



# National Institute of Standards & Technology

## Certificate

### Standard Reference Material® 1921b

#### Infrared Transmission Wavelength/Wavenumber Standard

This Standard Reference Material (SRM) is intended primarily for use in calibrating the wavelength/wavenumber scale of spectrophotometers in the infrared (IR) spectral region from 3.2  $\mu\text{m}$  to 18.5  $\mu\text{m}$  (540  $\text{cm}^{-1}$  to 3125  $\text{cm}^{-1}$ ). A unit of SRM 1921b consists of a matte finish polystyrene film approximately 38  $\mu\text{m}$  thick with a 25 mm diameter exposed area, centered 38 mm from the bottom of a cardboard holder, which is 5 cm  $\times$  11 cm  $\times$  0.2 cm in size.

**Certified Wavelength/Wavenumber Values:** The spectral transmittance of a statistically representative group of the polystyrene film SRM specimens was measured under both vacuum and purge conditions. The positions of absorption bands in the range of 3.2  $\mu\text{m}$  to 18.5  $\mu\text{m}$  were obtained using both a centroid method as well as a band minimum determination method. Thirteen of the band locations were selected for certification based on experimental and statistical analysis results. The certified wavelength values and associated uncertainties of these bands are shown in Tables 1 and 3 for the centroid and band minimum methods, respectively. The corresponding wavenumber values and associated uncertainties of the bands are shown in Tables 2 and 4, respectively. (See section entitled “Band Wavenumber and Wavelength Determination” for details). To aid the user in distinguishing among the bands during measurement, a spectrum is shown in Figure 1, with arrows identifying the certified bands. For band wavelength and wavenumber values measured in air or under purge conditions, see section entitled “Correction for Air/Nitrogen Purge”.

The expanded uncertainty,  $U$ , is provided for each certified band wavelength and wavenumber. It is the product of the coverage factor,  $k = 4$ , and the combined standard uncertainty. The combined standard uncertainty is the root sum of squares of all the uncertainty components [1,2].

**Expiration of Certification:** The certification of **SRM 1921b** is valid, within the measurement uncertainty specified, until **31 December 2021**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see “Instructions for Storage, Handling, and Use”). The certification is nullified if the SRM is damaged, contaminated, otherwise modified.

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

Overall direction and coordination of the technical measurements leading to certification were performed under the supervision of R.V. Datla and L.M. Hanssen of the NIST Sensor Science Division.

Technical measurements leading to certification were performed by R. Saunders and L.M. Hanssen of NIST.

Statistical consultation was provided by B. 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.

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*Certificate Revision History on Last Page*

Steven J. Choquette, Acting Director  
Office of Reference Materials

## INSTRUCTIONS FOR STORAGE, HANDLING, AND USE

**Storage and Handling:** When not in use, SRM 1921b should be kept in its accompanying protective cover. For storage, it is advisable to keep the SRM in a desiccator cabinet. The SRM should always be handled with care; the exposed film surface should never be touched by fingers or any other objects. Dust may be removed by blowing with clean, dry air.

**Measurement Conditions:**<sup>(1)</sup> The calibration measurements were made using a Bomem DA-3.02 Fourier transform spectrophotometer. The instrument room temperature was maintained at  $23\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  and the humidity ranged from 30 % to 50 % during the measurements. Calibration measurements were made under a purge gas of clean air (with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  removed) at atmospheric pressure. Details of the measurement methodology can be found in reference 2.

**Source of Material:** The polystyrene film used for SRM 1921b was taken from a single roll. It was manufactured by the Dow Chemical Company and donated by the Coblenz Society.

**Calibration Measurements:** Prior to calibration with SRM 1921b, the spectrophotometer should be set up under the following conditions:

- Step 1. Set the instrumental resolution to any value up to a maximum of  $4\text{ cm}^{-1}$ . For a resolution of  $4\text{ cm}^{-1}$  used with a Fourier transform spectrophotometer no (equivalent to Boxcar) apodization should be used in the Fourier transform processing [3,4]. For  $2\text{ cm}^{-1}$  or less resolution, other apodizations can be used. Within these constraints, the most appropriate resolution for calibration is the one that is used for typical sample measurements.
- Step 2. Set the source aperture to provide sufficient signal for measurement, yet not greater than that required to maintain measurement resolution. The setting should not be so large that the wavenumber shift error becomes significant [5] or the detector becomes significantly non-linear [6,7].
- Step 3. Close and purge or evacuate the sample chamber for a time suitable for the instrument to reach pressure and temperature equilibrium.
- Step 4. Obtain at least six transmittance spectra of SRM 1921b for statistical evaluation.
- Step 5. Analyze the resulting spectra for band locations as described in the next section.
- Step 6. When appropriate, apply the results to correct the spectrometer's wavelength/wavenumber scale as described in the last section.

The purpose of analysis in step 5 is to obtain band locations as discussed below.

**Band Wavenumber and Wavelength Determination:** Two methods have been used to obtain calibrated band locations: a centroid method with band fraction of 0.5 and a band minimum determination method. Both methods have been applied to spectra in wavenumbers. Wavelength values can be obtained from the wavenumber values through the relationship  $\lambda\nu = 1$ , where  $\lambda$  is the wavelength in cm (see also the description below on potential atmospheric corrections). The user can select either Tables 1 and 2 if they apply the centroid (with band fraction of 0.5) method, or Tables 3 and 4 if they apply any method designed to obtain the band minimum. Note that calibration values are now provided for the  $1943\text{ cm}^{-1}$  absorption band (#9), but only for use with a band minimum location method; this is new for SRM 1921b. (For band #9 use of the centroid method is associated with significantly greater uncertainties and is not recommended.)

### Centroid Method

The first method used to determine the band wavenumber ( $\nu$ ) and wavelength ( $\lambda$ ) values of SRM 1921b is the centroid (also known as the center of gravity) method [8,9]. This procedure is performed on the transmittance spectra using wavenumber values only. The wavenumber value is defined as the number of waves per unit length (cm). Refer to Figure 2 for the following band determination procedure description. The process is applied for each calibration band.

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<sup>(1)</sup> Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

First, the bounds of an initial wavenumber range ( $\nu_{\min}$  to  $\nu_{\max}$ ) enclosing the band are determined; they are the wavenumber values at which transmittance relative maxima occur on either side of the band. Next, the differences between the transmittance values at each bound and the transmittance at the band minimum,

$$\Delta T(\nu_{\max}) = [T(\nu_{\max}) - T(\nu_{\text{band min}})] \text{ and } \Delta T(\nu_{\min}) = [T(\nu_{\min}) - T(\nu_{\text{band min}})],$$

are determined. Then half the value of the smaller of  $\Delta T(\nu_{\max})$  and  $\Delta T(\nu_{\min})$ ,  $\Delta T_0/2$  is determined. The wavenumber range ( $\nu_1$  to  $\nu_2$ ) to be used in the centroid calculation is that between the wavenumber values where the transmittance values on either side of the band equal the minimum transmittance value plus  $\Delta T_0/2$ ,

$$\nu_{1,2} = \nu_{\text{band min}} \pm T_{1/2} \equiv T(\nu_{\text{band min}}) + \Delta T_0/2$$

The specific data end points of the spectrum,  $h = \nu_1$  and  $k = \nu_2$  are selected so that  $T_h \geq T_{1/2} > T_{h+1}$  and  $T_{k-1} < T_{1/2} < T_k$  for adjacent points. The centroid equation for finite sums (below) effectively averages data at the ends,  $\nu_1$  and  $\nu_2$ , to reduce the error due to the finite data spacing. The formula used is

$$\nu_{\text{Cen}} = \nu_k + \Delta \nu \left\{ \frac{\sum_{i=h-1}^k (i-k + \frac{1}{2}) \left[ \frac{(T_i + T_{i+1})}{2} - T_{1/2} \right]}{\sum_{i=h-1}^k \left[ \frac{(T_i + T_{i+1})}{2} - T_{1/2} \right]} \right\}$$

where  $\Delta \nu$  is the frequency spacing.

### Band Minimum Determination Method

A NIST-designed method is applied to determine accurately the band minimum (or maximum) value to obtain calibration values for SRM 1921b. This method is called the *extrapolated centroid method* [10,11]. It entails the calculation of centroid values for a set of fractions (approaching zero fraction) of the band and extrapolating a curve fit through the set of values to a value for zero fraction that corresponds to the band minimum (or maximum). Results of any method that is designed to find the band minimum should produce essentially the same result and hence be directly comparable [4,12].

**Correction for Air/Nitrogen Purge:** The NIST certification measurements were performed under clean air purge. However, it should be noted that the wavelength values reported in Table 1 are vacuum values where the index of refraction,  $n$ , equals 1. For instruments that operate under vacuum, calibration measurements of SRM 1921b can be directly compared to values in Table 1. Also, for instruments which give vacuum wavenumber and wavelength values (such as Fourier transform infrared (FTIR) spectrometers which use helium-neon lasers for determination of the wavenumber scale) even when operated under air or purge gas, as in our case, no corrections are necessary.

In all other cases when measurements of SRM 1921b are made under air, nitrogen, or other purge gas, the wavenumber and wavelength values need to be adjusted for the index of refraction of the gas ( $n = 1.00026$  for dry nitrogen gas at atmospheric pressure and  $T = 298$  K) [13,14]. Thus, for nitrogen purge, the user-measured wavenumber values should be divided by 1.00026, and the wavelength values should be multiplied by 1.00026 to compare to the certified values in Table 1.

**Corrections due to Sample Temperature:** The certified values in Tables 1 through 4 are for SRM 1921b at a nominal temperature of 23 °C (296 K). The expanded uncertainties include accommodation for a temperature range of  $\pm 5$  °C. For temperatures outside this range (18 °C to 28 °C), the user should correct the values using the temperature coefficients given in Table 5. The table only contains values for those bands where the temperature dependence is significant relative to the expanded uncertainties. Below 15 °C and above 35 °C, the appropriate corrections have not been determined and the user is advised not to exceed this range.

**Corrections to Instrument Wavenumber Scale:** The resulting  $N$  ( $N \geq 6$ ) values for each peak at wavenumber,  $\nu$ , should be averaged to obtain a single *band wavenumber value* (laboratory mean,  $\bar{y}_\nu$ ), and the standard deviation of the values,  $s_\nu$ , should be calculated. In order to determine whether or not the laboratory measurements are biased relative to SRM 1921a, calculate the difference,  $\delta_\nu$ , between the laboratory mean,  $\bar{y}_\nu$ , and the certified value,  $C_\nu$ , as follows:

$$\delta_\nu = \bar{y}_\nu - C_\nu$$

A practical limit for evaluating consistency with the certified value is:

$$\delta_c = 2\sqrt{\frac{s_\nu^2}{N} + \frac{U_{user}^2}{3} + \frac{U^2}{3}},$$

where  $U_{user}$  is the user's Type B evaluated expanded uncertainty [15] and  $U$  [1] is the uncertainty from Table 2. If  $|\delta_\nu| > \delta_c$ , then the difference is greater than can be explained by chance, and the wavenumber scale of the instrument should be corrected to the SRM. If this is the case, generally a linear least squares fit of  $\delta_\nu$  to  $\nu$  for the 13 peaks should provide a sufficient correction to the spectrophotometer scale. However, if  $|\delta_\nu| \leq \delta_c$ , the wavenumber scale of the spectrophotometer is considered to be accurate and correction is not advised.

Table 1. Certified Band Centroid Wavelength Values (in Vacuum)

Band Number	Band Wavelength ( $\mu\text{m}$ )	Expanded Uncertainty, $U$ ( $\mu\text{m}$ )
1	18.3512	$8.2 \times 10^{-2}$
2	11.8751	$1.8 \times 10^{-2}$
3	11.0276	$1.3 \times 10^{-3}$
4	9.7237	$2.5 \times 10^{-3}$
5	9.3522	$6.8 \times 10^{-3}$
6	8.6608	$7.0 \times 10^{-4}$
7	6.3169	$3.4 \times 10^{-4}$
8	6.2446	$4.1 \times 10^{-4}$
10	3.50853	$1.5 \times 10^{-4}$
11	3.33178	$1.0 \times 10^{-4}$
12	3.30421	$1.0 \times 10^{-4}$
13	3.26782	$9 \times 10^{-5}$
14	3.24442	$1.0 \times 10^{-4}$

Table 2. Certified Band Centroid Wavenumber Values (in Vacuum)

Band Number	Band Wavenumber ( $\text{cm}^{-1}$ )	Expanded Uncertainty, $U$ ( $\text{cm}^{-1}$ )
1	544.92	2.43
2	842.10	1.29
3	906.82	0.10
4	1028.42	0.27
5	1069.27	0.77
6	1154.62	0.09
7	1583.04	0.09
8	1601.38	0.11
10	2850.20	0.12
11	3001.40	0.09
12	3026.44	0.09
13	3060.14	0.09
14	3082.22	0.09

Table 3. Certified Band Minimum Wavelength Values (in Vacuum)

Band Number	Band Wavelength ( $\mu\text{m}$ )	Expanded Uncertainty, $U$ ( $\mu\text{m}$ )
1	18.5385	$9.0 \times 10^{-2}$
2	11.8793	$1.9 \times 10^{-2}$
3	11.0297	$4.3 \times 10^{-3}$
4	9.7250	$3.1 \times 10^{-3}$
5	9.3525	$8.7 \times 10^{-3}$
6	8.6617	$1.5 \times 10^{-3}$
7	6.3172	$3.7 \times 10^{-4}$
8	6.2448	$4.1 \times 10^{-4}$
9	5.1467	$1.7 \times 10^{-3}$
10	3.50938	$6.0 \times 10^{-4}$
11	3.33197	$2.0 \times 10^{-4}$
12	3.30467	$5.0 \times 10^{-4}$
13	3.26778	$2.6 \times 10^{-4}$
14	3.24435	$1.7 \times 10^{-4}$

Table 4. Certified Band Minimum Wavenumber Values (in Vacuum)

Band Number	Band Wavenumber ( $\text{cm}^{-1}$ )	Expanded Uncertainty, $U$ ( $\text{cm}^{-1}$ )
1	539.41	2.63
2	841.79	1.32
3	906.63	0.36
4	1028.27	0.33
5	1069.22	0.99
6	1154.50	0.20
7	1582.98	0.09
8	1601.29	0.10
9	1942.97	0.66
10	2849.48	0.49
11	3001.20	0.18
12	3025.99	0.46
13	3060.16	0.25
14	3082.26	0.16

Table 5. Temperature Coefficients for Band Locations

Band Number	Temperature Coefficient		Expanded Uncertainty	
	( $\text{cm}^{-1}/\text{K}$ )	( $\mu\text{m}/\text{K}$ )	( $\text{cm}^{-1}/\text{K}$ )	( $\mu\text{m}/\text{K}$ )
3	-0.008	$9.4 \times 10^{-5}$	0.003	$4.0 \times 10^{-5}$
7	-0.007	$2.8 \times 10^{-5}$	0.000	$1 \times 10^{-6}$
8	-0.010	$4.1 \times 10^{-5}$	0.000	$2 \times 10^{-6}$
11	-0.006	$7 \times 10^{-6}$	0.002	$2 \times 10^{-6}$
12	-0.009	$1.0 \times 10^{-5}$	0.002	$2 \times 10^{-6}$
14	-0.012	$1.2 \times 10^{-5}$	0.001	$1 \times 10^{-6}$

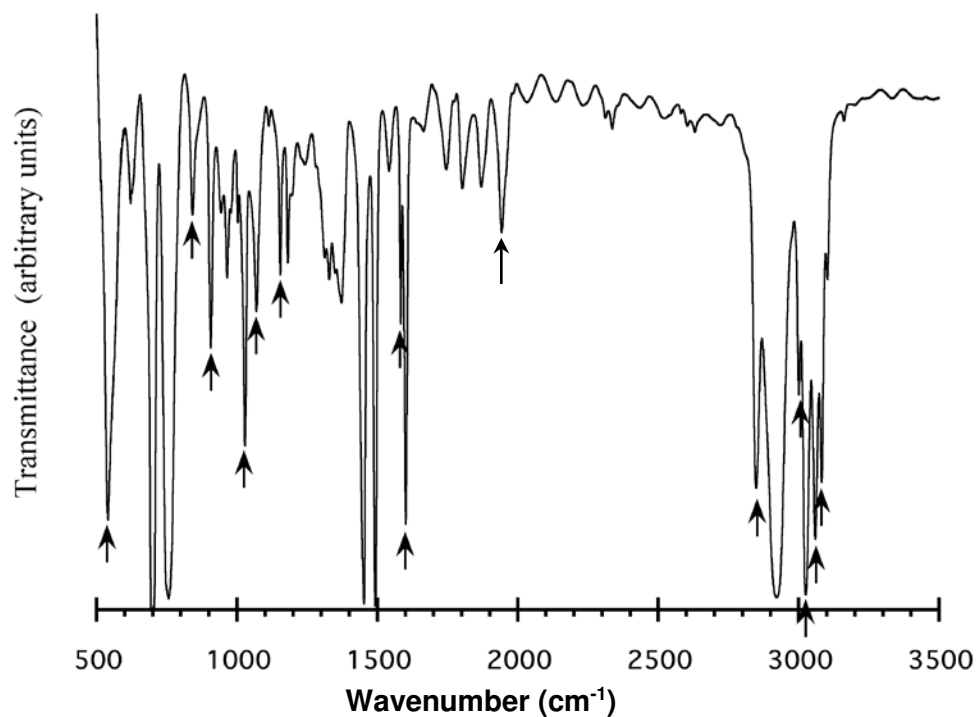


Figure 1. Spectrum of polystyrene film showing locations of certified absorption bands.

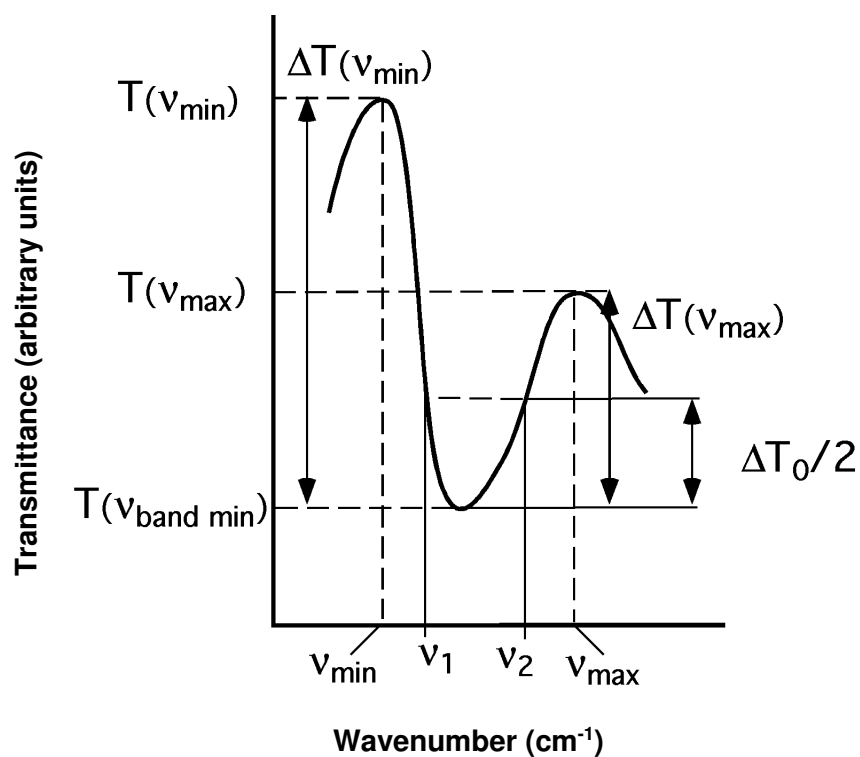


Figure 2. Diagram indicating parameters used in the band wavenumber determination method (see text for details).

## REFERENCES

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*Users of this SRM should ensure that the Certificate 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](mailto:srminfo@nist.gov); or via the Internet at <https://www.nist.gov/srm>.*