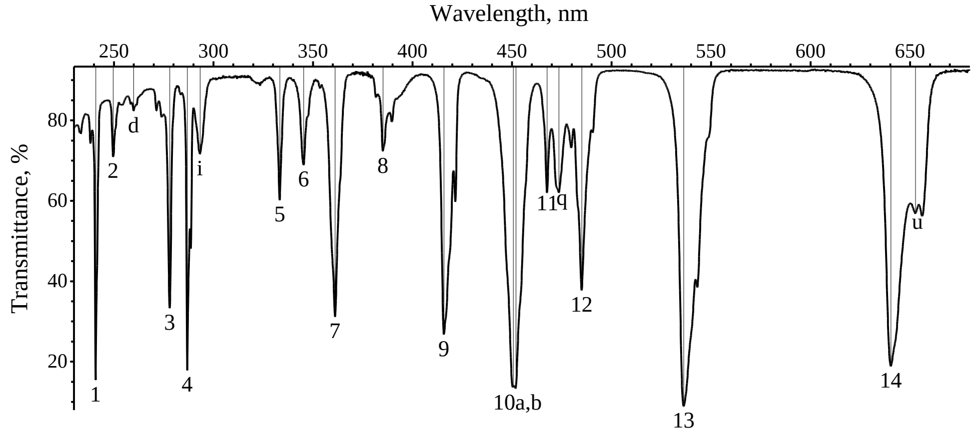
NIST Special Publication 260-192

Thirty-Year Stability of Standard Reference Material® 2034

Holmium Oxide Solution Wavelength Standard for Spectrophotometry



Melody V. Smith
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National Institute of Standards and Technology
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Thirty-Year Stability of Standard Reference Material® 2034

Holmium Oxide Solution Wavelength Standard for Spectrophotometry

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Abstract

Standard Reference Material (SRM) 2034 Holmium Oxide Solution Wavelength Standard (240 nm to 650 nm) was produced periodically from 1985 to 2015. Originally unstated, by 1996 an expiration period of ten years was established. This report describes a study of legacy samples from 13 production runs over the 30-year period that established that the band locations in all samples have not varied outside of their established uncertainties. These results support the extension of the expected stability of SRM 2034 holmium oxide solution in dilute perchloric acid to a period of at least 30 years.

Keywords

Holmium Oxide
Spectrophotometry
Stability Study
Standard Reference Material (SRM)
Wavelength Standard

Technical Information Contact for this SRM

Please address technical questions about this SRM to srms@nist.gov where they will be assigned to the appropriate Technical Project Leader responsible for support of this material. For sales and customer service inquiries, please contact srminfo@nist.gov.

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Background

Standard Reference Material (SRM) 2034 Holmium Oxide Solution Wavelength Standard (240 nm to 650 nm) was introduced in 1985 [1]. It was produced as needed from 1985 to 2015. The original certificate did not specify an expiration date. Units produced from 1996 to 2004 were certified with assigned expiration times of ten years. More specifically, the expiration date was taken as December 31 of the tenth year following the series designation. Hence, the expiration of Series 2004 on December 31, 2014, was the inspiration for comparing spectra of retained SRM 2034 samples from each of the production series from fiscal year1985 to 2015.

The intent of the comparison was to revise the expiration time of SRM 2034 and commercial CRMs based on the well-known holmium oxide solution from 10 years to 30 years. Table 1 lists the number of legacy samples available for production series from 1985 to 2004. One or more samples from each of these series were studied, along with four samples from the 2015 production series.

Table 1: Legacy Samples Available in 2015

Series	Expiry Time, Years	Number of Available Samples	Number of Samples Studied
1985	Not specified	4	3
1986	Not available	1	1
1988	Not available	2	2
1991	5	2	2
1994	8	6	3
1995	9	4	3
1996	10	5	3
1998	10	7	3
1999	10	4	3
2001	10	2	2
2002	10	2	2
2004	10	2	2

The band positions of holmium oxide in dilute perchloric acid when produced to the specifications of SRM 2034 were declared to be an intrinsic standard for wavelength by a multi-center study published in 2005 [2]. The study provides certified values for spectral bandwidths from 0.1 nm to 3.0 nm in increments of 0.1 nm. The present study does not revisit these values but uses them as a baseline to present the data for different bands on a common scale relative to the corresponding certified values.

Measurements

The spectral measurements for this study were obtained using the Cary 6000i Materials Measurement Laboratory Transfer Spectrophotometer (MMLTS) in early FY 2015 [3]. Twenty spectra were collected on each of three days in four runs of six samples each. Table 2 describes the experimental design of the study.

Table 2: SRM 2034 Experimental Protocol

Day	Run	Cell	Sample	Day	Run	Cell	Sample	Day	Run	Cell	Sample
1	1	1	Blank	2	1	1	Blank	3	1	1	Blank
		2	1985a			2	1985b			2	1985c
		3	2015w			3	2015w			3	2015w
		4	1986a			4	1986a			4	1986a
		5	Control			5	Control			5	Control
		6	1988a			6	1988b			6	1988a
1	2	2	1991a	2	2	2	1991b	3	2	2	1991a
		3	2015x			3	2015x			3	2015x
		4	1994a			4	1994b			4	1994c
		5	Control			5	Control			5	Control
		6	1995a			6	1995b			6	1995c
1	3	2	1996a	2	3	2	1996b	3	3	2	1996c
		3	2015y			3	2015y			3	2015y
		4	1998a			4	1998b			4	1998c
		5	Control			5	Control			5	Control
		6	1999a			6	1999b			6	1999c
1	4	2	2001a	2	4	2	2001b	3	4	2	2001a
		3	2015z			3	2015z			3	2015z
		4	2002a			4	2002b			4	2002a
		5	Control			5	Control			5	Control
		6	2004a			6	2004a			6	2004a

The letters after the production series designation are used to distinguish different samples from the same series. If three or more legacy samples were available, a different one was run on each of the three days. If fewer than three were available, then one sample was run more than once. One of the two available 2004 samples (unexpired at the time the spectra were obtained) was used as a control and internal calibration sample; the other was treated as a legacy sample. The four samples from the then-newly prepared 2015 series were each replicated four times, providing a total of 12 replicates for the 2015 series rather than the three replicates for the legacy series.

For each "run" in the experimental design, five samples were placed in cells 2 through 6 of the MMLTS's 6 × 6 sample chamber. The spectra were acquired from 670 nm to 230 nm in 0.1 nm wavelength increments, with a spectral band width (SBW) of 0.8 nm. This SBW was chosen to establish metrological traceability of the measurement results to those from the NIST high accuracy reference spectrophotometer (HAS II) with its fixed 0.8 nm SBW [4].

The data acquisition rate was 0.1 second per point (or 1 s/nm). With delays for filter changes and moving the grating, each spectral acquisition required approximately eight minutes. Thus, the first run of each day required 48 minutes. The other three runs did not require baseline acquisition and thus took about 40 minutes each. The temperature of the sample changer was controlled to 25 °C ± 0.1 °C using the MMLTS's closed-cycle circulating bath temperature controller accessory.

The intent was for the three days of acquisition to occur before series 2004 expired on December 31, 2014. However, an instrument malfunction shut down the acquisition after two days, and the third data set was acquired in January 2015 after repair. During repair, the technician found that the windows to the sample chamber needed cleaning for the instrument to pass the noise test.

The band minima for each spectrum were fitted using the five measured values nearest the "tip" of the band, fit to either the quadratic or cubic polynomial protocol described in [2]. The measured band locations for all 60 acquired spectra are provided in Appendix A.

Results

Figure 1 displays a segment of the spectrum from 230 nm to 300 nm for all data from Day 1, with the spectra offset in increments of 5 % for visual clarity.

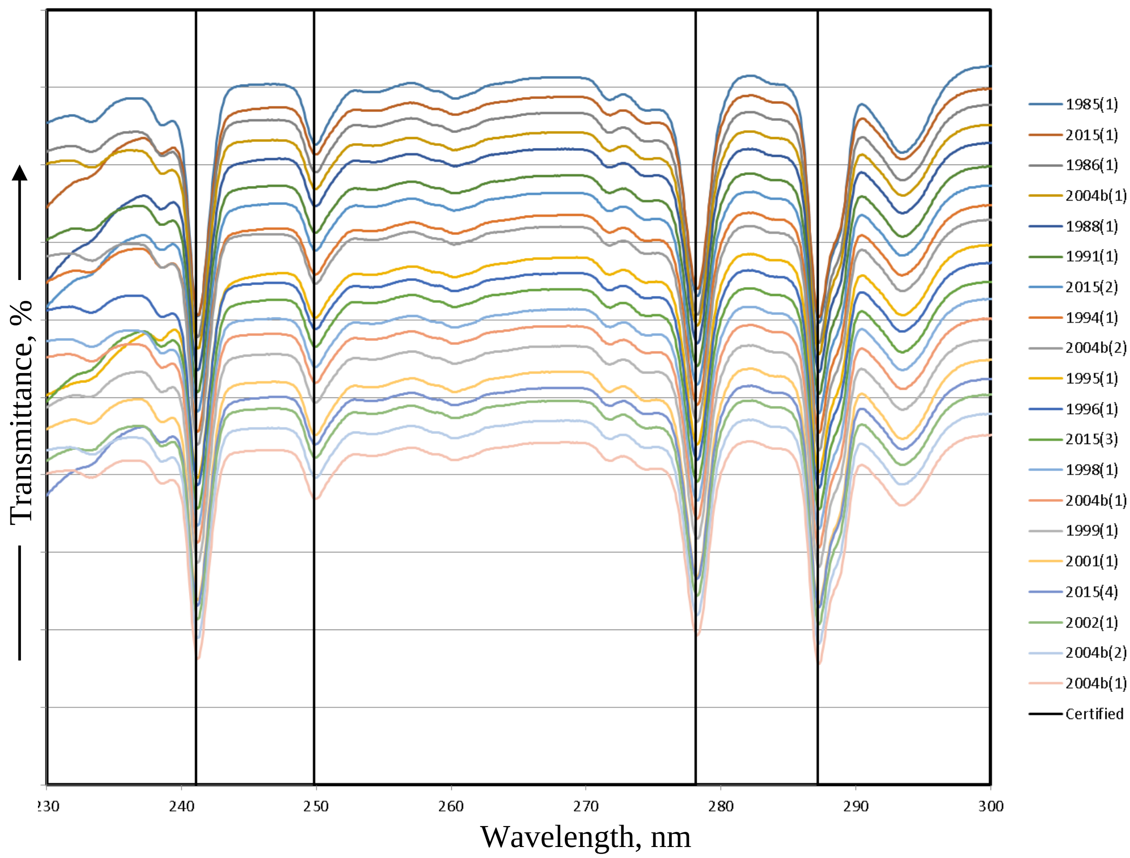

Figure 1: Stacked Plot of a Short-Wavelength Segment of the Data for Day 1.

The vertical lines represent certified values for the selected bands deemed suitable for certification within this wavelength region. Multiple "crossovers" in the baseline between 230 nm and 240 nm and the unequal spacing in other baseline regions results from differences in the transmittance and reflectivity of the fused silica used in cuvette construction over the past 30 years. A few crossovers in the bands result from minor concentration differences deemed to be within an acceptable range [3]. The bias of the native scale of the MMLTS with respect to the certified values is consistently 0.09 nm ± 0.02 nm. This bias is barely evident in the figure.

Figure 2 summarizes the differences between the measured and 0.8 nm SBW certified band locations averaged across all 20 spectra on each day.

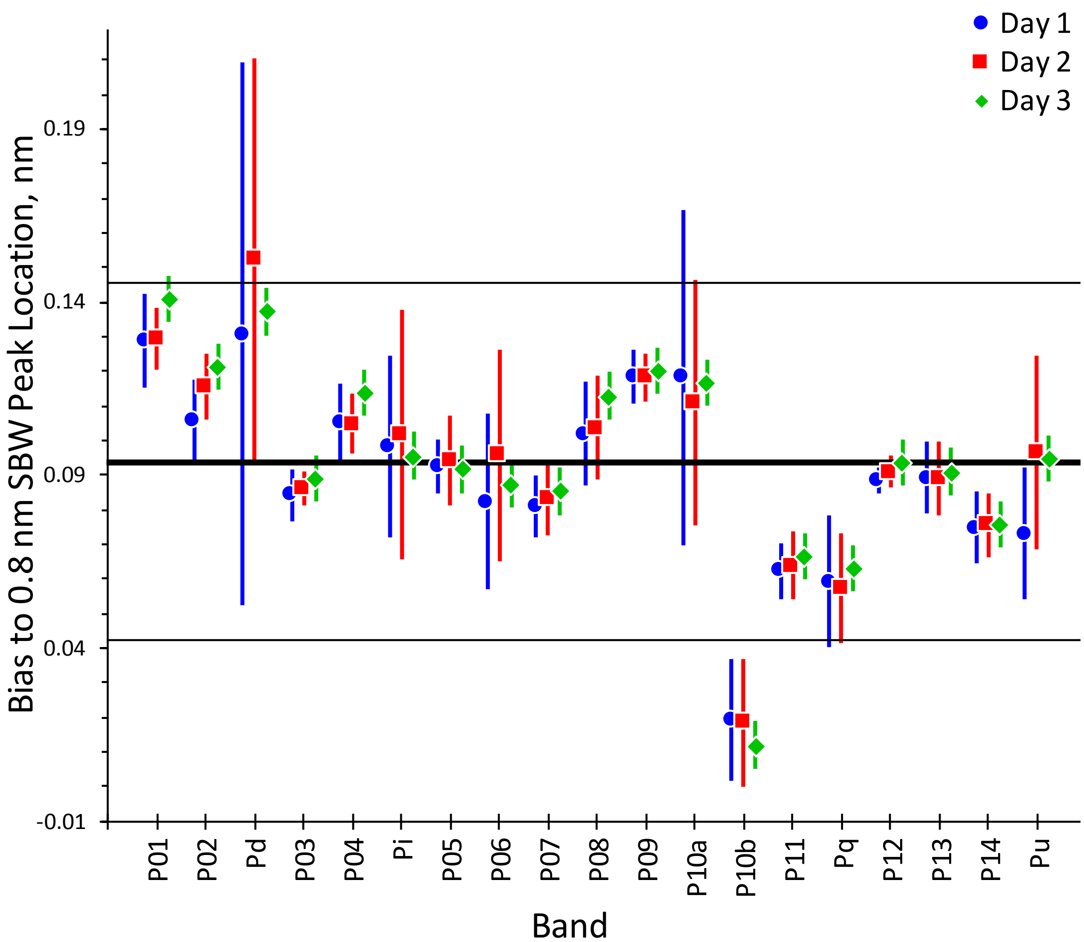

Figure 2: Observed Band Location Biases Relative to Intrinsic Values

The 14 bands for which the positions are certified are labeled P##, where ## = 01 to 14, except for band 10 which becomes a poorly resolved doublet at 0.8 nm SBW and blends into a singlet at bandwidths above about 1 nm. The bands are numbered from short to long wavelength (the spectral region shown in Figure 1 includes bands P01 to P04). The location of the short-wavelength doublet of P10, designated P10a, was very sensitive to spectral noise on Days 1 and 2 while its long-wavelength partner, designated P10b, was unexpectedly biased.

At 0.8 nm SBW, band 10 is insufficiently resolved for reliable wavelength calibration use. Bands labeled Pd, Pi, Pq, and Pu are candidate bands discussed in [3] but were considered too sensitive to spectral noise for confident certification. The locations for all bands except P10b were estimated using a quadratic polynomial fit; the location for the highly asymmetric P10b was estimated using a cubic polynomial.

For convenience, we classify the 13 bands deemed useful for instrument calibration at 0.8 nm SBW as “primary” and the remaining six as “secondary”. However, the band locations of all 19 bands are sufficiently stable for the purposes of this stability study.

The error bars in Figure 2 represent the estimated standard deviation of the 20 measurements of each fitted band position over the 12 legacy samples from 1985 to 2004, four measurements of the 2004 Control, and four measurements of the 2015 samples. These error bars represent a combination of random error components, which would accompany replicate measurements of a single sample, and errors due to sample differences resulting from age or any other factors (e.g., concentration, matrix, cuvette effects). The dramatic reduction in measurement error on the third day, especially for the less-well defined bands, is due to the window cleaning noted above.

Figure 3 displays the standard deviation of the 19 band position biases as a function of the mean bias value for each of the 60 acquired spectra. The codes used to identify the individual spectra are listed in Table 3.

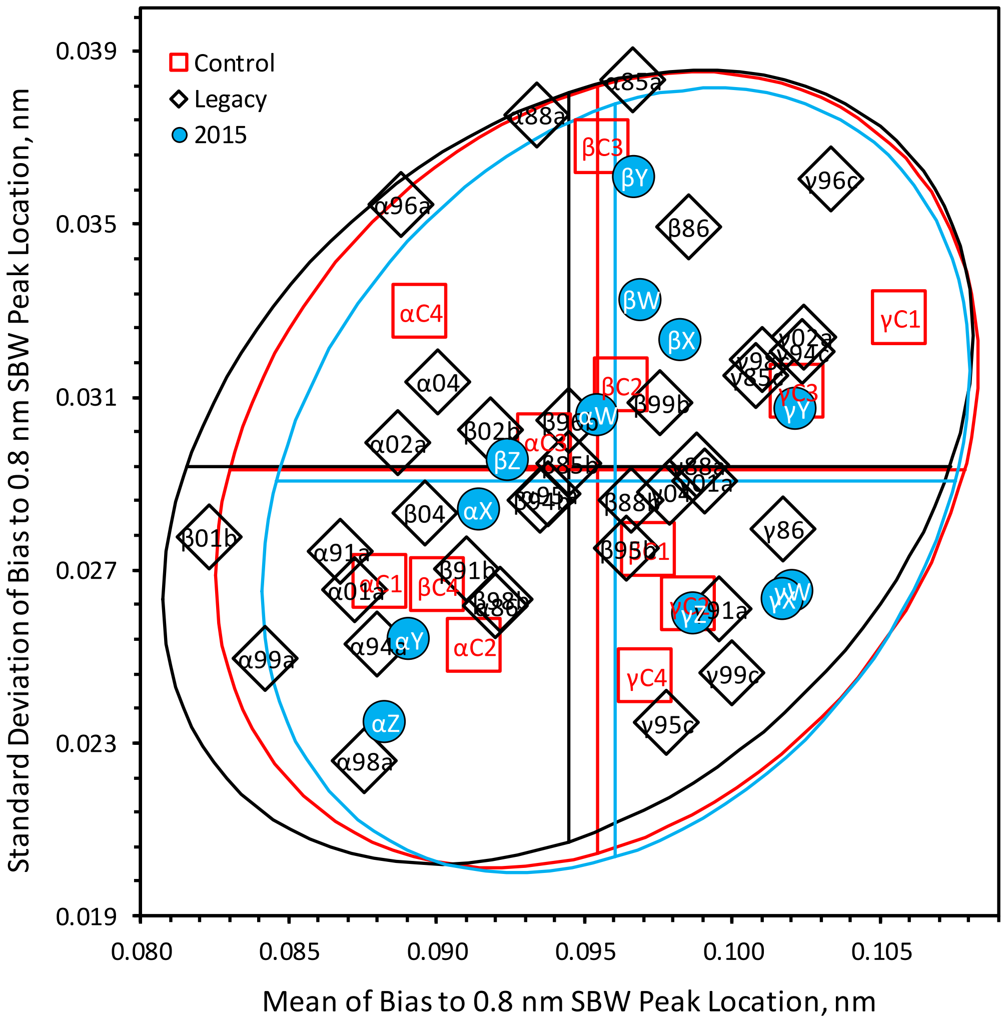

Figure 3: Standard Deviation vs Mean Band Location Bias Relative to Intrinsic Values

Table 3: Sample Codes Used in Figures 3 and 4

Day 1			Day 2			Day 3		
Code	Sample	Rep	Code	Sample	Rep	Code	Sample	Rep
α85a	1985a	1	β85b	1985b	1	γ85c	1985b	1
αW	2015w	1	βW	2015w	1	γW	2015w	1
α86	1986a	1	β86	1986a	1	γ86	1986a	1
αC1	Control	1	βC1	Control	1	γC1	Control	1
α88a	1988a	1	β88b	1988b	1	γ88a	1988b	1
α91a	1991a	1	β91b	1991b	1	γ91a	1991b	1
αX	2015x	1	βX	2015x	1	γX	2015x	1
α94a	1994a	1	β94b	1994b	1	γ94c	1994b	1
αC2	Control	2	βC2	Control	2	γC2	Control	2
α95a	1995a	1	β95b	1995b	1	γ95c	1995b	1
α96a	1996a	1	β96b	1996b	1	γ96c	1996b	1
αY	2015y	1	βY	2015y	1	γY	2015y	1
α98a	1998a	1	β98b	1998b	1	γ98c	1998b	1
αC3	Control	3	βC3	Control	3	γC3	Control	3
α99a	1999a	1	β99b	1999b	1	γ99c	1999b	1
α01a	2001a	1	β01b	2001b	1	γ01a	2001b	1
αZ	2015z	1	βZ	2015z	1	γZ	2015z	1
α02a	2002a	1	β02b	2002b	1	γ02a	2002b	1
αC4	Control	4	βC4	Control	4	γC4	Control	4
α04	2004a	1	β04	2004b	1	γ04	2004b	1

The samples are divided into three groups. The "Control" group (red open squares) denote the Series 2004 sample run with each of the four data sets acquired on each of the three days. The "Legacy" group (black open diamonds) denote the 12 samples from the 1985 to 2004 production series. The "2015" group (solid blue circles) denote the samples prepared in 2014 and identified as Series 2015 of SRM 2034. The red, black, and blue ellipses represent 95 % confidence bounds on the {standard deviation, mean} pairs for the Control, Legacy, and 2015 spectra. The point where the vertical and horizontal lines cross marks the center of each distribution.

Close examination of Figure 3 reveals a statistically significant but practically negligible wavelength shift between the Day 3 (γ) data and the other two days (α,β). For this reason, the data are replotted in Figure 4 with each band position expressed relative to the corresponding band position in the control sample for the run. Thus, the "Control" group of Figure 3 collapses to a point in Figure 4 and is not shown.

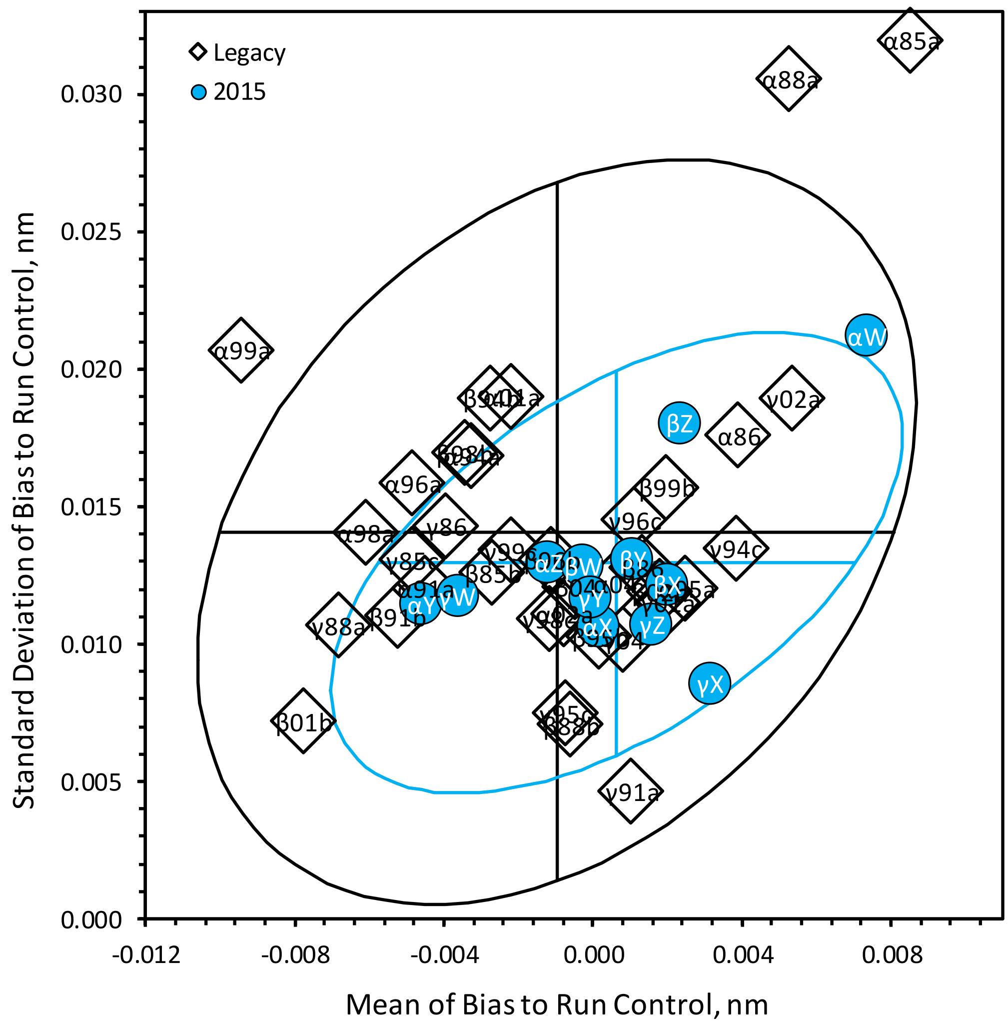

Figure 4. Standard Deviation vs Mean Band Location Bias Relative to Day Control

Conclusions

In Figures 3 and 4, the ellipses and crosses mark the 95% confidence region for color-coded sample groupings. Thus, the red-coded "Control" (2004a) region of Figure 3 represents the native experimental error in band location and wavelength repeatability, since this grouping represents repeated runs of the same solution. The congruence of the three color-coded confidence interval regions in Figure 3 argue that the “Legacy” and the “2015” groups are equivalent to the control and to each other.

Figure 4 does reveal a tighter confidence region for the four samples of the 2015 group than for the 28 samples of the legacy group. The results for of the legacy samples include slight variations in band depth (concentration) as revealed by spectral crossovers in the stacked plot of Figure 1. Here the practical equivalence of all series of SRM 2034 is supported by the overall extent of the axes of the figure, or 0.024 nm in the bias mean (abscissa) and 0.033 nm in the bias standard deviation (ordinate). These values should be compared with typical U_{95} values of 0.04 nm to 0.05 nm and P_{95} values of 0.17 nm to 0.22 nm for the certified values of these bands at 0.8 nm SBW listed in Table 4.

The data thus support the extension of the expected stability of the SRM 2034 holmium oxide solution in dilute perchloric acid to a period of at least 30 years.

Table 4: Intrinsic Band Locations at 0.8 nm Spectral Band Width

Band	Class[b]	Band Locations, nm[a]		
		x	$U_{95}(x)$[c]	$P_{95}(x)$[d]
P01	Primary	241.09	0.05	0.23
P02	Primary	249.85	0.05	0.22
P03	Primary	278.14	0.05	0.21
P04	Primary	287.16	0.05	0.21
P05	Primary	333.48	0.05	0.20
P06	Primary	345.40	0.05	0.20
P07	Primary	361.26	0.05	0.20
P08	Primary	385.56	0.04	0.19
P09	Primary	416.17	0.05	0.21
P11	Primary	467.81	0.04	0.17
P12	Primary	485.22	0.04	0.18
P13	Primary	536.51	0.04	0.18
P14	Primary	640.46	0.04	0.16
Pd	Secondary	260.13	0.06	0.25
Pi	Secondary	293.35	0.05	0.19
P10a	Secondary	450.96	0.06	0.23
P10b	Secondary	451.71	0.05	0.21
Pq	Secondary	473.60	0.04	0.19
Pu	Secondary	652.67	0.04	0.17

a Values from Reference 2. These values were estimated from spectra provided by 16 to 19 expert spectroscopists using trusted instruments.

b Primary: Band location suitable for use in wavelength calibration at 0.8 nm SBW; Secondary: Band location not suitable for use in wavelength calibration at 0.8 nm SBW due to sensitivity to spectral noise.

c Expanded 95 % confidence uncertainty. The true band locations are expected to be in the interval $x \pm U_{95}(x)$ with approximately 95 % confidence.

d Approximate 95 % confidence prediction uncertainty. A single measurement made using a well-calibrated, well-maintained analytical spectrophotometer is expected to be in the interval $x \pm P_{95}(x)$ with approximately 95 % confidence.

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Appendix A: Measured Band Locations

Table A1-1: Day 1 Measurements of Primary Bands

	Band Locations at 0.8 nm Fixed Bandwidth, nm												
Sample	P01	P02	P03	P04	P05	P06	P07	P08	P09	P11	P12	P13	P14
1985a	241.236	249.961	278.231	287.280	333.575	345.485	361.350	385.666	416.292	467.867	485.310	536.606	640.530
2015w	241.228	249.965	278.226	287.273	333.575	345.489	361.344	385.657	416.293	467.877	485.309	536.599	640.537
1986a	241.226	249.966	278.226	287.268	333.568	345.505	361.345	385.660	416.289	467.870	485.310	536.602	640.531
Control[a]	241.227	249.960	278.228	287.270	333.577	345.484	361.337	385.665	416.290	467.874	485.311	536.595	640.535
1988a	241.218	249.955	278.230	287.264	333.575	345.490	361.349	385.663	416.289	467.871	485.310	536.607	640.532
1991a	241.217	249.960	278.223	287.260	333.566	345.480	361.336	385.655	416.282	467.869	485.308	536.594	640.532
2015x	241.220	249.953	278.225	287.269	333.575	345.493	361.341	385.658	416.291	467.877	485.309	536.596	640.542
1994a	241.216	249.952	278.222	287.259	333.571	345.470	361.339	385.665	416.284	467.874	485.310	536.600	640.532
Control[a]	241.220	249.964	278.222	287.266	333.576	345.491	361.338	385.663	416.292	467.875	485.309	536.594	640.539
1995a	241.214	249.950	278.223	287.265	333.575	345.486	361.341	385.671	416.293	467.874	485.308	536.595	640.539
1996a	241.214	249.949	278.223	287.258	333.572	345.462	361.343	385.663	416.284	467.866	485.306	536.604	640.529
2015y	241.217	249.956	278.223	287.268	333.580	345.482	361.340	385.664	416.289	467.877	485.308	536.595	640.540
1998a	241.220	249.955	278.224	287.265	333.569	345.476	361.339	385.666	416.288	467.875	485.305	536.596	640.541
Control[a]	241.217	249.957	278.223	287.265	333.578	345.486	361.335	385.683	416.294	467.876	485.306	536.595	640.544
1999a	241.218	249.958	278.228	287.261	333.573	345.474	361.345	385.649	416.288	467.870	485.312	536.608	640.534
2001a	241.216	249.951	278.216	287.265	333.572	345.504	361.339	385.661	416.281	467.867	485.307	536.595	640.531
2015z	241.204	249.947	278.220	287.264	333.570	345.470	361.337	385.656	416.288	467.875	485.308	536.596	640.539
2002a	241.214	249.951	278.222	287.257	333.569	345.489	361.343	385.653	416.288	467.869	485.309	536.606	640.527
Control[a]	241.217	249.957	278.220	287.263	333.567	345.465	361.334	385.658	416.288	467.871	485.307	536.596	640.535
2004a	241.216	249.950	278.227	287.258	333.573	345.464	361.342	385.658	416.285	467.868	485.308	536.604	640.529

a Sample 2004a, used as a control and for internal calibration

Table A1-2. Day 2 Measurements of Primary Bands

Sample	Band Locations at 0.8 nm Fixed Bandwidth, nm												
	P01	P02	P03	P04	P05	P06	P07	P08	P09	P11	P12	P13	P14
1985b	241.224	249.963	278.230	287.267	333.574	345.532	361.352	385.663	416.291	467.870	485.310	536.607	640.535
2015w	241.220	249.961	278.232	287.266	333.579	345.485	361.354	385.663	416.290	467.870	485.312	536.611	640.532
1986a	241.229	249.973	278.228	287.271	333.579	345.494	361.342	385.669	416.292	467.877	485.314	536.600	640.537
Control[a]	241.224	249.973	278.227	287.269	333.584	345.503	361.344	385.671	416.289	467.877	485.313	536.597	640.535
1988b	241.219	249.971	278.226	287.266	333.580	345.494	361.338	385.660	416.289	467.878	485.312	536.599	640.534
1991b	241.219	249.963	278.225	287.263	333.574	345.487	361.340	385.666	416.287	467.875	485.311	536.597	640.532
2015x	241.221	249.969	278.227	287.269	333.577	345.524	361.341	385.662	416.289	467.879	485.313	536.599	640.539
1994b	241.226	249.959	278.226	287.270	333.573	345.507	361.340	385.662	416.290	467.878	485.311	536.599	640.541
Control[a]	241.226	249.968	278.225	287.269	333.578	345.477	361.343	385.670	416.293	467.879	485.309	536.594	640.541
1995b	241.213	249.959	278.225	287.268	333.580	345.508	361.341	385.676	416.290	467.878	485.311	536.597	640.541
1996b	241.215	249.963	278.224	287.260	333.570	345.499	361.349	385.652	416.288	467.867	485.311	536.605	640.533
2015y	241.216	249.960	278.223	287.263	333.579	345.500	361.339	385.665	416.287	467.875	485.311	536.596	640.532
1998b	241.219	249.965	278.226	287.264	333.577	345.491	361.339	385.657	416.290	467.876	485.310	536.595	640.540
Control[a]	241.219	249.968	278.228	287.263	333.575	345.491	361.348	385.654	416.287	467.871	485.313	536.608	640.536
1999b	241.217	249.972	278.227	287.262	333.574	345.492	361.338	385.675	416.287	467.876	485.312	536.596	640.536
2001b	241.215	249.961	278.223	287.257	333.565	345.485	361.340	385.654	416.277	467.862	485.304	536.592	640.523
2015z	241.219	249.966	278.224	287.265	333.573	345.489	361.346	385.662	416.288	467.876	485.310	536.594	640.538
2002b	241.218	249.966	278.228	287.262	333.570	345.487	361.340	385.671	416.289	467.875	485.310	536.596	640.538
Control[a]	241.215	249.964	278.225	287.259	333.558	345.497	361.351	385.653	416.287	467.866	485.309	536.602	640.534
2004b	241.219	249.965	278.224	287.260	333.564	345.471	361.340	385.668	416.286	467.874	485.310	536.596	640.532

a Sample 2004a, used as a control and for internal calibration

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Table A1-3. Day 3 Measurements of Primary Bands

Sample	Band Locations at 0.8 nm Fixed Bandwidth, nm												
	P01	P02	P03	P04	P05	P06	P07	P08	P09	P11	P12	P13	P14
1985b	241.224	249.963	278.230	287.267	333.574	345.532	361.352	385.663	416.291	467.870	485.310	536.607	640.535
2015w	241.220	249.961	278.232	287.266	333.579	345.485	361.354	385.663	416.290	467.870	485.312	536.611	640.532
1986a	241.229	249.973	278.228	287.271	333.579	345.494	361.342	385.669	416.292	467.877	485.314	536.600	640.537
Control[a]	241.224	249.973	278.227	287.269	333.584	345.503	361.344	385.671	416.289	467.877	485.313	536.597	640.535
1988b	241.219	249.971	278.226	287.266	333.580	345.494	361.338	385.660	416.289	467.878	485.312	536.599	640.534
1991b	241.219	249.963	278.225	287.263	333.574	345.487	361.340	385.666	416.287	467.875	485.311	536.597	640.532
2015x	241.221	249.969	278.227	287.269	333.577	345.524	361.341	385.662	416.289	467.879	485.313	536.599	640.539
1994b	241.226	249.959	278.226	287.270	333.573	345.507	361.340	385.662	416.290	467.878	485.311	536.599	640.541
Control[a]	241.226	249.968	278.225	287.269	333.578	345.477	361.343	385.670	416.293	467.879	485.309	536.594	640.541
1995b	241.213	249.959	278.225	287.268	333.580	345.508	361.341	385.676	416.290	467.878	485.311	536.597	640.541
1996b	241.215	249.963	278.224	287.260	333.570	345.499	361.349	385.652	416.288	467.867	485.311	536.605	640.533
2015y	241.216	249.960	278.223	287.263	333.579	345.500	361.339	385.665	416.287	467.875	485.311	536.596	640.532
1998b	241.219	249.965	278.226	287.264	333.577	345.491	361.339	385.657	416.290	467.876	485.310	536.595	640.540
Control[a]	241.219	249.968	278.228	287.263	333.575	345.491	361.348	385.654	416.287	467.871	485.313	536.608	640.536
1999b	241.217	249.972	278.227	287.262	333.574	345.492	361.338	385.675	416.287	467.876	485.312	536.596	640.536
2001b	241.215	249.961	278.223	287.257	333.565	345.485	361.340	385.654	416.277	467.862	485.304	536.592	640.523
2015z	241.219	249.966	278.224	287.265	333.573	345.489	361.346	385.662	416.288	467.876	485.310	536.594	640.538
2002b	241.218	249.966	278.228	287.262	333.570	345.487	361.340	385.671	416.289	467.875	485.310	536.596	640.538
Control[a]	241.215	249.964	278.225	287.259	333.558	345.497	361.351	385.653	416.287	467.866	485.309	536.602	640.534
2004b	241.219	249.965	278.224	287.260	333.564	345.471	361.340	385.668	416.286	467.874	485.310	536.596	640.532

a Sample 2004a, used as a control and for internal calibration

Table A2-1. Day 1 Measurements of Secondary Bands

	Band Locations at 0.8 nm Fixed Bandwidth, nm					
Sample	Pd	Pi	P10a	P10b	Pq	Pu
1985a	260.309	293.439	451.119	451.727	473.661	652.725
2015w	260.261	293.463	451.107	451.735	473.641	652.764
1986a	260.247	293.445	451.070	451.731	473.660	652.758
Control[a]	260.179	293.454	451.076	451.736	473.665	652.741
1988a	260.289	293.428	451.134	451.716	473.647	652.737
1991a	260.246	293.445	451.072	451.710	473.669	652.754
2015x	260.267	293.432	451.090	451.723	473.664	652.744
1994a	260.213	293.486	451.060	451.732	473.662	652.755
Control[a]	260.262	293.449	451.066	451.749	473.648	652.740
1995a	260.273	293.453	451.106	451.735	473.667	652.742
1996a	260.327	293.447	451.046	451.732	473.652	652.739
2015y	260.238	293.448	451.064	451.721	473.671	652.739
1998a	260.230	293.436	451.062	451.737	473.675	652.734
Control[a]	260.283	293.453	451.078	451.725	473.663	652.747
1999a	260.201	293.434	451.057	451.725	473.656	652.739
2001a	260.244	293.449	451.071	451.725	473.652	652.740
2015z	260.263	293.454	451.063	451.735	473.671	652.747
2002a	260.287	293.439	451.074	451.727	473.653	652.735
Control[a]	260.311	293.457	451.055	451.733	473.654	652.740
2004a	260.285	293.452	451.096	451.728	473.654	652.740

a Sample 2004a, used as a control and for internal calibration

Table A2-2. Day 2 Measurements of Secondary Bands

	Band Locations at 0.8 nm Fixed Bandwidth, nm					
Sample	Pd	Pi	P10a	P10b	Pq	Pu
1985b	260.277	293.433	451.059	451.735	473.653	652.749
2015w	260.313	293.461	451.069	451.730	473.651	652.772
1986a	260.322	293.458	451.070	451.731	473.655	652.759
Control[a]	260.270	293.464	451.071	451.734	473.664	652.766
1988b	260.287	293.474	451.061	451.737	473.661	652.778
1991b	260.258	293.458	451.071	451.728	473.653	652.749
2015x	260.303	293.464	451.064	451.727	473.655	652.774
1994b	260.234	293.449	451.098	451.721	473.655	652.768
Control[a]	260.290	293.474	451.061	451.733	473.650	652.779
1995b	260.280	293.456	451.063	451.731	473.663	652.781
1996b	260.301	293.462	451.061	451.733	473.657	652.775
2015y	260.328	293.453	451.062	451.724	473.657	652.796
1998b	260.268	293.457	451.062	451.740	473.645	652.762
Control[a]	260.323	293.431	451.095	451.727	473.641	652.769
1999b	260.302	293.478	451.070	451.739	473.659	652.774
2001b	260.252	293.419	451.054	451.713	473.657	652.741
2015z	260.239	293.423	451.125	451.730	473.671	652.747
2002b	260.266	293.452	451.062	451.705	473.669	652.771
Control[a]	260.276	293.427	451.063	451.733	473.668	652.753
2004b	260.254	293.442	451.081	451.719	473.660	652.766

a Sample 2004a, used as a control and for internal calibration

Table A2-3. Day 3 Measurements of Secondary Bands

Sample	Band Locations at 0.8 nm Fixed Bandwidth, nm					
	Pd	Pi	P10a	P10b	Pq	Pu
1985c	260.280	293.449	451.072	451.725	473.666	652.763
2015w	260.285	293.457	451.069	451.751	473.671	652.755
1986a	260.268	293.454	451.073	451.738	473.662	652.771
Control[a]	260.311	293.466	451.108	451.740	473.667	652.761
1988a	260.281	293.472	451.071	451.729	473.665	652.748
1991a	260.272	293.452	451.077	451.739	473.671	652.770
2015x	260.270	293.460	451.079	451.735	473.682	652.764
1994c	260.269	293.464	451.131	451.740	473.655	652.753
Control[a]	260.269	293.450	451.077	451.744	473.656	652.768
1995c	260.253	293.445	451.080	451.743	473.673	652.759
1996c	260.333	293.441	451.101	451.747	473.655	652.749
2015y	260.295	293.446	451.118	451.745	473.669	652.752
1998c	260.305	293.426	451.104	451.744	473.664	652.759
Control[a]	260.296	293.451	451.091	451.725	473.680	652.780
1999c	260.248	293.450	451.099	451.747	473.667	652.768
2001a	260.285	293.457	451.074	451.736	473.666	652.748
2015z	260.282	293.440	451.079	451.749	473.669	652.761
2002a	260.308	293.452	451.116	451.742	473.668	652.768
Control[a]	260.254	293.431	451.060	451.742	473.667	652.760
2004a	260.276	293.431	451.085	451.737	473.667	652.745

a Sample 2004a, used as a control and for internal calibration