



National Institute of Standards & Technology

Certificate

Standard Reference Material® 1921

Infrared Transmission Wavelength Standard

This Standard Reference Material (SRM) is intended primarily for use in calibrating the wavelength scale of spectrophotometers in the infrared (IR) spectral region from 3.2 μm to 18 μm (555 cm^{-1} to 3125 cm^{-1}). SRM 1921 is 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 x 11 cm x 2 mm in size. A unit of SRM 1921 consists of three polystyrene cards.

Certified Wavelength Values: The spectral transmittance of a representative group of samples of polystyrene film was measured in vacuum. The positions of absorption peaks in the range of 3.2 μm to 18 μm were obtained using a center of gravity method. Thirteen of these peak positions were selected for certification based on statistical analysis of experimental results. The wavelength values and associated uncertainties of these peaks are certified and are shown in Table 1. The corresponding peak wavenumber values are listed in Table 2. See Peak Wavenumber and Wavelength Determination for details. To aid the user in distinguishing among the peaks during measurement, a spectrum is shown in Figure 1, with arrows identifying the certified peaks. For peak wavelength and wavenumber values measured in air or under purge conditions, see Correction for Air/Nitrogen Purge.

The expanded uncertainty, U is provided for each certified peak wavelength and wavenumber. It is the product of a coverage factor at the 95 % level of confidence, and the combined standard uncertainty. The combined standard uncertainty is the root sum of squares of components of uncertainty due to detector, sample, run, and measurement [1,2].

Expiration of Certification: The certification of this SRM is deemed to be valid until April 1, 2003, provided the SRM is stored and handled in accordance with the Storage and Handling and Instructions for Use sections of this certificate. However, certification will be nullified if the SRM is damaged, contaminated, or exposed to excess humidity. The polystyrene films are being monitored (over a period of approximately four years there has been no significant change in wavelength positions). In the event that the certification becomes invalid, users will be notified by NIST.

Storage and Handling: When not in use, SRM 1921 should always 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.

The technical measurements leading to certification were performed by D. Gupta, L.M. Hanssen, and L. Wang of the NIST Radiometric Physics Division. The overall direction and coordination of the technical measurements leading to certification were performed under the supervision of J.J. Hsia, R. Datla, and L.M. Hanssen of the NIST Radiometric Physics Division.

The technical and support aspects involved in the original preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J.C. Colbert. Revision of this certificate was coordinated through the Standard Reference Materials Program by R.J. Gettings.

Gaithersburg, MD 20899

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4/13/94 (original certificate date); 5/19/94 (editorial revision); 4/6/95 (peak values less sensitive to the peak determination method were indicated); 2/23/96 (change in unit size)

*Update stability

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Statistical consultation was provided by S.B. Schiller of the NIST Statistical Engineering Division.

Measurement Conditions: The calibration measurements were made using a Bomem DA-3.02¹ Fourier transform spectrophotometer. The instrument room temperature was maintained near 22 °C and the humidity ranged from 30 % to 50 % during the measurements. Calibration measurements were made under vacuum level pressures of 50 Pa (0.4 Torr). Details of the measurements and data analysis can be found in Reference [3].

Source of Material: The polystyrene film used in SRM 1921, manufactured by the Dow Chemical Company, was taken from a single roll. The polystyrene film was donated by the Coblenz Society.

INSTRUCTIONS FOR USE

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

1. Set the instrumental resolution at 0.5 cm⁻¹ (if this is not achievable, the resolution should be set at the highest, (i.e., smallest value in cm⁻¹) achievable by the instrument).
2. Set the spot size on the sample to the maximum possible, yet not greater than that required to maintain measurement resolution and not greater than that at which the wavenumber shift error becomes significant [4] and not greater than that at which the detector becomes significantly non-linear [5,6].
3. Close and purge or evacuate the sample chamber for a time suitable for the instrument to reach pressure and temperature equilibrium.
4. Begin the calibration procedure with a "reference" measurement with no sample in the sample chamber.
5. Place SRM 1921 in the standard sample position, and make a "sample" measurement. The ratio of "sample" to "reference" spectra is the transmittance. This process (steps 3 to 5) should be repeated in sequence at least six (6) times. The resulting transmittance spectra should be analyzed for peak position as described below.

Peak Wavenumber and Wavelength Determination: The method used to determine the peak wavenumber (ν) and wavelength (λ) values of SRM 1921 is the center of gravity technique [7]. 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 when using the following peak determination procedure. First, the bounds of an initial wavenumber range (ν_{\min} to ν_{\max}) enclosing the peak are determined; they are the wavenumber values at which transmittance relative maxima occur on either side of the peak. Next, the differences between the transmittance values at each bound and the transmittance at the absorption peak

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

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 final wavenumber range (ν_1 to ν_2) to be used in the center of gravity calculation is that between the wavenumber values where the transmittance values on either side of the peak equal the minimum transmittance value plus $\Delta T_o/2$.

$$\nu_{1,2}(T = T(\nu_{\text{peak}}) + \Delta T_o/2)$$

A center of gravity calculation [8] on this region should be performed to obtain the peak wavenumber values to compare to the certified values. If another peak wavenumber determination method is used, a comparison with the certified values may not be valid. Four peak wavenumber values, noted in Tables 1 and 2, were found to be less sensitive to the technique used to derive them [1]. Peak values determined by other techniques may become available in the future. Wavelength values can be obtained from the wavenumber values through the relationship $\lambda\nu = 1$, where λ is the wavelength in cm.

¹Certain commercial material and equipment are identified in order to adequately specify the experimental procedure. Such identification does not imply a recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for this purpose.

Correction for Air/Nitrogen Purge: The calibration measurements were performed in vacuum. Hence, the wavelength values in Table 1 are vacuum values (where $n=1$, the index of refraction). For measurements of SRM 1921 made under nitrogen gas or air purge, the wavenumber and wavelength values need to be adjusted due to the index of refraction of the air or purge gas ($n=1.00026$ for dry nitrogen gas at atmospheric pressure and $T=298$ K) [9,10]. **Note:** For instruments which give vacuum wavenumber and wavelength values, do not adjust for the index of refraction of air or purge gas. The measured wavenumber values should be divided by 1.00026 and the wavelength values should be multiplied by 1.00026 to compare to the standard values.

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 "peak wavenumber value" (laboratory mean, \bar{y}_ν), 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 1921, calculate the absolute difference, Δ_ν , between the laboratory mean, \bar{y}_ν and the certified value, C_ν , as follows:

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

The uncertainty associated with this difference is:

$$\Delta_c = (t_{N-1, 0.95}) s_\nu / \sqrt{N} + U$$

where $t_{N-1, 0.95}$ is the critical value from the student's distribution with $N-1$ degrees of freedom for a two-sided 95 % confidence interval [11] and U [1,2] is the uncertainty from Table 2. For example, if $N=6$, $t_{5, 0.95} = 2.571$. 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 Δ_ν to ν for the thirteen 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.

REFERENCES

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- [5] ASTM E 1421-91 "Standard Practice for Describing and Measuring Performance of Fourier Transform Infrared FT-IR Spectrometers: Level Zero and Level One Tests," in Annual Book of ASTM Standards, **14.01**, (1991).
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Table 1. Certified Peak Wavelength Values (in vacuum)

Peak Wavelength (μm)	Expanded Uncertainty, U
18.3325	0.4129
11.8754	0.0070
11.0275	0.0080
9.7243	0.0026
9.3528	0.0040
8.6607*	0.0041
6.3166*	0.0002
6.2447*	0.0003
3.5086	0.0023
3.3318	0.0001
3.3042	0.0007
3.2680*	0.0002
3.2445	0.0001

Table 2. Certified Peak Wavenumber Values (in vacuum)

Peak Wavenumber (cm^{-1})	Expanded Uncertainty, U
545.48	12.29
842.08	0.49
906.82	0.66
1028.35	0.27
1069.20	0.46
1154.64*	0.54
1583.13*	0.06
1601.35*	0.07
2850.13	1.84
3001.40	0.12
3026.42	0.61
3060.03*	0.14
3082.19	0.12

*Peak values less sensitive to peak determination method [1].

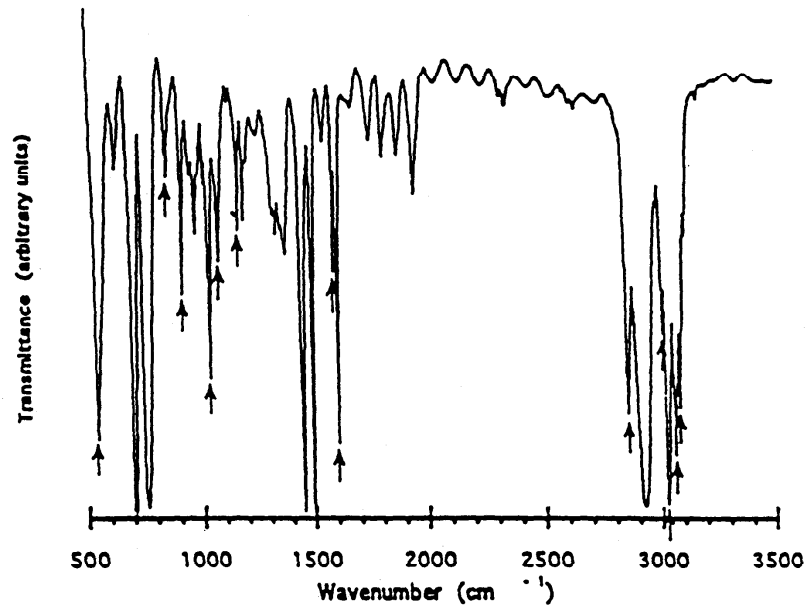


Figure 1. Spectrum of polystyrene film showing locations of certified peaks.

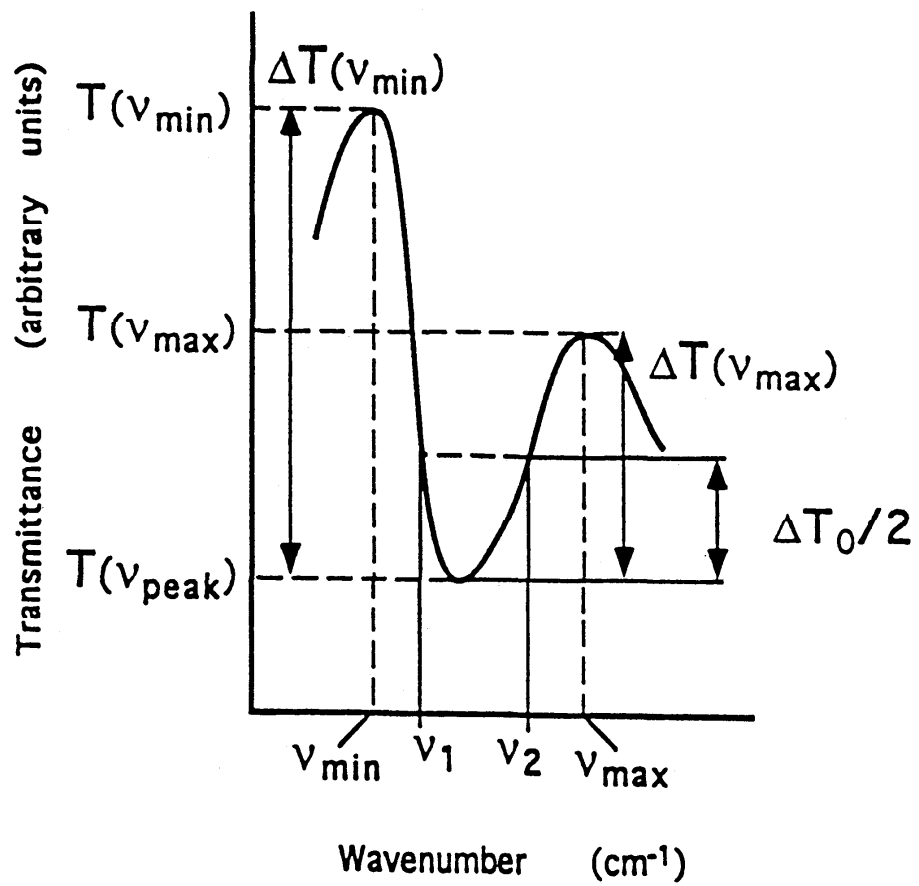


Figure 2. Diagram indicating parameters used in the peak wavenumber determination method (see text for details).