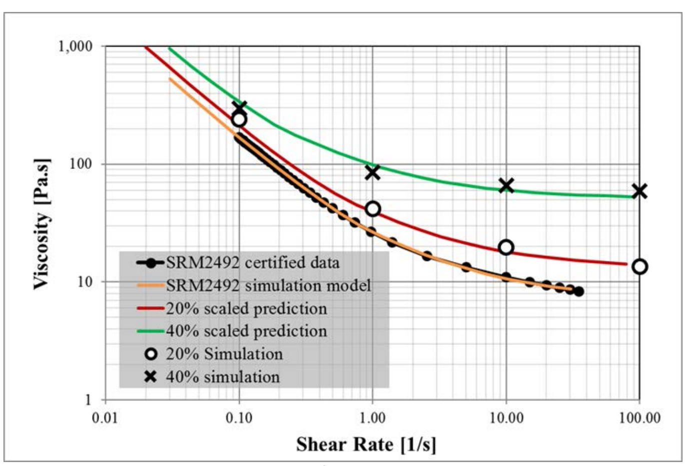

Figure 1: Simulation model data and predicted data from scaling parameters are compared to experimental data results. The uncertainty is about 10 % [4].

INSTRUCTIONS FOR STORAGE AND USE

Storage and Use: Store the bulk, unmixed material at room temperature. The SRM batch needs to be prepared by the operator before it can be used. Once the components are mixed as described below, the SRM should be stored at 23 °C ± 2 °C in a sealed plastic jar and used within 7 d.

Preparation: Follow the instructions below. The mixture's composition is:

- Corn syrup: 200 g
- Distilled water: 63.16 g
- Limestone: 458.1 g
- Glass beads (Considering a total paste volume of 320 cm^3 or see calculation below):

20 % by volume	196.8 g
40 % by volume	524.8 g

Mixing the material is a two phase process:

1) Prepare the paste fraction (limestone, corn syrup and water). The equipment and the method are described in ASTM C1738 [7], with the following sequence to introduce the ingredients. Pour the correct amount of distilled water in a jar that already contains the correct mass of corn syrup, and mix with a spatula until homogeneous. On average, it will take 5 min of mixing to dilute the visible glucose chains in the corn syrup. Assuring the syrup is diluted prior to adding it into the high shear blender results in a more effective transfer of the corn syrup into the mixture. Then, add all of the mixture into the high shear blender and proceed as described in ASTM C1738 to introduce the limestone and mix. The water baths of the high shear blender and the rheometer should be maintained at 23 °C ± 1 °C.
2) Tare a plastic container preferably made of polypropylene [8] and pour the mixed paste into it. Make sure that the container has a lid to avoid water evaporation. Measure the mass of the paste, P_m.
3) Addition of the beads.
   a. Calculate the mass of beads needed for the mixture using the formula below:

20 % beads	Mass beads = $0.329 * P_m$
40 % beads	Mass beads = $0.877 * P_m$

Note: the density of the paste is 1.87 ± 0.01 g/cm^3 and bead density is 2.46 g/cm^3

   b. The suggested method to mix the beads into the paste is to use a plunger mixer with a rotation speed of 31.4 rad/s (300 rpm). Add the calculated quantity of beads and mix for 5 minutes using the plunger mixer.

Note: Use a plunger mixer with a rotation speed of 31.4 rad/s (300 rpm) for 30 s to remix the prepared SRM before each use, especially if the mixture has rested for a few days.

How to use the SRM: The goal is to calibrate any rotational rheometer with a geometry selected by the user. The following steps need to be followed:

1) Prepare a paste or a mortar SRM, following the instructions above.
2) Place the SRM mixture in the rheometer to be calibrated and conduct a sweep-rotational speed-controlled test. Increase the speed from zero to any desired value (at least three decades of rotational speed, for instance, from 0.0104 rad/s to 10.4 rad/s (0.1 rpm to 100 rpm)) and then decrease it while recording the torque (N·m). Repeat at least three tests with a geometry of choice on a sample of SRM 2493, and find the average values from the produced torque and respective rotational speed.
3) Since the raw data ideally corresponds to the certified values, the torque and rotational speed can be scaled to match the known certified viscosity and shear rate. Comparison of the data obtained with either the paste, or the model data from this certificate, should be performed following either method A or B. A module is available on the NIST website to perform this calculation.

<u>Method A (based on Bingham parameters)</u>: It is assumed that the shear stress ($\boldsymbol{\tau}$), shear rate ($\dot{\boldsymbol{\gamma}}$), and apparent viscosity ($\boldsymbol{\mu}$) are fundamentally proportional to the torque ($\boldsymbol{\Gamma}$), rotational speed ($\mathbf{N}$), and angular momentum ($\boldsymbol{\Gamma/N}$), respectively. In other words, the *(Γ vs. N)* results from the new geometry are scaled to match the *(τ vs. $\dot{\gamma}$)* certified SRM 2493 values by calculating scaling factors $\mathbf{K_\tau}$ and $\mathbf{K_\mu}$. The scaling factors convert the three raw variables into fundamental rheology units by using the proportionality relationships. Also, if preferable, the two scaling factors listed are able to produce a direct shear rate scaling factor, $\mathbf{K_\gamma}$, by means of ***equation (4)*** which is derived from the known relationship for Bingham materials shown in ***equation (5)***. Figure 2 provides a schematic representation of the process.

$$\mu = \tau / \gamma \quad [\text{Pa·s}] \qquad (Eq.\ 4)$$

Thus, the shear rate scaling factor would be:

$$K_\gamma = K_\tau / K_\mu \qquad (Eq.\ 5)$$

Obtain the average of the raw data at any day between 1 d and 7 d. (Torque, **Γ** [μN·m] and rotational speed, **N** [rpm]) for at least 3 runs using an SRM 2493 mixture (0 %, 20 %, or 40 %). *Convert* **N** *units to [rad/s] and* **Γ** *to [N·m].*

↓

Use the average data to find the slope (**S**) and y-intercept (**I**) of the torque vs. rotational speed relationship. *Note: use only the linear part of the curve, with at least 10 data points.*

↓

Obtain known SRM 2493 certified values related to the mixture used from certificate. *For ex.:*

(Plastic viscosity) Slope = $\mu_{SRM2493}$

(Yield stress) Y-int. = $\tau_{0SRM2493}$

↓

Find calibration factors using these equations:

(Eq. 6)

$$K_\tau = \frac{\tau_{0,\ SRM2493}}{I} \quad [\text{Pa/N·m}]$$

(Eq. 7)

$$K_\mu = \frac{\mu_{,\ SRM2493}}{S} \quad [\text{Pa·s/N·m·s}]$$

↓

Calibrate raw data into shear stress (τ), shear rate (γ) and apparent viscosity (μ) using calibration factors:

$$\mu = K_\mu \frac{\Gamma}{N} \quad [\text{Pa.s}] \qquad (Eq.\ 8)$$

$$\gamma = K_\gamma N = \frac{K_\tau}{K_\mu} N \quad [\text{s}^{-1}] \qquad (Eq.\ 9)$$

$$\tau = K_\tau \Gamma \quad [\text{Pa}] \qquad (Eq.\ 10)$$

Figure 2: Schematic for the calibration of rheometer data from raw torque and rotational speed to fundamental rheological variables, viscosity and shear rate. A spreadsheet is available via NIST to execute this calibration process.

Note: This process is applied for calibration of any geometry used in a coaxial rheometer. The conversion from rpm to rad/s requires multiplication by 2π/60

Method B (based on the viscosity vs. shear rate curve): The viscosity vs. shear rate curve is extracted from this certificate and compared with the experimental data measured using the SRM 2493 paste. Then, a least square fit of the experimental data is calculated to determine the scaling factors, $\mathbf{L_\gamma}$, $\mathbf{L_\tau}$, and $\mathbf{L_\mu}$ (See figure 3 for the scheme).

Obtain the average of the raw data (Torque, **Γ** [μN·m] and rotational speed, **N** [rpm]) for at least three runs using an SRM 2493 mixture
Convert **N** *units to [rad/s] and **Γ** to [N·m].*

↓

Use the average data to calculate the ratio (**Γ** / **N** [N·m/(rad/s)]) for each **N** [rad/s].

↓

Fit the experimental data to model curve equation (3), and obtain two scaling factors $\mathbf{L_\gamma}$, and $\mathbf{L_\mu}$. The computer code in [5] can be used for this purpose.

↓

Calibrate raw data into shear stress (τ), shear rate ($\dot{\gamma}$) and apparent viscosity (μ) using the scaling factors:

$\boldsymbol{\mu} = \boldsymbol{L_\mu}\frac{\boldsymbol{\Gamma}}{\boldsymbol{N}}$	[Pa·s]	*(Eq. 11)*
$\dot{\boldsymbol{\gamma}} = \boldsymbol{L_\gamma}\,\boldsymbol{N}$	[s^{-1}]	*(Eq. 12)*
$\boldsymbol{\tau} = \boldsymbol{L_\mu}\,\boldsymbol{L_\gamma}\,\boldsymbol{\Gamma}$	[Pa]	*(Eq. 13)*

Figure 3: Schematic for the calibration of rheometer data from raw torque and rotational speed to fundamental rheological variables, viscosity and shear rate [5].
Note: This process is applied for calibration of any geometry used in a coaxial rheometer. The conversion from rpm to rad/s requires multiplication by 2π/60

Material Selection and Packaging: The limestone was purchased in bulk and the corn syrup was purchased in 1 gallon bottles. The packaging contains enough material to prepare two batches of material for testing. There is enough limestone in each jar for one batch and the glass bottle contains enough corn syrup for two batches. There are more than enough glass beads for both a 20 % and a 40 % by volume mortar preparation.

Homogeneity Assessment and Certification Analyses: Certification analyses for Bingham parameters were performed at NIST on 10 randomly selected units of the SRM. The uncertainty reported for the certified values includes allowances for random measurement variability, day-to-day variability, and material heterogeneity between units.

REFERENCES

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Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov*; or via the Internet at http://www.nist.gov/srm.*