



National Institute of Standards & Technology

Certificate

Standard Reference Material[®] 1921

Infrared Transmission Wavelength Standard

This Standard Reference Material (SRM) is intended 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 (w) x 11 cm (h) x 2 mm (t) 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 experimental and statistical analysis results. The wavelength values of these peaks are certified and are shown in Table 1 along with their associated uncertainties. The corresponding peak wavenumber values are listed in Table 2. See the section "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 the section "Correction for Air/Nitrogen Purge".

Measurement Conditions: The calibration measurements were made using a Bomem DA-3.02 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 [1].

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 when available. 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.

Expiration of Certification: The polystyrene films have been measured over a period of approximately one year, without significant change of any wavelength positions. The measured samples will be monitored over time, and in the event that the certification becomes invalid, users will be notified by NIST. Because of the finite measurement period, this certificate is valid for 3 years from the date of shipment from NIST.

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.

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

The technical and support aspects involved in the revision of this certificate were coordinated through the Standard Reference Materials Program by J.C. Colbert.

Gaithersburg, MD 20899
February 23, 1996
(Revision of certificate dated 4-6-95)

Thomas E. Gills, Chief
Standard Reference Materials Program

Source of Material: The polystyrene film used in SRM 1921 has been taken from a single roll and was manufactured by the Dow Chemical Company under the trade name Trycite¹, #DWF-6001. 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) the instrumental resolution should be set 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) the spot size on the sample should be set 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 [2] and not greater than that at which the detector becomes significantly non-linear [3,4]; 3) the sample chamber should be closed and purged or evacuated for a suitable time, for the instrument to reach pressure and temperature equilibrium; 4) the calibration procedure should begin with a "reference" measurement with no sample in the sample chamber; 5) SRM 1921 should be placed in the standard sample position, and a "sample" measurement should be made. 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 [5]. 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 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 $\Delta T(\nu_{\min})$, $\Delta T_0/2$ 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 $\Delta T_0/2$.

$$\nu_{1,2}(T = T(\nu_{\text{peak}}) + \Delta T_0/2)$$

A center of gravity calculation [6] 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 (see Reference 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.

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 adjusted² 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)) [7,8]. 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.

¹The use of a trade name on this certificate is for identification only and does not imply endorsement of the product by the National Institute of Standards and Technology.

²For instruments which give vacuum wavenumber and wavelength values, no adjustment for the index of refraction of air or purge gas should be performed.

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 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 :

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

The uncertainty associated with this difference is:

$$\Delta_\nu = (t_{N-1,0.95}) s_\nu / \sqrt{N} + U, [9]$$

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 and U [10,11] is the uncertainty from the certificate. 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 accurate and correction is not advised.

REFERENCES

- [1] Gupta, D., Wang, L., Hanssen, L.M., Hsia, J.J., and Datla, R.V., Standard Reference Materials: Polystyrene Films for Calibrating the Wavelength Scale of Infrared Spectrophotometers - SRM 1921, NIST Special Publication 260-122.
- [2] Griffiths, P.R., and DeHaseth, J.A., Fourier Transform Infrared Spectrometry, Chapter 1, p. 34, John Wiley & Sons, New York, (1986).
- [3] 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).
- [4] Hirschfeld, T., Fourier Transform Infrared Spectroscopy, Chapter 6, Ferraro, J.R. and Basile, L.J. eds., Applications to Chemical Systems, **2**, Academic Press, New York, (1979).
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- [8] Smith, F.G., ed., Atmospheric Propagation of Radiation, Chapter 1, p. 88, SPIE Optical Engineering Press, Bellingham, Washington, (1966).
- [9] Becker, D. et.al., "Use of NIST Standard Reference Materials for Decisions of Performance of Analytical Chemical Methods and Laboratories," NIST Special Publication 829, (1992).
- [10] "Guide to the Expression of Uncertainty in Measurement," ISBN 92-67-10188-9, 1st Ed., ISO, Geneva, Switzerland, (1993).
- [11] Taylor, B.N., and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Tech. Note 1297, (1994).

Table. 1 Certified Peak Wavelength Values (in vacuum)

| Peak Wavelength (μm) | Expanded Uncertainty, U^a |
|-----------------------------------|-----------------------------|
| 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^a |
|--------------------------------------|-----------------------------|
| 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 |

^aThe expanded uncertainty, a NIST associated uncertainty of the certified peak value, was calculated according to "The Guide to Expression of Uncertainty in Measurement" [10, 11]. 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.

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

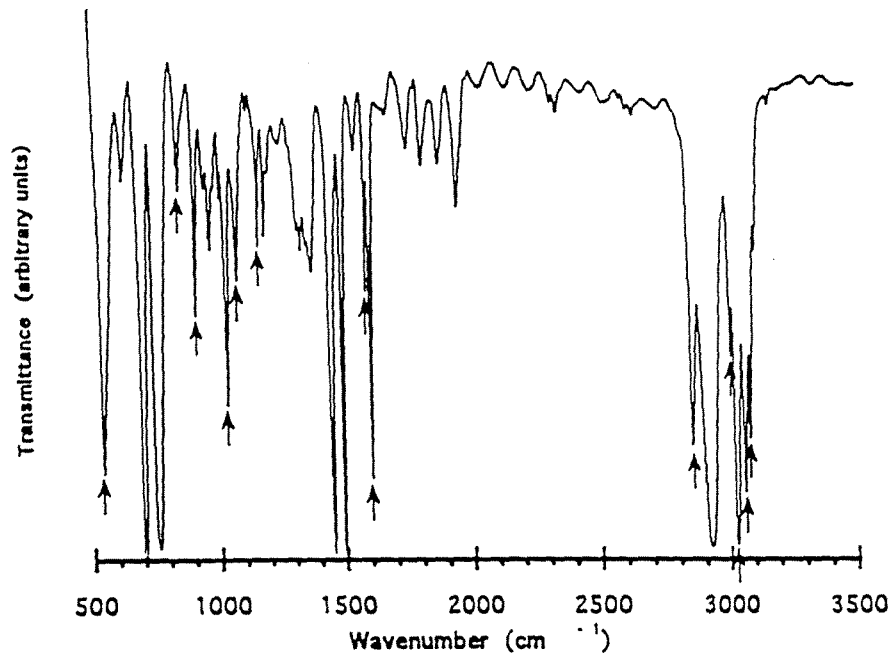


Figure 1. Spectrum of polystyrene film showing locations of certified peaks.

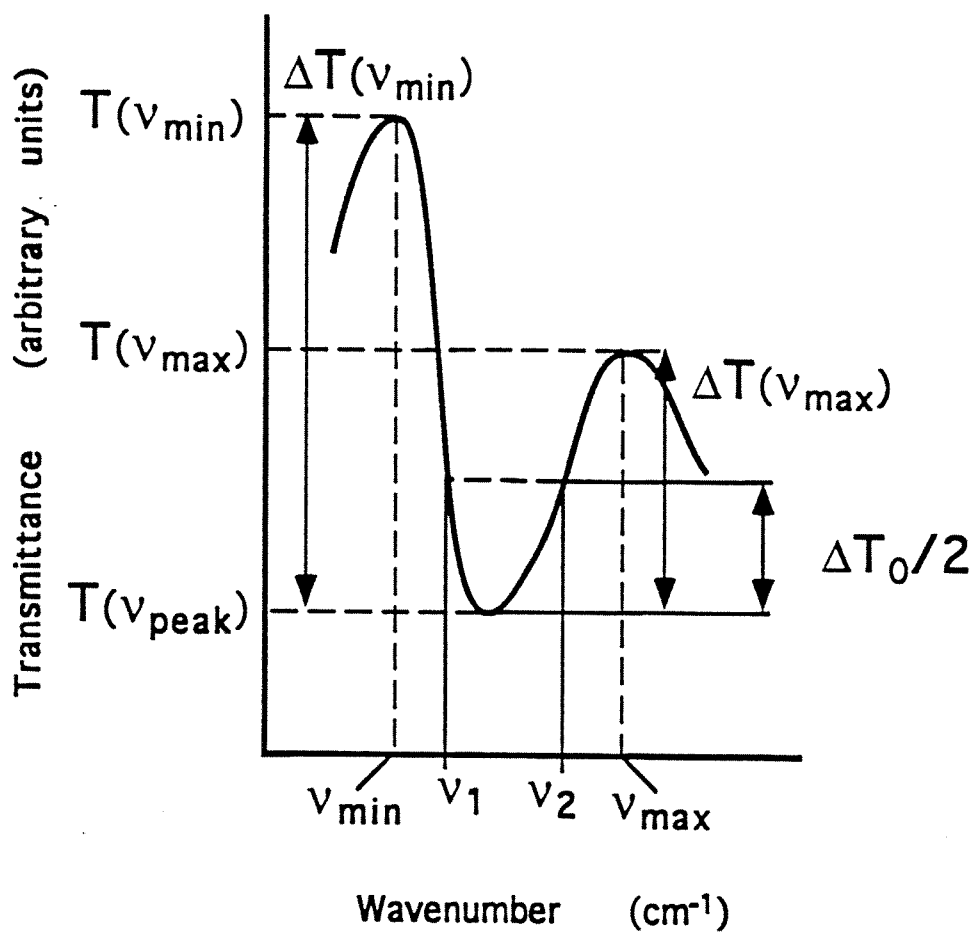


Figure 2. Diagram indicating parameters used in the peak wavenumber determination method (see text for details).