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## Challenges in providing standard reference materials for chemical and pharmaceutical process analysis

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### Abstract

The NIST Analytical Chemistry Division has supplied transmittance verification and wavelength calibration standard reference materials (SRMs) specialized to the needs of chemical and pharmaceutical spectrophotometric analysis since 1970. Growing demand for UV/visible standards stems from the increasingly routine use of spectrophotometers for pharmaceutical quality control and from the escalation in the documented use of standards for regulatory and voluntary quality control purposes. To meet the demand, NIST is studying ways to accelerate standards production. Projects include studies of the origin of transmittance drift (which necessitates aging during production), investigations of solid UV filters and of sealed liquid standards, and the development of an NIST-traceable reference material (NTRM<sup>TM</sup>) optical filters program to involve the private sector. Recently, we have revised the optical specifications of our solid filter standards to meet the requirements of reversed-geometry (post-dispersion) instruments. In the near-infrared, spectrochemical process control applications mandate the need for wavelength standards to support the stability and instrument-to-instrument transfer capability of multivariate analytical calibration models. We are presently producing one such standard and are investigating others. Finally, we are studying algorithms for locating peaks in wavelength standards to find a consistent means for making wavelength assignments from the UV through the mid-infrared. © 1999 Published by Elsevier Science B.V. All rights reserved.

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### 1. Introduction

The Analytical Chemistry Division (ACD) of NIST certifies a number of standard reference materials (SRMs) for verifying the accuracy of UV/visible/NIR spectrophotometers used for chemical and pharmaceutical applications. As shown in Fig. 1, most are designed to fit the ubiquitous holders for 12.5 mm

square cuvettes. The photometric (absorbance) standards are individually certified using the ACD reference spectrophotometer [1]. This instrument has operated since 1970 with little revision beyond the implementation of three generations of control computer. The optical design principles are common to several national reference instruments and are being maintained in a new instrument currently being assembled (Fig. 2). Our new instrument will hold more samples for automated measurement and will interface directly to our recently implemented filters database.

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Fig. 1. Representative SRMs.

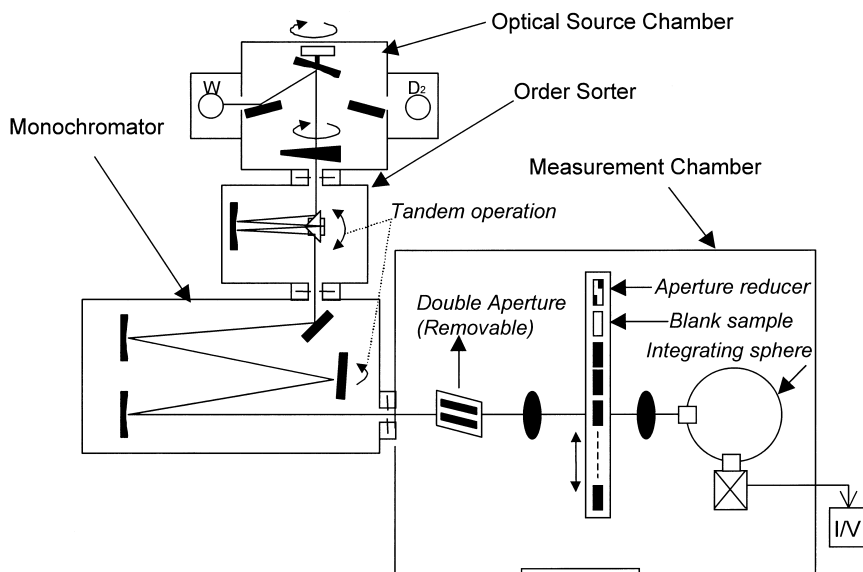


Fig. 2. New ACD reference spectrophotometer.

Despite the relative maturity of molecular absorption spectrometry, the spectrophotometric standards program has become particularly challenging in the present era. Especially noteworthy is the increase in demand for reference materials arising from the growth of quality systems (e.g., compliance with International Standards Organization (ISO), European Pharmacopoeia (EP), United States Pharmacopoeia (USP), etc., guidelines). The availability of affordable standards from NIST for nearly three decades has led to their incorporation into many standard operating procedures (SOPs) and into the expectations of many regulatory and accreditation inspectors. To address the need to expand the availability of standards in the face of limited resources, NIST is leveraging its measurement capability through the private sector by means of the NIST-traceable reference material (NTRM<sup>TM</sup>) program. This program presents an operational challenge of maintaining trustworthy traceability to the reference spectrophotometer while maintaining uncertainties sufficiently comparable with those of the SRMs.

Although maintaining traceability is certainly a technical challenge, we devote a section so entitled to several recent and ongoing measurement problems related more to maintaining or improving measurement quality than to expanding standard production capacity. Some of these challenges span the history of

photometric standards and others are of more recent origin, arising from the demands of new technologies and applications.

Before addressing either the NTRM program or assorted technical challenges, it is appropriate to provide an overview of the current SRM program.

## 2. Standard reference materials (SRMs<sup>®</sup>)

The SRMs offered by NIST for chemical spectrophotometry are summarized in Table 1. The letter following the SRM number is typically incremented for a new production run of a given standard. However, since most of the solid filter standards are effectively in continuous production, these letters are only incremented in the case of a noteworthy change. The table shows the current SRM identifications including the letter suffix, but the discussion below applies to all series of a given standard and omits the trailing letter.

Absorbance standards are intended for the *verification* of the absorbance scale of chemical spectrophotometers. These standards are certified at several wavelengths for their air-referenced optical transmittance ( $T$ ) and for their “transmittance density” (TD), defined by NIST as  $TD = -\log_{10}(T)$ . The TD is defined identically to absorbance, except it is based upon a

Table 1  
NIST standard reference materials for UV/visible spectrophotometry

SRM	Type	Wavelength range (nm) (no. of wavelengths)	Unit size
930e	Transmittance, neutral glass, $T_{\text{nom}}=0.1, 0.2, 0.3$	440–635 (5)	3 filters+1 holder
931e	Absorbance, liquid, 3 levels and blank	302–678 (4)	Set of 12 ampoules
935a	Absorbance, potassium dichromate powder, 10 levels	235–350 (4)	15 g
1930	Transmittance, neutral glass, $T_{\text{nom}}=0.01, 0.03, 0.5$	440–635 (5)	3 filters+1 holder
2030a	Transmittance, $T_{\text{nom}}=0.3$	465	1 filter+1 holder
2031a	Transmittance, metal-on-fused-silica, $T_{\text{nom}}=0.1, 0.3, 0.9$	250–635 (10)	3 filters+1 holder
2032	Stray light, potassium iodide	240–280 (9)	25 g
2034	Wavelength, holmium oxide solution	240–650 (14)	1 sealed cuvette
2035	Wavelength, rare-earth glass, to be available 1999	~1000–2000 (n.a.)	2.5 cm disk in 5 cm holder

transmittance that is referenced to air. (Absorbance in the normal analytical measurement is referenced to a blank contained in a cuvette such that reflective losses at the windows to the sample and the blank cancel in the transmittance ratio.) The user is directed to compare absorbances determined for the standards referenced to air with the certified values of TD. Instrument performance is judged satisfactory at a given wavelength and absorbance if the range determined by the mean of several measurements and a symmetric interval representing the instrument or application specification overlaps the range determined by the certified value and its expanded uncertainty (95% confidence) interval. The user is not instructed to use the SRM to “calibrate” the photometric axis, in the event of disagreement, but to contact the instrument manufacturer for advice or repair.

### 2.1. Solid absorbance standards

The earliest, most widely known and distributed NIST filters, the SRM 930 series, are made from Schott “NG” neutral density glasses to nominal transmittances of 10%, 20%, and 30% [2]. The later introduction of SRM 1930, made from the same series of glasses but to nominal transmittances of 1%, 3%, and 50%, extended the range covered by SRM 930 in both directions [3]. Spectra for representative filters of these SRMs are shown in Fig. 3. Although the glasses are formulated to be as “neutral” – or spectrally flat – as possible, it is evident that shallow local extrema are still present. These features result from mixing a “soup” of absorbing species for which the absorption peaks of some species fill the valleys of others.

These filters are certified at five visible wavelengths corresponding to local spectral extrema, as illustrated in Fig. 3. A convenient coincidence is that one extremum occurs at the wavelength of the 546.1 nm green line of atomic mercury. Standards are certified at positions of zero slope in order to minimize measurement error due to inaccuracy in the wavelength axis of the instrument under test. The uncertainty estimate includes a worst-case scenario of a 1 nm wavelength bias in the reference spectrophotometer, and users of the standards are advised to ensure wavelength accuracy to within 1 nm as well.

Neutral density filters to serve both the UV and visible spectral regions are typically constructed by coating thin, partially reflective metal films on fused silica substrates [4,5]. The NIST design is unique in using chromium and in optically contacting a fused silica cover plate over the thin metal film. The SRM 2031 series includes two such filters, nominally 10% and 30% transmitting, plus an uncoated fused silica plate referred to as a nominal 90% transmitting filter – with losses due to Fresnel reflections at the entry and exit faces. An empty filter holder, for use in the reference beam as the “blank”, is furnished with the set as well as with each set of SRMs 930 and 1930.

The chromium coating is less spectrally flat than the inconel or nichrome coatings used by other standards producers, but accommodates the optical contacting of the cover plate more readily. The cover plate improves the absorbance stability of the filter as well as simplifying the procedure for cleaning the filter. The spectral variation in chromium leads to a significant departure from the nominal transmittance at the spectral extremes, but is inconsequential for the standard

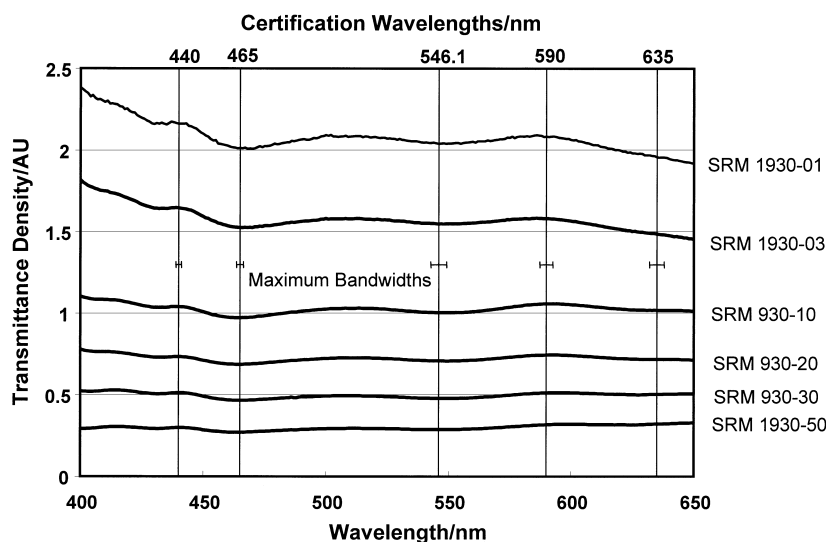


Fig. 3. Spectra of neutral glass filters.

since it is certified at 10 wavelengths across the UV and visible regions. Despite chromium's enhanced spectral response, its local spectrum is still sufficiently flat that the wavelength accuracy and bandwidth requirements for the certifying and tested instruments are generous. It is more noteworthy that the transmittance of such filters is determined largely by reflection rather than absorption. This leads to inter-reflection and stray light errors in some instruments.

### 2.2. Powder and liquid absorbance standards

NIST certifies two other absorbance standards, in part to provide UV-certified values determined primarily by absorption. Fig. 4 shows the spectra for one of the three certified absorbance levels of SRM 931 [6] and for one of the 10 certified levels of SRM 935 [7,8]. SRM 931 is a mixture yielding spectral features due to cobalt, nickel, and nitrate ion, and is available in sets of 10 ml ampoules containing three ampoules for each of the three certified levels and the blank. SRM 935 is high-purity potassium dichromate, and is available as a powder, certified for the absorbance per unit path-length relative to a specified blank at eight mass to volume ratios. The certification wavelengths, shown on the spectra, again correspond to local extrema to minimize bias resulting from wavelength error. The curvature of any given extremum determines the

maximum instrumental bandwidth for which the certification is valid.

### 2.3. UV/visible wavelength standard

NIST supplies a dilute holmium oxide solution, flame-sealed into a fused silica cuvette, as SRM 2034 [9]. The absorbance spectrum of this standard is shown in Fig. 5, along with that of a holmium oxide-doped glass, which is also widely used as a standard. The solution provides certifiable features at shorter wavelengths than the glass, and is stable for at least 10 years. Fourteen bands are certified for the position of minimum transmittance for six different instrumental bandwidths between 0.1 and 3 nm, with an expanded uncertainty (95% confidence interval) of 0.1 nm.

## 3. NIST-traceable reference materials (NTRMs)

The demand for NIST spectrophotometric performance standards has outstripped our capacity to produce them. Since our production capacity is unlikely to increase, we are exploring alternate schemes to provide measurement traceability from the end user to our reference spectrophotometer. Currently, we are defining an NTRM program to provide a defined traceability to NIST for optical filters made and

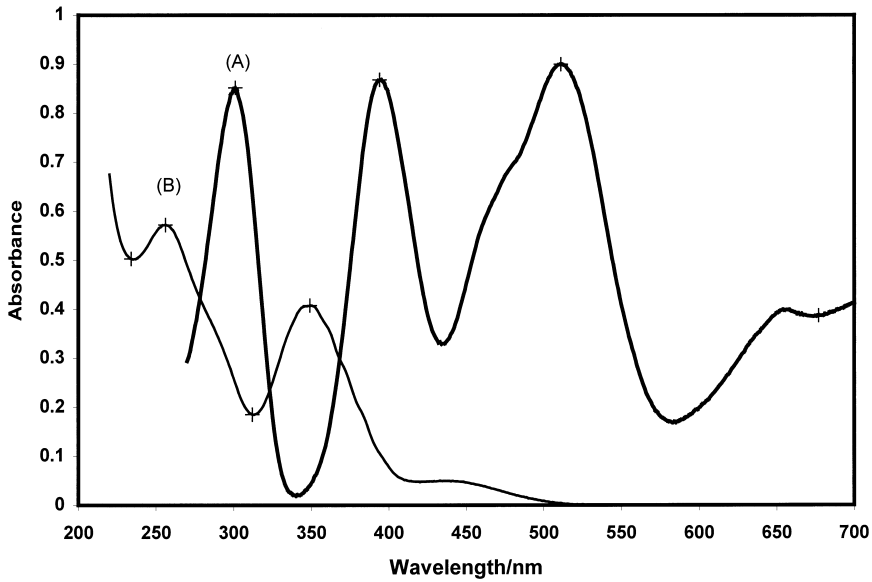


Fig. 4. Spectra of liquid standards: (A) SRM 931e, level III, and (B) SRM 935a at one of 10 mass fractions (0.04 g/kg) certified for specific absorptivity.

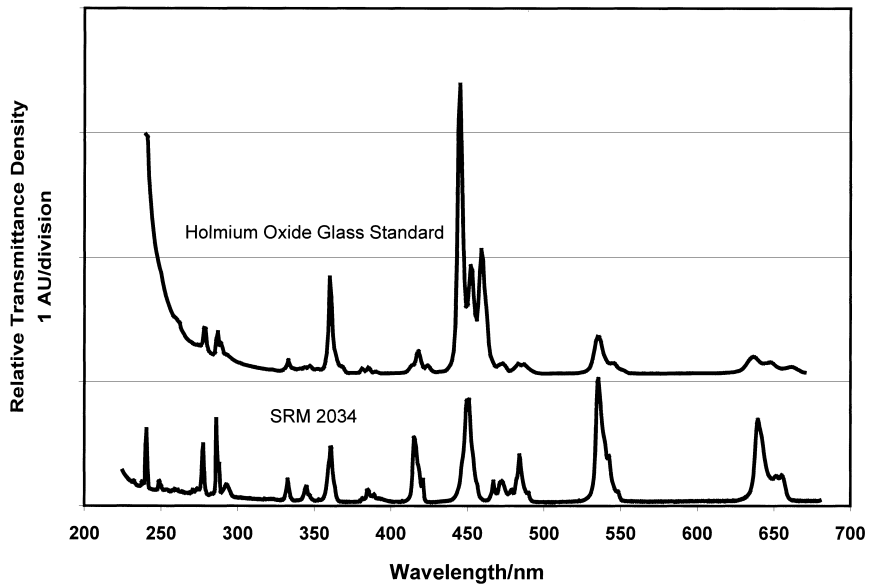


Fig. 5. Holmium oxide solution and glass spectra.

certified to our specifications by private-sector firms. Unfortunately, the expression “traceable to NIST” has been widely employed to describe a variety of protocols, many of which are ill defined and incompletely documented. The NTRM program concept,

which was first implemented about three years ago for NIST gas standards [10], defines the traceability of standards to NIST. NIST provides the quality assurance for such standards produced, certified, and distributed in the private sector. We are beginning our

NTRM program for spectrophotometric performance standards with the neutral density glass filters. To make this viable, NIST will inspect and certify the private-sector manufacturers who will follow defined protocols to assure the quality of their processes and measurements. In addition, NIST will monitor the certification and recertification measurement data from each of the NTRM filters made by each of the manufacturers.

### 3.1. NTRM workshops

A workshop on “NIST Traceability in Chemical Spectrophotometry” attracted 34 participants, including 10 from NIST, two from the US Food and Drug Administration (FDA), 15 from manufacturers of chemical spectrophotometers, about 10 from present producers or suppliers of spectrophotometric standards, and three from large-scale end user (chemical/pharmaceutical) companies. (Since some of the instrument manufacturers also supply standards, their representatives are counted twice.)

The sense of the workshop was to explore the NTRM concept further, with the caveat that NTRM standards would be effectively useless unless they were accepted as representing NIST traceability by regulatory (e.g., FDA, Environmental Protection Agency (EPA), etc.) and/or accreditation inspectors. The workshop participants agreed to two further meetings. The first would involve the subgroup of participants who might actually become NTRM providers, and the final meeting would reassemble the original participants for the finishing touches and recommendations. Final approval authority resides at NIST, but the input from the workshops is critical to NIST approval.

The smaller “working group” meeting held a few months later established some operational principles:

- NTRM providers would be accredited by the NIST-based National Voluntary Laboratory Accreditation Program (NVLAP).
- NTRM standards would be held to the same production specifications and inspection procedures as presently employed at NIST for SRM production.
- Initial NTRM filter standards would closely mimic SRM counterparts in nominal transmittance values, but an eventual goal would be for NTRM filters to fill gaps in the coverage afforded by SRMs.

- One-year recertification intervals will be recommended for NTRM neutral density glass filters, permitting expanded uncertainties equivalent to those for corresponding SRMs (which are certified by NIST for a two-year period).

The final workshop meeting, scheduled for early September 1998, is intended to review draft documentation being prepared by NIST on the basis of NVLAP requirements and the principles codified in the working group meeting. This workshop will also address the issue of “selling” the NTRM program to end users, regulators, and inspectors.

### 3.2. Assurance of traceability

Fig. 6 is a diagrammatic representation of some of the principles of the NTRM program. The linkage between NIST and NTRM producer/recertifiers is at the heart of the program. *Protocols* required will include one by which potential NTRM vendors would apply to NIST, one for initiation of an NTRM program, one for continuous production, and one for renewal of an NTRM program upon expiration of the approval period. *Artifact standards* will be used for intercomparison measurements between the NIST reference spectrophotometer and the spectrophotometer(s) used by the vendor for NTRM certification. These artifact standards will include NIST SRM filters spanning the required range as well as NTRM sets reserved by the producer as “batch standards”. The *quality control methods* indicated in the figure are largely dictated by the NVLAP program, which is based on ISO-25 compliance. Quality control will involve exhaustive documentation of every aspect of filter production, inspection, and certification and of the NIST-interaction protocols discussed above. It will involve rigorous adherence to schedules set up in the protocols for intercomparison measurements with NIST, as well as extensive record keeping with access by NIST.

Finally, the diagram indicates that some of the NTRM quality control procedures will involve blind testing. This part of the program is a necessary assurance to all parties concerned that measurements made to certify an NTRM set for an arbitrary customer are equivalent to those made for NIST intercomparisons.

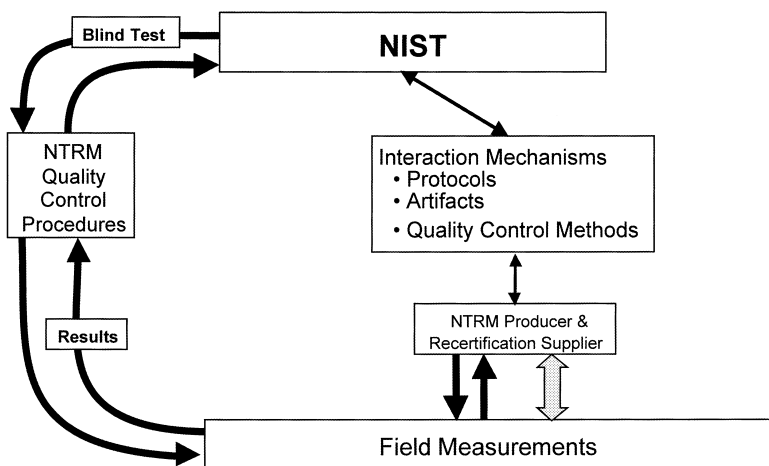


Fig. 6. Conceptual approach to NTRMs.

#### 4. Technical challenges

Two recent activities discussed below may be related in a general sense to the advent and growth of process analytical chemistry and to the suitability of molecular absorption spectrophotometry for non-destructive on-line, at-line, and in-line chemical analysis. The third topic discussed below concerns challenges involving the possible improvement and/or replacement of existing artifact standards.

##### 4.1. Optical wedge effects in standards and samples [11]

Scanning spectrophotometers typically employ a scanning monochromator before the sample in the optical train, to illuminate the sample and the blank with narrow-bandwidth light at a selected wavelength. In such instruments, the light transmitted by the sample and the blank is then optically relayed to the face of a detector. The geometry could be reversed, with broadband light passed first through the sample and the transmitted light relayed to the entrance slit of a monochromator with a detector mounted to the exit slit. An obvious reason to prefer the former geometry is to minimize heating of the sample by the measurement beam.

A less obvious reason is that the entrance slit of a spectrometer is a less forgiving target than the active surface of a reasonably large photodetector. Hence,

“reversed geometry” spectrophotometry is potentially sensitive to unbalanced (between the sample and the blank) beam deflection, physical (not wavelength) dispersion, and focal plane displacement. In spite of these disadvantages, post-sample wavelength dispersion is obviously the only available option for simultaneous measurements at many wavelengths with silicon-based array detectors.

Array detection has been developed more slowly for absorption spectrophotometry than for many other spectroscopic applications (e.g., ICP/OES) because of the disadvantages discussed above as well as the inability to employ double monochromators to minimize stray light. However, simultaneous detection “snapshot” spectra are vital to kinetic studies and to dynamic chemical process applications, and the market share of such instruments is growing rapidly.

Most of the problems associated with beam distortion can be addressed in single-beam operation by using the same cuvette in the same orientation for both the sample and the blank. This option is obviously not available for solid standards referred to air, and NIST standards have been problematic on two variations of diode array instruments. In the early diode array spectrophotometers offered by Hewlett-Packard (HP), focussed beam optics were used, and the optical path difference between the signal beam with the filter in place and the background beam referred to air resulted in differential focussing at the slit and concomitant absorbance bias.



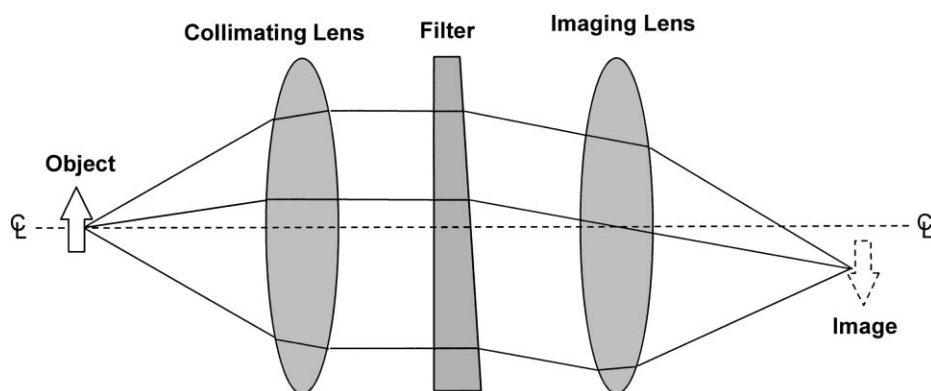


Fig. 7. Deflection of collimated beam by wedged sample.

The current generation Hewlett-Packard 8453<sup>1</sup> avoids having any sensitivity to optical pathlength through the sample by using collimated beam optics. This arrangement poses another problem for solid standards, as illustrated in Fig. 7. A slight optical wedge, or departure from parallelism between the entry and exit faces, translates the image of the source in the plane which contains the spectrometer entrance slit. For a small beam deflection,  $\alpha$ , and an imaging lens of focal length  $f$ , the image may be shown to be displaced by a distance  $d=f\alpha$ . The deflection angle can be shown to be related to the wedge angle,  $w$ , by  $\alpha=(n-1)w$ , where  $n$  is the index of refraction of the material. For a typical index of  $n=1.5$ , the deflection angle is seen to be about half of the wedge angle.

In the HP instrument, very short focal lengths are used. A focal length of about 20 mm gives a displacement of 20  $\mu\text{m}$  for a 1 mrad deflection angle. This distance is of the order of the slit width and pixel width in diode array instruments. The image of the continuum lamp overfills the entrance slit, such that the transmittance error introduced depends on the homogeneity of the particular source and cannot be predicted in general. To respond to this measurement challenge we have reduced the specification for NIST solid filters to 0.1 mrad in transverse wedge, thereby

reducing the displacement to a relatively small fraction of the slit width.

To test production filters for wedge, we employ a pair of autocollimators, arranged in a collimator-telescope configuration equivalent to Fig. 7 with the eyepiece lenses not shown. The 300 mm focal length objective lenses result in a resolution of about 0.01 mrad in wedge.

#### 4.2. NIR wavelength standard with peak location algorithm

Absorption and diffuse reflectance spectrophotometry in the near infrared (NIR) has become extremely popular for process analysis. The low absorption cross sections of the molecular overtone transitions are well suited to major and minor species determination with reasonable pathlengths. The coverage of species of interest is excellent, but this leads to difficulty in spectral interpretation, further complicated by broad natural bandwidths. Analytical results are extracted by chemometric models requiring extensive calibration with a sizeable set of carefully characterized application-specific standards which span the range of concentrations, temperatures, pressures, etc. expected for the process being monitored. In an ideal world, this extensive calibration procedure would be performed once for each application, could be used indefinitely on the same instrument, and even “downloaded” to other instruments.

In reality, the calibration is so sensitive to tiny changes in spectral features that changes in an instrument over time force expensive recalibrations, and

<sup>1</sup>To describe experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular products or equipment are necessarily the best available for that purpose.

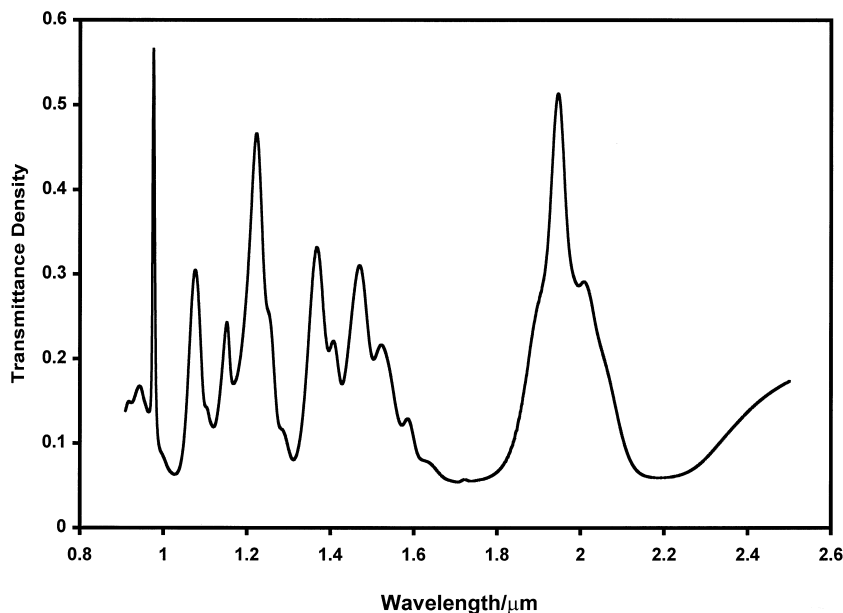


Fig. 8. Prototype NIR transmission wavelength standard.

transfer of calibration from instrument to instrument is rarely successful. Indeed, numerous papers have been published on the “calibration transfer” problem, and the generalized concept of forcing a variety of instruments to yield entirely equivalent drift-free spectra has been termed “instrument standardization.”

A rational place for instrument standardization to begin with is artifact standards. The abscissa (wavelength or wave number) is a less robust axis than the ratio-based absorbance ordinate. Consequently, we are preparing an NIR wavelength standard whose spectrum will resemble that of the prototype shown in Fig. 8. The standard is made from a glass doped with mole-percent-levels of four rare-earth oxides, which provide a distribution of reasonably resolved and sharp bands over the spectral region from 1 to 2  $\mu\text{m}$ .

The standard will be batch-certified using measurements on a statistical sample of the batch using a Fourier transform interferometer operating in the NIR. The FT spectrometer has inherent wave number accuracy of the order 99.99% derived from the well-known HeNe laser transition at 633 nm that is used to register the position of the moving arm. Nevertheless, we will employ absorption features from gas phase materials to further reduce the uncertainty.

The ability to transfer abscissa accuracy from NIST to the end user depends on more than the wave number accuracy with which the spectra are acquired, however. The method used to assign a unique “position” to each of the broad and asymmetric absorption bands is potentially the largest source of imprecision and inaccuracy. The modern era of computer-intensive spectroscopy presents an opportunity to improve precision for a given operator and to remove bias between operators by defining a common mathematical algorithm to be disseminated with the standard.

Many commercial data manipulation packages contain peak location algorithms, but these packages can give statistically distinct values from each other and can even give slightly variable results within a given program for different user-set parameters (thresholds, smoothing factors, etc.). Currently an algorithm is being tested both in the NIST Chemical Science and Technology Laboratory (CSTL) and the NIST Physics Laboratory (PL) to be eventually applied to the wavelength standards supported by both laboratories [12]. The algorithm is based upon the “center-of-gravity” (CoG) of a specified fraction of a band [13] and a variant was first employed at NIST in the certification of SRM 1921, Polystyrene Infrared

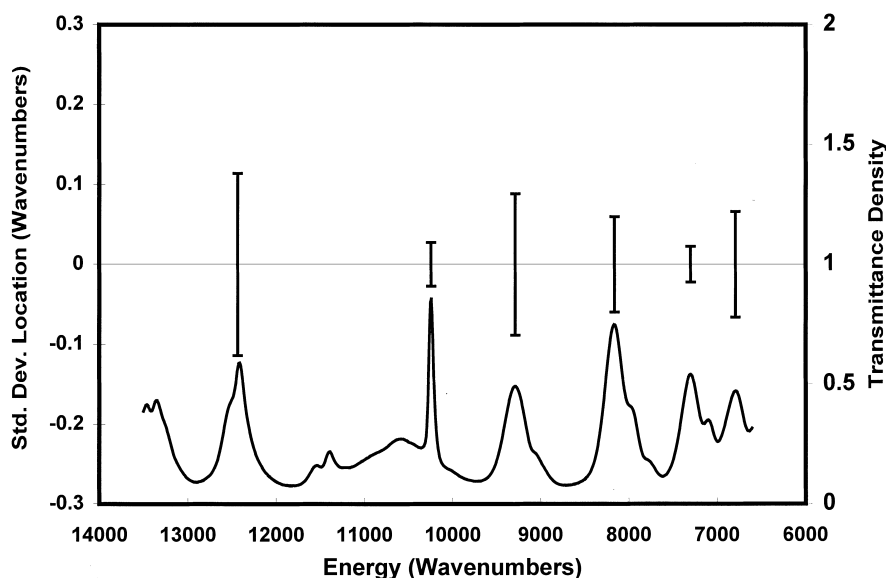


Fig. 9. Precision performance of peak location algorithm on earlier prototype.

Wavelength Standard, by the Optical Technology Division of the PL [14]. The peak fraction used was 0.5, which resulted in a “picked-position” visibly different from the transmittance minimum for very asymmetric peaks.

The area-based center-of-gravity algorithm is demonstrably more precise than amplitude- or derivative-based methods. Fig. 9 shows a study based on 60 separate spectra taken using 20 samples of an earlier prototype of the proposed wavelength standard. The peak location precision is seen to be of the order of tenths of a wave number for peaks of full width at half maximum (FWHM) of 65–300  $\text{cm}^{-1}$ . The FTS resolution was 4  $\text{cm}^{-1}$ , and the interferogram was zero-filled to Fourier interpolate the abscissa spacing to 1  $\text{cm}^{-1}$ . Thus, the peaks are located to about 0.1% of their width and about 2.5% of the instrumental resolution for four-fold zero filling. This precision was found to be approximately ten-fold better than several peak-picking algorithms based on fitting low order polynomials to the top of an absorbance peak. Analysis of variance (ANOVA) showed that some of the variance for two of the peaks was related to heterogeneity within the 20 samples, an effect not distinguishable with the other peak-picking algorithms.

To accommodate the desire of end users for a precise peak location assignment which corresponds

to a visual absorbance maximum or transmittance minimum for asymmetric peaks, the latest version of the NIST CoG algorithm calculates several peak locations as a function of peak fraction and fits the trend to extrapolate to a peak fraction of zero. This process degrades the precision slightly, but is still more robust than amplitude-based methods, while yielding a result that corresponds to a transmittance minimum or absorbance maximum.

#### 4.3. Future challenges

*Absorbance drift* has been known to exist in the solid filter standards for many years, and represents a significant uncertainty component in the two-year certification. Nevertheless, the drift is sufficiently small and too variable (from filter to filter) to model and perform bias correction. Furthermore, drift probably arises from both surface chemistry and surface contamination. It may be possible to solve the surface chemistry component eventually, but the contamination component will invariably call for periodic cleaning, and it is probably advisable to continue to combine cleaning with recertification.

Recent drift studies with covered and uncovered *metal-on-fused-silica filters* have clearly favored the continuation of the cover plates uniquely employed by

NIST for years. The “sandwich” design also simplifies cleaning, since the exposed fused silica is more robust than the thin metal film. The recent decision to hold NTRM filters to the same construction specifications as SRM filters implies that vendors will need to acquire the difficult optical contacting skill, or a different surface protection method must be found for both SRMs and NTRMs. Edge-glued cover plates and evaporative overcoatings are both under consideration.

A more agreeable option would be to replace the metal-on-fused-silica filters with *absorbing glass UV filters* that are roughly analogous to the visible neutral density filters. Such filters exist commercially, and are presumably derived from a phosphate base glass that transmits down to about 260 nm. Preliminary studies indicate high melt-to-melt variability, suggesting the need for extensive collaboration with a glass producer to assure a satisfactory standard.

In the long run, the best standards for chemical spectrophotometry may be *artifact-free standards*. This approach reflects the trend in standards, which has seen all but one of the seven basic SI units (mass) defined in terms of fundamental quantum standards. With the increasing automation of computer-intensive instruments, it is entirely possible to incorporate the same principles into commercial instruments that are employed by the standards laboratories for reference spectrophotometers. For the absorbance axis, the decades-old double aperture method is employed [15]. The apertures are not subject to contamination, surface chemistry, material inhomogeneity, or temperature dependence, and the fundamental principles are obvious and straightforward. For the wavelength axis, atomic wavelengths in vacuum are quantum standards, are sufficiently tabulated in the open literature, and are much narrower and more symmetric than solid or liquid molecular absorption standards. Pen lamp and double aperture calibration could be automated into processor-controlled instruments.

Even so, cost, convenience, and political, regulatory, and quality-driven considerations will prolong the existence of artifact standards.

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