

# Intrinsic Wavelength Standard Absorption Bands in Holmium Oxide Solution for UV/visible Molecular Absorption Spectrophotometry

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The transmittance minima of 18 absorption bands of a solution of 40 g/L holmium oxide in 10% (volume fraction) perchloric acid are certified as intrinsic traceable wavelength standards, by means of a multicenter measurement on material from a single source coupled with comparisons of a variety of preparations of the material evaluated on a single instrument. Fit-for-purpose artifact standards for the experimental calibration or validation of wavelength scales of chemical spectrophotometers can be carefully produced by end users themselves or by commercial standards producers. The intrinsic (data) standard confers traceability to the SI unit of length in place of costly transfer artifacts and repetitive calibration procedures. Certified values are provided for instrumental spectral bandwidths of 0.1–3.0 nm in 0.1 nm intervals, and information values are provided to a spectral bandwidth of 10 nm at wider intervals. Expanded uncertainties are typically less than  $\pm 0.1$  nm for certified band positions. © 2005 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [DOI: 10.1063/1.1835331]

Key words: certified wavelengths; holmium oxide solution; intrinsic standards; molecular absorption; reference materials; spectral convolution; UV/visible spectrophotometry; wavelength standards.

## Contents

1. Introduction.....	43
1.1. Background.....	43
1.2. Traceability.....	44
1.3. Instrument Dependence.....	45
2. Experiment.....	45
2.1. Multicenter Value Assignment of Band Positions.....	45
2.1.1. Samples.....	45
2.1.2. Measurement Conditions.....	45
2.2. Supplemental Experiments.....	46
2.2.1. Variation Within and Across SRM 2034 Preparations.....	46
2.2.2. Variation Across Sources.....	46
2.2.3. Temperature Dependence.....	46
2.2.4. Concentration Dependence.....	46
3. Results and Discussion.....	47
3.1. Consensus Band Positions.....	47
3.2. Deviation from Consensus Values.....	48
3.3. Slit Function.....	48
3.4. Band Shape and Location Uncertainty.....	49
3.5. Effect of Temperature.....	49
3.6. Variation Across Solution Preparations.....	49
3.7. Effect of Concentration.....	49
3.8. Intrinsic Spectrum.....	49
3.9. Interpolation by Theoretical Slit Function Convolution.....	50
4. Conclusions.....	55
5. Disclaimer.....	55
6. References.....	55

## List of Tables

1. Participant instruments and data supplied.....	46
2. Holmium oxide solution preparations other than NIST SRM 2034.....	46

3. Measured consensus band positions for three spectral bandwidths (SBWs).....	47
4. Locations of band minima as a function of SBW.....	51

## List of Figures

1. The transmittance spectrum of dilute acidic holmium oxide solution at 0.1 nm SBW.....	44
2. A comparison of the band positions as returned by a single participating instrument with the consensus mean values.....	48
3. “Single channel” (emission) spectra of the deuterium $D_{\alpha}$ line at spectral slit width settings.....	48
4. Summary of temperature dependence data at an SSW of 1.0 nm.....	49
5. Concentration dependence of the spectral position of the minimum of Band 1.....	50
6. A portion of the 0.1 nm SBW spectrum and as broadened by convolution of a triangle function to 1, 3, 5, and 10 nm SBW values.....	50
7. A graphical view of the computed SBW trajectories and their uncertainties, compared with the experimental SSW results.....	54

## 1. Introduction

The present work establishes the transmittance minima of 18 absorption bands of a solution of 40 g/L holmium oxide in 10% (volume fraction) perchloric acid as intrinsic wavelength standards, by means of an exhaustive multicenter measurement on material from a single source coupled with comparisons of a variety of preparations of the material evaluated on a single instrument. The wavelength location of each absorption band minimum is a fundamental property of the ideal absorption spectrum of the solution, in the absence of instrumental broadening.

### 1.1. Background

Dilute holmium oxide solutions permanently sealed into fused silica cuvettes have been widely adopted as reference

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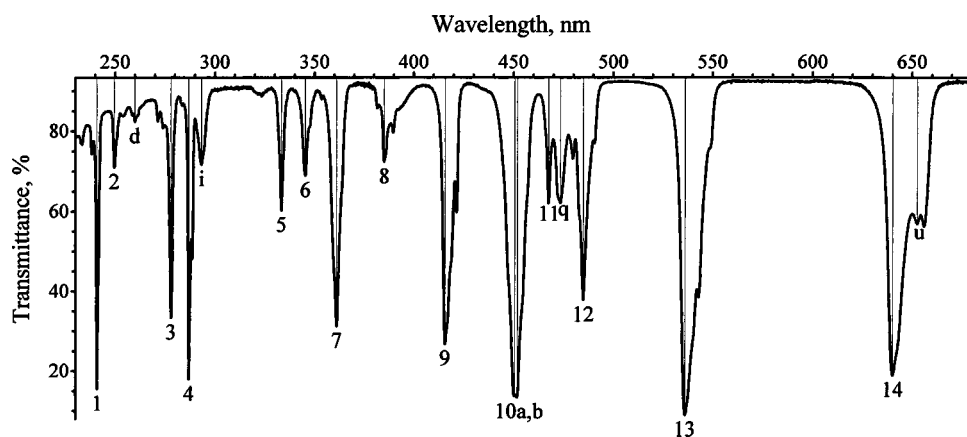


FIG. 1. The transmittance spectrum of dilute acidic holmium oxide solution at 0.1 nm SBW, identifying the absorption bands evaluated here as intrinsic wavelength standards.

materials for calibration or validation of the wavelength scale in chemical spectrophotometry.<sup>1-5</sup> The methods and procedures used in the initial development and study of National Bureau of Standards (NBS) Standard Reference Material (SRM) 2034 have been described in detail previously by Weidner *et al.*<sup>1</sup> and in NBS Special Publication 260-102.<sup>2</sup> Holmium is postulated to exist as the aquo ion of the general formula  $\text{Ho}(\text{H}_2\text{O})_n^{3+}$  (or  $\text{Ho}_{\text{aq}}^{3+}$ ) when  $\text{Ho}_2\text{O}_3$  is dissolved in aqueous perchloric acid.<sup>6,7</sup> The expression “holmium oxide solution” and the spectral band positions reported in this work refer to this chemical species, known also as “holmium perchlorate solution.”<sup>4,5</sup> The aqueous perchloric acid solvent was used from the beginning by NBS (now the National Institute of Standards and Technology, or NIST) since the coordination of the resulting  $\text{Ho}_{\text{aq}}^{3+}$  is relatively stable to changes in temperature and concentration.<sup>1,8</sup> The 14 certified bands of SRM 2034 (and a number of previously uncertified bands) in the spectral range from 240 to 650 nm are due to absorption of incident radiation by  $\text{Ho}_{\text{aq}}^{3+}$ . The spectrum of the holmium oxide solution is shown in Fig. 1, with the NIST-certified bands identified by number. A few additional bands identified by letters are candidates for certification based on a prior study.<sup>9</sup> Term assignments corresponding to the absorption bands may be found in the literature.<sup>10</sup>

The true location of the wavelength of a transmittance band minimum of a holmium oxide solution wavelength standard of a controlled composition is a spectroscopic property that should remain constant as long as the solution is chemically stable. If there is a significant change in the chemical composition of the material, however,  $\text{Ho}_{\text{aq}}^{3+}$  may form complexes that have different spectral characteristics. Absorption bands that show abnormal variations in response to the environment of rare earth ions are designated as “hypersensitive.”<sup>11</sup> For  $\text{Ho}_{\text{aq}}^{3+}$ , this designation is applied particularly to the  $^5\text{I}_8 \rightarrow ^5\text{G}_6$ ,  $^5\text{F}_1$  absorption band (Band 10 in Fig. 1)<sup>11,12</sup> and, to a lesser extent, to the  $^5\text{I}_8 \rightarrow ^5\text{G}_5$  (Band 9) and  $^5\text{I}_8 \rightarrow ^5\text{F}_5$  (Band 14) bands.<sup>13</sup>

Wavelength accuracy requirements for chemical analysis may be inferred from the Pharmacopoeial literature. For calibration with a transmission wavelength standard, the Japanese Pharmacopoeia specifies an accuracy of  $\pm 0.5$  nm.<sup>14</sup> The British and European Pharmacopoeias require an accu-

racy of  $\pm 1.0$  nm in the ultraviolet (UV) and  $\pm 3.0$  nm in the visible spectral region.<sup>4,5</sup> Other Pharmacopoeias suggest that analyte band maxima should be found experimentally to be within  $\pm 1$  nm<sup>3</sup> or  $\pm 2$  nm<sup>15</sup> of the value specified in the monograph.

In addition to the holmium oxide solution considered here, other materials utilized as wavelength standards in transmittance may be found by similar studies to provide intrinsic wavelength standard absorption bands. Several alternative wavelength standards provide coverage to both shorter and longer wavelengths than the holmium oxide solution. The most widely used artifact wavelength standards in transmittance are based upon various rare earth species in solution or in glass or crystalline matrices. These include holmium glass,<sup>15,16</sup> didymium glass,<sup>3,17</sup> a solution containing holmium and neodymium,<sup>18</sup> a proprietary rare earth solution,<sup>19</sup> and two proprietary rare earth-doped crystals.<sup>20</sup> Samples of the crystalline material known as the “Nelson standard” were made available to willing participants in the present study, and the results of that study will be published separately.

## 1.2. Traceability

Assertion of traceability of a measurement to the meter (metre) requires “an unbroken chain of comparisons all having stated uncertainties” relating the measurement to “stated references.”<sup>21</sup> For the certified band positions reported here, the stated references are atomic spectral lines widely regarded as traceable to the meter, and the evaluation of the uncertainties is supported by the large number of instruments and participants employed in the comparison of these references to the holmium oxide solution band positions.

Recent studies<sup>9,22,23</sup> suggest the possibility that certain band positions for holmium oxide solutions meeting carefully prescribed specifications could be assigned intrinsic values with uncertainties considered fit-for-purpose for many chemical measurements. The study reported here of solutions obtained from a variety of sources supports the intrinsic nature of the certified values for a limited range of holmium oxide concentration.

Artifact standards for the experimental calibration or validation of wavelength scales may thus be carefully produced

by end users themselves or by commercial standards producers, with traceability to the *Système International d'Unités* (International System of Units, or SI) conferred by the intrinsic (data) standard reported here in lieu of costly batch-certified transfer artifacts and repetitive traceable calibration procedures.

### 1.3. Instrument Dependence

Throughout this discussion, the term “spectral slit width” (SSW) is used to denote the intended full width at half maximum (FWHM) of the slit function of an instrument (or the product of the physical slit width and the reciprocal linear dispersion),<sup>24</sup> and the term “spectral bandwidth” (SBW) is used to denote the measured realization of the same quantity. The instrumental SBW is equivalent to the “resolution” as the term is used in the *International Vocabulary of Basic and General Terms in Metrology* (VIM).<sup>21</sup>

The bands of the holmium oxide solution are unresolved collections of transitions that form asymmetric features subject to changes in the apparent position of the band minimum when recorded by an instrument whose SBW is significant with respect to the spectral width of the absorption band. Experimental SBW values for this study range from 0.1 nm (negligible with respect to the narrowest spectral band of the native spectrum) to the relatively significant value of 3.0 nm.

The native (intrinsic) spectrum of the solution (taken to be revealed by the 0.1 nm spectral acquisitions) is convolved with an idealized triangular theoretical slit function to interpolate band positions smoothly between measured values. The resulting band locations given here may thus be used to calibrate instruments of SBW between 0.1 and 3.0 nm against certified, traceable values. Information values are given by theoretical extrapolation for SBWs from 3.0 to 10.0 nm.

## 2. Experiment

### 2.1. Multicenter Value Assignment of Band Positions

#### 2.1.1. Samples

One sample of the 2002 production series of NIST SRM 2034 was sent to each participant. For this series, a new 2 L solution was prepared by dissolving 80 g  $\text{Ho}_2\text{O}_3$  in deionized water and 200 mL high-purity perchloric acid. The dissolution was facilitated by moderate heat (below boiling) on a hot plate. The solution was covered and maintained overnight at room temperature, and was then diluted to calibrated volume with deionized water. The final aqueous solution contained 40 g/L  $\text{Ho}_2\text{O}_3$  in 10% (volume fraction)  $\text{HClO}_4$ .

The 99.99% pure holmium oxide, lot number Ho-0-4-007, was obtained in a prior year from Research Chemicals, Division of Nucor Corp., Phoenix, AZ. The perchloric acid was the NIST high-purity solution prepared by sub-boiling distillation.<sup>25</sup> The de-ionized water was from the NIST Advanced Chemical Sciences Laboratory pure water system.

Both the water and acid were checked spectrophotometrically for their UV absorption properties prior to use.

The fused-silica cuvettes of optical quality were tested for fluorescence with a hand-held source of ultraviolet light. The square cuvette has a nominal 10 mm pathlength and a fused-silica tubular end. One pair of opposing faces is transparent and the other pair of opposing faces is frosted. Cuvettes were filled using an automatic pipette, with approximately 3.5 mL per cuvette. Caps to be glued over the sealed-off necks of the cuvettes were machined from black Delrin in the NIST Fabrication Technology Division, using a numerically controlled mill. The hinged wooden box made to specifications for storing SRM 2034 contains a routed slot inside with foam and felt inserts to protect the cuvette.

#### 2.1.2. Measurement Conditions

The nominal measurement protocol followed that of the earlier studies,<sup>9,22</sup> except for the sample identity and allowances made for instrumental idiosyncrasies. Optimal fulfillment of the protocol called for replicate measurements on separate days of the full spectrum from 230 to 680 nm at a sampling interval of 0.1 nm, and for SBWs of 0.1, 1.0, and 3.0 nm. Wavelength calibration data were to be furnished by means of spectral scans of appropriate calibration lamps or as functional bias correction equations. Acceptable variations included partial scans covering band tips, final measured values of band positions, and alternative SBWs within the range of 0.1–3.0 nm. Optimal sample temperature was 25 °C, but participants were asked to report the actual temperature rather than attempt to control the temperature, due to the known low dependence of band position on temperature.<sup>1,2</sup> The instruments used and the data furnished are summarized in Table 1.

Positions were sought for the bands identified in Fig. 1 by numbers or letters, following the nomenclature of Ref. 1. The numbered bands have been certified in NIST SRM 2034 since 1985, and the lettered bands represent further possibilities (with some eliminated by the earlier study<sup>9</sup>). In spite of the 0.1 nm data interval, band positions were estimated to the nearest 0.01 nm by peak-location algorithms. Prior study has revealed the relative robustness of computer peak location with respect to the details of the algorithm.<sup>9</sup> NIST/Chemical Science and Technology Laboratory (CSTL) peak locations represent the minimum of a cubic polynomial fit to the minimum data point of a given band and the two nearest neighbors on each side. Table 1 indicates whether full spectra, region-of-interest scans (of the band tips), or calibrated band locations were furnished. If spectral scans and band positions were both furnished, the furnished band positions were used in the data analysis. If calibrated full or partial spectral scans were furnished without band position estimates, the NIST/CSTL five-point cubic peak location algorithm was used.

Two sets of spectra from the earlier study were obtained on instruments different from those the participants employed in the current study. After demonstrating that there were no location differences between NIST SRM 2034 Se-

TABLE 1. Participant instruments and data supplied

Country	Lab	Device <sup>a</sup>	SSW/nm	Data <sup>i</sup>
Canada	NRC	L900	0.1, 1, 3	S, P
Canada	NRC	L19	0.1, 1, 3	S, P
Finland	HUT	L900	0.1, 1, 3, 5	S
France	CNAM	PB <sup>b</sup>	0.1	P
Germany	PTB	PB <sup>c</sup>	0.1, 1, 3	P
Hungary	OMH	PB <sup>d</sup>	0.3, 1, 3	R
Japan	NMIJ	C500	0.1, 1, 3	S
Japan	NMIJ	U3410	0.1, 1, 3	S
Mexico	CENAM	L19	0.1, 1, 3	P
Mexico	CENAM	C5e	0.1, 1, 3	P
Republic of Korea	KRISS	C5e	0.1, 1, 3	S, P
South Africa	CSIR	PB <sup>e</sup>	2, 4	R, P
Spain	CSIC	L900	0.1, 1, 3	S
Spain	CSIC	L9	0.1, 1, 3	S
Sweden	SP	L900	0.1, 1, 3	R, S, P
Sweden	KUS	C400	0.1, 1, 3, 5	S
Switzerland	METAS	PB <sup>f</sup>	1	R, P
United Kingdom	NPL	C5e	0.1, 1, 3	S
USA	CSTL	L900	0.1, 1, 3	S
USA	CSTL	PB <sup>g</sup>	0.8	R
USA	PL	C5e	0.1, 1, 3, 5	S
USA	PL	PB <sup>h</sup>	1.5, 3.0	R

<sup>a</sup>C5=Varian Cary 5, C5e=Varian Cary 5e, C400=Varian Cary 400, C500=Varian Cary 500, L9=PerkinElmer Lambda 9, L19=PerkinElmer Lambda 19, L900=PerkinElmer Lambda 900, PB=Purpose built, U3410=Hitachi U3410.

<sup>b</sup>Reference Spectrophotometer based on 1.5 m *f*/12 monochromator with holographic 2000/mm grating.

<sup>c</sup>Reference spectrophotometer based on 0.6 m Jobin Yvon HRD1 single-pass double monochromator.

<sup>d</sup>Reference spectrophotometer based on Hillger–Watts double-grating monochromator.

<sup>e</sup>Spectroradiometer based on Jobin von H10D double monochromator.

<sup>f</sup>Reference spectrophotometer based on *f*/5.6 Jobin Yvon HR 640 monochromator.

<sup>g</sup>Reference spectrophotometer based on 1 m McPherson 2061 monochromator.

<sup>h</sup>Reference spectrophotometer based on 1 m McPherson 2051 monochromator.

<sup>i</sup>S=full spectral scan; R=region-of-interest scan about bands; P=band positions.

ries 02 and Series 99 materials (see below), these data were added to the current study (identified as two “L19” instruments in Table 1).

## 2.2. Supplemental Experiments

Supplemental studies were performed at NIST to establish the robustness of the values assigned to a single sample batch with respect to material properties and to temperature.

The instrument used for all of these studies was the NIST/CSTL PerkinElmer 900 spectrophotometer. Except for the temperature dependence experiment, the temperature was controlled to  $25 \pm 0.2$  °C in all cases. In all cases, replicate spectra were acquired for each sample, with removal and replacement of the sample in the instrument between runs. An SSW of 1.0 nm was employed, and band positions were extracted with the NIST/CSTL five-point cubic algorithm.

### 2.2.1. Variation Within and Across SRM 2034 Preparations

Eight samples of NIST SRM 2034 (Series 02) were chosen randomly to determine the variability of band position within a single material preparation. To study the same variability across different preparations of SRM 2034, spectra were acquired for at least one sample retained by NIST/CSTL for each year in which SRM 2034 has been produced since the introduction of the material in 1985. Samples included all series produced prior to 2002, designated by the last two digits of the production year with a letter appended to delineate separate batches: 85a, 85b, 86, 88, 91, 94, 95, 96, 98, 99, and 01. A sample from Series 02 was included as both a participant and a control for each run required using the nine-position sample carousel.

### 2.2.2. Variation Across Sources

Six samples of dilute, acidic holmium oxide solution were obtained from sources other than NIST, for comparison with the NIST SRM 2034 Series 02 sample (Table 2). Spectra of these samples were run following the protocol for all three bandwidths. Spectra were furnished by NPL for a control sample containing dilute holmium oxide and an additional rare earth oxide.

### 2.2.3. Temperature Dependence

Replicate scans for sample temperatures from 25 to 45 °C in 5 °C increments were acquired by using two samples of SRM 2034 (02) in the temperature-controlled sample carousel of the NIST/CSTL instrument. The range was limited to temperatures above ambient by malfunction of the cooling element. Data were acquired for both 0.1 and 1.0 nm SBWs.

### 2.2.4. Concentration Dependence

The dependence of band position on holmium oxide concentration was studied using samples of nominal 10, 20, 35, 40, and 60 g/L holmium oxide in solution. Samples at the

TABLE 2. Holmium oxide solution preparations other than NIST SRM 2034

Source	Designation	SSW/nm	Date
Perkin-Elmer	C005-0403	0.1, 0.25, 0.5, 1, 2, 3	1991
Merck KGaA	UV/vis Standard 6 (1.08166)	0.1, 0.25, 0.5, 1, 2, 3	1996
Starna Cells, Inc.	RM-HL	0.1, 0.25, 0.5, 1, 1.5, 2, 3	2002
Slovak Institute of Metrology	CRM J01	0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 11	1999
Stranaska, LLC	CRM 100	0.1, 0.25, 0.5, 1, 2, 3	2002
CENAM	CRM 41-e	0.1, 1, 3	2000

TABLE 3. Measured consensus band positions for three spectral bandwidths (SBWs)

Band	0.1 nm SBW				1.0 nm SBW				3.0 nm SBW			
	$N^a$	$\lambda_{\min}^b$	$\pm U_{95}^c$	$\pm P_{95}^d$	$N^a$	$\lambda_{\min}^b$	$\pm U_{95}^c$	$\pm P_{95}^d$	$N^a$	$\lambda_{\min}^b$	$\pm U_{95}^c$	$\pm P_{95}^d$
1	17	240.98	0.04	0.18	17	241.12	0.05	0.21	16	241.03	0.06	0.25
2	17	249.80	0.05	0.22	17	249.87	0.06	0.24	16	250.06	0.09	0.36
d	17	259.98	0.08	0.34	16	260.22	0.07	0.30	16	260.12	0.09	0.36
3	17	278.16	0.04	0.17	18	278.13	0.05	0.20	17	278.04	0.06	0.27
4	17	287.02	0.04	0.19	18	287.19	0.06	0.28	18	287.61	0.07	0.33
i	17	293.34	0.04	0.18	17	293.39	0.05	0.21	17	293.33	0.07	0.30
5	17	333.49	0.04	0.17	18	333.47	0.04	0.19	18	333.48	0.07	0.31
6	17	345.47	0.05	0.21	18	345.39	0.04	0.19	18	345.52	0.07	0.32
7	18	361.29	0.04	0.17	18	361.25	0.03	0.15	19	361.09	0.06	0.29
8	18	385.38	0.04	0.19	18	385.61	0.04	0.19	18	385.99	0.09	0.37
9	18	416.05	0.04	0.17	18	416.26	0.05	0.23	18	416.86	0.08	0.35
10a	18	450.63	0.04	0.17			NA <sup>e</sup>				NA <sup>e</sup>	
10b	18	452.02	0.04	0.17	17	451.40	0.05	0.23	19	451.28	0.05	0.23
11	18	467.78	0.03	0.15	18	467.82	0.03	0.11	18	468.11	0.06	0.22
q	18	473.75	0.05	0.21	18	473.52	0.03	0.12	19	473.53	0.06	0.24
12	18	485.21	0.04	0.17	18	485.23	0.04	0.16	19	485.21	0.06	0.23
13	18	536.43	0.04	0.16	18	536.56	0.04	0.17	19	537.19	0.07	0.29
14	18	640.43	0.03	0.13	18	640.50	0.03	0.12	19	641.11	0.06	0.25
u	18	652.68	0.05	0.21	18	652.69	0.04	0.14	15	653.12	0.18	0.65

<sup>a</sup>Number of spectrophotometers providing data for this band at this SBW.

<sup>b</sup>The mean (in nm) of the  $N$  values of the band transmittance minimum at this SBW.

<sup>c</sup>Approximate 95% confidence interval (Ref. 26) in nm, of the mean value:  $\pm t_{(0.025, N-1)} \times s / \sqrt{N}$ , where  $t_{(0.025, N-1)}$  is the two-sided student's  $t$  for 95% confidence at  $N-1$  degrees of freedom and  $s$  is the standard deviation of the  $N$  values. The true value for each transmittance minimum at this SBW is expected, with about 95% confidence, to be within this interval.

<sup>d</sup>Approximate 95% prediction interval (Ref. 26) in nm:  $\pm t_{(0.025, N-1)} \times s / \sqrt{(1+1/N)}$ . The next single measurement of the location of this peak at this SBW made using a measurement system from the same population as those used by the participants in this study is expected, with about 95% confidence, to be within this interval.

<sup>e</sup>There is no transmittance minimum at this SBW.

lowest two mass concentrations were prepared by dilution from the stock solution for SRM 2034 Series 02. Samples of nominal 20 and 60 g/L were found among the non-NIST preparations of holmium oxide solutions, with the mass concentrations inferred from the absorbance values. The 35 g/L nominal mass concentration sample was one of two batches of the original Series 85 of SRM 2034.

### 3. Results and Discussion

#### 3.1. Consensus Band Positions

The measured consensus band positions compiled from the multicenter measurement are summarized in Table 3 for the three SBWs of the study. The consensus value is taken as the unweighted mean, as the data is sparse (two spectra for each instrument and SBW) and the repeatability is unrelated to the bias. Uncertainty intervals  $\pm U_{95}$  are 95% confidence intervals for the true value, computed from the estimated standard deviation of the mean appropriately expanded for the number of data sets used.<sup>26</sup> Prediction intervals,  $\pm P_{95}$ , define the range in which a single future determination would be expected to fall with a level of confidence of 95%.<sup>26</sup> The prediction intervals are comparable to the uncertainties of prior studies with fewer participants,<sup>9,22</sup> and to the revised uncertainties for SRM 2034 (Series 01). They are also useful in assigning acceptable performance limits for

testing a single instrument on the basis of a single spectrum.

Determinations of band positions of absorption wavelength standards with a single instrument have required estimates of "type B" uncertainty components, formerly known as systematic errors, which are not subject to assessment by statistical methods but require an educated estimate. For NIST SRM 2034, these included an estimate of the inaccuracy of calibration of the measuring instrument with atomic pen lamps and an estimate of the inaccuracy of locating peak minima.<sup>1,2</sup> In the present case, the first of these is now confounded into the data experimentally by the use of multiple research grade instruments with skilled operators. The second is partially confounded by the use of multiple peak location algorithms, and was shown in an earlier study<sup>9</sup> to be negligible in comparison with the first. Temperature effects were originally found to be negligible over the range from 20 to 30 °C for SRM 2034,<sup>1,2</sup> and this finding is further supported below.

The present study supports a further potential source of calibration bias resulting from a difference in the optical alignment of the calibration pen lamp and the alignment of the system continuum lamp(s) to the spectrometer. This uncertainty is also confounded into the final result by the multicenter approach. We therefore assert that the uncertainties shown in Table 3 represent a complete description of the uncertainty budget for the intrinsic standard.

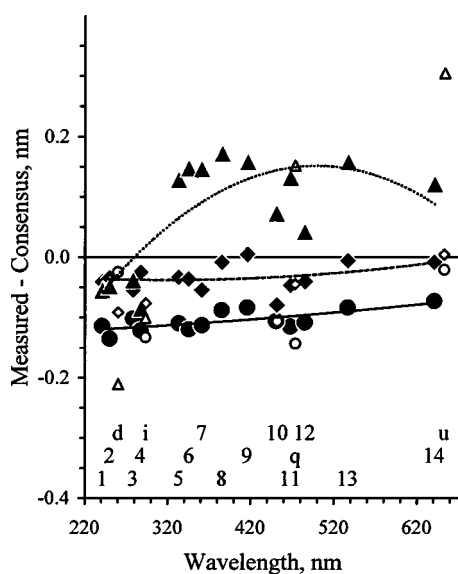


FIG. 2. A comparison of the band positions as returned by a single participating instrument with the consensus mean values. Symbols shapes indicate SBWs of 0.1 nm (circles), 1.0 nm (diamonds), and 3.0 nm (triangles). Symbols are filled for bands certified in NIST SRM 2034, and empty otherwise.

### 3.2. Deviation from Consensus Values

Wavelength bias as a function of wavelength and SSW is indicated for each participating instrument by comparison of the band positions returned by that instrument with the consensus band positions for all participants. Figure 2 shows such a comparison for one of the participating instruments. To put the illustrated deviations from consensus in context, the average ability to calibrate a given participant instrument based upon the consensus values (at the 95% confidence level) is reasonably well indicated by the average of the prediction intervals for a given SBW in Table 3. The similarity of this value for the 0.1 and 1.0 nm SSW data may carry either or both of two implications: (1) the ability to calibrate the instrument with atomic line pen lamps is roughly equivalent for SSW values below about 1 nm or (2) the observed spectrum of holmium oxide solution does not change radically over this range of SSWs.<sup>1,2</sup>

The example shown in Fig. 2 is typical of most of the instruments, inasmuch as the average bias (from the consensus) may exceed the scatter about the fit (residual standard deviation) for one or more of the three SSW values studied. This behavior supports the perhaps radical claim<sup>9</sup> that spectrophotometers can be more consistently calibrated with respect to each other by using the holmium oxide solution standard than by using atomic pen lamps. Given the superior nature of the atomic emission line profiles, the clear implication is that the absorbing standard accurately represents the axis defined by the optical train containing the continuum lamp(s), whereas the emission standard may not.

With few exceptions, the largest diversions from consensus were for the 3.0 nm bandwidth data as shown. This is expected since the wider slits permit wider angular alignment excursions and are more difficult to fill uniformly with

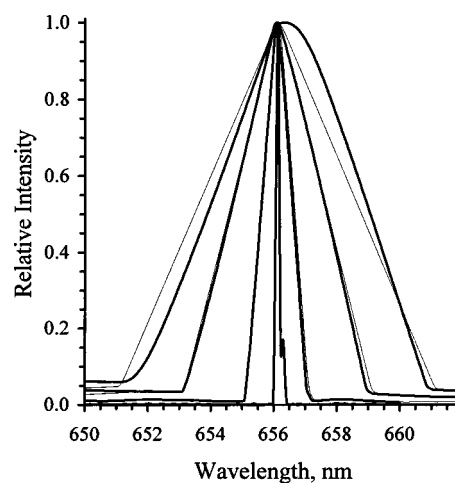


FIG. 3. "Single channel" (emission) spectra of the deuterium  $D_{\alpha}$  line at spectral slit width (SSW) settings of 0.1 nm (inside envelope), 1, 3, and 5 nm (outside envelope). The dark traces are experimental and the light traces are numerical convolutions. The 5 nm result illustrates the effect of nonuniform slit illumination when calibrating and using high-resolution instruments at large slit settings. At 0.1 nm SSW, the residual hydrogen  $H_{\alpha}$  line can be seen.

the image of the calibration lamp. The results from several instruments also showed the shift seen here between the data acquired with the visible lamp and that acquired with the UV lamp for the 3 nm SBWs, implying that the two lamps do not share completely a common optical axis or do not illuminate the entry slit in an equivalent fashion. (The abrupt transition at about 315 nm is ameliorated to the eye by the fitted smooth curve.)

### 3.3. Slit Function

Nonuniform illumination of the entry slit can result in deviations of the slit function from the triangular ideal, as is shown in Fig. 3 for the deuterium  $D_{\alpha}$  line at 656.1 nm<sup>27</sup> on one of the participating instruments. (At high resolution, the residual hydrogen  $H_{\alpha}$  line characteristic of these lamps is also seen.) In this case, the instrument performs well out to the 3 nm limit of this study, but demonstrates asymmetry and shift in the slit function at the extra SSW of 5 nm furnished by this participant. The digression from consensus at 3 nm shown in Fig. 2, as well as by several other instruments, indicates that the onset of nonuniform slit illumination may occur at lower SSWs for some instruments than for that of Fig. 3. Significant departures from symmetry and changes in apparent SBWs and wavelength calibration have been observed on the NIST/CSTL instrument for different pen lamp alignments.

Slit function symmetry is easiest to achieve with the smaller entry slits corresponding to 0.1 and 1.0 nm SBWs for research grade instruments such as these. For many small instruments used for routine analysis, the slit function may actually be closer to the ideal at large SBWs than for these instruments, since the physical slit width would be smaller than the image of the source lamp.



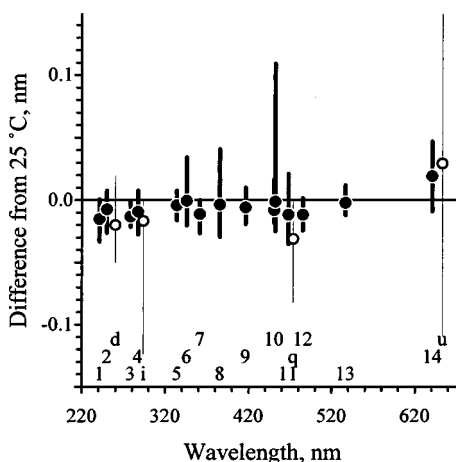


FIG. 4. Summary of temperature dependence data at an SSW of 1.0 nm. Each data point represents the average of four shifts of the position of a single band from the position determined at 25 °C to the position at 30, 35, 40, and 45 °C. The bar represents the range of these four temperature shifts. The solid symbols represent bands certified in SRM 2034 and the open symbols represent additional bands reported here.

### 3.4. Band Shape and Location Uncertainty

The two greatest residuals in Fig. 2, for features *d* and *u* at the 3 nm SSW, are not outliers but are illustrative of some of the larger prediction intervals of Table 3. Comparison of the band positions found by participant peak location algorithms with those found by the NIST/CSTL algorithm confirms the previous finding<sup>9</sup> that the algorithm is not responsible for the relatively large dispersion of results for particular bands. Rather, the fault lies in the shape and structure of these bands and on the possibility that false local minima may result from noise superimposed on relatively flat-tipped bands, as may be inferred from Fig. 3 of Ref. 9.

### 3.5. Effect of Temperature

The results of the temperature study at an SBW of 1.0 nm and over the temperature range of 25–45 °C are summarized in Fig. 4. At each wavelength, the data point is the average departure of the band location at the four other temperatures (30, 35, 40, and 45 °C) from the band location at 25 °C. The bars indicate the maximum and minimum deviations from the 25 °C band location. The dispersion implied by these bars is generally not distinguishable from the reproducibility of locating the bands for replicate measurements at the same temperature on a single instrument. The few maximum or minimum excursions exceeding 0.05 nm in magnitude are found to represent apparent wavelength shifts resulting from temperature-dependent amplitudes of adjacent features. For this reason it is prudent to restrict the temperature range for normal use to  $25 \pm 5$  °C as originally recommended by Weidner *et al.*<sup>1,2</sup> for SRM 2034.

### 3.6. Variation Across Solution Preparations

Example spectra from one sample of SRM 2034 prepared in each of the 12 batches prepared at NIST revealed minor differences in the baseline and absorption amplitude. Baseline effects have been attributed to the purity of the holmium oxide powder,<sup>1</sup> to organic impurities in the acid or water used, or to cuvette-specific effects resulting from local contamination and/or differences in cuvette windows. Amplitude differences result from minor concentration variations. Shifts in the apparent positions of the shortest-wavelength certified bands caused by baseline effects are trivial with respect to the uncertainties given in Table 3. The prior batches of SRM 2034 were prepared by the same individual using the same stock of holmium oxide powder, but with several variations of acid, water, and cuvette manufacturer.

Two of the holmium oxide preparations shown in Table 2 gave experimental evidence of being prepared at mass concentrations other than 40 g/L, and one yielded a significant baseline effect in the UV portion of the spectrum. In spite of these differences, band positions obtained from spectra of all of these samples are well within the stated uncertainties of those reported here for NIST SRM 2034 (Series 02). However, a distinguishable mass concentration effect for certain bands led to the study reported below.

### 3.7. Effect of Concentration

Figure 5 illustrates a slight concentration dependence in the spectral position of the minimum of Band 1. In the lower plot, data for 10, 20, and 60 g/L concentrations at 1 nm SSW have been normalized in absorbance space to overlay with the 40 g/L data to visualize the effect. The absolute wavelength excursion across this concentration range for Bands 1 and 4 is 0.05 nm. The minima for Bands 9, 13, and 14 also systematically shift with concentration but by less than 0.03 nm. This finding contradicts the original reports<sup>1,2</sup> and supports adherence to the nominal 40 g/L solution for the intrinsic standard.

### 3.8. Intrinsic Spectrum

The intrinsic spectrum is proposed here as a means of verifying that a preparation of holmium oxide solution is qualified to convey traceability through the certified band positions of Table 3.

The spectrum presented in Fig. 1 is wavelength calibrated to the consensus scale within  $\pm 0.1$  nm for all of the bands given in Table 3. The spectrum will be made available electronically through the NIST web site<sup>28</sup> for overlay with experimental spectra of candidate materials acquired with 0.1 nm SBWs and 0.1 nm data spacing. While the wavelength axes of these overlaid spectra may not coincide exactly, visual observation should verify that no additional features are present (contamination) and that the known features of holmium oxide solution are present in the desired proportions. Variation in the baseline from about 230 to 275 nm results from differences in cuvettes or contamination in the cuvette

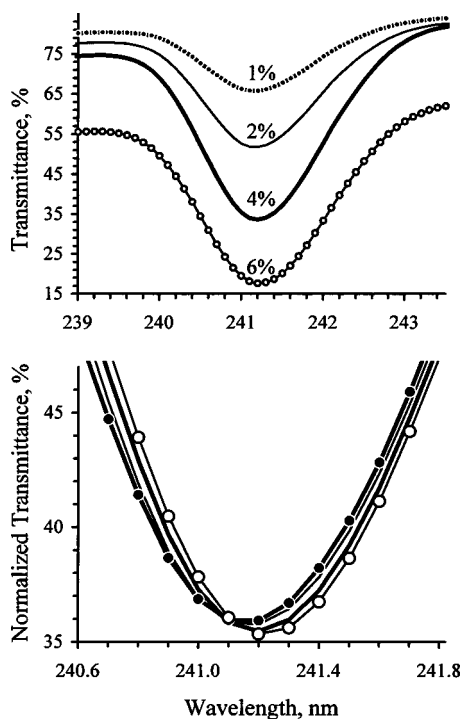


FIG. 5. Concentration dependence of the spectral position of the minimum of Band 1. The upper section displays the spectral segments of 10 g/L (1%), 20 g/L (2%), 40 g/L (4%), and 60 g/L (6%) solutions as acquired. The lower section displays the spectral segments at expanded graphical resolution and normalized in absorbance space to the 40 g/L spectrum. The band minima shift to higher wavelengths with increasing mass concentration.

or the solvent (the acid and/or water). Although some baseline variation is not critical to the accuracy of the short-wavelength band positions, solutions providing a transmittance value of less than 50% at 230 nm should be rejected and a fresh solution should be prepared with attention to avoiding organic contaminants.

### 3.9. Interpolation by Theoretical Slit Function Convolution

The effect of instrumental broadening on the high-resolution molecular spectrum of Fig. 1 is theoretically modeled by convolving the instrument slit function through the “single channel” spectrum of the light transmitted through the sample, similarly treating the spectrum of the light incident on the sample, and performing the point-by-point ratio of the two broadened spectra to compute the resulting broadened transmittance spectrum. As a practical matter, the continuum lamp spectrum is sufficiently featureless to neglect the effect of the instrument bandwidth on the shape of the incident spectrum. Further, dividing the broadened transmitted spectrum by the original incident spectrum pointwise is mathematically equivalent to simply convolving the instrument slit function (normalized to unit area) through the transmittance spectrum. (The normalization of the slit function compensates for not convolving the incident spectrum.) This latter approach is used here, with the instrumentally broadened transmittance at the  $i$ th wavelength channel  $\bar{T}_i$  related

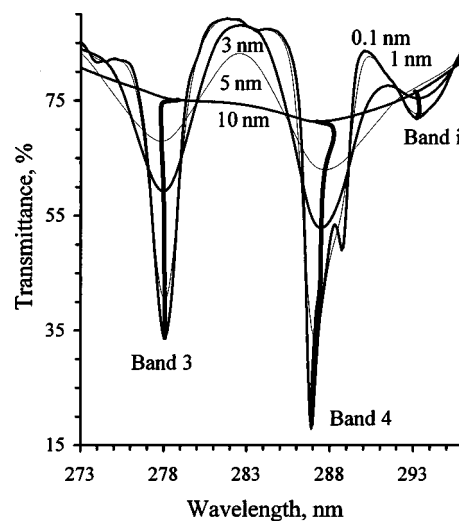


FIG. 6. A portion of the 0.1 nm SBW spectrum and as broadened by convolution of a triangle function to 1, 3, 5, and 10 nm SBW values. The dark lines denote the peak minima as a function of SBW “trajectories,” computed at every bandwidth from 0.1 to 10 nm at 0.1 nm intervals.

to the  $j$ th channel of the intrinsic spectrum  $T_j$  through the area-normalized instrument slit function  $S_k$ , with a maximum at  $k=0$  declining to zero at  $k = \pm n$

$$\bar{T}_i = \sum_{k=-n}^n S_k T_{i-k}, \quad (1)$$

where  $n$  is the number of data intervals required to span one half of the SSW. For an ideal grating spectrometer, the slit function is triangular, representing the image of an entrance slit (evenly illuminated with monochromatic light) being translated across an exit slit of the same size by the rotation of the grating. For convenience, we define the area-normalized theoretical slit function as

$$S_k = \frac{W - |k/10|}{10 \times W^2}, \quad (2)$$

$$k = -10W + 1, -10W + 2, \dots, 0, \dots, 10W - 2, 10W - 1,$$

where  $W$  is the SBW in nm represented as the FWHM of the triangular function and the factors of 10 are unique to the 0.1 nm data spacing employed in this study. [The obvious null end points of the triangle at  $k = \pm 10W$  are omitted because they are inconsequential to the value of Eq. (1)]. This function may be used to theoretically broaden the intrinsic spectrum to the expected experimental spectrum for any SBW that is an integral multiple of the 0.1 nm data spacing.

The NIST/CSTL five-point cubic band location algorithm used for experimental data is also used here to track the “trajectory” of the apparent peak location with theoretical SBW for discreet convolutions. Figure 6 overlays trajectories

TABLE 4. Locations of band minima as a function of SBW

SBW <sup>a</sup>	Band 1			Band 2			Band d			Band 3		
	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$
0.1	240.97	0.05	0.21	249.78	0.05	0.21	259.99	0.06	0.25	278.15	0.05	0.20
0.2	240.97	0.05	0.21	249.78	0.05	0.21	260.01	0.06	0.23	278.15	0.05	0.20
0.3	240.98	0.05	0.21	249.79	0.05	0.21	260.02	0.06	0.23	278.15	0.05	0.20
0.4	241.00	0.05	0.21	249.80	0.05	0.21	260.03	0.06	0.23	278.15	0.05	0.20
0.5	241.02	0.05	0.21	249.81	0.05	0.21	260.05	0.06	0.23	278.15	0.05	0.20
0.6	241.04	0.05	0.22	249.82	0.05	0.21	260.08	0.06	0.24	278.15	0.05	0.20
0.7	241.07	0.05	0.22	249.84	0.05	0.21	260.11	0.06	0.24	278.15	0.05	0.21
0.8	241.09	0.05	0.23	249.85	0.05	0.22	260.13	0.06	0.25	278.14	0.05	0.21
0.9	241.10	0.05	0.23	249.87	0.05	0.22	260.16	0.06	0.25	278.14	0.05	0.21
1.0	241.12	0.05	0.23	249.89	0.05	0.22	260.18	0.06	0.26	278.13	0.05	0.22
1.1	241.12	0.05	0.24	249.91	0.05	0.22	260.20	0.06	0.27	278.13	0.05	0.22
1.2	241.13	0.05	0.24	249.93	0.05	0.23	260.21	0.06	0.27	278.12	0.05	0.22
1.3	241.13	0.05	0.25	249.95	0.05	0.23	260.23	0.06	0.28	278.12	0.05	0.23
1.4	241.14	0.05	0.25	249.97	0.05	0.24	260.24	0.06	0.28	278.11	0.05	0.23
1.5	241.13	0.05	0.26	249.98	0.05	0.24	260.26	0.06	0.29	278.11	0.05	0.24
1.6	241.13	0.05	0.26	250.00	0.05	0.24	260.26	0.06	0.30	278.11	0.05	0.24
1.7	241.13	0.05	0.27	250.01	0.05	0.25	260.25	0.06	0.30	278.10	0.05	0.25
1.8	241.12	0.05	0.27	250.02	0.05	0.25	260.23	0.06	0.30	278.10	0.05	0.25
1.9	241.12	0.05	0.28	250.03	0.05	0.26	260.21	0.06	0.31	278.10	0.05	0.26
2.0	241.12	0.05	0.29	250.03	0.05	0.27	260.19	0.06	0.31	278.10	0.05	0.27
2.1	241.11	0.05	0.29	250.04	0.05	0.27	260.17	0.06	0.32	278.10	0.05	0.27
2.2	241.10	0.05	0.30	250.05	0.05	0.28	260.16	0.06	0.33	278.09	0.05	0.28
2.3	241.10	0.05	0.31	250.05	0.05	0.29	260.15	0.06	0.33	278.09	0.05	0.29
2.4	241.09	0.05	0.32	250.05	0.05	0.29	260.15	0.06	0.34	278.09	0.05	0.30
2.5	241.08	0.05	0.33	250.06	0.05	0.30	260.15	0.06	0.36	278.08	0.05	0.30
2.6	241.08	0.05	0.34	250.06	0.05	0.31	260.15	0.06	0.37	278.08	0.05	0.31
2.7	241.07	0.05	0.35	250.06	0.05	0.32	260.15	0.06	0.37	278.07	0.05	0.32
2.8	241.06	0.05	0.36	250.06	0.05	0.33	260.15	0.06	0.39	278.06	0.05	0.33
2.9	241.05	0.05	0.37	250.07	0.05	0.33	260.15	0.06	0.40	278.06	0.05	0.34
3.0	241.04	0.05	0.38	250.07	0.05	0.34	260.15	0.06	0.41	278.05	0.05	0.35
4.0	241.00	0.05	f	250.11	0.05	f	260.11	0.06	f	277.98	0.05	f
5.0	240.97	0.05	f	250.15	0.05	f	259.85	0.07	f	277.93	0.05	f
6.0	240.93	0.05	f	250.13	0.05	f	258.89	0.17	f	277.90	0.05	f
7.0	240.87	0.05	f	250.05	0.05	f		NA <sup>c</sup>		277.87	0.05	f
8.0	240.79	0.05	f		NA <sup>e</sup>			NA <sup>e</sup>		277.90	0.05	f
9.0	240.78	0.05	f		NA <sup>e</sup>			NA <sup>e</sup>		278.60	0.05	f
10.0	240.78	0.06	f		NA <sup>e</sup>			NA <sup>e</sup>		NA <sup>e</sup>		NA <sup>e</sup>

SBW <sup>a</sup>	Band 4			Band i			Band 5			Band 6		
	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$
0.1	287.03	0.05	0.20	293.32	0.05	0.21	333.48	0.04	0.18	345.46	0.05	0.20
0.2	287.03	0.05	0.20	293.32	0.05	0.19	333.48	0.05	0.18	345.46	0.05	0.19
0.3	287.04	0.05	0.20	293.33	0.05	0.19	333.47	0.05	0.18	345.45	0.05	0.19
0.4	287.06	0.05	0.20	293.33	0.05	0.19	333.47	0.05	0.19	345.44	0.05	0.19
0.5	287.08	0.05	0.20	293.33	0.05	0.19	333.47	0.05	0.19	345.43	0.05	0.19
0.6	287.10	0.05	0.20	293.34	0.05	0.19	333.48	0.05	0.19	345.42	0.05	0.19
0.7	287.13	0.05	0.21	293.34	0.05	0.19	333.48	0.05	0.19	345.41	0.05	0.20
0.8	287.16	0.05	0.21	293.35	0.05	0.19	333.48	0.05	0.20	345.40	0.05	0.20
0.9	287.19	0.05	0.21	293.37	0.05	0.20	333.48	0.05	0.20	345.39	0.05	0.20
1.0	287.22	0.05	0.22	293.38	0.05	0.20	333.48	0.05	0.20	345.38	0.05	0.20
1.1	287.24	0.05	0.22	293.39	0.05	0.21	333.49	0.05	0.21	345.38	0.05	0.21
1.2	287.28	0.05	0.22	293.41	0.05	0.21	333.49	0.05	0.21	345.38	0.05	0.21
1.3	287.31	0.05	0.23	293.42	0.05	0.22	333.49	0.05	0.22	345.38	0.05	0.22
1.4	287.35	0.05	0.23	293.43	0.05	0.22	333.49	0.05	0.22	345.38	0.05	0.22
1.5	287.40	0.05	0.24	293.43	0.05	0.23	333.49	0.05	0.23	345.38	0.05	0.23
1.6	287.44	0.05	0.24	293.44	0.05	0.23	333.48	0.05	0.23	345.39	0.05	0.23
1.7	287.47	0.05	0.25	293.44	0.05	0.24	333.48	0.05	0.24	345.39	0.05	0.23
1.8	287.50	0.05	0.26	293.44	0.05	0.25	333.48	0.05	0.24	345.40	0.05	0.24
1.9	287.51	0.05	0.26	293.44	0.05	0.25	333.47	0.05	0.25	345.41	0.05	0.25
2.0	287.52	0.05	0.27	293.43	0.05	0.26	333.47	0.05	0.26	345.42	0.05	0.25
2.1	287.53	0.05	0.27	293.43	0.05	0.26	333.47	0.05	0.26	345.43	0.05	0.26
2.2	287.54	0.05	0.28	293.42	0.05	0.27	333.47	0.05	0.27	345.44	0.05	0.26

TABLE 4. Locations of band minima as a function of SBW—Continued

SBW <sup>a</sup>	Band 4			Band i			Band 5			Band 6		
	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$
2.3	287.54	0.05	0.29	293.41	0.05	0.28	333.47	0.05	0.28	345.45	0.05	0.27
2.4	287.54	0.05	0.30	293.40	0.05	0.29	333.47	0.05	0.29	345.47	0.05	0.28
2.5	287.55	0.05	0.30	293.40	0.05	0.29	333.47	0.05	0.29	345.48	0.05	0.29
2.6	287.55	0.05	0.31	293.39	0.05	0.30	333.47	0.05	0.30	345.49	0.05	0.29
2.7	287.55	0.05	0.32	293.38	0.05	0.31	333.47	0.05	0.31	345.50	0.05	0.30
2.8	287.56	0.05	0.33	293.37	0.05	0.32	333.47	0.05	0.32	345.51	0.05	0.31
2.9	287.56	0.05	0.34	293.36	0.05	0.33	333.47	0.05	0.33	345.52	0.05	0.32
3.0	287.57	0.05	0.35	293.36	0.05	0.34	333.47	0.05	0.34	345.53	0.05	0.33
4.0	287.64	0.05	f		NA <sup>e</sup>		333.47	0.05	f	345.57	0.05	f
5.0	287.78	0.05	f		NA <sup>e</sup>		333.47	0.05	f	345.58	0.05	f
6.0	288.01	0.05	f		NA <sup>e</sup>		333.48	0.05	f	345.59	0.05	f
7.0	288.22	0.05	f		NA <sup>e</sup>		333.48	0.05	f	345.59	0.05	f
8.0	288.29	0.05	f		NA <sup>e</sup>		333.49	0.05	f	345.63	0.05	f
9.0	288.14	0.05	f		NA <sup>e</sup>		333.52	0.05	f	345.68	0.05	f
10.0	287.28	0.05	f		NA <sup>e</sup>		333.59	0.05	f	345.68	0.05	f
SBW <sup>a</sup>	Band 7			Band 8			Band 9			Band 10a		
	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$
0.1	361.27	0.05	0.19	385.36	0.05	0.19	416.02	0.05	0.21	450.62	0.05	0.19
0.2	361.27	0.05	0.19	385.37	0.05	0.18	416.03	0.05	0.21	450.63	0.05	0.19
0.3	361.27	0.05	0.19	385.39	0.04	0.18	416.04	0.05	0.20	450.65	0.05	0.19
0.4	361.27	0.05	0.19	385.42	0.04	0.18	416.05	0.05	0.20	450.68	0.05	0.19
0.5	361.27	0.05	0.19	385.45	0.04	0.18	416.07	0.05	0.21	450.72	0.05	0.19
0.6	361.27	0.05	0.20	385.49	0.04	0.18	416.10	0.05	0.21	450.78	0.05	0.20
0.7	361.27	0.05	0.20	385.53	0.04	0.18	416.13	0.05	0.21	450.84	0.05	0.20
0.8	361.26	0.05	0.20	385.56	0.04	0.19	416.17	0.05	0.21	450.96	0.06	0.23
0.9	361.25	0.05	0.21	385.59	0.04	0.19	416.21	0.05	0.21		NA <sup>e</sup>	
1.0	361.25	0.05	0.21	385.61	0.04	0.19	416.25	0.05	0.22		NA <sup>e</sup>	
1.1	361.23	0.05	0.21	385.63	0.04	0.20	416.29	0.05	0.22		NA <sup>e</sup>	
1.2	361.22	0.05	0.22	385.65	0.04	0.20	416.33	0.05	0.23		NA <sup>e</sup>	
1.3	361.21	0.05	0.22	385.67	0.04	0.21	416.36	0.05	0.23		NA <sup>e</sup>	
1.4	361.20	0.05	0.23	385.68	0.04	0.21	416.39	0.05	0.24		NA <sup>e</sup>	
1.5	361.18	0.05	0.23	385.70	0.04	0.21	416.42	0.05	0.24		NA <sup>e</sup>	
1.6	361.17	0.05	0.24	385.72	0.04	0.22	416.45	0.05	0.25		NA <sup>e</sup>	
1.7	361.16	0.05	0.24	385.74	0.04	0.22	416.48	0.05	0.25		NA <sup>e</sup>	
1.8	361.14	0.05	0.25	385.76	0.04	0.23	416.51	0.05	0.26		NA <sup>e</sup>	
1.9	361.13	0.05	0.25	385.78	0.04	0.23	416.54	0.05	0.26		NA <sup>e</sup>	
2.0	361.12	0.05	0.26	385.80	0.04	0.24	416.57	0.05	0.27		NA <sup>e</sup>	
2.1	361.11	0.05	0.26	385.82	0.04	0.25	416.60	0.05	0.28		NA <sup>e</sup>	
2.2	361.11	0.05	0.27	385.84	0.04	0.25	416.64	0.05	0.28		NA <sup>e</sup>	
2.3	361.10	0.05	0.27	385.86	0.04	0.26	416.67	0.05	0.29		NA <sup>e</sup>	
2.4	361.10	0.05	0.28	385.88	0.04	0.27	416.71	0.05	0.30		NA <sup>e</sup>	
2.5	361.09	0.05	0.29	385.90	0.04	0.27	416.74	0.05	0.31		NA <sup>e</sup>	
2.6	361.09	0.05	0.30	385.92	0.04	0.28	416.78	0.05	0.32		NA <sup>e</sup>	
2.7	361.10	0.05	0.30	385.94	0.04	0.29	416.81	0.05	0.32		NA <sup>e</sup>	
2.8	361.10	0.05	0.31	385.96	0.04	0.30	416.84	0.05	0.33		NA <sup>e</sup>	
2.9	361.10	0.05	0.32	385.98	0.04	0.30	416.87	0.05	0.34		NA <sup>e</sup>	
3.0	361.11	0.05	0.33	386.00	0.04	0.31	416.89	0.05	0.35		NA <sup>e</sup>	
4.0	361.14	0.05	f	386.31	0.05	f	417.07	0.05	f		NA <sup>e</sup>	
5.0	361.13	0.05	f	386.44	0.05	f	417.32	0.05	f		NA <sup>e</sup>	
6.0	361.11	0.05	f	386.60	0.05	f	417.37	0.05	f		NA <sup>e</sup>	
7.0	361.09	0.05	f	386.84	0.05	f	417.37	0.05	f		NA <sup>e</sup>	
8.0	361.06	0.05	f	387.10	0.05	f	417.36	0.05	f		NA <sup>e</sup>	
9.0	361.05	0.05	f	387.32	0.06	f	417.35	0.05	f		NA <sup>e</sup>	
10.0	361.04	0.05	f	387.50	0.07	f	417.35	0.05	f		NA <sup>e</sup>	
SBW <sup>a</sup>	Band 10b			Band 11			Band q			Band 12		
	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$
0.1	452.02	0.05	0.19	467.78	0.04	0.15	473.73	0.05	0.19	485.20	0.04	0.17
0.2	452.00	0.05	0.19	467.79	0.04	0.16	473.72	0.05	0.19	485.20	0.04	0.17

TABLE 4. Locations of band minima as a function of SBW—Continued

SBW <sup>a</sup>	Band 10b			Band 11			Band q			Band 12		
	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$
0.3	451.98	0.05	0.19	467.79	0.04	0.16	473.71	0.05	0.18	485.21	0.04	0.17
0.4	451.95	0.05	0.19	467.79	0.04	0.16	473.70	0.04	0.18	485.21	0.04	0.17
0.5	451.91	0.05	0.19	467.80	0.04	0.16	473.68	0.04	0.19	485.21	0.04	0.17
0.6	451.86	0.05	0.19	467.80	0.04	0.16	473.66	0.04	0.19	485.21	0.04	0.17
0.7	451.79	0.05	0.20	467.81	0.04	0.16	473.63	0.04	0.19	485.22	0.04	0.18
0.8	451.71	0.05	0.21	467.81	0.04	0.17	473.60	0.04	0.19	485.22	0.04	0.18
0.9	451.59	0.05	0.23	467.82	0.04	0.17	473.57	0.04	0.19	485.23	0.04	0.18
1.0	451.45	0.05	0.24	467.82	0.04	0.17	473.54	0.04	0.20	485.23	0.04	0.19
1.1	451.38	0.05	0.22	467.83	0.04	0.17	473.50	0.04	0.20	485.24	0.04	0.19
1.2	451.35	0.05	0.21	467.83	0.04	0.18	473.48	0.04	0.20	485.24	0.04	0.19
1.3	451.34	0.04	0.21	467.84	0.04	0.18	473.45	0.04	0.20	485.25	0.04	0.20
1.4	451.33	0.04	0.21	467.85	0.04	0.19	473.44	0.04	0.21	485.25	0.04	0.20
1.5	451.33	0.04	0.21	467.86	0.04	0.19	473.44	0.04	0.21	485.26	0.04	0.21
1.6	451.32	0.04	0.21	467.87	0.04	0.20	473.44	0.04	0.22	485.26	0.04	0.21
1.7	451.32	0.04	0.22	467.87	0.04	0.20	473.44	0.04	0.22	485.26	0.04	0.21
1.8	451.32	0.04	0.22	467.88	0.04	0.21	473.45	0.04	0.23	485.26	0.04	0.22
1.9	451.32	0.04	0.23	467.89	0.04	0.21	473.46	0.04	0.23	485.25	0.04	0.23
2.0	451.32	0.04	0.23	467.90	0.04	0.21	473.47	0.04	0.24	485.25	0.04	0.23
2.1	451.32	0.04	0.24	467.92	0.04	0.22	473.48	0.04	0.24	485.24	0.04	0.24
2.2	451.32	0.04	0.24	467.93	0.04	0.23	473.49	0.04	0.25	485.24	0.04	0.24
2.3	451.32	0.04	0.25	467.94	0.04	0.23	473.50	0.04	0.25	485.23	0.04	0.25
2.4	451.33	0.04	0.26	467.96	0.04	0.24	473.50	0.04	0.26	485.22	0.04	0.26
2.5	451.33	0.04	0.26	467.98	0.04	0.25	473.51	0.04	0.27	485.22	0.04	0.26
2.6	451.33	0.04	0.27	468.00	0.04	0.25	473.52	0.04	0.27	485.22	0.04	0.27
2.7	451.34	0.04	0.28	468.02	0.04	0.26	473.52	0.04	0.28	485.21	0.04	0.28
2.8	451.35	0.04	0.29	468.05	0.04	0.27	473.53	0.04	0.29	485.21	0.04	0.29
2.9	451.35	0.04	0.29	468.08	0.04	0.28	473.54	0.04	0.30	485.21	0.04	0.29
3.0	451.36	0.04	0.30	468.11	0.04	0.28	473.54	0.04	0.30	485.21	0.04	0.30
4.0	451.41	0.04	<sup>f</sup>		NA <sup>e</sup>		473.53	0.04	<sup>f</sup>	485.26	0.04	<sup>f</sup>
5.0	451.40	0.04	<sup>f</sup>		NA <sup>e</sup>		473.35	0.04	<sup>f</sup>	485.25	0.04	<sup>f</sup>
6.0	451.42	0.04	<sup>f</sup>		NA <sup>e</sup>		472.76	0.04	<sup>f</sup>	485.21	0.04	<sup>f</sup>
7.0	451.41	0.04	<sup>f</sup>		NA <sup>e</sup>		472.89	0.04	<sup>f</sup>	485.14	0.04	<sup>f</sup>
8.0	451.38	0.04	<sup>f</sup>		NA <sup>e</sup>		473.15	0.04	<sup>f</sup>	485.04	0.04	<sup>f</sup>
9.0	451.36	0.04	<sup>f</sup>		NA <sup>e</sup>		473.51	0.04	<sup>f</sup>	484.87	0.04	<sup>f</sup>
10.0	451.34	0.04	<sup>f</sup>		NA <sup>e</sup>			NA <sup>e</sup>		484.56	0.04	<sup>f</sup>

SBW <sup>a</sup>	Band 13			Band 14			Band u		
	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$
0.1	536.42	0.04	0.17	640.41	0.04	0.15	652.69	0.06	0.23
0.2	536.42	0.04	0.17	640.41	0.04	0.15	652.69	0.06	0.22
0.3	536.43	0.04	0.17	640.41	0.04	0.15	652.69	0.05	0.21
0.4	536.44	0.04	0.17	640.42	0.04	0.15	652.69	0.05	0.20
0.5	536.45	0.04	0.17	640.43	0.04	0.15	652.68	0.05	0.19
0.6	536.47	0.04	0.18	640.44	0.04	0.16	652.68	0.04	0.18
0.7	536.48	0.04	0.18	640.45	0.04	0.16	652.68	0.04	0.17
0.8	536.51	0.04	0.18	640.46	0.04	0.16	652.67	0.04	0.17
0.9	536.53	0.04	0.18	640.48	0.04	0.16	652.67	0.04	0.17
1.0	536.56	0.04	0.19	640.50	0.04	0.16	652.67	0.04	0.17
1.1	536.59	0.04	0.19	640.52	0.04	0.16	652.66	0.04	0.17
1.2	536.61	0.04	0.19	640.54	0.04	0.16	652.66	0.04	0.17
1.3	536.64	0.04	0.20	640.56	0.04	0.17	652.66	0.04	0.17
1.4	536.68	0.04	0.20	640.59	0.04	0.17	652.66	0.04	0.18
1.5	536.71	0.04	0.20	640.62	0.04	0.17	652.65	0.04	0.18
1.6	536.74	0.04	0.21	640.65	0.04	0.18	652.65	0.04	0.18
1.7	536.77	0.04	0.22	640.68	0.04	0.18	652.65	0.04	0.18
1.8	536.80	0.04	0.22	640.71	0.04	0.19	652.65	0.04	0.19
1.9	536.83	0.04	0.23	640.75	0.04	0.19	652.65	0.04	0.19
2.0	536.86	0.04	0.23	640.79	0.04	0.20	652.66	0.04	0.20
2.1	536.89	0.04	0.24	640.83	0.04	0.20	652.66	0.04	0.20
2.2	536.93	0.04	0.25	640.86	0.04	0.21	652.67	0.04	0.21
2.3	536.96	0.04	0.25	640.90	0.04	0.21	652.69	0.04	0.21
2.4	536.99	0.04	0.26	640.94	0.04	0.22	652.71	0.04	0.22

TABLE 4. Locations of band minima as a function of SBW—Continued

SBW <sup>a</sup>	Band 13			Band 14			Band u		
	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$	$\lambda_{\max}^b$	$U_{95}^c$	$P_{95}^d$
2.5	537.03	0.04	0.27	640.98	0.04	0.22	652.74	0.04	0.23
2.6	537.06	0.04	0.28	641.01	0.04	0.23	652.79	0.04	0.23
2.7	537.10	0.04	0.28	641.05	0.04	0.23	652.86	0.04	0.25
2.8	537.14	0.04	0.29	641.08	0.04	0.24	652.96	0.04	0.26
2.9	537.18	0.04	0.30	641.11	0.04	0.25	653.16	0.05	0.34
3.0	537.21	0.04	0.31	641.15	0.04	0.25	653.46	0.11	0.56
4.0	537.58	0.04	f	641.42	0.04	f	653.54	0.05	f
5.0	537.91	0.04	f	641.66	0.04	f		NA <sup>e</sup>	
6.0	538.28	0.04	f	641.88	0.04	f		NA <sup>e</sup>	
7.0	538.50	0.04	f	642.09	0.04	f		NA <sup>e</sup>	
8.0	538.64	0.04	f	642.32	0.04	f		NA <sup>e</sup>	
9.0	538.75	0.04	f	642.57	0.04	f		NA <sup>e</sup>	
10.0	538.83	0.04	f	642.86	0.04	f		NA <sup>e</sup>	

<sup>a</sup>Spectral band width (in nm).

<sup>b</sup>The expected location of the transmittance minimum (in nm) calculated as the mean of 0.1 nm SBW spectra from 13 instruments convolved with an idealized triangular slit function of width SBW.

<sup>c</sup>Approximate 95% confidence interval (Ref. 26) (in nm) of the expected transmittance minimum:  $\pm t_{(0.025, N-1)} \times s / \sqrt{13}$ , where  $t_{(0.025, 13-1)}$  is the two-sided student's  $t$  for 95% confidence at 12 degrees of freedom and  $s$  is the standard deviation of the 13 convolved spectra at the given SBW. The true value for each transmittance minimum at each given SBW is expected, with about 95% confidence, to be within this interval.

<sup>d</sup>Approximate 95% prediction interval (Ref. 26) (in nm):  $\pm t_{(0.025, 13-1)} \times s \times \text{MEF} / \sqrt{(1+1/13)}$ , where MEF is the empirically determined multiplicative expansion factor  $1 + 0.025 \times \text{SBW} + 0.080 \times \text{SBW}^2$  that accounts for the uncertainty of calibrating real instruments at large SBW. The next single measurement of the location of this peak at this SBW made using a measurement system from the same population as those used by the participants in this study is expected, with about 95% confidence, to be within this interval.

<sup>e</sup>There is no transmittance minimum at this SBW.

<sup>f</sup>Due to the empirical derivation of MEF,  $P_{95}$  cannot be reliably calculated for SBW greater than 3.0 nm.

.for three bands with a portion of the broadened spectrum at several bandwidths for illustration. The trajectories are computed using every bandwidth from 0.1 to 10 nm at 0.1 nm intervals, and not just the few shown in the figure.

Table 4 reports the positions of all bands studied here at SBWs from 0.1 to 3.0 nm in 0.1 nm intervals, with a few

representative values given for larger SBW values. The calculation represented in the table utilized all calibrated full spectra furnished by participants at an SBW of 0.1 nm ( $N = 13$ ). Each spectrum was convolved to the SBWs shown and the band locations were extracted for each SBW. The central value, uncertainty, and prediction interval were com-

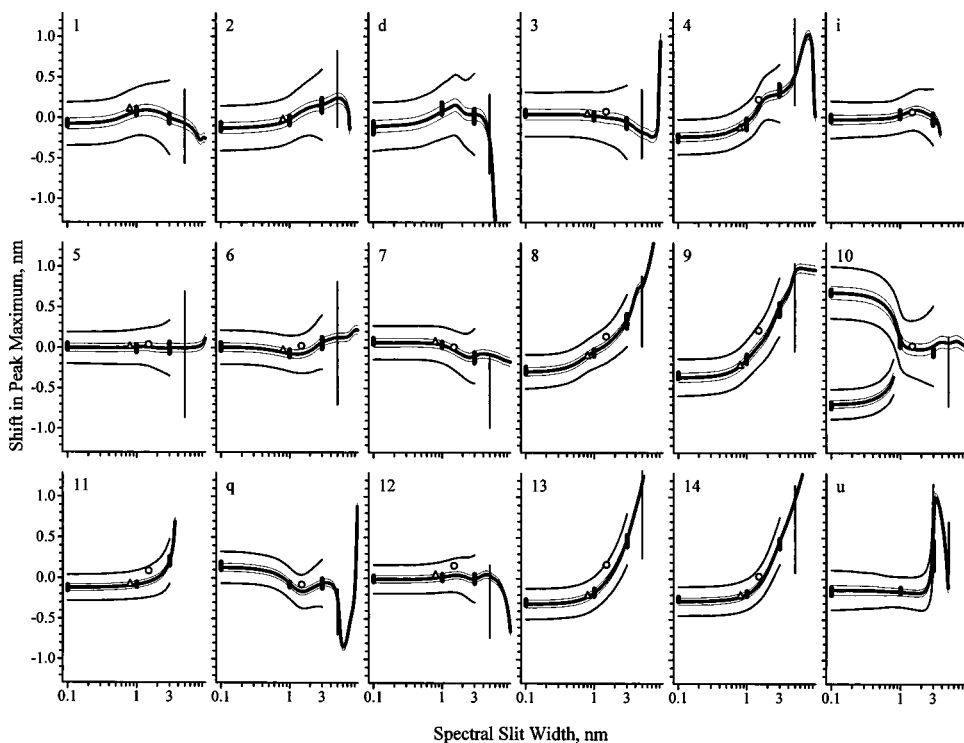


FIG. 7. A graphical view of the computed SBW trajectories (see Fig. 6) and their uncertainties, compared with the experimental SSW results. Mean-centered band positions are computed from theoretically broadened experimental spectra (Table 4) and are shown with 95% confidence (inner band) and 95% prediction (outer band) intervals. The measured SBW values at 0.1, 1.0, and 3.0 nm reported in Table 3 are plotted with their approximately 95% confidence interval uncertainties. The open circles represent individual instruments reporting data at other SBW values.

puted in the same manner as discussed for Table 3, except for the use of a multiplicative expansion factor for the prediction interval. The expansion function used for the prediction interval is a quadratic function with a  $Y$  intercept of 1.0, fitted to the relative  $U_{95}$  values of Table 3 (normalized to  $U_{95}$  at 0.1 nm SBW for each measured band) and is included to represent the loss of calibration accuracy in these instruments at increasing SBW. The calculation of  $P_{95}$  in Table 4 is terminated at a SBW of 3.0 nm, since the experimental data does not support the estimation of the empirical function beyond that limit. Minor differences in the 0.1 nm SBW bandwidth values in Tables 3 and 4 result from the lower value of  $N$  for Table 4, and from the fact that Table 3 uses band locations extracted from each of two spectra for each SBW and instrument and Table 4 averages the spectra before convolution and band position extraction.

The validity of the theoretical convolution used to generate Table 4 may be tested by comparison of the predicted and measured values at 1.0 and 3.0 nm in Table 3. A graphical view of the trajectories and comparisons with experimental values is provided in Fig. 7. Here the data are mean centered for ease of display, but the figure is useful for observing the qualitative behavior of the various spectral features with bandwidth. The central line for each subfigure represents the mean-centered band shift as a function of SBW. The innermost pair of lines about each trajectory, from 0.1 to 3.0 nm, is the 95% confidence interval, and the outermost line pair represents the 95% prediction interval for a single future determination. Vertical bars plotted at 0.1, 1.0, and 3.0 nm represent the  $U_{95}$  for the measured values reported in Table 3. Additional symbols represent individual instruments reporting data at other SBW values.

For SBWs from 0.1 to 3.0 nm, the values in Table 4 represent certified values as validated by the experimental data of the multicenter experiment. For SBWs between 3.0 and 10.0 nm, the values are considered to be "information values" for which the uncertainty is less well characterized.

## 4. Conclusions

The establishment of specified absorption bands of a solution of 40 g/L holmium oxide in 10% (volume fraction) perchloric acid as certified intrinsic wavelength standards that are fit-for-purpose for most applications in chemical spectrophotometry is supported by various conclusions:

- (1) Realistic uncertainties are furnished by the multicenter approach, which experimentally confounds calibration uncertainty into the end result.
- (2) Intrinsic band positions as continuous functions of instrumental spectral bandwidth may be supplied by means of the theoretical broadening of the intrinsic (narrow-band) spectrum as validated through the consensus measurements at discreet spectral bandwidths.
- (3) Band positions of different preparations of holmium oxide solution are robust with respect to the origin of materials and to  $\pm 20\%$  variations in concentration.

We therefore recommend the certified band positions in Table 4 as intrinsic wavelength standards in the sample temperature range of  $25 \pm 5$  °C, applicable to samples of holmium oxide in perchloric acid prepared in the manner described herein and with a high-resolution spectrum shown to be congruent with the intrinsic spectrum reported here.

## 5. Disclaimer

Certain commercial equipment, instruments, or 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, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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- <sup>15</sup> *Pharmacopoeia of the People's Republic of China*, Volume II (Chemical Industry Press, Beijing, 2000), Appendix IV A (English Edition 2000).
- <sup>16</sup> Originally produced as Corning 3130 and 3131 glasses. Produced as Kopp Glass 3131 since the early 1980s. Available from numerous resellers and from the NIST Calibration Program as "Wavelength Standard" (38050C) in 51 mm by 51 mm format or (38051C) in cuvette format.
- <sup>17</sup> Produced as Kopp Glass 5121 and available through optical filter distributors.
- <sup>18</sup> European Reference Material ERM-FB010a is produced and sold by LGC Promochem through LGC, Middx TW11 0LY, U. K. It is a mixture of holmium and neodymium oxides dissolved in dilute perchloric acid. Certified values are provided for the wavelengths of minimum transmittance of 16 features spanning the range 219–865 nm at spectral bandwidths of 0.5, 1.0, and 2.0 nm.
- <sup>19</sup> J. Webster, *The Application Notebook (Supplement to Spectroscopy)*, February 2004, p. 30.
- <sup>20</sup> The "McCrone Standard" is a monocrystalline Nd-doped YAG crystal produced by McCrone Scientific Ltd, 155a Leighton Road, London NW5 2RD, U. K. The "Nelson M-42" standard is a monocrystalline erbium-doped YAG [(Y<sub>1.5</sub>Er<sub>1.5</sub>)Al<sub>2</sub>(AlO<sub>4</sub>)<sub>3</sub>] crystal produced by Nelson Gemological Instruments, 1 Lyndhurst Road, London NW3 5PX, U. K. The

- National Physical Laboratory (NPL), Middx TW11 0LW, U. K. can also supply these materials and will calibrate the wavelengths of minimum transmittance of particular features specified by the customer.
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