Viscosity Measurements of NIST SRM 1617b

A Research Report

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Measurements

The measurements reported here serve a synergistic purpose. One is to include NIST Standard Reference Material® (SRM) 1617b *Sulfur in Kerosene (High Level)* in the large-scale research effort toward characterizing the thermophysical properties of kerosene-based fuels (for rocket and aircraft applications) in progress at the National Institute of Standards and Technology (NIST) and other facilities [1]. Conversely, adding viscosity, density, and speed of sound data to the certificate, enhances the usefulness of the SRM by broadening its potential applications. In a first step, the kinematic viscosity of NIST SRM 1617b was measured with an open gravitational capillary viscometer (miniAV from Cannon Instrument Comp., State College, PA*). The temperature range was from 20 °C to 100 °C in increments of 5 °C. The pressure was ambient, i. e. on average 0.083 MPa at Boulder, Colorado. The instrument had been calibrated and adjusted as described in a previous publication [2]. The sample liquid had been provided by the NIST Analytical Chemistry Division. An aliquot was poured into a clean new glass vial which was then mounted on the viscometer. The measurement criterion for the viscometer was to perform at least three consecutive effluxes so that the measured efflux time intervals varied by less than 0.25 %. The criterion was met within the first three repetitions at each temperature. The highest standard deviation of the measured efflux times was 0.06 %.

Uncertainty Calculations - General

The uncertainty intervals outlined in this document require the assumption that the material is homogeneous. If this assumption is not correct, alternative uncertainty intervals must be used.

There are several equations that are used repeatedly when computing uncertainty. We provide here general forms of these equations and refer back to them below.

The sample standard deviation of n observations is given by

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}, \tag{1}$$

where $\bar{x}$ is the sample mean,

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* In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' names or labels. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \; . \tag{2}$$

If the combined standard uncertainty of a measurement result having N influence quantities is

$$u_c(y) = \sqrt{\sum_{i=1}^{N}(a_i^2 \cdot u(x_i)^2)} \; , \tag{3}$$

where

$$a_i = \frac{\partial y}{\partial x_i} \; , \tag{4}$$

and the influence quantities are independent of each other, then the effective degrees of freedom associated with the combined standard uncertainty can be computed using the Welch-Satterthwaite approximation [3,4],

$$df = \frac{u_c^4}{\sum_{i=1}^{N} \dfrac{a_i^4 \cdot u(x_i)^4}{df_i}} \; , \tag{5}$$

where df_i represents the degrees of freedom for the ith uncertainty component.

The effective degrees of freedom are used to determine the value from the Student's t table needed to compute the expanded uncertainty. In general, the equation for expanded uncertainty is

$$U = t_{1-\alpha/2 \, ; \, df} \cdot u(y) \; , \tag{6}$$

corresponding to a $100(1-\alpha)$ % uncertainty interval. Typically, $\alpha = 0.05$.

Uncertainty Calculation for the Viscosity Measurements with the Open Gravitational Capillary Viscometer

The calibration and adjustment of the capillary viscometer involves fitting known kinematic viscosities v of certified viscosity standards versus measured efflux time intervals τ as described in a previous publication [2]. We fit efflux time intervals in the range $40 \text{ s} \le \tau \le 110 \text{ s}$. The working equation of the capillary viscometer is

$$v = \hat{c}\,\tau - (\hat{\varepsilon} / \tau^2). \tag{7}$$

The estimates for the capillary constants $\hat{c}$ and $\hat{\varepsilon}$ and their associated uncertainties are listed for each bulb in Table 1. The notation with accent circumflex is used to indicate estimates of model parameters, in this case the viscometer constants c and ε. This convention is used in the remainder of this report.

Table 1: Estimated capillary constants and associated uncertainties to obtain in eq. (7) kinematic viscosities in units of $mm^2 \cdot s^{-1}$ from measured efflux time intervals τ in seconds.

Parameter	Units	Bulb 1	Bulb 2
$\hat{c}$	$mm^2 \cdot s^{-2}$	0.086076	0.01052
$u(\hat{c})$	$mm^2 \cdot s^{-2}$	$43.0 \cdot 10^{-6}$	$2.686 \cdot 10^{-6}$
$\hat{\varepsilon}$	$mm^2 \cdot s$	27.0675	61.1251
$u(\hat{\varepsilon})$	$mm^2 \cdot s$	9.2136	6.8303
$u(\hat{c}, \hat{\varepsilon})$		$2.854 \cdot 10^{-4}$	$4.4 \cdot 10^{-6}$

The covariance $u(\hat{c}, \hat{\varepsilon})$ listed in Table 1 is used to account for the relationship between the two parameters. Information regarding the estimation of the covariance matrix for least-squares parameter estimates is provided in references [5] and [6]. All measurements discussed in this document were taken using Bulb 2.

In our adjustment of the capillary constants $\hat{c}$ and $\hat{\varepsilon}$, the known kinematic viscosity of a certified standard is the dependent variable, and the measured efflux time interval is the independent variable. In least-squares regression, the independent variable is usually "known", and the dependent variable is usually measured. A least-squares regression with errors in the independent variable may have considerable bias in the estimated parameters if the errors are very large. We performed both orthogonal distance regression [7, 8] and least-squares regression of the calibration data. We determined that the errors in efflux time were negligible, because the parameter estimates and their uncertainties were very close for both methods. Thus, we use the ordinary least-squares model parameters.

For the measurement of unknown liquids, the appropriate calibration parameters $(\hat{c}, \hat{\varepsilon})$ are used to obtain the viscosity of the sample. From the working equation (7), the combined standard uncertainty is

$$u(v) = \sqrt{ \left(\frac{\partial v}{\partial \hat{c}} \right)^2 u^2(\hat{c}) + \left(\frac{\partial v}{\partial \hat{\varepsilon}} \right)^2 u^2(\hat{\varepsilon}) + 2 \left(\frac{\partial v}{\partial \hat{c}} \right) \left(\frac{\partial v}{\partial \hat{\varepsilon}} \right) u(\hat{c}, \hat{\varepsilon}) + \left(\frac{\partial v}{\partial \tau} \right)^2 u^2(\tau) } \ . \qquad (8)$$

The uncertainties $u(\hat{c})$, $u(\hat{\varepsilon})$, and $u(\hat{c}, \hat{\varepsilon})$ are determined from the least-squares fit of the calibration data. The partial derivatives of the kinematic viscosity v with respect to the calibration constants and the efflux time interval in the working equation (7) are

$$\left(\frac{\partial v}{\partial \hat{c}} \right) = \tau \ , \qquad (9)$$

$$\left(\frac{\partial v}{\partial \hat{\varepsilon}} \right) = -\tau^{-2} \ , \qquad (10)$$

$$\left(\frac{\partial v}{\partial \tau} \right) = \hat{c} + 2 \hat{\varepsilon} \tau^{-3} \ . \qquad (11)$$

We typically use the Welch-Satterthwaite approximation to compute the effective degrees of freedom for $u(v)$; however, the approximation is valid only if the terms in the uncertainty are uncorrelated. To obtain independent terms in $u(v)$, we must separate our uncertainty into two parts: the three terms associated with the adjustment of the working equation

$$u^2(v_{adj}) = \left(\frac{\partial v}{\partial \hat{c}} \right)^2 u^2(\hat{c}) + \left(\frac{\partial v}{\partial \hat{\varepsilon}} \right)^2 u^2(\hat{\varepsilon}) + 2 \left(\frac{\partial v}{\partial \hat{c}} \right) \left(\frac{\partial v}{\partial \hat{\varepsilon}} \right) u(\hat{c}, \hat{\varepsilon}) \ , \qquad (12)$$

 and the term associated with efflux time interval

$$u^2(v_\tau) = \left(\frac{\partial v}{\partial \tau} \right)^2 u^2(\tau) \ . \qquad (13)$$

Thus, the combined standard uncertainty is obtained from

$$u^2(v) = u^2(v_{adj}) + u^2(v_\tau) \ . \qquad (14)$$

We can now apply the Welch-Satterthwaite approximation, eq. (5), to compute the effective degrees of freedom,

$$df_v = \frac{u^4(v)}{\dfrac{u^4(v_{\mathrm{adj}})}{df_{v\,\mathrm{adj}}} + \dfrac{u^4(v_\tau)}{df_\tau}} \,, \tag{15}$$

where $df_{v\,\mathrm{adj}}$ is the number of observations in the regression fit minus the number of parameters in the model. The expanded uncertainty of $u(v)$ is computed according to eq. (6).

The calculation of $u(\tau)$ and df_τ will be discussed next. The efflux time measurement equation is

$$\tau = \delta(T) + \theta + \omega \,, \tag{16}$$

where $\delta(T)$ is the correlated efflux time interval for a given bath temperature, θ is the repeatability error, and ω represents the manufacturer's specified error in the timing measurement system. The combined standard uncertainty is

$$u(\tau) = \sqrt{u^2(\delta(T)) + \tfrac{1}{n_\tau} s_\tau^2 + u^2(\omega)} \,, \tag{17}$$

where s_τ is the sample standard deviation of n_τ efflux measurements, $u(\delta(T))$ is the uncertainty in the correlated efflux for a given bath temperature, and $u(\omega)$ is the uncertainty associated with the timing measurement system. The term s_τ^2/n_τ represents the uncertainty due to repeatability error θ.

The value of $u(\omega)$ is given by the instrument manufacturer as 0.02 s, and we will assume $df_\omega = 30$. The degrees of freedom, df_τ, associated with $u(\tau)$ are computed using the Welch-Satterthwaite approximation, eq. (5).

We use an empirical model to quantify the relationship between $\delta(T)$ and the bath temperature, T. The model can be used to predict $\delta(T)$ and its associated uncertainty $u(\delta(T))$, for any value of T. The empirical model was selected using commercially available, automated curve fitting and equation discovery software. We selected the simplest possible, three-parameter model that provided the best overall fit to the data based on the residual standard deviation. Adding a fourth parameter did not substantially improve the model fit. The empirical model for the efflux time interval data set of SRM 1617b is

$$\delta(T) \;=\; \left[\beta_0 + \beta_1/\ln(T/T_0) + \beta_2/T^{1.5} \right]^{-1}, \tag{18}$$

with $T_0 = 1$ K to non-dimensionalize the argument of the logarithm. The estimated model parameters and their associated uncertainties are listed in Table 2.

Table 2:   Estimated parameter values β_i and their associated uncertainties in parentheses for the relationship between efflux time interval and bath temperature for SRM 1617b. Units are seconds for $\delta(T)$ and kelvins for temperature T.

$\hat{\beta}_0 \left(u(\hat{\beta}_0)\right)$	Units	$\hat{\beta}_1 \left(u(\hat{\beta}_1)\right)$	Units	$\hat{\beta}_2 \left(u(\hat{\beta}_2)\right)$	Units
0.57354 (0.00127)	s^{-1}	-3.53626 (0.00835)	s^{-1}	272.72681 (0.99141)	$K^{1.5}s^{-1}$

We use propagation of errors to determine the value of $u(\delta(T))$. For the three-parameter model, the squared, standard uncertainty is

$$u^2(\delta(T)) = \left(\frac{\partial \delta(T)}{\partial \hat{\beta}_0}\right)^2 u^2(\hat{\beta}_0) + \left(\frac{\partial \delta(T)}{\partial \hat{\beta}_1}\right)^2 u^2(\hat{\beta}_1) + \left(\frac{\partial \delta(T)}{\partial \hat{\beta}_2}\right)^2 u^2(\hat{\beta}_2)$$

$$+ 2\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_0}\right)\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_1}\right)u(\hat{\beta}_0,\hat{\beta}_1) + 2\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_0}\right)\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_2}\right)u(\hat{\beta}_0,\hat{\beta}_2)$$

$$+ 2\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_1}\right)\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_2}\right)u(\hat{\beta}_1,\hat{\beta}_2) + \left(\frac{\partial \delta(T)}{\partial T}\right)^2 u^2(T) \qquad . \qquad (19)$$

To compute the degrees of freedom associated with $u(\delta(T))$, we need to divide $u^2(\delta(T))$ into two parts,

$$u^2(\delta(T)_{\text{model}}) = \left(\frac{\partial \delta(T)}{\partial \hat{\beta}_0}\right)^2 u^2(\hat{\beta}_0) + \left(\frac{\partial \delta(T)}{\partial \hat{\beta}_1}\right)^2 u^2(\hat{\beta}_1) + \left(\frac{\partial \delta(T)}{\partial \hat{\beta}_2}\right)^2 u^2(\hat{\beta}_2)$$

$$+ 2\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_0}\right)\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_1}\right)u(\hat{\beta}_0,\hat{\beta}_1) + 2\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_0}\right)\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_2}\right)u(\hat{\beta}_0,\hat{\beta}_2)$$

$$+ 2\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_1}\right)\left(\frac{\partial \delta(T)}{\partial \hat{\beta}_2}\right)u(\hat{\beta}_1,\hat{\beta}_2) \qquad , \qquad (20)$$

and

$$u^2(\delta(T)_{\text{temp}}) = \left(\frac{\partial \delta(T)}{\partial T}\right)^2 u^2(T), \tag{21}$$

so that

$$u^2(\delta(T)) = u^2(\delta(T)_{\text{model}}) + u^2(\delta(T)_{\text{temp}}). \tag{22}$$

The degrees of freedom associated with $u(\delta(T))$ are

$$df_{\delta(T)} = \frac{u^4(\delta(T))}{\dfrac{u^4(\delta(T)_{\text{model}})}{df_{\delta(T)\text{model}}} + \dfrac{u^4(\delta(T)_{\text{temp}})}{df_{\delta(T)\text{temp}}}}. \tag{23}$$

Eqs. (22) and (23) are analogous to eqs. (14) and (15). The uncertainties in the estimated model parameters are easily obtained from the regression fit, and $df_{\delta(T)\text{model}}$ is the number of observations used in the regression fit minus the number of parameters in the model.

The uncertainty in the temperature measurement, $u(T)$ is a type B uncertainty [3, 4], defined as the combination of manufacturer's specified error, long-term fluctuations in the bath temperature, and uncertainty due to the distance from the thermometer to the bulb. The uncertainty due to manufacturer's specified error and the uncertainty due to the bath temperature are both 0.01 K. Based on heat transfer considerations, the uncertainty due to the distance from the thermometer to the capillary is assumend to increase linearly from 0.02 K at 20 °C to 0.1 K at 100 °C, so that the uncertainty is $0.001\ \text{K} \cdot (°\text{C})^{-1} \cdot t$, where t is the temperature in °C. We estimate the temperature uncertainty to be

$$u(T) = \sqrt{(0.01)^2 + (0.01)^2 + (0.001 \cdot t)^2}, \tag{24}$$

We will assume that we have a fairly high degree of confidence in our estimate of $u(T)$, so that $df_{\delta(T)\text{temp}} = 30$. The value of $df_{\delta(T)}$ from eq. (23) is used to obtain the expanded uncertainty $u(v)$ for measurements with the capillary viscometer, according to eq. (6).

Results

Measured average efflux time intervals and the resulting kinematic viscosities of NIST SRM 1617b are listed in Table 3 for temperatures ranging from 20 °C to 100 °C. The table also includes details of the uncertainty analysis such as combined standard uncertainties, effective

degrees of freedom, coverage factors at 95 % confidence level, and expanded uncertainties, both absolute and relative. The viscosity-temperature dependence is illustrated in Figure 1.

References

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Table 3: Kinematic viscosities of NIST SRM 1617b and their uncertainties as measured with the open gravitational capillary viscometer at ambient atmospheric pressure (0.083 MPa).

NIST SRM 1617b Sulfur in Kerosene (High Level)

| Temperature t	Average[*] Efflux Time $\bar{\tau}$	Adjusted Kinematic Viscosity $\bar{v}$	Combined Standard Uncertainty $u(\bar{v})$	Effective Degrees of Freedom df	Coverage Factor k at 95 % uncertainty	Expanded Uncertainty $U(\bar{v})$	Relative Expanded Uncertainty $U(\bar{v})/\bar{v}$
°C	s	mm²·s⁻¹	mm²·s⁻¹	—	—	mm²·s⁻¹	%
20	186.28	1.958	0.0007	6	2.4469	0.0018	0.091
25	170.76	1.794	0.0005	24	2.0639	0.0011	0.060
30	157.37	1.653	0.0007	4	2.7765	0.0021	0.13
35	145.56	1.528	0.0005	23	2.0687	0.0011	0.07
40	135.28	1.420	0.0005	24	2.0639	0.0011	0.07
45	126.21	1.323	0.0007	10	2.2281	0.0015	0.11
50	118.05	1.237	0.0006	23	2.0687	0.0012	0.10
55	110.74	1.160	0.0006	22	2.0739	0.0013	0.11
60	104.36	1.091	0.0008	15	2.1315	0.0016	0.15
65	98.47	1.029	0.0008	19	2.0930	0.0016	0.16
70	93.28	0.9737	0.0009	18	2.1009	0.0018	0.19
75	88.47	0.9228	0.0009	18	2.1009	0.0019	0.20
80	84.13	0.8762	0.0010	18	2.1009	0.0021	0.23
85	80.25	0.8341	0.0011	19	2.0930	0.0023	0.28
90	76.59	0.7955	0.0012	17	2.1098	0.0024	0.31
95	73.31	0.7598	0.0013	17	2.1098	0.0027	0.35
100	70.32	0.7270	0.0014	17	2.1098	0.0029	0.40

[*] Average of repetitive measurements of one sample.
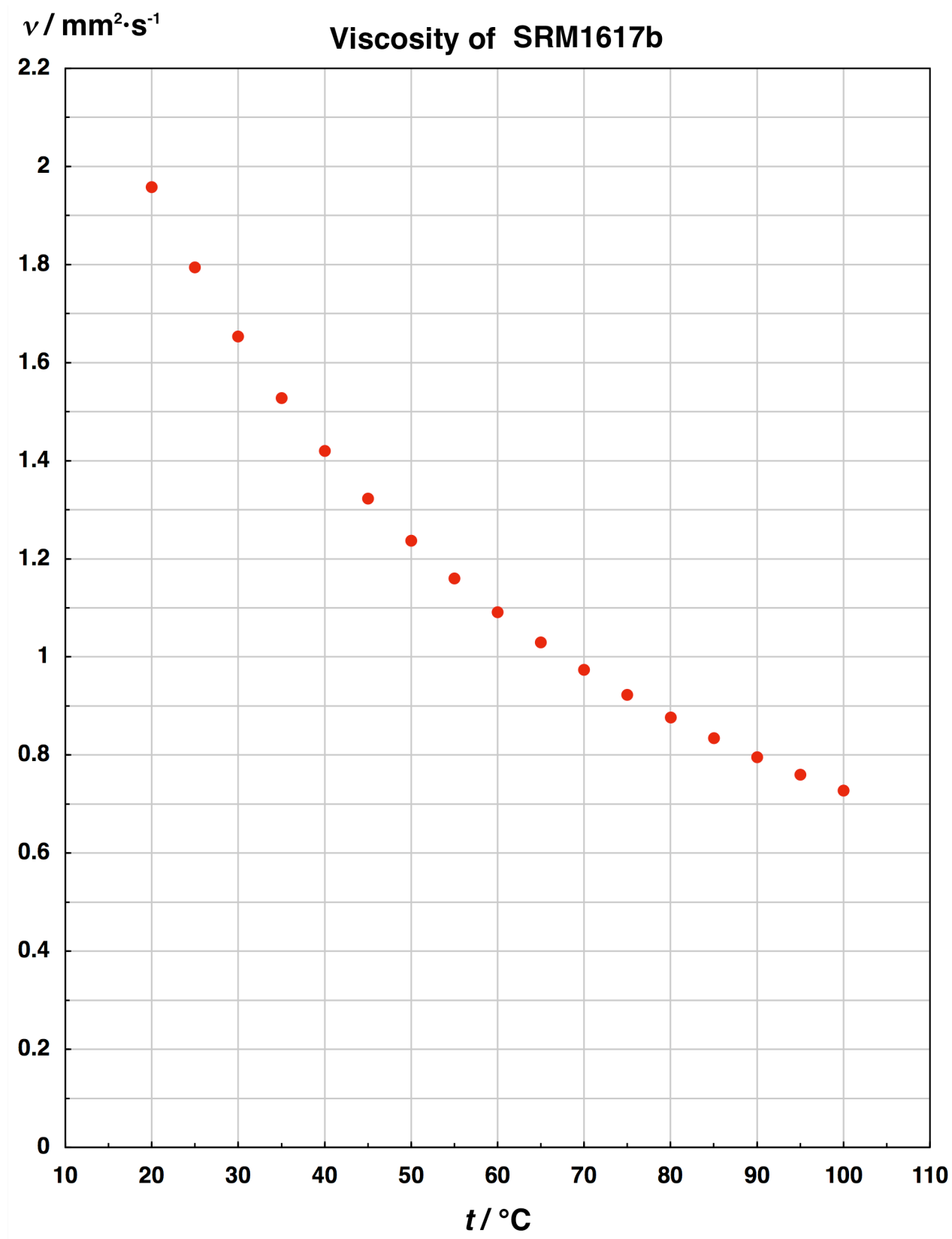
Figure 1: Measured kinematic viscosities of NIST SRM 1617b as a function of temperature at ambient atmospheric pressure (0.083 MPa). The uncertainties of the data are smaller than the symbol size.