Studies of a Polystyrene Wavenumber Standard for Infrared Spectrophotometry

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Standard Reference Material (SRM) 1921 is a matte finish polystyrene film available from NIST for use in calibrating the wavenumber scale of spectrometers in the infrared spectral region from 545 cm^{-1} to 3082 cm^{-1}. New results of the dependence of the calibrated peak values on measurement resolution and peak determination method are presented. Appropriate zero filling of the interferogram was found to significantly decrease peak value dependence on resolution. For any resolution $\leq$ 4 cm^{-1}, as determined by the center of gravity method, the peak values differ by amounts less than 0.01 cm^{-1}, the least significant digit of the calibration values specified in Ref. [2]. A method of extrapolating the peak minimum for an absorption band in the transmission spectrum was carried out through a chi square fit on a series of peak values obtained at different peak fractions of the same band. The extrapolated minimum peak values are presented for the first three bands of polystyrene.

INTRODUCTION

The center of gravity (CG) method is a peak value determination algorithm described by D. G. Cameron, J. K. Kauppinen et al in reference [1]. For an absorption band in a transmission spectrum, its center of gravity, ν_{CG}, is given by

$$\nu_{CG} = \frac{\int_{\nu_i}^{\nu_k} \nu [T_f - T(\nu)] d\nu}{\int_{\nu_i}^{\nu_k} [T_f - T(\nu)] d\nu} \qquad (1)$$

where f is a fraction of the peak height as determined by the smaller peak side, $T(\nu)$ is the transmittance, and ν_i and ν_k are the wavenumbers at which $T(\nu) = T_f$. The uncertainty associated with the use of the CG method to determine a peak value is at its minimum near f = 0.5 [1]. Since NIST first made available polystyrene as SRM 1921 in 1994 [2], others [3] have studied the dependence of the calibrated wavenumber values on various parameters such as resolution and temperature. We have expanded on those efforts with a view to make this standard more useful to the community. Here we present some of the results.

RESULTS AND ANALYSIS

First an extensive investigation was conducted on the influence of resolution (r) on peak position value for the CG algorithm. Twelve polystyrene samples were measured sequentially six times (72 measurements in all) under purge using a Bomem DA3 FT-IR spectrometer [4]. The instrumental conditions were as follows: r = 0.5 cm^{-1}, aperture = 0.1 mm, scan speed = 0.5 cm/s, gain = 4, scan number = 100, Hamming apodization, KBr beamsplitter, globar source, and MCT detector.

In order to eliminate the effects caused by measurement-to-measurement variation, the lower resolution (i.e. 1.0, 2.0 and 4.0 cm^{-1}) spectra were obtained by appropriate truncation of the interferograms acquired at a resolution of 0.5 cm^{-1}. The influence of resolution change on a representative polystyrene absorption band at 1028 cm^{-1} (FWHH = 11.1 cm^{-1}) can be seen in Fig. 1. Significant peak position shifts are observed. For example, the

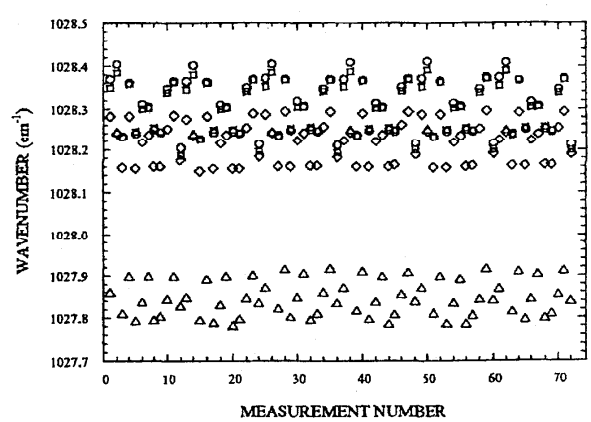

FIGURE 1. 1028 cm^{-1} peak values of polystyrene, measured at: ○, r = 0.5 cm^{-1}; □ , r = 1.0 cm^{-1}; ◇, r = 2.0 cm^{-1} and △, r = 4.0 cm^{-1} without zero filling.

average peak value difference between that of r = 0.5 cm^{-1} and r = 4.0 cm^{-1} is about 0.42 cm^{-1} which surpasses the

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maximum of the measurement-to-measurement variation (which is nearly all due to sample-to-sample variation) of ~ 0.2 cm^{-1} for this band.

This peak value shift of 0.42 cm^{-1} with resolution degradation is caused by the data point interval increase. Having fewer data points along the band contour results in a weight distribution shift when the CG method is applied. To examine this effect more carefully, the original interferograms were processed in such a way as to maintain the data point interval while degrading the spectral resolution. This was done by substituting zeros for the truncated portions of the interferograms. This corresponds to zero filling the lower resolution interferograms so that all the resulting spectra have the same data point interval. For the 1028 cm^{-1} band of polystyrene, the resulting peak values obtained from the different resolution spectra for any individual measurement are almost identical as shown in Fig. 2.

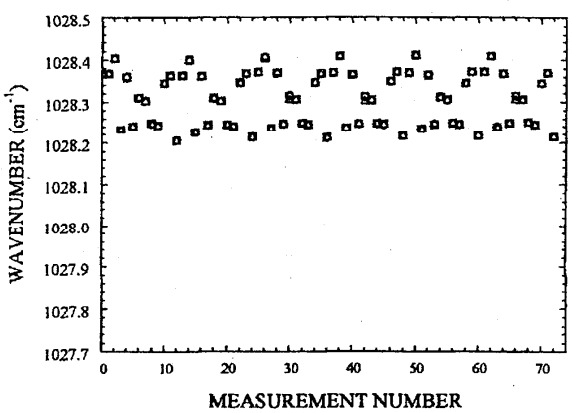

FIGURE 2. 1028 cm^{-1} peak values of polystyrene, measured at: ○, r = 0.5 cm^{-1}; □, r = 1.0 cm^{-1}; ◇, r = 2.0 cm^{-1} and △, r = 4.0 cm^{-1} with zero filling.

This significant result of the independence of peak value from resolution, when using the CG method, was observed for all 13 calibration bands of the polystyrene. The 13 peak mean ($\bar{\nu}$) differences between those measured for r = 0.5 cm^{-1} and r = 1.0, 2.0 or 4.0 cm^{-1} are summarized in Table 1. Each mean represents the average of all 72 measurements (12 samples measured 6 times).

To accommodate users who have access only to software which locates the peak minima, we have employed an extrapolated center of gravity method to produce peak minima values for SRM 1921. For each band, a series of peak values were obtained using the CG method with different peak fraction, f. These data were used to extrapolate to the band minimum at f = 0. Since the portions of the peaks used in the CG calculation for the smaller fraction contains fewer data points (than f = 0.5), a higher level of zero filling is required to produce good results. This can be seen in Fig. 3. Thus, all the spectra were zero filled to a level equivalent to that for spectrum of resolution 0.06 cm^{-1}.

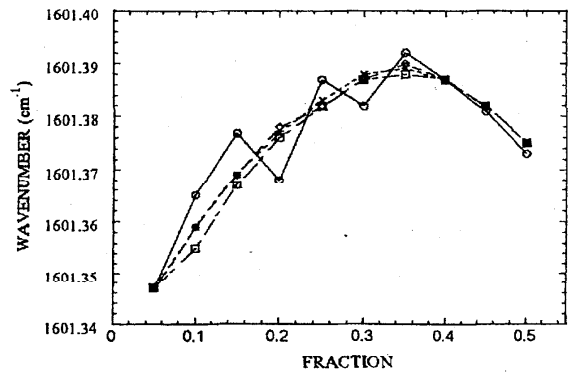

FIGURE 3. Effect of different levels of zero filling on the 1601 cm^{-1} band when r = 0.5 cm^{-1} and the peak fraction is changed from 0.05 to 0.5. The zero filling level is changed as: ○, 1 times; □, 2 times; ◇, 4 times, and ×, 8 times.

Peak value vs. Fraction plots for 4 bands of polystyrene from a single spectrum are shown in Fig. 4. One can observe the following:

(1) Each band has its own wavenumber vs. fraction curve pattern which is determined by the peak contour.

(2) The peak values associated with the different resolutions, tend to vary more as the CG fraction is reduced. The peak value at f = 0.5 is one of the stable points which are the least affected by resolution change.

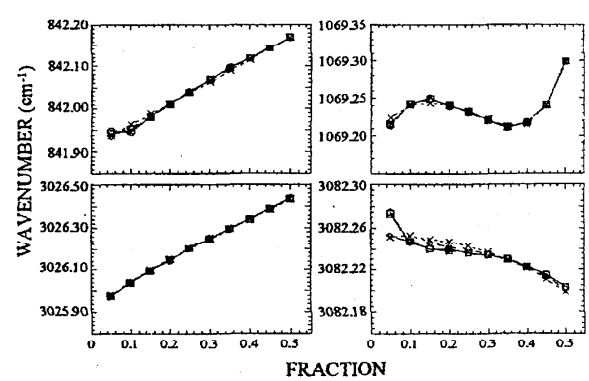

FIGURE 4. Dependence of peak values of 4 polystyrene bands on CG fraction and resolution. The different resolution results are shown as: ○, r = 0.5 cm^{-1}; □, r = 1.0 cm^{-1}; ◇, r = 2.0 cm^{-1}; and , ×, r = 4.0 cm^{-1}.

TABLE 1. 13 Peak Mean Differences Between That Measured at Resolution = 0.5 cm^{-1} and at Lower Resolutions

peak (cm^{-1})	without zero filling			with zero filling		
	$\bar{\nu}_{r=0.5}-\bar{\nu}_{r=1.0}$	$\bar{\nu}_{r=0.5}-\bar{\nu}_{r=2.0}$	$\bar{\nu}_{r=0.5}-\bar{\nu}_{r=4.0}$	$\bar{\nu}_{r=0.5}-\bar{\nu}_{r=1.0}$	$\bar{\nu}_{r=0.5}-\bar{\nu}_{r=2.0}$	$\bar{\nu}_{r=0.5}-\bar{\nu}_{r=4.0}$
545	0.0300	-0.3403	-1.3639	-0.0018	-0.0049	-0.0059
842	0.0403	0.0081	-0.1388	0.0005	0.0005	0.0006
906	0.0317	0.0159	-0.0222	0.0001	0.0002	0.0001
1028	0.0317	0.0865	0.4244	-0.0002	-0.0002	-0.0015
1069	0.0415	0.0199	0.0980	0.0002	0.0002	0.0000
1154	0.0195	-0.0215	-0.4097	0.0000	-0.0007	-0.0016
1583	0.0836	0.0593	-0.3846	-0.0001	-0.0009	-0.0035
1601	0.0067	0.0150	0.1545	-0.0002	-0.0001	0.0002
2850	-0.0547	0.0317	-0.0715	-0.0002	0.0002	-0.0002
3001	0.0081	0.0322	-0.3992	0.0002	-0.0002	-0.0002
3026	-0.0500	0.0276	0.1096	0.0000	0.0000	0.0005
3060	-0.0171	0.0005	0.0549	0.0002	-0.0002	0.0002
3028	-0.0146	0.1155	1.2263	0.0005	0.0002	0.0005

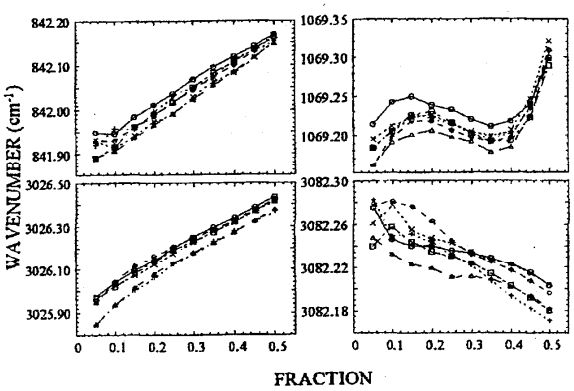

FIGURE 5. Six measurements of the same sample at r = 0.5 cm^{-1}. In the plot, the measurement number are as follows: ○, 1; □, 2; ◇, 3; ×, 4; +, 5; and △, 6.

The peak value vs. CG fraction for 6 measurements of the same sample with resolution of 0.5 cm^{-1} is shown in Fig. 5. In each case, the measurement-to-measurement variation of peak value is larger than that due to resolution change (Fig. 4).

Now we proceed to extrapolate the peak fraction results to find the peak minimum values. Since it is difficult to fit irregular curves such as some of these shown in Fig. 4, the extrapolated minimum operation was performed on a reduced range of CG fraction ($0.01 \le f \le 0.1$). The peak values obtained at this range of CG fraction for the 906 cm^{-1} of polystyrene are shown in Fig. 6. The dashed line in this plot represent the mean of 6 measurements of the same sample and error bars stand for the standard deviation of the mean. To make the extrapolation more accurate at lower fraction, chi square fit, a linear curve fit with weighting by the inverse of the standard deviation, was applied to the data. This fit is shown as a solid line in Fig. 6. Table 2 summarizes the chi square fitting results of the first three bands of polystyrene for r = 0.5, 1.0, 2.0 and 4.0 cm^{-1}.

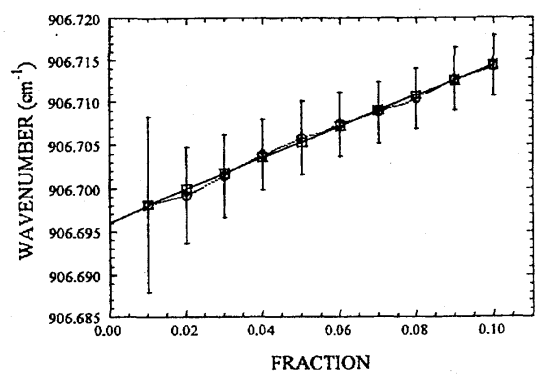

FIGURE 6. Chi square fitting on mean of 6 measurements with standard error as error bars at r = 0.5 cm^{-1}. In the plot, the dashed line with ○ represents the mean of 6 measurements and the solid line with □ stands for chi square fitting result.

CONCLUSIONS AND FUTURE WORKS

Appropriate zero filling is a very effective way to improve peak value determination for spectra measured at low resolution, especially for the CG method and specifically with f = 0.5.

The approach of the extrapolated CG method to obtain the peak minimum will be used to provide another set of reference data to SRM 1921. We will extend the

TABLE 2. Chi Square Fit on Mean Peak Value vs. Fraction Plots of Three Bands of Polystyrene, Comparison of Extrapolated Peak Minimum with Peak Value at f = 0.5

Peak (cm^{-1})	r (cm^{-1})	Slope (cm^{-1}/f)	Extrapolated Peak Minimum (cm^{-1})	Chi ^{2}	Peak Values (cm^{-1}) at f = 0.5
545	0.5	8.4487	539.855	0.17782	547.071
545	1	8.3836	539.872	0.19366	547.052
545	2	8.4154	539.875	0.09036	547.055
545	4	8.3842	539.879	0.05103	547.048
842	0.5	0.09729	841.916	0.17188	842.161
842	1	0.09714	841.917	0.32188	842.158
842	2	0.29563	841.901	0.09881	842.158
842	4	0.57009	841.875	0.00152	842.158
907	0.5	0.18028	906.696	0.01081	906.841
907	1	0.18208	906.699	0.01808	906.839
907	2	0.17629	906.696	0.01101	906.839
907	4	0.17671	906.697	0.02009	906.839

extrapolated CG method to all of our polystyrene data and generate calibrated minimum values for the SRM 1921.

Comparison of this method with other commercially available minimum find algorithms will be carried out. We will also extend the ongoing investigation of the effects of temperature change on peak value.

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