

Holmium Oxide Solution as a Prototype Intrinsic Standard in Molecular Absorption Spectrophotometry

John C. Travis and David L. Duewer

National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-8394

ABSTRACT

Intrinsic standards can become an efficient mechanism for providing traceable reference materials for chemical spectrophotometry. The sealed holmium oxide (Ho_2O_3) in dilute acidic aqueous solution used by the U.S. National Institute of Standards and Technology as Standard Reference Material 2034 is a candidate material for an intrinsic wavelength standard in the ultraviolet and visible spectral regions. Low mass fractions of Ho_2O_3 in glass and as $\text{Ho}^{3+}(\text{aq})$ solutions have long been favored for use as wavelength calibration materials in molecular absorption spectrophotometry on the basis of their spectral coverage and absorption band shape. Three national metrology institutes of the North American Cooperation in Metrology evaluated the performance of $\text{Ho}^{3+}(\text{aq})$ certified reference materials under “routine” operating conditions using commercial instrumentation. The resulting data show a substantial level of agreement while also demonstrating that the wavelength comparability of the five instruments used by the participants can actually be improved by calibrating all of the instruments to the consensus band locations of $\text{Ho}^{3+}(\text{aq})$ solution. A similar approach is being considered to establish intrinsic absorbance standards.

Keywords: intrinsic standard, wavelength calibration, molecular absorption, holmium oxide, reference material.

1. INTRODUCTION

The U.S. National Institute of Standards and Technology (NIST) has operated two separate programs providing regular transmittance traceability for chemical and physical applications for over three decades. In establishing a suite of artifact standards suitable for validating spectrophotometers for use in chemical applications, the Chemical Science and Technology Laboratory (CSTL) of NIST has inadvertently assumed a production role that is incompatible with the efficient delivery of traceability, unnecessarily redundant with calibration services performed by the NIST Physics Laboratory, and in competition with commercial standards producers. Given the prospect of, at best, fixed resources, CSTL now faces the problem of how to satisfy the traceability needs of established spectrophotometric technologies while advancing measurement science in emerging technologies.

The NIST traceability policy was formalized in 2001.¹ This policy adopts the definition of the International Standards Organization (ISO) that traceability is the “property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.”² Following this guideline, CSTL is pursuing two strategies to leverage chemical spectrophotometric traceability beyond our walls.

One of these strategies, the NIST Traceable Reference Materials (NTRM) program, is described in detail elsewhere.^{3,4} NTRM producer/certifiers follow NIST-defined procedures^{5,6} to produce commercial versions of the NIST neutral glass filters, Standard Reference Materials (SRMs) 930e and 1930 Glass Filters for Spectrophotometry.^{7,8} Following verification of compliance and quality, NIST formally endorses the traceability assertion for these materials. Producers/certifiers of certified reference materials (CRMs) outside of the NTRM program are encouraged to assert traceability by careful adherence to the NIST traceability policy statement.

The second strategy involves the establishment of *intrinsic* standards that are “based on well characterized laws of physics, fundamental constants of nature, or invariant properties of materials and make ideal stable, precise, and accurate measurement standards if properly designed, characterized, operated, monitored, and maintained.”⁹ Such fundamental standards as the *second* and the *meter* are intrinsic, based upon stated atomic properties. On a more humble plane, certain

band positions of the $\text{Ho}^{3+}(\text{aq})$ ion in dilute acidic aqueous solutions of Ho_2O_3 appear to be sufficiently invariant to qualify this material as an intrinsic wavelength scale standard for molecular absorption spectrophotometry. A recent study by three national metrology institutes (NMIs) of the North American Cooperation in Metrology (NORAMET) supports both the value of absorption-based wavelength standards and the use of multi-center assessment for certifying properly prepared $\text{Ho}^{3+}(\text{aq})$ solution as an intrinsic wavelength standard.¹⁰ It may be possible to similarly establish intrinsic spectrophotometric absorbance scale standards for use with chemical applications.

2. BACKGROUND

The Ultraviolet Spectrometry Group (UVSG) of the U.K. celebrated its 50th anniversary and announced its dissolution at the third Oxford Conference in 1999. The anniversary was also marked by the publication of a book whose first half is devoted to standards in absorption spectrometry.¹¹ Chapters are devoted to physical and chemical standards for the validation of absorbance accuracy, the evaluation of stray radiant energy, and the calibration of the wavelength scale. The most widely used standards today are not intrinsic and require individual certification; however, a limited number of the historical artifact standards for absorbance and wavelength may be expected to be sufficiently invariant to qualify as intrinsic standards. New materials should be evaluated for potential utility as well.

In spite of their popularity, glass-matrix absorbance standards are labor-intensive – requiring individual certification and the perpetual maintenance of national scales of regular transmittance as defined by purpose-built reference spectrophotometers. Neutral density glass standards for the visible spectral region¹² utilize commercial glasses that are subject to grinding tolerances and whose composition varies slightly between and within melts. Metal-on-fused-silica neutral density filters¹² covering the entire UV/visible/near infrared range are difficult to produce and suffer inter-reflection effects. Both types of solid filters drift due to natural surface chemistry and the accumulation of surface contamination; both must be periodically cleaned and recertified. Glasses also provide a popular matrix for absorption-based wavelength standards, utilizing low concentrations of rare earth elements to provide the sharp absorption features needed as wavelength markers.¹³ These filters are widely available, although often relying upon published band positions for a generic type of glass. While band positions are little affected by changes in filter surface, high-accuracy work requires the certification and/or validation of individual filters.¹³

Simple chemical solutions offer the most obvious possibilities for intrinsic standards for chemical spectrophotometry. For both the absorbance and wavelength scales, such standards are easily used with “routine” measurement geometry and mechanisms. Fresh solution standards can be easily prepared as and where needed with gravimetric accuracy. Disadvantages include effects of impurities in the chemicals used to prepare the solutions, possible toxicity and chemical disposal difficulties, and significant temperature coefficients.

A particularly robust and forgiving solution-based wavelength standard is presented here as a prototype intrinsic standard for chemical spectrophotometry: $\approx 4\%$ (mass fraction) Ho_2O_3 in $\approx 10\%$ (volume fraction) perchloric acid in water. The resulting $\text{Ho}^{3+}(\text{aq})$ ions yield sharp absorption bands with minimal band position temperature dependence over a temperature range of $25\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$.¹⁴ The locations of the major bands from 240 nm to 640 nm are remarkably robust with respect to $\text{Ho}^{3+}(\text{aq})$ concentration over a mass fraction range of 2% to 6% and minor variation in the absorbance baseline. NIST and the Centro Nacional de Metrología (CENAM) of Mexico provide this solution contained in flame-sealed, nonfluorescent, fused-silica cuvettes.^{15,16} Similar materials are available from a number of commercial sources. NIST has certified ten “series” of SRM 2034 Holmium Oxide Solution Wavelength Standard from 240 nm to 640 nm, beginning in 1985; although the same supply of Ho_2O_3 powder was used in all, each series represents at least one preparation of the solution using different acid, water, and cuvettes. The CENAM standard DMR 41e Filtro de Óxido de Holmio is prepared from source materials different from those used at NIST.

3. NORAMET EVALUATION OF HOLMIUM OXIDE SOLUTION WAVELENGTH STANDARDS

3.1. Purpose

Beginning in June 2000, five groups within the three NORAMET NMIs evaluated the performance of NIST and CENAM $\text{Ho}^{3+}(\text{aq})$ CRMs under “routine” operating conditions using commercial instrumentation. The study was designed to (1)

evaluate wavelength measurement comparability among research-grade commercial instruments, (2) demonstrate the comparability between NIST and CENAM CRMs, (3) acquire a database of $\text{Ho}^{3+}(\text{aq})$ spectral data from a variety of spectrophotometers for use in a NIST study of wavelength-assignment algorithms, (4) establish realistic uncertainties on the measurement of band locations in these CRMs, and (5) critically assess the NIST-certified SRM 2034 band location values.

3.2. Protocol

Five research-grade commercial spectrophotometers were employed by the three participating NMIs, each operated by different individuals. The participating personnel and instruments are fully described elsewhere.¹⁰ A single sample kit of two CENAM and two NIST CRMs was circulated among the participants; a complete data set was acquired by the NIST/CSTL coordinating laboratory at the beginning and end of the study. Thus, a total of six “data sets” were acquired. Participants were asked to calibrate the wavelength axis of their instrument using pen lamp discharges. Such atomic emission features constitute ideal intrinsic wavelength standards for many spectroscopic applications, but their use is often problematic in commercial spectrophotometers with only continuum lamps built in. The NIST/CSTL instrument is calibrated using pen lamps in the source position normally occupied by the system deuterium lamp.

Participants were asked to submit complete spectral scans, from 230 nm to 680 nm, in increments of 0.1 nm for all four CRMs on each of two days and at each of three different spectral slit width (SSW) settings of the instrument. Thus, each data set consists of 24 complete spectra. The data were all processed identically by NIST/CSTL and calibration corrections furnished by participants were applied to extracted band locations. A representative spectrum for a 0.1 nm SSW is shown in Figure 1.

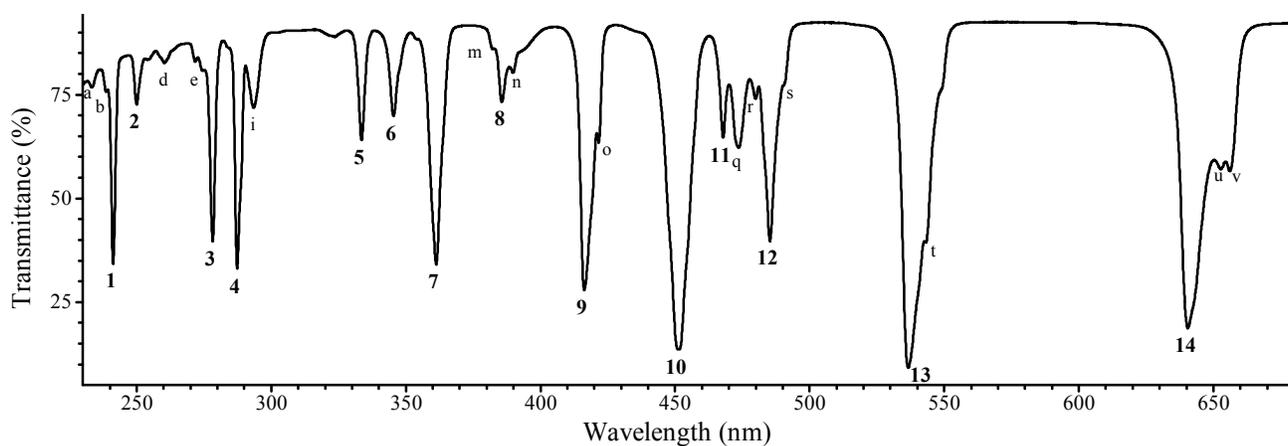


Figure 1. Representative 0.1 nm SSW UV-Visible spectrum of 4 % mass fraction Ho_2O_3 in 10 % volume fraction perchloric acid in water. Bands having certified SRM 2034 and DMR 41 locations are labeled “1” through “14”; other spectral features evaluated are labeled “a” through “v”.

3.3. Band Location Algorithms

Three band location algorithms were evaluated; they are illustrated in Figure 2. The *local minimum* is the simplest, represented by the discreet data point with the lowest transmittance in the band in question. This method is obviously limited to spectra for which the sampling interval is smaller than the required wavelength accuracy tolerance. The *interpolated minimum* is common to many software packages that accompany commercial instruments. A cubic polynomial fit to five data points, including the local minimum and the two neighboring data points on each side, provided results that agree closely with peak location data provided by participants using similar peak location algorithms. The *bisection* method was used in the original NIST certification of SRM 2034.¹⁴ The method is better suited to strip-chart recordings than to digitized spectra, but a bisection curve can be defined using the midpoints of a series of horizontal chords that connect points of equal transmittance on each side of the band envelope. The band location is given by the intersection of this bisection curve with the band envelope at the bottom of the band. The computer implementation strikes a horizontal chord from each data point, whereas the original version used the grid of the chart paper.

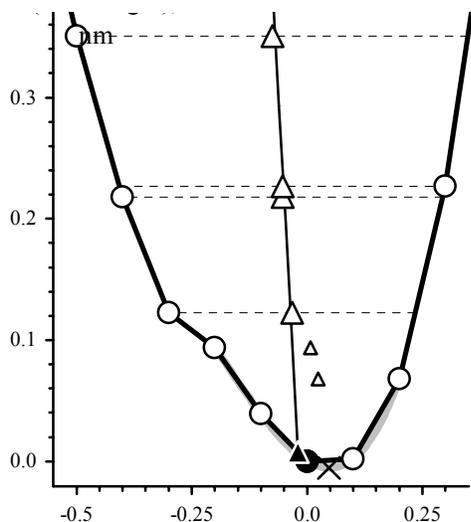


Figure 2. Band location estimation algorithms for a representative band of a 0.1 nm SSW spectrum. The zero of the wavelength (horizontal) and the transmittance (vertical) axes is defined by the lowest-transmittance datum. Observed data are denoted by open circles and are connected by a thick solid line; the local minima (lowest observed transmittance) is denoted by the closed circle. The cubic fit to the five data centered on the local minima is represented by a thick gray line; the interpolated minimum (lowest calculated transmittance of the fitted curve) is denoted by the symbol “x”. Representative bisector chords are shown as horizontal dashed lines; the chord midpoints are denoted with large open triangles. The band bisector defined by all “smoothly connected” midpoints is represented by the thin vertical line. The bisection minimum (the intersection of the band bisector and the band envelope) is denoted with a solid triangle. The small open triangles denote chord midpoints that were excluded from use in defining the band bisector.

The results of the study favor the interpolated minimum method, with the happy consequence that the details of the algorithm are relatively unimportant. Differences between values returned by the interpolated minimum and the bisection method favor the re-assignment of band positions for SRM 2034, which have not been modified since the original certification of the first series in 1985 using the bisection algorithm.

3.4. Spectral Slit Width Effects

At 0.1 nm SSW, there are at least 36 transmittance minima of at least 1 nm baseline width between 230 nm and 680 nm in a typical $\text{Ho}^{+3}(\text{aq})$ spectrum (Figure 1). All of these observed minima were *post facto* evaluated in all spectra acquired for this study. While a number of these spectral minima proved to be too sensitive to photometric noise for consistent characterization, 29 proved unambiguously present in all of the study’s 0.1 nm spectra. Although the 14 minima certified in SRM 2034 are present in all three SSWs, as illustrated in Figure 3 only the most symmetrical retain the same location and many fuse or “wash out” at the larger SSWs.

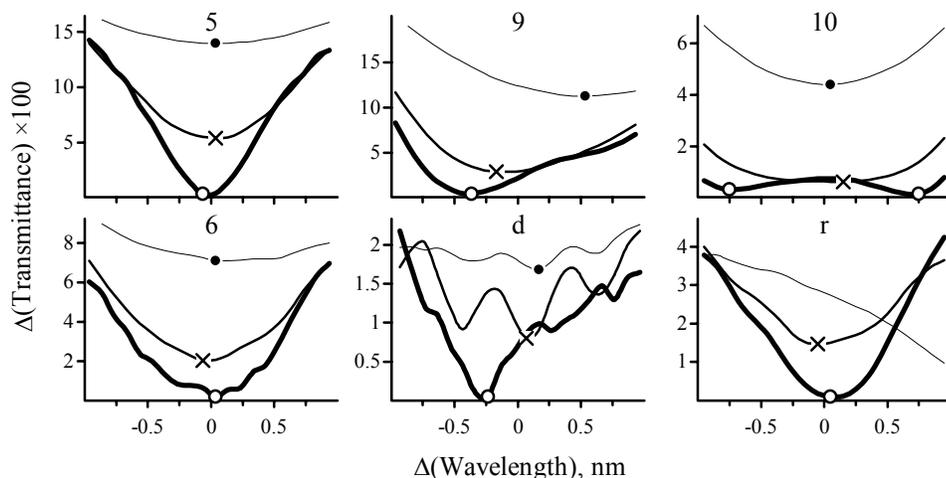


Figure 3. Representative spectra minima at SSWs of 0.1 nm (dark line, open circle), 1 nm (medium line, x) and 3 nm (light line, solid circle), where the symbols denote the location of transmittance band minima. The wavelength axis of each window is centered on the mean location of all the band minima displayed within the window; the transmittance axis of each window is scaled to the smallest and largest displayed transmittance.

3.5. Uncertainties

The combined standard uncertainty^{17,18} for the position of a given spectral minimum is modeled as:

$$u_{total} = \sqrt{u_{replicate}^2 + u_{set}^2 + u_{sample}^2}$$

where $u_{replicate}$ estimates the short-term replication variability, combining inter- and intra-session effects, u_{set} estimates the among-instrument variability and/or long-term operational differences for a given instrument, and u_{sample} estimates the variability in band location among the four samples.¹⁰ Figure 4 displays the uncertainties at 1 nm SSW for all features.

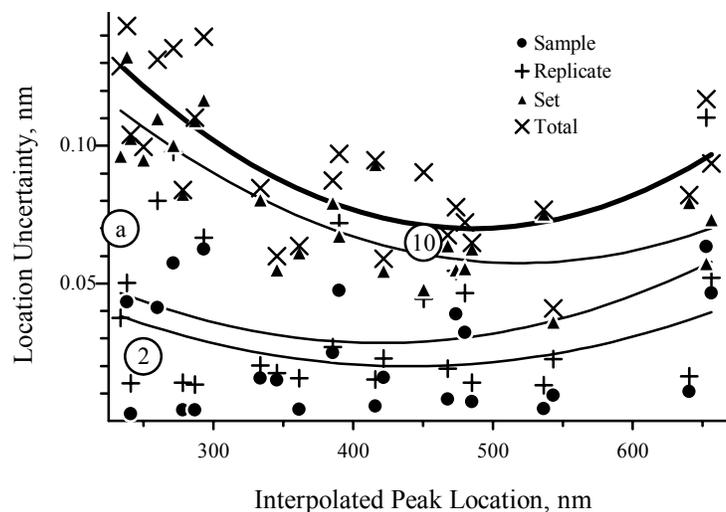


Figure 4. Estimates of the uncertainty components for the interpolated 1.0 nm SSW minimum locations: u_{sample} , $u_{replicate}$, u_{set} , and u_{total} . The labeled open circles denote features for which $u_{sample} > u_{replicate}$.

The u_{sample} is almost always smaller than $u_{replicate}$, indicating that the four samples are statistically indistinguishable from each other with respect to the location of the transmittance minima. In particular, CENAM and NIST CRMs provide virtually identical band locations. This supports the hypothesis that the locations of most of the $\text{Ho}^{+3}(\text{aq})$ transmission minima are effectively invariant with respect to minor production differences.

The u_{total} for different transmission minima range from ≈ 0.05 nm to ≈ 0.15 nm. Thus, the 95% confidence limits for some bands are greater than the ± 0.2 nm overlap expected from the ± 0.1 nm uncertainty asserted in the original SRM 2034 certification and the uncertainty of about ± 0.1 nm asserted as the measurement accuracy by each participant.

Since u_{set} is the dominant source of variability, it is useful to examine this source of variation in greater detail. The left side of Figure 5 displays the average bias of the 1.0 nm SSW transmittance minima locations for each of the six data sets relative to the all-set means. Quadratic polynomial correction/calibration curves for each set are also displayed, each defined from the relative biases for bands 3, 5, 7, 9, 12, and 14. The right side of Figure 5 displays the biases after correction to these calibration curves. Removal of these systematic biases reduces the pooled u_{set} for the bands not used in the calibration from 0.086 nm to 0.039 nm – roughly the same magnitude as u_{sample} and u_{set} for these bands.

The original SRM 2034 certified uncertainties thus do not account for the practical uncertainties involved in emission-line calibrations of different instruments as performed by skilled operators. This assessment is not intended as a judgement on the scientific quality of the original work, but to bring the uncertainty statements into accordance with recent uncertainty guidelines.^{17,18} The results of this NORAMET study have already been incorporated in the quoted uncertainties for SRM 2034, Series 01, produced in 2001.

3.6. Locations

The consensus mean values for the locations of bands 1 through 14 agree with the certified values for SRM 2034 within a tolerance defined by the overlap of the ± 0.1 nm uncertainty originally quoted for SRM 2034 and the 95% uncertainty bounds

of the present data. Nevertheless, the inadequacies of the originally used bisection location algorithm demonstrated in Figure 2 suggest the advisability of a reevaluation of the certified positions for SRM 2034, Series 02, to be produced in the year 2002. Given the among-instrument biases demonstrated in Figure 5, the value assignment should involve comparative measurements on different instruments.

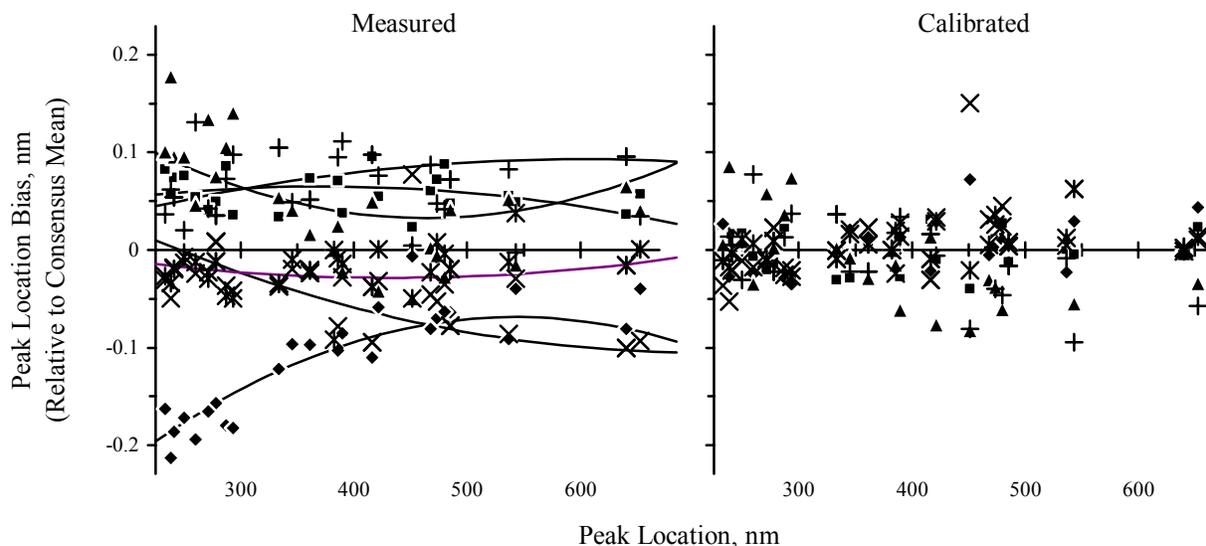


Figure 5. Location biases at 1 nm SSW. The left side segment displays location bias measured for each data set relative to the consensus means. Biases are estimated as the interpolated location difference averaged over all spectra. Quadratic polynomial calibration curves of the measured biases to the consensus locations are also displayed. Each symbol type denotes results for one of the six data sets. The right side segment displays the residual bias data after quadratic calibration.

An unexpected conclusion that may be drawn from Figure 5 is that use of dilute acidic H_2O_2 solution absorption standards may provide better calibrations for even high-end commercial spectrophotometers than can be easily achieved using atomic emission lines. We speculate that broad absorption peaks improve calibration consistency for SSWs of 0.1 nm or greater by minimizing the influence of slit function asymmetry. In any case, the use of an absorbing standard ensures that the optical axis of importance is the same for calibration as it is for applications.

4. MULTI-CENTER WAVELENGTH ASSESSMENT TO ESTABLISH AN INTRINSIC STANDARD

4.1. Rationale and Proposed Use of an Absorption-Based Intrinsic Wavelength Standard

Wavelength accuracy is ultimately traceable to the SI unit of the meter, itself an intrinsic standard based upon an atomic property. The first link in the practical traceability chain is provided by intrinsic secondary length standards – atomic wavelengths from gas discharge lamps. The use of the traceable wavelengths of light from such lamps is widely recommended for the calibration of dispersive spectrometers.¹³ Instruments calibrated in this manner are used to value-assign the transmittance minima of absorption-based artifact standards for the wavelength calibration of spectrophotometers not equipped to accommodate discharge lamps. Each link in the traceability chain – from pen lamp to spectrometer to CRM – involves the evaluation of additional uncertainty components beyond those passed from the prior link. Nonetheless, the resulting uncertainty of $\approx \pm 0.25$ nm suggested by the NORAMET study for the interpolated band minima is acceptable for a wide variety of chemical applications that require traceability to satisfy regulatory or quality-control mandates.

The traceability requirement applied to ever smaller and less expensive utility-grade molecular absorption spectrophotometers implies a monotonically increasing work load for NMIs supporting traceability through calibration services or certified reference materials. The establishment of an appropriate intrinsic standard represents a rational

mitigation of the calibration/certification treadmill for the bulk of requirements relating to utility instruments. Applications requiring wavelength accuracies on the order of 0.1 nm would still require NMI calibration services.

The intrinsic standard does not replace the artifact for the end user, but supplies a ready traceability resource for commercial producers of reference materials. The responsibility of the commercial standards producer is to furnish evidence that the reference material has been prepared in absolute conformance to the conditions stipulated in the documentation of the intrinsic standard. For dilute acidic holmium oxide solution, the proof that the material has been properly prepared lies in the spectrum itself. The simple proof is to acquire back-to-back spectra of the candidate solution and a previously certified solution such as NIST SRM 2034 on the same instrument, and verify that the spectra overlay within a tolerance prescribed by the intrinsic standard documentation. This method does not require that the spectrophotometer used be perfectly calibrated, but does require the availability of the previously certified artifact. A second method compares the spectrum from the candidate solution with an electronically tabulated version of the approved spectrum of the intrinsic standard. This method does require that the instrument be well calibrated. For this purpose, the candidate material can be used as the calibrant, and the experimental spectrum with the calibrated wavelength axis should overlay the intrinsic "pattern" within the required tolerance. Interpolation may be required to examine difference spectra on an expanded scale.

Three studies are proposed: (1) a multi-center evaluation of band locations in one exemplar material at selected SSWs, (2) verification of the validity of mathematical convolution techniques for establishing band locations as continuous functions of SSW, and (3) characterization of the acceptable material spectral profile.

4.2. Proposed Protocol for Band Location Evaluation at Selected SSWs

The proposed protocol is quite different from that used in the NORAMET study, although soliciting similar information. Participation has been invited from nearly every region of the world. The NMIs that have agreed to participate plan to use a variety of instruments that can be calibrated with one or more atomic spectral lines, including a few custom-built national reference spectrophotometers. Different samples of a single preparation of NIST SRM 2034 will be sent to each participant. For scanning double-beam instruments, participants are asked to furnish complete spectra at a data spacing of 0.1 nm for SSWs of 0.1 nm, 1.0 nm, and 3.0 nm. Participants are also asked to furnish calibration information, either as bias correction polynomials and/or suitably high-density spectral scans of atomic discharge lamps. Where such complete scans are impractical, participants are asked to provide results in the most convenient form – from "region-of-interest" discontinuous scans about the transmittance minima to extracted and calibrated transmittance minima. For instruments that do not allow data acquisition at the three desired SSWs, participants are asked to provide the results they can achieve.

The samples that will be distributed, part of the SRM 2034 Series 02 production, have been prepared and individually characterized by CSTL. A collaborative report describing all acquired data, data analysis techniques, and consensus band locations and their uncertainties will be prepared for publication in a suitable peer-reviewed journal.

4.3. Proposed Protocol for Band Location at Arbitrary SSWs

Observed spectra are convolutions of an infinitely well-resolved fundamental spectrum with the instrument's slit function. Given that a 0.1 nm SSW $\text{Ho}^{+3}(\text{aq})$ spectrum is adequately close to fully resolved and that modern chemical spectrophotometric instruments employ slit functions that can be well approximated as slightly flattened isosceles triangles, band locations can be mathematically calculated as continuous functions of SSW.¹⁹ We propose to use the 0.1 nm SSW spectra acquired in the above multi-center phase as the basis for these calculations, and to validate the calculations with band locations observed at other SSWs. Spectrophotometers have been identified that can provide experimental validation for SSWs up to 16 nm. A report will be prepared expressing $\text{Ho}^{+3}(\text{aq})$ band locations and their uncertainties as low-order polynomials with respect to SSW.

4.4. Proposed Protocol for Material Quality Assessment

CSTL has initiated a single-instrument evaluation of archival samples of all the SRM 2034 series, all units of SRM 2034 Series 02, a number of units of CENAM's DMR 41e, and exemplars of other available $\text{Ho}^{+3}(\text{aq})$ standard solutions. A report will describe the spectral variability encountered and the effect on certified band positions, and the envelope of acceptable spectral tolerance will be made web-accessible.

5. POTENTIAL FOR ADDITIONAL INTRINSIC STANDARDS

Solid neutral density filters mounted in cuvette-simulating frames have long been the most popular medium for validating the absorbance axis of UV/visible spectrophotometers.¹² Beam attenuation in the visible spectral region is provided by commercial glasses that have been doped in the melt with a recipe of absorbing species so as to produce a nominally constant specific absorptivity over the visible spectrum. In the UV, such neutral density filters are provided by thin metallic films deposited on a fused silica substrate, attenuating as much by specular reflectance as by absorption.¹² In either case, these filters must be individually calibrated to provide the required accuracy for instrument validation, and are thus not candidates to become intrinsic standards. The popularity of these filters derives largely from (1) the ease of use, (2) the lifetime (though periodic recertification is advised), and (3) the relative spectral neutrality (flatness), permitting calibration at the same wavelength(s) as the application for which the instrument is being validated.

The challenge in identifying intrinsic absorbance standards is to identify simple chemical solutions that offer competitive advantages to the individually certified neutral density filters. Spectral neutrality is immediately sacrificed, with the closest analogy being a requirement for spectrally broad and smooth absorption bands providing for minimal interaction with the wavelength accuracy and SSW of the instrument under test. Intrinsic absorption coefficients for such materials would be furnished at local absorbance maxima and/or minima (with local spectral neutrality); these wavelengths would not necessarily correspond to desired application wavelengths. For this purpose, end users must be educated that wavelength matching of the application may well be an excessive requirement, as long as the application and the standard are within the range of the same continuum lamp (normally deuterium or tungsten). Users should understand that instruments must be validated for absorbance accuracy and stray radiant energy²⁰ in each spectral region defined by the use of a different lamp or detector, but that matching the exact wavelength of applications is generally impractical and unnecessary.

The convenience of solid filters is matched by chemical solutions permanently sealed into cuvettes. Sealed solutions can be certified gravimetrically by commercial standards producers using an intrinsic standard “recipe,” although there are several caveats. The first of these is that the solution be stable under normal use conditions, preferably for a period of years. A second is that reflective losses from the cuvette walls be compensated by a “blank” sealed into an adequately matched cuvette. A third is a realistic assessment of gravimetric uncertainties and material purity factors. Solutions sealed into ampoules provide an option that mitigates the cuvette-correction problem, since the sample and blank may be sequentially measured in the same cuvette. However, the other two caveats remain, and the user is faced with chemical disposal needs as well as the depletion of the standard.

The obvious choice for the ultraviolet region is potassium dichromate (in acidic solution), which has long been advanced as a UV absorbance standard.^{21,22} This material is available from NIST in powder form as SRM 935a Crystalline Potassium Dichromate for Use as an Ultraviolet Absorbance Standard²³ or sealed into ampoules as SRM 1935 Potassium Dichromate Solution for Use as Ultraviolet Absorbance Standard.²⁴ The standard is certified at absorbance valleys at 235 nm and 313 nm, and at absorbance peaks at 257 nm and 350 nm. For use with instruments of SSW greater than 2 nm, correction factors would be required for the measured values or the uncertainties. To be qualified as an intrinsic standard, this material would require studies of purity requirements for the base material, water, and acid; further studies on the storage life in various formats; and a multi-center re-evaluation of the specific absorptivity values. Variations on potassium dichromate as well as other candidate materials for the UV spectral region are discussed in a recent book chapter.²²

NIST SRM 931 Liquid Absorbance Standard for Ultraviolet and Visible Spectrophotometry²⁵ provides a starting point for intrinsic standards for the visible region, with $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ions providing an absorbance maximum at 512 nm and $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ ions providing an absorbance maximum at 395 nm and a broad plateau at 650 nm to 700 nm. This NIST SRM is extremely stable sealed into ampoules. A reference material available from the Laboratory of the Government Chemist using these ions is furnished sealed into cuvettes.²⁶ The preparation of these materials is described as “not easy”;²² the first step in designing an appropriate intrinsic standard based on these materials would be to identify user-friendly gravimetric chemical procedures.

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