Wavenumber Standards for Mid-infrared Spectrometry

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1 INTRODUCTION

Accuracy of the wavenumber scale of spectroscopic instrumentation is important for most applications. Most modern Fourier transform infrared (FT-IR) spectrometers incorporate HeNe lasers that are used to set the wavenumber scale for the instrument. The frequency of these lasers is typically known to within 0.01 cm^{-1}. Yet a variety of error sources can result in much larger wavenumber scale errors for actual sample measurements. Hence, a calibration is required to guarantee the accuracy of the wavenumber scale. Wavenumber standards are the primary tool of a spectroscopist or instrument manufacturer for establishing valid wavenumber uncertainty levels and calibration of the scale.

A number of standards have been investigated and developed over time, including solid-, liquid-, and gas-phase forms. These are ultimately tied to fundamental frequency standards maintained at national metrology institutes (NMIs) such as the National Institute of Standards and Technology (NIST) (formerly the National Bureau of Standards (NBS)) in the USA, the National Physical Laboratory (NPL) in the UK, the National Research Council (NRC) in Canada, and others. For the infrared (IR) spectral range, the only wavenumber standards available from the NMIs are polystyrene. They are designed for use with medium-resolution instruments that represent the vast majority of FT-IR spectrometers.

For a considerable period of time, calibration of the highest-resolution (grating) instruments in the IR employed the same standards as are used for the visible and near-infrared, namely atomic emission lines from gas discharge lamps. The main difference was the use of higher-order reflections off the gratings for the IR as opposed to the fundamental for the visible region. The overall uncertainty of this method includes a larger component from use of the higher-order reflection. This method of wavenumber calibration was used for many of the first measurements of molecular gas vibrational and rotational absorption spectra. Over time as these spectra became better understood the absorption lines themselves began to be used as standards for calibration. Further improvements have primarily been in the methods used to characterize the frequencies and wavenumbers of the various gas species absorption lines. More recently these methods have become tied to the fundamental unit of time.

Additionally, other materials have been investigated for potential use as wavenumber standards including both liquids and solids. The absorption spectra associated with condensed-phase materials are naturally broader in wavenumber and hence more appropriate to lower-resolution instruments such as prism and low-resolution grating monochromators (earlier on) and FT-IR spectrometers (in more recent decades). Thin-film polystyrene has been a popular material for wavenumber calibration in the IR beyond 2.5 µm since at least 1950, when Plyler and Peters[1] characterized its absorption bands. Since then it has become available as a calibrated standard from NMIs.

2 VAPOR-PHASE STANDARDS

Vapor-phase absorption measurements in the IR date from the late 1800s. Several authors published comprehensive studies of gases, liquids and solids, including Coblentz.[2] As spectrometer instrumentation improved and the physics of

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the energy level transitions, which are evidenced by absorption and emission spectra, became better understood, the accuracy of the absorption line wavenumber determinations improved significantly.

Compilations of wavenumber standards representing accumulations of high-accuracy high-resolution measurement results from numerous researchers have expanded and improved over time. These include two editions of a handbook sponsored by the International Union of Pure and Applied Chemistry (IUPAC) in 1961[3] and in 1977 edited by Cole,[4] along with handbooks by Rao *et al.*[5] in 1966, Guelachvili and Rao[6] in 1983 as well as a second volume[7] in 1993. By 1996 the amount of data had expanded to such an extent that the IUPAC produced a Technical Report by Guelachvili *et al.*[8] that does not list specific absorption line values, but rather summarizes the molecular species and their absorption spectral ranges and refers the reader to an extensive list of references in the literature.

The highest accuracy standards for frequency calibration are determined by heterodyne techniques.[9] The uncertainties associated with absorption line wavenumbers measured by Doppler-limited heterodyne methods are commonly 10^{-2} to $10^{-7}\,\mathrm{cm}^{-1}$, and saturated absorption heterodyne methods 10^{-5} to $10^{-9}\,\mathrm{cm}^{-1}$.[10–13] The calibration data from heterodyne measurements can be used to correct high-resolution Fourier transform (FT) spectrometer measurements, yielding expanded ($k = 2$) uncertainties for the broad range of wavenumbers in the most recent IUPAC recommended wavenumber standards of 10^{-3} to $10^{-6}\,\mathrm{cm}^{-1}$.[8] The IUPAC recommended absorption line data for wavenumber calibration are summarized by Guelachvili *et al.*[8] They list recommended molecular species and associated spectral ranges that are summarized in Table 1 and Figure 1. For each set of recommended lines it provides the associated reference along with a correction coefficient

Table 1. Gas spectra lines for wavenumber calibration (IUPAC).[8]

Gas species	Spectral range (cm^{-1})
CH_4	1218–4134
C_2H_2	2630–6685
C_2H_4	2925–3000
CH_3Cl	1309–3831
CH_3I	3849–6237
CH_3OH	100–350
CO	1948–6388
CO_2	839–2391
CS_2	1460–1551
Fe I, Fe II	2350–23 600
H_2	354–1447
HCN	6378–6395
HCl	2086–5825
HF	205–7997
H_2O	25–7639
I_2	7220–11 200
NH_3	719–5234
NO	1741–1952
NO_2	523–5130
OCS	486–3120

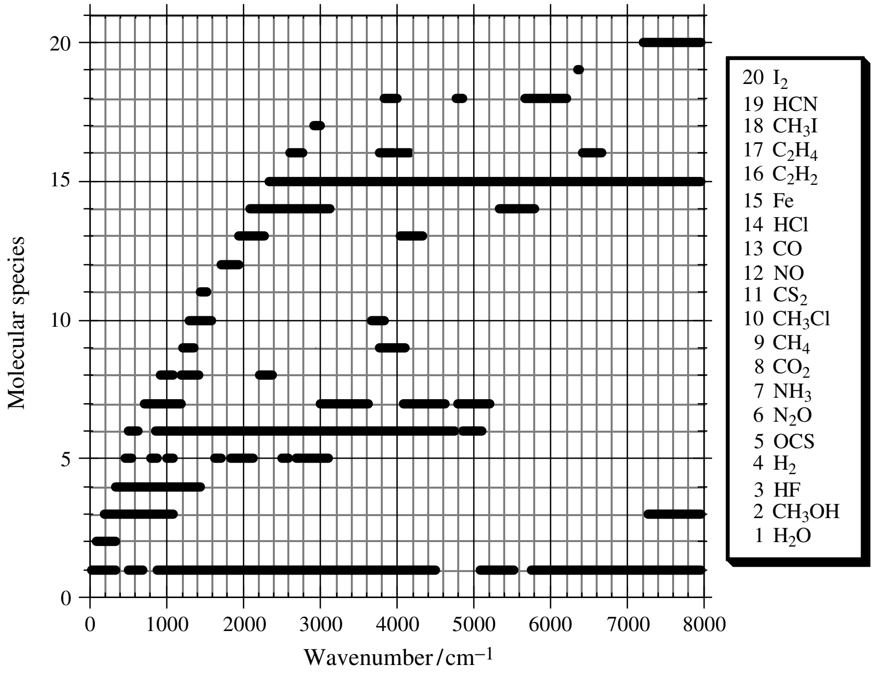

Figure 1. Overview of spectral bands containing the IUPAC[8] recommended wavenumber standard absorption lines for 20 species that are listed in Table 1.

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(to be applied to all lines in the set) obtained from heterodyne data that are also described and referenced. Each species in Figure 1 is listed in order of increasing minimum wavenumber along with the number code identifying it on the ordinate scale. Species 15 (Fe emission spectra) and 20 (I_2) extend to higher wavenumbers not shown in the figure ($23\,600\,\mathrm{cm}^{-1}$ and $11\,200\,\mathrm{cm}^{-1}$, respectively). The overall spectral range of each species (listed in alphabetical order) is also presented in Table 1.

In 1973 a popular database of atmospheric gas absorption line information known as HITRAN (high-resolution transmission molecular absorption database) was first made available in electronic format.[14] Since then it has been continuously expanded to encompass 37 species with absorption lines and spectral coverage from the ultraviolet (UV) through the far-infrared. It is designed to be used to model transmission and emission in the atmosphere. Much of the data in published handbooks of IR standards are included in the database. Information provided in the database includes transition identification, line wavenumber, half-width, intensity, linewidth temperature coefficient, line shift pressure coefficient, and more.[15] Table 2 lists the 37 gas species in the 1996 version of HITRAN with the overall spectral range for each species. The HITRAN database is useful for a number of modeling applications, but not all the lines in it are appropriate for calibration purposes. Species suitable for calibration of moderate-resolution spectrometers ($>0.1\,\mathrm{cm}^{-1}$) are indicated by *, species more appropriate for higher-resolution spectrometers are indicated by †, and two species requiring extra safety precautions are indicated by ‡.

For moderate-resolution instruments with resolution capability of $0.5\,\mathrm{cm}^{-1}$ or better, the handbook and database information are useful tools for wavenumber scale calibration, especially for measurement of samples with similar narrow band spectral structure. Calibration can be performed with appropriately filled gas cells, under residual pressure conditions in vacuum systems, or under atmospheric pressure purge conditions with consideration of the pressure dependence of line positions for the highest accuracy results.

Table 2. Gas spectra lines available in the HITRAN database.[15]

Gas species	Spectral range (cm^{-1})
CH_4*	0–6185
C_2H_2*	604–3375
C_2H_6†	720–3001
CH_3Cl	679–3173
ClO	0–1208
$ClONO_2$	763–798
CO*	3–6418
CO_2*	442–9649
COF_2	725–1982
HBr*	16–9759
HCN‡	2–3422
H_2CO†	0–2999
HCOOH†	1060–1162
HCl*	20–13 458
HF*	41–11 536
HI	12–8488
HO_2	0–3676
H_2O	0–22 657
H_2O_2†	0–1500
HOBr	0–316
HOCl†	0–3800
HNO_3	0–1770
H_2S	2–2892
N_2	1922–2626
NH_3*	0–5295
NO†	0–3967
NO^+	1634–2531
N_2O*	0–5132
NO_2†	0–2939
O	68–159
O_2	0–15 928
O_3	0–4033
OCS*	0–2089
OH	0–9997
PH_3‡	708–1411
SF_6	940–953
SO_2†	0–4093

3 CONDENSED-PHASE STANDARDS

In 1950 Plyler and Peters[1] at NBS reported on several materials specifically studied for use as wavelength standards for prism spectrometers (low to medium resolution) in the IR range from 1.6 to 24 µm. Absorption band wavenumbers were presented for both liquid and solid standards. Liquids included 1,2,4-trichlorobenzene, methanol, methylcyclohexane and toluene. The solid standard was 25 µm thick polystyrene. Work covering the wavelength range of 0.6 to 2.6 µm, with additional bands of polystyrene and dydymium glass solid standards, as well as 1,2,4-trichlorobenzene and carbon disulfide liquids, was presented two years later by Acquista and Plyler.[16] Refined calibration measurement results, including those of a 50 µm thick polystyrene film, along with uncertainties for most of the bands, were presented by Plyler *et al.*[17] in 1957, and then again in 1960 with $0.03\,\mathrm{cm}^{-1}$ instrumental uncertainty.[18] Repeated measurements on polystyrene samples over more than a decade showed no evidence of any shift of the bands examined between 6 and 14.4 µm ($1600\,\mathrm{cm}^{-1}$–$700\,\mathrm{cm}^{-1}$).[18]

The IUPAC 1961 handbook of recommended wavenumber standards included one solid (polystyrene) and one liquid (indene).[3] The wavenumber values for 7 and 70 µm

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thick polystyrene were referenced to Plyler *et al.*[18] and Jones and Nadeau, and consisted of 14 bands covering the spectral range of 700–3030 cm^{-1}. The values for indene (indene with 0.8% camphor–cyclohexanone) in 30 µm film form were from Jones *et al.*[19] from NRC. The polystyrene data were retained by IUPAC in the second edition in 1977, while the indene (0.8% camphor–cyclohexanone) spectrum with 77 bands covering a range of 700–4000 cm^{-1} was supplemented by indene–camphor–cyclohexanone (equal parts) with eight absorption bands extending the wavenumber range down to 300 cm^{-1}.[4] Discussion of the good stability over 16 years and uniformity of the indene standards along with uncertainties (0.5 cm^{-1} or 1.0 cm^{-1} for all 85 bands) for the wavenumber values were described by Jones and Nadeau.[20]

Another standards organization, the American Society of Testing and Materials (ASTM) has produced *Recommended Practices* for dispersive spectrophotometer characterization beginning in 1965[21,22] and most recently in 1989[23] that specified the use of polystyrene or indene for wavenumber scale calibration. Subsequently another series of *Recommended Practices* for FT-IR characterization were also published beginning in 1991.[24–26] These listed only polystyrene for wavenumber scale calibration.

During that period, the number of users of spectrometers for IR spectroscopy, especially low to moderate resolution instruments, has continued to increase. This has led to an increasing demand for certified wavenumber standards that are also easy to use and relatively stable. In the early 1990s, NPL and NIST performed the requisite analyses and characterization to produce polystyrene film wavenumber standards.

The polystyrene wavenumber standards available from NPL are calibrated individually.[27] The absorption bands for which calibration values are provided are listed in Table 3, along with those provided by NIST, as well as ASTM, IUPAC, and the original NBS recommended bands, for comparison. The polystyrene material is a matte finish 40 µm thick material, originally provided by Perkin-Elmer Ltd. and later produced by NPL. Matte finish polystyrene provided by both NPL and NIST has no and minimal (respectively) discernible interference fringes within the spectral range of 500–3200 cm^{-1}, as can be seen in Figures 2 and 3. Interference fringes in the spectrum of clear polystyrene can add up to 1.5 cm^{-1} uncertainty to calibrated values due to their sensitivity to beam geometry and temperature.[28] Many of the absorption bands were found to be temperature dependent and exhibit spectral shifts with modest temperature variation. The uncertainties for the NPL wavenumber values include a component to allow for a temperature range of ±10 °C from the nominal room temperature value of 30 °C. The expanded uncertainties ($k = 2$) for all the NPL wavenumber values listed in Table 3 are 0.4–0.6 cm^{-1}. The calibration values are valid for any measurement resolution below (better than) 4 cm^{-1}.[29]

Table 3. Polystyrene bands for wavenumber calibration.

Absorption band wavenumber (cm^{-1})	NBS (1957)	IUPAC (1961 and 1977)	ASTM (1991, 1994, 1999)	NPL (1992)	NIST (1993)
540			X		X
698		X			
842					X
906	X	X	X		X
1028	X	X	X	X	X
1069	X	X			X
1154	X	X		X	X
1181		X		X	
1493	X				
1583		X		X	X
1601	X	X	X	X	X
1802	X	X			
1871	X	X			
1944	X	X	X		
2850	X	X	X	X	X
2924	X	X			
3001	X				X
3026	X	X	X		X
3060	X		X	X	X
3082	X		X		X
3104	X				

NPL uses a Perkin-Elmer 983 G grating spectrophotometer for the polystyrene calibration measurements. Calibration of the spectrophotometer is performed on a regular basis using gas absorption lines from a number of gases that provide a thorough coverage of the spectral range, including atmospheric water vapor and

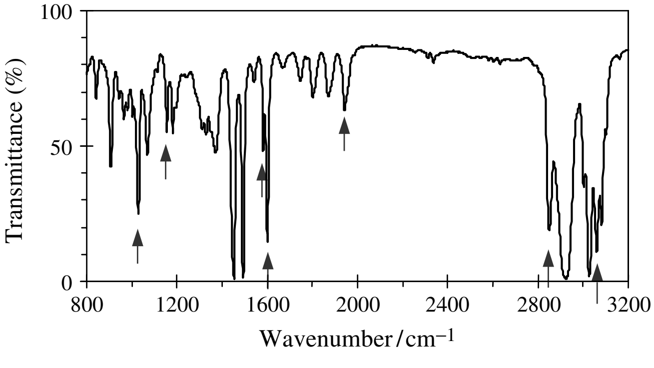

Figure 2. NPL polystyrene standard spectrum. The arrows identify the locations of the calibrated absorption bands listed in Table 3. (© Crown copyright, 1999. Reproduced by permission of the Controller of the HMSO.)

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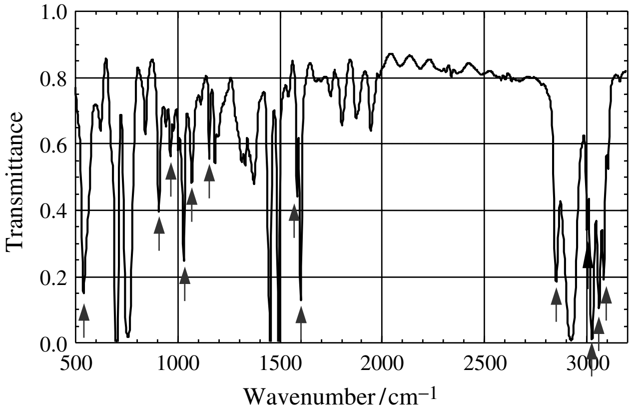

Figure 3. NIST polystyrene standard spectrum. The arrows identify the locations of the calibrated absorption bands listed in Table 3.

carbon dioxide as well as sealed cells with various gas mixtures.[28] In addition, short-term drift of the instrument is accounted for via an automatic wavenumber scale check that is performed interspersed within each calibration measurement sequence.[30] Instrument calibration measurements are made in a nitrogen purge at 0.5 cm^{-1} resolution. Polystyrene calibration measurements are made at about 1.3 cm^{-1} resolution with additional cubic piecewise smoothing applied to obtain the transmittance minima values.

NIST began the process of establishing a polystyrene standard (standard reference material SRM 1921A)[31] after receiving a request for calibrated standards and obtaining a large roll of matte finish polystyrene from the Coblentz Society in the late 1980s. A portion of the material was made into a large number of standard samples. NIST has used a Bomem DA FT-IR to perform batch calibrations of the polystyrene, characterizing approximately 100 random samples out of a total number of 2000 in each batch on two occasions.[32,33] Certain commercial equipment, instruments and materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology. The absorption bands for which certified wavenumbers are provided are listed in Table 3. The associated expanded uncertainties ($k = 2$) for the 13 bands vary considerably from 0.06 cm^{-1} to 0.66 cm^{-1} (with the exception of two bands with 1.9 cm^{-1} and 12 cm^{-1} uncertainty). The NIST polystyrene exhibits weak fringes in the spectrum seen in Figure 3. The effects of these fringes on absorption band location are effectively incorporated into the uncertainties through the batch calibration process. The fringe structure is sensitive to sample thickness, which varies from sample to sample sufficiently to cycle through them. Hence the mean spectrum of all samples exhibits minimal interference structure, and the sample-to-sample variance in wavenumber values are included in the combined and expanded uncertainties. NIST has not concluded temperature coefficient measurements. However, Spragg and Billingham[34] measured the temperature coefficients for several bands of the NIST standard.

NIST uses residual water vapor and carbon dioxide absorption lines to calibrate its DA FT-IR spectrometer. This has been repeated on a yearly basis under both vacuum and clean-air purge conditions. The largest deviation has been found to be 0.01 cm^{-1} at 2300 cm^{-1} for a scan performed with 0.02 cm^{-1} resolution.[32] The calibration results have been very reproducible. Further studies of the resolution dependence of the polystyrene absorption band wavenumber values have established the applicability of the high-resolution calibration results to lower-resolution measurements.[35]

Although oxidation and other degradation of polystyrene films can occur over time,[18,26] shifts in wavenumber values of calibrated absorption bands of the standards and reference samples have not been observed by NBS or NIST over extended periods approaching a decade or more.[18,33]

4 CALIBRATION METHODOLOGY

4.1 Sources of error

A number of parameters involved in the measurement process of obtaining spectra, especially in the FT processing steps, can affect the wavenumber scale accuracy. These include the source aperture size, selection of single- versus double-sided interferogram measurement, method of generating the double-sided interferogram for subsequent FT processing (when measuring only single-sided interferograms), apodization and size of the spectrum used for phase correction, apodization of the full interferograms, level of zero-filling, etc. Finally, the method used for obtaining the peak values can significantly affect the wavenumber results.

The most straightforward mechanisms for wavenumber scale error in FT-IR interferometers are geometrical in nature. The wavenumber scale is most often generated by keeping track of interference fringes obtained from a stabilized HeNe laser beam that travels through the interferometer along much the same path as the IR source light used for the spectral measurements. If the HeNe and IR source light do not travel through the interferometer in identical ways, the angular misalignment of the two beams will lead to a corresponding wavenumber scale error. In fact, any mechanism that leads to the divergence of light or a change of the divergence through the interferometer will alter the wavenumber scale to some degree. Hence,

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the use of a finite size internal source aperture or Jacquinot stop leads to a wavenumber shift that can be calculated. A calculated correction taking into account the source aperture is automatically performed in some FT-IR instrument software. In addition, other downstream vignetting of the IR beam can lead to wavenumber scale errors.

The ambient conditions of the measurement also need to be taken into account. The index of refraction of air or N_2 purge gas differs from that of vacuum by approximately 2.7×10^{-4}. The exact index is wavelength, temperature and humidity dependent.[36] For prism-grating spectrometers this index difference needs to be taken into account for the wavenumber or wavelength scale. For FT-IR spectrometers that use HeNe lasers to set the wavenumber scale, only the difference in index of the purge gas between the IR wavelength being measured and that of the HeNe laser need be corrected for to obtain the vacuum wavenumber scale.

Other sources of error, such as variation in scan mirror speed, detector non-linearity, inter-reflection between sample, detector and interferometer components, etc., can lead to wavenumber scale error in the processed spectrum. Guelachvili presented a thorough review of a number of these error sources in 1981.[37]

4.2 Use of low- versus high-resolution standards

The basic need for calibration of the photometric and wavenumber scales of the spectra resulting from measurements is the same irrespective of the type of measurement instrument. However, the form and type of error in these scales may differ significantly depending on the spectrometer type. Specifically, prism monochromators, grating monochromators, and interferometers produce wavenumber scales in different ways. The spectrometers built around these elements have sources of error that affect the scales in different ways as well. The optimal calibration procedure necessarily will vary according to spectrometer design and type. For instance, grating instruments tend to have an error in the wavenumber scale that has a non-linear dependence on wavenumber. In addition, errors occur upon grating and source changes within a spectral scan. On the other hand, interferometers tend to have wavenumber error that is linear in wavenumber that also could vary upon beam splitter, source or detector interchange.

An interesting point to consider for interferometers is the spectral resolution capability of the instrument and the width of the standard lines or bands used for wavelength calibration. It is a common view that polystyrene, for instance, is only useful for calibration of instruments incapable of the higher resolution required for seeing the much narrower gas absorption lines. In fact, it is possible for an FT-IR spectrum to have narrow gas lines that are correctly located and yet in the same spectrum have polystyrene bands that are significantly shifted in wavenumber from calibrated values. Such a case is demonstrated in Figure 4.

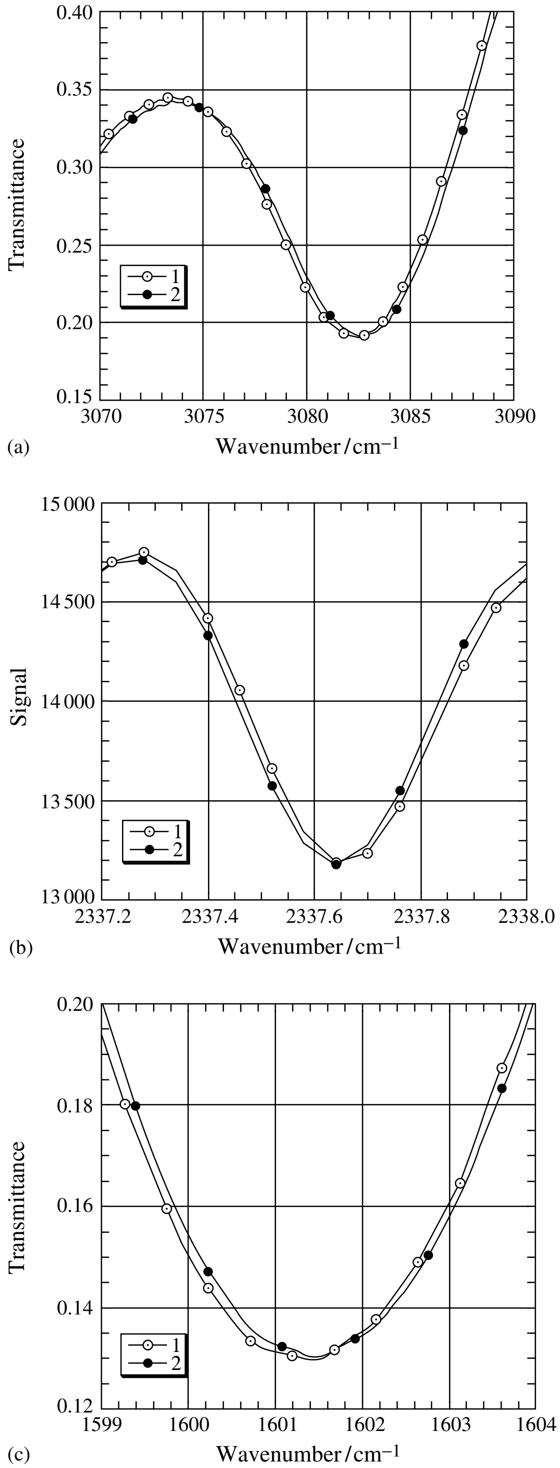

Figure 4. Wavenumber scale error evidenced by shifts in the CO_2 line (b) at 2337.65 cm^{-1} and polystyrene absorption bands (a) at 3083 cm^{-1} and (c) at 1601 cm^{-1}.

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Two spectra of polystyrene taken at $0.5\,\mathrm{cm}^{-1}$ resolution under clean air purge are shown overlaid. A CO_2 absorption line at $2337.65\,\mathrm{cm}^{-1}$ in Figure 4(b) is spectrally bracketed by polystyrene absorption bands at $3083\,\mathrm{cm}^{-1}$ (Figure 4a) and $1601\,\mathrm{cm}^{-1}$ (Figure 4c). All three plots exhibit some offset between curves #1 and #2. However, the gas line shift is only $0.02\,\mathrm{cm}^{-1}$, while the polystyrene bands have clear shifts in the opposite direction of $0.1\,\mathrm{cm}^{-1}$ and $0.3\,\mathrm{cm}^{-1}$, respectively. The overlaid spectra shown in Figure 4 were obtained from the same initial interferograms. The difference between them is merely a difference in the size of the portion of the interferogram used for phase correction in the FT processing. Several authors have examined the phase correction process and the effects of phase error on spectra including line or band positions.[38–40] One may conclude that a high-resolution calibration may not always be the most appropriate for spectra with low-resolution structure.

A thorough wavenumber calibration procedure for FT-IR spectrometers may require a number of standards that provide calibration using spectral structure over a range of linewidths. Failing the availability of such an ideal set of standards, the user must select an available standard that most nearly matches the type of samples they typically need to measure (i.e. gas lines for gas spectra, etc.). The widths of the bands in the spectrum of polystyrene vary from 4 to $40\,\mathrm{cm}^{-1}$. When combined with gas spectra, the user can span a very broad range of desired widths.

4.3 Absorption band (peak) wavenumber evaluation methods

The importance of the method used to obtain wavenumber values from absorption spectra is frequently overlooked. Often no discussion, or just a brief mention, of the method used to obtain the calibration values from the absorption spectra is found, whether from chart paper or from digital data. Only a few of the papers and handbooks concerning wavenumber standards have anything to say about the wavenumber value determination process. Plyler *et al.*[18] mention that the calibrated values correspond to the center of the 3/4 point of the symmetrical absorption bands, and the ASTM documents on FT-IR testing and calibration specifically recommend the use of the center of gravity (centroid) method for application to the polystyrene standard.

In 1995 NIST organized an intercomparison among nine laboratories (including six FT-IR manufacturers) to evaluate the effect of the method used to obtain wavenumber values from polystyrene absorption spectra.[41] A variety of FT-IR systems and 16 evaluation methods/software programs were represented. Despite starting with identical polystyrene spectra (in ASCII format), the variation in absorption band wavenumber values ranged from $0.5\,\mathrm{cm}^{-1}$ to more than $1\,\mathrm{cm}^{-1}$. These results indicated the importance of the absorption wavenumber algorithm and the manner of its implementation in software to the useful application of a medium-resolution wavenumber standard.

A number of methods are available to the user for characterizing an absorption line or band by a single wavenumber value. These include fitting to functional forms determined by the physics and chemistry of the absorption processes, such as a Lorentzian, Gaussian or Voigt form. Other methods are not related to the underlying physical processes. These are based on mathematical evaluations of the spectral structure. These latter methods come in two varieties: those that determine the location of the minimum or maximum; and those that determine an average value over some fraction of the line or band, such as the centroid and bisecting methods.

NIST has employed the centroid method applied to 50% (0.5 fraction) of the absorption band to obtain wavenumber values for the calibrated bands in its polystyrene standard. (The centroid method is also commonly referred to as the “center of gravity” method despite the absence of gravity or mass as the measured quantity in most spectra.) The centroid method has been recognized as a useful tool for the application of wavenumber scale calibration since first discussed by Van den Akker in 1943.[42] It was implemented in the development of dydymium glass wavelength standards for the visible and near-infrared by Venable and Eckerle[44] in 1979. Cameron *et al.* carefully studied the effects of various parameters on the centroid method determination of wavenumber values and demonstrated that for optimum precision the appropriate fraction of a line to evaluate lies within the region of values centered at 0.5 (50%).[44] Henry Buijs of Bomem, Inc. implemented the centroid method, with 0.5 fraction, for the software for the DA series of FT-IR spectrometers in the early 1980s. The most recent ASTM *Recommended Practice* for FT-IR testing presents in the appendix the equations for and a detailed description of the 0.5 fraction centroid method employed by NIST.[26]

Using the spectral data set obtained from the batch calibration of the polystyrene standards (960 spectra), Zhu and Hanssen at NIST have performed a number of investigations of the effects of important parameters on the calibrated wavenumber values.[33,35,45] A study of the dependence of band wavenumber values on measurement resolution revealed two important facts.[35] (1) For the polystyrene standards, although calibration measurements were originally performed at $0.5\,\mathrm{cm}^{-1}$ resolution, the calibrated centroid values are effectively independent of measurement resolution up to $4\,\mathrm{cm}^{-1}$. (2) The resolution dependence that

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appears in the straightforward generation of results is an artefact of the decreased data spacing (along the wavenumber axis) associated with standard (common) FT processing. When zero-filling is used to maintain the same number of points in the spectra for low resolution as for high resolution, then fact (1) is realized. The relative insensitivity of band location to resolution is because the bands are spectrally resolved: the narrowest calibrated band in the polystyrene spectrum has a full width at half-height (FWHH) of 4.4 cm^{-1}. Boxcar apodization must be used for the lowest-resolution (4 cm^{-1}) case. Due to the associated degradation of effective resolution, 2 cm^{-1} becomes the recommended limit when relatively strong apodization functions, such as Hamming or triangle, are applied. A simple analysis of the effects of data spacing on all 13 NIST calibrated polystyrene absorption bands revealed an expected dependence of band location error on data spacing interval and bandwidth (inversely proportional).[33] Results showing the maximum error due to the digitization of the wavenumber scale for the 0.5 fraction centroid method are plotted in Figure 5. A universal formula that would apply to all 13 bands requires an appropriate quantification of the lack of symmetry in the bandshape. The analysis can be used to select an appropriate level of zero-filling to limit the error from finite data spacing. Although the study was performed on values obtained from the 0.5 fraction centroid method, analogous behavior would be expected from other methods as well.

A comparison of methods for absorption band wavenumber determination has also been performed on the NIST polystyrene data.[45] Seven methods were applied to the data and evaluated for all 13 calibrated bands. A comparison of the methods' results for the 1601 cm^{-1} band is shown in Figure 6. The resolution and apodization conditions for the three plots are (a) 0.5 cm^{-1} and Boxcar, (b) 0.5 cm^{-1} and Hamming, and (c) 4.0 cm^{-1} and Boxcar. The methods used are: (1) extrapolated centroid (EC), (2) extrapolated bisecting (EB), (3) 30-point quadratic fit, (4) 4-point cubic spline fit, (5) GRAMS[46] peak fit with 49-point smoothing, (6) GRAMS peak fit with no smoothing, and (7) centroid with 0.5 peak fraction. (The EC and EB methods are described in Zhu and Hanssen.[35,45] The EC and EB methods use wavenumber values calculated from successively smaller fractions of the absorption band to extrapolate to zero fraction, i.e. to an effective minimum (or maximum) value. These methods combine derivation of the line minimum (or maximum) with the reduced sensitivity to spectral noise characteristic of the fixed fraction centroid method.) The results are shown for the 1601 cm^{-1} polystyrene absorption band. The seven methods were not necessarily completely optimized for the study, since the goal was not to select a *best* method, but rather to establish

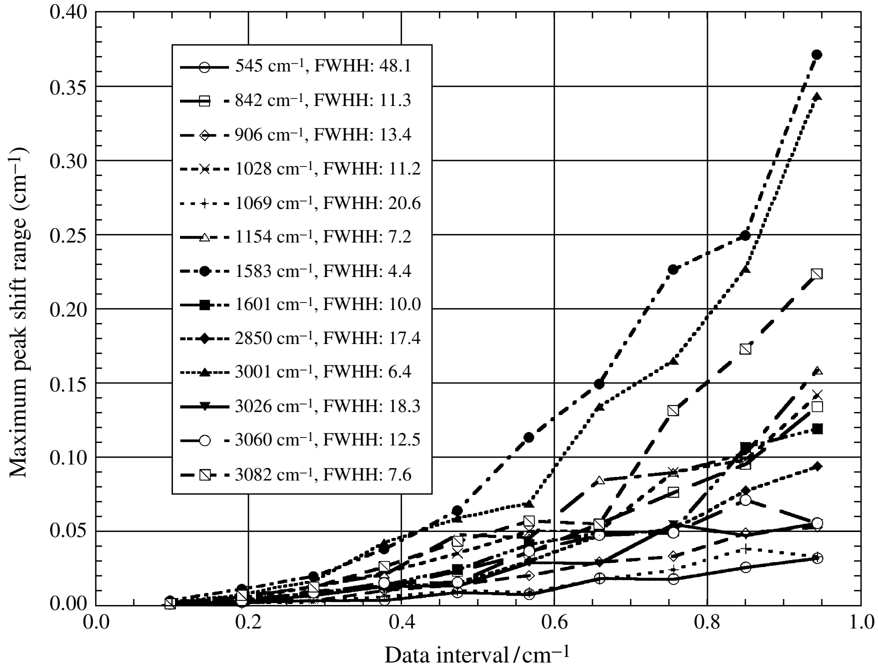

Figure 5. Maximum error in location of transmittance minima of 13 absorption bands of NIST polystyrene standards due to finite data interval. The minima are determined using a centroid method (with 0.5 fraction). The plotted curves are identified along with the width of each band. [Reproduced by permission of the International Society of Optical Engineering from C. Zhu and L. M. Hanssen, in 'Optical Diagnostic Methods for Inorganic Transmissive Materials', eds R. U. Datla and L. M. Hanssen, *Proc. Soc. Photo.-Opt. Instrum. Eng.*, **3425**, 111 (1998).]

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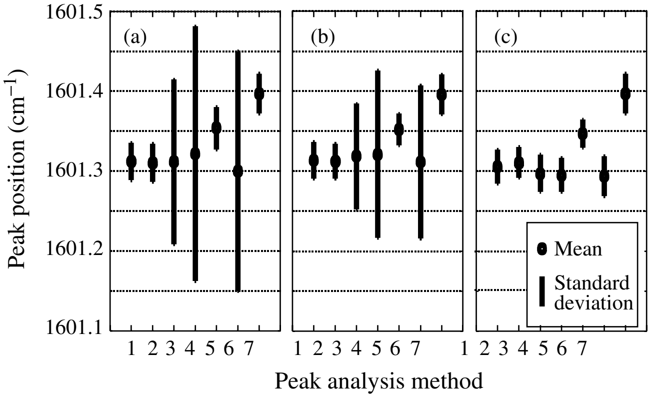

Figure 6. Comparison of methods for wavenumber evaluation applied to the 1601 cm^{-1} band of polystyrene. [From C. Zhu and L. M. Hanssen, in 'Optical Diagnostic Methods for Inorganic Materials II', ed. L. M. Hanssen, *Proc. Soc. Photo.-Opt. Instrum. Eng.*, **4103**, 62 (2000).]

a level of *agreement* between all the selected methods. Method (7) was included for comparison purposes only and should not be expected to agree with the other six methods. The EC method has been developed for providing users with calibration values associated with band or line minima (or maxima) that can be compared directly with those obtained from most peak analysis software. In the future, calibration values obtained from the EC method will be provided along with those currently available from the 0.5 fraction centroid method for the NIST polystyrene standard 1921A.

5 CONCLUSIONS

IR wavenumber standards for the vapor phase have steadily improved over the past century. Currently, the accuracy of frequency measurements and the knowledge of numerous gas absorption line wavenumber values enable very good calibration of high-resolution spectrometers for similar high-resolution measurements over large portions of the IR spectral range. In the future, more complete knowledge of an increasing number of gas species spectral absorption lines should fill in the remaining gaps in the spectral coverage. Polystyrene has proved to be a useful wavenumber standard for calibration of moderate- to low-resolution spectral measurements. However, the need for physical wavenumber standards with uncertainties less than or equal to 0.1% is unlikely to diminish over time. This necessitates the development of new standards and/or improvements in the current one. It also will require either the use of a standard method for calibrated absorption band analysis, or the demonstrated equivalence of a number of methods used for producing wavenumber values.

ABBREVIATIONS AND ACRONYMS

ASTM	American Society of Testing and Materials
EB	Extrapolated Bisecting
EC	Extrapolated Centroid
HITRAN	High-resolution Transmission Molecular Absorption Database
IUPAC	International Union of Pure and Applied Chemistry
NBS	National Bureau of Standards
NIST	National Institute of Standards and Technology
NMI	National Metrology Institute
NPL	National Physical Laboratory
NRC	National Research Council

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