National Institute of Standards and Technology
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Standard Reference Material® 1921b
Infrared Transmission Wavelength/Wavenumber Standard
CERTIFICATE

Purpose: The certified values delivered by this Standard Reference Material (SRM) are intended for use in calibrating the wavelength/wavenumber scale of spectrophotometers in the infrared (IR) spectral region from 3.2 µm to 18.5 µm (540 cm^{-1} to 3125 cm^{-1}).

Description: A unit of SRM 1921b consists of a matte finish polystyrene film approximately 38 µm thick with a 25 mm diameter exposed area, centered 38 mm from the bottom of a cardboard holder, which is 5 cm × 11 cm × 0.2 cm in size.

Certified 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 µm to 18.5 µm 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. The certified values in Tables 1 through 4 are at a nominal temperature of 23 °C (296 K) and the expanded uncertainties include accommodation for a temperature range of ± 5 °C. Table 5 includes the temperature coefficients for the user to use to correct the values when temperatures are outside this range (18 °C to 28 °C). (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 certified values are metrologically traceable to the International System of Units (SI) [1].

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 [2,3].

Period of Validity: The certified values delivered by **SRM 1921b** are valid within the measurement uncertainty specified until **31 December 2025**. The certified values are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

Maintenance of Certified Values: NIST will monitor this SRM over the period of its validity. If substantive technical changes occur that affect the certification, NIST will issue an amended certificate through the NIST SRM website (https://www.nist.gov/srm) and notify registered users. SRM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the SRM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (https://www.nist.gov/srm).

Gerald T. Fraser, Chief	Steven J. Choquette, Director
Sensor Science Division	Office of Reference Materials

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

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

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

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

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

Band Number	Band Wavenumber (cm^{-1})	Expanded Uncertainty, *U* (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

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: The calibration measurements were made using a Bomem DA-3.02 Fourier transform spectrophotometer. The instrument room temperature was maintained at 23 °C ± 1 °C and the humidity ranged from 30 % to 50 % during the measurements. Calibration measurements were made under a purge gas of clean air (with CO_2 and H_2O removed) at atmospheric pressure. Details of the measurement methodology can be found in reference 3.

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 Coblentz 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 cm^{-1}. For a resolution of 4 cm^{-1} used with a Fourier transform spectrophotometer no (equivalent to Boxcar) apodization should be used in the Fourier transform processing [4,5]. For 2 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 [6] or the detector becomes significantly non-linear [7,8].
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 λ 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 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 (υ) and wavelength (λ) values of SRM 1921b is the centroid (also known as the center of gravity) method [9,10]. 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.

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 $\Delta T(\nu_{\min})$, $\Delta T_o/2$ is determined. The wavenumber range (ν_1 to ν_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 $\Delta T_o/2$,

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

The specific data end points of the spectrum, $h = \upsilon_1$ and $k = \upsilon_2$ 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, ν_1 and ν_2, to reduce the error due to the finite data spacing. The formula used is

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

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* [11,12]. 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 [5,13].

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 l. 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 = 1.000 26 for dry nitrogen gas at atmospheric pressure and T = 298 K) [14,15]. Thus, for nitrogen purge, the user-measured wavenumber values should be divided by 1.000 26, and the wavelength values should be multiplied by 1.000 26 to compare to the certified values in Table l.

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 ± 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.

Table 5. Temperature Coefficients for Band Locations

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

Corrections to Instrument Wavenumber Scale: The resulting N ($N \geq 6$) values for each peak at wavenumber, ν, should be averaged to obtain a single *band wavenumber value* (laboratory mean, $\bar{y}_\nu$), and the standard deviation of the values, s_ν, should be calculated. In order to determine whether or not the laboratory measurements are biased relative to SRM 1921a, calculate the difference, δ_ν, between the laboratory mean, $\bar{y}_\nu$, and the certified value, C_ν, 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 [16] and U [2] is the uncertainty from Table 2. If $\left|\delta_\nu\right| > \delta_c$, 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 δ_ν to ν 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.

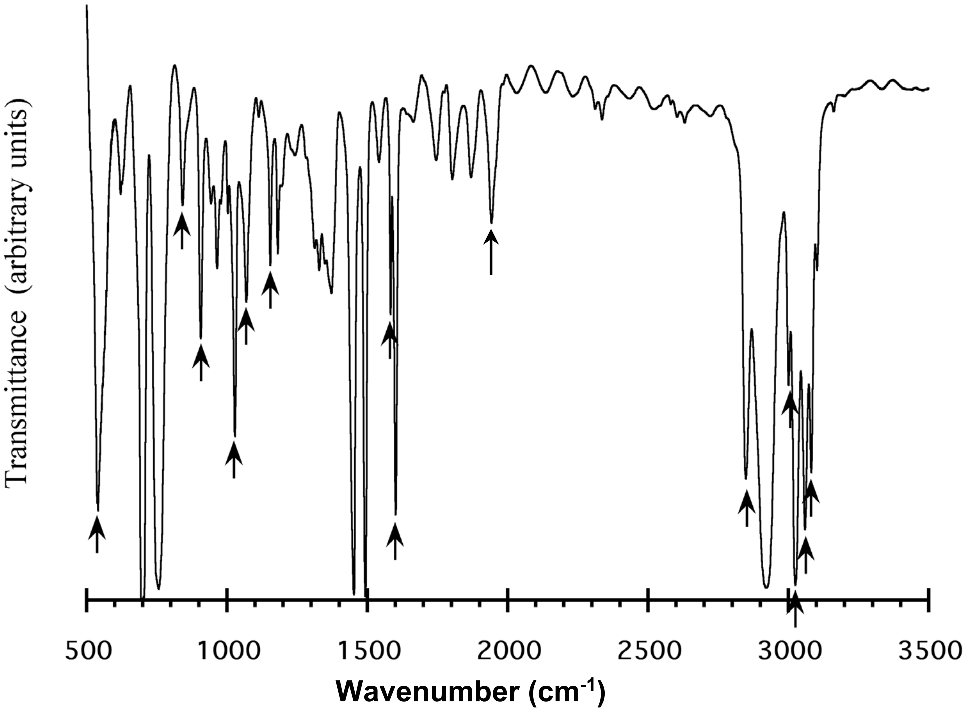

Figure 1. Spectrum of polystyrene film showing locations of certified absorption bands.

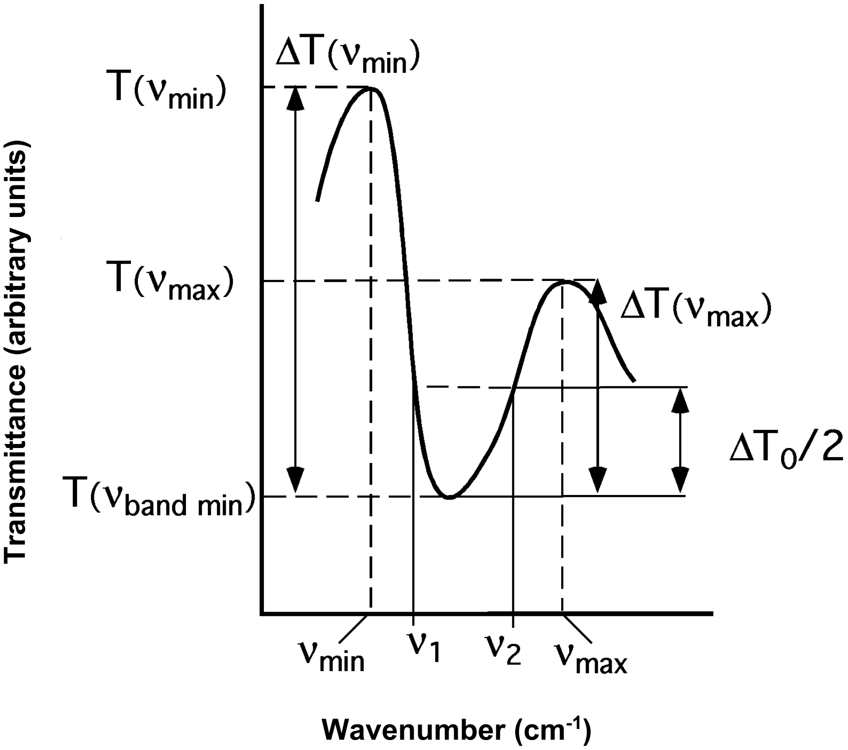

Figure 2. Diagram indicating parameters used in the band wavenumber determination method (see text for details).

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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 Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at https://www.nist.gov/srm.

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APPENDIX A

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

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