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National Institute of Standards and Technology

Standard Reference Materials:

Glass Filters as a Standard Reference Material for Spectrophotometry— Selection, Preparation, Certification, and Use of SRM 930 and SRM 1930

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[2]Some elements at Boulder, CO 80303.

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Preface

Standard Reference Materials (SRMs), as defined by the National Institute of Standards and Technology (NIST), are well-characterized materials produced in quantity and certified for one or more physical or chemical properties. They are used to assure the accuracy and compatibility of measurements throughout the Nation. SRMs are widely used as standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. They are also used extensively in the fields of environmental and clinical analysis. In many applications, traceability of quality control and measurement processes to the national measurement system is carried out though the use of SRMs. For many of the Nation's scientists and technologists, it is therefore of more than passing interest to know the details of the measurements made at NIST in arriving at the certified values of the SRMs produced. The NIST Special Publication 260 Series is a collection of publications reserved for this purpose.

The 260 Series is dedicated to the dissemination of information on different phases of the preparation, measurement, certification, and use of NIST SRMs. In general, much more detail will be found in these publications than is generally included in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing the greatest care and accuracy. These publications also should provide sufficient additional information so SRMs can be utilized in new applications in diverse fields not foreseen at the time the SRM was originally issued.

Inquiries concerning the technical content of this publication should be directed to the author(s). Other questions concerned with the availability, delivery, price, and so forth, of NIST SRMs will receive prompt attention from:

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Abstract

This publication describes the various factors that can affect the proper functioning of a spectrophotometer and suggests procedures to assess and control these factors. Particular consideration is given to the long- and short-term stability of a spectrophotometer, wavelength accuracy, spectral bandpass, stray radiation, and the accuracy of the transmittance or absorbance scale. A description is given of the Standard Reference Materials (SRMs) that can be used to control these factors. The methods for the preparation, certification, and use of two such materials (SRM 930 and SRM 1930) are also presented. The results obtained in the actual use of these SRMs are examined in some detail. An Appendix contains the reproduction of several publications and Certificates relevant to the subject discussed in this publication.

Keywords: Accuracy in absorption spectrophotometry; glass filters; spectral bandpass; spectrophotometry; standard reference materials; stray radiation; testing of spectrophotometers; transmittance (absorbance) accuracy; wavelength accuracy.

Disclaimer

Foreword

Since its inauguration in 1901, the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), has issued nearly 2000 different Standard Samples or Standard Reference Materials (SRMs). Many of these have been renewed several times; others have been replaced or discontinued as technology changed. Today, over 1000 SRMs are available, together with a large number of scientific publications related to the fundamental and applied characteristics of these materials. Each material is certified for chemical composition, chemical properties, or its physical or mechanical characteristics. Each SRM is provided with a Certificate or a Certificate of Analysis that contains the essential data concerning it properties or characteristics. The SRMs currently available cover a wide range of chemical, physical, and mechanical properties, and a corresponding wide range of measurement interests in practically all aspects of fundamental and applied science. These SRMs constitute a unique and invaluable means of transferring to the user accurate data obtained at NIST, and provide essential tools that can be used to improve accuracy in practically all areas where measurements are performed.

In addition to SRMs, the National Institute of Standards and Technology issues a variety of Reference Materials (RMs) which are sold, but not certified by NIST. They meet the ISO Guide 30-1981 (E) definition for RMs, and many meet the definition for CRMs. The documentation issued with these materials is either a: (1) "Report of Investigation," the sole authority being the author of the report. RMs are intended to further scientific or technical research on particular materials. The principal consideration in issuing RMs is to provide a homogeneous material so that investigators in different laboratories are assured that they are investigating the same material. (2) "Certificate," issued by the certifying agency (other than NIST), e.g., other national laboratories, other government agencies, other standardizing bodies, or other non-profit organizations. When deemed to be in the public interest and when alternate means of national distribution do not exist, NIST acts as the distributor for such materials.

Further information on the reference materials available from NIST may be obtained from the Standard Reference Materials Program, National Institute of Standards and Technology. Information on other NIST services may be obtained from Technology Services, National Institute of Standards and Technology, Gaithersburg, MD 20899.

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Part One

1. GENERAL

The need for reference materials to verify the accuracy of measurements in molecular absorption spectrometry (or spectrophotometry*) has been associated with the early stages of development of this analytical technique since its beginning. It is only in the recent years, however, that accurately calibrated Standard Reference Materials (SRMs) have become available to verify the accuracy of the transmittance and wavelength scales of conventional spectrophotometers and to assess the amount of stray radiant energy in those instruments.

To underline the importance of this factor, it is perhaps useful to remember that in the field of clinical chemistry alone, more than 1,000,000 spectrophotometric tests were performed daily in the United States in the late 1960's and early 1970's. Today, at an estimated growth rate of 15 percent per year, the number of analytical measurements performed in the clinical laboratories in this country is on the order of several billion per year [2].

Solid materials in the form of glasses with adequate optical transmittance characteristics, such as Chance ON-10, Schott NG-4, etc., or liquid compounds such as pyrene or p-nitrophenol, and solutions of inorganic compounds such as potassium dichromate, cobalt ammonium sulfate, or holmium oxide were used extensively in *intralaboratory* tests to assess the precision of spectrophotometers used within a particular laboratory. When these materials were used to verify the proper functioning of such instruments on an *interlaboratory* basis, however, the results indicated that rather poor accuracy was obtained for both wavelength and transmittance values. This situation was confirmed by numerous and extensive interlaboratory tests, and the detailed results were described in a number of publications. The critical paper by Rand in 1969 [3], the extensive monograph edited by Burgess and Knowles [4], the papers cited in references 5-9, and the more recent work edited by Burgess and Mielenz [10] are relevant.

All determinations that use spectrophotometry are based on the measurement of the optical transmittance of the analytical samples. The accurate measurement of this parameter is an essential requirement, especially when used to establish the optical characteristics of the material, such as the molar absorptivity, and also in enzyme studies and dosimetry. Transmittance accuracy is also indispensable for interlaboratory exchange and comparison of analytical data. As a result of this situation and the numerous requests from the users of spectrophotometers, and from clinical chemists in particular, the National Bureau of Standards (NBS) initiated in 1969 a project to study the various factors that affect the accuracy of spectrophotometric measurements, and to provide means to identify, assess, monitor, and, if possible, decrease the uncertainty of such measurements [11]. In fact, this project was an extension of the pioneering activity in the general field of spectrophotometry that existed at the National Bureau of Standards since the early 1920's [12] and has continued uninterrupted to the present time.

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* The nomenclature used in this paper is defined in reference 1.

The sources of variance that are responsible for the uncertainty of spectrophotometric measurements were identified as wavelength accuracy, spectral bandpass, radiation pathlength, stray radiant energy, transmittance scale accuracy, and polarization effects of the instrument. Since no adequate instrumentation was available to study these parameters individually in a quantitative manner and with a proven accuracy, it was decided to design and construct a special high-accuracy spectrophotometer for this purpose. This research instrument was completed and tested in 1970, and it has been used since then for the certification of all the SRMs for transmittance and stray radiant energy produced to date at NIST. A condensed description of this instrument is given in the following section.

1.1 Description of the High-Accuracy Spectrophotometer

The high-accuracy spectrophotometer [13-16], located in the Inorganic Analytical Research Division (IARD), is a single-beam instrument and is illustrated in figure 1. Its major components, described only briefly here, are: (a) a radiation source; (b) a monochromator; (c) a sample holder; (d) a system to verify the accuracy of the transmittance measurements; (e) an integrating sphere-photomultiplier unit connected to a digital voltmeter; and (f) a data acquisition and display system. A circular neutral wedge, located between the radiation source and the entrance slit of the monochromator, is used to select various levels of radiation flux required by the measurements. Quartz-lithium fluoride achromats are used as objectives to produce the necessary beam geometries.

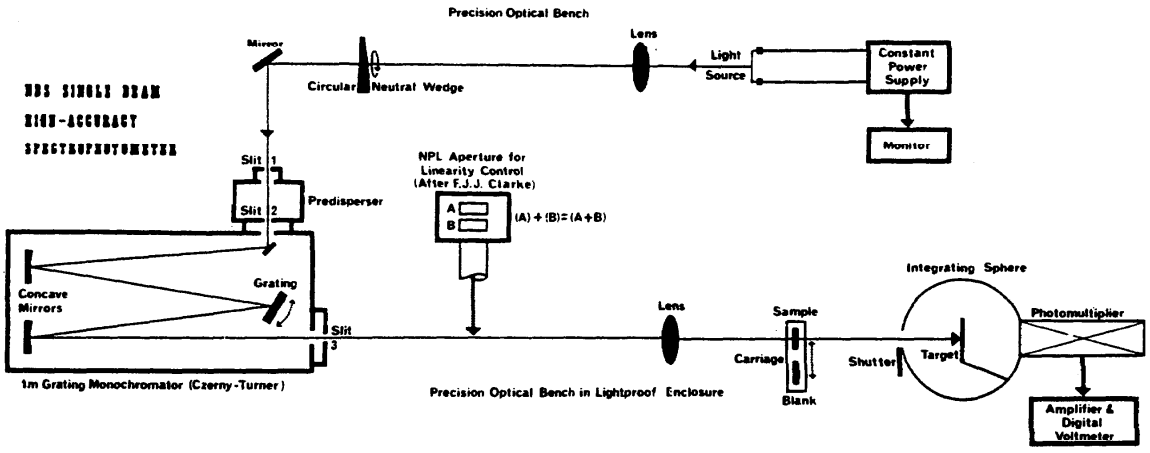


Figure 1. Schematic illustration of the IARD single-beam, high-accuracy spectrophotometer. The double-aperture unit is placed on the optical bench only when linearity measurements are performed.

The radiation source for the spectral range of 400-1000 nm is a ribbon tungsten filament lamp powered by a constant current source. The stability of this current is monitored with a potentiometer capable of detecting changes of 2-3 parts in 10^6. For the ultraviolet region from 200 to 400 nm, a deuterium discharge lamp is used. These two light sources are interchangeable, and their images can be directed onto the entrance slit of the monochromator using a mirror at 45°.

The monochromator is a 1-m Czerny-Turner grating instrument provided with a quartz prism predisperser, functioning as a double monochromator to reduce stray radiant energy. These parts are illustrated in figure 2.

The sample-carrying system provides for manual measurements of one sample and its blank, or of seven samples and eight blanks in a sequential order. They can be operated manually or automatically using a microcomputer. The integrating sphere, placed at the end of the optical path, is made from a hollow aluminum sphere provided with a target coated on the inside with $BaSO_4$. The image of the exit slit of the monochromator is projected onto the target of the integrating sphere (see fig. 3) to which an end-on photomultiplier (PM) tube detector is attached.

The data acquisition and presentation system consists of a digital voltmeter capable of taking 40 readings per second. The radiation fluxes obtained for the sample I, and for the reference beam I_o passing through air ($I_{o\ air}$) for solid materials or the blank sample ($I_{o\ blank}$) for solutions, are used by the microcomputer to calculate transmittance T, $\left[\frac{I}{I_{o\ air}}\right]$, or internal transmittance T_i, $\left[\frac{I}{I_{o\ blank}}\right]$, and the corresponding values of transmittance density, $(-\log_{10}T)$, or absorbance, $(-\log_{10}T_i)$, respectively. The microcomputer also controls all of the measuring sequences including wavelength settings, neutral wedge adjustments, stepping of the sample carousel, and transmittance measurements.

An essential element of this instrumentation is the system for verifying the accuracy of the transmittance measurements. As mentioned previously, the radiation fluxes passing through the sample and reference channels generate corresponding photocurrents i and i_o, respectively, at the photomultiplier. These photocurrents are substituted for I and I_o in the above transmittance expression, and their ratio is the optical transmittance value for the material measured. If these photocurrents can be measured accurately, then the optical transmittance value will be accurate, provided wavelength accuracy, radiation pathlength accuracy, adequate spectral bandpass, and freedom of stray radiant energy have been achieved.

A necessary relationship, which is implicit for the accurate measurement of photocurrent, is that the detector photocurrent be a linear function of the radiation flux. This is illustrated in

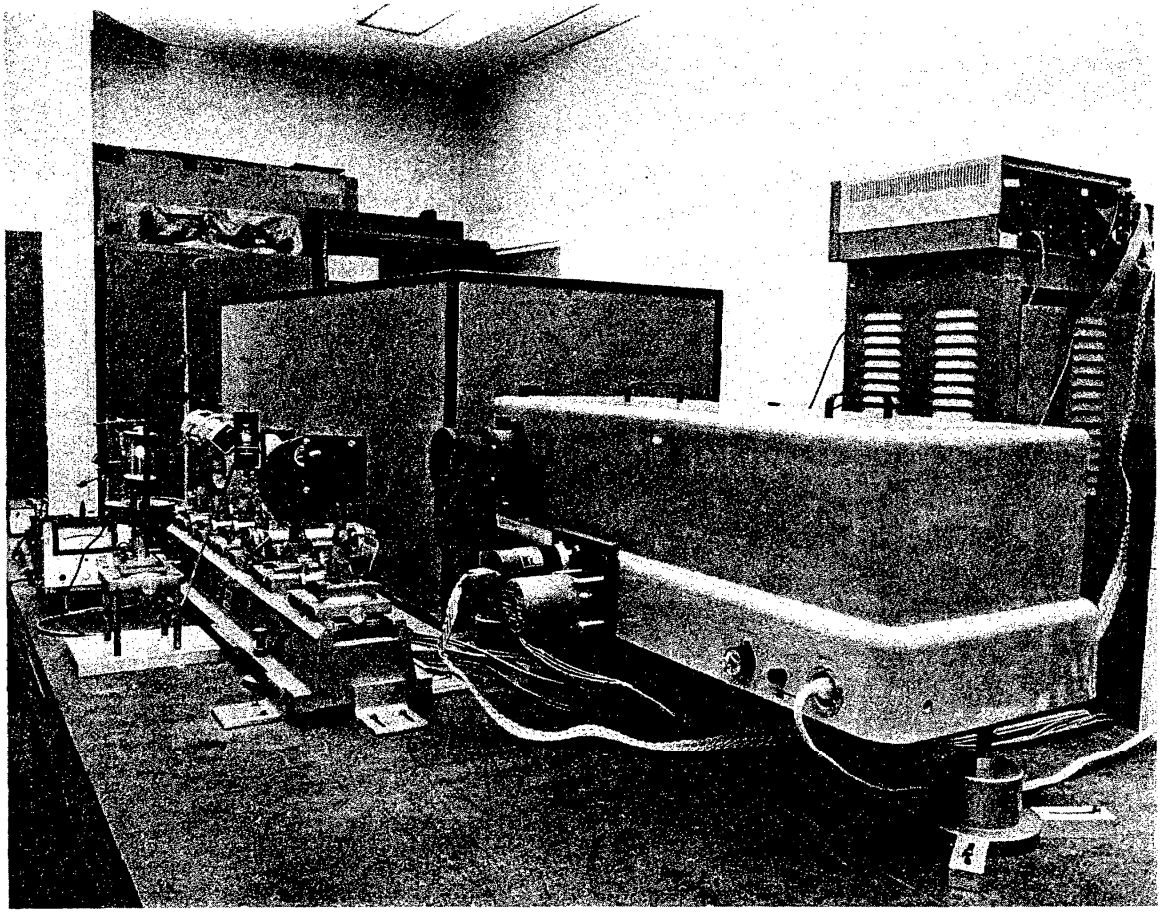


Figure 2. Arrangement of the two radiation sources used with the IARD high-accuracy spectrophotometer. A low power laser beam is used to verify the alignment. At left: the tungsten filament lamp for measurements in the visible. On the optical bench: deuterium low pressure discharge source for measurements in the ultraviolet. Also on the optical bench: the 45° mirror and the circular neutral wedge. At right: the 1-m Czerny-Turner spectrometer provided with the predisperser and stepping motor shaft encoder. The sample holder, integrating sphere-photomultiplier unit, and the two achromat objectives are placed on optical bench located in the light-tight enclosure visible at the rear. Also at right: the console containing the electronic and pneumatic controls.

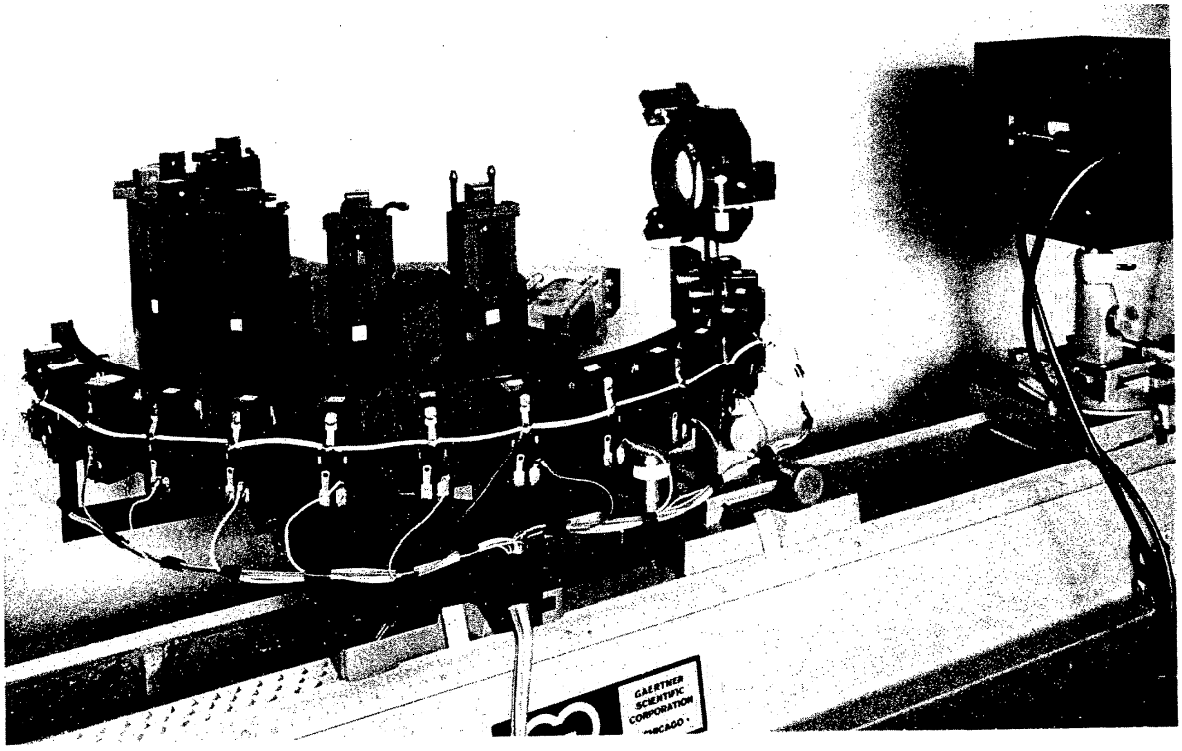


Figure 3. Circular platform holding seven cuvettes or filter holders. An improved unit (not illustrated) is provided with eight additional cuvettes or filter holders for the blank samples. At right: one of the two lithium fluoride-quartz achromats and the integrating sphere-photomultiplier unit.

the simple graph in figure 4. The abscissa represents arbitrary radiation fluxes F, and the ordinate represents the relative photocurrent signals I. In the ideal case, when $F=0$, then $I=0$. For a certain value of F, called here arbitrarily 100 percent, there corresponds a maximum value of the photocurrent I. These determine two fixed points on the graph, and any measurement of radiant flux will be accurate if it falls on the straight line which connects the origin 0 with the 100-percent point.

Various methods may be used to measure the linearity of these photocurrents. A technique based on the radiation-addition principle using two apertures was selected for its simplicity and freedom from errors [17]. The two-aperture system consists of a metal plate provided with two rectangular windows A and B (see fig. 5). Each window can be closed by shutters operated remotely through pneumatic controls. This aperture system is placed past the

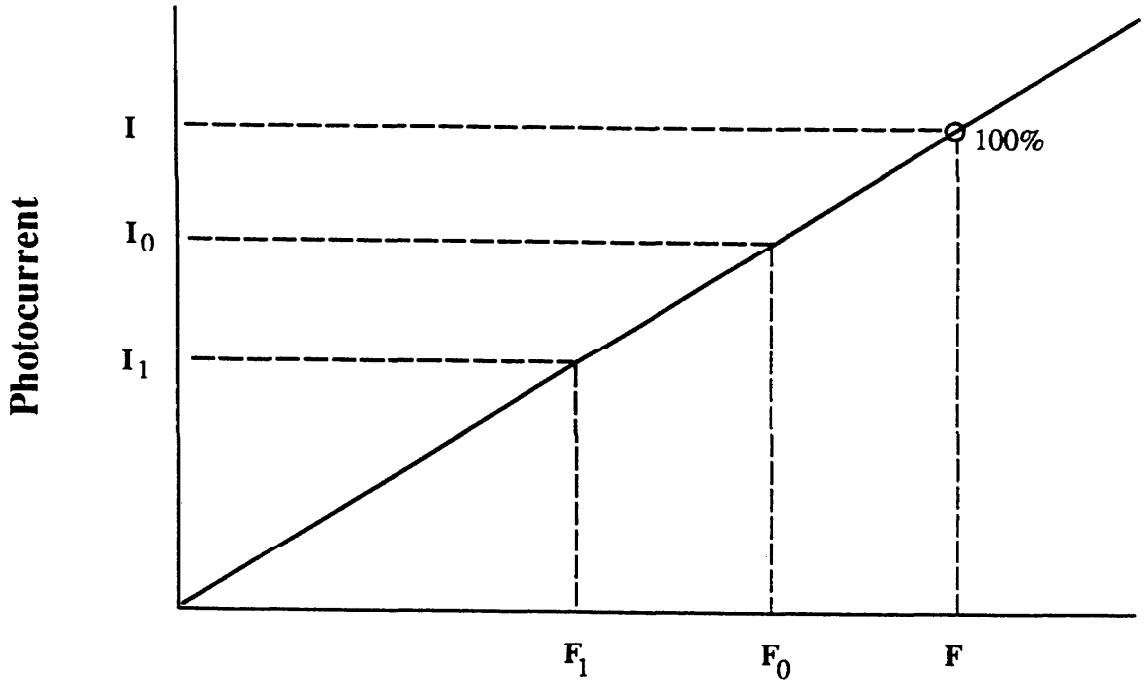


Figure 4. Illustration of the relation between radiation fluxes F and corresponding photocurrents I in an ideal case.

exit slit of the monochromator and always within the optical solid angle of the instrument. The image of the apertures is then produced on the target of the integrating sphere.

The linearity verification consists of measuring the photocurrent produced with aperture A open and B closed; then B open and A closed; and finally with both apertures A and B open. If the system is linear, the sum of the photocurrents obtained with apertures A and B open separately should be equal to the photocurrent obtained when both apertures A and B are open at the same time. If this is not the case, the system shows a nonlinearity which is proportional to the amount by which the sum of (A) + (B) differs from (A + B). This difference is then used to correct the transmittance measurements. This operation is repeated over the range of transmittance levels needed. During the individual measurement of (A), (B), and the combined (A + B), experimental conditions must not change (see Appendix 2). A critical study by K.D. Mielenz and K.L. Eckerle [18] has concluded that the possible causes of errors generated by optical diffraction and interferences occurring at the apertures of the double-aperture unit will not affect the accuracy of the measurements at 1 part in 10^5.

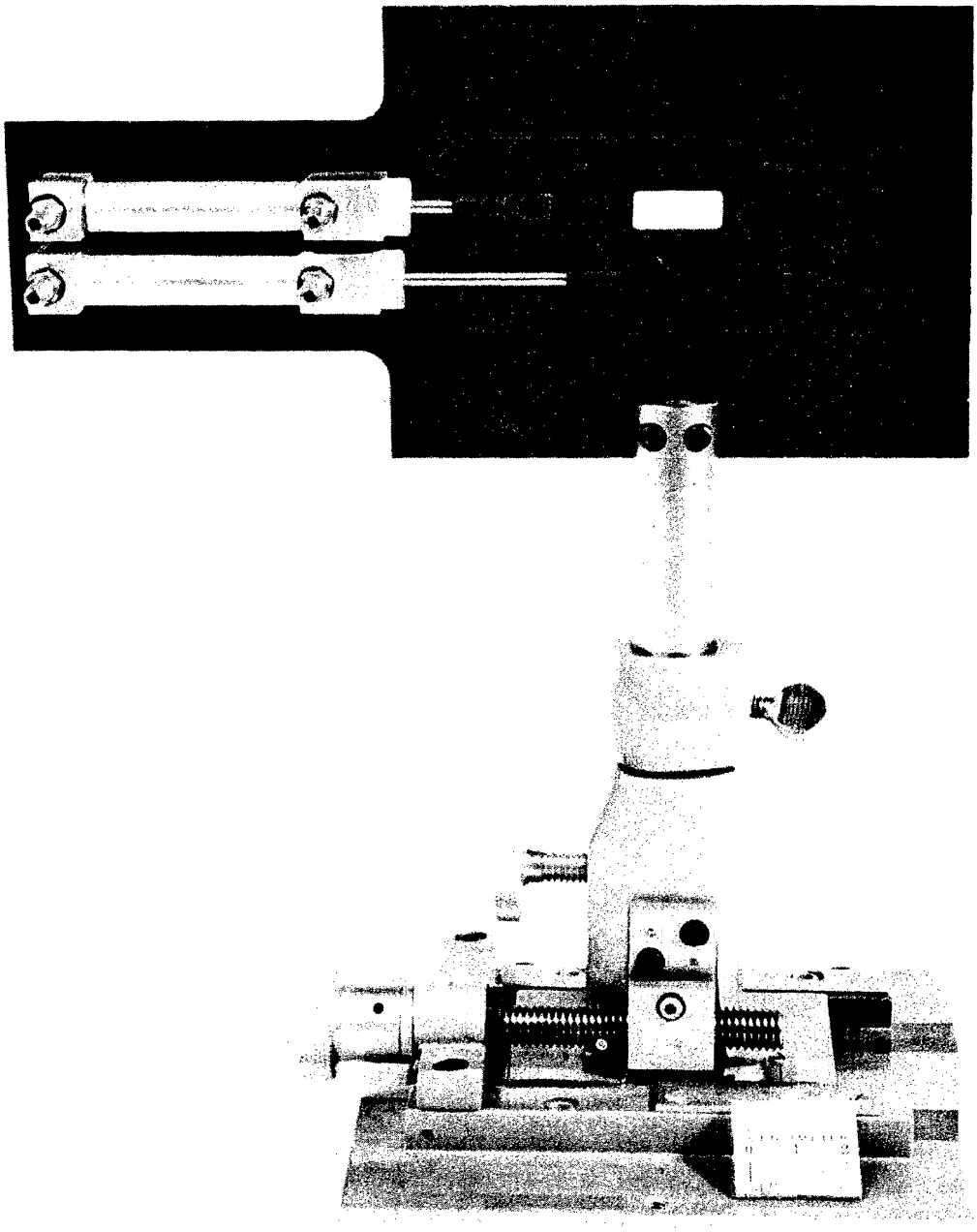


Figure 5. View of the double-aperture unit for linearity testing. The two pneumatically-controlled shutters are located on the plate. One aperture is open, the other is closed.

The stability of the various electronic and optical parts of the IARD high-accuracy spectrophotometer was determined and the results are summarized in table 1. From these data it can be concluded that the transmittance of a stable glass filter, which has a nominal percent transmittance ranging from 10%T to 50%T, can be determined with an uncertainty of 1 part in 10^4. Since the same uncertainty is obtained when the linearity of the photocurrent is measured as described above, the accuracy of the transmittance is also assessed with an uncertainty of 1 part in 10^4 over this same transmittance range.

Table 1. Summary of the Functioning Characteristics of the IARD High-Accuracy Spectrophotometer

• Stability of the electronic system	1 to 2 parts in 10^5
• Stability of the electronics and PM tube (dark)	4 parts in 10^5
• Stability of electronics, PM tube, and radiofluorescent source	7 parts in 10^5
• Stability of electronics, PM tube, and tungsten ribbon filament	2.2 parts in 10^4
• Reproducibility of transmittance measurements	1 part in 10^4

A similar high-accuracy spectrophotometer, designed by K.D. Mielenz et al. [19], was constructed and is used in the NIST Radiometric Physics Division (RPD) for the study of various physical parameters in spectrophotometry [20]. This RPD instrument differs from the IARD spectrophotometer described here in that it uses reflecting rather than refracting optics. Some of the parameters studied on the RPD research instrument are: interreflection phenomena, polarization, homogeneity of the photomultiplier sensitive surface, effectiveness of integrating spheres and diffusers, scatter and homogeneity of transparent solid optical filters, calibration of glass wavelength filters, etc. The RPD reference instrument is also used from time to time to verify the transmittance measurements performed with the IARD high-accuracy spectrophotometer.

1.2 Standard Reference Materials

The high-accuracy spectrophotometer housed in the Inorganic Analytical Research Division is described in this publication because it is a primary transmittance standard. The only way known to us by which the accurate transmittance values determined with this instrument can be transferred to the users of spectrophotometers is with the help of Standard Reference Materials, or SRMs. These SRMs are defined as "reference materials, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body," and their objective is to assure the accuracy and compatibility of measurements by transferring to the user the accurate values obtained at NIST.

A number of liquid and solid optical SRMs for the spectral range from 200-800 nm have been prepared and certified at NIST for the verification of the accuracy of the wavelength and transmittance scales of conventional spectrophotometers, and for assessing the stray radiant energy. Standard Reference Materials for fluorescence spectrometry are also available. A summary of the major characteristics of these optical filter SRMs, together with information on the publications prepared at NIST that describe in detail the selection, characteristics, preparation, calibration procedures, and uses of these materials, is given in table 2. This publication gives a detailed description of the materials and methods used to produce and certify SRM 930 and SRM 1930, Glass Filters for Spectrophotometry.

The reader who is interested in the more fundamental problems associated with high-accuracy spectrophotometry and luminescence measurements is advised to consult the publications listed in references 21 and 22, including the papers mentioned in those publications. Reprints from several papers closely related to the subject discussed in this publication are reproduced here in the Appendices as a convenience to the reader. The Certificates for the optical SRMs described in table 2 are also reproduced in the Appendices.

Table 2. Standard Reference Materials for Spectrophotometry Provided by the National Institute of Standards and Technology

SRM	Material	Composition
Transmittance (Solids)		
SRM 930 Glass Filters for Spectrophotometry	Solid filters made of Schott NG-4 and NG-5 optically neutral glass. Obtained from the Schott-Jenaer Glaswerk, Mainz, Germany	Three filters with nominal percent transmittances of 10, 20 or 30%. Each filter is mounted in a black-anodized aluminum alloy holder provided with front and rear shutters. The filters are stored in a cylindrical aluminum alloy container.
SRM 1930 Glass Filters for Spectrophotometry	Solid filters made of Schott NG-3 and NG-11 optically neutral glass. For further information, see above.	Three filters with nominal percent transmittances of 1, 3 or 50%. For further information, see above.
SRM 2031 Metal-on-Quartz Filters for Spectrophotometry	Solid filters made of semi-transparent, evaporated chromium-on-fused silica (non-fluorescent) plates.	Three filters with nominal percent transmittances of 10, 30 or 90%. Each filter is made from two fused-silica plates assembled by optical contact. The 90%T filter is made from one clear plate. The 10%T and 30%T filters are made by assembling a fused-silica plate which carries a film of semi-transparent chromium to produce the desired transmittance, and a clear plate. Each filter is placed in a metal alloy holder provided with front and rear shutters.
Absorbance (Liquids)		
SRM 931 Liquid Absorbance Standards for Ultraviolet and Visible Spectrophometry	Liquid filters made from a solution of Co and Ni metals dissolved in a mixture of nitric-perchloric acids. The pH of the solution is about 1. Prepared in the NIST Inorganic Analytical Research Division.	Three solutions and a blank are issued in sealed ampoules and have a nominal absorbance of 0.3, 0.6, or 0.9.
SRM 935 Crystalline Potassium Dichromate for Use as an Ultraviolet Absorbance Standard	Crystalline potassium dichromate of established purity obtained from the J.T. Baker Chemical Co., Phillipsburg, NJ	The crystalline material of reagent grade purity is offered in glass bottles provided with plastic screw caps.
Stray Radiant Energy		
SRM 2032 Potassium Iodide for Use as a Stray Light Standard	Crystalline potassium iodide of established purity obtained from the J. T. Baker Chemical Co., Phillipsburg, NJ.	The reagent-grade, crystalline KI is 99.8% pure as indicated by the manufacturer. Moisture is 0.007%. Homogeneity was determined by absorbance measurements at wavelengths 265, 267 and 270 nm, and was found adequate.

Certification	Use	Remarks
The transmittance of each filter is measured with the high-accuracy spectrophotometer at wavelengths 440, 465, 546.1, 590 and 635 nm using spectral bandpasses not exceeding 2.2, 2.7, 6.5, 5.4 and 6.0 nm, respectively.	This SRM is intended as a reference source for the verification of the transmittance or absorbance scales of conventional spectrophotometers in the visible spectral region.	The use of this SRM is limited to the visible spectrum and requires narrow spectral bandpasses. For further details, consult the Certificate included in Appendix 9.
For further information, see above.	For further information, see above.	For further information, see above; also, consult the Certificate included in Appendix 10.
The transmittance of each filter is measured with the high-accuracy spectrophotometer at wavelengths 250, 280, 340, 360, 400, 465, 500, 546.1, 590 and 635 nm.	This SRM is intended as a reference source for the verification of the transmittance and absorbance scales of conventional spectrophotometers in the ultraviolet and visible spectral regions.	SRM 2031 has good optical neutrality and can be used to calibrate spectrophometers with wide spectral bandpasses from 250 to 635 nm (with possible extension to about 3 μm). For further details, consult the Certificate included in Appendix 11; also, see NBS Special Publication 260-68.
The absorbance of each solution was measured at wavelengths 302, 395, 512 and 678 nm with the high-accuracy spectrophotometer using spectral bandpasses not exceeding 1.5, 2.0, 3.3 and 8.5 nm, respectively.	This SRM is intended for the verification of the accuracy of transmittance or absorbance scales of conventional spectrophotometers in the ultraviolet and visible spectral regions.	SRM 931 requires the use of narrow spectral bandpasses, and provides only one certified value in the ultraviolet spectral region. For further details, consult the Certificate in Appendix 12.
The apparent specific absorbance is certified for ten concentrations at wavelengths 235, 257, 313, 345 and 350 nm using spectral bandpasses not exceeding 1.6 nm.	This SRM is intended to be used as a reference standard for the verification of the accuracy and linearity of the absorbance scale of conventional spectrophotometers in the ultraviolet spectral region.	SRM 935 requires accurate preparation of solutions of potassium dichromate in 0.001N perchloric acid. SRM 935 requires the use of narrow spectral bandpasses, and provides certified values only in the ultraviolet spectral region. For further details, consult the Certificate in Appendix 13; also, see NBS Special Publication 260-54.
The specific absorbances were measured with the high-accuracy spectrophotometer at wavelengths 240, 245, 250, 255, 260, 265, 270 and 275 nm at 23.5°C using a spectral bandpass of 0.2 nm.	SRM 2032 is to be used to assess heterochromatic stray light in the ultraviolet region below 260 nm in absorption spectrophotometers.	SRM 2032 should be stored in the original low-actinic glass bottle and cardboard container, protected from exposure to light and humidity. The estimated stability is 3 years. For further details, consult the Certificate in Appendix 14.

Table 2. Standard Reference Materials for Spectrophotometry Provided by the National Institute of Standards and Technology (Continued)

SRM	Material	Composition
Stray Radiant Energy (Continued)		
SRM 2033 Potassium Iodide for Use as a Stray Light Standard with Radiation Attenuator	Crystalline potassium iodide of established purity, and two semi-transparent evaporated metal-on-fused silica filters contained in a metal alloy holder provided with two shutters. The KI was obtained from the J. T. Baker Chemical Co., Phillipsburg, NJ. The filters were made in the NIST Fabrication Technology Division.	Potassium iodide as for SRM 2032. Two semi-transparent chromium-on-fused silica (non-fluorescent) filters of optical quality.
Wavelength		
SRM 2009a Didymium Glass Filter for Checking the Wavelength Scale of Spectrophotometers	The didymium glass was prepared by Corning Glass Works, Corning, NY, as Corning 5120 Filter Glass.	Rare earth oxides in a glass matrix. This filter is 1 cm wide, 3 cm high and 3 mm thick. Each filter is placed in a metal alloy holder which fits into the cuvette holder of the spectrophotometer.
SRM 2034 Holmium Oxide for Use as Wavelength Standard in Spectrophotometry	Holmium oxide of established purity dissolved in perchloric acid.	Holmium oxide is offered as solutions sealed in 10-mm fused-silica, non-fluorescent cuvettes of optical quality.
Fluorescence		
SRM 936 Quinine Sulfate Dihydrate	The quinine sulfate dihydrate was a special lot of material obtained from J. T. Baker Chemical Co., Phillipsburg, NJ.	SRM 936 contains 1.7% impurities determined by liquid chromatography and believed to be dihydroquinine sulfate dihydrate. The water content is 4.74 ± 0.05% determined by the Karl Fisher method, and 4.57 ± 0.04% by weight loss. The theoretical value is 4.60%.
SRM 1931 Fluorescence Corrected Emission Spectra	Solid, sintered mixtures of inorganic phosphors in polytetrafluoroethylene resin.	The four inorganic phosphors are: ZnS:Ag; Zn_2SiO_4Mn; ZnCdS:Ag; and $CaSiO_3$:Pb,Mn. Each sample is mounted in black-anodized aluminum alloy holders stored in a red anodized cylindrical aluminum alloy container. A blank sample is also provided.

Certification	Use	Remarks
Same as for SRM 2032. The transmittance of the evaporated metal-on-fused silica filters was measured at 255 nm with the high-accuracy spectrophotometer. The nominal value is 10%T for each filter, and a combined value of 1%T.	SRM 2033 is to be used to assess heterochromatic and isochromatic stray light in absorption spectrophotometers.	Same as for SRM 2032. The two semi-transparent, evaporated metal-on-fused silica filters in the metal holder should be stored in the plastic container provided with SRM 2033. Consult the Certificate in Appendix 15.
The wavelengths of maximum absorption were determined with a high-precision spectrophotometer for bandwidths in the range 1.5 to 10.5 nm and for 14 to 24 wavelengths in the range 400 to 760 nm. The instrument has a wavelength accuracy of 0.04 nm.	The filters are to be used in calibrating the wavelength scale in the visible spectral region for spectrophotometers having nominal bandwidths in the range 1.5 to 10.5 nm.	SRM 2009a was not measured individually. It is recommended for most applications. For further details, consult NBS Special Publication 260-66, and the Certificate in Appendix 16.
The wavelengths of maximum absorption of holmium oxide solutions in perchloric acid is determined for various spectral bandpasses at the nominal wavelengths: 241, 249, 278, 287, 333, 345, 361, 385, 416, 451, 467, 485, 536, and 640 nm.	This SRM is to be used as a reference standard for the verification of the accuracy of the wavelength scale of absorption spectrometers, in the ultraviolet and visible spectral regions.	Holmium oxide solutions in perchloric acid were selected as a wavelength standard because the absorption bands are narrower than those of the holmium oxide glass. Consult the Certificate in Appendix 17; also, see Appendix 4 and NBS Special Publication 260-102.
The material is certified for the relative molecular emission spectrum $E(\lambda)$, in radiometric units for a solution of 1.28×10^{-6} mol/L in 0.105 mol/L perchloric acid, using an excitation wavelength of 347.5 nm. The certified values of the molecular emission spectrum at 5-nm intervals from 375 to 675 nm are given. This certification was made with the NIST reference fluorescence spectrometer.	This SRM is to be used for evaluation of methods and calibration of fluorescence spectrometers. A solution of 0.1 mg/mL in 1000 mL 0.105 mol/L perchloric acid is recommended. It should be stored in the dark in a well-stoppered glass bottle. This solution is stable for three months. SRM 936 is for "in vitro" diagnostic use only.	The material should be kept in its orginal bottle and stored in the dark at 30°C or less. Under these conditions SRM 936 is stable for three years. See NBS Special Publication 260-64, and Certificate in Appendix 18.
The nominal maximum emission spectra are 450, 530, 580 and 620 nm. All measurements are made with the NIST reference fluorescence spectrometer.	These materials are intended for the evaluation of methods and calibration of fluorescence spectrometers in the spectral range from about 420 to about 675 nm.	A NIST Special Publication in the SP 260 series describing the production and certification of this SRM is in preparation. For further information, consult the reprint in Appendix B, and the Certificate in Appendix 19.

Part Two

2. FACTORS AFFECTING THE PROPER FUNCTIONING OF A SPECTROPHOTOMETER

There are a number of factors that can affect the proper functioning of a spectrophotometer and prevent the acquisition of meaningful data. Some of these factors are described below.

2.1 Short- and Long-Term Stability

Short- and long-term stability is related to the instrument's mechanical, optical, and radiation measuring design and to the quality of the materials and workmanship used to implement the design. The conditions under which the instrument is operated, such as vibration, humidity and temperature, dust and corrosion, will also affect its stability. Other critical factors are the short- and long-term stability of the radiation source, the reproducibility of the positioning of the sample holder and carriage, and the stability of the read-out system.

2.2 Wavelength Accuracy

Wavelength accuracy is a function of the stability of the optical system and of the accuracy of the wavelength scale, or wavelength cam, and its reproducibility.

2.3 Spectral Bandpass

The spectral bandpass of a spectrophotometer is the spectral interval $\Delta\lambda$ in wavelength that emerges through the exit slit of width w of the instrument: $\Delta\lambda = w \frac{d\lambda}{dx}$ where $\frac{d\lambda}{dx}$ is the reciprocal linear dispersion of the spectrophotometer. Spectral bandpass is a parameter that depends on the optical design and of the associated elements: grating, prism, or filters used in the instrument. The magnitude of the spectral bandpass for a specific spectrophotometer over the whole spectral range of the instrument is important information that is provided by the manufacturers of the particular instrument.

2.4 Stray Radiations

Stray radiations can originate in the spectrometer and in the sample compartment. The stray radiation produced in the spectrometer is the radiant flux at wavelengths different from those of the nominal spectral bandpass transmitted through the instrument at a particular wavelength. The stray radiation produced in the sample compartment is the radiant flux that

reaches the photosensitive detector without passing through the absorbing sample. The former is the heterochromatic stray radiation, while the latter is the isochromatic stray radiation.

2.5 Accuracy of the Transmittance or Absorbance Scales

Accuracy of the transmittance or absorbance scales refers to the capability of a spectrophotometer to measure ratios of radiant fluxes with a known accuracy and to produce true transmittance (T) or absorbance (A) measurements. This fundamental parameter is determined ultimately by the linearity of the detection system when the other parameters such as wavelength accuracy, adequate spectral bandpass, and photometric precision are in control.

2.6 Conditions Associated with the Stability of the Analytical Sample (Color Reaction) and its Homogeneity

Conditions associated with the stability of the analytical sample (color reaction) and its homogeneity include dissociation and association reactions, radiation scatter inside the sample, polarization, fluorescence, temperature, particulate matter, and surface conditions. These conditions are characteristics of the analytical sample and of the chemical reactions involved in the spectrophotometric process, and are to a large extent independent of the spectrophotometer used for the measurements. Since these factors can affect in a significant manner the precision and accuracy of the measurement, however, they are mentioned here to remind the analyst that he must be aware of their existence, and that he must evaluate their magnitude in the particular analytical process considered before proceeding with the actual measurement. As a result of this knowledge, the analyst must be able to select the most adequate analytical procedure for the matrix and chemical species under consideration, and to establish ways to eliminate, minimize, or compensate for these causes of errors. From the factors mentioned above, those which are relevant to the subject discussed in this publication will be examined in more detail.

3. PROCEDURES TO ASSESS AND CONTROL SOME OF THE FACTORS THAT AFFECT THE PROPER FUNCTIONING AND ACCURACY OF A SPECTROPHOTOMETER

3.1 Short- and Long-Term Stability

The short- and long-term stability of a spectrophotometer can be verified and monitored by using glass filters specially selected for this purpose. Stable radiation sources, such as tritium-activated luminescent materials, could be considered for the same purpose [16]. The use of such a source, however, is not always possible due mainly to problems associated with the design and operation of the instrument.

Of the several kinds of glass filters that can be used, those constituting SRM 930 and SRM 1930 are most suitable. The optical characteristics of these glass filters are discussed in Section 4. Since the stability of a spectrophotometer is the first test that should be carried out, however, we will describe their use for this purpose now.

As a general rule, it is desirable to place the spectrophotometer in a clean laboratory and in an area where the temperature is as constant and reproducible as possible, protected from direct sunlight, sudden changes of temperature, corrosive atmosphere, dust, and vibration. The tests should be carried out after the instrument has been verified by the manufacturer, and it is found to perform well and to meet all the required specifications.

After an initial warming-up period, the "0%T" and "100%T" readings on the scale are verified following the procedure described by the manufacturer of the particular instrument. The wavelength dial is set at a selected value, usually the one at which the transmittance of the analytical sample will be determined, e.g., 635.0 nm. One of the SRM 930 glass filters in its metal holder, e.g., the filter having the nominal percent transmittance of 30%T, is inserted in the sample compartment. An empty filter holder is positioned in the reference compartment, or the compartment is left empty. The transmittance of the glass filter is measured following the method specified by the manufacturer, and the results are recorded. This procedure is repeated at all wavelengths at which the analytical samples will be measured. Similar transmittance measurements are performed using the glass filters having nominal percent transmittances of 20%T and 10%T. The temperature at which these measurements are made should also be recorded. In this manner, the performance of the instrument is determined over the working spectral range for a transmittance interval and at a temperature that covers most of the conditions of analytical determinations under consideration. Similar measurements can also be made using SRM 1930.

The values obtained are displayed in a graphical form by plotting on the ordinate the transmittance found for every wavelength, and on the abscissa the date at which these measurements were made. An example of such a graph is given in figure 6 for two wavelengths, 635.0 nm and 590.0 nm. Similar graphs should be made for the other wavelengths of interest for the nominal 10%T, 20%T, and 30%T filters. The results for the measurements shown in figure 6 were obtained in a laboratory in which the surrounding temperature was maintained at 24.0 °C $\pm$ 1 °C. This temperature was recorded on the graphs as a common value for all measurements. When solutions are measured, the temperature of the liquid in the cuvette should be determined. Where the temperature changes from measurement to measurement, its value should be recorded and written on the graph under the corresponding transmittance value so that temperature corrections can be made if necessary. The procedure described above should be performed every time the spectrophotometer is used: before, and preferably after, the analytical work is carried out.

The data plotted in figure 6 were obtained with a commercial spectrometer provided with a quartz prism double spectrometer, and a transmittance scale divided in 1000 units between 0 and 100 percent transmittance. The size of each division, and the stability and reproducibility of

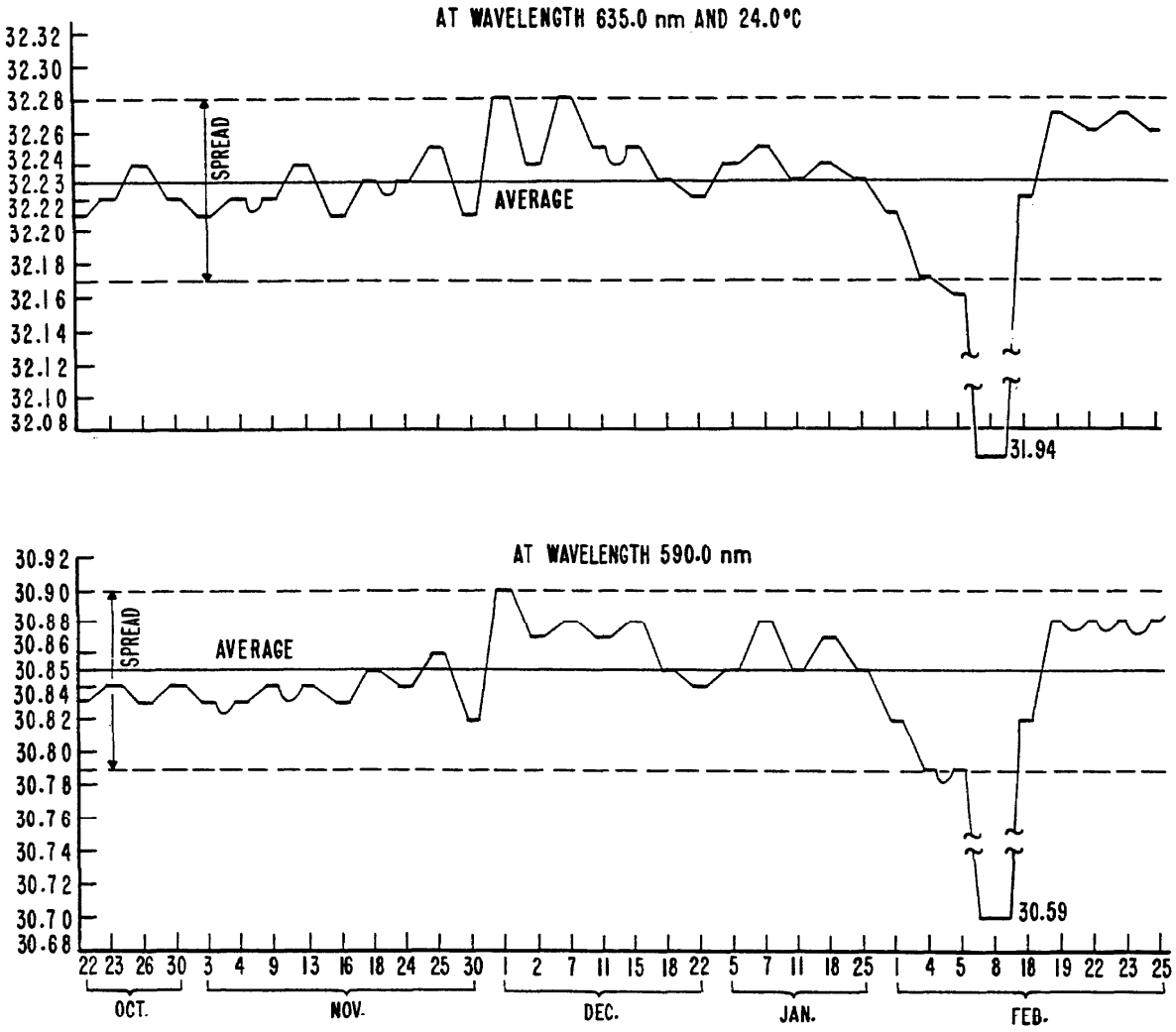


Figure 6. Control chart for a spectrophotometer showing the variation of transmittance at 24.0 °C as a function of time for a neutral glass filter at 635.0 nm and 590.0 nm.

the instrument is such that it permits visual interpolation between each division, to fractions of a division; hence, the ordinate scale on the graphs in figure 6 was selected to reflect this resolution.

An examination of the data shows that the stability of the instrument, as expressed by percent transmittance, when operated at 24.0 °C from October 22 to February 5, varied from 32.17 %T to 32.28 %T, with an average of 32.23 %T at 635.0 nm. At 590.0 nm, the equivalent values were 30.79 %T, and 30.90 %T, respectively, with an average of 30.85 %T.

The spread, 0.11 %T for both wavelengths, results from the inherent instability of the instrument and of the glass filters used. This situation changed markedly on February 8 when transmittances of 31.94 %T and 30.59 %T were found at 635.0 nm and 590.0 nm, respectively. Since these values largely exceeded the specified spread established for this particular instrument by the manufacturer, a field engineer from the manufacturer was called in. An examination of the spectrophotometer revealed that a potentiometer was malfunctioning. After replacement of this faulty part the instrument was tested again on February 18, and the transmittance values measured on the same glass filters were within the established spread of the instrument as originally established. As shown in figure 6, the results indicate that the spectrophotometer was again performing according to its specifications.

This example illustrates the usefulness of the short- and long-term stability tests as well as data presentation using control charts. This test procedure permits the detection and diagnosis of possible malfunctions in an instrument before such malfunctions would affect the validity of measurements. It is obvious that similar control charts can be prepared using absorbance values instead of transmittance values.

The periodic verification of the stability of spectrophotometers, as described above and illustrated in figure 6, is used routinely in the NIST laboratories. This procedure is highly recommended to all users of such instruments, and it is performed as previously mentioned with the help of specially selected glass filters. It should be mentioned here that the precision of such tests, however, cannot exceed the stability of the glass filters, which will be discussed in Section 5 for the materials used in this work.

3.2 Wavelength Accuracy

Although the test discussed in section 3.1. may show that a spectrophotometer exhibits good instrument stability, large errors in the accuracy of its wavelength scale may produce unreliable measurements. The wavelength accuracy of a spectrophotometer can be verified by the use of (a) an emission source capable of producing discrete radiations of suitable intensity and adequate wavelength spacing throughout the spectral range of interest, e.g., 200 to 800 nm, or (b) glass filters or solutions with sharp absorption bands.

(a) Adequate sources of discrete radiations at well-known wavelengths, most suitable for use in the calibration of the wavelength scale of a spectrophotometer, are the low-pressure quartz discharge tubes containing mercury vapor, helium, or neon. Such tubes are available commercially from the manufacturers of laboratory instrumentation at reasonable prices. One type of a low-pressure discharge tube has a cylindrical shape with the total length of 120 mm from which a 50-mm portion constitutes the quartz discharge tube. This tube should be placed immediately in front of the entrance slit of the spectrometer.

(b) Wavelength calibrations can also be made by using a glass filter having a number of strong and narrow absorption bands suitably spaced over the spectral range of interest. Two

materials have been used or suggested for this purpose: glasses containing rare-earth oxides such as didymium glasses (mixture of praeseodymium and neodymium oxides) and holmium oxide glasses. They have been used for many years at the National Institute of Standards and Technology. The transmittance characteristics of the didymium and holmium oxide glasses are illustrated in figures 7 and 8, respectively.

A detailed description of the properties and use of low-pressure discharge tubes and of glass filters with sharp absorption bands is given in NBS Letter Circular LC-1017, "Standards for Checking the Calibration of Spectrophotometers," by K.S. Gibson, H.J. Keegan, and J.C. Schleter, reissued in January 1967. Part of this paper is reproduced in Appendix 3. Further recommended practice can be found in the Manual on Recommended Practices in Spectrophotometry, published by the American Society of Testing and Materials, 1916 Race Street, Philadelphia, PA 19103. A comprehensive chapter by Vinter on wavelength calibration is found in reference 23.

3.2.1 SRM 2009a, Didymium Glass

As seen in table 2, SRM 2009a is issued by NIST as a wavelength standard. It consists of a didymium glass filter having the nominal spectral transmittances shown in figure 7. This filter is produced in a nominal size of 10x30x3 mm thick. It is mounted in a metal holder that fits into the cuvette holder of the spectrophotometer. The spectral bandpass-wavelength dependence is described in detail in Special Publication 260-66 and in the Certificate that accompanies each standard. The 14 to 24 certified wavelengths are in the spectral range 400 - 760 nm and are given for spectral bandpasses from 1.5 - 10.5 nm (see Certificate in Appendix 16).

3.2.2 SRM 2034, Holmium Oxide Solution

Since SRM 2009a is used to verify the wavelength accuracy in the visible spectral range only, it was necessary to produce an SRM that could be used in the ultraviolet as well. An adequate material for use in the ultraviolet and visible spectral range was obtained by dissolving holmium oxide in dilute perchloric acid [24]. The spectral transmittance of the aqua ion $Ho(H_2O)_n^{3+}$ [25], obtained when holmium oxide is dissolved in a 10 percent aqueous perchloric acid solution, is illustrated in figure 2 of the paper reproduced in Appendix 4 [24]. The 14 sharp transmittance minima are evenly distributed throughout the spectrum from 240 to 640 nm, and provide a means of verifying the wavelength accuracy of conventional spectrophotometers over that spectral range. The wavelengths corresponding to the 14 transmittance minima for several bandwidths and temperatures are given in Appendix 4.

A list of the wavelengths of minimum transmittance of the holmium oxide solution reported by other workers is given in table 6 of the paper in Appendix 4. The details of these measurements are given in reference 4. The data shown in this table indicate that values obtained by workers in different laboratories are generally in good agreement, and that the NIST data also agree well with these workers' previously published data. These workers also

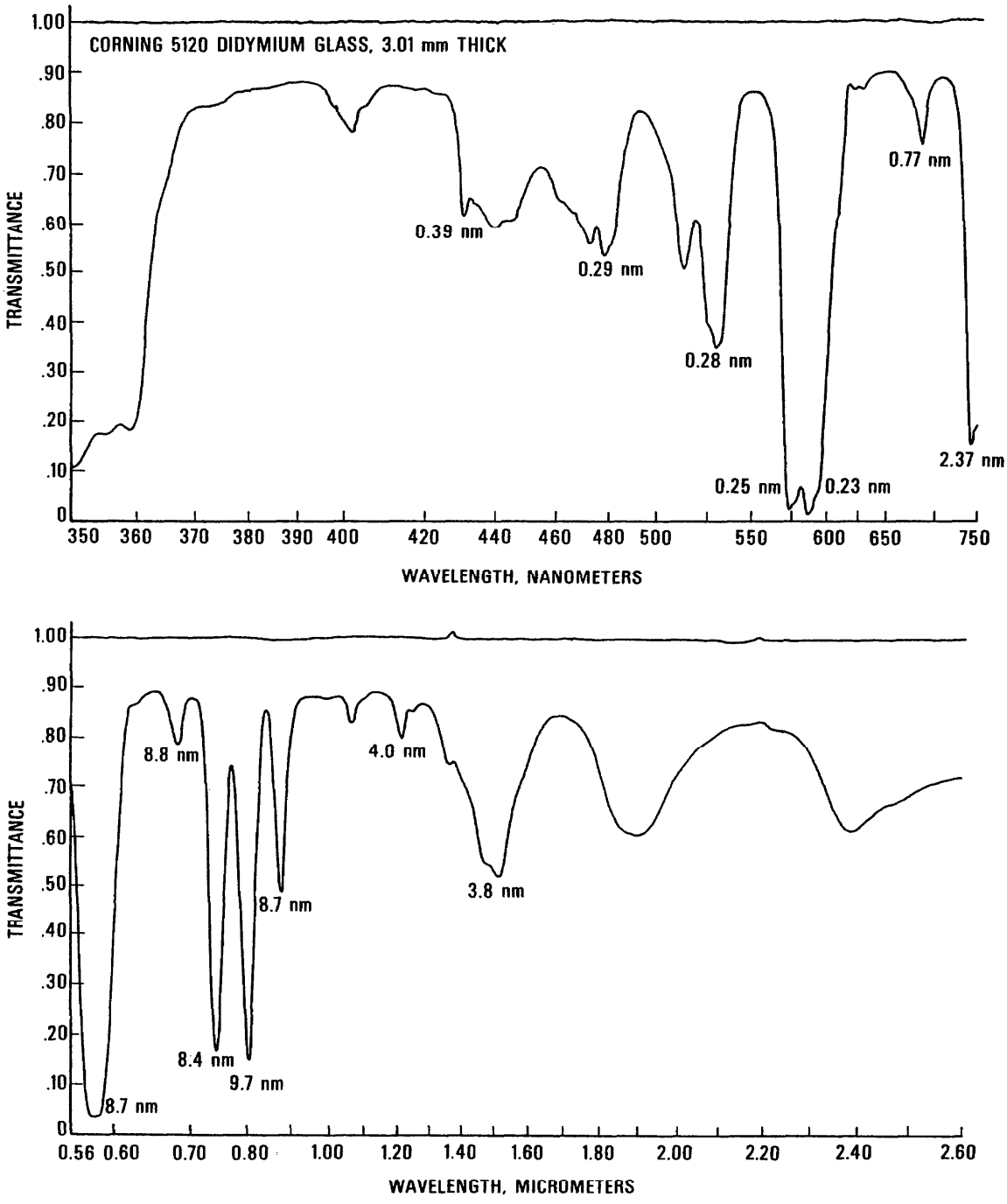


Figure 7. Transmittance of a didymium glass filter. The spectral bandpass used is marked at the corresponding transmittance minimum. Courtesy of Corning Glass Works.

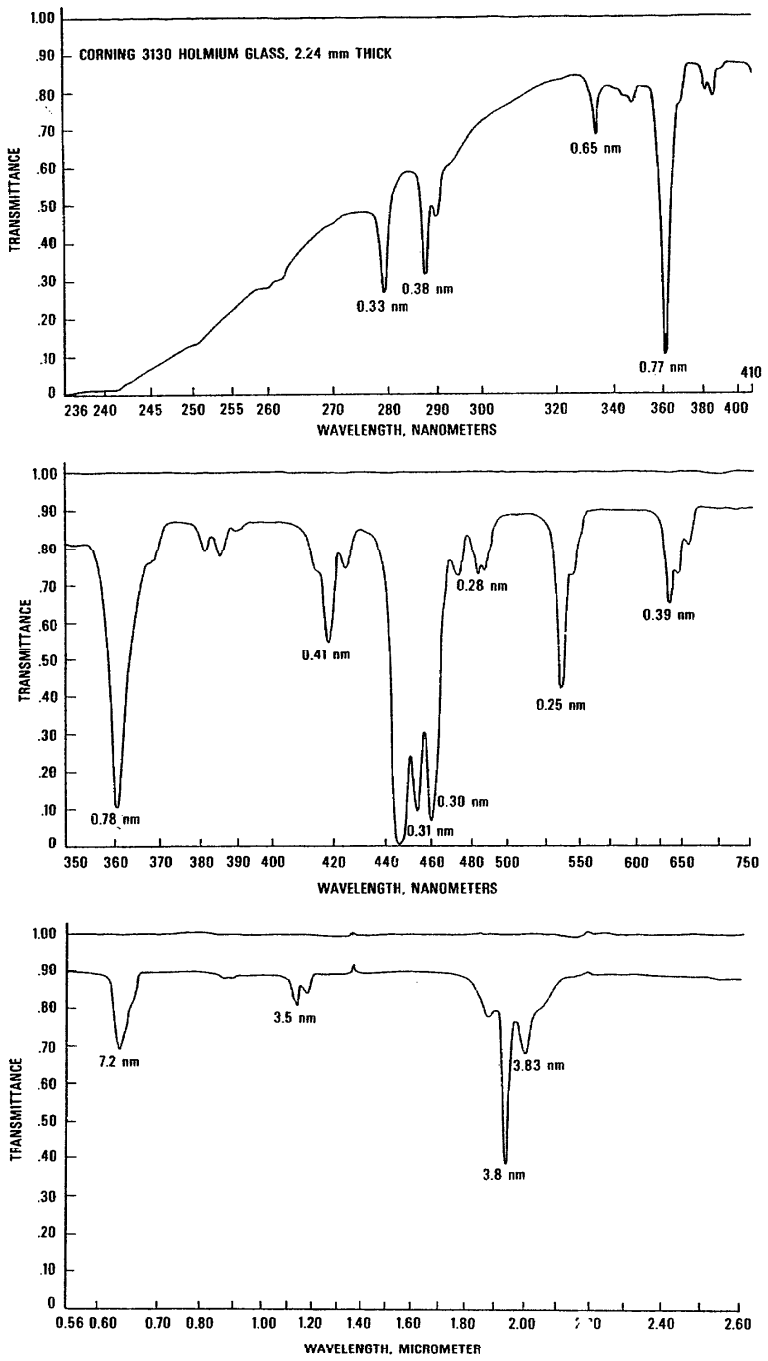


Figure 8. Transmittance of a holmium oxide glass filter. The spectral bandpass used is marked at the corresponding transmittance minimum. Courtesy of Corning Glass Works.

found that the wavelengths of minimum transmittance of holmium oxide in similar solutions of perchloric acid are not sensitive to variations in temperature and concentration. They also concluded that the wavelengths of minimum transmittance were least affected by changes in spectral bandwidth for bandwidths less than 1 nm, but that large shifts can be encountered at bandwidths exceeding 1 nm.

The reported wavelengths of minimum transmittance of the holmium oxide solutions appearing in Appendix 4 are estimated to be uncertain by no more than $\pm$ 0.1 nm at the 95 percent confidence limit. These wavelengths of minimum transmittance were found to be essentially unaffected by changes in temperature at 25 °C $\pm$ 5 °C. They were also unaffected by variations in the concentration for solutions containing 2 percent, 4 percent, and 6 percent by weight of holmium oxide. The critical parameter affecting the measured values of minimum transmittance was found to be the spectral bandwidth setting of the spectrophotometer. For spectral bandwidths less than 1 nm, the wavelength shift is generally less than 0.2 nm.

As a result of this work, SRM 2034, "Holmium Oxide Solution as an Ultraviolet and Visible Wavelength SRM," was issued in 1985. It consists of an all-fused-silica rectangular cuvette with a 10-mm nominal lightpath, provided at one end with a fused silica tube for filling the cuvette with a solution of 4 percent holmium oxide by weight in 10 percent aqueous perchloric acid. The purity of the holmium oxide is 99.99 percent (as indicated by the manufacturer) and the perchloric acid and distilled water are pure reagent grade prepared at NIST by sub-boiling distillation. After filling the cuvette, the tubular end is sealed by fusion. As far as it is known, the solution is stable under typical laboratory conditions for at least 5 years.

Users of SRM 2034 can most effectively determine the wavelength error associated with their instrument by using the NIST certified data listed in Special Publication 260-102 (also in Appendix 4) that are representative of the spectral bandwidth setting ordinarily used with the instrument (see certificate in Appendix 17). The wavelengths of minimum transmittance of the holmium oxide solution for spectral bandwidths greater than 3 nm have not been evaluated.

3.3 Spectral Bandpass

As mentioned in Section 2.3, the spectral bandpass over the entire spectral range for various slit widths is an instrumental parameter which should be provided by the manufacturer. For spectrophotometers with prisms or gratings, the spectral bandpass ($\Delta\lambda$) is related to reciprocal linear dispersion ($d\lambda/dx$) and slit width (w) by the equation given in Section 2.3. For example, for an instrument with a reciprocal linear dispersion of 15 nm/mm and a slit width of 0.2 mm, the bandpass is 3.0 nm. For prism instruments, the reciprocal linear dispersion and, therefore, the bandpass vary with wavelength. The following discussion will be limited to the influence of this important parameter, which is often neglected, on the measurements of transmittance for the glass filters discussed in this publication.

Three types of glass filters having a transmittance that varies only moderately with wavelength were used: the Chance ON-10, Corning 8364, and Schott NG-4 optically neutral glasses. The transmittance characteristics of these glasses as a function of wavelength in the spectral interval of 350 nm to 700 nm were obtained using a Cary 14 spectrophotometer with an adequate spectral bandpass. The results are illustrated in figure 9, where it can be seen that the Corning 8364 and Chance ON-10 glasses exhibit similar characteristics. Figure 9 also shows that these two glasses have an absorbance, or transmittance, more dependent on wavelength than the Schott NG-4 glass. Since the Corning filter produced results similar to those found for the Chance ON-10 glass, these two filters will be discussed collectively.

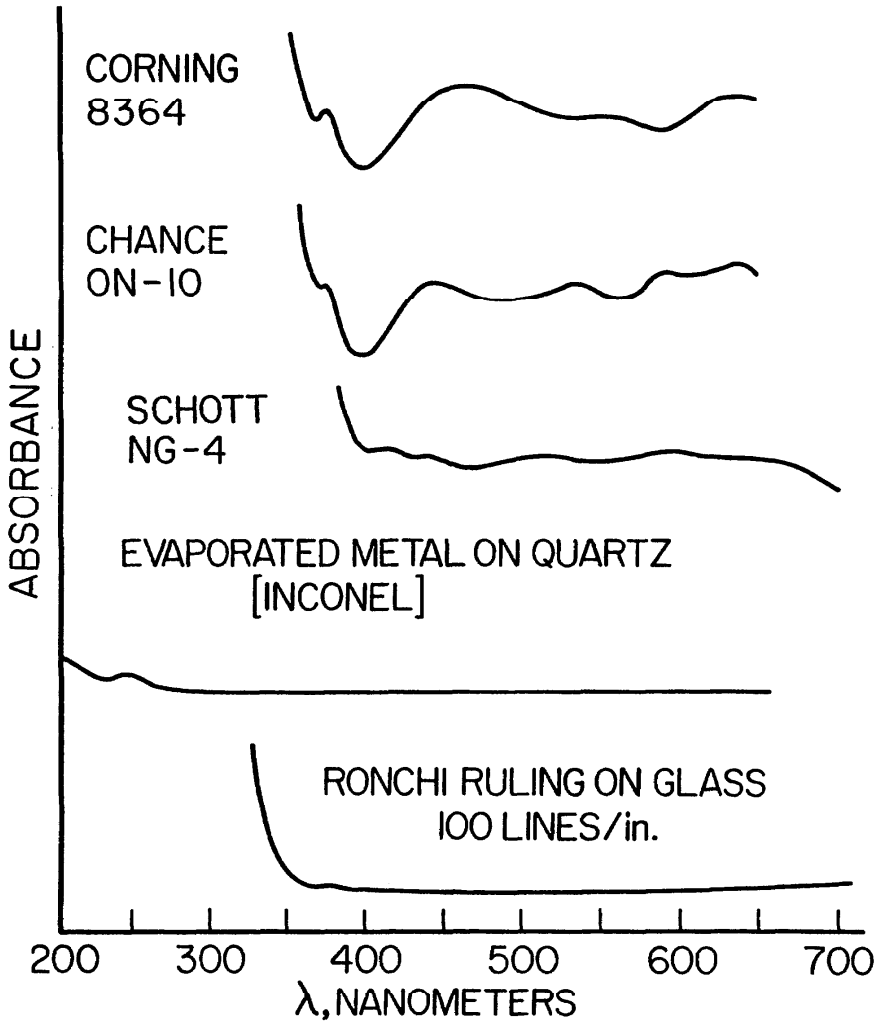


Figure 9. Spectral characteristics for five transparent materials from 200 nm to 700 nm [11].

Using a Cary 16 spectrophotometer, the transmittances of the Chance ON-10 and Schott NG-4 glasses were measured, as indicated in figures 10 and 11, respectively, at four wavelengths using variable slit widths, and consequently, various spectral bandpasses from 0.5 nm to 100.0 nm. Figure 10 illustrates the dependence of the transmittance for the Chance ON-10 (and Corning 8364) glass filter on the spectral bandpass at 400.0, 445.0, 490.0, and 590.0 nm. It can be seen that the transmittance varies with the bandpass, and that this dependence is stronger at the wavelengths where the glass has a stronger and sharper absorption band. For instance, at 400.0 nm a rather narrow spectral bandpass of 0.5 nm will be required for this type of glass to obtain an accurate transmittance value, with everything else being equal, in particular the wavelength and photometric scale accuracy. At 490.0 nm, however, a spectral bandpass of 15 nm would be adequate. The same dependence, but to a smaller extent, is illustrated in figure 11 for a Schott NG-4 glass. It can be seen here that larger spectral bandpasses could be used to produce accurate transmittance values.

This transmittance-spectral bandpass dependence is summarized in the graph in the upper left corner of figure 10, where it can be seen that the use of wider spectral bandpasses will produce the inaccurate T_1 and T_2 values when compared with T_1' and T_2', which are the transmittance values obtained using an infinitesimal spectral bandpass. As a general rule, the value of the spectral bandpass required to produce accurate transmittance measurements with an uncertainty not greater than 0.1 percent should be 1/20 of the symmetrical natural spectral bandwidth, at half intensity, of the material to be analyzed and at the wavelength at which the measurement is performed. When this information is not available, it can be determined by measuring the transmittance (or absorbance) of the material at the wavelength of interest, using various spectral bandpasses (or slit widths) as illustrated in figures 10 and 11. The largest bandpass or slit width that can be used is given by the value found at the end of the horizontal portion of the transmittance-spectral bandpass curve. The selection and use of adequate spectral bandpass is one of the indispensable conditions that must be fulfilled to obtain true transmittance values.

3.4 Stray Radiations

An instrumental parameter that can measurably affect the accuracy of transmittance measurements is the stray radiant energy (SRE) or stray light. This can be defined generally as unwanted radiation that is measured by the photodetector. Stray radiant energy contributes to the degradation of optical transmittance measurements and to the reduction of specificity, sensitivity, and linearity of absorbance measurements.

As mentioned briefly in Section 2.4., two major types of SRE can be identified: heterochromatic and isochromatic. The former originates in the spectrophotometer and can be defined as radiation transmitted by the spectrometer that is of a wavelength different from the spectral bandpass for which the instrument was set. The latter originates in the sample compartment and can be defined as radiation of the same wavelength as that which falls on the sample, but reaches the photodetector of the spectrophotometer without passing through the analytical sample.

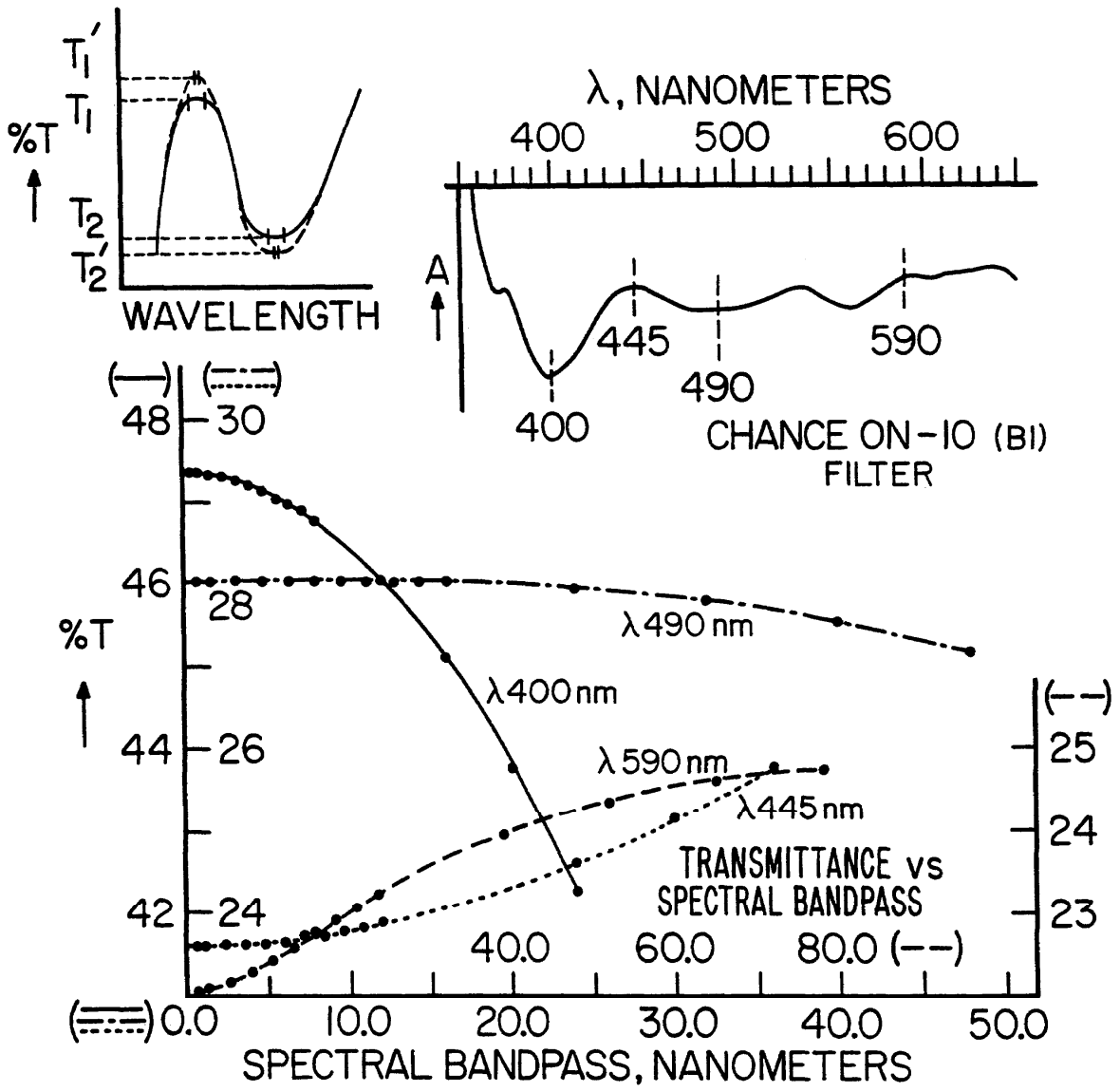


Figure 10. Influence of spectral bandpass on the transmittance of a Chance ON-10 glass filter measured at 400.0, 445.0, 490.0 and 590.0 nm. The graph at left, upper corner, describes in general the relation between spectral transmittance and spectral bandpass. Measurements made with a smaller bandpass | | provide accurate T values when compared with those made with a larger spectral bandpass | | [11].

From these simple definitions it might be concluded that both types of stray light can be assessed easily. Unfortunately, this is not the case. Actually, the accurate measurement of stray light is subject to ambiguity and is difficult to define and measure [26].

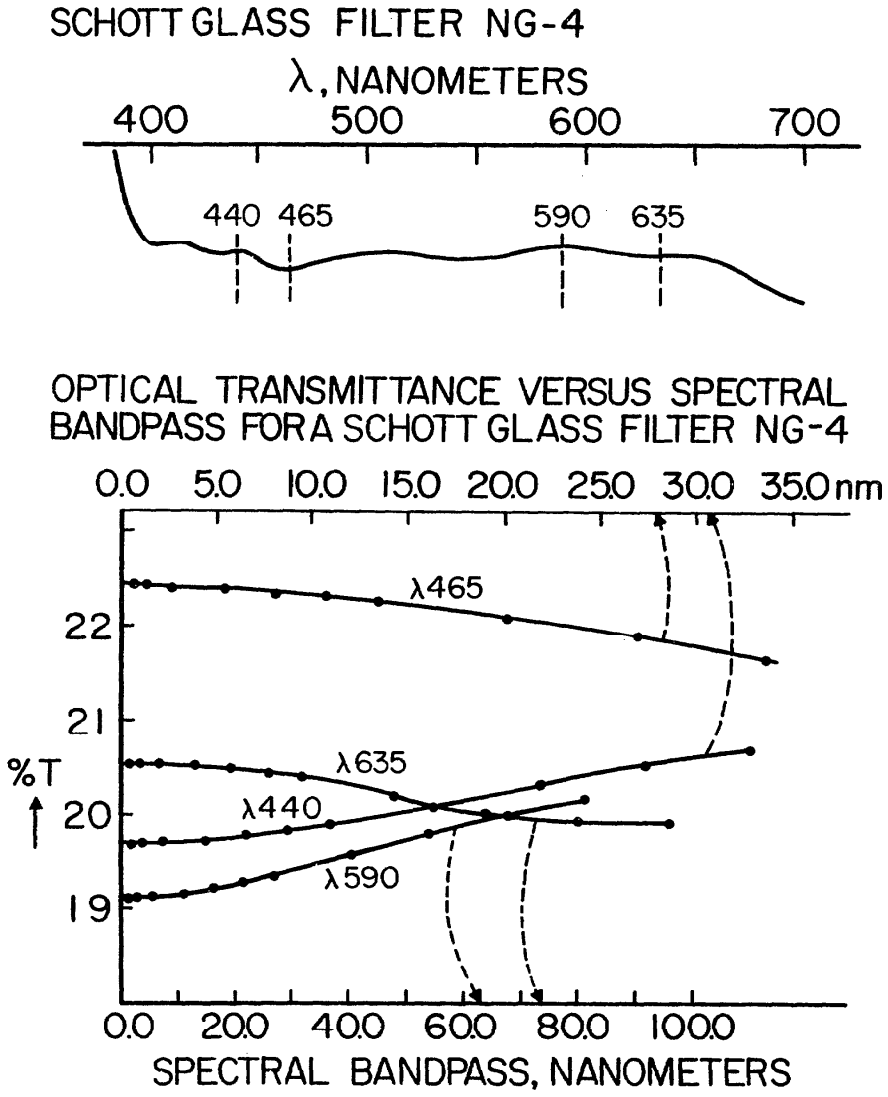


Figure 11. Influence of spectral bandpass on the transmittance of a Schott NG-4 glass filter measured at 440.0, 465.0, 590.0 and 635.0 nm [11].

3.4.1 SRMs 2032 and 2033

At the present time, two SRMs (SRMs 2032 and 2033) are available to assess both the heterochromatic and isochromatic stray light. Heterochromatic stray light can be measured by using a variety of techniques, including the use of blocking optical filters, and this approach was selected to produce SRM 2032. This material consists of crystalline potassium iodide of reagent-grade purity which has sharp cutoff absorption near 260 nm, and can be used to assess the stray light below this wavelength. Solutions from this compound were certified for their

specific absorbances at eight wavelengths from 240 - 275 nm in increments of 5 nm with an uncertainty of 5 percent. The measurement consists of setting the spectrometer at a wavelength below 260 nm, say 255 nm, and placing in the sample compartment a quartz cuvette containing the potassium iodide solution. Any appreciable amount of light detected is assumed to be heterochromatic stray light. See also the Certificate for SRM 2032 in Appendix 14.

Isochromatic stray light can be assessed using SRM 2033. This material consists of two filters made from a semi-transparent evaporated metal on a fused silica substrate each of which has a nominal percent transmittance of 10%T. One filter is mounted in a metal holder that can be inserted in the sample compartment of the spectrophotometer. This holder is provided with a front and rear shutter, one of which has a window in which the second filter is mounted. This system is used to assess the maximum isochromatic stray light in the sample compartment that results from reflections of the incident radiation at the surfaces of the sample and various optical components and reaches the photodetector without passing through the sample.

The isochromatic SRE test measurement is performed by placing this unit in the sample beam of the spectrophotometer with the opaque shutter at the rear of the filter holder. Under these conditions, if a signal is detected, it is caused by reflections at the surface of the filter exposed to the incident radiation. This radiation is scattered from the walls and other components of the sample compartment and reaches the photodetector without passing through the sample. The signal is the isochromatic stray light. See also the Certificate for SRM 2033 in Appendix 15.

3.4.2 A New Method for Measurement of Stray Radiant Energy

A different approach to the measurement of heterochromatic stray light in ultraviolet absorption spectrometry was described recently by Mielenz, Weidner, and Burke [27]. The principle and application of the new method is discussed in detail in the publication reproduced in Appendix 5, and since it appears to have particular merit, it is briefly summarized below.

The test method uses the same solution filters with sharp UV absorption edges as specified in ASTM Test Method E387, but one measures the apparent absorbance of a 10-mm pathlength cell in the sample beam relative to a 5-mm pathlength cell in the reference beam. Scanning toward shorter wavelengths, an apparent absorbance maximum, which is a direct measurement of the heterochromatic stray light, is recorded. This method was found to be in satisfactory agreement with the ASTM method in comparative tests of several spectrophotometers at different wavelengths between 200 and 390 nm, using potassium chloride, potassium iodide, sodium iodide, acetone, and sodium nitrate solution filters. The new method proved to be simpler than the ASTM method when small amounts of stray light were measured, the main advantage being that the apparent absorbance maximum occurs at considerably lower scale values than the corresponding absorbance plateau measured by the ASTM method. This reduces the need for successive attenuations of the reference beam every time the spectrophotometer runs off scale; in many instances, the new method required no attenuation.

3.5 Accuracy of the Transmittance or Absorbance Scales

Optical transmittance is due to an intrinsic property of matter and characterizes a particular transparent material. Since this parameter is not known a priori, it must be determined by experimental procedures. Photometric accuracy is an essential condition that must be fulfilled by a spectrophotometer for the production of accurate transmittance or absorbance values.

As mentioned earlier, true transmittance values can be obtained only by using accurate measuring techniques and by taking into consideration all factors that can affect and distort the data. In this discussion the optical transmittance T of a solid material includes the reflection losses that occur at the air-solid interface. The internal transmittance T_i is defined as the transmittance of the material corrected for reflection losses. This internal transmittance can be calculated in principle from the transmittance by using the well-known Fresnel equations as shown in the reprint of Appendix 2. The internal transmittance is obtained experimentally when the measurements are made using a blank sample in the reference beam of the spectrophotometer. When a blank is not available, as in the case of SRMs 930 and 1930, the measurements are made against air in the reference beam. Under these circumstances the resulting transmittance value includes the reflection losses (which are about 8 percent for a glass filter having an index of refraction of 1.5). A discussion of this subject by Mielenz is given in reference 20. The absorbance A of a material is related to the internal transmittance T_i by the expression $A = -\log_{10}T_i$ while the transmittance density D is related to the transmittance T by the expression $D = -\log_{10}T$.

Transmittance is the ratio of two radiant fluxes. It is therefore necessary that the transmittance scale of the spectrophotometer be accurate. The transmittance of a particular material is also a function of wavelength; hence the wavelength scale of the monochromator should also be accurate, and appropriate spectral bandpasses should be used. These conditions were examined in the previous sections. For highest accuracy, the measurements should be made using collimated radiation. Such radiations define unambiguously the actual pathlength through the transmitting medium, the reflection losses, and eliminate the effects of polarized radiations that are produced at the surface of the sample (see Appendices 2 and 6). Other important factors, already mentioned, that must be considered are: the homogeneity, flatness, parallelism, and stability of the sample, radiation scatter inside the sample, interference phenomena, stray radiation, polarization, fluorescence, temperature, particulate matter, and surface conditions. Since transmittance measurements depend on a diversity of factors, meaningful values can be obtained only by defining the experimental conditions for obtaining transmittance data.

Spectrophotometers are used to perform two types of measurements:

(1) Quantitative determination of chemical species using the relation between optical transmittance of the material and the concentration as a measuring parameter. Under these circumstances, the photometric scale of the spectrophotometer is calibrated in meaningful units,

using a series of reference solutions having known concentrations of the species to be determined, rather than values of optical transmittance.

The accuracy of the measurements is related to the accuracy with which the concentrations of the reference solutions are known and to the precision (stability, sensitivity) of the spectrophotometric method and instrument used. The accuracy of the transmittance or absorbance scale per se, is not a critical factor in such measurements.

The precision and stability of the instrument are, however, important parameters that should be verified before and after each series of measurements. This can be done, as already discussed, by the careful use of selected solid or liquid reference filters having well established and stable transmittance values.

(2) Determination of the optical transmittance characteristics of solid or liquid materials, and the determination of certain physicochemical constants such as molar absorptivity and equilibrium constants. In all of these cases, the accuracy of the transmittance or absorbance scales of the measuring instrument, among other things, is essential to provide true values. Ways to establish and check this important parameter are critically needed. For example, current interest in molar absorptivity values, as an index of the purity of biological or clinical materials, requires greater accuracy of measurement. Also, the accuracy of the determination of equilibrium constants of chemical reactions in solutions and the determination of enzyme activity in international units is dependent on true values of their molar absorptivities.

4 STANDARD REFERENCE MATERIALS FOR TRANSMITTANCE IN SPECTROPHOTOMETRY

4.1 Description and Selection of Materials for Use as Standard Reference Materials in Spectrophotometry

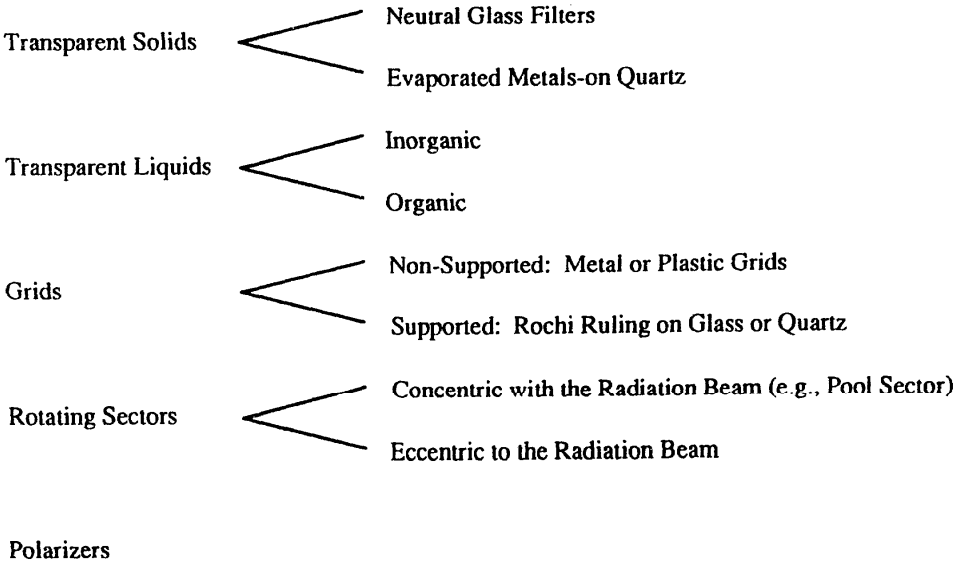
Such materials should fulfill the following conditions: (a) be transparent in the spectral range of interest, usually between 200 nm and 800 nm; (b) have a transmittance independent of wavelength (optically neutral); (c) have a spectral transmittance independent of temperature; (d) have low reflectance and be free of interferences; (e) be non-fluorescent; (f) be stable, homogeneous, and free of strain; (g) have mechanical stability for the size used (thickness, length, width) and be easy to fabricate by conventional techniques used in optical shops; (h) be simple to use in conjunction with the conventional spectrophotometers available today in analytical laboratories; (i) be readily available and relatively inexpensive.

These conditions are fulfilled to a smaller or larger extent by several different materials including transparent solids and liquids, grids, rotating sectors, and polarizers. Of these materials, the neutral optical glass filters mentioned in the first group below, most nearly satisfied the required conditions and constitute the most acceptable compromise when compared with the other materials.

Several neutral glasses were examined, and from these the Corning 8364, the Chance ON-10, and the Schott NG-4 glasses were initially selected. As illustrated in figure 9, the spectral transmittances of these glasses are compared with the transmittances of an evaporated metal-on-quartz filter (non-fluorescent fused silica of optical quality) and a Ronchi ruling on a glass substrate. The transmittances of the latter two materials exhibit the least dependence on wavelength from 200 nm to over 700 nm. The Ronchi ruling transmittance below 350 nm is limited only by the transmittance of the glass substrate and not by the nature of the ruling itself. For the evaporated metal-on-quartz filter, the attenuation of radiations is produced by reflection rather than absorption. This material, therefore, was not selected since there is a possibility that reflected radiation is generated in conventional spectrophotometers. The Ronchi ruling was rejected since it is subjected, by its nature, to diffraction phenomena. From the remaining glasses, the Schott NG glass was finally selected since this material exhibits the best optical neutrality. Excluding its limited spectral transmittance range to the visible and near-infrared spectral domain, the Schott NG glass is the best material that satisfies the other conditions enumerated above.

A number of procedures were developed and used for the preparation of SRM 930 and SRM 1930, and these were tested under a variety of conditions. Of these procedures, only those that were finally selected and are used for the preparation of these SRMs will be described here.

The optically neutral NG glasses for the filters were produced by Schott of Mainz, Germany, and are designated as "Jena Colored and Filter Glass." The following Schott NG glasses were selected: NG-3, NG-4, NG-5, and NG-11. This choice permits stepwise coverage of a nominal transmittance range from 1%T, 3%T, 10%T, 20%T, 30%T to 50%T, using nominal glass thickness of 1.5 to 2.0 mm. All glass material was received from the manufacturer in the form of 150x150 mm (6x6") square plates. From this raw material the individual filters were obtained by adequate cutting, grinding, and fine polishing in the optical shops at NIST.



4.2 Preparation of the Glass Filters

Each glass filter is cleaned manually with distilled water using a piece of optical lens paper. This is followed by a preliminary examination for visible defects using a stereo-microscope with 12X magnification. This examination is performed in an all-polypropylene hood provided with a vertical laminar flow of filtered air, illustrated in figure 12.

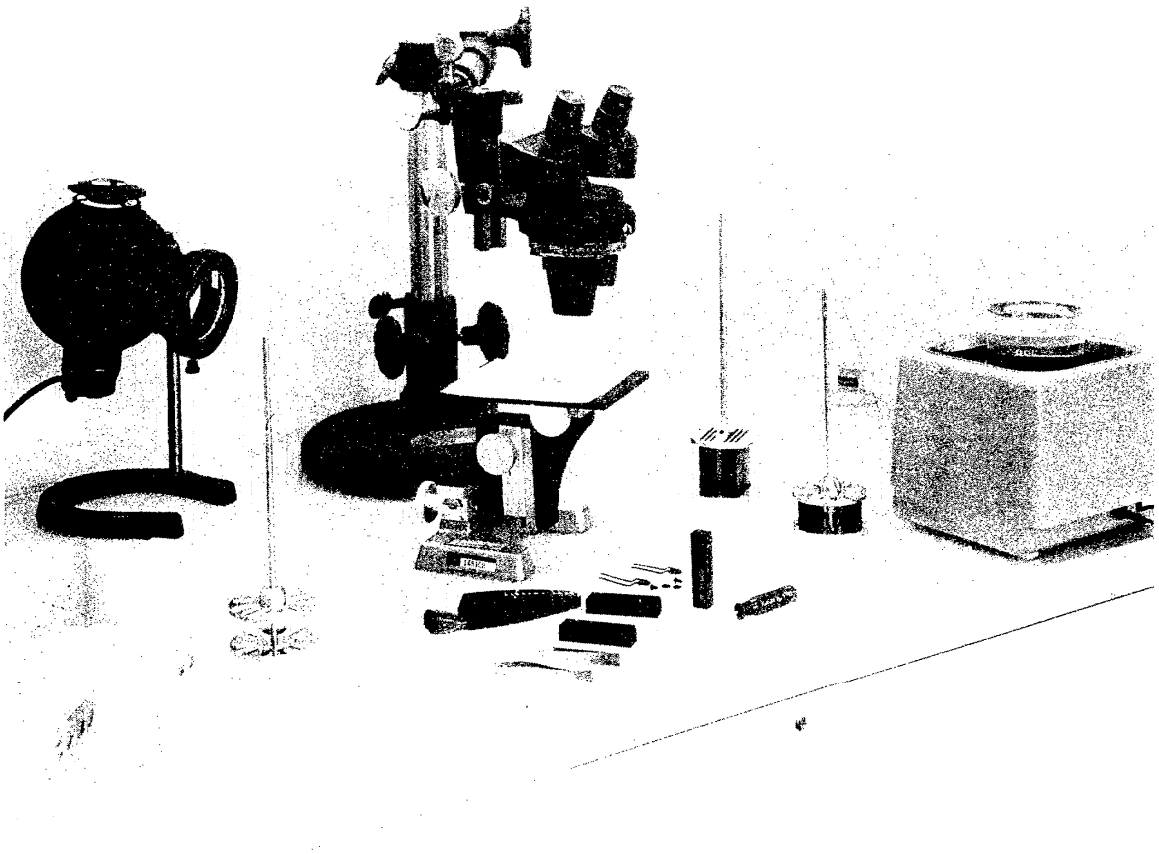


Figure 12. Instrumentation to examine, clean, and mount the glass filters used to produce SRMs 930 and 1930. The entire equipment is placed and used in an all-polypropylene hood provided with vertical clean air flow.

4.2.1 Flatness and Parallelism

During the recent years, additional measurements have been performed to determine the flatness, parallelism, and optical homogeneity of the glass material. The flatness is assessed by observing the fringe pattern obtained against a flat quartz plate. This is accomplished by using a conventional instrument (Type "U" reflex viewer 6" capacity from The Van Keuren Co., 176 Waltham Street, Watertown, MA 02172) illustrated in figure 13 (left side). The parallelism is measured with a thickness mechanical gauge provided with an electronic sensor capable of a resolution of 0.1 μm (Model 7008A made by the Federal Products, a unit of Esterline Corp., Providence, R.I.) illustrated in figure 13 (right side).

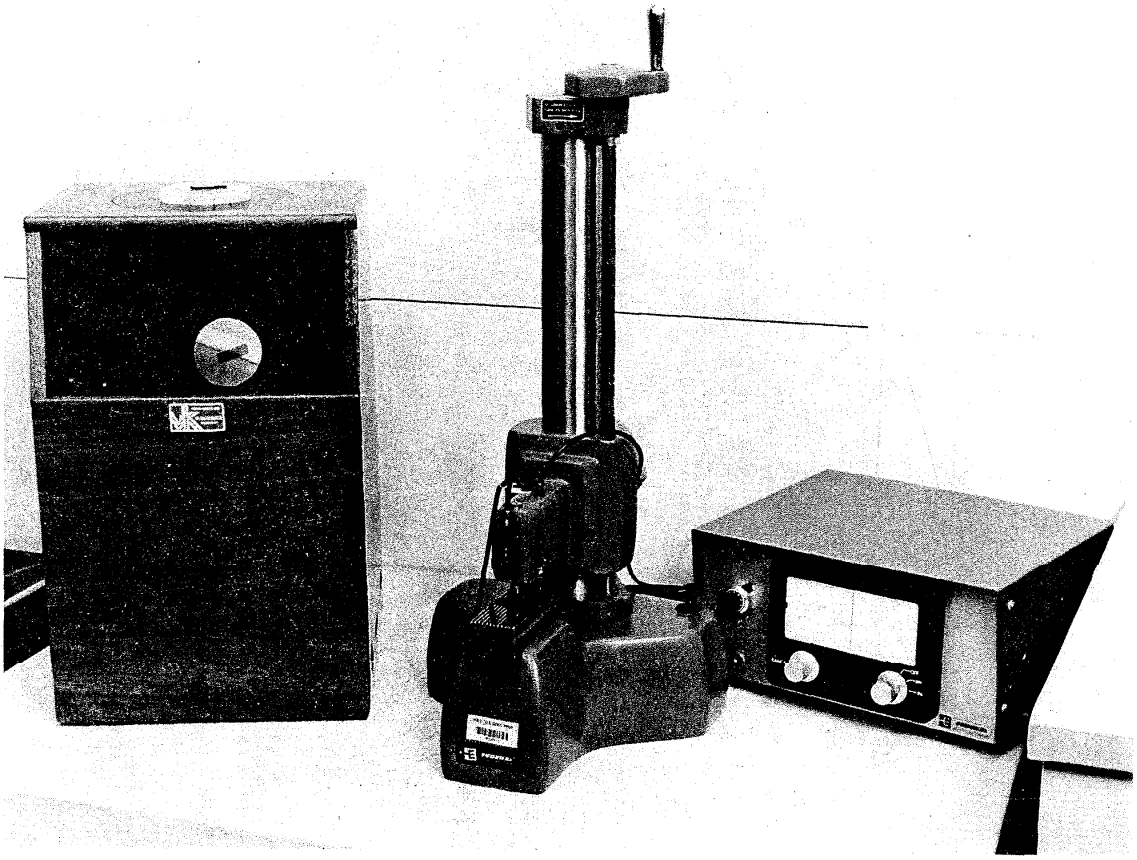


Figure 13. Conventional instruments for observing the figure patterns of a glass filter (left) and for determining the thickness of a glass filter.

4.2.2 Optical Homogeneity

The homogeneity of the glass is determined by measuring the optical transmittance with densitometer designed for this purpose. The densitometer, illustrated schematically in figure 14a, and pictorially in figures 14b and 14c, is a single-beam arrangement having as a major characteristic a constant radiation source S made of a tritium-activated phosphor (12.3 years half-life) with a maximum emission at 560 nm. A mechanical chopper *C* is placed after the light source to produce an ac signal (75 cps). A glass lens *L* forms a reduced image (1x4 mm) of the source at the filter *F*. The filter *F* under investigation is placed in a holder that can be moved in the x-y directions by two micrometer screws (0.5 mm/turn) operated by individual stepping motors (200 steps/revolution). The radiation is received on a Budde diffuser [28] followed by a photomultiplier tube, conventional digital electronics, and printer.

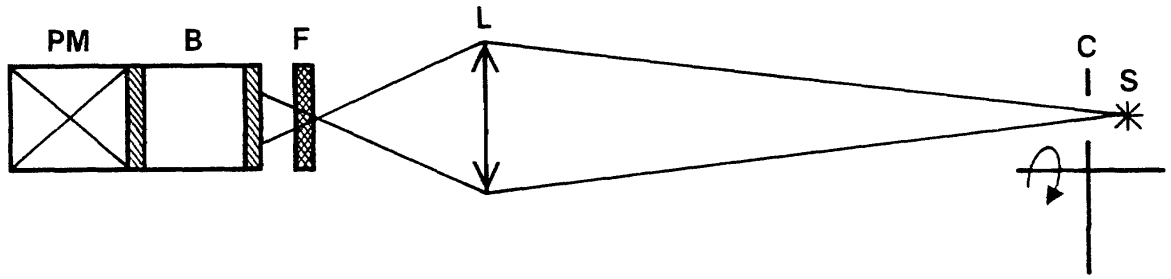


Figure 14a. Schematic of densitometer for the determination of transmittance homogeneity of glass filters. S = radiation source made of a tritium-activated phosphor, C = mechanical light chopper; L = glass lens; F = glass filter under investigation placed in a holder that can be moved in the x-y directions by two stepping motors attached to micrometer screws; B = Budde's diffuser; PM = photomultiplier tube.

Scanning of the glass filter is performed by operating the stepping motors of the x-y system through a microcomputer programmed to measure the transmittance at nine selected points on the 10x30 mm filter [29]. The use of this measuring tool provides a means to individually test each filter and to select the ones that conform to specifications. An example of this transmittance homogeneity check is illustrated by the data from table 3.

The distribution of the test points on the face of the filter is

1	2	3
4	5	6
7	8	9

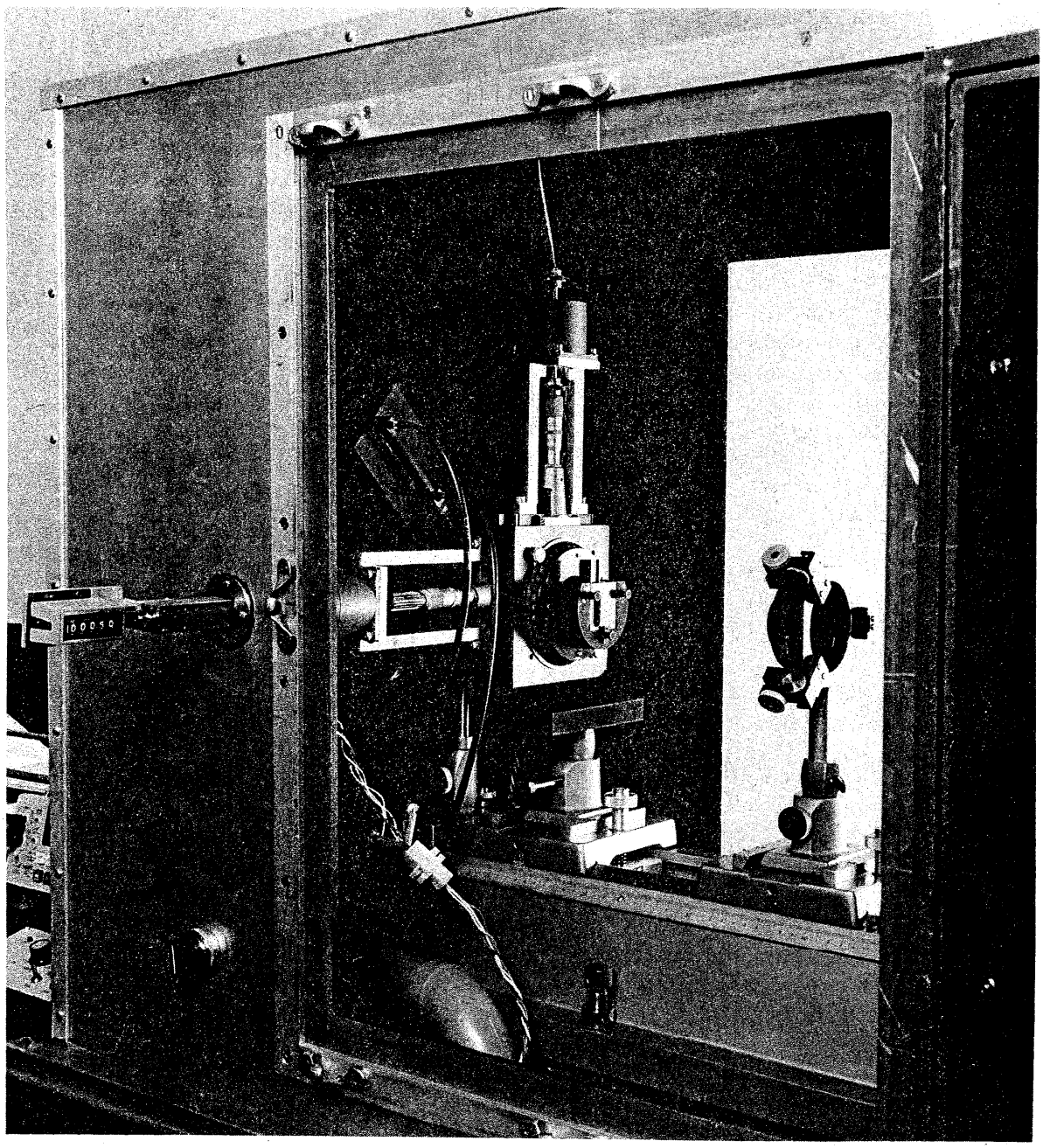


Figure 14b. Densitometer placed in a light-tight enclosure. From right to left: lens producing the image of the light source at the filter; filter holder with x-y scanning capability operated by stepping motors; counter for the x movement; pneumatic shutter followed by Budde's diffuser and photomultiplier tube. At bottom left: pneumatic "off" and "on" valve for operating shutter.

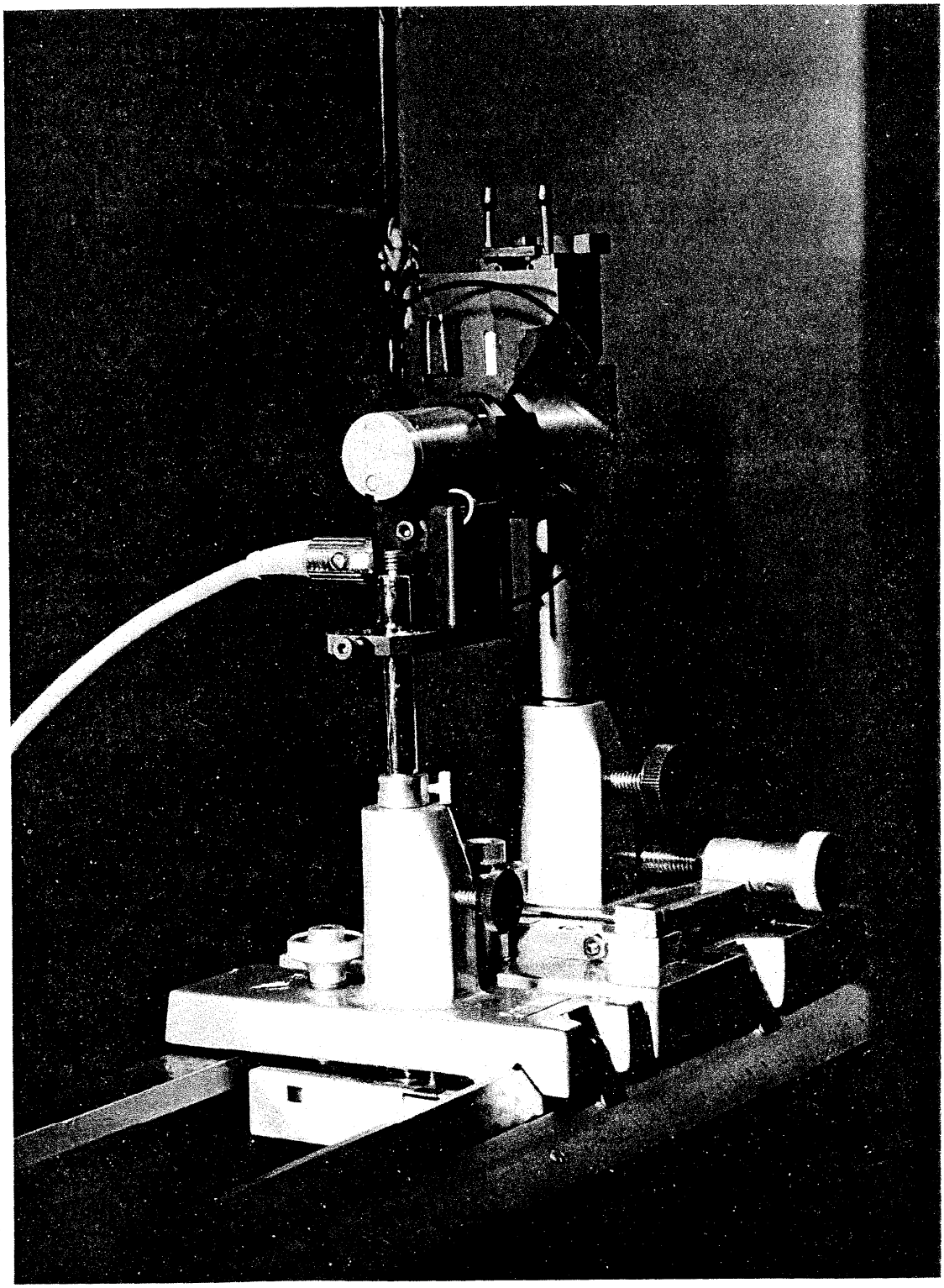


Figure 14c. Light source for densitometer. From right to left: tritium-activated luminescence light source in a holder; light chopper.

Table 3. Homogeneity of a Glass Filter with a Nominal 20 Percent Transmittance (Filter Number 20-1245)

	Mean	Standard Deviation	Adjusted Mean	Delta Center	Relative Delta
Test Point [5]	0.94664	0.00026	0.94664	0.00000	0.00000
Test Point [4]	0.94713	0.00123	0.94714	0.00050	0.05283
Test Point [1]	0.94718	0.00043	0.94720	0.00056	0.05864
Test Point [2]	0.94661	0.00037	0.94664	0.00000	0.00001
Test Point [3]	0.94728	0.00018	0.94732	0.00068	0.07142
Test Point [6]	0.94689	0.00059	0.94694	0.00030	0.03125
Test Point [9]	0.94643	0.00031	0.94649	-0.00015	-0.01633
Test Point [8]	0.94595	0.00031	0.94602	-0.00062	-0.06592
Test Point [7]	0.94727	0.00035	0.94735	0.00071	0.07503
Test Point [8]	0.94682	0.00053	0.94691	0.00027	0.02818
Test Point [5]	0.94654	0.00021	0.94664	0.00000	0.00000

4.3 Cleaning of the Glass Filters

Each glass filter which passes the inspections is washed manually with a diluted aqueous solution of a nonionic detergent such as alkyl phenoxy polyethoxy ethanol (Triton X-100, Rohm and Haas), rinsed with distilled water, and dried in air. The filters are then transferred in a 12-unit stainless steel holder and placed in a Soxhlet extractor, as illustrated in figures 15 and 16, respectively.

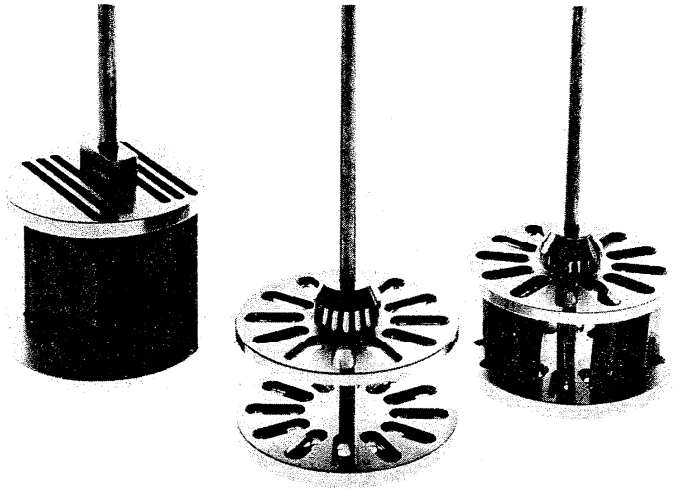


Figure 15. Stainless steel holders for six 50×50 mm, and twelve 30×10 mm glass filters.

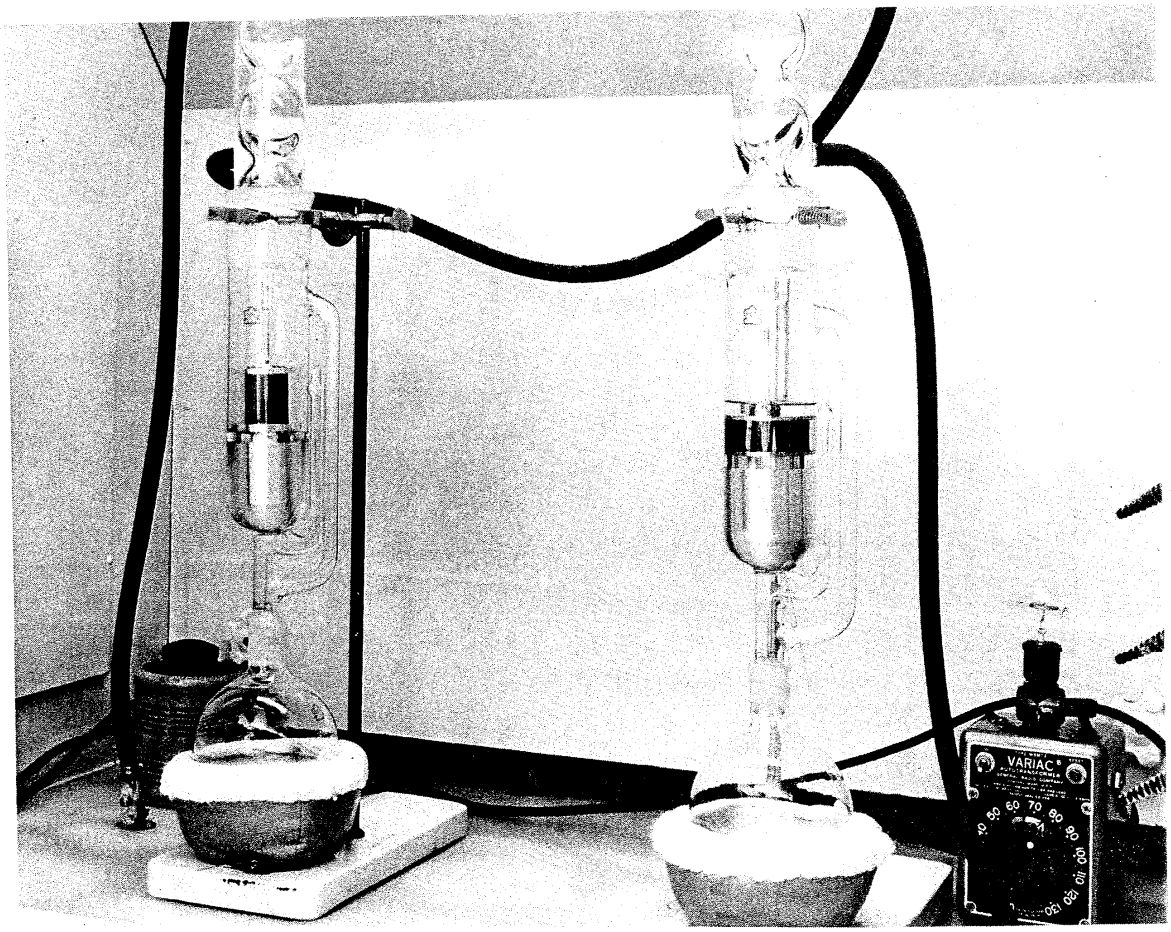


Figure 16. Soxhlet extractors used for the final cleaning of the 50×50 mm and 30×10 mm glass filters with electronic-grade isopropyl alcohol.

An aluminum slug is inserted at the bottom of each extraction flask to reduce the volume of solvent required for the functioning of the extractor and to shorten the syphoning time. To avoid bumpy boiling, followed sometimes by an undesirable overflow of the isopropyl alcohol from the boiling flask into the extraction vessel, a side tube provided at the bottom with a coarse glass frit is inserted through the side of each flask. A steady stream of clean air, from a compressed gas cylinder equipped with a gas regulator and needle valve, is passed through the tube to produce a continuous and gentle bubbling. The glass filters are then washed for three hours, at a rate of three syphonings per hour, using isopropyl alcohol of electronic grade (see references 30 and 31). After this period the glass filters are dried in air in the laminar flow hood.

Following the cleaning procedure, the glass filters are placed individually in the special aluminum alloy holders made at NIST in the instrument shops. This operation is performed by using the tools illustrated in figure 12, which include an anti-static brush and plastic-tipped tweezers. The mounted filters are placed in a covered plexiglass box and are aged for at least

2 weeks in the laminar flow hood where they are exposed continuously to the radiation of the fluorescent lamps provided at the top (total 120 watts, arbitrarily chosen). Since the individual metal holder contributes significantly to the usefulness of the glass filters, it will be described in the next section.

4.4 Filter Holders

The shape and dimensions of these metal holders are given in figures 17 through 22. Established in conformance to the dimensions of the rectangular sample compartments of most conventional spectrophotometers, the holders were designed to hold the glass filters without producing mechanical strains in the glass material, as determined by a polariscope examination. The metal material used for the holder is an aluminum alloy 2024 (4.5% Cu, 1.5% Mg, 0.6% Mn). The two-pronged retaining spring is made of phosphor bronze. The metal holder and retaining spring are both anodized flat black. The spring is secured by a screw and washer made of black nylon. The dimensions and shape of the window were selected to avoid vignetting even for spectrophotometers having a low-pass radiation beam. Each filter comprising SRM 930 and SRM 1930 is provided with a removable front and rear shutter made from flat black Delrin.

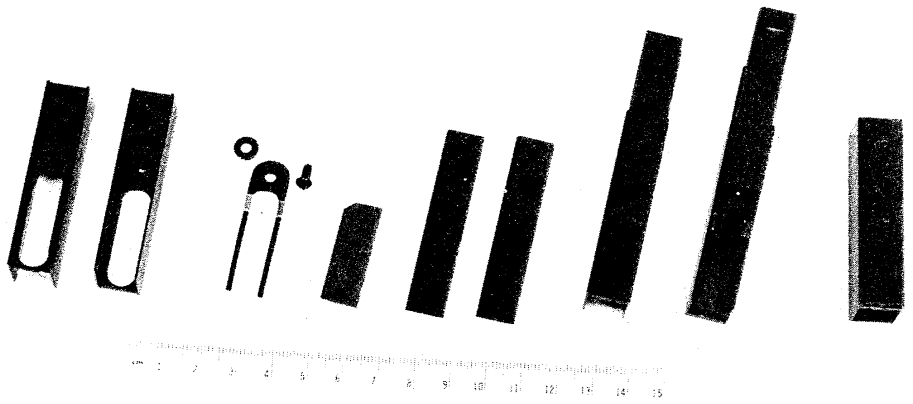


Figure 17. Filter holder with removable shutters. From left to right: front and rear view of the holder body provided with dove-tail grooves; retaining spring with nylon screw and washer; Schott NG glass filter; two shutters; front view of the filter holder with front shutter, rear view of the filter with rear shutter; filter holder with both shutters closed.

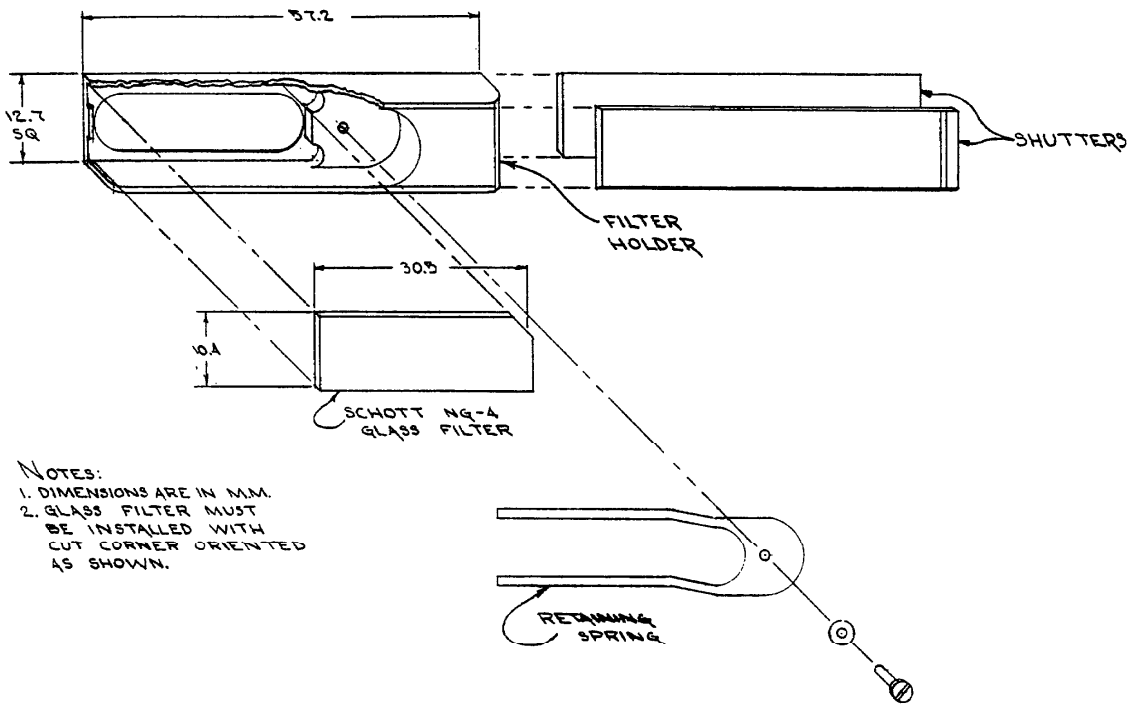


Figure 18. Aluminum alloy filter holder. The retaining spring and the front and rear shutters are illustrated. Dimensions are given in mm.

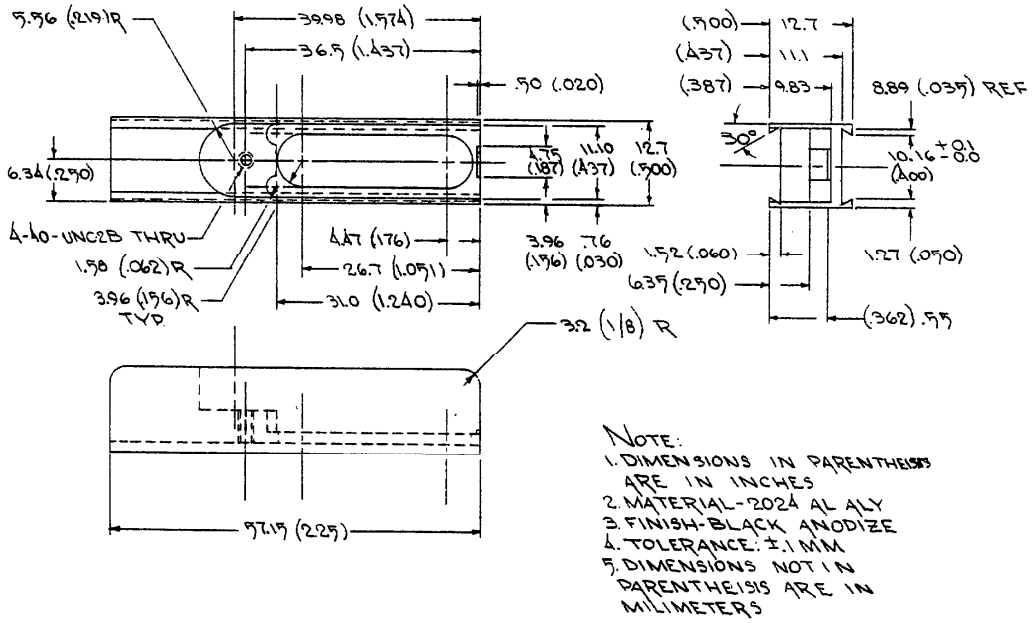


Figure 19. Details of the aluminum alloy filter holder body. Dimensions in parentheses are in inches. Dimensions not in parentheses are in mm. (Tolerance ±0.2 mm.)

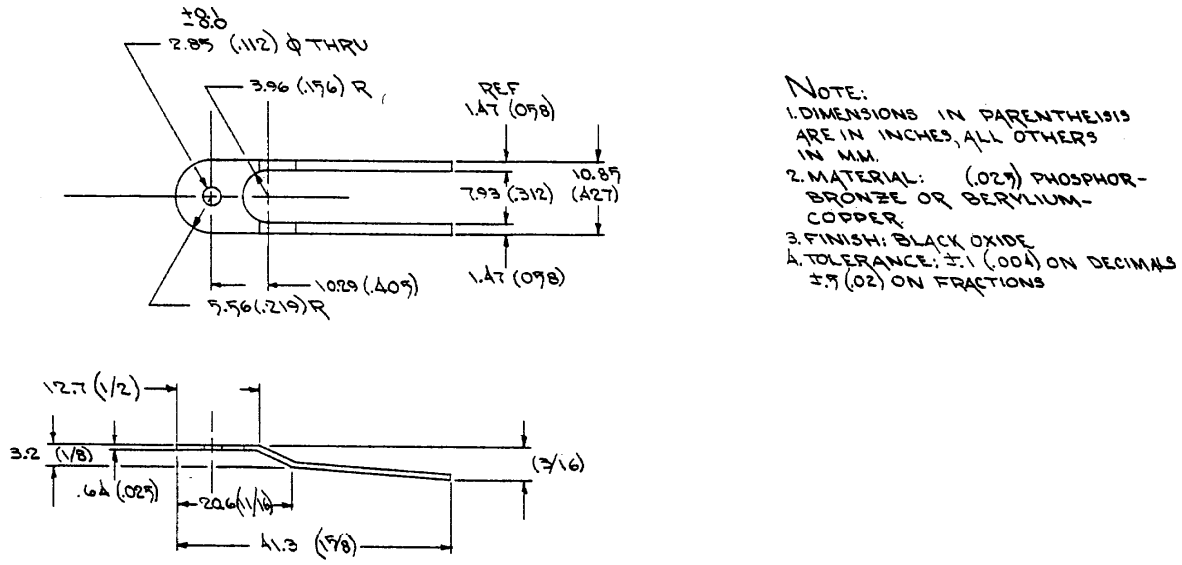


Figure 20. Details of the retaining spring used with the filter holder unit from figure 19. Material: phosphor-bronze or beryllium-copper. Finish: black oxide. Tolerance: ±0.1 mm. Dimensions in parentheses are given in inches, all others are in mm.

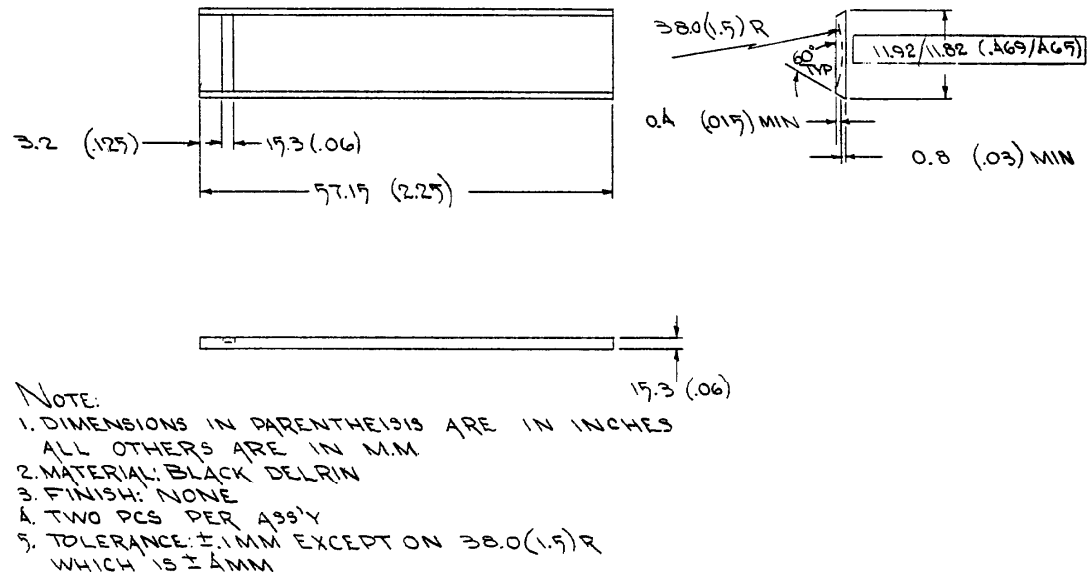


Figure 21. Details of the front and rear shutters used with the filter holder unit from figure 19. Material: black Delrin, two pieces for every filter holder. Dimensions in parentheses are in inches, all others are in mm. Tolerance: ±0.1 mm except on 38.0 (1.5) R.

SRM 930, consisting of three glass filters with nominal percent transmittances of 10, 20, and 30%T, is stored in a cylindrical black-anodized container for protection (see fig. 22). SRM 1930, consisting of three glass filters with nominal percent transmittances of 1, 3, and 50%T, is stored in cylindrical blue-anodized containers identical to those used to store SRM 930. Each glass filter comprising SRMs 930 and 1930 is placed in an individual metal holder. An empty metal filter holder, also included in SRMs 930 and 1930, should be placed in the reference beam of the spectrophotometer to provide identical transmittance measuring conditions.

The anodizing process used to produce the flat black layer, which coats the aluminum alloy filter holders and the cylindrical containers, was examined by Heslin and Hunkeler [32] for possible degassingof undesirable chemical species thatcould affect in time the transmittance properties of the glass filters. The results of this study indicate that no such deleterious effect occurs.

Figure 22. Illustration of SRM 930, Glass Filters for Spectrophotometry, showing the black-anodized aluminum alloy container for storing three filters in their holders and an empty filter holder. One of the three glass filters, Schott NG-4, is shown disassembled with the retaining spring, nylon screw, washer, and the filter holder with the front and rear shutters.

5. STABILITY OF SRM 930

As a rule, before taking measurements with the IARD high-accuracy spectrophotometer, a warmup period of one hour is required. The room temperature is kept at 21 °C ± 1 °C, and the relative humidity is about 35 percent. The particulate matter is controlled through special filters that rates the room in the 100,000 class.

5.1 Reproducibility of Transmittance Measurements

Seven Schott NG glass filters having nominal percent transmittances ranging from 10%T to 50%T were placed in the sample-holder carousel of the high-accuracy spectrophotometer and measured in six replications. The results, given in table 4 (see also Appendix 2), show that these measurements can be reproduced with a pooled relative standard deviation of 0.010 percent.

Table 4. Reproducibility of Transmittance Measurements on Seven Schott NG Glass Filters: Numbers 2, 4, 6, 8, 10, 12, and 14

Replication No.	Percent Transmittance						
	2	4	6	8	10	12	14
1	33.327	21.711	12.236	50.990	33.377	20.906	13.473
2	33.325	21.710	12.237	50.983	33.377	20.903	13.471
3	33.321	21.711	12.241	50.992	33.383	20.900	13.474
4	33.320	21.708	12.240	50.998	33.375	20.901	13.470
5	33.323	21.710	12.239	50.983	33.379	20.901	13.474
6	33.325	21.710	12.238	50.986	33.377	20.904	13.470
Average	33.324	21.710	12.238	50.987	33.378	20.902	13.472
Rel. Percent σ	0.0080	0.0051	0.0150	0.0072	0.0083	0.0108	0.0141
Ave. Rel. Percent σ				0.010			

5.2 Temperature Dependence

The temperature dependence of the transmittance was determined for the same Schott NG type of glass by measuring the transmittance at a room temperature of 20.5 °C and 25.5 °C and at 440.0 nm, 465.0 nm, 546.1 nm, 590.0 nm, and 635.0 nm. The results are given in table 5. From these data, it can be concluded for the type of glass used that the transmittance dependence on temperature over the tested temperature range, in the spectral interval from 440.0 nm to 635.0 nm, is insignificant. For a variation of ±1 °C to 2 °C, this dependence averaged less than 0.2 percent of the measured transmittance values. The influence of temperature on the transmittance of glass filters is discussed by A.T. Young [33].

Table 5. Influence of Temperature on the Transmittance of Seven Schott NG Filters at Five Wavelengths

Wavelength (nm)	Percent Transmittance						
	25.5 °C			20.5 °C			Average Difference
	Date			Date			
	1-14	1-15	1-17	1-23	1-22	1-24	
440.0	9.30	9.29	9.30	9.32	9.32	9.32	+0.02
	18.70	18.69	18.70	18.73	18.72	18.73	+0.03
	29.08	29.07	29.09	29.11	29.10	29.11	+0.03
	32.95	32.96	32.95	32.96	32.95	32.96	+0.01
	9.89	9.89	9.89	9.91	9.91	9.91	+0.02
	18.53	18.53	18.53	18.54	18.54	18.54	+0.01
	29.15	29.15	29.17	29.20	29.20	29.20	+0.04
465.0	11.03	11.04	11.04	11.05	11.05	11.06	+0.01
	21.06	21.08	21.08	21.09	21.10	21.09	+0.02
	32.20	32.21	32.22	32.24	32.25	32.24	+0.03
	35.62	35.61	35.61	35.61	35.61	35.61	0.00
	11.69	11.69	11.69	11.70	11.70	11.70	+0.01
	20.92	20.91	20.92	20.93	20.92	20.92	0.00
	32.27	32.27	32.30	32.32	32.33	32.33	+0.05
546.1	9.94	9.95	9.95	9.93	9.93	9.93	-0.02
	19.59	19.60	19.61	19.57	19.58	19.57	-0.03
	30.69	30.69	30.70	30.67	30.68	30.67	-0.02
	33.76	33.76	33.76	33.70	33.71	33.71	-0.05
	10.55	10.57	10.57	10.54	10.53	10.54	-0.02
	19.43	19.47	19.48	19.43	19.43	19.44	-0.03
	30.74	30.76	30.78	30.75	30.73	30.75	-0.02
590.0	8.82	8.82	8.83	8.79	8.80	8.80	-0.02
	18.02	18.04	18.04	18.00	18.00	18.00	-0.03
	27.62	27.65	27.65	27.62	27.62	27.62	-0.02
	31.20	31.22	31.22	31.14	31.14	31.14	-0.07
	9.37	9.38	9.38	9.34	9.35	9.35	-0.03
	17.89	17.90	17.90	17.86	17.86	17.86	-0.04
	27.69	27.70	27.71	27.68	27.67	27.68	-0.02
635.0	9.85	9.86	9.86	9.83	9.83	9.83	-0.03
	19.47	19.48	19.49	19.45	19.44	19.45	-0.03
	27.74	27.74	27.76	27.72	27.71	27.73	-0.03
	32.65	32.67	32.66	32.59	32.60	32.60	-0.06
	10.44	10.44	10.44	10.40	10.41	10.42	-0.03
	19.34	19.35	19.35	19.30	19.31	19.31	-0.04
	27.78	27.80	27.80	27.77	27.77	27.78	-0.02

5.3 Accelerated Visible Radiation Exposure Test

The stability of the Schott NG glass to visible radiations was tested by exposing three filters having a nominal percent transmittance of 10, 20, or 30%T to the high intensity radiation of a source with a spectral distribution similar to the conventional fluorescent lamps used for the illumination of laboratories. Each high intensity exposure lasted 21 hours and was equivalent to 21,000 hours of normal exposure. The transmittance measurements listed in table 6 were made before and after each of the two exposures. For each wavelength, the first of the six columns gives the transmittance of the glass filters before the exposure, and the second column gives the transmittance measurements after the 21 hours of accelerated exposure. The percent difference between these two measurements is given in the third column. The same filters were exposed again for another 21 hours. Column 4 gives the transmittance values before this exposure, while column 5 gives these values after this second 21-hour accelerated exposure. The percent difference between these data (columns 4 and 5) is given in column 6.

Transmittance measurements were made at 440.0 nm, 465.0 nm, 590.0 nm, and 635.0 nm. From these data it can be concluded that the Schott NG type of glass tested exhibits an acceptable stability when exposed to the visible radiation experiment described. Similar stability tests performed on other neutral glasses have indicated that these glasses were less stable by a factor of four when compared with the Schott NG glass. Consequently, the Schott NG material was selected for SRMs 930 and 1930.

Table 6. Percent Transmittance of Three Schott NG Glass Filters Before and After Exposure to Accelerated Visible Radiation Test

Filter	440.0 nm						465.0 nm					
	Before	After	% Diff.	Before	After	% Diff.	Before	After	% Diff.	Before	After	% Diff.
1	12.96	12.96	0.0	12.97	12.96	0.08	15.22	15.22	0.0	15.22	15.21	0.07
2	20.53	20.53	0.0	20.52	20.52	0.0	23.23	23.23	0.0	23.23	23.22	0.04
3	34.45	34.43	0.06	34.43	34.42	0.03	37.34	37.32	0.05	37.32	37.31	0.03

Filter	590.0 nm						635.0 nm					
	Before	After	% Diff.	Before	After	% Diff.	Before	After	% Diff.	Before	After	% Diff.
1	12.19	12.19	0.0	12.20	12.17	0.25	13.36	13.36	0.0	13.37	13.35	0.15
2	19.61	19.60	0.05	19.61	19.59	0.10	21.03	21.03	0.0	21.04	21.01	0.14
3	33.44	33.42	0.06	33.43	33.40	0.09	35.02	34.98	0.11	35.01	34.98	0.09

5.4 Transmittance as a Function of Time

The variation of transmittance as a function of time for the Schott NG type of glasses (NG-4 and NG-5) was determined by using three filters, which constitute our own reference set, and measuring them over a period of four years. Table 7 presents the results obtained at 440.0 nm, 465.0 nm, 590.0 nm, and 635.0 nm.

Table 7. Stability of Transmittance Measured on SRM 930 as a Function of Time

Wavelength (nm)	Date	Percent Transmittance		
		1	2	3
440.0	05-18-71	32.87	19.80	11.59
	07-12-72	32.88	19.83	11.62
	08-30-73	32.91	19.81	11.59
	11-16-73	32.96	19.84	11.61
	01-09-74	32.98	19.84	11.62
	08-01-74	32.94	19.84	11.61
	01-13-75	32.95	19.84	11.62
465.0	05-18-71	35.53	22.59	13.56
	07-12-72	35.54	22.62	13.59
	08-30-73	35.54	22.62	13.59
	11-16-73	35.62	22.62	13.58
	01-09-74	35.63	22.63	13.58
	08-01-74	35.60	22.62	13.57
	01-13-75	35.60	22.62	13.58
590.0	05-18-71	31.13	19.16	10.37
	07-12-72	31.14	19.20	10.41
	08-30-73	31.14	19.20	10.41
	11-16-73	31.21	19.19	10.40
	01-09-74	31.21	19.20	10.41
	08-01-74	31.18	19.20	10.40
	01-13-75	31.19	19.20	10.41
635.0	05-18-71	32.55	20.60	11.37
	07-12-72	32.59	20.65	11.39
	08-30-73	32.59	20.65	11.39
	11-16-73	32.66	20.65	11.40
	01-09-74	32.68	20.67	11.41
	08-01-74	32.63	20.66	11.41
	01-13-75	32.64	20.66	11.40

The largest difference observed after 4 years of use did not exceed about 3 parts in 1000. The measurements also seem to indicate a trend toward an increase of the transmittance of these glass filters. This is in accordance with the known property of glass surfaces to produce a layer of SiO when exposed to atmospheric conditions. This phenomenon is called "blooming" of the glass, and the thin SiO deposit which is formed acts as an anti-reflection layer, resulting in an apparent increase of the transmittance of the glass.

Similar measurements were made on another set of three glass filters over a period of two years. The results of these transmittance measurements, which are listed in table 8, confirm the data in table 7.

Table 8. Comparison of Transmittance Measurements Performed on a Set of Three Schott NG Glass Filters Over a Period of Two Years

Filter Identification	Wavelength (nm)	Percent Transmittance		
		1971 May	1972 December	1973 April
10%T	440.0	11.59	11.62	11.60
	465.0	13.56	13.59	13.57
	590.0	10.37	10.40	10.39
	635.0	11.36	11.40	11.39
20%T	440.0	19.80	19.83	19.81
	465.0	22.59	22.62	22.60
	590.0	19.16	19.20	19.19
	635.0	20.60	20.65	20.65
30%T	440.0	32.87	32.88	32.92
	465.0	35.53	35.54	35.59
	590.0	31.13	31.14	31.20
	635.0	32.55	32.58	32.64

The transmittances of several sets of SRM 930 were determined, after several years of use under routine laboratory conditions, to assess the effect of time and handling on this parameter. Table 9 presents the results obtained for Set No. 106, certified in 1972. The column marked T_1 contains the transmittance values as certified on November 29, 1972. This set was measured again on February 27, 1974, in an "as received" condition; the transmittance values obtained are given in the column marked T_2. The difference between these measurements is given in the column marked ΔT_1. The transmittance of these glass filters, after about 2 years of use in a laboratory, is lower than the certified values, suggesting a possible contamination of the glass surface. This supposition was verified by submitting the filters to the cleaning

procedure described previously. The filters were remeasured, and the data obtained are given in the column marked T_3, which represent the average of four series of measurements carried out over a period of three days. The difference between the T_3 measurements (after cleaning) and the T_1 measurements (original certification) is given in the column marked ΔT_2. The ΔT_2 results, which indicate a positive difference, confirm the hypothesis of a surface contamination of the glass during their use and verify the natural tendency of the glass to cover itself with a layer of SiO as was already discussed. As mentioned above, the results of this phenomenon is an apparent increase of the transmittance of the material.

Table 9. Percent Transmittance of SRM 930, Set 106, After Two Years of Use in a Laboratory

Filter Number	Wavelength (nm)	T_1 As Certified (11/29/72)	T_2 As Received (2/27/74)	ΔT_1 (T_2-T_1)	T_3 (Cleaned and Remeasured)	ΔT_2 (T_3 - T_1)
1-106	440.0	9.23	9.23	0.00	9.27	+0.04
	465.0	10.95	10.92	-0.03	10.99	+0.04
	590.0	8.77	8.74	-0.03	8.78	+0.01
	635.0	9.83	9.80	-0.03	9.84	+0.01
2-106	440.0	16.53	16.51	-0.02	16.58	+0.05
	465.0	18.78	18.73	-0.05	18.82	+0.04
	590.0	15.00	15.84	-0.06	15.92	+0.02
	635.0	17.33	17.25	-0.08	17.33	0.00
3-106	440.0	30.02	29.98	-0.04	30.12	+0.10
	465.0	33.37	33.29	-0.08	33.47	+0.10
	590.0	29.91	29.81	-0.10	29.94	+0.03
	635.0	30.90	30.78	-0.12	30.90	0.00

Additional data concerning the stability of SRM 930 are collected from measurements performed on filter sets that are returned to NIST for verification and, where needed, for recalibration. Since their issuance in 1971, about 100 sets of SRM 930 have been sold each year in the United States and overseas and, to date, over 1700 sets have been produced. A number of users routinely return the filters for verification on an annual basis, as suggested in the Certificate. Other users request recalibration less frequently. At the present time at least 50 sets are verified per year.

From the pool of recalibration data, about 85 percent of the sets indicate that the transmittance values stay within the 0.5 percent relative uncertainty noted in the Certificate. The remaining 15 percent of the sets show a change larger than 0.5 percent relative; none has shown a change that exceed 1.5 percent relative.

In some cases an excellent transmittance stability is demonstrated. For instance, Set No. 100, issued in 1974, has been measured over a period of 19 years in our laboratory. The transmittances measured on these glasses from 1974 through 1992 are given in table 10. The transmittance data in 1992 reproduce the initial values in 1974 with differences that exceed 0.5 percent relative only in one case (nominal 10%T filter at 635 nm, table 10a).

Table 10a. Comparison of Percent Transmittance Values Obtained From 1974 to 1992 for SRM 930, Set No. 100, Filter with a Nominal 10% Transmittance

Date	Wavelength				
	440 nm	465 nm	546.1 nm	590 nm	635 nm
1974	9.45	11.18	10.12	8.94	10.00
1975	9.45	11.19	10.12	8.94	10.01
1976	9.45	11.19	10.12	8.95	10.01
1977	9.44	11.18	10.11	8.93	10.01
1978	9.45	11.19	10.11	8.93	10.00
1979	9.45	11.19	10.12	8.94	10.00
1980	9.45	11.19	10.12	8.94	10.00
1981	9.45	11.19	10.12	8.94	10.01
1982	9.46	11.21	10.14	8.96	10.03
1983	9.45	11.19	10.13	8.94	10.01
1984	9.47	11.21	10.14	8.96	10.02
1985	9.46	11.19	10.13	8.96	10.01
1986	9.48	11.22	10.16	8.99	10.05
1987	9.47	11.21	10.14	8.97	10.03
1988	9.47	11.21	10.15	8.98	10.04
1989	9.48	11.22	10.15	8.98	10.06
1990	9.48	11.22	10.15	8.97	10.04
1991	9.48	11.22	10.14	8.97	10.03
1992	9.49	11.23	10.16	8.98	10.06
Rel. % Change	+0.42	+0.45	+0.40	+0.45	+0.60

Table 10b. Comparison of Percent Transmittance Values Obtained From 1974 to 1992 for SRM 930, Set No. 100, Filter with a Nominal 20% Transmittance

Date	Wavelength				
	440 nm	465 nm	546.1 nm	590 nm	635 nm
1974	17.48	19.78	18.37	16.78	18.21
1975	17.49	19.80	18.39	16.79	18.23
1976	17.48	19.79	18.39	16.80	18.23
1977	17.48	19.77	18.37	16.78	18.22
1978	17.49	19.79	18.37	16.78	18.22
1979	17.50	19.79	18.38	16.79	18.23
1980	17.49	19.79	18.39	16.79	18.23
1981	17.50	19.80	18.41	16.81	18.23
1982	17.50	19.82	18.42	16.82	18.25
1983	17.49	19.79	18.39	16.80	18.23
1984	17.49	19.80	18.40	16.81	18.24
1985	17.49	19.79	18.40	16.82	18.25
1986	17.51	19.81	18.43	16.84	18.28
1987	17.51	19.82	18.42	16.84	18.27
1988	17.52	19.82	18.43	16.84	18.28
1989	17.52	19.82	18.42	16.84	18.28
1990	17.52	19.81	18.40	16.82	18.26
1991	17.53	19.82	18.40	16.82	18.27
1992	17.51	19.81	18.40	16.82	18.26
Rel. % Change	+0.17	+0.15	+0.16	+0.24	+0.27

All the measurements discussed thus far indicate clearly that the glass filters can be used as a secondary transfer optical transmittance standard with an uncertainty of ≤ 0.5 percent relative. We would like to briefly mention, however, a case where the glass material exhibited a greater instability [34]. This property was recorded on several sets of SRM 930b where an instability with time of about twice the certified uncertainty was observed. This instability was traced to the initial grinding and polishing of the glass material by the manufacturer. The problem was eliminated by fine grinding and polishing at the NIST optical shops, and by aging the material in our laboratory for a least six months before its issuance as an SRM. Further information concerning the stability of the optical transmittance of glass filters is found in a paper by W.R. Blevin [35].

Table 10c. Comparison of Percent Transmittance Values Obtained From 1974 to 1992 for SRM 930, Set No. 100, Filter with a Nominal 30% Transmittance

Date	Wavelength				
	440 nm	465 nm	546.1 nm	590 nm	635 nm
1974	30.85	34.22	32.73	30.60	31.55
1975	30.86	34.25	32.78	30.66	31.60
1976	30.82	34.20	32.75	30.64	31.61
1977	30.81	34.20	32.72	30.62	31.59
1978	30.85	34.19	32.72	30.62	31.58
1979	30.84	34.23	32.76	30.65	31.61
1980	30.85	34.24	32.78	30.66	31.61
1981	30.83	34.23	32.78	30.67	31.62
1982	30.82	34.22	32.80	30.68	31.64
1983	30.81	34.21	32.76	30.67	31.61
1984	30.81	34.19	32.77	30.66	31.61
1985	30.80	34.20	32.77	30.67	31.61
1986	30.84	34.23	32.82	30.71	31.66
1987	30.83	34.22	32.81	30.71	31.67
1988	30.84	34.25	32.82	30.73	31.69
1989	30.83	34.22	32.79	30.70	31.67
1990	30.81	34.19	32.74	30.65	31.63
1991	30.81	34.20	32.74	30.66	31.64
1992	30.80	34.20	32.73	30.65	31.63
Rel. % Change	-0.16	-0.06	0.00	+0.16	+0.25

5.5 Interlaboratory Transmittance Measurements

A set of SRM 930 was measured at NIST and at the National Physical Laboratory (NPL) in England by F.J.J. Clarke and his associates using their high-accuracy instrument. Both NIST and NPL measurements were made with noncollimated, convergent-beam geometry. A rectangular surface area of the filter, about 3x8 mm, was used at NPL. At NIST, a surface area of about 8x0.5 mm was used for the transmittance measurements. The results given in table 11 indicate that an average difference of 0.19 percent of the measured values was obtained between the measurements carried out at NPL and at NIST.

Table 11. Comparison of Transmittance Measured on Three Schott NG Glass Filters at NPL and NIST

Wavelength (nm)	%T		Relative Percent Difference (NIST-NPL)
	NIST	NPL	
440.0	12.92	12.93	-0.08
465.0	14.97	15.01	-0.27
590.0	11.67	11.67	0.00
635.0	12.70	12.72	-0.16
440.0	19.60	19.62	-0.10
465.0	22.37	22.43	-0.27
590.0	19.01	19.01	0.00
635.0	20.41	20.47	-0.29
440.0	32.88	32.98	-0.30
465.0	35.53	35.66	-0.36
590.0	31.13	31.21	-0.26
635.0	32.54	32.62	-0.25
Average relative percent difference			-0.19%

Another comparative study, which included three clinical laboratories, was performed to determine the reproducibility of transmittance measurements on the Schott NG glass filters. Three filters having nominal percent transmittances of 10, 20, and 30%T were first measured at four wavelengths on a conventional spectrophotometer at NIST. This instrument included a double monochromator with quartz prisms used in a double-beam mode, and a transmittance scale with 1000 divisions between 0 and 100 percent transmittance. The transmittance accuracy of this scale was established using SRM 930. The same filters, including instructions describing the technique to be used in measuring their transmittances, were then sent to three laboratories, arbitarily designated A, B, and C.

The results obtained are summarized in table 12 and include the average percent transmittance (%T) values, the standard deviation (S.D.), the percent relative standard deviation (%R.S.D.), and the percent difference (% Diff.). The percent difference values were calculated using the NIST data as the reference values. This study demonstrates that transmittance data can be reproduced under actual laboratory conditions with a general uncertainty of less than 1 percent. From the total of 36 transmittance measurements, only 3 measurements exceed 1 percent (all by laboratory B), and this was due probably to inadequate spectral bandpass of the particular spectrophotometer used.

Table 12. Comparison of Transmittance Measurements Performed by Four Laboratories on Three Schott NG Glass Filters

Laboratory A		%T			
Filter No.		440 nm	465 nm	590 nm	635 nm
1	Ave.	12.91	14.99	11.68	12.71
	S.D.	0.0063	0.004	0.008	0.005
	% R.S.D.	0.049	0.027	0.070	0.041
	% Diff.	-0.4	-0.07	-0.6	-0.5
2	Ave.	19.61	22.37	19.06	20.50
	S.D.	0.004	0.010	0.004	-
	% R.S.D.	0.021	0.046	0.022	-
	% Diff.	-0.5	-0.3	-0.3	-0.1
3	Ave.	32.81	35.44	31.12	32.58
	S.D.	0.0080	0.0080	0.0050	0.0050
	% R.S.D.	0.023	0.023	0.017	0.016
	% Diff.	+0.3	+0.3	+0.1	+0.2

Laboratory B		%T			
Filter No.		440 nm	465 nm	590 nm	635 nm
1	Ave.	12.91	14.87	11.56	12.59
	S.D.	-	0.041	0.041	-
	% R.S.D.	-	0.276	0.36	-
	% Diff.	-0.4	-0.9	-1.6	-1.4
2	Ave.	19.59	22.39	18.90	20.51
	S.D.	-	-	0.053	-
	% R.S.D.	-	-	0.281	-
	% Diff.	-0.6	-0.2	-1.1	-0.05
3	Ave.	32.58	35.23	30.90	32.36
	S.D.	-	0.093	-	-
	% R.S.D.	-	0.264	-	-
	% Diff.	-0.4	-0.3	-0.6	-0.4

Table 12. Comparison of Transmittance Measurements Performed by Four Laboratories on Three Schott NG Glass Filters (Continued)

Laboratory C		%T			
Filter No.		440 nm	465 nm	590 nm	635 nm
1	Ave.	12.88	14.96	11.66	12.65
	S.D.	-	0.014	0.011	0.018
	% R.S.D.	-	0.09	0.09	0.15
	% Diff.	-0.6	-0.3	-0.8	-0.9
2	Ave.	19.54	22.34	19.12	20.37
	S.D.	-	-	0.024	-
	% R.S.D.	-	-	0.13	-
	% Diff.	-0.9	-0.4	+0.05	-0.7
3	Ave.	32.88	35.40	30.97	32.43
	S.D.	-	-	-	-
	% R.S.D.	-	-	-	-
	% Diff.	+0.5	+0.1	-0.4	-0.2

NIST Laboratory		%T			
Filter No.		440 nm	465 nm	590 nm	635 nm
1	Ave.	12.96	15.00	11.75	12.77
	S.D.	0.0053	0.0037	0.0048	0.0057
	% R.S.D.	0.041	0.025	0.041	0.045
2	Ave.	19.71	22.44	19.11	20.52
	S.D.	0.0049	0.0052	0.0038	0.0049
	% R.S.D.	0.025	0.023	0.020	0.024
3	Ave.	32.72	35.35	31.09	32.50
	S.D.	0.0045	0.0056	0.0040	0.0043
	% R.S.D.	0.014	0.016	0.013	0.013

6. SCATTER, HOMOGENEITY, POLARIZATION, AND POSITIONING OF SCHOTT NG GLASS FILTERS

The conditions required for a material to be useful as a reference standard were enumerated at the beginning of this work. Among those mentioned earlier, and which will be discussed further here, include: freedom of scatter and polarization, and homogeneity.

6.1 Influence of Scatter, Homogeneity, and Polarization on Transmittance

Scatter and homogeneity measurements in polarized radiation were performed on three Schott NG glass filters by K.L. Eckerle in the Radiometric Physics Division at NIST using the instrument described in reference 36. All measurements were performed at 546.1 nm, and the results are given in table 13.

Table 13. Measurement of Scatter, Homogeneity, and Polarization on Three Schott NG Glass Filters

(x,y)	Ω	T(0°)	ΔT_R(0°)	T(90°)	ΔT_R(90°)	T(Ave)	ΔT_R(Ave)
Set #537 Filter 1							
(+1,0)	0.0045	0.10038	0.000014	--	--	--	--
(-1,0)	0.0045	0.10047	0.000015	--	--	--	--
(0,0)	0.0045	0.10042	0.000012	0.10042	0.000012	0.10042	0.000008
(0,0)	0.0012	0.10046	0.000013	0.10042	0.000026	0.10044	0.000015
(0,0)	0.014	0.10039	0.000013	0.10035	0.000020	0.10037	0.000012
Set #537 Filter 2							
(+1,0)	0.0045	0.19240	0.000023	--	--	--	--
(-1,0)	0.0045	0.19216	0.000031	--	--	--	--
(0,0)	0.0045	0.19254	0.000022	0.19250	0.000028	0.19252	0.000018
(0,0)	0.0012	0.19252	0.000026	0.19249	0.000021	0.19251	0.000017
(0,0)	0.014	0.19237	0.000024	0.19239	0.000027	0.19238	0.000018
Set #537 Filter 3							
(+1,0)	0.0045	0.30875	0.000024	--	--	--	--
(-1,0)	0.0045	0.30872	0.000019	--	--	--	--
(0,0)	0.0045	0.30877	0.000020	0.30874	0.000028	0.30875	0.000017
(0,0)	0.0012	0.30875	0.000042	0.30874	0.000049	0.30874	0.000032
(0,0)	0.014	0.30848	0.000028	0.30847	0.000035	0.30847	0.000023

The quantities (x,y) are the coordinates of the center of the illuminating spot with respect to the center of the filter in millimeters when looking in the direction of the source. The parameter, Ω, is the approximate solid angle in steradians. The quantities T(0°), T(90°), and T(Ave) are the transmittances for the electric vector of the illuminating radiation horizontal, vertical, and average of horizontal and vertical, respectively, measured at 546.1 nm. Their respective standard errors are $\Delta T_R(0°)$, $\Delta T_R(90°)$, and $\Delta T_R(Ave)$.

The radiation scatter measurements were made by determining the transmittance of the filters successively at distances from the averaging sphere of 210 mm, 370 mm, and 715 mm corresponding to solid angles of about 0.014, 0.0045, and 0.0012 steradians, respectively. The diameter of the circular entrance aperture at the averaging sphere was 28 mm. To assess the uniformity of the filters, the transmittance measurements were made at a constant solid angle of 0.0045 steradians. From the data in table 13 it can be concluded that, within the experimental measuring conditions, there is no significant change of transmittance produced by scatter and polarization, and that the Schott NG glass has good homogeneity.

The absence of polarization influence on transmittance was verified, again on a set of SRM 930, as shown in table 14. This table shows a comparison of transmittance measurements performed on the same SRM 930 set at 465.0 and 546.1 nm using the two high-accuracy spectrophotometers at NIST in the Inorganic Analytical Research Division (IARD) and the Radiometric Physics Division (RPD).

Table 14. Transmittance of a Set of SRM 930 at Two Wavelengths Obtained at NIST Using the IARD and the RPD High-Accuracy Spectrophotometers

High-Accuracy Instrument	Nominal 30%T Filter		Nominal 20%T Filter		Nominal 10%T Filter	
	465.0 nm	546.1 nm	465.0 nm	564.1 nm	465.0 nm	546.1 nm
IARD	0.3427	0.3280	0.1980	0.1840	0.1120	0.1014
RPD	0.3430	0.3284	0.1983	0.1844	0.1121	0.1015
Δ(RPD)*	-0.00002	-0.00007	-0.00008	-0.00005	-0.00001	-0.00002

* The difference, Δ(RPD), is the difference in transmittances measured by illuminating the filters with polarized radiation having the electric vector in either the horizontal or vertical direction.

6.2 Influence of Positioning of the Filters on Transmittance

The transmittance error resulting from positioning the glass filter at various angles to the incident radiation beam was determined. In these measurements, the filter was placed in the high-accuracy spectrophotometer on a vertical holder attached to a 10-cm diameter rotary horizontal table. This table had a scale divided into 360° with a vernier reading to 5 min, and was held on the single-sample carriage of the spectrophotometer with a vertical mounting rod. This remote-controlled carriage has a smooth transversal movement, and the sample positioning in and out of the beam can be reproduced to within 0.025 mm.

Table 15 presents the comparative results for transmittance measurements made at 590.0 nm on a Schott NG neutral glass filter, 2-mm thick, having a nominal percent transmittance of 30%T, for normal incidence and for angles of 3°, 6°, and 9°. From these results it can be concluded that a deviation of up to 3° from a normal incidence position can be tolerated. Since this parameter is instrument dependent, however, the results from table 15 are valid only for the high-accuracy spectrophotometer used to perform these measurements.

Table 15. Percent Transmittance Measured at 590.0 nm on a Schott NG Glass Filter, 2-mm Thick, Having a Nominal 30% Transmittance for Normal Incidence and for Angles of 3°, 6°, and 9°

Angle	%T
0°	28.13
3°	28.10
6°	28.03
9°	27.98

7. EXAMPLE OF USING SRM 930 FOR TRANSMITTANCE SCALE VERIFICATION AND CALIBRATION

In another series of tests, a set of SRM 930 was used to verify and correct the transmittance scale of a conventional spectrophotometer. The difference in scales was determined by measuring the transmittances of the certified glass filters on the tested instrument, and by comparing the results with the certified values. These results are presented in table 16.

Table 16. Comparison of Percent Transmittance Measurements Performed on a Schott NG Filter Using the NIST Inorganic Analytical Research Division Instrument and a Conventional Spectrophotometer

Wavelength (nm)	NIST Instrument	Conventional Instrument	Difference	Relative % Difference
440.0	32.82	32.75	-0.07	-0.21
465.0	35.51	35.40	-0.11	-0.31
590.0	30.98	30.93	-0.05	-0.16
635.0	32.38	32.32	-0.06	-0.19
Average Relative % Difference				-0.22

From the data in table 16, it can be concluded that the transmittance scale of this conventional spectrophotometer provides transmittances that are lower than the accurate values by an average difference of 0.22 percent. This average difference can be added to the measurements made with the conventional instrument to obtain the accurate transmittance values. Another method to perform the correction is to use an interpolation procedure using a graph established by plotting on the abscissa the accurate transmittance (or absorbance) values of SRM 930, and on the ordinate the values found on the instrument for this material. In this discussion it was implicitly assumed that all other parameters that can affect the transmittance accuracy have been considered and minimized. The stability of the instrument, the wavelength accuracy, the spectral bandpass, stray light, and temperature are the parameters that require special attention. Correction of the transmittance or absorbance scale of a spectrophotometer should be applied only when these conditions are fulfilled.

8. TRANSMITTANCE TRANSFER STANDARDS FROM THE NATIONAL PHYSICAL LABORATORY IN GREAT BRITAIN AND THE PHYSICS AND ENGINEERING LABORATORY, DSIR, IN NEW ZEALAND

The National Physical Laboratory in Teddington, Great Britain, is issuing on a regular basis semi-transparent evaporated metal filters on fused-silica substrates as transfer standards in the ultraviolet, visible, and near-infrared spectral ranges. The metal used is a specially selected nichrome alloy. The exposed metal surface of these filters is not protected. These filters are certified at any selected densities over the spectral range as required by the user. Neutral optical glasses of the Schott NG type are also available for work in the visible spectral range, and those available from stock have nominal absorbances of 0.04, 0.15, 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 [37-39].

Neutral glass filters, similar to the NIST SRM 930 discussed in this publication, are described by Bittar and Havelin. They are certified using a high-accuracy spectrophotometer designed and built at the Physics and Engineering Laboratory in New Zealand [40].

9. SUMMARIZING REMARKS

The acquisition of meaningful measurements by spectrophotometry requires that every phase of the chemical processes involved in the analytical procedure, and every parameter of the instrumental spectrophotometric technique be well-known and understood. The analyst must be able to assess the importance of these two factors in a quantitative manner, and to evaluate their individual contributions to the uncertainty of the final measurement. Some of the parameters involved in the instrumental spectrophotometric technique have been examined in this publication, and particular attention was given to those instrumental parameters that play a more significant role: the short- and long-term instrumental stability, the wavelength accuracy, the spectral bandpass problem, stray radiation, and the transmittance accuracy. Means and methods have been discussed, and Standard Reference Materials have been described and produced, that permit to determine to a large extent the magnitude of these important parameters and to assess and correct their individual contributions toward the deterioration of spectrophotometric precision and accuracy.

Instrumental stability, wavelength accuracy, adequate spectral bandpass, freedom of stray radiation, and transmittance accuracy are basic parameters that play a determinant role in accurate transmittance measurements of a transparent material in the spectral range of interest. Without the fulfillment of these conditions no accurate transmittance measurements could be performed. SRMs 930 and 1930 seem to be a useful means to assume that the measurements are accurate.

The usefulness of glass filters has also been established by the fact that they are used by several manufacturers of spectrophotometers to establish and monitor the accuracy of the transmittance scale of their instruments. While the use of SRM 930 and SRM 1930 do not solve all problems in spectrophotometry, their availability have contributed appreciably to the production of more accurate and, therefore, more meaningful measurements in all fields where spectrophotometry is applied.

The production of accurate chemical analytical data, that is the capability to determine accurately the amount of a particular chemical species in a given matrix, requires, on the other hand, spectrophotometric precision, as determined by the instrumental stability and sensitivity. The accuracy of the analytical measurements is determined in this case by the accuracy achieved in the preparation of the analytical samples and in the establishment of the reference curve. These in turn depend on the stability of the chemical reactions involved in the spectrophotometric process, and on the ability to prepare adequate reference solutions having accurately known concentrations of the chemical species of interest in a matrix identical to that of the analytical sample. Under these circumstances, analytical accuracy can be achieved using

spectrophotometers which exhibit good stability and sensitivity. The wavelength accuracy, the spectral bandpass, and the accuracy of the transmittance or absorbance scale play a lesser role in this analytical application. The lack of accuracy of these parameters could affect the sensitivity and linearity, and in some cases, the specificity of spectrophotochemical analyses.

Standard Reference Materials 930 and 1930, Glass Filters for Spectrophotometry, are transfer standards that are calibrated for transmittance, in the spectral range from 440.0 nm to 635.0 nm, using a high-accuracy spectrophotometer which is a primary transmittance standard. The transmittance values were certified with a relative uncertainty of 0.7 to 0.3 percent, depending on the transmittance level of the filter. The validity of these transmittance values with time will depend on the stability of the glass and the conditions under which it is used. The measurements from table 10 prove that the intrinsic stability of the certified transmittance values are reproducible, within the uncertainty indicated, over a length of time of at least 19 years. This assumes that the filters have been used with proper care, following the instructions given in the Certificate. Deviations from these instructions could result in degradation or loss of accuracy. In particular, the glass surface should never be touched with the fingers, the filters should not be exposed to dust or corrosive reagents, and when not in use, they should always be kept in the container provided for this purpose and with the shutters inserted.

Should the glass surface of the filters become accidentally contaminated, no attempts should be made to wash it, since the user does not have means to determine if this cleaning treatment has not altered the properties of the glass surface and degraded the accuracy of the certified transmittance values. Since SRMs 930 and 1930 are transfer standards, the only means available to determine their integrity is by remeasuring their transmittance with a primary standard instrument, and this can be done only with a high-accuracy spectrophotometer like the one described in this work. Should there be a need to verify the accuracy of the certified transmittance data, the glass filters may be returned to NIST for verification of the transmittance data assigned to that particular set, and for cleaning and recalibration if necessary. Before returning the glass filters, it is recommended that proper arrangements be made by contacting the Atomic and Molecular Spectometry Group in the Inorganic Analytical Research Division at NIST to establish the best conditions in which such a verification can be made.

SRMs 930 and 1930 are delicate and costly units that have required an appreciable amount of careful work for preparation and certification. These materials should be handled with great attention to ensure the production of accurate measurements and long life. This is particularly true when the working conditions in certain laboratories require frequent use of these SRMs. To protect these reference materials in such cases, it might prove desirable to produce "in house" secondary glass standards derived from SRMs 930 and 1930, and use these secondary standards for daily control of the spectrophotometers used in the laboratory. When these standards indicate a significant change in the measurements, only then should SRMs 930 and 1930 be used as final verification of the data.

Secondary glass standards could be produced by purchasing the optically neutral glass used for the production of SRMs 930 and 1930, cut to size as described in this publication, and placed in holders similar to those illustrated in detail in figures 17 through 21. The transmittance of these filters should be established at the desired wavelengths with the best

spectrophotometer available in the laboratory after its transmittance scale was verified with SRMs 930 and 1930.

10. UNCERTAINTY ESTIMATION FOR SRM 930D

The uncertainty estimation for SRM 930d is detailed in the table below. The source of each estimated uncertainty component in SP 260-116 is indicated in the table, and each is discussed by number in the text. Uncertainty components for items 1-6 are derived from an estimate of the range, $\pm a_i$, with the assumption that the uncertainty is uniformly distributed. The (normally distributed) standard uncertainty component is then approximated as $a_i/\sqrt{3}$.[41] Items 2-4 have ranges not symmetrically distributed about zero, but are estimated in the same fashion, and the negative going components (items 3 and 4) combine in quadrature to yield the same uncertainty as the positive going component (item 2), so the three are combined as a single uncertainty component, normally designated as "stability/geometry".

Table 17. Estimation of Overall Uncertainty for SRM 930d

i	Description of Standard Uncertainty Component, u_i	note	u_i (Rel.%)
1	Uniformity of Filter over Designated Area	a	0.173
2	Two-year Stability of Filter	b	0.140
3	Filter Orientation with respect to Optical Axis	c	
4	Exposure to Light and Laboratory Atmosphere	d	
5	Temperature Effects over Permitted Range	e	0.115
6	Instrumental Linearity	f	0.058
7	Short-Term Reproducibility	g	0.010
Overall Estimated Uncertainty, U		h	0.515

a. Acceptance value for optical homogeneity test described in Section 4.2.2.
b. Estimated from a graphical study of Tables 7, 8, and 10 in Section 5.4.
c. Estimated from the data of Table 15, Section 6.2.
d. Estimated from Table 6, Section 5.3, p. 44, and Table 9, Section 5.4.
e. Estimated from a graphical study of the data in Table 5, Section 5.2.
f. Appendix 2, Figure 16 and related discussion.
g. Table 4, Section 5.1.
h. See "Overall estimated uncertainty" below for the error propagation formula used.

1. The reference spectrophotometer irradiates an area of approximately 8 mm by 1 mm, which is approximately centered in the filter. Users instruments may irradiate an area of either different size, different location, or both. To cover this eventuality, the filters are

tested for homogeneity in a densitometer as described in section 4.2.2. The irradiation area in the densitometer is approximately 1 mm by 4 mm, and the 9 locations examined span an area of 5 mm by 24 mm. A filter is rejected if the transmittance at any of the eight peripheral sampling locations differs from that at the center location by 0.3% relative or more. Many commercial instruments irradiate an area which is below the centerline of the cuvette, to better accomodate partially filled cuvettes.

2. The time dependence of filter transmittance in tables 7, 8, and 10 is confounded with other error components, such as u_3 and u_5. However, the data of these tables reveal a clear increase in transmittance with time, in accord with the proposed explanation discussed in Section 5.4. A fit of the data of table 7 averaged over all wavelengths and all three transmittance values is consistent with a possible change in transmittance of 0.25% relative over the period of time between 0.5 years and 2.5 years following the grinding and polishing of a filter. Since the filter is aged for 0.5 years at NIST before the final certification, and is certified for a period of 2 years, this figure is taken as an appropriate estimate of the positive (increasing transmittance) uncertainty component. If the filter is returned to NIST for cleaning and recalibration on 2-year intervals, as is recommended, the time drift effect should be considerably lower over 2-year intervals subsequent to the first one.

3. The transmittance of the filter is a function of angle of incidence because the reflectance from the entrance and exit surfaces increases with increasing deviation from normal incidence. From the data of table 15, it may be determined that a loss in transmittance (negative bias) of 0.2% accomodates a tolerance of ± 4 degrees of arc in the alignment of the filter with respect to normal. Furthermore, the f/10 converging optics in the NIST reference spectrophotometer imply that the angle of incidence in the irradiating light varies from normal to as much as the half-angle of the illuminating cone --- or $\arctan(0.1/2) \approx 3$ degrees of arc --- off of normal. This negative bias in the IARD spectrophotometer used to certify SRM 930 may account for the consistent negative bias indicated by table 14 for intercomparisons with the reference instrument located in the Radiometric Physics Division (RPD), which employs collimated beam optics.

4. From tables 6 and 9, it is evident that the effect of exposure to light and laboratory atmosphere is to reduce the transmittance fractionally. The error estimate here is somewhat subjective, and is designed with the intent that the true value of transmittance fall within the stated uncertainty limits over the two-year period of certification, assuming that the user has handled the filters as recommended, and kept them stored in the containers provided for the majority of the time between infrequent calibrations. Each of the exposures of table 6 represents three years of around-the-clock exposure to typical ambient light levels, so that this effect is essentially negligible for the recommended procedure. On the other hand, the estimated error component is less than the effect of laboratory atmosphere indicated by the data of table 9, especially considering the offsetting effect of error component u_2. The anecdotal data set of table 9 is thus considered to be less compelling than the experience with NIST reference filters kept in-house over a period of 19 years.

5. A graphical study of the data of table 5 reveals that the relative percent difference between a transmittance measured at 25.5 °C and at 20.5 °C is clearly a function of both the wavelength and the nominal transmittance of the filter. The value given is scaled linearly

from the result of the experiment to the total tolerance of 4 °C (±2 °C) considered acceptable for use of the filter. The temperature effect is most notable for low transmittance and for the extremes of wavelength certified. Users operating outside of the recommended temperature range of 21±2 °C may expect to encounter difficulties with the nominal 10%T filter at the wavelength extremes.

6. The inherent accuracy of a single measurement of the apparent transmittance of a filter or sample depends on the accuracy of the zero (intercept) and the linearity of the detector response, as well as the stability of the source during the measurement of the incident and transmitted intensities. The NIST spectrophotometer is nulled frequently to ≤0.01% of the full scale reading for the incident light, which approaches 0.1% relative for the worst case and the 10 %T filter. The linearity of the detector was evaluated initially using the double aperture method as described in Section 1.1 and Appendix 2, and a polynomial correction function was fitted and incorporated into the measurement system. The linearity is periodically confirmed by means of the double-aperture method, and has been found to be stable. Every transmittance is computed from a measured transmitted intensity and two bracketing measurements of the incident intensity (blanks), with the measurements made at time intervals of approximately six seconds. Thus, the incident intensity at the time of measurement of the transmitted intensity is a linear interpolation of two values measured at twelve second intervals. The absolute accuracy of this estimate of incident intensity depends on any drift in lamp intensity being linear over this time period.

7. This value represents a pooled estimated standard deviation of the measured transmittance for 6 replications using 7 filters (35 degrees of freedom), reported in table 4, Section 5.1, and is probably dominated by photon shot noise, or the random Poisson distribution of photon statistics.

10.1 Overall Estimated Uncertainty

The expanded uncertainties of the certified transmittance values, U, are given in relative percent, as determined from the component standard uncertainties (i.e., estimated standard deviations) and a coverage factor k=2 based on the t-distribution for infinite degrees of freedom. The expanded uncertainty defines an interval within which the unknown value of the transmittance can be asserted to lie with a level of confidence of approximately 95 percent. This uncertainty includes "Type A" uncertainties, which are evaluated by statistical methods (item 7 in the table), and "Type B" uncertainties, which are evaluated by other means (items 1-6 in the table). The uncertainties are combined by the root-sum-of-squares method. The methods used to treat uncertainties are described in NIST Technical Note 1297[41].

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Note

This work is a revised and augmented edition of an earlier NBS-SP 260-51 publication issued in 1975 on the selection, preparation, certification and use of SRM 930 "Glass Filters for Spectrophotometry" [14]. To the material included in this early work, an appreciable amount of new data, mainly from references 15 and 16, were incorporated in this updated edition which includes a description of the new Standard Reference Material 1930 issued in 1987. SRM 1930 extends the transmittance range of SRM 930, issued in 1971, by providing three neutral glass filters having nominal percent transmittances of 1, 3, and 50%T.

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Appendix 1

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Comments on Spectrometry Nomenclature

Sir: As an optical physicist who collaborates with analytical chemists in the development and use of absorption and luminescence spectrometers, I have become increasingly aware of the fact that our vocabularies are not always the same. Although some of these differences have been pointed out before (*1*) it seems worthwhile to familiarize the readers of this journal with the currently prevailing terminology of physical optics. Perhaps the following comments may be helpful to editors, authors, and nomenclature committees in establishing a common and consistent terminology that can be used in all branches of spectrometry and would save readers a good deal of puzzlement and reading between lines. The main purpose of these comments is to emphasize the need for interdisciplinary efforts in defining spectrometry nomenclature without perpetuating the inconsistencies that exist at present. They do not represent an official position of the National Bureau of Standards.

The basic concept of modern optical terminology (*2, 3*) is to combine nouns and adjectives in order to describe quantities and properties as explicitly as necessary, rather than using glossaries of short names for them. This "Chinese Restaurant" method of nomenclature (*4*) offers flexibility in introducing new terms, and has recently been extended to include the photon quantities used in photochemistry and similar disciplines dealing with the interaction of light and matter (*5*).

The basic list of nouns describing the transport of energy according to the laws of geometrical optics is:

Energy, Q.

Energy density, $u = dQ/dV$. Energy per unit volume.

Flux, $\Phi = dQ/dt$. Time rate of energy flow.

Flux density, $W = d\Phi/dA$. Flux per unit area.

Intensity, $I = d\Phi/d\Omega$. Flux per unit solid angle.

Sterance, $L = d^2\Phi/d(A\cos\Theta)d\Omega$. Flux per unit projected area and unit solid angle.

(A number of alternative and additional terms have been proposed. For example: *pointance* to replace the continually misused term *intensity; incidance* and *exitance*, or *incident areance* and (*transmitted, emitted*, etc.) *areance* for the flux densities arriving at and leaving a surface; *sterisent* for the sterance generated per unit path length by emission or scattering into the direction of propagation; and *fluence* for the surface energy density incident upon a volume element irradiated from within a large solid angle of rays (F. E. Nicodemus, private communication). As these have not yet been accepted generally, they were not included here. However, the new term *sterance* was included as it avoids the misnomer *photon radiance* that has appeared in papers on luminescence spectrometry.)

These nouns are modified by the adjective *radiant*, and the above symbols are written with a subscript 'e' (for energy), when radiometric units are used. The modifiers *luminous* and *photon* are used in conjunction with subscripts 'v' (for visual) and 'p' (for photon) to indicate the use of photometric and photon units, respectively. For example:

Radiant energy density, u_e[J m^{-3}].

Luminous intensity, I_v[lm sr^{-1}].

Photon sterance, L_p[E m^{-2} sr^{-1} s^{-1}].

(The basic unit for photon energy used here is the *einstein* [E], defined as one mole of photons. It is not an SI unit, but is used so extensively in photochemistry and photobiology that its acceptance as a supplementary SI unit may be desirable.)

The additional modifier *spectral* and subscripts λ and σ are used to denote derivatives of radiometric and photon quantities with respect to wavelength and wavenumber, respectively. Thus:

Spectral radiant energy density, $u_{e,\lambda} = du_e/d\lambda$ [J m^{-4}]. Radiant energy density per unit wavelength interval.

Spectral photon intensity, $I_{p,\sigma} = dI_p/d\sigma$ [E sr^{-1} s^{-1} m]. Photon intensity per unit wavenumber interval.

Any of these can be modified further; such as: *fluorescence photon flux, transmitted spectral radiant flux density*, or *absorbed luminous energy*. Usually, it is possible to drop most of the modifying adjectives as well as the subscripts e, v, or p, once the context has been clearly established or whenever a distinction is not necessary.

The same method of nomenclature also provides a simple and logical way of specifying the precise meaning of the quantities and material properties commonly measured in analytical spectrometry. Thus *radiant absorptance* α_e and *photon absorptance* α_p should be used for the ratios of the radiant or photon fluxes absorbed by a sample to those incident upon it, when measured with a large bandwidth so that these two ratios are not the same. On the other hand, *spectral absorptance* $\alpha(\lambda)$ is sufficiently accurate in the case of measurements made with a small bandwidth. Similarly, luminescence yields (the ratios of the radiant or photon fluxes emitted by a sample to those absorbed by it) should be designated as *radiant yield* η_e or *photon yield* η_p (not *energy yield* or *quantum yield*). In this case, *spectral radiant yield*, $\eta_{e,\sigma} = d\eta_e/d\sigma$, and *spectral photon yield*, $\eta_{p,\sigma} = d\eta_p/d\sigma$, are different quantities even in the limit of infinitely narrow bandwidths, and thus should be referred to by these names.

[The dependence on wavelength or wavenumber is indicated by a subscript ($\eta_{p,\sigma}$) when the spectral distribution is defined as a derivative, but in functional form [$\alpha(\lambda)$] in the case of spectral distributions that are not derivatives. This is an important distinction that must also be borne in mind in the presentation of spectra. The positions of the peaks and valleys in derivative spectra depend on the units used, so that these should not be published in the form of a single graph with dual scales (such as wavelength and wavenumber, or spectral radiant and photon yield).]

In addition to this general description of current optical terminology, the following comments are made in direct reference to the nomenclature list in the December 1975 issue of *Analytical Chemistry* (*6*).

1) This list cautions not to use *optical density* instead of *absorbance*, but defines the latter as "the logarithm to the base ten of the reciprocal of transmittance"—which is the definition of optical density. *Internal transmittance* should have been substituted for *transmittance* in this def-

inition of absorbance. The International Lighting Vocabulary suggests *transmission density* and *internal transmission density* instead of optical density and absorbance. This is more determinative, and also fits into a general scheme where *reflection density* is defined as the negative logarithm to the base ten of reflectance. On the other hand, transmission and reflection density are operational quantities that merely express measured data on a logarithmic scale, whereas absorbance is directly related to molecular constants through the Lambert–Beer and Strickler–Berg equations. Thus, in my opinion, it should be retained as a separate term. I believe that all confusion would be avoided by defining:

Transmittance, τ. Ratio of the flux transmitted by a sample to the flux incident upon it.

Internal transmittance, τ_i. Transmittance exclusive of losses at boundary surfaces and effects of interreflections between them.

Transmittance density, $D = -\log_{10}\tau$. Negative logarithm to base ten of transmittance.

Absorbance (Internal transmission density), $A = -\log_{10}\tau_i$. Negative logarithm to base ten of internal transmittance.

2) The definitions of *absorptivity* in chemistry and physics are not the same. In chemistry, it means absorbance per unit path length and unit concentration (A/bc), whereas the International Lighting Vocabulary (2) defines it as internal absorptance per unit path length ($d\alpha_i/db$). Similarly, it specifies *transmissivity* as internal transmittance per unit path length and *reflectivity* as the reflectance of a thick layer (so that a further increase in thickness will no longer change its value). Generally, terms ending in *-ance* represent sample properties, whereas terms ending in *-ivity* denote material properties that are independent of sample geometry. The quantity A/bc does not fall in this latter category as it is also independent of sample concentration. The International Union for Pure and Applied Chemistry, apparently aware of this discrepancy, has suggested calling it *absorption coefficient*. However, as this name has been given different and mutually inconsistent meanings in the past, a less ambiguous word—perhaps *specific absorbance*—would have been better. Therefore it is proposed to define:

Absorptivity, $a = d\alpha_i/db$ [m^{-1}]. Internal absorptance per unit path length.

Specific absorbance, $\epsilon = A/bc$ [$kg^{-1}\ m^2$]. Absorbance per unit path length and unit concentration.

Specific molar absorbance, $\epsilon_m = A/bc_m$ [$mol^{-1}\ m^2$]. Absorbance per unit path length and unit molar concentration.

3) The December 1975 nomenclature list also implies that the Beer–Lambert laws are the same. The correct definitions are:

Beer's law: Absorbance is proportional to concentration.

Lambert's law: Absorbance is proportional to path length. Also called *Bouguer's law.*

4) The definition of the *ångström* unit in terms of the red line of cadmium has been abrogated several years ago. It is now defined as 10^{-10} m, exactly. However, the ångström is not an SI unit, and has been sanctioned by the International Committee on Weights and Measures only as a supplementary unit that will eventually be abandoned (7). Therefore, authors should be encouraged to use *micrometers* or *nanometers.*

5) The December 1975 list defines *spectrometry* as the "measurement of spectra", but restricts the meaning of *spectrometer* to "instrument with an entrance slit, a dispersing device, and with one or more exit slits . . .". As this excludes non-dispersive and slit-less instruments, such as Fourier and Girard spectrometers, it would be more consistent to call any instrument used for spectrometry a *spectrometer.* Therefore:

Spectrometer: Instrument for the measurement of spectra.

The general term for instruments that measure spectral distributions of radiometric quantities is *spectroradiometer.* However, as this implies measurements in absolute units, *spectrometer* is a better term for the simpler, usually ratio-forming instruments used in analytical spectrometry. Thus, a *spectrophotometer* could also be called *absorption spectrometer,* and *fluoroescence spectrometer* would end the controversy of *spectrofluorimeter* vs. *spectrofluorometer.*

(Strictly speaking, the word *spectrophotometer* is a misnomer. A *photometer* is an instrument that measures luminous flux in lumens. Since the adjective *luminous* implies the integral effect of visual radiation as perceived by the human eye, the spectral analysis of luminous flux has no physical meaning. However, in view of the firmly established meaning of *spectrophotometer,* it is not suggested to change it, although a scanning of the recent literature shows an increasing usage of *absorption spectrometer.*)

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Appendix 2

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An Accurate Spectrophotometer for Measuring the Transmittance of Solid and Liquid Materials

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(May 31, 1972)

The optical transmittance of solids and liquids as well as the molar absorptivity of various chemical species are parameters of fundamental significance in characterizing these materials. Meaningful transmittance data can be obtained only when the measurements are performed with well-known accuracy and precision. To perform such measurements, a high accuracy spectrophotometer was designed and assembled at NBS, Analytical Chemistry Division, and will be described in this paper. This single-beam instrument is composed of a constant radiation source, a monochromator, a sample carriage, an integrating sphere-photomultiplier assembly followed by appropriate electronics, and a read out system consisting of a digital voltmeter and a computer data acquisition and handling provision. The accuracy of transmittance measurements is determined by the light-addition principle used in conjunction with a two-aperture arrangement. The spectrophotometer can be used in manual or automatic modes of operation. A detailed discussion of the data obtained with this instrument, used in both modes, will be presented together with its application to the certification of solid and liquid Standard Reference Materials for checking the photometric scales of conventional spectrophotometers.

Key words: Absorbance; automation of accurate spectrophotometer; instrumentation, spectrophotometric; spectrophotometry, high accuracy; standard reference material in spectrophotometry; transmittance.

I. Introduction

Optical transmittance is due to an intrinsic property of matter and characterizes a particular transparent material. Since this parameter is not known a priori, it must be determined by experimental procedures.

True transmittance values can be obtained only by using accurate measuring techniques and by taking into consideration all factors which can affect and distort the data.[1]

Transmittance is the ratio of two radiation flux intensities. It is therefore necessary that the photometric scale of the spectrophotometer used to perform the measurements be accurate. The transmittance of a particular material is also a function of wavelength; hence the wavelength scale of the monochromator should also be accurate, and appropriate spectral bandpasses should be used. The measurements should be made using collimated radiations. Such radiations define unambiguously the actual path length through the transmitting medium, the reflection losses, and eliminate the effects of polarized radiations that are produced at the surface of the sample. Other important factors which must be considered are: homogeneity and stability of the sample, radiation scatter inside the sample, interference phenomena, stray radiation, polarization, fluorescence, temperature, particulate matter, and surface conditions. Since transmittance measurements depend on a diversity of factors, meaningful values can be obtained only by defining the experimental conditions for obtaining transmittance data [1, 2].[2] Spectrophotometers are used to perform two types of measurements:

(1) Quantitative determination of chemical species using the relation between optical transmission of the material, and the concentration as a measuring parameter. Under these circumstances, the photometric scale

[1] The optical transmittance of a solid material includes the reflection losses which occur at the air-solid interface.

The internal transmittance is defined as the transmittance of the material corrected for reflection losses (2). This internal transmittance can be calculated in principle from the transmittance by using the well known Fresnel equations (1, pp. 98 to 100).

For collimated radiation the reflectance R, for a material with an index of refraction, n, and an absorptivity, a, at wavelength, λ, is given through:

$$R_\lambda = \frac{(n_\lambda - 1)^2 + n_\lambda^2 a_\lambda^2}{(n_\lambda + 1)^2 + n_\lambda^2 a_\lambda^2}.$$

For a nonabsorbing material and collimated radiation:

$$R_\lambda = \frac{(n_\lambda - 1)^2}{(n_\lambda + 1)^2}.$$

For glass, n is approximately 1.5 in the visible region of the spectrum, and R will be about 4 percent at every air-glass interface.

When noncollimated radiation is used:

$$R_\lambda^\perp = \frac{\sin^2(\alpha - \beta)_\lambda}{\sin^2(\alpha + \beta)_\lambda}$$

for perpendicular polarized radiation, and

$$R_\lambda^{\parallel} = \frac{\tan^2(\alpha - \beta)_\lambda}{\tan^2(\alpha + \beta)_\lambda}$$

for parallel polarized radiation, where α and β are the angles of incidence and refraction, respectively.

In collimated radiation and in air, $\alpha = \beta = 0$ and $R^\perp = R^{\parallel} = R$.

[2] Figures in brackets indicate the literature references at the end of this paper.

of the spectrophotometer is calibrated in meaningful units, using a series of reference solutions having known concentrations of the species to be determined, rather than values of optical transmittance.

The accuracy of the measurements is related solely to the accuracy with which the concentration of the reference solutions is known and to the precision (stability, sensitivity, reproducibility) of the spectrophotometric method and instrument used. The accuracy of the photometric scale per se, is not a critical factor in such measurements.

The precision, stability, and reproducibility of the instrument can be checked before each series of measurements by careful use of solid or liquid reference filters having well established transmittance values.

(2) Determination of the optical transmission characteristics of solid or liquid materials, and the determination of molar absorptivities of chemical compounds. In both cases the accuracy of the photometric scale of the measuring instrument, among other things, is essential to provide true values. Ways to establish and check this important parameter are critically needed.

Since conventional spectrophotometers do not provide means to check photometric accuracy or to evaluate the possible sources of systematic errors, it was decided in 1969 to design and construct a research spectrophotometer on which transmittance measurements could be performed with well defined accuracy. Such an instrument would be used to determine optical transmittance of selected solids and liquids at various wavelengths. These materials can be used as standard reference materials (SRM's) to check the accuracy of the photometric scale of conventional spectrophotometers. The same certified SRM's could likewise be used to monitor the precision, stability, and reproducibility of those instruments [3, 4].

After a comprehensive examination of the literature in this field [5 to 34] arranged in chronological order, an instrument was developed which is similar in principle to the instrument at the National Physical Laboratory (NPL), Teddington, England, where a long tradition of high accuracy spectrophotometry exists. The instrument described in this work performs measurements of radiant energy in the visible and ultraviolet region of the spectrum, with well established and high photometric accuracy. Transmittance measurements on solids and liquids can be made with this instrument using collimated as well as noncollimated beam geometry. The wavelength accuracy and spectral bandpass achievable are adequate to avoid degradation of photometric accuracy, and the other interferences mentioned have been given careful consideration, and, in most cases, have been assessed quantitatively.

The transmittance measurements on the optically neutral glass filters discussed in this work have been made with a noncollimated beam geometry corresponding to an aperture of about f:10. The image of the exit slit of the monochromator (8 mm x 0.5 mm) was produced at the center of the entrance face of the filter. All measurements have been made against air for the nonattenuated radiation flux, and no correction for reflection losses was made. Transmittance measurements made with noncollimated radiation by projecting the image of the exit slit of the monochromator on the entrance face of the sample using an opening of f:10 (total angle of about 7° or 8°), may differ by several parts in 10^4 of the value when compared with similar measurements made with collimated radiations, as indicated in this Journal by K. Mielenz.

Noncollimated beam geometry was applied in this work to approach the measuring conditions used in most of the conventional spectrophotometers which are available today. A brief description of this instrument was given earlier in reference [3].

II. Description of the Instrument[3]

The high accuracy spectrophotometer, completed and tested in 1970, is a single beam instrument which contains the following components: (a) a constant radiation source, (b) a monochromator, (c) a sample holder, (d) a system to check the accuracy of the photometric measurements, (e) an integrating sphere attached to a photomultiplier-digital voltmeter unit, and (f) the data presentation system. Figure 1 illustrates schematically the arrangement of these various components. A circular neutral wedge is placed after the light source to select various levels of radiation intensities required for measurements. A description of the components is presented in the following sections.

a. **The Radiation Source.** Since the instrument is a single-beam type, it is essential that the radiation source be constant and homogeneous. Additional desirable conditions are: capability of monitoring the current supplied to the source and radiation similar to that from a Planckian radiator. The source is similar in design to that developed and used at NBS by H. J. Kostkowski and R. D. Lee of the Institute for Basic Standards. This source was duplicated in our instrument with the kind assistance of its developers.

The source is used in the spectral range 360 nm to 800 nm and consists of a tungsten incandescent filament lamp with a tungsten ribbon 8 mm long by 2 mm wide. The connections to the lamp terminals are soldered to minimize contact problems (see fig. 6). The direct current required to operate this lamp at approximately 3000 K is 18 A across a 6 V drop; our source is operated at 5 V and 15 A. The d.c. power supply is capable of delivering 15 V and 50 A, and can be operated in constant current or constant voltage modes. To achieve the constant current mode an external sensing resistor of 0.1Ω and 50 A and a current control circuit are placed in series with the power supply. A feedback voltage across this resistor is connected to the sensing system. The character

[3] The commercial instruments and parts used in the construction of the spectrophotometer are identified in the addendum.

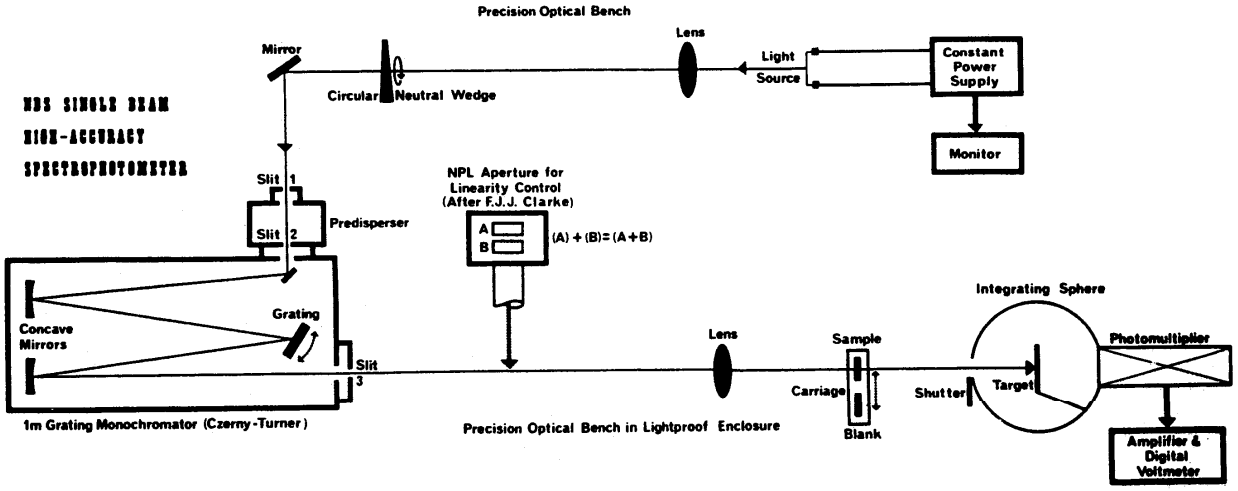

FIGURE 1. Principle of the single beam high accuracy spectrophotometer. The aperture unit is placed on the optical bench only when linearity measurements are performed.

istic of this function is the ability to automatically change its output voltage to maintain a constant current to the load resistor, which, in our case, is the lamp source. The nominal current regulation obtained is better than 0.01 percent, and the stability over an 8 hour period, at constant load temperature, is better than 0.02 percent. The stability of the current delivered to the lamp is monitored with a high accuracy potentiometer used in conjunction with a null meter. This meter is sensitive to variations in the current supplied to the lamp from 1 part in 1000 to 1 part in 1,000,000 per division (fig. 1 and fig. 14). The potentiometer is connected to the current source across a resistor (0.01Ω and 100 A) placed in series with the lamp.

The demagnified (2 to 1) image of the ribbon filament is projected on the entrance slit of the predisperser by a fused quartz (nonfluorescent SiO_2) lens whose focal distance is 254 mm and diameter is 44 mm. This and the other lenses used in the optical system, were calculated by K. Mielenz of the Institute for Basic Standards at NBS. The lenses are mounted in carriers which permit orientation in any position. A circular neutral wedge is placed between the light source and the predisperser. This wedge, evaporated inconel on a fused quartz disc (150 mm diam), is linear in density and provides a light attenuation of 100 to 1. The wedge is motor driven (1 rev. per s) to select proper radiation intensity levels as required by the measurements (figs. 2, 3, and 4). The radiation source used for measurements in the ultraviolet region to 275 nm is a single coil tungsten-bromine incandescent lamp (fig. 5) supplied by an adequate power source; below 275 nm, a deuterium discharge lamp is contemplated.

b. **The Monochromator.** The monochromator is a 1-m Czerny-Turner type grating instrument with a dispersion of 0.8 nm/mm. The flat grating has 1200 grooves per mm covering a surface of 100 x 100 mm. The monochromator is provided with a predispersing attachment to reduce the stray light (fig. 3). This pre-

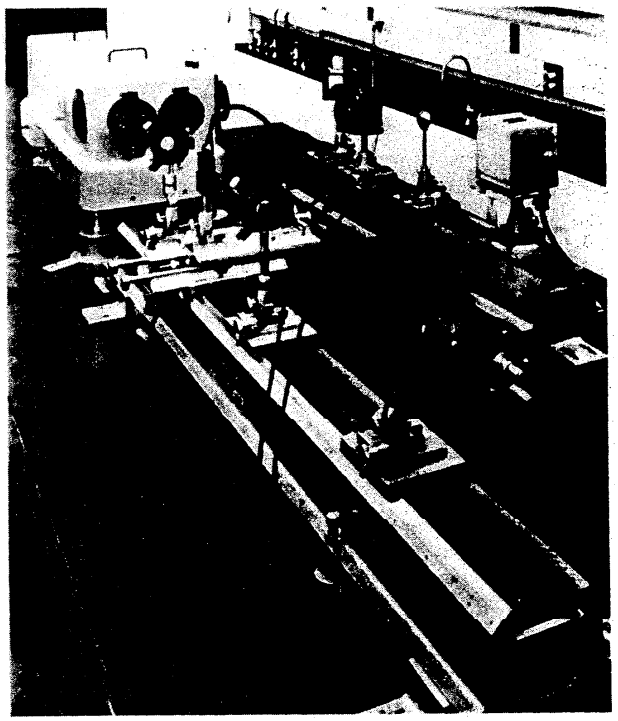

FIGURE 2. General views of the spectrophotometer. Rear: optical bench carrying the tungsten-halogen radiation source used for checking the alignment of optical components, followed by a quartz lens, the circular quartz neutral wedge, and a flat mirror. Left: the 1-m Czerny-Turner grating monochromator (the predisperser is not illustrated here). Front: optical bench carrying a quartz lens, the single-sample and blank carriage, a second quartz lens, and the integrating sphere with the photomultiplier housing.

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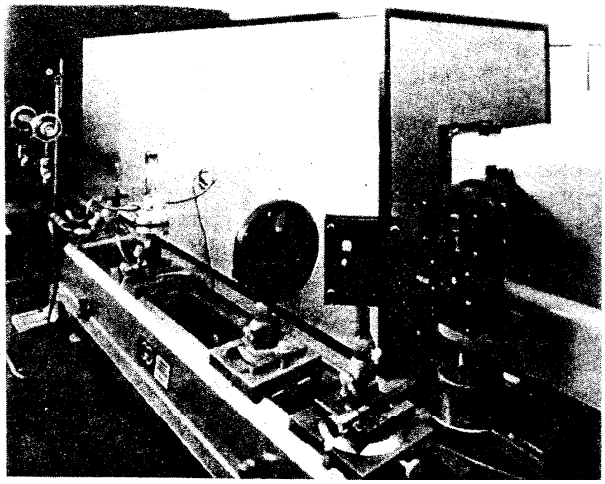

FIGURE 3. Close view of the tungsten ribbon filament lamp on its adjustable holder, followed by the quartz lens—circular neutral wedge assembly, and by the flat mirror in its adjustable holder. The 30° quartz prism Littrow-type predisperser is located at the entrance slit of the 1-m grating monochromator. Extreme left: neon gas laser used to check the optical alignment, and mercury discharge lamp for wavelength calibration. When in use, the tungsten ribbon lamp is surrounded by an enclosure with black walls (50 cm x 50 cm x 70 cm high). Rear: enclosure containing the optical units illustrated in figure 2.

disperser is a small quartz prism monochromator connected to the scanning system of the 1-m instrument. A wavelength counter permits readings to 0.1 nm and the scanning speed can be varied from 0.05 nm to 200 nm/min by a 12 speed synchronous electric motor.

The optical components are placed on precision lathe bed type optical benches which are 160 and 120 cm long, and are equipped with appropriate carriers provided with *x-y-z* adjustments.

c. **Sample Carrying Systems.** The spectrophotometer is provided with two sample carrying systems. One system measures one sample and its blank, while the other system permits sequential measurements for seven samples and eight reference reading positions against air, and can be operated manually or automatically through a computer interfaced with the instrument.

The single sample carrying unit consists of a platform provided with two vertical holders which can accept $\frac{3}{4}$-in (14 mm) rods and a variety of sample supports (fig. 2). These holders can be moved laterally through a rack and pinion arrangement. The platform is mounted on 4 ball bushings which ride on two horizontal rods and can be moved pneumatically across the optical axis. The pneumatic operation was recommended by G. E. Moore and J. T. Sterling of the Institute for Materials Research at NBS and by L. Owen, a guest worker at NBS. The travel distance is 8 in (20 cm) and the linear movement is smooth; the position of the platform and the sample in and out of the optical beam, can be reproduced within 0.025 mm. This unit is illustrated in figure 2

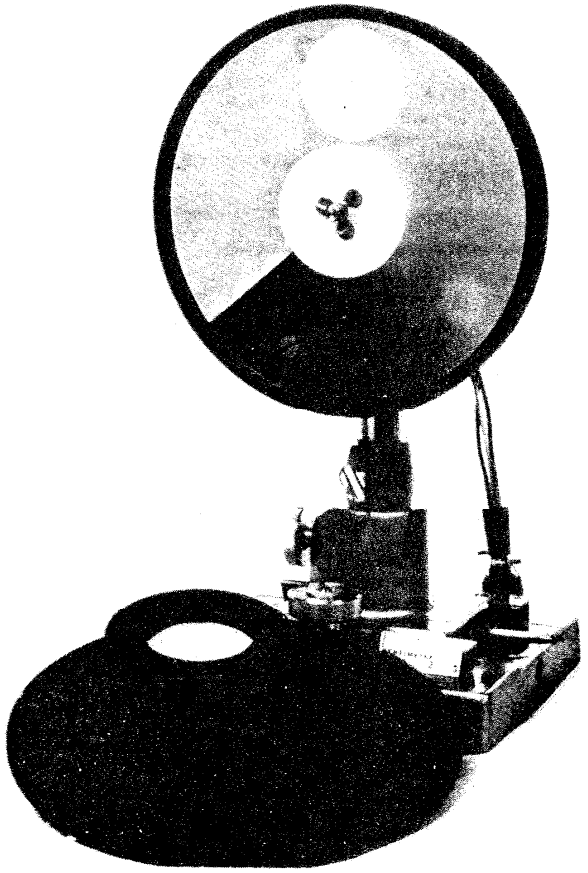

FIGURE 4. Close view of the circular, neutral wedge. The front plate which carries the fused silica lens was removed to show the fused silica disc with the evaporated metal layer.

and is located between the two quartz lenses. The sample holder is designed to accept conventional solid or liquid filter holders which fit most spectrophotometers. These holders are provided with a thermostating jacket, and can be rotated in the horizontal plane through a 10 cm diameter rotating table.

A filter holder which permits the rotation and scanning of the sample in the x–y direction is also available (fig. 7). It is provided with micrometer screws having a total linear motion of 25 mm with 0.01 mm per division. The seven-sample carrying unit is illustrated in figures 8 and 9 and consists of a semicircular aluminum-alloy plate placed horizontally on an appropriate carrier on the optical bench along the optical axis. This plate, which is 32 cm in diameter and 2.5 cm thick, can be rotated clockwise through a pneumatically operated precision ratchet system in increments of 12°. The stepwise rotation utilizes a solenoid valve which is operated electrically by a switch located outside the enclosure. This switch can be operated manually or automatically by computer (fig. 14).

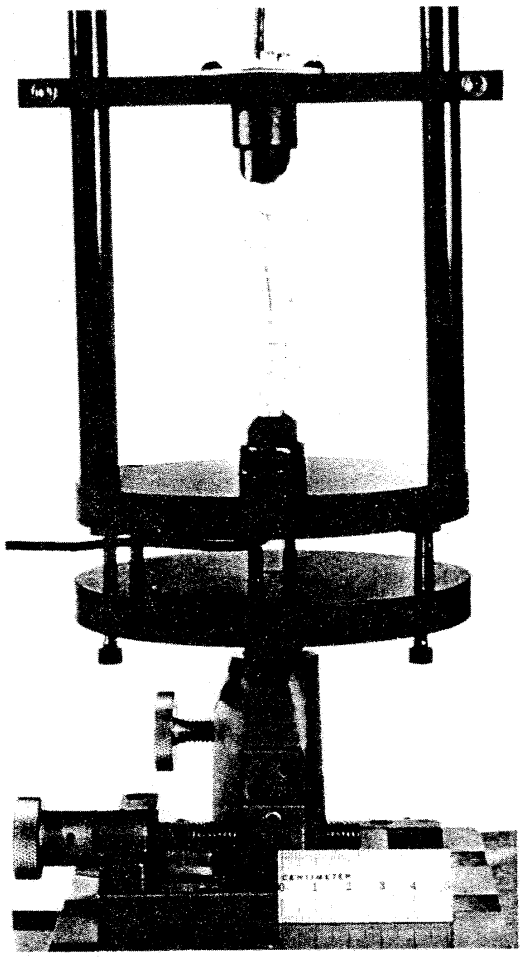

FIGURE 5. Single coil tungsten halogen lamp in the adjustable holder.

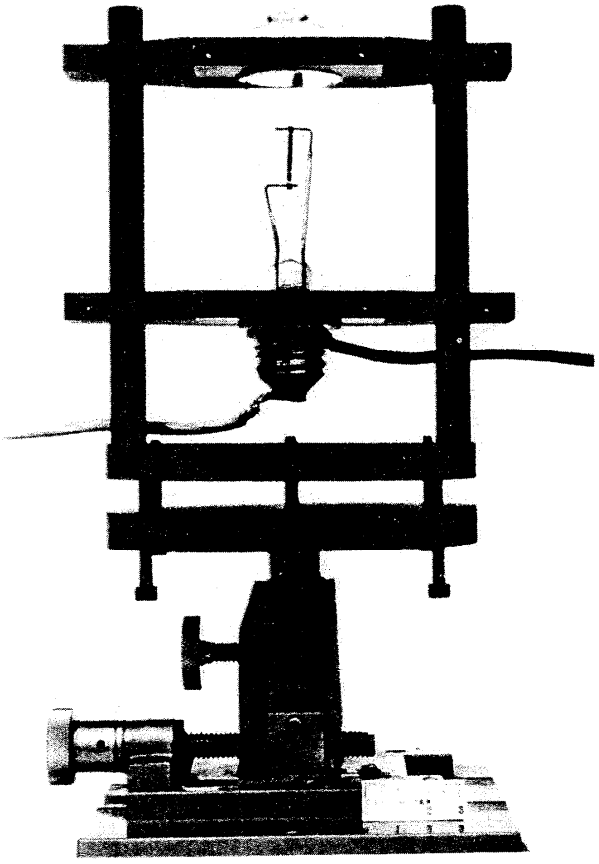

FIGURE 6. The tungsten ribbon filament lamp in the newly designed adjustable holder. The platform which carries the lamp is similar to that described in figure 5 and can be oriented in the horizontal plane through the six screws spaced around the edges of the platform at 60° intervals. Three screws push the platform while the other three pull.

The current-supplying wires are soldered directly to the lamp terminals to eliminate contact problems.

The semicircular plate carries seven sample holders similar to those used for the single sample system described earlier. The holders are placed at 24° intervals and are separated by blank spacings. About 1 atm of air pressure is used to operate the plate and the rotation is set at 2 s per 12° step when the automatic computer operating mode is used.

d. **System to Check the Accuracy of the Photometric Reading.** Since the high accuracy spectrophotometer is single beam, accurate photometric data are obtained when there is a linear relation between the measured radiation flux and the corresponding response of the photodetector.

Linearity of photodetectors can be measured by several means: the inverse square law [7, 15]; the use of optical elements having a known transmittance which can be determined by other means [17] and the light addition principle of Elster and Geitel using a plurality of light sources [5, 6, 8, 9, 10, 13, 18, 19, 20, 28, 31, 33, 34] or multiple apertures [11, 12, 14, 16, 21, 23, 25, 26, 27, 30]. A novel approach to the problem of accurate photometric measurements was described by O. C. Jones and F. J. J. Clarke [24, 29] and by F. Desvignes and J. Ohnet [32]. A critical discussion of some aspects of accurate spectrophotometry will be found in an NBS manuscript by Gibson and associates [22]. The radiation addition principle, using two apertures with one source of radiation, was chosen for our work. The aperture method for checking the linearity of photometric data was in use at the National Physical Laboratory from about 1930 onwards, and one form of it was described by Preston and Cuckow [11] in conjunction with a single beam spectrophotometer, using a five aperture screen. One year later, Buchmüller and König [12] described and used a two aperture unit. At NBS, Barbrow [14] used a 10 aperture arrangement, while Harding [16] and Cordle and Habell [25] at NPL described a two aperture system. Multiapertures were used by Hoppmann [21], Bischoff [23], Sanders [26] and Nonaka and Kashima [27]. Finally, Clarke [30]

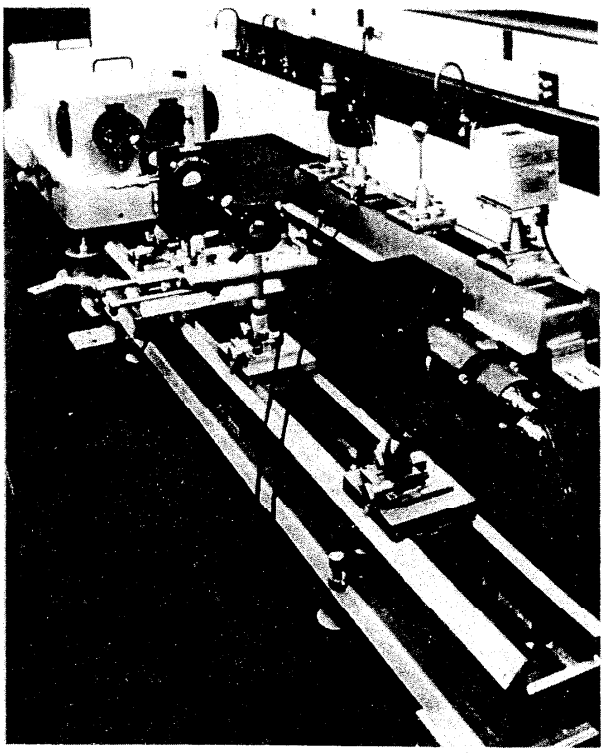

FIGURE 7. Same as figure 2 except for the sample holder which in this case is capable of rotating the sample 360° and to displace it in the x-y direction through the micrometer screws.

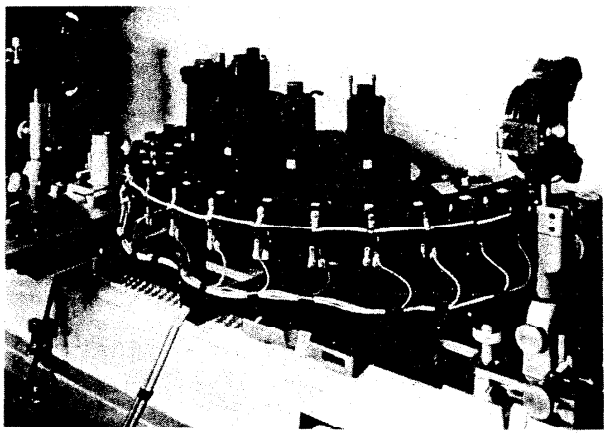

FIGURE 8. Circular platform carrying seven filter holders. The 15 position switches (7 sample positions and 8 blank positions) are visible along with the two quartz lenses. The exit slit of the monochromator is at left.

discussed in detail the use of a two aperture system to check the accuracy of photometric data obtained on the spectrophotometer at NPL. It is this two aperture system which is used at NBS.

The two aperture unit consists of a metal plate (130 mm by 100 mm) containing two rectangular

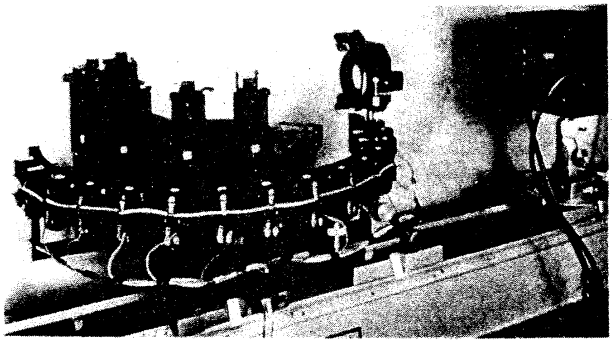

FIGURE 9. Same as figure 8. The pneumatic cylinder which rotates the circular platform through a ratchet mechanism is visible at the rear of the platform. The integrating sphere with its pneumatic shutter is seen at right.

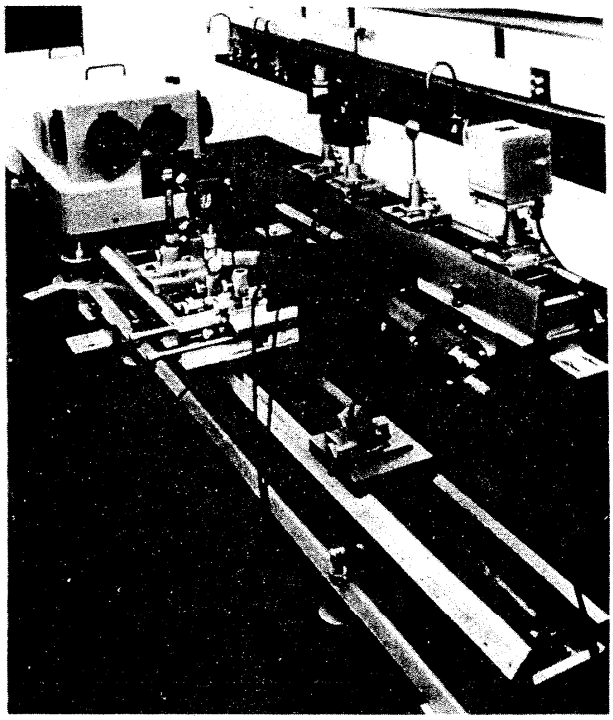

FIGURE 10. Same as figure 2. In this case the dual-aperture unit for linearity control is located on the optical bench after the exit slit of the monochromator.

windows, A and B, (20 mm by 8 mm) located one above the other (figs. 10, 11. 12). Each aperture can be closed by a light-tight shutter which is operated pneumatically by remote control (fig. 14). The aperture plate is placed in the optical path after the exit slit of the monochromator and *within* the optical solid angle of the instrument. The image of the apertures is then projected on the target of the integrating sphere. A fused quartz lens with a focal distance of 190 mm and a diameter of 60 mm is used for this purpose. The arrangement is illustrated in figure 10. No optical element

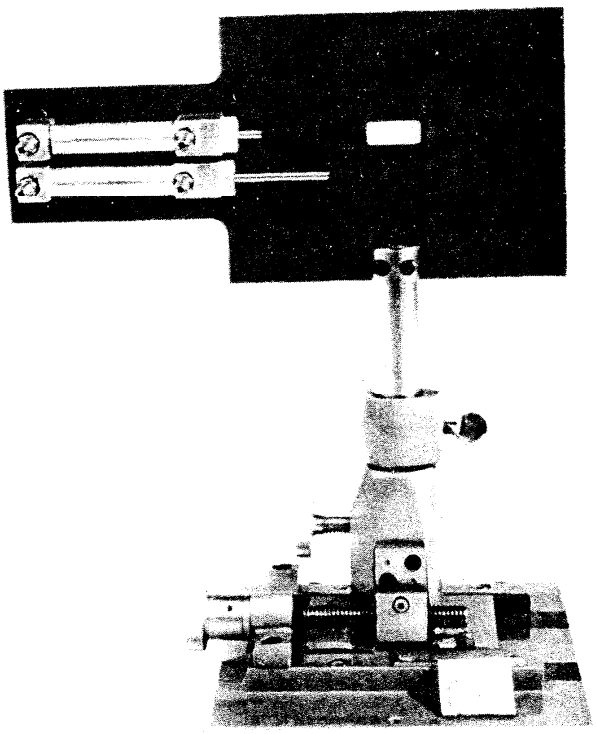

FIGURE 11. Detail of the dual-aperture unit showing its construction and the pneumatic system which operates the two shutters. One aperture is open, the other is closed.

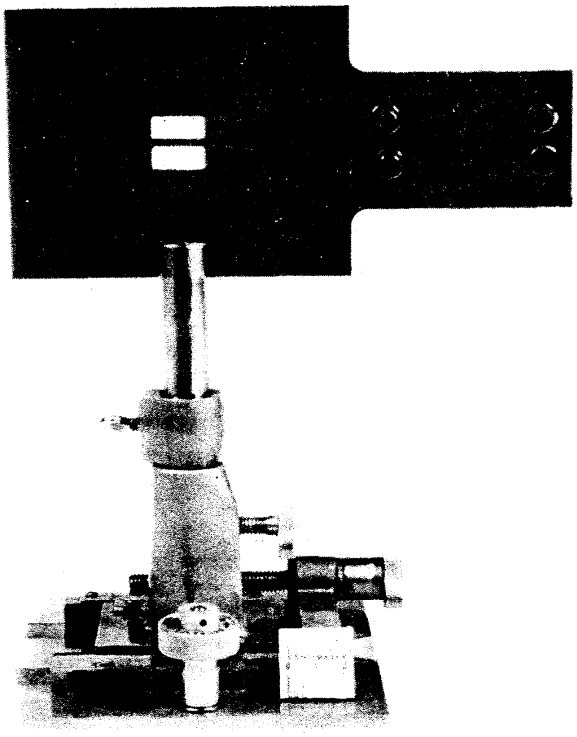

FIGURE 12. Front view of the dual-aperture unit, with both apertures open.

should be placed between the aperture plate and the monochromator. The linearity check consists of measuring the photocurrent produced when aperture A is open then closed, and then aperture B is open and then closed. The value of $(A)+(B)$ is compared with the values obtained with both apertures $(A+B)$ open. If the system is linear these two values should be identical:

$$(A)+(B)=(A+B).$$

If this is not the case, the system shows nonlinearity which is proportional to the amount by which the sum of $(A)+(B)$ differs from $(A+B)$. This difference is then used to correct the transmittance values measured on the solid or liquid filters.

c. **Integrating Sphere and Photomultiplier Arrangement.** The radiations emitted from the exit slit of the monochromator and passing through the aperture or the filter are received on the target of the integrating sphere. This sphere is illustrated in figures 2, 7, 9, and 10. A block of aluminum made from identical halves was cut to produce a half sphere in each block. The halves were joined together to form a hollow sphere. Its diameter is 125 mm and a target, made from a circular plate, 35 mm in diameter, is located at the center of the sphere. The front surface of the sphere has a 20 mm diameter opening. This opening can be closed by a shutter which is operated remotely by a pneumatic system. A 50 mm diameter opening is at the opposite end to which the housing of the photomultiplier is attached by an "O" ring to provide a light-tight joint. The inside of the sphere is coated using a suspension of $BaSO_4$; the outside is painted black.

Under these circumstances the sensitive surface of the photodetector receives the radiations originating from the exit slit of the monochromator only after these radiations have undergone at least two diffuse reflections.

The photomultiplier is a 50 mm flat-faced, silica end window tube with a 44 mm cathode and 11 venetian blind dynodes having CsSb secondary emitting surfaces. The cathode is an S–20 or tri-alkali type. The spectral range of this tube is from below 200.0 nm to 850.0 nm. The operating voltage used is 850 V. The photomultiplier output is supplied to a current-to-voltage converter consisting of an operational amplifier with high precision feedback resistors with values of 10^6, 3×10^6, 10^7, 3×10^7, and $10^8\Omega$. Dark current compensation is also available. This electronic system, described in figure 13 was designed and assembled by K. W. Yee of the NBS Electronic Instrumentation Section. The output from the current-to-voltage unit is connected to a digital voltmeter, illustrated in figure 14, with one microvolt resolution on the 1 V full scale range.

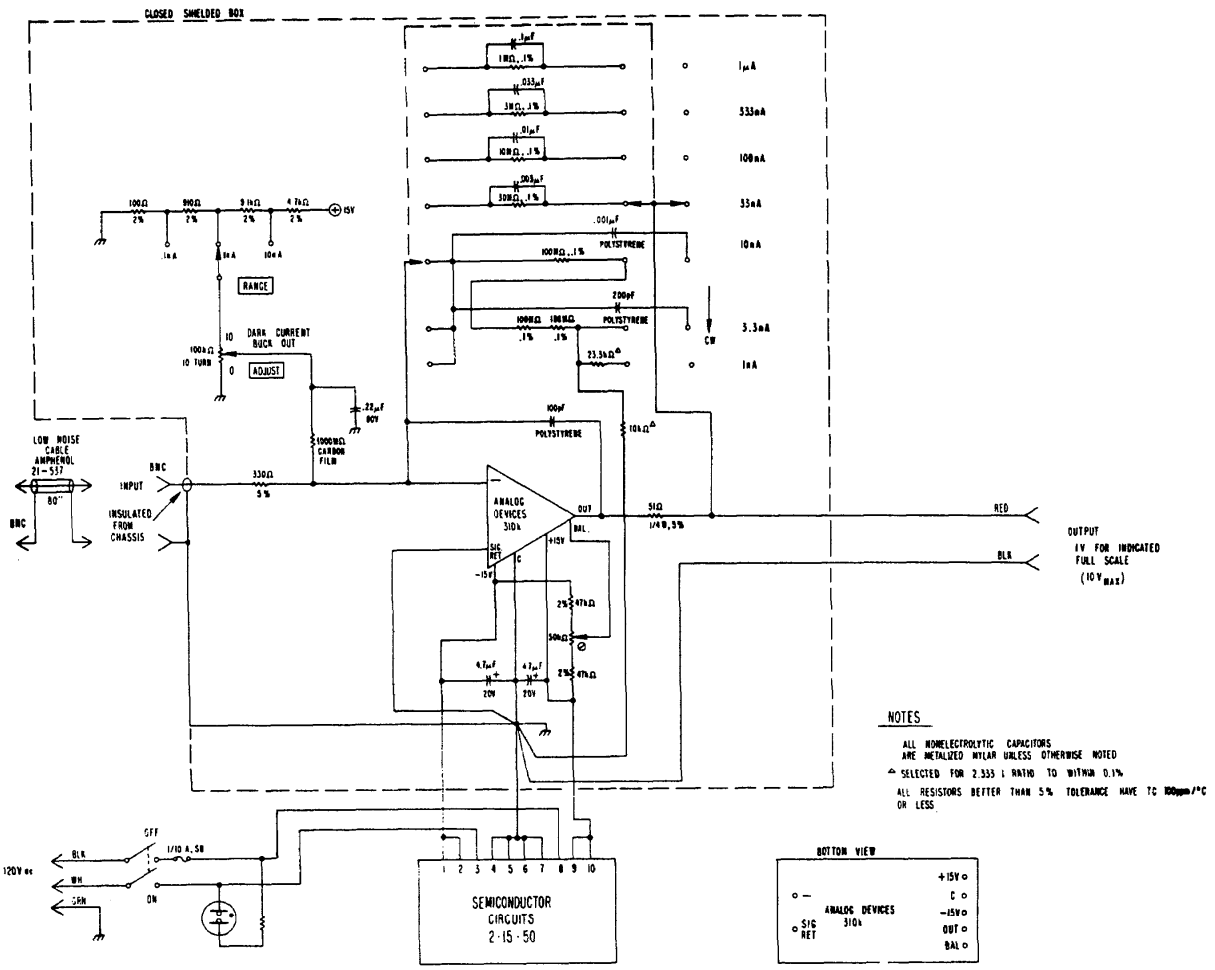

FIGURE 13. Schematic of the current-to-voltage circuitry. Courtesy of K. W. Yee.

The optical components located after the exit slit of the monochromator, including the photomultiplier tube, are enclosed in a light-tight box 200 cm long, 70 cm wide and 76 cm deep (fig. 3). The removable front panel is provided with a sliding door to permit rapid access to the filter-holder system. The box contains outlets for the compressed air which operates the apertures, sample carriage and integrating sphere shutter, and for the electrical connection from the photomultiplier. The inside walls are lined with thermal insulation painted black. When in use, all nonblack metal parts are covered with a black cloth to reduce stray light. The entire equipment is placed on a vibration isolation table 3.66 m by 1.52 m. The optical benches and the monochromator are secured by stops which are attached to the table surface. The alignment of the optical parts is made and checked periodically with a low-power laser shown in figure 3 (CW gas laser, output power 2 mW, λ 6328 Å) and with a high intensity tungsten-halogen lamp shown in figure 5.

f. **Data Collection and Presentation Systems.** The data output from the digital voltmeter (DVM), corresponding to the current generated at the photomultiplier tube by the radiations passing through the aperture system (A, B, $A+B$) or the samples (I) and blanks (I_0), can be obtained by visual means or computer operation. Both methods have been used in this work with good results. In the visual mode, the operator examines the digital voltmeter display and takes a mental average of the data. The display rate is adjusted to about one reading per second.

When measurements are taken by computer, the display of the digital voltmeter is adjusted to a faster rate; for instance, 10 to 20 data per second, depending on the capabilities of the instrument and measurement requirements. In our work, we use 10 data per second and collect 50 individual data for each measurement. This information is fed to the computer which calculates and prints the results as averages with the corresponding standard deviation, relative standard

FIGURE 14. Console containing the power supply for the photomultiplier tube, the dc null detector, the current-to-voltage converter, the digital voltmeter, the command panel for computer operation, and the command panel for the pneumatic operation of the shutter, aperture system, and single sample carriage. The electric switches for operating the circular neutral wedge are also located on this panel.

Middle right: potentiometer for monitoring the dc current supplied to the tungsten ribbon filament lamp.

At bottom left: teletype for data presentation.

Right: light panel which indicates the position of the automatic seven sample holder.

CALIBRATION OF SRM930 AT 440 NM 2-2-72
SAMPLE NUMBER AND POSITION:
1-70 IN 2; 1-79 IN 4; 2-79 IN 6; REFERENCE IN 8; 3-79 IN 10;
1-91 IN 12; 3-91 IN 14

POS	AV	S	S/AV	PERCENT T
1	.2001700E 01	.4388E-03	.2192E-03	
2	.6413441E 00	.3256E-03	.5077E-03	
3	.2001230E 01	.4320E-03	.2159E-03	32.044
4	.6528346E 00	.4804E-03	.7359E-03	
5	.2001040E 01	.4254E-03	.2126E-03	32.623
6	.4221110E 00	.2293E-03	.5432E-03	
7	.2000995E 01	.3041E-03	.1520E-03	21.095
8	.6560142E 00	.3189E-03	.4861E-03	
9	.2001402E 01	.4476E-03	.2236E-03	32.781
10	.2358762E 00	.1425E-03	.6039E-03	
11	.2001539E 01	.4114E-03	.2055E-03	11.785
12	.6739426E 00	.2848E-03	.4226E-03	
13	.2001205E 01	.4678E-03	.2338E-03	33.674
14	.2386761E 00	.1064E-03	.4456E-03	
15	.2001101E 01	.4150E-03	.2074E-03	11.927
1	.2001622E 01	.3187E-03	.1592E-03	
2	.6412983E 00	.1321E-03	.2060E-03	
3	.2002043E 01	.6139E-03	.3067E-03	32.036
4	.6526482E 00	.2474E-03	.3790E-03	
5	.2001551E 01	.4756E-03	.2376E-03	32.603
6	.4222282E 00	.2174E-03	.5149E-03	
7	.2001507E 01	.4355E-03	.2176E-03	21.095
8	.6562004E 00	.3344E-03	.5095E-03	
9	.2001529E 01	.5337E-03	.2667E-03	32.785
10	.2339933E 00	.1866E-03	.7979E-03	
11	.2001634E 01	.4532E-03	.2264E-03	11.790
12	.6741099E 00	.3418E-03	.5070E-03	
13	.2001589E 01	.6368E-03	.3182E-03	33.678
14	.2386828E 00	.1604E-03	.6720E-03	
15	.2001829E 01	.3388E-03	.1693E-03	11.924
1	.2002214E 01	.2826E-03	.1412E-03	
2	.6413472E 00	.3518E-03	.5486E-03	
3	.2001882E 01	.3882E-03	.1939E-03	32.035
4	.6526177E 00	.2513E-03	.3851E-03	
5	.2001741E 01	.3841E-03	.1919E-03	32.601
6	.4223418E 00	.2957E-03	.7000E-03	
7	.2002075E 01	.4892E-03	.2443E-03	21.097
8	.6562083E 00	.1365E-03	.2081E-03	
9	.2001871E 01	.3708E-03	.1852E-03	32.778
10	.2358786E 00	.1596E-03	.6767E-03	
11	.2002130E 01	.5036E-03	.2515E-03	11.762
12	.6740563E 00	.3022E-03	.4484E-03	
13	.2001997E 01	.4545E-03	.2270E-03	33.668
14	.2386354E 00	.1704E-03	.7133E-03	
15	.2002478E 01	.2975E-03	.1485E-03	11.928

FIGURE 15. Computer data presentation.

deviation, and sample position number to identify the measurement. When transmittance measurements are made on individual samples or when linearity checks are performed, the readings are initiated manually for every position. When the seven sample holder is used for sequential measurements, the operation is performed automatically by the computer. It is programmed to take a predetermined number of individual DVM readings (50), print the arithmetic average, followed by the standard deviation, relative standard deviation, percent transmittance and sample position (fig. 15). At the conclusion of each measurement, the computer initiates a signal which rotates the holder to the next position. This is followed by the data taking and sample changing sequence until the measurements are stopped manually or automatically by a provision made in the computer program.

The programming of the entire computer operation was developed by J. Aronson, R. Freemire, and J. Wing. The computer-instrument interfacing was performed by F. Ruegg and R. Shideler of the NBS Analytical Chemistry Division, Technical Service Group, under the supervision of J. DeVoe.

III. Stability of the Electronic System

As a rule, before taking measurements with the spectrophotometer, a warmup period of one hour is required. The room temperature is kept at 24 ± 1 °C, and the relative humidity is 35 percent. The particulate matter is controlled through special filters which rates the room in the 100,000 class.

The dark current of the photomultiplier tube was measured by taking 15 replications each consisting of the average of 50 individual digital voltmeter readings. These measurements were made using 850 V at the anode. The average dark current under these circumstances produced 0.000682 V with a relative standard deviation of 0.71 percent.

In all of our work, a dark current buck-out arrangement was used. A series of measurements were performed to determine the stability of this dark current compensation. To this effect, 15 consecutive measurements, each representing the average of 50 indi-

vidual digital voltmeter readings, were made and the average dark current value was 0.000024 V with a relative standard deviation of 23.1 percent.

Four tests were made to determine the stability of the electronic system and the radiation source using the computer data acquisition mode.

a. Stability of the Current-to-Voltage Converter. A constant voltage was supplied to the converter using the dark current compensation provided on the unit. Fifty individual measurements were taken every 5 seconds and the average value was printed along with its percent standard deviation. The measurements were then repeated 15 times and an average of the 15 values was calculated along with the corresponding percent standard deviation. These measurements were then repeated three times. The results are summarized in table 1. This table also presents the values for the first group and the average values and corresponding percent standard deviation for the two consecutive groups. It can be seen from the stability of the current-to-voltage unit that measurements can be performed with a reproducibility of about 0.0012 (at the 67% confidence level) expressed as percent standard deviation for a single determination. The time interval between the first and last group of measurements was 15 min.

TABLE 1. Stability of the current-to-voltage converter alone measured in three groups of 15 replications each

Replication	Average of 50 individual measurements; volts	Percent standard deviation
1	1.003494	0.0013_6
2	1.003496	0.0012_9
3	1.003482	0.0014_6
4	1.003507	0.0011_1
5	1.003515	0.0013_4
6	1.003508	0.0013_6
7	1.003497	0.0011_8
8	1.003498	0.0013_3
9	1.003505	0.0011_0
10	1.003510	0.0014_2
11	1.003518	0.0013_3
12	1.003521	0.0012_0
13	1.003522	0.0013_1
14	1.003507	0.0012_6
15	1.003527	0.0013_7
Average of replications	1.003507	First group
Percent standard deviation	0.0012	First group
Average of replications	1.003535	Second group
Percent standard deviation	0.0015	Second group
Average of replications	1.003545	Third group
Percent standard deviation	0.0010	Third group

b. Stability of the Current-to-Voltage Converter Plus the Photomultiplier Tube Supplied with 850 V and in Total Darkness. The measurements were made as previously described and the results are presented in table 2.

c. Stability of the Current-to-Voltage Converter and the Photomultiplier Tube Supplied with 850 V and Exposed to the Radiation of a Tritium Activated Fluorescence Source. A constant radiation source consisting of a tritium activated phosphor was placed before the integrating sphere and a series of measurements were taken following the technique described above. Table 3 shows the results.

d. Stability of the Current-to-Voltage Converter, the Photomultiplier Tube Supplied with 850 V, and the Tungsten Ribbon Filament Lamp. The same measuring procedure as mentioned in a, b, and c was used here. In this case, however, the incandescent tungsten lamp was used as the source of radiation. Table 4 summarizes the results of four groups of measurements over a period of 20 min. This last series of measurements indicate that the single-beam spectrophotometer is capable of producing measurements of radiation fluxes with a percent standard deviation of about 0.022_5 for single measurements with 2.00 V at the photomultiplier tube anode.

TABLE 2. Stability of the current-to-voltage converter and the photomultiplier tube at 850 V in total darkness

Replication	Average of 50 individual measurements; volts	Percent standard deviation
1	1.012329	0.027_1
2	1.012342	0.048_8
3	1.012322	0.027_2
4	1.012320	0.033_8
5	1.012394	0.043_5
6	1.012421	0.015_3
7	1.012404	0.018_4
8	1.012406	0.029_6
9	1.012365	0.019_6
10	1.012402	0.019_1
11	1.012465	0.025_2
12	1.012412	0.061_5
13	1.012451	0.023_5
14	1.012417	0.029_8
15	1.012481	0.024_8
Average of replications	1.012395	First group
Percent standard deviation	0.0050	
Average of replications	1.012467	Second group
Percent standard deviation	0.0033	
Average of replications	1.012510	Third group
Percent standard deviation	0.0035	

In these measurements the stability of the direct current (nominal 5 V; 14 A) supplied to the tungsten ribbon lamp was monitored with the potentiometer, and the variation of this current was less than one part in 10^5 during a series of 15 consecutive measurements (5 min).

Following the four stability tests discussed earlier, a consecutive series of six measurements were made to determine the reproducibility of transmittance measurements. To this effect seven Schott NC–4 neutral glass filters were placed in the automatic sample carrying system and the data acquisition and sample changing operations were performed automatically through the computer unit. As mentioned previously, the sample carrying system can accept seven samples in positions 2; 4; 6; 8; 10; 12; 14, and eight intermediate positions 1; 3; 5; 7; 9; 11; 13; 15. The odd numbers correspond to measurements of the nonattenuated radiation beam passing through air and are marked I_0, while the even numbers correspond to measurements of the attenuated radiations after passing through the absorbing material and are marked I. The uncorrected transmittance, T, is then

$$T=\frac{I}{I_0}.$$

The radiation flux from the tungsten ribbon filament lamp was attenuated with the circular neutral wedge until a photocurrent corresponding to about 2.0020 V was obtained for the nonattenuated beam I_0. The photomultiplier tube was supplied with 850 V and the 30 MΩ resistor was used at the current-to-voltage converter. For every position, 50 digital voltmeter readings were taken by the computer at a rate of 10 to 15 per second. The average value was printed along with the sample position, the standard deviation, the relative standard deviation, and the transmittance values for the glass filters 2; 4; 6; 8; 10; 12; and 14:

$$T_2=\frac{I_2}{\frac{I_1^0+I_3^0}{2}};\quad T_4=\frac{I_4}{\frac{I_3^0+I_5^0}{2}};\quad T_6=\frac{I_6}{\frac{I_5^0+I_7^0}{2}};\ \text{etc. . . .}$$

until the seven glass filters were measured. This sequence was repeated six times and the results are given in table 5.

As can be seen from these data, the reproducibility of sequential transmittance measurements can be performed with an average standard deviation of 0.010 percent for a single determination.

IV. Wavelength Calibration

The wavelength scale of the monochromator is provided with a counter which indicates wavelength directly in ångstroms. This counter is checked for

TABLE 3. Stability of the current-to-voltage converter and the photomultiplier tube at 850 V and exposed to the radiation of a tritium activated fluorescent source

Replication	Average of 50 individual measurements; volts	Percent standard deviation
1	1.536345	0.027_5
2	1.536326	0.030_2
3	1.536196	0.022_8
4	1.536289	0.023_5
5	1.536106	0.030_9
6	1.536117	0.031_4
7	1.535916	0.025_1
8	1.536065	0.023_8
9	1.536179	0.029_3
10	1.536003	0.023_0
11	1.536083	0.021_5
12	1.535961	0.026_3
13	1.536052	0.031_3
14	1.536095	0.026_6
15	1.536092	0.026_2
Average of replications	1.536122	First group
Percent standard deviation	0.0082	
Average of replications	1.535768	Second group
Percent standard deviation	0.0095	
Average of replications	1.535522	Third group
Percent standard deviation	0.0054	

accuracy with a low pressure mercury discharge lamp placed before the entrance slit of the monochromator. The following wavelengths were used for calibration: 3650.2 Å; 4046.6 Å; 4077.8 Å; 4339.2 Å; 4347.5 Å; 4358.4 Å; 4916.0 Å; 5460.7 Å; 5769.6 Å; and 5790.7 Å. If additional reference wavelengths are needed, a Cd-Hg or a He-discharge lamp could be used for calibration. The wavelength counter was then checked using the procedure recommended by Gibson [2], and a slit of 0.1 mm which is equivalent to an effective spectral bandpass of 0.08 nm. The deviation of the wavelength counter from the true value was found to be less than ± 0.1 nm; hence no wavelength correction was applied to the measurements discussed here.

V. Stray Radiation

Tests were made to determine the stray radiant energy (SRE) in the monochromator proper, as well as in the photometric arrangement. The measurement of stray radiation in the monochromator, that is, the radiation energy at wavelengths different from those of the nominal spectral bandpass transmitted through the instrument, is not easy or infallible. A detailed discussion of this instrumental parameter was given in an ASTM Tentative Method [35] and the procedure recommended in this work was used to determine SRE in the blue and yellow spectral range. In this procedure, a solution of methylene blue, which has a strong absorption in the range from λ 600 to 660 nm is used. The SRE using a slit of 1 mm (0.8 nm) was equal to or less than five parts in 10^5.

The SRE generated inside the photometric system is defined as the radiant energy which falls on the photosensitive detector without passing through the absorbing sample. This SRE is usually produced by reflections and scattering of radiations on the optical and mechanical parts located between the exit slit of the monochromator and the integrating sphere. The measurements were performed using a slit of 1 mm by placing a front surface mirror at the sample position, which reflects to the instrument all radiations received from the exit slit imaged at the mirror surface. The size of this image was about 8 mm high and 1 mm wide. In this way, a maximum SRE was generated in the spectrophotometer. The measurements were then performed at λ 577.3 nm, using a radiation flux intensity five times greater than that used in routine transmittance measurements, by determining the dark current of the photomultiplier with the shutter in the closed position at the integration sphere. An average dark current of 0.040 mV was observed. The mirror was then placed at the sample position, the shutter

TABLE 4. Stability of the current-to-voltage converter, the photomultiplier tube at 850 V, and the tungsten ribbon filament lamp

Replication	Average of 50 individual measurements; volts	Percent standard deviation
1	2.002395	0.038_0
2	2.001356	0.022_6
3	2.002145	0.024_7
4	2.000975	0.026_2
5	2.001944	0.020_7
6	2.000925	0.028_1
7	2.001832	0.026_1
8	2.000825	0.023_5
9	2.001551	0.026_3
10	2.000960	0.021_2
11	2.001739	0.023_1
12	2.000851	0.024_4
13	2.001729	0.028_2
14	2.000825	0.023_0
15	2.001557	0.024_4
Average of replications	2.001441	First group
Percent standard deviation	0.026	First group
Average of replications	2.001517	Second group
Percent standard deviation	0.012	Second group
Average of replications	2.000826	Third group
Percent standard deviation	0.025	Third group
Average of replications	2.001268	Fourth group
Percent standard deviation	0.027	Fourth group

TABLE 5. Reproducibility of transmittance measurements on seven Schott NG–4 glass filters No. 2; 4; 6; 8; 10; 12; and 14

Replication No.	Percent transmittance						
	2	4	6	8	10	12	14
1	33.327	21.711	12.236	50.990	33.377	20.906	13.473
2	33.325	21.710	12.237	50.983	33.377	20.903	13.471
3	33.321	21.711	12.241	50.992	33.383	20.900	13.474
4	33.320	21.708	12.240	50.988	33.375	20.901	13.470
5	33.323	21.710	12.239	50.983	33.379	20.901	13.474
6	33.325	21.710	12.238	50.986	33.377	20.904	13.470
Average	33.32	21.710	12.238	50.987	33.378	20.902	13.472
Percent σ	0.0080	0.0051	0.0150	0.0072	0.0083	0.0108	0.0141
Average percent σ				0.010			

was opened and measurements were made again. The average value found was 0.037 mV. This indicated that no SRE could be detected under the experimental circumstances.

VI. Linearity Control

The single-beam static optical system described in this work permits the unequivocal use of the radiation

addition principle by means of the double-aperture method for determining departure from linearity of the entire optical, photometric, and electronic system, and thus of the photometric accuracy of transmittance measurements.

The double-aperture and its positioning on the optical bench was described earlier. Its use will now be illustrated, and follows the procedure developed and used at the National Physical Laboratory.

Since the linearity of photometric data for a given photomultiplier tube depends on the anode voltage, the values at the current-to-voltage converter, and the ambient temperature, all measurements were made using identical experimental conditions. These same conditions were maintained when transmittance measurements were performed. Since the linearity is, within 1 part in 10^4, not usually a function of wavelength [36], all measurements were performed at λ 565.0 nm. A recent study of this parameter at NBS by Mielenz and Eckerle indicates that there may be a relation between wavelength and linearity at the level of 1 part in 10^5 [38].

The intensity of the radiation flux produced by the tungsten ribbon lamp was attenuated with the circular neutral wedge until a photocurrent equivalent to 2.0020 V was obtained when both apertures, A and B, were open. A setting of 850 V was used at the photomultiplier tube with a 30 MΩ resistor at the current-to-voltage converter. Fifty individual DVM readings were taken and the average value for $(A+B)$ was printed. Aperture B was then closed, and 50 DVM readings were taken. The average value for aperture A was printed. The average value for aperture B was then obtained in a similar manner by closing aperture A and opening aperture B. This sequence was repeated three times, ending with an $(A+B)$ value.

Identical measurements were made over a range of attenuation corresponding to 4 cascaded steps of 2 to 1 as illustrated in the actual example which follows:

Step 1	$(A+B)$	A	B
	2.0014_7	1.0159_6	0.9864_1
	2.0015_6	1.0159_9	0.9864_0
	2.0020_6	1.0160_9	0.9862_5
	2.0021_1	$1.01598 + 0.98635 = 2.00233$	
Av.	2.00181		
Diff.	$2.00233 - 2.00181 = +0.00052$		
% Corr.	$= -0.026$		

Step 2	$(A+B)$	A	B
	1.0004_9	0.5102_0	0.4910_8
	1.0007_8	0.5099_6	0.4909_1
	1.0006_6	0.5100_4	0.4911_5
	1.0009_0	$0.51007 + 0.49105 = 1.00112$	
Av.	1.00071		
Diff.	$1.00112 - 1.00071 = +0.00041$		
% Corr.	$= -0.041$		

Step 3	$(A+B)$	A	B
	0.5006_2	0.2565_7	0.2443_0
	0.5005_6	0.2567_3	0.2443_6
	0.5007_0	0.2566_5	0.2443_2
	0.5006_2	$0.25665 + 0.24433 = 0.50098$	
Av.	0.50063		
Diff.	$0.50098 - 0.50063 = +0.00035$		
% Corr.	$= -0.069$		

Step 4	$(A+B)$	A	B
	0.2502_0	0.1287_2	0.1217_5
	0.2502_8	0.1285_6	0.1216_8
	0.2501_9	0.1285_4	0.1216_6
	0.2502_3	$0.12861 + 0.12170 = 0.25031$	
Av.	0.25023		
Diff.	$0.25031 - 0.25023 = +0.00008$		
% Corr.	$= -0.031$		

The correction curve is established from these data by plotting voltages on the abscissa and the corresponding additive correction value on the ordinate. These are tabulated below and illustrated in figure 16.

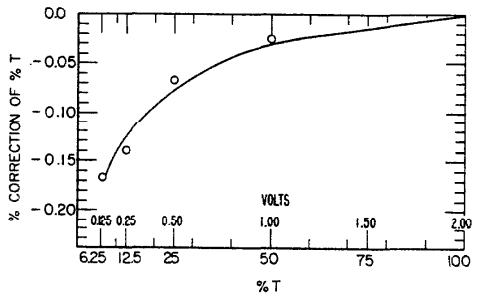

FIGURE 16. Linearity correction curve.

Voltage	% T	% Correction of % T
2.00	100	0.0
1.00	50	0.026
0.50	25	0.067
0.25	12.5	0.14
0.125	6.25	0.167

When transmittance measurements are performed, the I_0 reading is initially set with the circular neutral wedge to a value near 2.0020 V. The I value is then measured. If the initial $I_0 = 2.00214$ V and final $I_0 = 2.0022_8$ V and $I = 0.54220$ V, then percent T is:

$$\frac{0.54220}{\frac{2.00214 + 2.00228}{2}} \times 100 = 27.081$$

which is the noncorrected value. To correct this value, one takes from the ordinate of figure 16 the value corresponding to 0.54220 on the abscissa which, in this case, is 0.072. The corrected percent T value is then:

$$27.081 - \left(\frac{27.081 \times 0.072}{100}\right) = 27.061.$$

Mielenz and Eckerle have studied recently the louble aperture method for testing photometric inearity, and have used a curve-fitting procedure ior finding the nonlinearity correction rather than the method described earlier (38).

VII. Sample Position

A series of measurements were performed to determine the magnitude of error which could occur when the sample is oriented with its entrance face at an angle to the incoming radiation beam. The single sample holder provided with the rotating table, as described in section II, paragraph c, was used. Transmittance measurements were performed by producing the image of the exit slit of the monochromator at the entrance face of the sample (aperture f:10). The data are shown in table 6. The consequence of this condition on transmittance measurements is discussed by Mielenz in this Journal.

TABLE 6. Percent transmittance (*%T*), measured on three neutral glass filters 1.0; 1.5; and 2.0 mm thick at $\lambda = 440$ nm, at three angles of incidence

Angle of incidence	Filter 1.0 mm	Filter 1.5 mm	Filter 2.0 mm
Normal incidence	32.91_5	19.83_8	11.60_6
1°	32.89_9	19.83_3	11.60_4
2°	32.89_7	19.81_9	11.59_9
3°	32.88_1	19.81_2	11.58_9

Similar measurements were made to determine the identity of positions on the seven-sample automatic changer described in section II, paragraph c. For this experiment, seven neutral glass filters A; B; C; D; E; F; and G were used and were positioned in holders 2; 4; 6; 8; 10; 12; and 14 in three different arrangements as described by Garfinkel, Mann and Youden [39].

TABLE 7. Evaluation of the identity of the seven stations of the automatic sample changer

Percent Transmittance (*%T*) at station number (St. No.) 2; 4; 6; 8; 10; 12; and 14 for filters A, B, C, D, E, F, and G at $\lambda = 465.0$ nm

Run No.		A	B	C	D	E	F	G
I	*%T*	27.08	16.44	46.39	26.12	15.22	37.34	23.23
	St. No.	2	4	6	8	10	12	14
II	*%T*	27.07	16.40	46.39	26.11	15.21	37.34	23.23
	St. No.	14	2	4	6	8	10	12
III	*%T*	27.08	16.43	46.39	26.11	15.21	37.33	23.23
	St. No.	10	12	14	2	4	6	8

Transmittance measurements were then performed on all filters for the three different arrangements and the results are given in table 7. From these data it can be concluded that the seven stations are interchangeable and will produce measurements which will not differ by more than one part in one thousand.

VIII. Influence of Polarized Radiations on Transmittance Measurements

This effect was determined by measuring the transmittance of a Schott NG–4 neutral glass filter at four wavelengths using radiations emerging from the predisperser-monochromator unit, and by projecting the image of the exit slit (8 by 0.5 mm) at the entrance face of the filter with a convergent beam geometry corresponding to an f:10 opening. The glass filter was checked prior to measurements with a polariscope for freedom of internal tensions. Column one of table 8 shows the results obtained when transmittance measurements were made using the radiations produced by the spectrophotometer. Column two shows the results obtained when a polarizing sheet, with the vibration plane horizontal, was placed in front of the glass filter. The measurements obtained with the vibration plane in vertical position, are given in column three.

These measurements show that polarized radiations can affect transmittance measurements of solid glass filters when noncollimated beam geometry is used. This effect is predicted by the Fresnel equations mentioned in the introduction and should disappear when collimated radiations are used (1, pg. 100).

XI. Comparison of Transmittance Measurements

Two sets of solid filters were used in a comparative test to determine the reproducibility of transmittance measurements between two laboratories. One set was made from three neutral glass Schott NG–4 filters having nominal percent transmittances of 10; 20; and 30. The second set was made as described elsewhere [4]. Three evaporated metal (Inconel) on fused quartz (nonfluorescent) plates having nominal percent

TABLE 8. Effect of polarization on percent transmittance (%T) measured at four wavelengths on a Schott NG–4 glass filter

Wavelength nm	%T			% Difference
	Produced by spectrophotometer	Polarizer, plane of vibration horizontal	Polarizer, plane of vibration vertical	$\%T_1 - \%T_3$
	1	2	3	
440.0	19.81_8	19.80_0	19.78_8	− 0.15
465.0	22.59_7	22.60_0	22.56_9	− 0.12
590.0	19.17_8	19.17_0	19.09_9	− 0.41
635.0	20.61_1	20.60_2	20.54_7	− 0.31

transmittances of 25; 50; and 75 were used. The transmittance measurements were performed on two sets of filters at the National Physical Laboratory (NPL) in England using their high accuracy spectrophotometer, and at NBS on the instrument described in this paper. The measurements at NBS were carried out before and after the measurements at NPL. All measurements were made with noncollimated convergent beam geometry. A rectangular surface of the filter about 3 mm by 8 mm was used at NPL and the beam was only slightly convergent. At NBS an area about 8 mm by 0.5 mm was used for the transmittance measurements.

The results given in table 9 indicate that an average difference of −0.19 percent of the values was obtained between the measurements carried out at NPL and at NBS. An average difference of −0.30 percent of the value was found when similar measurements were performed on the inconel-on-quartz filters, as shown in table 10.

X. Standard Reference Materials for Spectrophotometry

The need for providing means and materials to check the proper functioning of a spectrophotometer was discussed in some detail in previous publications [3, 4]. At that time it was established that the accuracy of the photometric scale is a critical and most demanding parameter in spectrophotometry. Hence, particular attention was given to a number of ways for checking this parameter. Investigations showed that solid colored glass filters, exhibiting optical neutrality over the spectral range from 400.0 nm to 700.0 nm, would constitute an acceptable Standard Reference Material (SRM). From the various colored glass filters available, Schott NG–4 "neutral glass" was selected, prepared and characterized. It is now offered by NBS as a means to check the photometric scale of spectrophotometers.

TABLE 9. Comparison between the percent transmittances (%T) measured on three Schott NG–4 glass filters at NPL and NBS

Wavelength nm	NBS, %T March 12, 1971	NBS, %T May 18, 1971	NBS, %T average	NPL, %T February 1971	% Diff. NBS to NPL
440.0	12.92	12.91	12.91_5	12.93	− 0.11
465.0	14.96_5	14.98	14.97_3	15.01	− 0.25
590.0	11.70	11.64	11.67	11.67	0.0
635.0	12.72	12.68	12.70	12.72	− 0.16
440.0	19.62_5	19.58	19.60_3	19.62	− 0.09
465.0	22.38_5	22.35	22.36_7	22.43	− 0.28
590.0	19.06	18.95	19.00_5	19.01	− 0.03
635.0	20.45_5	20.37	20.41_3	20.47	− 0.23
440.0	32.89	32.86	32.87_5	32.98	− 0.32
465.0	35.52	35.54	35.53	35.66	− 0.36
590.0	31.16_5	31.10	31.13_3	31.21	− 0.25
635.0	32.56_5	32.52	32.54_3	32.62	− 0.24

Average difference between NBS and NPL percent T values = − 0.19 percent.

TABLE 10. Comparison between the percent transmittances (%T) measured on three inconel-on-silica filters at NPL and NBS

Wavelength nm	NBS, %T 1	NBS, %T 2	NBS, %T average	NPL, %T	% Diff. NBS to NPL
450.0	24.87	24.88	24.87_5	24.93	− 0.18
550.0	23.78	23.82	23.80	23.86	− 0.25
650.0	23.38	23.39	23.38_5	23.46	− 0.32
450.0	49.35	49.33	49.34	49.56	− 0.44*
550.0	47.60	47.60	47.60	47.81	− 0.44
650.0	46.85	46.85	46.85	47.14	− 0.64
450.0	72.17	72.20	72.18_5	72.30	− 0.16
550.0	72.05	72.11	72.08	72.20	− 0.17
650.0	72.20	72.34	72.27	72.33	− 0.08

Average difference between NBS and NPL percent T values = − 0.30 percent.

*This filter had a flaw in the form of a crack which was sometimes visible and other times invisible. The larger differences found in the measurements of this filter may be due to this flaw.

SRM 930, developed in the Analytical Chemistry Division and available since March 1971 consists of three glass filters. Each filter bears an identification number, and the upper left corner has been removed to indicate correct orientation in the metal holder (fig. 17).

The transmittance measurements were made with the high accuracy spectrophotometer described in this paper, and are certified with an uncertainty of ±0.5 percent of the value. This uncertainty is the sum of the random errors of ±0.1 percent (2SD limit) and of estimated biases which are ±0.4 percent. These biases are due to possible systematic errors originating principally from the inherent inhomogeneity and instability of the glass as well as from positioning of the filter. Measurements were made at 24 °C, and variations within several degrees Celsius of this temperature will not significantly affect the calibration of the filters. The neutral NG−4 glass for the filters was provided by Schott of Mainz, Germany and is designated as "Jena Colored and Filter Glass." Nominal transmittance for a filter 1.5 mm thick is 20 percent at 400.0 nm wavelength and 32 percent at 700.0 nm wavelength. Between these limits the transmittance varies in a monotonic manner.

The filter is held in a frame and the size and shape of the filters and frames were selected, for practical considerations, to conform to the dimensions of the standardized cuvettes for which holders are supplied in most conventional spectrophotometers. The filters are approximately 1.0, 1.5, and 2.0 mm thick. Corresponding to these thicknesses are nominal transmittances of 30, 20, and 10 percent, respectively. These thicknesses were selected to provide a means for calibrating the photometric scale at three different levels.

The effective spectral bandpasses used to determine the certified values were equal to or smaller than 2.2 nm at 440.0 nm; 2.7 nm at 465.0 nm; 5.4 nm at 590.0 nm; and 6.0 nm at 635.0 nm. The transmittance measurements are made by producing the image of the slit (about 8 mm by 0.5 mm) using a convergent beam geometry with an opening of f:10 corresponding to an angle of 7° to 8° in the middle of the entrance face of the filter. This beam geometry was used to reproduce the average experimental conditions found in most of the conventional spectrophotometers available today. Prior to the certification, each filter is examined for surface defects and thoroughly cleaned. If, through handling, the surface of the filter becomes contaminated, it may be cleaned with a small soft brush attached to a rubber tube connected to a vacuum source [40]. If contamination results from fingerprints, they must be removed before making measurements. This may be accomplished by removing the filter from its holder, breathing lightly on it, and rubbing the surface gently with optical lens tissue. The clean filter is then properly positioned in its holder. To remove and replace the filter in the holder, the spring-loaded plate should be lifted with care to prevent damage to the filter. As little handling as possible is recommended. SRM 930 should be used according to the directions on the certificate; consult the manufacturer of the instrument if differences are obtained that exceed those specified by the manufacturer.

Under no circumstances should other cleaning procedures which make use of detergent solutions, organic solvents, etc. be applied.

When a filter has become contaminated beyond cleaning by the procedure described in the certificate, it should be forwarded to NBS. After proper cleaning, the filters will be checked and, if needed,

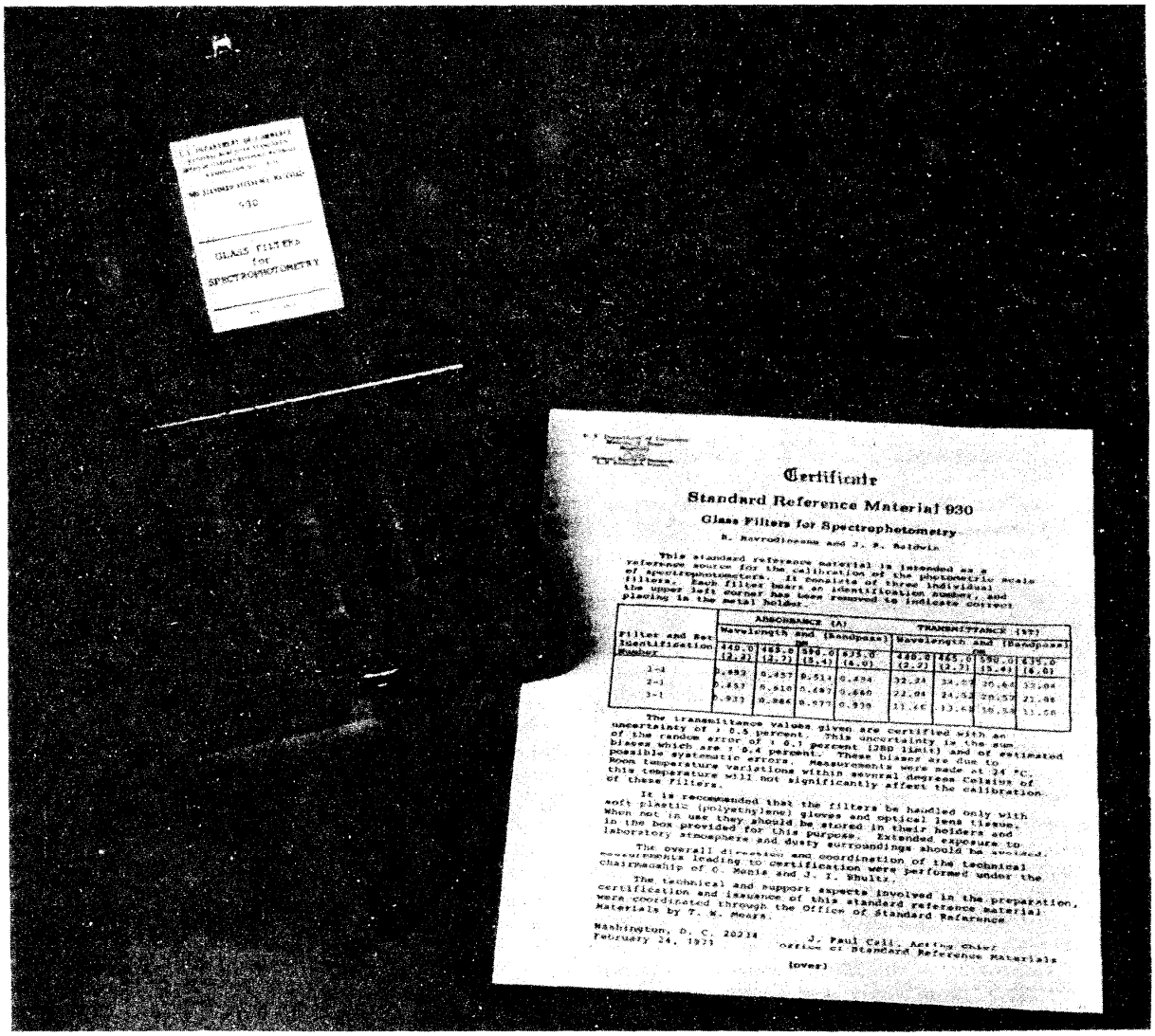

FIGURE 17. NBS Standard Reference Material 930 and calibration certificate.

recalibrated using the high accuracy spectrophotometer described in this work.

It was already stated that the accuracy of photometric scales defines only one of the parameters required for obtaining accurate transmittance values and molar absorptivities. Other factors must also be established. These are wavelength accuracy, adequate spectral bandpass, stray light, cell parameters (when solutions are measured), fluorescence, polarization, reflection, and temperature coefficient. Some of these variables were discussed in NBS Technical Notes 544 and 584 and are also examined in this paper.

The transmittance data given in the certificate which accompanies each SRM 930 depend not only on the intrinsic properties of the glass and the experimental measurement conditions, but on the surface state of the glass. This parameter varies with time and exposure conditions. When glass is exposed to normal room atmosphere and temperature, its surface is corroded to an extent depending on the composition, time of exposure, concentration, temperature and nature of the glass surface acting agents. This action produces a change in the reflecting and transmitting properties of the material [41]. For instance, a well-known phenomenon called "blooming" of the glass is due to the formation of an SiO layer at the surface of the glass. This layer, which increases the transmittance, acts as an antireflection coating. The speed with which such a layer is formed varies with the composition of the glass, the atmosphere and time. Generally speaking, several years are needed for a fresh surface to reach equilibrium. This, and similar

phenomena are presently being studied, along with means to stabilize the surface state of glass filters. Until more information is acquired in this field, we recommend that the colored glass filters issued as SRM 930 be rechecked annually to determine whether any physicochemical changes, which might affect the transmittance values, have occurred.

Another important factor is the need for defining and producing a clean glass surface. Until now the final cleaning of the NG–4 filters was made with redistilled ethyl alcohol and pure water (thermally distilled and deionized). Other cleaning procedures are under consideration. The use of isopropyl alcohol in vapor or liquid form associated with mild ultrasonic action is being investigated [41].

The transmittance characteristics of the SRM 930 limit the use of this material to the visible region of the spectrum from about 400 nm to the near infrared. Since the ultraviolet region, from about 200 nm is also important to the analyst who uses spectrophotometric methods, exploratory work is underway to select and certify solid material for checking the photometric scale in this spectral region. Optical filters exhibiting small transmittance-wavelength dependence in the spectral range 200 nm to near infrared can be obtained by evaporating thin semitransparent layer of a metal on a suitable transparent substrate [42, 4], and such filters have been considered in this work. The metals selected were inconel and chromium which exhibit adequate transmission characteristics and good adhesion to the substrate. The substrate was nonfluorescent fused quartz. A series of filters were prepared by the optical shop at NBS according to the following specifications: a number of nonfluorescent optical quality fused quartz plates, 10 mm × 25 mm and 1 mm thick, were cut and polished, Inconel or chromium metal was evaporated on the surface to produce nominal transmittances of 25, 50, and 75 percent. The surface bearing the evaporated metal was coated with a layer of optical cement which was transparent to the visible and ultraviolet radiations down to 230 nm. A clear plate of the same material was used to cover and protect the evaporated metal layer.

The filter assembly was then marked at one corner to insure its proper positioning and the finished filter was placed in a metal holder of conventional size (approximate o.d. 13 x 13 x 57 mm) fitting the cuvette holder found in most spectrophotometers. The metal holder was also marked at one side to permit positioning of the filter in a reproducible manner.

In addition to the evaporated metal filters, a number of units were prepared using only the clear uncoated fused quartz plates and assembled with the same optical cement. When desired, these clear filter assemblies could be used as reference samples in the blank compartment.

Before submitting the evaporated metal filters to transmittance measurements, a study was made of the effect of radiations on their transmittances. A filter was exposed to an accelerated test in which radiations had the same spectral distribution as the fluorescent lighting of the laboratory, except that they were 1000 times more intense. The filter was exposed for an equivalent of 36,000 hours of continuous irradiation. This test was made on a radiation accelerator made available by the Building Research Division of NBS. The percent transmittance was measured before and after the exposure and gave the following results:

	Transmittance, percent			
Wavelength, nm	250	380	500	650
Before exposure	44.48	51.35	48.90	47.41
After exposure	44.11	51.34	48.92	47.47

The relative standard deviation for a single determination of these measurements was 0.01 percent. As can be seen, the only significant relative change in transmittance of about 0.84 percent of the value occurred at 250 nm.

Several sets of these filters were calibrated at five selected wavelengths, 250 nm; 350 nm; 450 nm; 550 nm; and 650 nm, using the cleaning and measuring procedures outlined for Schott NG–4 colored glass neutral filters. The results indicated that the reproducibility of transmittance measurements is good (percent standard deviation 0.009 to 0.024) and is comparable to those obtained for the colored glass filters at all wavelengths except 250 nm. From the experimental data, it is evident that the transmittance of the evaporated metal filter at 250 nm is critical and, at present, no satisfactory explanation for this phenomenon can be given. A limitation of the evaporated metal filters is that they attenuate the intensity of radiation by *reflecting* a part of it, rather than absorbing. This can produce, in certain circumstances, undesirable stray light in the instrument and make the transmission measurements dependent on the geometry of the optical beam. However, since these filters are closer to optical neutrality than the colored glass filters, and since they can be used in the ultraviolet region as well, they were included in this work.

This limitation was apparent from the data obtained in a cooperative study conducted at C. Zeiss by A. Reule using conventional spectrophotometers. On the other hand, a similar comparative test, made on the same filters by F. J. J. Clarke at NPL has produced the results presented in table 10. One can observe that, in spite of the limitations mentioned above, an agreement within −0.30 percent of the value was obtained between NBS and NPL measurements at the indicated wavelength.

Further studies will be needed to assess unambiguously the transmittance characteristics of evaporated metal-on-quartz filters, with or without a protective quartz plate, and to assess their suitability as Standard Reference Materials to check the photometric scale of spectrophotometers in the ultraviolet and visible part of the spectrum.

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XI. Addendum

The identification of commercial instruments and products, is given in the Addendum only to permit reproduction of the work described in this paper. In no instances does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the particular equipment or product is necessarily the best available for the purpose.

Radiation source for visible—Microscope lamps, type 18A/T10/1P–6V: General Electric Co., Lamp Division, Nela Park, Cleveland, Ohio 44112. For ultraviolet: Atlas single coil halogen (Bromine) lamp, type P1/8, 30V, 250W: GTE Sylvania, Inc., 6610 Electronic Drive, Springfield, Virginia 22151.

Power supply for microscope lamp, Kepco, Model JQE 15–50–M–VP: Kepco, Inc., 131–38 Sanford Avenue, Flushing, New York 11352. For tungsten-halogen single filament lamp: same manufacturer, Model JQE–36–30 Mt–VP.

Potentiometer: Leeds and Northrup Model K3 with null meter and power supply. Resistors: Leeds and Northrup 0.1, 50 A and 0.01, 100 A: Leeds and Northrup, Sumneytown Pike, North Wales, Pa. 19454.

Nonfluorescent fused silica: Dynasil Corporation of America, Berlin, New Jersey 08009.

Neutral Density Attenuator and $BaSO_4$ white paint: Eastman Kodak Co., Special Products Sales, Kodak Apparatus Division, Elmgrove Plant, Rochester, New York 14650.

Monochromator with predisperser: McPherson Instrument Corp., 530 Main Street, Acton, Massachusetts 01720.

Optical benches with carriers and $x-y$ sample holder with micrometer control: Gaertner Scientific Corp., 1201 Wrightwood Ave., Chicago, Illinois 60614.

Lens holders: Ardel Instrument Co., Inc., P. O. Box 992, Jamaica, New York 11431.

Ball bushing and rails: Thompson Industries, Inc., Manhasset, New York 11030.

Pneumatic cylinders and accessories: Clippard Instrument Laboratory, Inc., Cincinnati, Ohio 45239.

Rotating table: Ealing Optics Division, 2225 Massachusetts Avenue, Cambridge, Massachusetts 02140.

Thermostating holders for glass cells and glass filters: Cary Instruments, 2724 South Peck Road, Monrovia, California 91016.

Pneumatic ratchet system: Allenair Corp., P. O. Box 350, 255 East 2nd Street, Mineola, New York 11501.

Black paint—Nextel 101–c 10 Black: Reflective Products Division 3M, 2501 Hudson Road, St. Paul, Minnesota 55101.

Photomultiplier tube EMI–9558QA: Gencom Division, 80 Express Street, Plainview, New York 11803.

Power supply for photomultiplier tube: Model 415B and digital voltmeter 8400A: John Fluke Manufacturing Co., P.O. 7428, Seattle, Washington 98133.

Thermal insulation: Photoshroud, Shumway Optical Instruments Corp., 2118 Beechgrove Place, Utica, New York 13501.

Vibration isolation table: Lansing Research Co., 705 Willow Avenue, Ithaca, New York 14850.

Low power laser; Model 195 cw gas laser, output power 2 mw: Optics Technology, Inc., 901 California Avenue, Palo Alto, California 94304.

Tritium activated fluorescent source, Beta light Marker HM–110: Canrad Precision Industries, Inc., 630 Fifth Avenue, New York, New York 10020.

Colored glass neutral filters, Schott NG–4: Fish-Schurmann Corp., 70 Portman Road, New Rochelle, New York 10802.

Spectral lamp: Oriel Optics Corp., 1 Market Street, Stamford, Connecticut 06902.

Polarization filters: Polaroid Corp., 119 Windsor Street, Cambridge, Massachusetts 02139.

Computer: 24K memory and 16 bit words. EMR computer, Division of Weston Instruments, Inc., Schlumberger Co., 8001 Bloomington Freeway, Minneapolis, Minnesota 55420.

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(Paper 76A5–729)

Appendix 3

January 1955

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C. 20234

Letter Circular LC-1017

Re-issued January 1967

STANDARDS FOR CHECKING THE CALIBRATION OF SPECTROPHOTOMETERS (200 to 1000 nm)

Contents

1. Introduction.

In continuation of a type of activity carried on for many years at the National Bureau of Standards, there is described in this letter circular the various types of standards that are available for issuance by the Bureau for the purpose of checking or maintaining the over-all reliability of spectrophotometers in the ultraviolet, visible and near-infrared regions of the spectrum. Certain other information of similar purpose is also included.

Experience has shown that spectrophotometers can easily get out of adjustment. Although repeated trials may give the same values over and over again, indicating high sensitivity and precision, and the instrument may otherwise appear to be functioning perfectly, gross errors in wavelength may nevertheless be rendering the values obtained highly unreliable. Other causes of error may likewise be present and unsuspected, particularly with the photoelectric spectrophotometers now comprising so large a percentage of the total in use. The use of the various standards described herein has been found of considerable assistance in detecting and eliminating errors that would otherwise be present, or in confirming that the instrument is in fact giving reliable results.

Reference is made in this letter circular to the NBS test fee schedules currently in effect. Those relating to spectrophotometry are designated as 202.105, Spectrophotometric Standards, and 202.106, Spectrophotometric Measurements. These schedules are obtainable from the National Bureau of Standards.

2. Checking the Wavelength Scale.

Most of the present-day spectrophotometers have a direct-reading wavelength scale; that is, the scale, instead of being divided in uniform linear or circular measure, is divided and engraved directly in nanometers (formerly called millimicrons). This greatly facilitates setting the instrument at any desired wavelength. The accuracy of many of these direct-reading wavelength scales is remarkably good, when put in the best average adjustment, considering the difficulties of quantity production of such scales. When so adjusted, it is not uncommon to find them in error by not more than 1 nm throughout the ultraviolet and visible spectrum. However, if one wishes the uncertainties in his wavelength settings to be of the order of 0.1 nm, a careful check of these direct-reading scales is necessary.

Certain sources and wavelengths that have proved especially suitable for the calibration of various types of spectrophotometers are listed in tables 1a and 1b which are similar in scope and purpose to table 1 of Circular 484 (1)*.

*Numbers in parentheses refer to the References.

All values of tables 1a and 1b are consistent with those published in the M.I.T. wavelength tables (2). Which of these sources to use, and which wavelengths of the several sources are the most suitable, will depend on the type of instrument. Furthermore, the procedure will vary importantly depending on whether the instrument is a non-recording or a recording spectrophotometer.

Table 1a. Wavelengths of Sources Suitable for Calibration of Spectrophotometers.

Wavelength (nm)	Note	Wavelength (nm)	Note	Wavelength (nm)	Note	Wavelength (nm)	Note
Mercury Arc in Quartz (Same wavelengths in glass above 300 nm)							
205.29		253.48	3*	296.73	*	398.40	
222.47		253.65		302.15	6*	400.63	
223.41		257.63		302.35		404.66	*
225.88		260.32		302.56		407.78	*
230.21		265.20	4*	302.75		435.83	*
232.32		265.37		312.57	*	491.60	
235.25		265.51		313.15	7*	546.07	*
237.83	*	269.95		313.18		576.96	9*
239.94	1*	275.28	*	334.15	*	579.07	
239.97		275.97		349.28		623.44	
244.69		280.35	5*	365.01	8*	671.62	
246.41		280.45		365.48		690.72	
248.20		284.78		366.29		1014.0	*
248.27	2*	289.36	*	366.33		1128.7	
248.38		292.54		390.64			
Helium Discharge Tube in Glass							
318.77		396.47		447.15	*	667.81	*
361.36		402.62		471.31	*	706.52	*
363.42		412.08		492.19		728.13	
370.50		414.38		501.57	*	1083.0	*
381.96		438.79		504.77			
388.86	*	443.75		587.56	*		

* These lines have been found most useful on the Beckman DU spectrophotometer.

1. A value of 239.95 is recommended for the unresolved pair.
2. A value of 248.3 is recommended when the 3 lines are unresolved.
3. The intensity of 253.48 is negligible compared to that of 253.65. The latter value should be used when the lines are unresolved.
4. The 265.20 line is somewhat stronger than the others and a value of 265.3 is recommended when the three lines are unresolved.
5. These two lines are of approximately the same intensity and a value of 280.40 is recommended for the unresolved pair.
6. The two shorter lines are considerably stronger than the other two. It is probable that a value of 302.25 should be used for the unresolved lines.
7. A value of 313.16 is recommended for the unresolved pair.
8. With the arc used on the Beckman DU spectrophotometer the ratio of intensities for 365.01 : 365.48 : 366.33 is 100 : 48 : 36, approximately. The intensity of the 366.29 line appears negligible relative to that of 366.33.
9. These two lines are of approximately the same intensity and a value of 578.0 is recommended for the unresolved pair.

Table 1b. Wavelengths of Sources Suitable for Calibration of Spectrophotometers

Neon Discharge Tube		Aluminum Spark in Air	Hydrogen Arc
Wavelength (nm)	Relative Intensity	Wavelength (nm)	Wavelength (nm)
585.25	5	216.88	434,05
588.19	4	217.40	486.13
594.48	8	220.46	656.28
597.55	2	221.00	
603.00	2	226.35	
607.43	8	226.91	Sodium Arc
609.62	13	236.71	Wavelength
614.31	25	237.21	(nm)
616.36	6	237.31	589.00
621.73	4	237.34	589.59
626.65	11	237.84	
630.48	4	256.80	
633.44	20	257.51	Cesium Arc
638.30	23	257.54	Wavelength
640.22	100	263.16	(nm)
650.65	39	265.25	852.11
653.29	8	266.04	894.35
659.90	12	281.62	
667.83	23	308.22	
671.70	14	309.27	
692.95	23	358.69	
702.41	2	394.40	
703.24	45	396.15	
705.91	--		
717.39	5		
724.52	17		
743.89	4		
748.89	--		
753.89	--		
754.40	--		

2.1 Non-Recording Spectrophotometers.

The best procedure for checking the wavelength scale of a non-recording spectrophotometer is by direct use of a source of radiant energy having spectral lines of suitable intensity and adequately spaced throughout the spectral range of interest. Various sources are available and can be recommended for such purpose. How many sources, or how many wavelengths, to use in such a calibration depends, of course, on the desires of the individual investigator.

In this connection it should be noted that the number of significant figures of importance in spectrophotometry (including "absorption spectroscopy") is of a different order of magnitude than that used in emission spectroscopy or in standard wavelength tables. In the visible spectrum with the usual type of spectrophotometer it seems impossible to maintain the wavelength calibration with uncertainties less than about 0.1 nm. While the uncertainty may be less in the ultraviolet with a prism instrument, there seems no purpose served in giving standard wavelengths to better than 0.01 nm for spectrophotometric calibration.

Two suitable sources for wavelength calibration are the mercury lamp and the helium lamp. A mercury lamp in a quartz envelope is by far the best single source for wavelength calibration from 205 to 1014 nm. A mercury lamp in a glass envelope provides the same spectral lines except that below about 300 nm they are not transmitted by the glass envelope.

The helium lines are especially well placed for wavelength calibration in the visible spectrum, and the strong lines at 388 and 1083 nm are also often very useful. Many other sources, flame or arc, are available for visual wavelength calibration (2, 3) but most of these are too unstable for accurate calibration with a photoelectric detector.

These same sources and many others are also useful for the wavelength calibration of spectrographs used in photographic spectrophotometry. Between 200 and 400 nm the series of doublets obtained from the aluminum spark in air is very useful because they are so readily recognized.

Not all of the lines for any of the sources are given in tables 1a and 1b but only those that are considered especially suitable for the purpose. Furthermore, not even all of those listed for any one source may be suitable for any one particular instrument. The mercury arc in quartz is an example. All of the lines listed (and still others) can be used for wavelength calibration of a photographic spectrophotometer over the range of sensitivity of the plate used. The lines from 404.7 to 690.7 nm can be used for visual calibration of a spectrophotometer. But not all of the lines are suitable for calibration of a photoelectric instrument, and those that prove adequate will depend on the sensitivity and slit widths characteristic of any particular instrument. One must be very careful that other lines are not included, in addition to the one on which the settings are supposedly being made, of sufficient intensity to affect the wavelength setting.

Special attention should perhaps be called to the use of a cesium arc at 852.1 and 894.3 nm (4). From tables 1a and 1b it is apparent that there are few suitable lines between 706.5 and 1014.0 nm, particularly from steady sources necessary or desirable in the calibration of photoelectric spectrophotometers. The neon discharge tube gives many lines between 750 and 1000 nm (2) but these have not been found satisfactory in the calibration of photoelectric spectrophotometers. In the orange and red the neon lines are useful for visual calibration and many of these can be used to calibrate photoelectric spectrophotometers (5) if the sensitivity is such that very narrow slits can be used. The relative intensities (6) given in table 1b will help in case of overlapping.

The best technique to use in wavelength calibration of non-recording spectrophotometers, given a suitable source, will vary from instrument to instrument and method to method. A few general principles can be given here, however.

In photographic spectrophotometry it usually is sufficient to photograph a known spectrum at the top and bottom of the plate, unless the source used for the absorption spectra itself carries such known reference lines. A few of these reference lines will then serve to correlate that particular plate with whatever complete calibration curve has previously been established by more extensive measurements with the various sources.

On visual and photoelectric non-recording spectrophotometers, it usually is necessary, for highest precision, to have a basic reference line to which all of the other wavelengths are compared by direct check. At the Bureau the Hg yellow lines have proved most suitable for the König-Martens visual spectrophotometer (7). At the slit widths used the overlapping of the two lines gives a central brighter "line" taken as 578.0 nm with a luminous background against which the slit jaws are readily seen. A luminous background, or slight illumination of the ocular slit, always facilitates calibration when an eyepiece is used. Visual calibration without an eyepiece is usually less precise unless very narrow slits are used.

Two techniques have been used at the Bureau in the calibration of non-recording photoelectric spectrophotometers. On the Gibson spectrophotometer (8) the slits are always 0.1 mm wide or greater and the most reliable calibration is obtained by plotting galvanometer deflections at closely adjacent wavelengths. The most probably value for the wavelength reading is given by the intersection of the two straight lines resulting from a plot of the data for any given line, the correction being given by the difference between this value and the true wavelength. This is illustrated in reference (1).

On the Beckman DU spectrophotometer the same method has been used (9), but at the Bureau it has seemed preferable and is much more rapid, to calibrate with a narrow slit and record the wavelength dial reading for the maximum left deflection of the galvanometer needle as the wavelength dial is slowly turned. The most suitable reference line on two of the Bureau's instruments has proved to be the Hg green line at 546.07 nm (5).

2.2 Recording Spectrophotometers.

The initial wavelength calibration of a recording spectrophotometer, such as the manufacturer must carry out in connection with cutting his cams or preparing his reading scale, is not here considered, but only the check of such a calibration by the user of the instrument.

Such a user can, of course, follow the procedure prescribed above for checking the wavelength calibration of non-recording spectrophotometers. However, there are two important reasons for following a different procedure for recording spectrophotometers. For such instruments it is desirable to have a calibration that is made with the instrument operating. It is further desirable in most kinds of work to have this calibration appear on the graph sheet so that difficulties connected with positioning of the sheet, expansion or contraction of the paper with humidity or temperature, or instrumental variations can be eliminated.

Wavelength calibrations of this kind can be made if a material is available having a number of strong and narrow absorption or transmission bands suitably spaced over the spectral range of interest. Two materials have been used or suggested for this purpose: (a) Glasses containing rare-earth oxides, such as didymium glasses and holmium oxide glasses, have been used for many years at the National Bureau of Standards (10, 11), (b) quartz-Polaroid combinations have been proposed (12) and may prove useful for such work.

The use of a didymium glass or a holmium oxide glass in this manner would not in general be accurate unless it is calibrated at nearly the same slit widths as are to be used. Most of the absorption bands that are usable for the purpose are multiple bands and the wavelengths of maximum absorption often depend on the slit widths. This has been illustrated in previous publications (1, 10).

While the use of a didymium glass or a holmium oxide glass for checking the wavelength calibrations of a recording spectrophotometer is highly recommended, there are two other uses of these glasses which are not recommended. First, these glasses are not well suited for checking the photometric scale of any spectrophotometer, recording or non-recording. Transmittances at the peaks of the absorption bands are too dependent on slit widths, and transmittances on the steep parts of the curve are too dependent on slight wavelength errors, both as illustrated in Fig. 1 of reference (10) and in Fig. 8 of reference (1). Second, the use of these glasses to check the wavelength calibration of a non-recording spectro-

photometer is considered much inferior from the standpoints of time, convenience and reliability to the direct use of line sources as described in Sec. 2.1. The National Bureau of Standards has consistently refused to accept didymium glasses or holmium oxide glasses for calibration for either of these two purposes.

2.2.1. General Electric Recording Spectrophotometer.

The NBS didymium glass standards were carefully calibrated by point-by-point measurements on the König-Martens visual and Gibson photoelectric spectrophotometers with slit widths approximating the 10- and 20- nanometer slits used on the NBS General Electric spectrophotometer. Some of these values have been published (13).

The most suitable didymium glass for the purpose, considering type of curve and availability, is a Corning 5120 glass of 3.0 mm thickness. While it is not known how much the wavelengths of maximum absorption of this 5120 glass might vary from melt to melt, glasses from at least three melts have been measured, and there has never been any certain variation among the samples tested. For much work it is probably safe to use the values given in table 2.

Table 2. Wavelengths of maximum absorption for Corning 5120 glasses of 3.0 mm thickness as obtained at the National Bureau of Standards for the slit widths indicated.

Wavelength of Maximum Absorption (nm)	Approximate Spectrum Interval Transmitted by Slits (nm)
441.0	10
475.5	10
528.7	10
585.0	10
684.8	10
743.5	10
745.	20
808.	20
883.	20
1067.	20

For those who wish greater certainty, however, the Bureau has obtained a supply of Corning 5120 glass in 2-inch polished squares and of 3.0 mm thickness. These are measured and the values reported in accordance with NBS test fee schedule 202.105, items d to f. The measurements consist of recording a curve of the test glass on the same sheet as the curve of the NBS standard glass and deriving values of the wavelengths of minimum transmittance of the former relative to

those of the latter. The over-all uncertainties of the values so reported are considered to be not greater than ±1 nm from 441.0 nm to 743.5 nm, and not greater than ± 2 nm from 745 to 1067 nm.

Methods of use of a calibrated didymium glass on a G. E. recording spectrophotometer are described in references (1), (10), and (13).

2.2.2. Cary Model 14 recording spectrophotometer.

The NBS holmium oxide glass standards were carefully calibrated by using a Cary Model 14 recording spectrophotometer, the wavelength indicating dial of which had previously been calibrated by means of a number of sources having wavelengths throughout the ultraviolet and visible spectral regions. Measurements of the wavelengths of minimum transmittance were made as functions of slit width over the range 0.06 to 5.0 nanometers of spectral width. Eleven sharp absorption bands were found to be sufficiently symmetrical that the wavelengths of minimum transmittance indicated by the recorder remained constant for slit widths up to about 2 nanometers.

The most suitable holmium oxide glass for the purpose is a Corning 3130 glass of approximately 2.5 mm thickness. It is not known how much the wavelengths of minimum transmittance of this 3130 glass might very from melt to melt. It is known that, for some 3130 glasses, the absorption of the base glass prevents the use of the glass for wavelength calibration in the ultraviolet near 241 nanometers. For much work it is probably safe to use the values given in the following table.

Wavelengths of minimum transmittance for Corning 3130 glasses of 2.5 mm thickness as obtained at the National Bureau of Standards for slit widths less than 2 nm.

Useful wavelengths between 240 and 370 nm	Useful wavelengths between 360 and 650 nm
241.5	360.8
279.3	385.8
287.6	418.5
333.8	453.4
360.8	459.9
	536.4
	637.5

For those who require that the base glass of the standard transmit sufficiently for the standard to be useful at 241 nanometers, the Bureau has obtained a supply of Corning 3130 glass in 2-inch polished squares and of 2.5 mm thickness. These are measured and the values reported in accordance with NBS test fee schedule 202.105, items g to i.

The measurements consist of recording a curve of the test glass on the same sheet as the curve of the NBS standard glass and deriving values of the wavelengths of minimum transmittance of the former relative to those of the latter. The over-all uncertainties of the values so reported are considered to be not greater than $\pm$ 0.5 nm. The present supply of holmium oxide glass contains striae, and in some cases strains, which have not appreciably altered the wavelengths of minimum transmittance.

The methods of use of a calibrated holmium oxide glass on a Cary Model 14 recording spectrophotometer are similar to those described in references (1), (10), and (13) relating to the method of use of a didymium glass on a G. E. recording spectrophotometer.

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Appendix 4

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Spectral Transmittance Characteristics of Holmium Oxide in Perchloric Acid Solution

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The work describes the methods and procedures used to determine the wavelengths of minimum transmittance of holmium oxide in perchloric acid solution. Measurements of spectral transmittance of the solutions were made by means of a high precision spectrophotometer over the wavelength range 200 nm to 680 nm. The wavelength scale accuracy of this instrument was verified by extensive measurements of mercury and deuterium emission lines. The measurements of spectral transmittance of the holmium oxide solutions were made as a function of temperature, purity, concentration, and spectral bandwidth. Analysis of the uncertainties associated with these parameters and the uncertainties associated with the calibration of the instrument wavelength scale and the data analysis have resulted in an estimated uncertainty of ±0.1 nm for the determination of the wavelengths of minimum transmittance of the holmium oxide solution.

Key words: holmium oxide; spectral bandwidth; spectrophotometer calibration; spectral transmittance; wavelength calibration; wavelength standard.

1. Introduction

This work describes the methods and procedures used to determine the wavelengths of minimum spectral transmittance of holmium oxide (Ho_2O_3) in perchloric acid ($HClO_4$) solution in the spectral region 200 to 680 nm. The object of this activity was to develop a standard for verifying the wavelength scale of uv/visible spectrophotometers, and to provide assistance toward improving the accuracy of measurements in the fields of molecular absorption spectrometry or spectrophotometry [1][1].

Holmium oxide in a glass matrix has been issued by the National Bureau of Standards (NBS) as a wavelength standard for the ultraviolet and visible spectrum since 1961 [2]. Didymium glass wavelength standards have been issued since 1945. The didymium glass wavelength standards are available from NBS as Standard Reference Material 2009; 2010; 2013; and 2014 [3].

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2. Experimental

2.1 Instrumentation

Measurements of spectral transmittance of the holmium oxide solutions were made by means of a Varian Cary Model 2390 recording spectrophotometer[2].

[1]Numbers in brackets indicate literature references.

[2]Certain commercial equipment or products are mentioned in this paper in order to adequately document the work. In no case does this imply that the equipment or product is being endorsed by NBS or that it is necessarily the best equipment or product for the application.

The optical system of this double beam instrument consists of a filter predisperser and a double-pass double-sided grating monochromator. A deuterium lamp is used over the wavelength range 185 to 340 nm and a tungsten-halogen lamp is used over the wavelength range 340 to 3150 nm as a source. The spectral bandwidths are selectable from 0.07 nm to 3.6 nm. Data can be recorded by a digital readout system with thermal printer and an analog chart display.

2.2 Materials

2.2.1 Holmium Oxide

The holmium oxide solutions were prepared by dissolving the powder in a 10% perchloric acid in distilled water. The purity of the holmium oxide specimens used in the preparation of these solutions was indicated by the manufacturer [4] to be 99.99% (Lot No. Ho-0-4-007) and 99.999% (Lot No. Ho-0-5-007). Solutions were prepared with 2%, 4%, and 6% holmium oxide. These solutions were placed in 10 mm pathlength nonfluorescent fused silica cuvettes.

The actual form in which Ho is formed when Ho_2O_3 is dissolved in $HClO_4$ is that of an aquo ion of the general formula $Ho(H_2O)_n^{3}+$. The term "holmium oxide" and the spectral transmittances reported in the manuscript refer to this chemical species. Aqueous solutions of perchloric acid are used in this study to dissolve Ho_2O_3 since the resulting aquo ion is least likely to form complexes when subjected to changes in temperature and concentration [5].

The holmium oxide powder is stated by the manufacturer to have an average particle size of about 2 micrometers. The perchloric acid was a nominal 70-72% reagent grade (considered here as 100%). The distilled water was produced by thermal distillation. The aqueous solutions of holmium oxide in 10% perchloric acid were prepared by weighing 2, 4, or 6 g of the oxide and adding 10 mL of distilled water and 10 mL of perchloric acid. The holmium oxide was dissolved by heating at about 80 °C for one hour. The clear solution was transferred quantitatively to a 100 mL volumetric flask and was brought to volume with distilled water at room temperature.

2.2.2 Cells

The cells used for the transmission measurements of the holmium oxide solutions were conventional nonfluorescent, fused silica, cuvettes with a nominal pathlength of 10 mm. These cuvettes were provided with graded quartz-to-pyrex tubes with rubber caps.

2.3 Measurement Techniques

2.3.1 Calibration of the Spectrophotometer Wavelength Scale

The spectophotometer wavelength scale error was evaluated by measuring the emission spectrum of the instrument's deuterium lamp and the emission spectrum of a mercury pen lamp [6,7,8].

The wavelength calibration was performed at the beginning of the holmium oxide solution measurements and again at the completion of the measurements. A number of emission lines of mercury and two emission lines of deuterium were used over the wavelength range 230 nm to 690 nm (see fig. 1). The wavelength scale errors were determined for spectral bandwidths of 0.1 nm, 1 nm, 2 nm, and 3 nm.

Each emission line was scanned at a rate of 0.01 nm per second and recorded on a scale of 0.2 nm per centi-

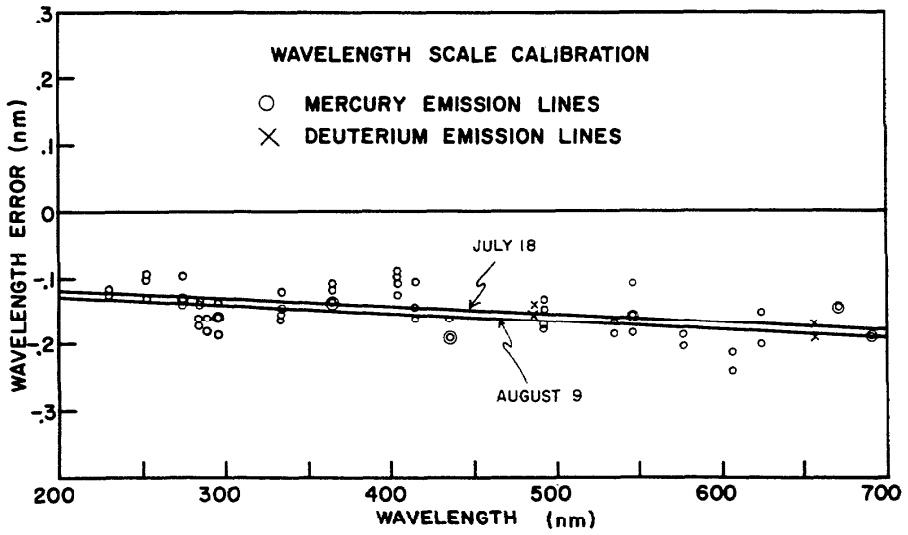


Figure 1-Wavelength scale calibration of the spectrophotometer.

meter. The recorded emission peaks were bisected, using a proportional divider, to determine the wavelengths at the center of the recorded triangular lines. Using this technique, the wavelength scale was read to the nearest 0.01 nm with a precision of ±0.005 nm. The differences between the measured wavelengths of mercury emission lines and the true wavelengths are plotted in figure 1. A linear least squares fit of these wavelength differences for the two dates July 18 and August 9 (also shown in fig. 1) was used to correct the measured values of the holmium oxide transmission minima for errors in the wavelength scale of the instrument.

The wavelength error of the instrument was essentially the same for spectral bandwidths less than 1 nm. However, at spectral bandwidths of 2 nm and 3 nm, the wavelength error was slightly different and a different correction was required.

The deuterium lamp emission lines were measured at two wavelengths each day during the holmium oxide solution characterization to verify the accuracy of the wavelength scale. These measurements showed that the calibration of the wavelength scale is constant to ±0.02 nm after a nominal warm-up of one hour. These results, as well as the repeatability of the calibration with the mercury line source, indicate that the overall stability of the instrument wavelength scale was better than ±0.05 nm during the period of time required to complete the wavelength characterization of the holmium oxide solution.

The mercury pen lamp is mounted in the lamp positioning device that ordinarily holds the deuterium lamp of the spectrophotometer. The arc tube of the mercury pen was aligned parallel to the entrance slit of the monochromator. The lamp holder is equipped with screw adjustments for vertical and horizontal alignment of the source. The entrance slit cannot be directly observed. Therefore, the source was adjusted with instrument operating in the single-beam mode until a maximum signal is observed. To test the effect of the positioning of the mercury line source on the observed emission line maxima, the pen lamp was moved horizontally across the field of view of the entrance slit to the monochromator in approximately 0.22 mm steps for a total of 12 steps or a 2.64 mm distance. The results of this experiment showed that the recorded emission maxima varied by less than ±0.01 nm for lamp positions within ±1 mm of the center position. The center position corresponded to the position of maximum signal.

2.3.2 Confirmation of Spectral Bandwidths

The mercury line source was used to confirm the spectral bandwidth settings of the spectrophotometer. The mercury emission line at 435.8 nm was scanned for spectral bandwidths of 0.1 nm, 0.25 nm, 0.5 nm, 1 nm, 2 nm and 3 nm. The emission peak was normalized to 100% on the chart recorder by adjusting the instrument gain. The bandwidth at half peak height is approximately equal to the spectral bandwidth. The natural bandwidth of the emission line is much less than the instrument bandwidth. The recorded curve has a triangular symmetry for all settings of the monochromator slitwidths. For the above-mentioned nominal spectral bandwidth settings of the spectrophotometer, the measured spectral bandwidths were 0.092 nm, 0.228 nm, 0.468 nm, 1.04 nm, 2.18 nm, and 3.20 nm, respectively. This technique for determining spectral bandwidths has some uncertainties due to assumptions made. However, it serves to confirm that the desired spectral bandwidths are closely approximated when the instrument is programmed to provide those settings; hence the effect on the transmittance minima is negligible.

2.3.3 Determination of the Wavelengths of Minimum Transmittance

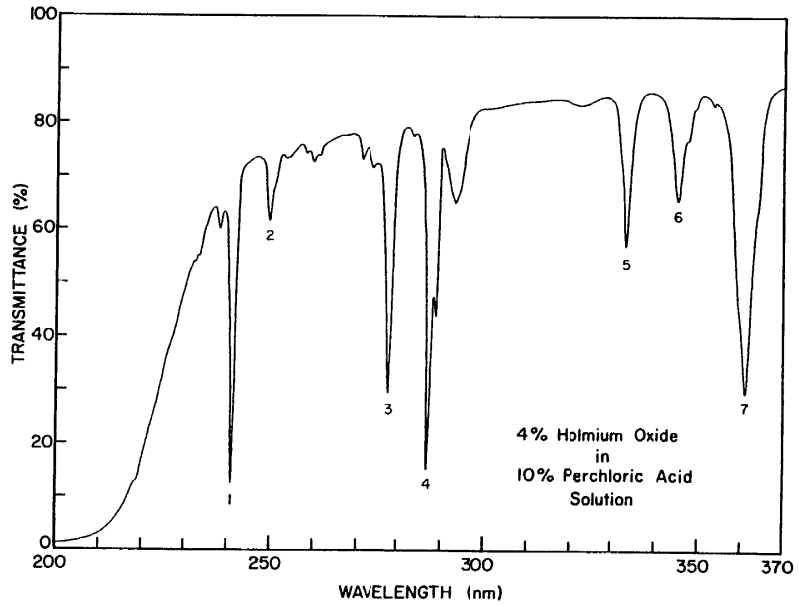
The spectral transmittance of holmium oxide in an aqueous solution of perchloric acid exhibits many absorption bands in the ultraviolet and visible spectrum. The spectrum is shown in figure 2 for a 0.1 nm spectral bandwidth scan. The total number of observed absorption bands varies as a function of the spectral bandwidth used during the recording of the spectrum. There are approximately 14 major absorption features or bands between 200 and 650 nm that can be observed clearly for a wide range of spectral bandwidth settings. Most of the major absorption bands have lesser bands between them or in close association. These smaller bands are better resolved at bandwidths less than 1 nm. Only the major absorption bands that could be of use as possible wavelength standards were selected for detailed study. The various parameters affecting the measured wavelengths of minimum transmittance of the holmium oxide solution are discussed in section 3. These include such parameters as temperature, purity, concentration, and spectral bandwidth.

The spectral transmittance of the holmium oxide solution was digitally recorded on a thermal printer at 0.1 nm intervals with the monochromator scanning at a rate of 0.05 nm/s. The transmittance was simultaneously recorded on a chart with a wavelength display of 0.5 nm/cm.

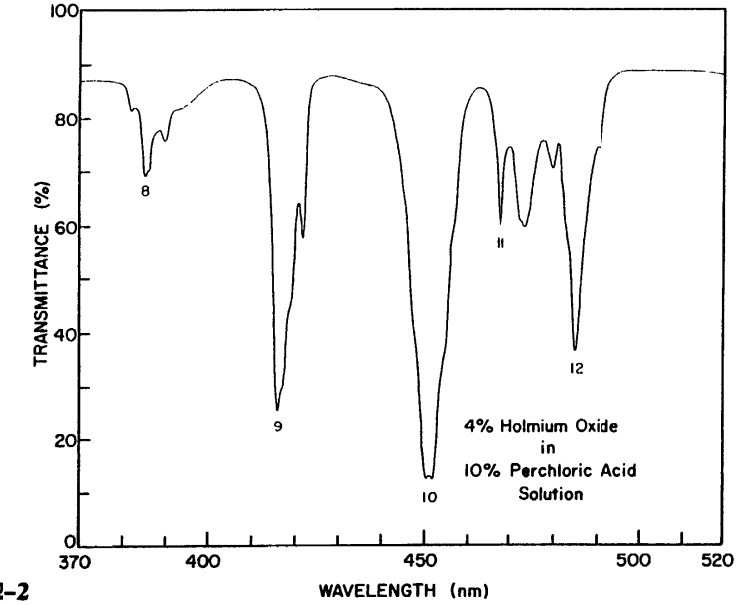
The holmium oxide solution was contained in a 10 mm pathlength fused silica cuvette. The transmittance of the solution in this cuvette was measured relative to an air-only path in the reference beam.

The determination of the wavelengths of the transmittance minimum of the holmium oxide solution was derived from an analysis of the recorded digital output. The 0.1 nm interval transmittance data were plotted on

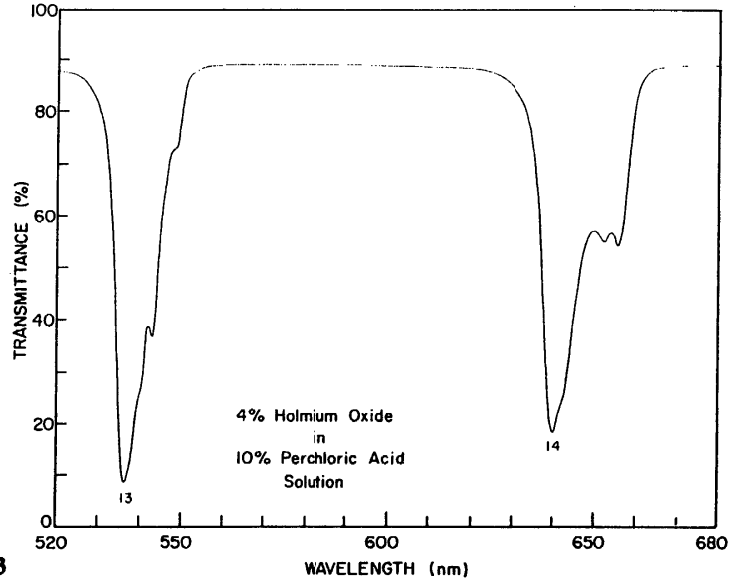
Figure 2–Spectral transmittance of a 4% solution of holmium oxide in 10% perchloric acid in water, beginning at right.



2-1



2-2



2-3

graph paper on a scale of 0.1 nm per cm with subdivisions of 0.01 nm per mm so that the wavelength interval of this plotted digital data could be read to the nearest 0.01 nm between the measured data points. The location of the wavelength of minimum transmittance for a given holmium oxide band was determined graphically (fig. 3) by drawing a curve through the data points and bisecting the horizontal grid lines between the two slopes of the curve representing the absorption feature. Several of these bisection points locate the line between the two slopes that intersects the minimum transmittance point, (usually at the lowest point of the curve). The wavelength at this point of intersection was taken as the measured wavelength of minimum transmittance for the absorption feature. The true wavelength of the minimum was determined by applying a wavelength correction to the instrumental wavelength scale, as determined in section 2.3.1.

2.3.4 Accuracy of the Wavelengths of Minimum Transmittance

The overall uncertainty in the location of the wavelengths of minimum transmittance is believed to be no greater than ±0.1 nm at the 95% confidence limit. This conclusion is based on the reproducibility of the following calibration procedures:

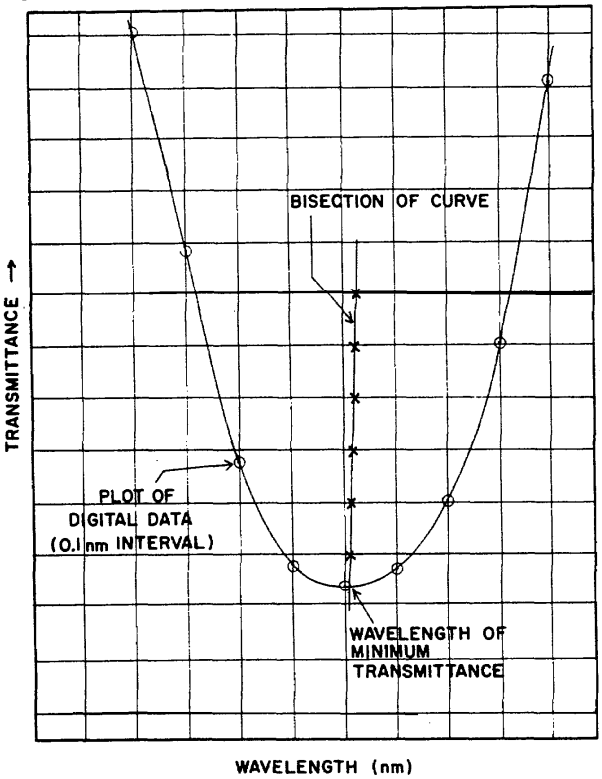


Figure 3–Graphical technique used to determine the transmittance minima from digital spectral transmittance data.

- The uncertainty of the calibration of the instrument wavelength scale using the mercury and deuterium lamps, and the long-term and day-to-day instabilities of the instrument wavelength scale (less than ±0.05 nm).
- The imprecision of the graphical technique for deriving the measured wavelengths of minimum transmittance. (±0.02 nm).
- The dependence of the measured wavelengths of minimum transmittance on variations in temperature or concentration of the solution. (±0.02 nm).

These uncertainties have been discussed in section 2.3.1. The imprecision of the graphical technique is illustrated in table 1, where data are shown for three absorption features. Ten sets of digital results were produced by the instrument for each of these features. The digital data were plotted and the wavelengths of minimum transmittance for each absorption feature were determined for the 10 sets of data by the graphical technique. The standard deviation and standard error for the 10 determinations is also given in table 1.

3. Measurements

3.1 Influence of the Blank Cuvette, Solvent, and Water

The spectral transmittances of an empty fused silica cuvette, a cuvette filled with distilled water, and a

Table 1. Ten cycle repetitive measurements of three holmium oxide transmittance minima. Listed minima are obtained by graphical techniques, using the digitally recorded 0.1 nm interval transmittance measurement.

	(spectral bandwidth=0.1 nm)		
Cycle	Minima No. 1	Minima No. 12	Minima No. 14
1	240.88 nm	485.08 nm	640.28 nm
2	240.87	485.10	640.30
3	240.86	485.11	640.30
4	240.84	485.11	640.30
5	240.85	485.10	640.29
6	240.84	485.11	640.30
7	240.85	485.11	640.29
8	240.85	485.11	640.30
9	240.84	485.10	640.30
10	240.85	485.11	640.29
Average:	240.853	485.104	640.295
Standard Deviation:	0.0134	0.0097	0.0071
Standard Error:	.0042	.0031	.0022

Note: The data shown in this table have not been corrected for the wavelength scale error of the spectrophotometer.

cuvette filled with the diluted perchloric acid (without holmium oxide) are illustrated in figure 4. These measurements are relative to an air path in the reference beam.

Measurements of the wavelength of minimum transmittance for the band at 241 nm were made with the holmium oxide in perchloric acid solution versus a cuvette containing only the perchloric acid in the reference beam. The wavelength of minimum transmittance of this band was found to be the same when the holmium oxide solution was measured relative to air in the reference beam and when it was measured relative to a cuvette containing the perchloric acid solution. Since the 241 nm band is within the spectral range showing a slope in the transmittance of the cuvette–perchloric acid spectra, (see fig. 4) it was considered to be the band most likely to be influenced by this slope. However, no measurable influence was detected in the location of the wavelength of minimum transmittance of this band due to these spectral features associated with the solvent or cuvette.

3.2 Influence of Temperature

The wavelengths of minimum transmittance of the holmium oxide solution were determined at 20 °C, 25 °C, and 30 °C for spectral bandwidths of 0.1 nm and 1 nm. If there is a temperature-related influence on the location of the wavelengths of minimum transmittance, it was not detected within these temperature ranges. The measured differences were attributed to random uncertainties.

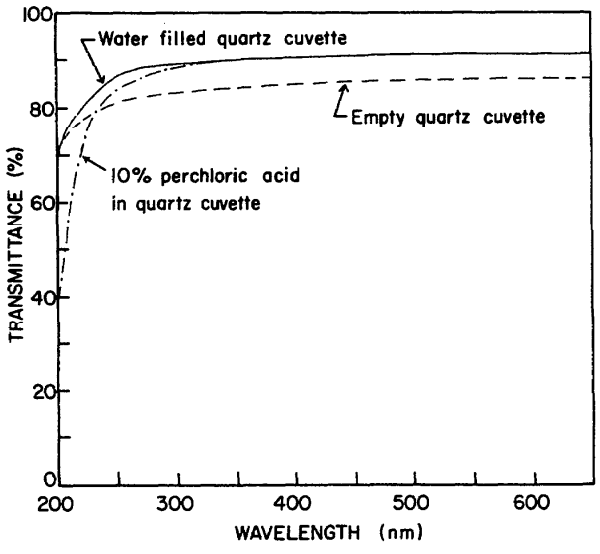


Figure 4–Spectral transmittances of an empty fused silica cuvette, a cuvette filled with water, and a cuvette filled with a solution of 10% perchloric acid in water.

3.3 Influence of Purity

Complete spectral scans of solutions made with the 99.99% and 99.999% purity holmium oxides showed no spectral differences except in the extreme ultraviolet cut-off at wavelengths less than 230 nm. The differences are illustrated in figure 5 for the wavelength range 200 to 300 nm. The wavelengths of the minimum transmittances for the 14 selected absorption bands were found to be the same for solutions prepared from these two lots of holmium oxide.

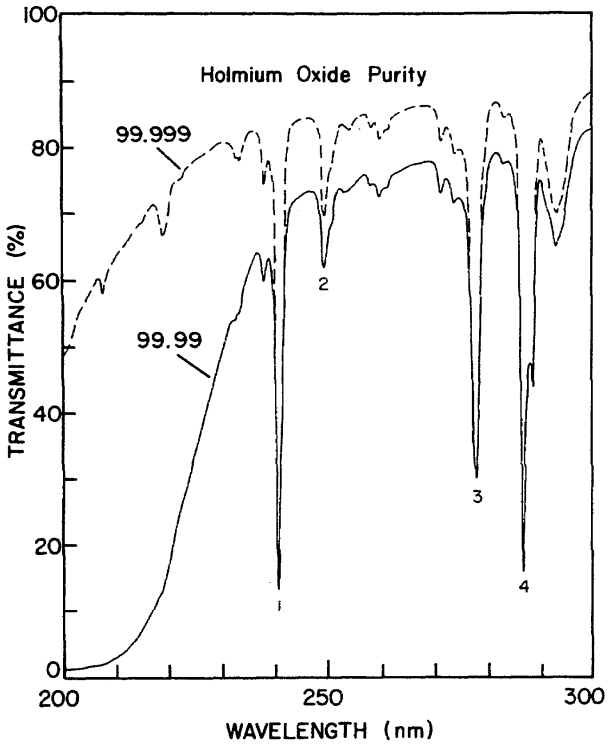


Figure 5–Spectral differences of solutions prepared from holmium oxide specimens of 99.99% purity and 99.999% purity.

3.4 Influence of Concentration

The location of the wavelengths of minimum transmittance of the holmium oxide solution as a function of concentration was tested with concentrations of 2%, 4%, and 6% in the perchloric acid solution. The general spectral scan indicated that the changes in concentration affected the measured transmittance as would be expected but did not influence the location of the transmittance minima. To verify this further, three of the bands were evaluated by the graphical technique described in section 2.3.1. The results of these concentration measurements for these bands are shown in table 2.

Table 2. Influence of holmium oxide concentration on the wavelengths of minimum transmittance.

	(spectral bandwidth=0.1 nm)		
Holmium oxide concentration	Minima No. 1	Minima No. 12	Minima No. 14
2 %	240.84 nm	485.11 nm	640.30 nm
4 %	240.86	485.11	640.32
6 %	240.84	485.12	640.31

Note: The data shown in this table have not been corrected for the wavelength scale error of the spectrophotometer.

3.5 Influence of Spectral Bandwidth

The wavelengths of minimum transmittance of the holmium oxide solution were determined for spectral bandwidths of 0.1 nm, 0.25 nm, 0.5 nm, 1 nm, 2 nm, and 3 nm. Measurement of the instrumental spectral bandwidths is discussed in section 2.3.2. The influence of spectral bandwidth was by far the most important parameter affecting the location of the measured wavelengths of minimum transmittance. The results of this study are shown in figures 6 through 19 for the 14 minima identified in figures 2-1, 2-2, and 2-3. The data for bandwidth effects are also listed in tables 3 and 4. The measurements indicate that for most of the holmium oxide bands, the location of the wavelengths of minimum transmittance does not change significantly for spectral bandwidths of less than 1 nm. From these data it can be seen that a 0.1 nm spectral bandwidth is adequate to define the wavelengths of minimum transmittance within the stated uncertainties. For some bands the location of the minimum transmittance shifts only slightly for spectral bandwidths greater than 1 nm. However, many do show large shifts for larger bandwidth settings. These results indicate that for instruments with spectral bandwidth settings of less than 1 nm, the holmium oxide solution can serve as an excellent wavelength standard. For instruments having bandwidth settings between 1 nm and 3 nm the standard can still be of use if the instrument bandwidth is known.

4. Results

4.1 Transmittance of Holmium Oxide Solution

The general spectral signature of the holmium oxide solution is illustrated in figures 2-1, 2-2, and 2-3 for a spectral bandwidth of 0.1 nm. Some of the finer spectral features shown in these figures will be absent when the spectrum is recorded at bandwidths greater than 1 nm. The major transmittance minima selected for this study are indicated by numbers 1 through 14 as shown in these figures. These band numbers are used throughout the manuscript as a key to associate the data in the tables with the spectral features illustrated in the figures.

4.2 Selection of Useful Wavelengths of Minimum Transmittance

The selection of holmium oxide bands that are considered useful for calibration purposes was based on the influence of spectral bandwidth on the location of these minima. The transmittance minima of small side bands associated with major absorption features usually shift in wavelength with bandwidth setting or are not resolved over the normal instrumental bandwidth range. The 14 major absorption bands are listed in tables 3 and 4. The absorption bands not listed in the tables are not considered useful for wavelength calibration purposes.

4.3 Numerical Data

The wavelengths of minimum transmittance of the 4% holmium oxide solution are listed in tables 3 and 4 for six spectral bandwidths. The results of the measurements as a function of temperature are also listed for 0.1 nm and 1 nm spectral bandwidths at temperature settings of 20 °C, 25 °C, and 30 °C.

The shift in wavelengths of minimum transmittance as a function of spectral bandwidth is shown in figures 6 through 19 for the 14 selected minima. The recommended values of minimum transmittance are listed in table 3 and 4 for the measurements made at 25 °C.

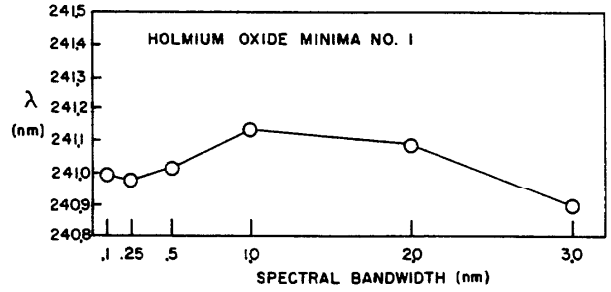
4.4 Uncertainty of Measured Wavelengths

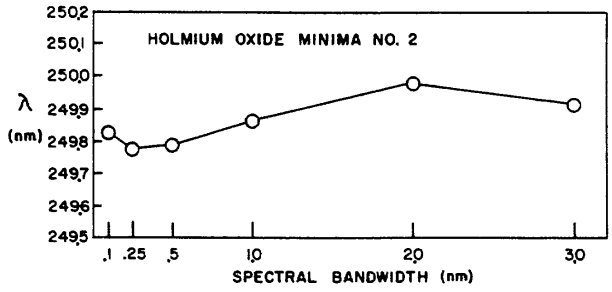
The uncertainties associated with the data listed in tables 3 and 4 have been discussed in section 2.3.4. The uncertainty in the determination of the wavelengths of minimum transmittance for the holmium oxide solution is believed to be no greater than ±0.1 nm at the 95% confidence limit using the instrumentation and techniques described in this paper.

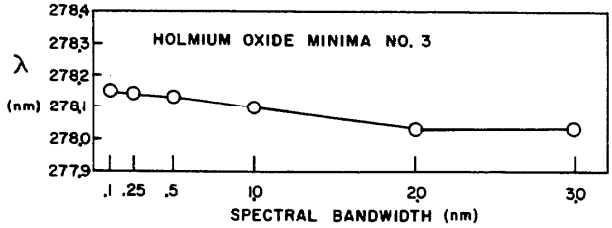
4.5 Comparison of Results with Measurements Made on the NBS Reference Spectrofluorimeter

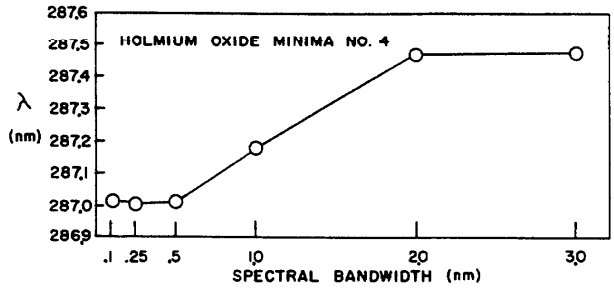
The wavelengths of minimum transmittance of several absorption bands of holmium oxide solution were determined by analysis of spectral data obtained with the NBS Reference Spectrofluorimeter [9]. This reference instrument is primarily designed to be used as a research tool for high accuracy spectral analysis of fluorescent materials and in the development of standards for use in this area of research. The versatile design of the instrument allows for its use as a high accu-

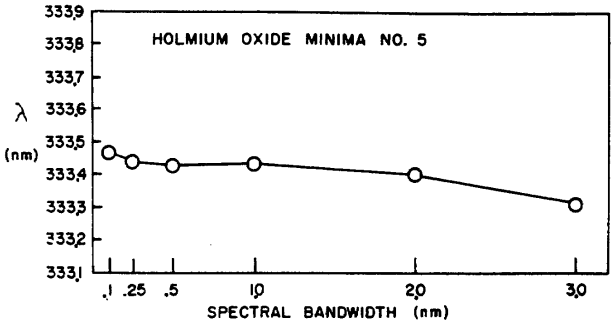
Figures 6-19—Fourteen holmium oxide transmittance minima as a function of spectral bandwidth.

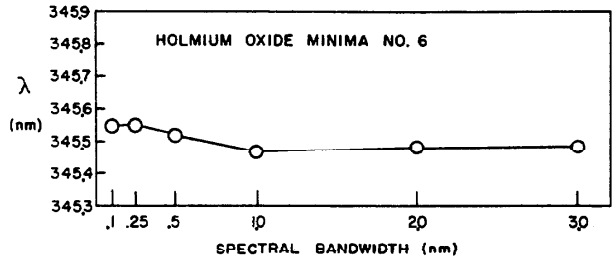


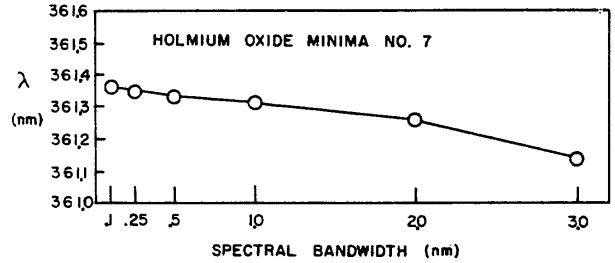


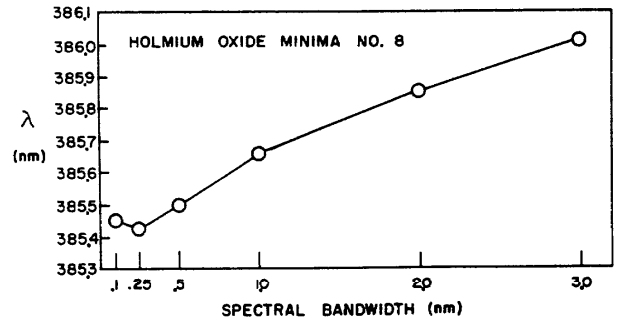


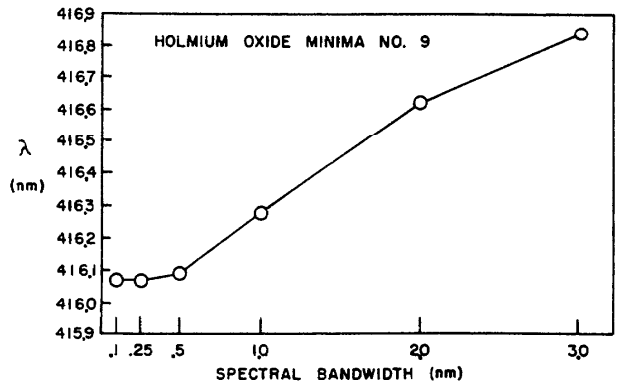












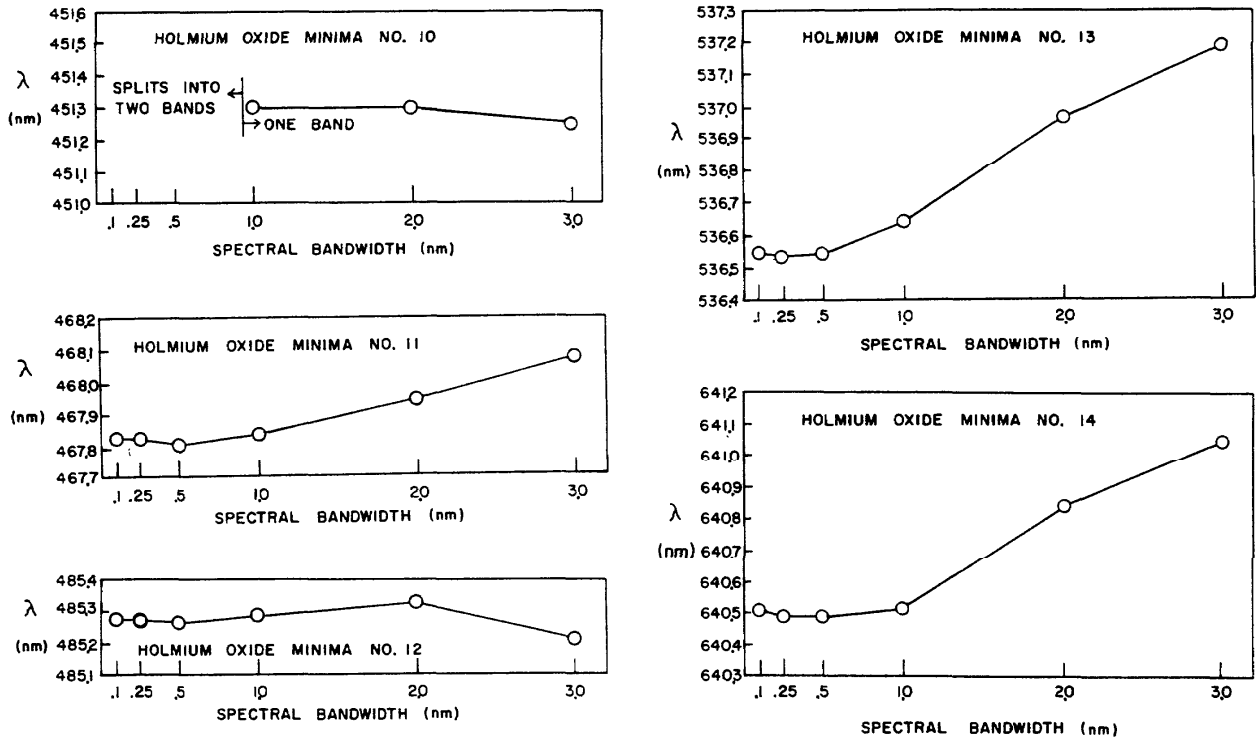


Table 3. Results of holmium oxide solution analysis for transmittance minima 1 through 7 for spectral bandwidths of 0.1, 0.25, 0.5, 1, 2, and 3 nm. 4% holmium oxide in a 10% perchloric acid solution.

Minimum	Temp	Spectral Bandwidths					
No.	(°C)	0.1 nm	0.25 nm	0.5 nm	1 nm	2 nm	3 nm
1	20	240.99 nm			241.13 nm		
1	25	240.99	240.97 nm	241.01 nm	241.13	241.08 nm	240.90 nm
1	30	240.99			241.15		
2	20	249.79			249.88		
2	25	249.83	249.78	249.79	249.87	249.98	249.92
2	30	249.79			249.86		
3	20	278.14			278.09		
3	25	278.15	278.14	278.13	278.10	278.03	278.03
3	30	278.14			278.09		
4	20	286.99			287.17		
4	25	287.01	287.00	287.01	287.18	287.47	287.47
4	30	287.01			287.18		
5	20	333.48			333.45		
5	25	333.47	333.44	333.43	333.44	333.40	333.32
5	30	333.48			333.45		
6	20	345.57			345.47		
6	25	345.55	345.55	345.52	345.47	345.49	345.49
6	30	345.62			345.49		
7	20	361.38			361.33		
7	25	361.36	361.35	361.33	361.31	361.16	361.04
7	30	361.38			361.31		

Note: The uncertainty in the wavelengths of minimum transmittance is ±0.1 nm. An extra decimal place is given for rounding purposes.

Table 4. Results of holmium oxide solution analysis for transmittance minima 8 through 14 for spectral bandwidths of 0.1, 0.25, 0.5, 1, 2, and 3 nm. 4% holmium oxide in a 10% perchloric acid solution.

Minimum No.	Temp. (°C)	Spectral Bandwidths 0.1 nm	0.25 nm	0.5 nm	1 nm	2 nm	3 nm
8	20	385.45 nm			385.66 nm		
8	25	385.45	385.42 nm	385.50 nm	385.66	385.86 nm	386.01 nm
8	30	385.44			385.68		
9	20	416.10			416.27		
9	25	416.07	416.07	416.09	416.28	416.62	416.84
9	30	416.13			416.30		
10	20	-----*			451.30		
10	25	-----*	-----*	-----*	451.30	451.30	451.24
10	30	-----*			451.34		
11	20	467.83			467.84		
11	25	467.82	467.82	467.80	467.83	467.94	468.07
11	30	467.84			467.84		
12	20	485.30			485.29		
12	25	485.28	485.28	485.27	485.29	485.33	485.21
12	30	485.31			485.30		
13	20	536.53			536.65		
13	25	536.54	536.53	536.54	536.64	536.97	537.19
13	30	536.45			536.63		
14	20	640.48			640.52		
14	25	640.51	640.49	640.49	640.52	640.84	641.05
14	30	640.52			640.49		

* Splits into 2 minima for spectral bandwidths less than 1 nm.

Note: The uncertainty in the wavelengths of minimum transmittance is ±0.1 nm. An extra decimal place is given for rounding purposes.

racy spectrophotometer in some applications. The wavelength scale of the spectrofluorimeter has been carefully calibrated by extensive measurements of emission line sources and is known to have an uncertainty of ±0.1 nm for spectral bandwidth of 0.1 nm.

This reference instrument was used to confirm the results obtained with the calibrated high-precision commercial spectrophotometer used for the holmium oxide measurements. A comparison was made to confirm the results for three of the transmittance minima at one spectral bandwidth setting. The results of this comparison are shown in table 5. The two instruments provided data for these three transmittance minima that agree to within 0.1 nm. The wavelength scale uncertainty for both instruments is ±0.1 nm.

Table 5. Comparison of values for holmium oxide transmittance minima with values obtained with the NBS Reference Spectrofluorimeter.

Instrument	(spectral bandwidth=0.1 nm) Minima No. 1	Minima No. 7	Minima No. 14
Varian (Cary) Model 2390	240.995 nm	361.361 nm	640.507 nm
NBS Reference Spectrofluorimeter	240.970 nm	361.313 nm	640.469 nm

4.6 Other Measurements Outside NBS

A list of the wavelengths of minimum transmittance of the holmium oxide solution reported by other workers is given in table 6. (Ref. 10 offers details of these measurements.)

The data shown in table 6 indicate that workers in other laboratories are in generally good agreement with one another and that the NBS data also agree well with these workers' previously published data. These workers also found that the wavelengths of minimum transmittance of holmium oxide in similar solution in perchloric acid are not sensitive to variations in temperature and concentration. They also concluded that the wavelengths of minimum transmittance were least affected by changes in spectral bandwidth for band-

Table 6. Comparison of values for holmium oxide transmittance minima with values obtained by other workers (see Reference [10]).

Min. No.	NBS Transmittance Minima		(1)	(2)	(3)	(4)
1	240.99 nm	*	241.15 nm	241.0 nm	241.1 nm	241.1 nm
2	249.83	*	249.75	250.0	249.7	249.7
3	278.15	*	278.2	277.8	278.7	278.2
4	287.01	*	287.15	287.5	287.1	287.2
5	333.47	*	333.5	333.3	333.4	333.3
6	345.55	*	345.6	345.5	345.5	345.0
7	361.36	*	361.5	361.0	361.5	361.2
8	385.45	*	385.6	385.6	385.5	385.6
9	416.07	*	416.2	416.0	416.3	416.6
10	451.30	#	450.7	450.4	450.8	451.0
11	467.82		467.75			468.0
12	485.28		485.25	485.2	485.8	485.2
13	536.54		536.3			536.8
14	640.51		640.5			

* Spectral bandwidth = 0.1 nm
# Spectral bandwidth = 1 nm

widths less than 1 nm, but that large shifts can be encountered at bandwidths in excess of 1 nm.

5. Conclusions

The reported wavelengths of minimum transmittance of the holmium oxide solution appearing in tables 3 and 4 are estimated to be uncertain by no more than ±0.1 nm at the 95% confidence limit. These wavelengths of minimum transmittance were found to be essentially unaffected by changes in temperature at 25 °C ±5 °C. They were also unaffected by variations in the concentration for solutions containing 2%, 4%, and 6% holmium oxide. The critical parameter affecting the measured values of minimum transmittance was found to be the spectral bandwidth setting of the spectrophotometer. For spectral bandwidths less than 1 nm the wavelength shift is generally less than 0.2 nm. Users can most effectively determine the wavelength error associated with their instrument by using the NBS data listed in tables 3 and 4 that are representive of the spectral bandwidth setting ordinarily used with the instrument. The wavelengths of minimum transmittance of the holmium oxide solution for spectral bandwidths greater than 3 nm have not been evaluated.

The authors gratefully acknowledge the assistance of Chenq-Tsong Chang, guest worker from Taiwan, for his contribution in measuring the transmittance minima of the holmium oxide solution on the NBS Reference Spectrofluorimeter; Jack J. Hsia, for constructive discussions; Robert W. Burke, for assistance in the preparation of various Ho_2O_3 solutions; and the NBS Optical Shop for preparation of the fused silica cuvettes.

6. References

[1] The terminology used in this work was defined earlier by K. D. Mielenz in Anal. Chem. **48**, 1093 (1976).

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Heterochromatic stray light in UV absorption spectrometry: a new test method

K. D. Mielenz, V. R. Weidner, and R. W. Burke

A new method of estimating the amount of heterochromatic stray light in UV spectrophotometers is described. The method uses the same solution filters with sharp UV absorption edges as ASTM Test Method E387, but one measures the apparent absorbance of a 10-mm path-length cell in the sample beam relative to a 5-mm cell in the reference beam. Scanning toward shorter wavelengths, one records an apparent absorbance maximum which is a direct measure of the stray light. This method was found to be in satisfactory agreement with the ASTM method in comparative tests of several spectrophotometers at different wavelengths between 200 and 390 nm, using KCl, KI, NaI, acetone, and $NaNO_2$ solution filters. The new method proved to be simpler, the main advantage being that the apparent absorbance maximum occurs at considerably lower scale values than the corresponding absorbance plateau measured by the ASTM method. This reduces the need for successive attenuations of the reference beam every time the spectrophotometer runs off scale. In many instances the new method required no attenuation at all.

I. Introduction

Stray light (stray radiant energy or SRE) is a common problem in spectrophotometry. Edisbury[1] called it "villainous company that hath been the spoil of me" (Shakespeare, Henry IV) as it has caused a good deal of grief to spectrophotometrists, from biased absorbance readings to nonlinear Beer's law plots and false absorption peaks. These errors are often unsuspected and may not be apparent to the user unless stray-light tests have been performed to ensure that the spectrophotometer meets specifications and is used properly.

The practical importance of such tests is manifest from a 1975 survey conducted by Beeler and Lancaster[2] to assess the extent of stray-light problems in routine clinical spectrophotometry. When the absorbance of solutions of sodium iodide at 240 nm was measured by the 159 laboratories which participated in this survey, 15% of these laboratories reported results that suggested a problem caused by stray-light levels in excess of 1%. The laboratories also measured the absorbances of acid potassium dichromate, alkaline potassium chromate, and nickel sulfate solutions between 240 and 563 nm. Those that had stray-light problems reported absorbances that were skewed in distribution and showed low mean values as well as wide instrument-to-instrument variation. On the other hand, the laboratories without stray-light problems reported results which followed a symmetrical distribution, showed less instrument-to-instrument variation, and provided an accurate estimate of the true absorbance of the solutions. Beeler and Lancaster emphasized that this survey showed how stray light in a spectrophotometer "can quickly be identified by a single reading on a single solution at single wavelength."

While stray light at the 1% level is easily detected, the determination of smaller percentages is more difficult. The stray light in a well-designed modern spectrophotometer is typically only a small fraction of 1%, and for double-monochromator instruments it is often <0.001%. As the measurement of such a small percentage falls outside the normal operating range of spectrophotometers, special test methods are required. In general, these methods involve tedious procedures poorly suited for routine testing. The new method described in this paper is simpler and, therefore, more likely to be carried out by practicing spectrophotometrists.

II. Definitions

In general terms, stray light is spurious radiant energy that has departed from its regular path in a spectrophotometer and then reenters the path so that it is sensed by the detector and causes false readings of transmittance and absorbance. The kind of stray light most often encountered in routine spectrophotometry

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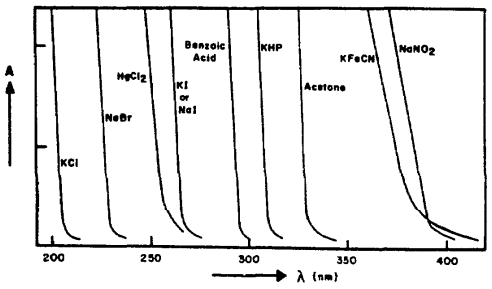

Fig. 1. Absorption spectra of solution cutoff filters suitable for stray-light testing in the UV.

is heterochromatic SRE, i.e., stray radiant energy comprised of wavelengths outside the nominal bandpass of the monochromator. It usually arises from scatter and spurious reflections inside the monochromator. Therefore, it consists predominantly of wavelengths λ', where the source flux $\Phi_{\lambda'}$, the monochromator transmittance $T(\lambda')$, and the detector responsivity $R(\lambda')$ are high, and is most detrimental for nominal wavelength settings λ where these parameters fall off to produce a decrease in the main signal without a commensurate decrease of the stray-light signal. In general, these conditions occur near the wavelength limits of a spectrophotometer so that the stray light that matters most in practical UV absorption spectrometry is heterochromatic SRE from near-UV and visible wavelengths λ', which is present at short-UV wavelength settings $\lambda < \lambda'$. This type of heterochromatic SRE can be detected readily with a sharp cutoff filter that absorbs the nominal wavelength λ while transmitting the longer stray wavelengths λ'. If such a filter is placed in the sample compartment of a spectrophotometer and the monochromator is scanned to a wavelength λ below the cutoff, the instrument will register an apparent transmittance of

$$x(\lambda) = \left[\int_{\lambda'>\lambda} \Phi_{\lambda'} T(\lambda') R(\lambda') d\lambda'\right] \Big/ [\Phi_\lambda T(\lambda) R(\lambda) \Delta\lambda], \quad (1)$$

where $\Delta\lambda$ is the nominal bandwidth. This quantity x is called the instrumental stray-light ratio of the spectrophotometer at the wavelength λ.

Figure 1 shows the absorption spectra of several cutoff filters suitable for this purpose. One of these, potassium iodide, is available as NBS Standard Reference Material SRM No. 2032.[3]

III. ASTM Test Method E387

The usually recommended method of estimating stray light in UV spectrophotometry is ASTM Test Method E387,[4] which is quite simple in concept: a cutoff filter of the type mentioned above is used as the sample, the spectrophotometer is scanned toward short wavelengths until an apparent absorbance plateau A' is recorded, and hence the stray-light ratio defined by Eq. (1) is given by $x = 10^{-A'}$.

In practice, this test method poses the problem that most spectrophotometers run off-scale long before the final absorbance plateau is reached. When this happens, the scan must be halted to place an attenuating screen into the reference beam. The attenuation thus introduced must be noted, and then the scan can be resumed until the constant absorbance reading is obtained or (more likely) the instrument runs off-scale again. In the latter case another attenuator must be added, and often this procedure must be repeated several times.

Figure 2 shows an example in which two attenuators were needed to test a double-monochromator instrument with a maximum absorbance readout of 3.0, using a 10 g/liter aqueous solution of KI as the cutoff filter near 255 nm. The two attenuation steps were 1.92 and 1.13 absorbance units, respectively, and the final absorbance reading was 2.37. Thus, the actual absorbance plateau was $A' = 1.92 + 1.13 + 2.37 = 5.42$, and hence the stray-light ratio was calculated as $x = 10^{-A'} = 3.8 \times 10^{-6}$. Practical details on the ASTM method will be found in Sec. V.

IV. The New Method

The new test method to be described originated from an idea to use a gradual attenuation of the reference beam instead of the step-wise attenuation recommended by ASTM. It was thought that a shorter path-length of the cutoff solution could provide this gradual attenuation. Thus, the same solution cutoff filters are used but one measures a 10-mm path-length cell in the sample beam against a 5-mm cell placed in the reference beam. Again scanning toward high absorbances, one should obtain a zero reading (100% transmittance) at the longer wavelengths, where both cells are transparent, and once more at the shorter wavelengths, where they are opaque to the main beam but transmit equal stray-light fluxes. Hence, it is intuitively clear that an apparent absorbance maximum A'' should be recorded at some intermediate wavelength λ, and that this maximum should represent a direct measure of the heterochromatic stray-light ratio of the spectrophotometer. Furthermore, the spectrophotometer should be less likely to run off scale, since only

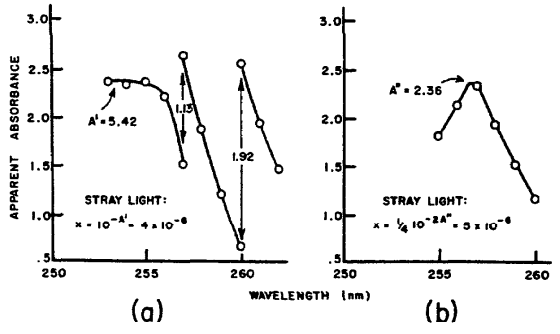

Fig. 2. Stray-light tests of a single-beam, double-monochromator spectrophotometer with 0–3 absorbance scale, using KI cutoff filters near 255 nm: (a) ASTM Test Method E387, (b) new method. The ASTM method required two screens in the reference beam for successive attenuations of 1.92 and 1.13 absorbance units, respectively.

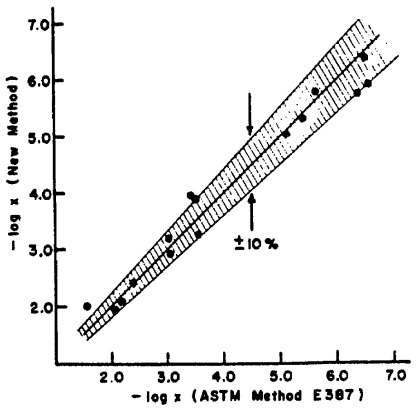

Fig. 3. Comparative results obtained in fifteen stray-light tests by the new method and by ASTM Test Method E387, showing the equivalence of both methods within ±10%.

one-half of the absorbance of a 10-mm cell is seen by the spectrophotometer and since it is well known that stray-light effects are amplified in differential spectrophotometry.[5] These ideas were tested in a series of test runs. In the example shown in Fig. 2(b), a maximum of only 2.36 absorbance units was recorded for the same test conditions as in Fig. 2(a).

Mathematically, this apparent absorbance maximum is given as follows. Let x be again the stray-light ratio defined by Eq. (1), τ the true transmittance of the 10-mm cutoff solution, and $\sqrt{\tau}$ that of the 5-mm solution. Then, if these solutions are transparent to the stray light, the sample and reference signals will be proportional to $(\tau + x)$ and $(\sqrt{\tau} + x)$, respectively, so that the apparent transmittance recorded by the spectrophotometer is

$$\tau' = (\tau + x)/(\sqrt{\tau} + x). \tag{2}$$

Setting the derivative $d\tau'/d\tau$ equal to zero, we find

$$\sqrt{\tau} + x = \tfrac{1}{2}(\tau + x)\sqrt{\tau}, \qquad \tfrac{1}{2}\tau = x(\tfrac{1}{2} + \sqrt{\tau}).$$

Thus, if $\sqrt{\tau} \ll \frac{1}{2}$, the minimum apparent transmittance, $\tau'' = \tau'_{\min}$, occurs where the transmittance of the 10-mm cell is equal to the stray-light ratio x, then $\tau = x$. Equation (2) then shows that $\tau'' = 2\sqrt{x}/(1 + \sqrt{x})$ or, since $\sqrt{x} \ll 1$, the ratio becomes $\tau'' = 2\sqrt{x}$. Hence, the stray-light ratio can be calculated as follows in terms of τ'' or in terms of the corresponding absorbance maximum $A'' = -\log(\tau'')$:

$$x = \tfrac{1}{4}(\tau'')^2 = \tfrac{1}{4}\,10^{-2A''}. \tag{3}$$

In the case of Fig. 2(b), this expression gave a stray-light ratio, $x = 4.6 \times 10^{-6}$, which agrees well with the corresponding result obtained by the ASTM method.

V. Comparison

In addition to the comparison illustrated by Figs. 2(a) and 2(b), further tests were performed to compare both methods. All in all, a series of fifteen measurements was completed on the following four types of spectrophotometer:

Single-beam, single-prism monochromator, meter readout from 0 to 3 absorbance units.

Single-beam, single-grating monochromator with prism predisperser, unlimited digital readout.

Single-beam, double- (prism-grating) monochromator, meter readout from 0 to 3.

Double-beam, double- (prism/prism) monochromator, chart recording from 0 to 2.

The tests were performed at several wavelengths between ~200 and 400 nm, using the following solution cutoff filters: 10 g/liter KCl, 10 g/liter KI, 10 g/liter NaI, acetone, and 50 g/liter $NaNO_2$. Each test was done according to the ASTM recommendations for Test Method E387, and then repeated by the new method. The relative (10 vs 5 mm) absorbances were obtained directly on the double-beam spectrophotometer and by taking the difference of separate absorbance readings for each cell with the single-beam instruments. Readings were taken in 1- or 2-nm intervals in the direction of decreasing wavelength.

The results of these comparative tests are shown in Fig. 3 in the form of a logarithmic plot of the stray-light values obtained by the new method vs those given by the ASTM method. The average ratio of the corresponding values of $-\log(x)$ is 1.01 ± 0.10. Hence, these data can be represented by the 45° line shown in the figure, and it can be concluded that both methods give equivalent results within random experimental errors. The standard deviation of ±10% of this mutual agreement was judged satisfactory in view of the low signal levels being measured.

As expected, the use of either method was straightforward as long as the spectrophotometer stayed on scale during the test, but the new method proved to be considerably simpler when small amounts of stray light were measured.

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Appendix 6

JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
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Reflection Correction for High-Accuracy Transmittance Measurements on Filter Glasses

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(July 27, 1973)

Multiple reflections in the sample compartment of a spectrophotometer constitute a source of systematic bias in transmittance measurements on filter glasses. This bias may be removed by applying a numerical correction obtained from measurements on tilted samples in polarized light. For a high-accuracy spectrophotometer, this correction was found to be of the order of several 10^{-4} transmittance units, independent of polarization, but slightly wavelength dependent.

Key words: Correction for reflections; reflections, multiple; spectrophotometry, high accuracy; systematic bias in spectrophotometry; transmittance, correction.

1. Introduction

The sample compartment of most spectrophotometers is designed such that the monochromator exit slit is focused into the sample by a lens, and is refocused into the detector by another lens (fig. 1). This beam geometry is preferred by instrument designers for intensity reasons and other convenience gains, but may constitute a source of significant systematic errors of the measured data. One of these errors is caused by multiple reflections between the two lenses and the sample surfaces [1, 2, 3].[1]

For high-accuracy applications this error can be eliminated by means of a numerical correction, ΔT, which converts the measured transmittance, T_M, into the correct value

$$\tau = T_M + \Delta T. \quad (1)$$

[1] Figures in brackets indicate the literature references at the end of this paper.

A simple but accurate method to determine this correction is described in this paper.

The specific spectrophotometric application discussed is the measurement of the transmittance of glass filters to an accuracy of $\pm 10^{-4}$ transmittance units. For the particular high-accuracy spectrophotometer used [4], the correction ΔT was found to be of the order of several 10^{-4} transmittance units, independent of polarization throughout the visible spectrum, and applicable for filters with widely different indices of refraction. The correction was found to be slightly wavelength dependent.

2. Theoretical Background

A detailed discussion of the reflection errors affecting the measurement of filter transmittances may be found in reference [3]. A summary is given here in order to provide the theoretical foundation for the experimental work described in section 3.

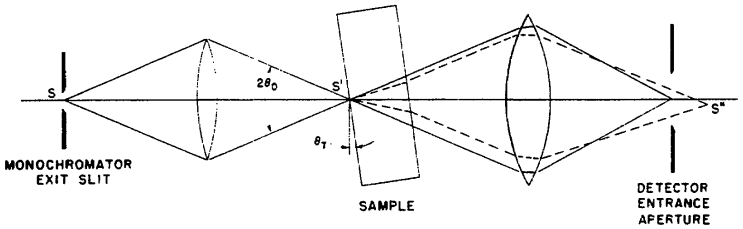

FIGURE 1. *Sample-compartment optics of a focused-beam spectrophotometer.*

The purpose of the measurement is assumed to be the determination of the normal-incidence transmittance,

$$\tau=\frac{\tau_i(1-r)^2}{1-r^2\tau_i^2}, \tag{2a}$$

of a glass filter surrounded by air. The filter is characterized by its thickness t and complex refractive index $n(1+i\kappa)$, so that for each wavelength λ the normal-incidence internal transmittance τ_i and Fresnel reflectance r appearing in eq (2a) are given by

$$\tau_i=e^{-4\pi n\kappa t/\lambda}, \tag{2b}$$

$$r=\left(\frac{n-1}{n+1}\right)^2. \tag{2c}$$

This quantity τ can be measured accurately with specially designed instrumentation in which the sample is placed normal to a collimated beam of light, the collimation being effected by off-axis mirror optics in a manner which reduces reflection errors to a negligible level [3, 5]. A conventional spectrophotometer does not permit such a direct measurement of τ because of the above-mentioned reflection error, even if its lenses were arranged to produce a collimated rather than the usual focused beam.

The cause of this error is illustrated in figures 2a and 2b. According to the first of these, the radiant flux received by the detector during the clear-space measurement is

$$\phi_0=T_1T_2(1+R_1R_2+\ldots), \tag{3a}$$

where the initial flux is taken as unity, and where T_1, R_1, T_2, and R_2 are the fractional fluxes transmitted or reflected into the detector by all components (lenses, slit jaws, detector housing, etc.) in front of and behind the sample area, respectively. When a sample with transmittance T and reflectance R is inserted, the flux into the detector is

$$\phi=T_1TT_2(1+R_1R_2T^2+RR_2+R_1R+\ldots), \tag{3b}$$

as indicated in figure 2b. Within the approximation that all contributions due to four or more reflections are considered negligibly small, the measured transmittance is

$$\begin{aligned}T_M&=\phi/\phi_0\\&=T[1+(R_1+R_2)R-R_1R_2(1-T^2)].\end{aligned} \tag{3c}$$

The correction which must be applied to T_M to eliminate the reflection bias is

$$T-T_M=\Delta T+\Delta T', \tag{4a}$$

where

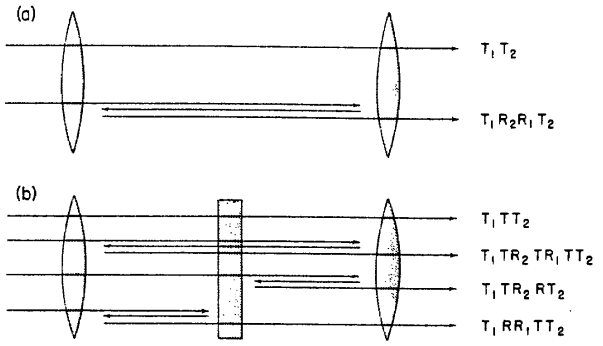

FIGURE 2. *Reflected beams in a spectrophotometer with lenses.*

$$\Delta T=-(R_1+R_2)RT, \tag{4b}$$

$$\Delta T'=R_1R_2T(1-T^2). \tag{4c}$$

The first of these two error terms, ΔT, is due to the fact that the insertion of the sample has created the two additional beams shown at the bottom of figure 2b. This error is greatest when the sample is normal to the optic axis, and may be eliminated by sufficiently tilting the sample so that these two beams no longer reach the detector. The other error component, $\Delta T'$, arises from the fact that the second beam from the top in figure 2b passes the sample three times, whereas the direct beam passes it only once. Since this residual error cannot be avoided by tilting the sample, it is clear that tilting is an effective means to eliminate reflection errors only if $\Delta T'$ is substantially smaller than ΔT. Equations (4b, c) suggest that this should be the case for any well-designed spectrophotometer for which these reflection errors are not unduly large. To show this, we assume that R_1 and R_2 are both of the order of a few percent, and that glass filters with an average transmittance $T\sim 0.5$ and reflectance $R\sim 0.08$ are used as samples. This leads to $\Delta T/\Delta T'\sim 10$, showing $\Delta T'$ to be a significantly smaller error in such circumstances. Whether or not this estimate holds must be ascertained individually for any given spectrophotometer.

Tilting the sample introduces obliquity errors, and therefore does not yield an accurate measurement of the normal-incidence transmittance τ unless further corrections are applied. These errors arise from a decrease of internal transmittance due to increased pathlengths in the sample for oblique light incidence and, secondly, from a variation of reflection losses at the sample boundaries with angle of incidence. The latter also introduces a dependence of measured transmittance on polarization.

For glass filters measured with a conventional spectrophotometer in which the monochromator exit slit is imaged onto the sample, these errors are given by

$$T=\tau[1+(1/2n^2)\,(\ln\tau_i)\,(\theta_T^2+\tfrac{2}{3}\,\theta_0^2)\pm(4r/n)\,\theta_T^2+\ldots], \tag{5}$$

where T is the measured transmittance (corrected for reflection errors); τ, τ_i, and r are the normal-incidence values of transmittance, internal transmittance, and Fresnel reflectance as given by eqs (2a, b, c); θ_T and θ_0 are the tilt angle and the cone angle of the incident light; and where the upper and lower signs of the last term pertain to the two cases in which the light is S or P polarized in the tilt plane. Equation (5) was derived in reference [3] under the assumption that the monochromator exit slit is sufficiently short to approximate a point source, and that the focusing lens is underfilled so that the grating or prism constitutes the limiting aperture. This aperture is assumed to be square, subtending the same angle $2\theta_0$ in the horizontal and vertical planes. The sample is assumed to be tilted only in one of these planes. The small-angle approximation given in eq (5) is estimated to be accurate to 10^{-4} transmittance units for angles θ_T and θ_0 up to about 10°.

For average transmittances and tilt angles of a few degrees, these obliquity effects are of the order of 10^{-3} transmittance units. Since this is the same magnitude as estimated above for the reflection error, it is clear that for a spectrophotometer with lenses an accurate measurement of the normal-incidence transmittance τ cannot be achieved without numerical correction for either source of error. If the sample is tilted in order to reduce the reflection error, an obliquity correction must be applied. Vice versa, a reflection correction is necessary if the sample is normal to the optic axis so that obliquity effects are minimized. Although these two alternatives are equivalent, the latter was chosen in this work since it constitutes the simpler approach for routine measurements of transmittance.

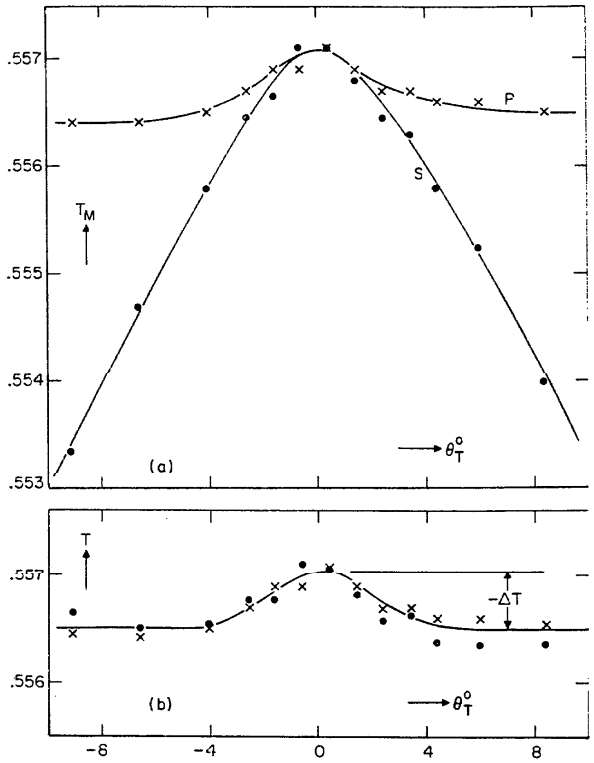

FIGURE 3. *(a) Measured transmittance* T_M *versus tilt angle* θ_T *for 55 percent filter in* S *and* P *polarized light at* $\lambda = 574$ *nm. (b) The same data after application of tilt correction.*

3. Experimental Procedure

The preceding theoretical discussion does not permit a precise calculation of the required reflection correction. Representing fractional fluxes which actually reach the detector, the quantities R_1 and R_2 appearing in equations (4b, c) are complicated and generally unknown functions of the relative positions of sample compartment elements, lens curvatures, location of aperture stops, and other beam-geometry factors. This makes it necessary to measure the correction. Such a measurement may be performed as follows.

Each of a series of filters with different transmittances is measured for different known tilt angles θ_T, and for S and P polarization of the incident light. This yields a set of raw data T_M, such as plotted in figure 3a. These are transformed into corrected data T by adding the tilt-correction given by eq (5),

$$(\Delta T)_{\text{tilt}} = -T_M\left[(1/2n^2)\ \ln\left(\frac{T_M}{1-2r}\right) \pm (4r/n)\right]\theta_T^2, \quad (6)$$

where the approximate values T_M and $T_M/(1-2r)$ were substituted for τ and τ_i on the right-hand side, and where estimates of n and r may be used. As indicated by figure 3b, these corrected transmittances T are constant for sufficiently large positive or negative tilt angles, but near normal incidence exhibit the 'reflection hump' whose height represents the desired reflection correction ΔT to be applied for this particular value of transmittance. From the measurements performed on all of the filters one may then determine the dependence of ΔT on T, as illustrated by figure 4. According to eq (4b), this dependence should be linear. In the work described here, these measurements were made as follows.

A series of four Schott NG–4 glass filters with nominal transmittances 0.1, 0.2, 0.3, and 0.5, an evaporated metal-on-glass filter with a nominal transmittance 0.4, and a clear glass plate were used. All of these samples were 50 mm × 50 mm × 2 mm in size, and flat and plane-parallel to within a few fringes of mercury-green light. The spectrophotometer used to perform the measurements was fully described in a previous issue of this journal [4], and will not be discussed here. The filters were placed in the sample compartment of this spectrophotometer on a vertical rectangular holder adapted to a rotary horizontal table with 10 cm diameter. This table had a scale divided in 360° with a vernier reading to 5 min, and was held on the single-sample carriage of the spectrophotometer (see ref. [4], fig. 2) with a vertical mounting rod. This sample carriage unit consists of a platform provided with vertical holders which can be moved laterally by a

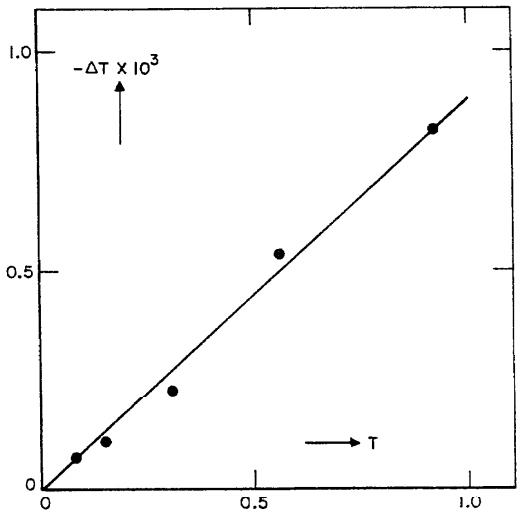

FIGURE 4. *Reflection correction* ΔT *versus* T *for* λ *= 574 nm.*

rack and pinion arrangement. The platform, mounted on four ball bushings which ride on two horizontal rods, can be moved pneumatically across the optical axis. This remote-controlled movement is smooth, and the sample position in and out of the beam is reproducible within 0.025 mm.

A sheet polarizer of 9.5 cm diam was used to produce the S and P polarized radiation. This polarizer was held in a ball bearing rotating mount with a circular scale divided from 0 to 360°. It was placed on the optical bench in front of the entrance slit of the predisperser-monochromator aggregate of the spectrophotometer between the circular neutral wedge and the flat front-surface mirror (see ref. [4], fig. 3). This placement of the polarizer on the source side of the spectrophotometer avoids the additional reflection errors which would occur if the polarizer were put in the sample compartment of the spectrophotometer, but requires that the monochromator does not significantly depolarize the incident radiation or rotate its plane of polarization. This was ascertained by testing the monochromator between crossed polarizers at the wavelengths at which the measurements were performed.

Each transmittance measurement was performed in S and P polarized radiation and for tilt angles varying by $\pm 10°$ about the normal position. Each measurement resulted from the ratio I/I_0 of the attenuated to the unattenuated radiation value, each I and I_0 being the average of 50 individual measurements. The measurements were repeated four times.

4. Results

Using the procedures outlined in section 3, the numerical values of the reflection correction ΔT were determined for the four neutral-density glass filters and the clear glass plate, at the wavelength $\lambda = 574$ nm. This yielded the result represented by the straight line in figure 4; namely,

$$\Delta T/T = -8.9 \times 10^{-4}, \qquad \text{for } \lambda = 574 \text{ nm}. \tag{7a}$$

Each of the individual values of ΔT could be measured to a precision better than 10^{-4} transmittance units. There was no evidence suggesting a dependence of ΔT on polarization.

Secondly, the measurements on the clear glass plate were repeated for $\lambda = 400$ nm and 650 nm. Together with the previously obtained result for 574 nm, this showed the wavelength dependence indicated in figure 5. This dependence is also linear, and may be expressed as

$$\Delta T/T = -1.26 \times 10^{-6}(\lambda - 574 \text{ nm}), \qquad \text{for } T = 0.92. \tag{7b}$$

These results were then combined into the final empirical expression.

$$\Delta T/T = -8.9 \times 10^{-4}[1 + 1.4 \times 10^{-3}(\lambda - 574 \text{ nm})], \tag{8}$$

for the correction ΔT to be applied for different transmittances T and wavelengths λ. This formula agrees with all individual measurements of ΔT to within $\pm 5 \times 10^{-5}$ transmittance units.

The correction ΔT so obtained represents only the first of the two error terms appearing in eq (4a), above. The exact value of the second term $\Delta T''$ cannot be determined within the context of this paper, but a quantitative estimate may now be obtained as follows. From eqs (4b) and (7a) it may be seen that, for this spectrophotometer and for the appropriate value $R \sim 0.08$ for the filters used,

$$\frac{1}{2}(R_1 + R_2) \sim 6 \times 10^{-3}. \tag{9a}$$

Provided that this arithmetic average of R_1 and R_2 is not substantially different from their geometric average $(R_1R_2)^{1/2}$, it follows from eq (4b) that

$$\Delta T'' \sim 3.6 \times 10^{-5}\, T(1 - T^2), \tag{9b}$$

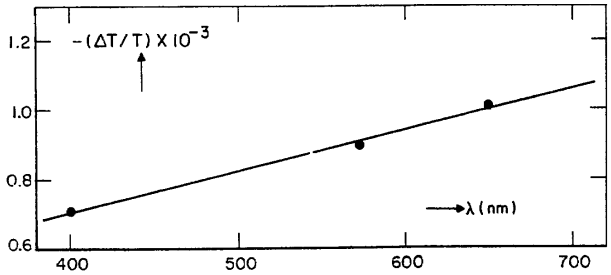

FIGURE 5. *Reflection correction* ΔT *versus* λ *for* T = *0.92*

or $\Delta T' \sim 1.4 \times 10^{-5}$ for $T = 0.577$, for which this error is a maximum. Although this argument is not mathematically exact, it suggests that the residual reflection error $\Delta T'$ is entirely negligible for the spectrophotometer used here.

According to eq (4b), the correction ΔT depends on the reflectance R and, therefore, on the refractive index n of the sample. Using eqs (4b) and (2c) it is easily seen that

$$d(\Delta T) = -\frac{8r(R_1 + R_2)T}{(n+1)^2}\, dn. \tag{10}$$

For $n = 1.5$, $r = 0.04$, $T = 0.5$, and the above value (9a) for $(R_1 + R_2)$, this is reduced to $d(\Delta T) \sim 3 \times 10^{-4}\, dn$, showing that ΔT will not be affected by more than 10^{-4} transmittance units as long as $dn < 0.3$, or $1.2 < n < 1.8$. Hence it may be concluded that the above values of ΔT are applicable to virtually all filter glasses. Other types of samples, such as coated glasses, will of course require a different correction. For example, measurements on the evaporated metal-on-glass filter with transmittance 0.4 at 474 nm yielded a value, $\Delta T = -1.4 \times 10^{-3}$, which is about four times larger than indicated by figure 3 for uncoated samples.

5. Conclusion

Based upon this work, all transmittance measurements on glass filters with this high-accuracy spectrophotometer are performed with the sample accurately aligned normal to the optic axis. In addition to the reflection correction given by eq (8) and the detector nonlinearity correction discussed in reference [4], an f-number correction is applied to remove the residual bias due to the nonparallel radiation in the sample compartment. This latter correction is given by eq (5) as

$$(\Delta T)_f = -(T/3n^2)\left(\ln \frac{T}{1-2r}\right)\theta_0^2;$$

its magnitude is 1.3×10^{-4} transmittance units, or less, for the $f/10$ cone of light ($\theta_0 = 0.05$ rad) used. With these corrections applied, all measurements made with this high-accuracy spectrophotometer yield the normal-incidence transmittance τ defined by eq (2a) within a 10^{-4} limit of instrumental accuracy.

This spectrophotometer was designed and constructed to permit calibration of solid and liquid filters for transmittance with a well-defined accuracy (4). These filters are used as Standard Reference Materials (SRM's) to check the photometric scale of conventional spectrophotometers. SRM 930a consists of a set of three glass filters (Schott NG–4) with nominal transmittances 0.1, 0.2, and 0.3. Their transmittance values are certified to ± 0.5 percent of the value, this uncertainty being the sum of random and systematic errors. The latter are principally due to the inherent inhomogeneity and instability of the glass, surface effects, and positioning the filters. They exceed by a large margin the instrumental corrections discussed in this paper. Hence, the certified transmittances of previously issued standard filters remain unaffected by these corrections.

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(Paper 77A6–792)

Appendix 7

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Adaptation of a High-Accuracy Spectrophotometer for Ultraviolet Work

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(May 31, 1974)

A high-accuracy spectrophotometer, originally designed for work at visible wavelengths, was modified to permit measurements in the ultraviolet without degradation of its original performance. This was accomplished by equipping the spectrophotometer with a stable deuterium arc source, a highly efficient averaging sphere with fluorescent wavelength converter, a new grating, and achromatic sample-compartment optics. The modified spectrophotometer will be used for the development of new Standard Reference Materials, as well as for materials research, in the region between 200 and 300 nm.

Key words: Averaging sphere; deuterium arc lamp; fluorescent wavelength converter; grating; spectrophotometry; standard reference materials; ultraviolet; UV achromats; visible.

1. Introduction

A primary goal of the current NBS program in spectrophotometry has been the design of high-accuracy instrumentation for the certification of calibration standards and the development of improved measurement techniques. For transmittance measurements at visible wavelengths, this goal was accomplished by specially constructing two highly accurate single-beam spectrophotometers [1, 2],[1] which are presently used in the Institutes for Materials Research (IMR) and Basic Standards (IBS) for standards work at visible wavelengths (400 to 800 nm, approximately). The instrumental accuracy achieved with these spectrophotometers is 10^{-4} transmittance units (0.01 percent). Although similar in some design aspects, these two spectrophotometers differ significantly in others, and therefore can be employed for in-house comparisons to ensure the accuracy and consistency of all spectrophotometric measurements at NBS. The purpose of this work was to extend these capabilities into the ultraviolet spectral region by developing the means for modifying either spectrophotometer for applications down to about 200 nm.

The particular instrument that was modified was the IMR spectrophotometer described in reference [1]. As originally designed, this spectrophotometer employed a current-stabilized, 100-W tungsten ribbon lamp as the radiation source; a 1-meter, f/8.7 Czerny-Turner grating monochromator (1200 lines/mm, 500-nm blaze) with a fused-silica prism predisperser as the dispersing element; and an 11-stage, S-20 photomultiplier tube attached to a 125-mm, $BaSO_4$-coated averaging sphere as the signal detector. The tungsten lamp is imaged on the predisperser entrance slit by a fused-silica lens. Two additional fused-silica lenses are used in the sample compartment to focus the monochromator exit slit at the sample, and to refocus it into the averaging sphere [3]. The photomultiplier signal is measured by means of a current-to-voltage converter and a digital voltmeter, interfaced with a computer.

It may be estimated that, for a spectrophotometer of this type, a clear-space signal of at least 10^{-7} A is required if measurements are to be made with a standard deviation of at least 10^{-4} transmittance units [4]. The actual clear-space signal current obtained with this spectrophotometer at different wavelengths and for typical values of tungsten-lamp power, monochromator slit width, photomultiplier anode voltage, etc. is shown as curve (a) in figure 1, and thus indicates an inadequate performance of the instrument in the spectral region below approximately 370 nm. In order to effect the desired improvement of ultraviolet performance, the spectrophotometer was equipped with a deuterium arc source, a re-designed averaging sphere, and a differently blazed grating. These components were chosen to achieve a wide spectral range (200 to 800 nm) of the modified spectrophotometer, requiring only a change back to the tungsten lamp for work above 400 nm. In order to facilitate the usage of the instrument throughout this extended range, it was necessary to replace the two sample-compartment lenses by fused-silica, lithium-fluoride achromats.

*This paper describes a cooperative project on the part of the three authors. The basic design concepts and the accomplishment of a functioning instrument are due to K. D. Mielenz and R. Mavrodineanu. The optimization of the fluorescent wavelength converter for the averaging sphere was achieved by E.D. Cehelnik.

[1] Figures in brackets indicate the literature references at the end of this paper.

NOTE. See also USA Patent 3,968,363, July 6, 1976

2. Modification of Spectrophotometer

2.1. Deuterium Arc Lamp

To a significant extent, the sharp drop of ultraviolet signal level shown by curve (a) in figure 1 is attributable to the tungsten lamp of the original spectrophotometer. A rapid decrease of radiant intensity with decreasing wavelength is typical for incandescent filament lamps, and therefore makes any source of this kind a poor choice for work at short wavelengths [5]. In contrast, a deuterium arc lamp exhibits an increase of radiant intensity with decreasing wavelength, and thus provides much better power levels in the ultraviolet.

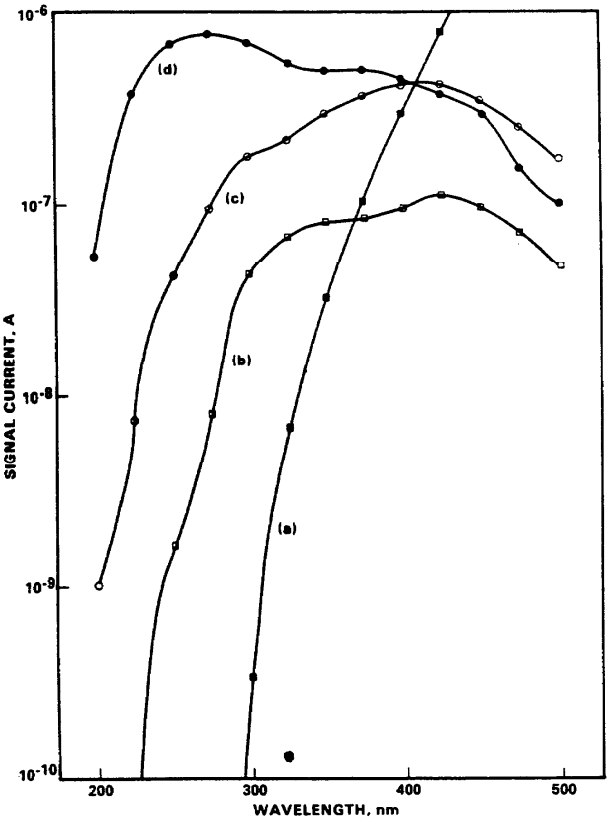

FIGURE 1. *Successive improvement of clear-space signal level of original spectrophotometer (curve a) obtained by: (b) deuterium arc lamp, (c) improved averaging sphere, and (d) new grating.*

A 60-W deuterium lamp with high-purity fused-silica window was chosen for the modified spectrophotometer. This lamp has a line-free continuous emission in the ultraviolet extending to below 180 nm, and is rated to have the same output at 200 nm as a 150-W xenon arc lamp. In comparison to a 250-W tungsten-bromide filament lamp, its output is about 1000 times greater at 250 nm, and 4 times greater at 300 nm. For work above 400 nm, tungsten lamps are preferable because of the decreasing intensity of the deuterium-arc spectrum and its line structure in the visible. The clear-space signal obtained after the deuterium lamp was installed in the spectrophotometer is shown as curve (b) in figure 1.

The stability of the radiant-intensity output of the deuterium lamp was tested by performing regularly repeated measurements of the spectrophotometer signal over extended periods of time. The long-term stability of lamp power so observed may be seen from figure 2, showing a gradually decreasing signal drift at the rates of 1.5, 0.6, and 0.08 percent per hour after the lamp had been operated for 1, 3, and 5 h, respectively. The average short-term instability (random noise plus drift) of the deuterium lamp was found to be 0.02 percent for a total of 15 sets of 20 individual readings, taken at 5-s intervals and at arbitrary times during an 8-h period of lamp operation. Since all data obtained with this spectrophotometer are derived by averaging a large number of individual measurements of transmittance, performed in a time-symmetrical sequence which eliminates the effects of drifting, this stability of the deuterium lamp is adequate for routine

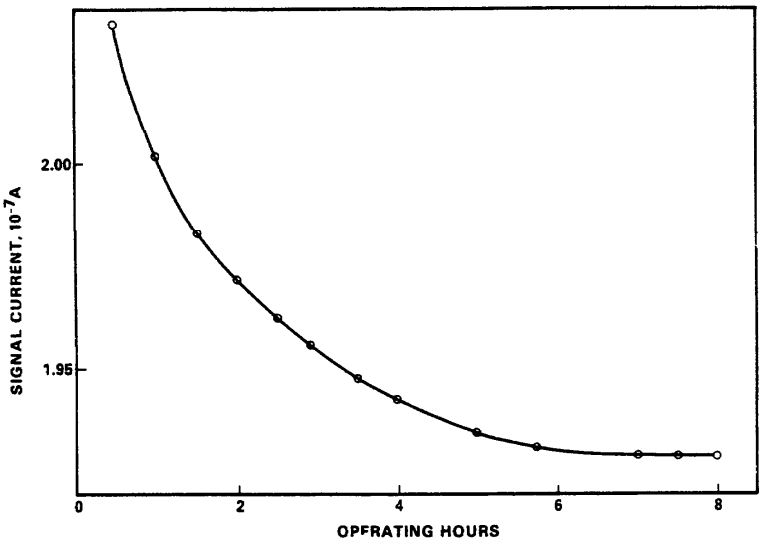

FIGURE 2. *Long-term signal drift observed with deuterium lamp.*

measurements with a precision better than 10^{-4} transmittance units. The above results for the deuterium lamp compare favorably with the stability data found for a current-stabilized tungsten lamp [2].

2.2. Averaging Sphere

The original averaging sphere of the spectrophotometer was designed as shown in figure 3a. It has an internal diameter of 125 mm, and circular entrance and exit ports 20 and 50 mm in diameter, respectively. The circular target, 35 mm in diameter, is located at the center of the sphere. The inside of the sphere, both sides of the target, and the thin target support rod are coated with several layers of specially prepared barium sulfate and polyvinyl alcohol coatings as developed by Grum and Luckey [6]. The photomultiplier tube is attached to the sphere, so that its 50-mm cathode is located 16 mm behind the exit port. The efficiency of this sphere was determined by successively measuring photomultiplier signals obtained at different wavelengths with and without sphere, using the deuterium arc lamp. These measurements showed a steep decrease of sphere efficiency from about 15 percent for visible wavelengths near 500 nm to less than 0.1 percent at 200 nm, and thus indicated the necessity to equip the spectrophotometer with an improved, more efficient sphere [7].

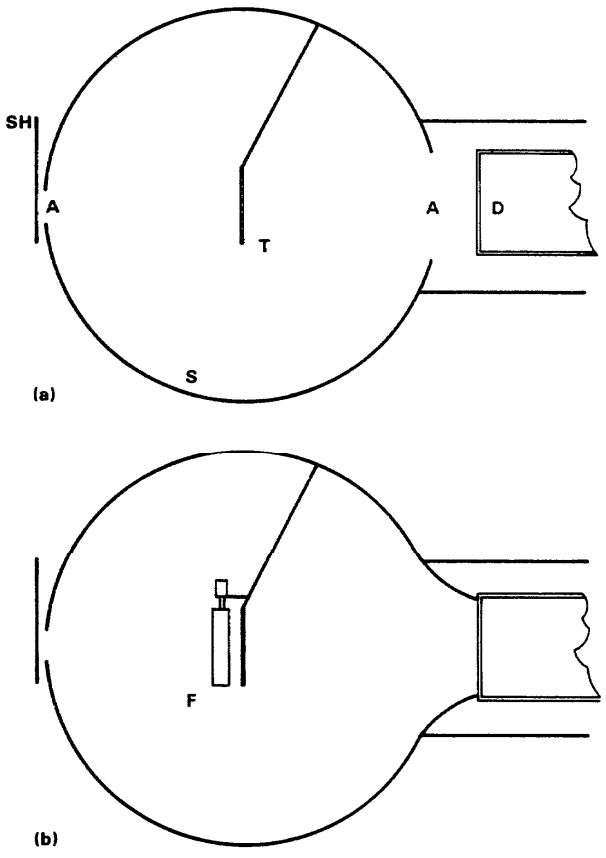

FIGURE 3. *Geometry of (a) original averaging sphere and (b) improved sphere.*

A: entrance port, A': exit port, D: detector, F: fluorescent dye cell, S: sphere wall, SH: shutter, T: target.

According to theory [8], the efficiency of an averaging sphere of the type considered is, approximately,

$$\phi_D/\phi = [r^2/(1-r)](1-e/d)d^2/16s^2 \qquad (1)$$

where

ϕ = radiant flux into sphere,
ϕ_D = flux reaching detector,
r = wall reflectance (assumed close to, but not equal to unity),
s = sphere radius,
d = radius of sensitive area of detector (assumed equal to radius of exit-port)
e = distance between exit port and detector.

It may be seen from this equation that, to a large extent, the poor efficiency of the original spectrophotometer sphere is due to inadequate coupling of exit port and detector. The collection efficiency of the detector (i.e.; the fraction of the diffuse flux from the exit port which actually reaches the photocathode) appears in Eq (1) as the factor $(1-e/d)$, which in this case has the numerical value 0.64 and thus shows that more than one third of the available flux is lost through the gap between exit port and detector. Therefore, a large increase in efficiency could be gained by modifying the sphere as shown in figure 3b. The sphere wall was tapered in a pear-like fashion and was extended into the detector housing, so that the exit port is butted directly against the photocathode. This simple modification of the sphere resulted in a large increase of efficiency (from 15 to 70 percent at 500 nm). However, the efficiency in the ultraviolet (now 2.5 percent at 200 nm) was still inadequate.

The averaging effectiveness of this sphere was tested by Mr. K. L. Eckerle of the Optical Radiation Section of NBS. The sphere was found to be insensitive to beam displacements from the target center of ± 1.5 mm within a $\pm 10^{-4}$ limit of signal variation. This is to be compared with a ± 5 percent variation for a ± 1 mm beam displacement on the same photomultiplier used without the sphere.

The high efficiency of the modified sphere in the visible suggested that a near-optimal sphere geometry had been achieved, and that the limiting factor in the ultraviolet was now the reduced reflectance of the barium-sulfate sphere coating. In order to overcome this remaining difficulty, a fluorescent dye was used to shift the incident short-wave radiation into the longer wavelength region for which the reflectance of barium sulfate is high. This dye, which is contained in a cell placed in front of the sphere target as shown in figure 3b, had to be chosen such that virtually all of the incident flux at short wavelengths is absorbed and is converted into fluorescence with a quantum efficiency as nearly equal to unity as possible. In order to avoid impairing the high sphere efficiency at longer wavelengths, it was also required that visible light be not absorbed, so that it passes through the dye unaffected and is reflected from the target as before. The fluores-

cent material selected was a 0.923 g/l solution of 2,5-diphenyloxazole (PPO) in *n*-hexane in a 10 × 10 × 2 mm high-purity fused-silica cell. It is effectively transparent for wavelengths above 360 nm, and below 340 nm absorbs more than 99 percent of the incident radiation. Its estimated quantum efficiency is 0.9, with the peak emission occurring near 370 nm. The use of this dye proved highly successful, and resulted in a sphere efficiency of 20 percent at 200 nm.

The marked enhancement of signal level obtained with this improved sphere is shown by comparing curve (c) in figure 1 with curve (b). The measured efficiency of the sphere is roughly constant and equal to 20 percent between 200 and 300 nm, followed by a gradual increase to a constant level between 60 and 65 percent for wavelengths from 400 to beyond 650 nm. A further increase of sphere efficiency was obtained in a final design by reducing the sphere diameter and further optimization of the dye [8].

It was also ascertained that the fluorescence wavelength converter did not affect the linearity of the detection system. Theoretically, the radiant intensity of fluorescence from the dye can be expressed as

$$I_e = QI_a, \tag{2a}$$

where Q is the quantum efficiency of the dye and I_a is the intensity absorbed. The latter is given by Beer's law as

$$I_a = I_o(1 - 10^{-\epsilon c b}) \tag{2b}$$

where I_o is the initial intensity, and where ϵ, c, and b denote molar absorptivity, concentration, and path length, respectively. Thus, I_e is proportional to I_o under the applicable assumptions that Beer's law is valid and that the quantum efficiency of the dye is independent of intensity. This conclusion was verified by measuring the linearity of the detection system at one wavelength (250 nm) for which the dye is effective, and at another (400 nm) for which it is not. These two measurements, which were made using the double-aperture method [9], yielded indistinguishable results within the limits of experimental uncertainty, and also agreed with previously performed linearity measurements of the same photomultiplier tube at 575 nm [1].

2.3. Grating

The previously obtained clear-space signal level, curve (c) in figure 1, was still judged inadequate for accurate work at short wavelengths. Since the original grating of the spectrophotometer (blazed for 500 nm in the first order) had been chosen for work in the visible, it was obvious that a further improvement could be effected by substitution of another grating. This new grating has 600 lines/mm, is blazed for 200 nm in the first order, and resulted in the final clear-space signal current plotted as curve (d) in figure 1. Since the signal level near 200 nm can easily be raised by adjusting the photomultiplier gain, the original goal of achieving a clear-space signal of at least 10^{-7} A throughout the ultraviolet had thus been accomplished.

The loss of signal level in the visible due to the change of gratings [curves (d) and (c) in figure 1] is relatively small, and is more than offset by the higher efficiency of the new sphere [curves (c) and (b)]. Thus the modified spectrophotometer can be used above 400 nm by merely interchanging deuterium and tungsten lamps, without need to substitute gratings.

2.4. Achromatic Sample-Compartment Optics

In view of the wide spectral range of the modified spectrophotometer, the chromatic aberration of the original sample-compartment lenses proved to be a limiting factor of instrumental performance. Significant losses of signal level were caused by the fact that these lenses, when initially focused by eye, were out of focus in the ultraviolet and thus caused less-than-optimal illumination of sample and detector.

If the monochromator exit slit is focused at the sample with unit magnification at a wavelength λ_0, the diameter of the blur circle in the sample plane for a wavelength $\lambda < \lambda_0$ can easily be shown to be equal to

$$\delta = D[2f(\lambda_0)/f(\lambda) - 1], \tag{3}$$

where f is the focal length and D is the effective diameter of the focusing lens. For the particular lenses of the original spectrophotometer [f(200 mm) = 168 mm, f(500 nm) = 200 nm, D = 38 mm], and assuming that the focusing was done at 500 nm, the computed blur-circle diameter at 200 mm is 14 mm. This numerical example illustrates the large defocusing caused by chromatic lenses in the sample compartment, although it should be pointed out that due to the opposing effect of the second lens a smaller blur circle is incurred at the detector. Nevertheless, it was found empirically that the ultraviolet signal level of the spectrophotometer could be improved as much as 30 percent by repositioning the sample-compartment lenses.

The most effective way to overcome this deficiency of the spectrophotometer would have been to use mirror optics, but since this would have required a redesign of the sample compartment and its enclosure it was more expedient to employ achromatic lenses. The lenses selected are f/3 lithium-fluoride, fused-silica (non fluorescent) achromats with 200 mm focal length, best correction for longitudinal chromatic aberration between 200 and 400 nm, and with anti-reflection coating for 400 nm.

On account of the limited spectral regions for which the deuterium and tungsten lamps of the modified spectrophotometer are employed, it was not found necessary to use an achromat in the source compartment as well.

3. Conclusion

As a result of the work reported here, the modified high-accuracy spectrophotometer is now used, throughout the spectral region between 200 and 800 nm, for

the certification of solid and liquid Standard Reference Materials for routine applications in spectrophotometry, as well as for materials research aimed at establishing inorganic and organic molar absorptivity standards.

The modified spectrophotometer may also serve as a model for improved commercial instrumentation. In particular, it is anticipated that the development of a highly efficient averaging sphere for visible and ultraviolet wavelengths will lead to a more widespread use of spheres in routine spectrophotometry.

4. References and Notes

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[3] The systematic error due to interreflection between the sample-compartment lenses is accounted for in all measurements made with this spectrophotometer. See Mielenz, K. D., and Mavrodineanu, R., J. Res. Nat. Bur. Stand. (U.S.), **77A** (Phys. and Chem.), No. 6, 699–703 (Nov.–Dec. 1973).

[4] K. D. Mielenz, J. Res. Nat. Bur. Stand. (U.S.), **76A** (Phys. and Chem.). No. 5, 455–467 (Sept.–Oct. 1972).

[5] Although tungsten-halogen lamps are frequently used in ultraviolet spectrophotometry, such a source was unsuitable for this application. A 250-W, single-coil tungsten-bromide lamp was tried, but merely resulted in an over-all increase of signal level which could also have been achieved by choosing a more intense tungsten lamp or increasing the photomultiplier gain. The tungsten-bromide lamp exhibited essentially the same steep drop of signal toward shorter wavelengths as the tungsten lamp, and was found to be inadequate for accurate work below 320 nm. A further difficulty is that tungsten-halogen lamps are generally too unstable for high-accuracy spectrophotometry in a single-beam geometry. See Clarke, F. J. J., J. Res. Nat. Bur. Stand. (U.S.), **76A** (Phys. and Chem.), No. 5, 375–403 (Sept.–Oct. 1972).

[6] Grum, F., and Luckey, G. W., Appl. Optics **7**, 2289–2294 (1968).

[7] A significant improvement of the visible and ultraviolet signal levels was found with a flux averager consisting of two double-ground fused-silica plates, 1 mm in thickness and spaced by a diffusely reflecting, cylindrical Al_2O_3 tube with 50 mm length and internal diameter. Although this type of averager has been used successfully for other applications (See Budde, W., Proc. Fourth Imeko Symposium, Prague 1969, p. 167), the averaging effectiveness of the particular unit used in this work was inadequate for this application since a beam displacement of ± 1 mm at the entrance window of the averager still caused a 0.4 percent change in the photomultiplier signal. These measurements were performed by Mr. K. L. Eckerle of the Optical Radiation Section of NBS.

[8] Mielenz, K. D., Mavrodineanu, R., and Cehelnik, E. D., Appl. Optics (to be published).

[9] Mielenz, K. D. and Eckerle, K. L., Appl. Optics **11**, 2294–2303 (1972).

(Paper 78A5–838)

Appendix 8

Sintered mixtures of phosphors in polytetrafluoroethylene resin for fluorescence standards

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U.S. National Bureau of Standards, Gaithersburg, Maryland 20899

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Applied Optics
25,No.6, 828 (1986)

The National Bureau of Standards is investigating the fluorescence properties of sintered mixtures of inorganic phosphors and polytetrafluoroethylene (PTFE) resin as possible reference materials for fluorescence standards. Four phosphors were selected from a collection of NBS standard phosphors[1] that produce emission spectra in the blue, green, yellow, and orange wavelength regions of the visible spectrum. The spectral properties of PTFE make it ideal for this application because of its low absorption in the UV and visible spectrum.

Analysis of the fluorescence properties of these specimens was done on the NBS Reference Spectrofluorimeter.[2] The initial testing involved an examination of the specimen stability under exposure to UV radiation. Figure 1 shows the emission spectra of the four phosphor–PTFE specimens before and after an 8-h exposure to a 450-W xenon source at a distance of 15 cm. The observed differences between the emission spectra before and after the exposure to the xenon source were too small to be shown in Fig. 1. The sintered specimens appear to be unaffected by this intensity of exposure. Further studies are being conducted to determine the effects of phosphor concentration on the measured emission spectra and the effects of varying the excitation wavelengths.

The emission spectra illustrated in Fig. 1 were obtained from specimens containing 10% phosphor by weight in PTFE. The sintered specimens were produced in 2-mm thick disks of ~50-mm diameter in crucibles of the design shown in Fig. 2. The powder mixture is pressed to a density of 1 g/cm^3 between two ceramic disks in the crucible. The specimen volume shrinks by ~10% during the sintering process, which takes place in an electric furnace at 370°C. The specimen temperature is monitored by means of a thermocouple probe inserted into the base of the crucible. The process requires ~3 h for the temperature of the crucible to rise to 370°C, after which it remains at this temperature for ~1 h before being allowed to cool. The powder specimen is placed between ceramic disks to reduce the chances of contamination from the metal parts of the crucible that develop an oxidation coating during the high-temperature cycle. After removal from the crucible, the specimen is buffed on an abrasive cloth to remove surface irregularities and produce a flat diffuse surface on the finished disk. Rectangular specimens are sliced from the sintered disk and mounted in 10-mm square cuvette holders for analysis. These cuvette holders have apertures on all four sides so that the specimen can be illuminated by the excitation radiation through one aperture and the emission radiation viewed through an aperture at 90° from the optical axis of the excitation beam. The specimen is mounted so that the incident excitation beam is 60° from the normal to the plane of the specimen. This geometry allows the specular component of the reflected excitation radiation to be excluded from measurement of the fluorescence spectra.

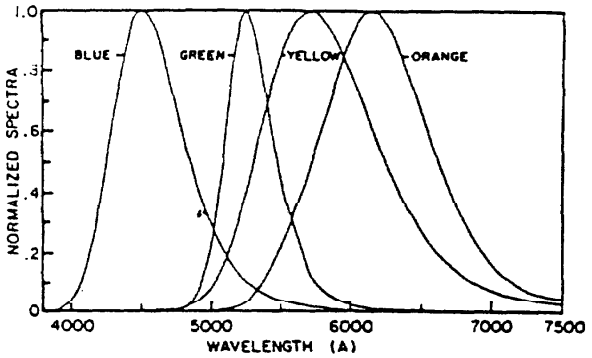

Fig. 1. Emission spectra of four sintered specimens containing 10% phosphor in PTFE resin.

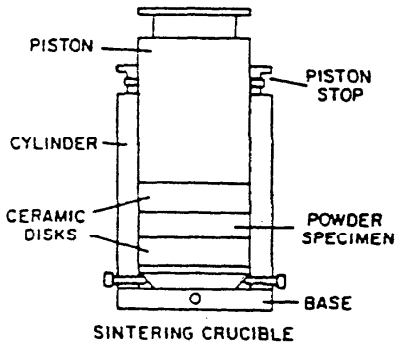

Fig. 2. Design of the crucible used to sinter the mixtures of phosphors in the PTFE resin.

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2. K. D. Mielenz in *Measurement of Photoluminescence*, K. D. Mielenz, Ed. (Academic New York, 1982), pp. 17–19.

Appendix 9

National Institute of Standards & Technology

Certificate

Standard Reference Material 930d

Glass Filters for Spectrophotometry

This Standard Reference Material (SRM) is intended for use in the verification of the transmittance and absorbance scales of spectrophotometers in the visible spectral domain. SRM 930d consists of three individual glass neutral density filters in separate metal holders and one empty filter holder. The exposed surface of the glass is approximately 29 x 8 mm, measuring from a point 1.5 mm above the base of the filter holder (see figure 1). The filter holders are provided with shutters that protect the glass filters when not in use. Each filter-containing holder bears a set identification number and a filter number (10, 20, or 30), which corresponds to the nominal % transmittance (100 x transmittance) of the filter.

Certified Transmittance Values: Certified transmittance values independently determined for each filter at five wavelengths in the visible portion of the electromagnetic spectrum are given in Table 1. The relative uncertainty of the certified transmittance values is $\pm$ 0.5% at 21 $\pm$ 2 °C for a period of two years from the date of certification specified below in Table 2. This uncertainty includes the effects of the random and systematic errors of the calibration procedure, as well as estimated systematic errors associated with alignment of the filters and material properties (e.g. aging of the glass which may cause some filters to change transmittance by about + 0.25% over the two-year period). Uncertainty estimation is described in the NIST Special Publication 260-116. [1]

Certified Transmittance Densities: The transmittance densities given in Table 2 are calculated from the certified transmittance (T) as $-\log_{10} T$. These values should be indicated by the absorbance (A) scale of the spectrophotometer if the filters are measured against air. The overall uncertainty in transmittance density is $\pm$ 0.002 absorbance units (AU) for a period of two years from the date of certification below Table 2.

The research, development, and initial production of this SRM were conducted in the NIST Inorganic Analytical Research Division by R. Mavrodineanu and J.R. Baldwin.

The transmittance measurements were performed in the NIST Inorganic Analytical Research Division by J.C. Travis, M.V. Smith, and N.K. Winchester.

The overall direction and coordination of technical measurements leading to certification were performed in the NIST Inorganic Analytical Research Division by J.C. Travis and R.L. Watters, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J.C. Colbert.

Gaithersburg, MD 20899
October 18, 1993
(Revision of certificate dated 9-27-93)

Thomas E. Gills, Acting Chief
Standard Reference Materials Program

(over)

NOTICE AND WARNINGS TO USERS

Storage and Handling: SRM 930d is stored in a black anodized aluminum container fitted with a threaded cap made of the same metal. Contamination of the glass filter surface with particulate matter due to static charge is minimized by the metallic nature of the container. Each filter is placed in a cylindrical cavity to prevent any contact between the filter face and the walls of the storage container. Each filter holder is provided with a flat leaf spring which is inserted into the cylindrical cavity to minimize damage during transportation. These springs can be removed during normal use in the laboratory. Improper storage or handling of the filters may cause changes in the transmittance. [1] It is recommended that the filters in the holders be handled only by the edges with soft plastic (polyethylene) gloves and optical lens tissue. When not in use they should be stored in their holders and in the container provided for this purpose. Extended exposure to laboratory atmosphere and dusty surroundings should be avoided. Should the surface of the glass filter become contaminated, no attempt should be made to clean it unless the user has the facilities to demonstrate that the cleaning treatment has not altered the glass surface or compromised the certified values. As this SRM is a transfer standard, the only means available to verify its integrity is by remeasuring its transmittance with a primary standard instrument similar to that used in this certification. [2-4]

Expiration of Certification: This certification is valid for 2 years from the date of certification specified below in Table 2.

Recalibration: The filters should be returned to NIST for cleaning and recalibration at two-year intervals to revalidate the filters. For recalibration, please contact M.V. Smith at (301) 975-4115 or N.K. Winchester at (301) 975-3152. Filters for recalibration should be shipped to M.V. Smith, NIST, Bldg. 222, Rm. B222, Gaithersburg, MD 20899.

Instrument Dependence Warning: Some samples of SRM 930d may cause a small (<0.02 AU) increase in the apparent absorbance, resulting from a minor deviation of the optical axis, in instruments for which wavelength dispersion occurs after the light has passed through the filter. If such effects are detected or suspected, the user should contact J.C. Travis, NIST Inorganic Analytical Research Division at (301) 975-4117, for assistance and instructions.

Source and Preparation of Material: The neutral glasses for the filters were provided by Schott of Mainz, Germany, and are designated as "Jena Color and Filter Glass." Glass material of types NG-4 and NG-5 were selected for best homogeneity and a minimum of inclusions and striae. The filters were cut from plates which were ground and polished in the NIST optical shop to appropriate thicknesses to achieve the nominal transmittances of 0.1, 0.2, and 0.3. [1,5] Prior to certification measurements, the glass filters were aged at NIST for at least six months and each filter was examined for surface defects and thoroughly cleaned. [1]

Determination of Transmittances: The transmittance measurements were made against air (an empty filter holder) at an ambient temperature of 21.0 ± 1.0 °C using the high-accuracy spectrophotometer designed and built in the NIST Inorganic Analytical Research Division. [2] This instrument represents the primary transmittance standard; its transmittance accuracy was established using the double-aperture method of linearity testing. [1,2,6,7] The effective spectral bandpass used to determine the certified values was 0.8 nm. The transmittance measurements were made by producing the vertical image of the slit (about 8 mm by 1 mm), using a convergent beam geometry with an aperture ratio f:10, in the middle of the entrance face of the glass filter. The filter is mounted in a multiple-filter carousel in the spectrophotometer. Each transmittance value reported in Table 1 is the average of three transmittances determined over an eight-min period required for three carousel rotations. The transmittance is measured in this way several times during an aging period of at least six months, and only the final measurement is reported. Each transmittance measurement is calculated from a measurement of the intensity transmitted through

the filter and bracketing measurements of the intensity transmitted through an empty filter holder, with a settling time of approximately 5 s and a signal integrating time of approximately 1 s for each measurement. The filters were measured in the spectrophotometer in a position perpendicular to the incident light beam as shown in figure 1.

Uniformity: The transmittance uniformity of each filter comprising SRM 930d was established over an area 5 mm wide by 24 mm long and located symmetrically about the center face of each filter. The transmittance was required to vary by less than the estimated systematic error component for uniformity of 0.3%, relative, over the specified area.

Instructions for Use: The transmittance of the filters depends upon the intrinsic properties of the material, wavelength, spectral bandpass, geometry of the optical beam, and can be affected by other factors such as stray light, temperature, and positioning of the filter. A change of ambient temperature of $\pm$ 2 °C from 21.0 °C will not significantly affect the calibration. [1] Changes in the transmittance may be caused by changes in surface conditions, aging of the glass, exposure to a harmful atmosphere or careless handling as indicated under "Storage and Handling". [1,3,5,6] The spectral bandpass values indicated in parentheses in this certificate are maximum values that should not be exceeded when accurate measurements are contemplated. The empty filter-holder is provided to be used in the reference beam of the spectrophotometer so that approximately equivalent conditions of stray radiation are achieved for both beams. The shutters provided with each filter must be removed at the time of measurement and be replaced after the measurements have been completed. Measurements performed outside of these specified conditions, and the optical geometry described under "Determination of Transmittances", will produce transmittance values that might differ from the certified data.

The cooperation of G.N. Bowers, Jr., M.D., of Hartford Hospital, Hartford, CT; R.N. Rand, Ph.D., of the Eastman Kodak Co. Research Laboratories, Rochester, NY; D.S. Young, M.D. and Ph.D., of the Mayo Clinic, Rochester, MN; and B. Mueller, Ph.D, of Hewlett-Packard GmbH, Waldbronn, Germany are gratefully acknowledged.

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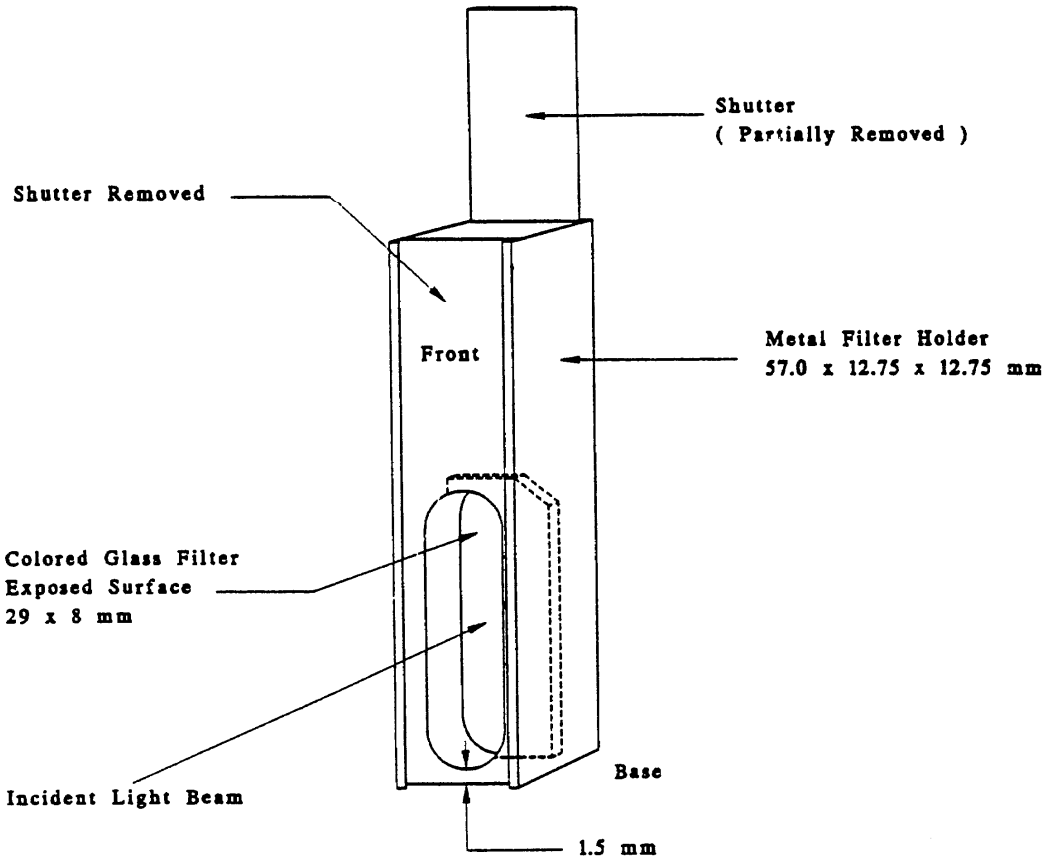
[7] Mielenz, K.D., and Eckerle, K.L., Spectrophotometer Linearity Testing Using the Double-Aperture Method, Appl. Optics 11, pp. 2294-2303, (1972).

Figure 1. Metal Holder for the Colored Glass Filters



National Institute of Standards & Technology

Certificate

Standard Reference Material 1930

Glass Filters for Spectrophotometry

This Standard Reference Material (SRM) is intended as a reference source for the verification of the transmittance and absorbance scales of spectrophotometers in the visible spectral domain. It is complementary to SRM 930d, providing levels of transmittance/absorbance that are outside the range covered by that SRM. SRM 1930 consists of three individual glass neutral density filters in separate metal holders and one empty filter holder. The exposed surface of the glass is approximately 29 x 8 mm, measuring from a point 1.5 mm above the base of the filter holder (see figure 1). The filter holders are provided with shutters that protect the glass filters when not in use. Each filter-containing holder bears a set identification number and a filter number (1, 3, or 50), which corresponds to the nominal % transmittance (100 x transmittance) of the filter.

Certified Transmittance Values: Certified transmittance values independently determined for each filter at five wavelengths in the visible portion of the electromagnetic spectrum are given in Table 1. The relative uncertainty of the certified transmittance values is $\pm$ 1.2% for filters 1 and 3 and $\pm$ 0.4% for filter 50, for a period of two years from the date of certification specified below Table 2. This uncertainty includes the effects of the random and systematic errors of the calibration procedure, as well as estimated systematic errors associated with alignment of the filters and material properties (e.g. aging of the glass which may cause some filters to change transmittance by as much as 0.4% over the two-year period). Uncertainty estimation is described in the NIST Special Publication 260-116. [1]

Certified Transmittance Densities: The transmittance densities given in Table 2 are calculated from the certified transmittances (T) as $-\log_{10} T$. These values should be indicated by the absorbance (A) scale of the spectrophotometer if the filters are measured against air. The overall uncertainty in transmittance density is $\pm$ 0.003 absorbance units (AU) for filters 1 and 3 and $\pm$ 0.0015 AU for filter 50, for a period of two years from the date of certification below Table 2.

The research, development, and initial production of this SRM were conducted in the NIST Inorganic Analytical Research Division by R. Mavrodineanu and J.R. Baldwin.

The transmittance measurements were performed in the NIST Inorganic Analytical Research Division by J.C. Travis, M.V. Smith, and N.K. Winchester.

The overall direction and coordination of technical measurements leading to certification were performed in the NIST Inorganic Analytical Research Division by J.C. Travis and R.L. Watters, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J.C. Colbert.

Gaithersburg, MD 20899
September 27, 1993
(Revision of certificate dated 3-30-93)

Thomas E. Gills, Acting Chief
Standard Reference Materials Program

(over)

NOTICE AND WARNINGS TO USERS

Storage and Handling: SRM 1930 is stored in a blue anodized aluminum container fitted with a threaded cap made of the same metal. Contamination of the glass filter surface with particulate matter due to static charge is minimized by the metallic nature of the container. Each filter is placed in a cylindrical cavity to prevent any contact between the filter face and the walls of the storage container. Each filter holder is provided with a flat leaf spring which is inserted into the cylindrical cavity to minimize damage during transportation. These springs can be removed during normal use in the laboratory. Improper storage or handling of the filters may cause changes in the transmittance. [1] It is recommended that the filters in the holders be handled only by the edges with soft plastic (polyethylene) gloves and optical lens tissue. When not in use they should be stored in their holders and in the container provided for this purpose. Extended exposure to laboratory atmosphere and dusty surroundings should be avoided. Should the surface of the glass filter become contaminated, no attempt should be made to clean it unless the user has the facilities to demonstrate that the cleaning treatment has not altered the glass surface or compromised the certified values. As this SRM is a transfer standard, the only means available to verify its integrity is by remeasuring its transmittance with a primary standard instrument similar to that used in this certification. [2-4]

Expiration of Certification: This certification is valid for 2 years from the date of certification specified below Table 2.

Recalibration: The filters should be returned to NIST for cleaning and recalibration at two-year intervals to revalidate the filters. For recalibration, please contact M.V. Smith at (301) 975-4115 or N.K. Winchester at (301) 975-3152. Filters for recalibration should be shipped to M.V. Smith, NIST, Bldg. 222, Rm. B222, Gaithersburg, MD 20899.

Instrument Dependence Warning: Some samples of SRM 1930 may cause a small (<0.02 AU) increase in the apparent absorbance, resulting from a minor deviation of the optical axis, in instruments for which wavelength dispersion occurs after the light has passed through the filter. If such effects are detected or suspected, the user should contact J.C. Travis, NIST Inorganic Analytical Research Division at (301) 975-4117, for assistance and instructions.

Source and Preparation of Material: The neutral glasses for the filters were provided by Schott of Mainz, Germany, and are designated as "Jena Color and Filter Glass." Glass material of types NG-3 and NG-11 were selected for best homogeneity and a minimum of inclusions and striae. The filters were cut from plates which were ground and polished in the NIST optical shop to appropriate thicknesses to achieve the nominal percent transmittances of 1, 3, and 50%. [1,5] Prior to certification measurements, the glass filters were aged at NIST for at least six months and each filter was examined for surface defects and thoroughly cleaned. [1]

Determination of Transmittances: The transmittance measurements were made against air (an empty filter holder) at an ambient temperature of 21.0 ± 1.0 °C using the high-accuracy spectrophotometer designed and built in the NIST Inorganic Analytical Research Division. [2] This instrument represents the primary transmittance standard; its transmittance accuracy was established using the double-aperture method of linearity testing. [1, 2, 6, 7] The effective spectral bandpass used to determine the certified values was 0.8 nm. The transmittance measurements were made by producing the vertical image of the slit (about 8 mm by 1 mm), using a convergent beam geometry with an aperture ratio f:10, in the middle of the entrance face of the glass filter. The filter is mounted in a multiple-filter carousel in the spectrophotometer. Each transmittance value reported in Table 1 is the average of three transmittances determined over an eight-min period required for three carousel rotations. The transmittance is measured in this way several times during an aging period of at least six months, and only the final measurements are reported. Each transmittance measurement is calculated from a measurement of the intensity transmitted through the filter and bracketing measurements of the intensity transmitted through an empty filter holder, with a settling time of approximately 5 s and a signal integrating time of approximately 1 s for each measurement. The filters were measured in the spectrophotometer in a position perpendicular to the incident light beam as shown in figure 1.

Uniformity: The transmittance uniformity of each filter comprising SRM 1930 was established over an area 5 mm wide by 24 mm long and located symmetrically about the center face of each filter. The transmittance was required to vary by less than the estimated systematic error component for uniformity of 0.9%, relative, for filter 1, 0.8% for filter 3 and 0.2% for filter 50, over the specified area.

Instructions for Use: The transmittance of the filters depends upon the intrinsic properties of the material: wavelength, spectral bandpass, geometry of the optical beam, and can be affected by other factors such as stray light, temperature, and positioning of the filter. A change in ambient temperature of ± 2 °C from 21.0 °C will not significantly affect the calibration. [1] Changes in the transmittance may be caused by changes in surface conditions, aging of the glass, exposure to a harmful atmosphere or careless handling as indicated under "Storage and Handling". [1,3,5,6] The spectral bandpass values indicated in parentheses in this certificate are maximum values that should not be exceeded when accurate measurements are contemplated. The empty filter-holder is provided to be used in the reference beam of the spectrophotometer so that approximately equivalent conditions of stray radiation are achieved for both beams. The shutters provided with each filter must be removed at the time of measurement and be replaced after the measurements have been completed. Measurements performed outside of these specified conditions, and the optical geometry described under "Determination of Transmittances", will produce transmittance values that might differ from the certified data.

The cooperation of G.N. Bowers, Jr., M.D., of Hartford Hospital, Hartford, CT; R.N. Rand, Ph.D., of the Eastman Kodak Co. Research Laboratories, Rochester, NY; D.S. Young, M.D. and Ph.D., of the Mayo Clinic, Rochester, MN; and B. Mueller, Ph.D, of Hewlett-Packard GmbH, Waldbronn, Germany are gratefully acknowledged.

REFERENCES

[1] Mavrodineanu, R., et al., Glass Filters as a Standard Reference Material for Spectrophotometry - Selection, Preparation, Certification, and Use, SRM 930 and SRM 1930, NIST Spec. Publ. 260-116, (1993).

[2] Mavrodineanu, R., An Accurate Spectrophotometer for Measuring the Transmittance of Solid and Liquid Materials, NBS Journal of Research 76A, No. 5, pp. 405-425, (1972).

[3] Collected Papers from NBS Conference on Accuracy in Spectrophotometry and Luminescence Measurements, NBS Journal of Research 76A, No. 5, pp. 375-510, (1972).

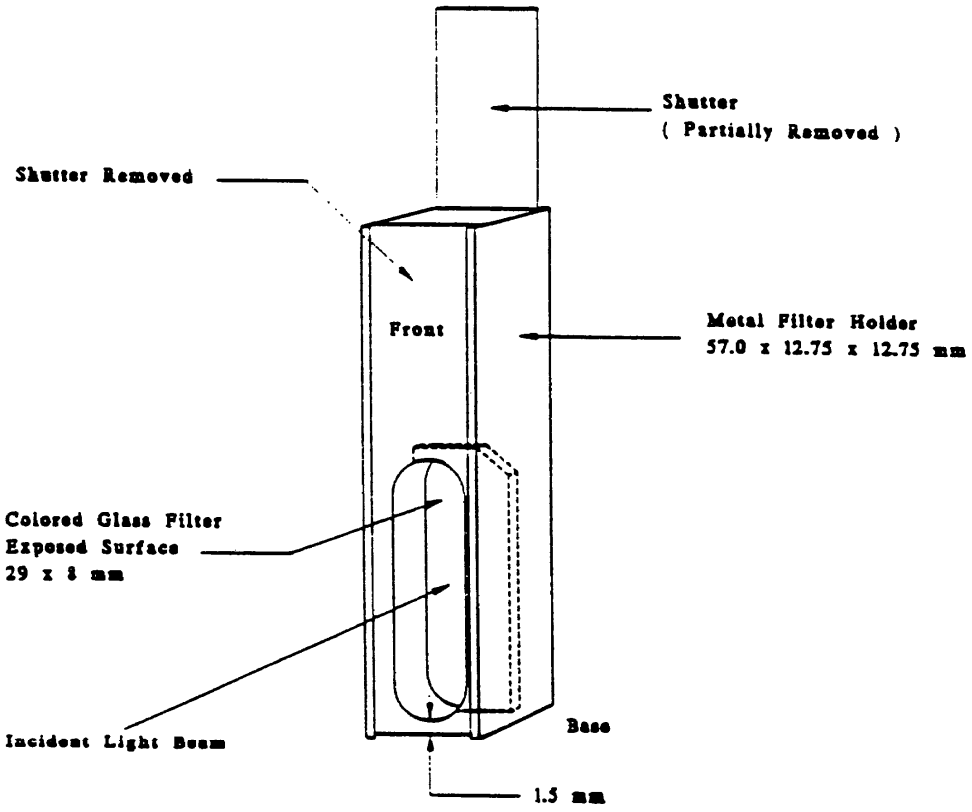
[4] Burke, R.W., and Mavrodineanu, R., Accuracy in Analytical Spectrophotometry, NBS Spec. Publ. 260-81, (1983).

[5] Mavrodineanu, R., Solid Materials to Check the Photometric Scale of Spectrophotometers, NBS Tech. Note 544, Menis, O., and Shultz, J.I., eds., pp. 6-17, (Sept. 1970); ibid, NBS Tech. Note 584, pp. 2-21, (December 1971).

[6] Gibson, K.S., Spectrophotometry, NBS Circ. 484, (Sept. 1949).

[7] Mielenz, K.D., and Eckerle, K.L., Spectrophotometer Linearity Testing Using the Double-Aperture Method, Appl. Optics 11, pp. 2294-2303, (1972).

Figure 1. Metal Holder for the Colored Glass Filters



Appendix 11

National Institute of Standards & Technology

Certificate

Standard Reference Material 2031

Metal-on-Quartz Filters for Spectrophotometry

This Standard Reference Material (SRM) is intended for use in the verification of the transmittance and absorbance scales of conventional spectrophotometers at selected wavelengths in the ultraviolet and visible spectral domains. SRM 2031 consists of three individual neutral density filters in their metal holders and one empty filter holder. The exposed surface of each filter is approximately 29 x 8 mm, measuring from a point 1.5 mm above the base of the filter holder (see Figure 1). The metal holders for these filters are provided with shutters to protect the filters when not in use. Each filter containing holder bears a set identification number and a filter number (10, 30, or 90), which corresponds to the nominal percent transmittance (100 x transmittance) of the filter.

Certified Transmittance Values: Certified transmittance values independently determined for each filter at ten wavelengths in the visible and ultraviolet spectral domains are given in Table 1. The relative uncertainties of the certified transmittance values are ± 1.0% for filters 10 and 30, and ± 0.5% for filter 90 at an operational temperature range of 21 ± 2 °C for a period of two years from the date of certification specified under Table 2. These uncertainties include 0.5% for random and systematic errors of the calibration procedure for all three filters in the set, as well as 0.5% for error sources unique to the metal film filters (numbers 10 and 30). The estimates are based on a study of 19 filter sets [1], and include the inherent effects of temperature and humidity variation, positional reproducibility, and apparent changes in the transmittance over a two-year period. In addition, the uncertainty includes components to account for potential differences between the NIST and user measurement conditions. These differences might include a wider temperature range, non-normality of the filter with respect to the optical axis (± 3 degrees of arc), the size of the spectrophotometer beam, and its position on the filter (see **"Uniformity"**, page 3).

Certified Transmittance Densities: The transmittance densities given in Table 2 are calculated from the certified transmittance (T) as $-\log_{10} T$. These values should be indicated by the absorbance (A) scale of the spectrophotometer when the filters are measured against air. The overall uncertainty in transmittance density is ± 0.004 absorbance units (AU) for filters 10 and 30, and ± 0.002 AU for filter 90 for a period of two years from the date of certification under Table 2.

The research, development, and initial production of this SRM were performed in the NIST Inorganic Analytical Research Division by R. Mavrodineanu and J.R. Baldwin.

The transmittance measurements were performed in the NIST Inorganic Analytical Research Division by M.V. Smith, N.K. Winchester, and J.C. Travis.

The overall direction and coordination of technical measurements leading to certification were performed in the NIST Inorganic Analytical Research Division by J.C. Travis and R.L. Watters, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J.C. Colbert.

Gaithersburg, MD 20899
October 28, 1993
(Revision of certificate dated 1-25-93)

Thomas E. Gills, Acting Chief
Standard Reference Materials Program

(over)

NOTICE AND WARNINGS TO USERS

Storage and Handling: SRM 2031 is stored in a black-anodized aluminum container provided with a threaded cap made of the same metal. Each filter is placed in a cylindrical cavity to prevent any contact between the filter face and the walls of the storage container. Contamination of the filter surface with particulate matter due to static charges is minimized by the metallic nature of the container. A flat leaf spring is inserted into the cylindrical cavity with each filter holder to minimize damage during transportation. These springs can be removed during normal use in the laboratory. Changes in the transmittance of the filters may be caused by surface conditions, aging of the material, exposure to a harmful atmosphere, or careless handling.[3,5-7] It is recommended that the filters in the holders be handled only by the edges with soft plastic (polyethylene) gloves and optical lens tissue. When not in use, the filters should be stored in their holders with the shutters in place and in the metal container provided for this purpose. Extended exposure to laboratory atmosphere and dirty surroundings should be avoided. Should the surface of the filter become contaminated, no attempt should be made to clean it unless the user has the facilities to demonstrate that the cleaning treatment will not alter the surface or degrade the accuracy of the certified values. As SRM 2031 is a transfer standard, the only means available to verify its integrity is to remeasure its transmittance with a primary standard instrument similar to that used in this certification.[1,3]

Expiration of Certification: Normal surface degradation and aging of the metallic film may cause the transmittance of the filters to change by an appreciable fraction of the certified uncertainty over a period of two years. This certification is therefore valid for 2 years from the date of certification under Table 2.

Recalibration: The filters should be returned to NIST for cleaning and recalibration at two-year intervals to validate the filters' integrity. For recalibration, please contact M.V. Smith at (301) 975-4115 or N.K. Winchester at (301) 975-3152. Filters for recalibration should be shipped to M.V. Smith, NIST, Bldg. 222/Rm 222, Gaithersburg, MD 20899.

Instrument Dependence Warning: In some commercial instruments, the metal-on-quartz filters can generate reflection effects in the sample compartment that can degrade the accuracy of the measured transmittances. During the development of SRM 2031, the presence and magnitude of reflection effects were studied and were found negligible, within the uncertainty specified, in all spectrophotometers tested (see Ref. 3, pp. 16-30 for additional details of this study). However, for certain instruments these effects could become significant. If such effects are detected or suspected, the user should contact J.C. Travis, NIST Inorganic Analytical Research Division at (301) 975-4117, for assistance and instructions.

Source and Preparation of Material: The evaporative coating of quartz substrates with thin chromium films was performed by Evaporated Metal Films, Ithaca, NY. The quartz plates were provided by Dynasil Corp. of America, Berlin, NJ. Except for the chromium coatings, the filters that constitute SRM 2031 were fabricated by the NIST Optical and Instrument Shops. Two filters, having nominal transmittances of 0.1 and 0.3, were produced by evaporating different thicknesses of chromium metal onto 1.5 mm thick fused silica plates that had been precision ground and polished. These metal films are protected by 1.5 mm thick clear fused silica cover plates optically contacted to the base plates. The third filter is a single fused silica plate 3 mm thick, having a nominal transmittance of 0.9. Prior to certification measurements, the filters were aged at NIST for at least six months and each filter was examined for surface defects and the condition of the optical contact.[3]

Determination of Transmittances: The transmittance measurements were made against air (an empty filter holder) at an ambient temperature of 21.0 ± 1.0 °C using the high-accuracy spectrophotometer designed and built in the NIST Inorganic Analytical Research Division.[5] This instrument is a primary transmittance standard; its transmittance accuracy was established using the double-aperture method of linearity testing.[5-7] The effective spectral bandpass used to determine the certified values was 1.6 nm in the ultraviolet and 0.8 nm in the visible region. Transmittance measurements for SRM 2031 were made by producing the vertical image of the slit (about 8 mm x 1.5 mm), using a convergent beam geometry with an aperture ratio f:10, in the middle of the entrance face of the filter. The filter is mounted in a multiple-filter carousel in the spectrophotometer, and is perpendicular to the incident light beam when in the measurement position. Each transmittance value reported in Table 1 is the average of three transmittances determined over an eight-min period required for three carousel rotations. The transmittance is measured in this way several times during an aging period of at least six months, and only the final measurement is reported. Each transmittance measurement is calculated from a measurement of the intensity transmitted through the filter and bracketing measurements of the intensity transmitted through an empty filter holder, with a settling time of approximately 5 s and a signal integrating time of approximately 1 s for each measurement.

Uniformity: The transmittance uniformity of each filter comprising SRM 2031 was established over an area 5 mm wide by 24 mm long and located symmetrically about the center face of each filter. The variation in transmittance over the specified area was less than 0.8% for filters 10 and 30, and 0.2% for filter 90. Further information concerning the selection, preparation, and properties of SRM 2031 will be found in reference. [1]

Instructions for Use: The measured transmittance of the filters depends upon the intrinsic properties of the material, wavelength, spectral bandpass, geometry of the optical beam, and can be affected by other factors such as stray light, temperature, and positioning of the filter. While changes of ± 2 °C in ambient temperature from 21.0 °C have not significantly affected the calibration, the effect of temperature variations exceeding ± 2 °C have not been investigated. The empty filter holder provided is to be used in the reference beam of the spectrophotometer so that approximately equivalent conditions of stray radiation are achieved for both beams. The shutters provided with the filters must be removed at the time of measurement and be replaced after the measurements have been completed. Because the transmittance of these filters exhibits an appreciable optical neutrality, the dependence of transmittance on bandpass is not critical, and wider bandpasses than that employed for certification (see **"Determination of Transmittances"**, page 3) may be used in routine measurements. For a quantitative discussion of this subject, the user should consult reference [1], p. 32. Measurements performed outside of the specified conditions, and the optical geometry described under **"Determination of Transmittances"**, will produce transmittance values that might differ from the certified data.

We wish to acknowledge the cooperation of G.N. Bowers, Jr., M.D., of Hartford Hospital, Hartford, CT; R.N. Rand, Ph.D., of the Eastman Kodak Co. Research Laboratories, Rochester, NY; and D.S. Yound, M.D., Ph.D., of the Mayo Clinic, Rochester, MN. H.E. Bennett and J.M. Bennett of the Michelson Laboratory, Physical Optics Branch, Naval Weapons Center, China Lake, CA, who helped in the initial production of SRM 2031, are also gratefully acknowledged.

REFERENCES

[1] Mavrodineanu, R. and Baldwin, J.R., Metal-on-Quartz Filters as a Standard Reference Material for Spectrophotometry, SRM 2031; NBS Special Publication 260-68; (1979).

[2] Mavrodineanu, R., Solid Materials to Check the Photometric Scale of Spectrophotometers, NBS Tech. Note 544, Menis, O. and Shultz, J.I., eds., pp. 6-17, (Sept. 1970); ibid, NBS Tech. Note 584, pp. 2-21, (Dec. 1971).

[3] Mavrodineanu, R., Considerations for the Use of Semi-Transparent Metallic Thin Films as Potential Transmittance Standards in Spectrophotometry. NBS Journal of Research 80A, No. 4, pp. 637-641, (1976).

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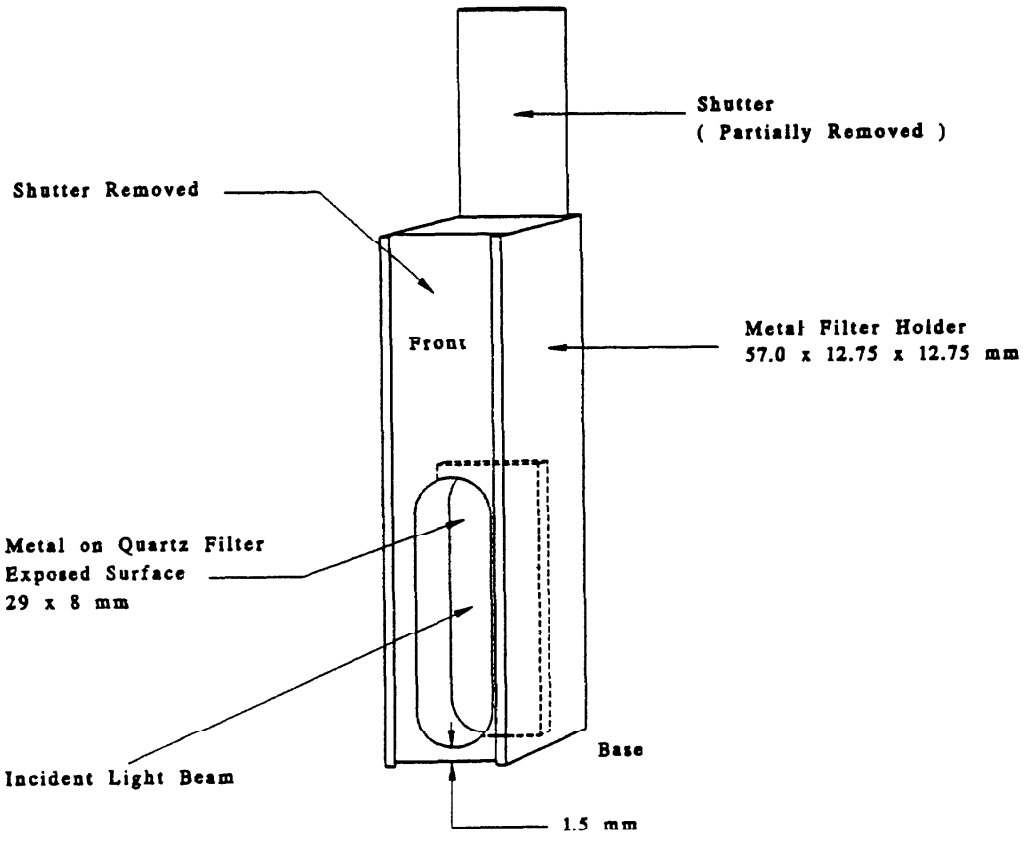
[5] Mavrodineanu, R., An Accurate Spectrophotometer for Measuring the Transmittance of Solid and Liquid Materials; NBS Journal of Research 76A, No. 5, pp. 405-425, (1972).

[6] Gibson, K.S., Spectrophotometry, NBS Circ. 484; (Sept. 1949).

[7] Mielenz, K.D. and Eckerle, K.L., Spectrophotometer Linearity Testing Using the Double-Aperture Method, Appl. Optics 11, pp. 2294-2303, (1972).

Figure 1. Metal Holder for the Metal-on-Quartz Filters



Appendix 12

National Institute of Standards & Technology

Certificate

Standard Reference Material 931e

Liquid Absorbance Standard for Ultraviolet and Visible Spectrophotometry

This Standard Reference Material (SRM) is intended primarily for routine critical evaluation of daily working standards used in spectrophotometry, and for use in the calibration and checking of accuracy of the photometric scale of spectrophotometers that provide a narrow effective spectral bandpass, not to exceed 1.5 nm at 302 nm, 2.0 nm at 395 nm, 3.3 nm at 512 nm, and 8.5 nm at 678 nm. [1]

SRM 931e is certified as solutions of known net absorbances at four (4) specific spectral wavelengths for a 10.00-mm measurement pathlength (see Preparation of Filter Solutions for details). Each unit of SRM 931e consists of 3 sets of liquid filters (12 ampoules total), each set consisting of a blank solution and 3 absorbance levels (I, II, and III) of the filter (nominal absorbances of 0.3, 0.6, and 0.9, respectively, for a 10-mm pathlength). Approximately 10 mL of each liquid filter is individually flame-sealed in a glass ampoule which has been prescored for easy opening. Each set of liquid filters in the SRM unit is individually packaged in a tray.

The certified net absorbances are given below for the three solution levels at four wavelengths, for a 10.00-mm pathlength cell and a temperature of 22 ± 1 °C. The uncertainties of the certified values include all known sources of random and possible systematic errors (see Certification of Net Absorbance for 10.00-mm pathlength).

	Wavelength, nm			
Filter	302	395	512	678
Level I	0.2978 ± 0.0015	0.3060 ± 0.0015	0.3013 ± 0.0015	0.1153 ± 0.0015
Level II	0.5946 ± 0.0025	0.5954 ± 0.0025	0.6001 ± 0.0025	0.2245 ± 0.0015
Level III	0.9160 ± 0.0035	0.9009 ± 0.0035	0.9055 ± 0.0035	0.3402 ± 0.0015

Note: All certified values have been corrected for absorbances due to the blank solution.

The preparation of the filter solutions and the performance of the transmittance measurements for the certification process were performed in the NIST Inorganic Analytical Research Division by J.D. Messman.

The overall coordination of technical measurements leading to certification was performed in the NIST Inorganic Analytical Research Division by R.L. Watters, Jr. and J.C. Travis.

The statistical analysis of the data was performed in the NIST Statistical Engineering Division by S.B. Schiller .

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Standard Reference Materials Program by J.C. Colbert.

Gaithersburg, MD 20899
May 26, 1993
(Revision of certificate dated 3-3-93)

Thomas E. Gills, Acting Chief
Standard Reference Materials Program

(over)

NOTICE AND WARNINGS TO USER

Stability and Expiration of Certification: While no long-term stability studies have been made on this lot (931e), studies on previous lots (931, 931a, 931b, and 931c) over three-year periods showed no degradation of the material when stored in the original sealed ampoules. Therefore, this material is certified only for use within three years following the date of shipment from NIST.

Preparation of Filter Solutions: The filter solutions were prepared by dissolving high-purity cobalt and nickel in a mixture of nitric and perchloric acids. The absorbance of nitrate ion was adjusted to a comparable level by evaporation and, if necessary, subsequent addition of small amounts of nitric acid. The nominal weights of the cobalt and nickel metals and the typical volumes of nitric and perchloric acids used in the preparation of the three absorbance levels of solutions are given below for information. The pH of these solutions is about 1.

Liquid Filter	Cobalt (g)	Nickel (g)	HNO_3 (mL)	$HClO_4$ (mL)
Level I	7.4	6.9	30	50
Level II	14.7	13.9	45	90
Level III	22.1	20.7	65	125

To facilitate dissolution of the metals and removal of excess nitric acid, the requisite weights of metal needed to produce the 20-L volume of solution for each absorbance level were divided into ten equal portions.

The dissolutions were performed in 1-L glass beakers. Following dissolution and evaporation of excess nitric acid for each portion on a hot plate, the solutions were filtered through Whatman No. 2 filters directly into 2-L volumetric flasks to remove any residual insoluble particles. The solutions were then diluted to calibrated volume with distilled water and mixed thoroughly. The ten 2-L portions for each absorbance level were combined in a 20-L glass carboy and the contents were swirled thoroughly to produce the final solutions. The blank solution (0.1N $HClO_4$ in distilled water) was produced by preparing ten 2-L portions of distilled water containing 18 mL of $HClO_4$ and combining the portions in a 20-L glass carboy.

Following preparation of the 20-L volumes of the blank solution (0.1N $HClO_4$) and the three absorbance level solutions, the solutions were ampouled, each containing approximately 10 mL of solution.

The maxima in the absorbance spectrum (see figure 1) at 302 and 512 nm are due to absorbance by NO_3^- and $Co(H_2O)_6^{++}$, respectively. The maximum at 395 nm and the plateau at 650-700 nm are due to $Ni(H_2O)_6^{++}$.

Certification of Net Absorbance for 10.00-mm Pathlength: The transmittance measurements leading to the certification of this SRM were performed at an ambient temperature of 22 $\pm$ 1 °C using the NIST high accuracy spectrophotometer. The design and construction of this instrument have been described previously.[2] The instrument is a primary transmittance standard; its accuracy has been verified using the double aperture radiation-addition principle. The effective spectral bandpass used to determine the certified values was 0.8 nm. The transmittance measurements were made by producing the vertical image of the slit (about 8 mm by 0.5 mm), using a convergent beam geometry with an aperture ratio f:10, in the middle of the entrance face of the sample cuvette. The cuvette was oriented in a position perpendicular to the incident light beam.

The liquid absorbance filter solutions were calibrated at the wavelengths and conditions indicated by measuring the transmittance, T, of the "Blank" and solutions "I", "II", and "III" against air as a reference. Each transmittance measurement is calculated from a measurement of the intensity transmitted through a 10-mm cuvette containing the SRM solution and bracketing measurements of the intensity transmitted through an empty cuvette holder, with a settling time of approximately 5 s and a signal integrating time of approximately 1 s for each measurement.

For the certification measurements, 18 ampoules were randomly selected from each of the four solutions (blank and 3 absorbance levels). Randomized measurements were made in four runs on each of three days. In each run, six unknown samples (SRM 931e) and one control sample (SRM 931d) were measured in triplicate using cuvettes with the pathlength known to $\pm$ 0.0005 mm. On each day, six samples from each of the four levels (blank and levels I, II, and III) were measured. Two samples from three of the four levels were measured in each run. A blank was run in each cuvette on each day.

The values of T were used to calculate the corresponding values of the apparent absorbance, A, using the relationship $A = -\log_{10}T$. The net absorbances were obtained by subtracting the apparent absorbance of the blank solution from the apparent absorbances calculated for solutions I, II, and III. The certified net absorbances are the grand mean values for the three levels and four wavelengths. Statistical analysis revealed no apparent "day" or "cuvette" effects in the data. A small apparent "run" effect was consistent with the temperature coefficients given below, and with the normal temperature variation in the laboratory. The random error (95% confidence interval) was about a third of the total estimated error given in the table, which includes systematic error estimates to accommodate a ± 1 °C temperature variation and a small angular uncertainty in cuvette orientation.

Temperature Dependence: Absorbances at various temperatures (17° to 35 °C) may be calculated using the equation:

$$A_T = A_{22}[1+C_A(T-22)]$$

where: A_T = Absorbance at temperature T (°C)
A_{22} = Absorbance certified at 22.0 °C
C_A = Fractional change in absorbance per °C

The values of C_A, at the four wavelengths, are given below.

Note: At wavelength 302 nm, absorbance decreases with increasing temperature; at the other wavelengths, absorbance increases with increasing temperature.

Wavelength, nm	C_A
302	- 0.0014
395	+0.0014
512	+0.0018
678	+0.0014

Wavelength Accuracy and Bandpass Requirements: Due to the spectral features in the absorbance spectrum (see figure 1), the absorbances of these liquid absorbance standards will depend not only on the accuracy of the photometric scale, but also on the wavelength accuracy and the spectral bandpass of the spectrophotometer. A mercury lamp is recommended for checking the wavelength scale. In addition, for those spectrophotometers having a hydrogen (H) or deuterium (D) source, the two emission lines at 486.1 and 656.3 nm (H) or 486.0 and 656.1 nm (D) may provide a convenient check at these wavelengths. To ensure that the measured absorbances are not significantly different from the certified values, the wavelength scale of the spectrophotometer should be calibrated to within ± 0.5 nm, and the effective spectral bandpass should not exceed 1.5, 2.0, 3.3, and 8.5 nm at 302, 395, 512, and 678 nm, respectively.

Instructions for Use: This Standard Reference Material should be kept in the original sealed ampoules. Once opened, the material should be used immediately. No attempt should be made to reseal the ampoule.

The instructions below are for use with the standard 10-mm rectangular cuvette, and apply to either single-beam or double-beam spectrophotometers. For calibration of the several spectrophotometric systems used in various automated instruments, the user is referred to the instruction manual for the particular instrument.

1. Select a clean 10.00-mm cuvette, free of scratches and fitted with a ground glass or Teflon stopper, for all SRM measurements.

2. Mark the cuvette to assure reproducible orientation in the spectrophotometer in case the cuvette should need to be removed during the calibration procedure (not recommended).

3. Place the cuvette in the sample holder and fill with distilled water. (Borosilicate Pasteur-type pipettes fitted with rubber bulbs are recommended for transferring all solutions to and from the cuvettes. Soft glass pipettes, which are available commercially, contain residual amounts of ultraviolet absorbing material, but may be used after proper cleaning. Several rinses, first with isopropyl alcohol and then with distilled water, are generally adequate).

4. Obtain the apparent absorbance of the cuvette containing distilled water against air (nothing in the reference holder) at 302, 395, 512, and 678 nm, using an effective spectral bandpass not to exceed 1.5 nm, 2.0 nm, 3.3 nm, and 8.5 nm at the respective wavelengths.

5. Empty the cuvette by suction without removing it from the sample holder (if at all possible), refill with distilled water and measure the apparent absorbance against air *again* at each of the above wavelengths.

6. Repeat the emptying and refilling operation until constant apparent absorbance readings are obtained. Empty the cuvette by suction without removing it from the sample holder.

7. Using the liquid filters provided, measure, in turn, the apparent absorbance of the "Blank" and of solutions "I", "II", and "III" against air in the following manner. Shake each ampoule before opening to remix any condensate which may have been collected in the neck. (The ampoules have been prescored directly below the gold band to facilitate opening.) Rinse the sample cuvette in the sample holder with at least two complete fillings of the SRM solution from each 10-mL ampoule before taking final apparent absorbance readings for that ampoule at the wavelengths and bandwidths of step 4.

8. Subtract the apparent absorbance of the "Blank" from the apparent absorbances obtained for solutions "I" "II", and "III" to yield the net absorbances for the three levels. These net absorbances should agree with the certified values within the uncertainties specified. Consult the manufacturer of the instrument if they do not.

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[2] Mavrodineanu, R., J. Research, Nat. Bur. Stand. 76A, 405-425 (1972).

Note: References [1, 2] are also published in NBS Special Publication 378, Accuracy in Spectrophotometry and Luminescence Measurements, R. Mavrodineanu, J.I. Shultz, and O. Menis, Editors, U.S. (1973).

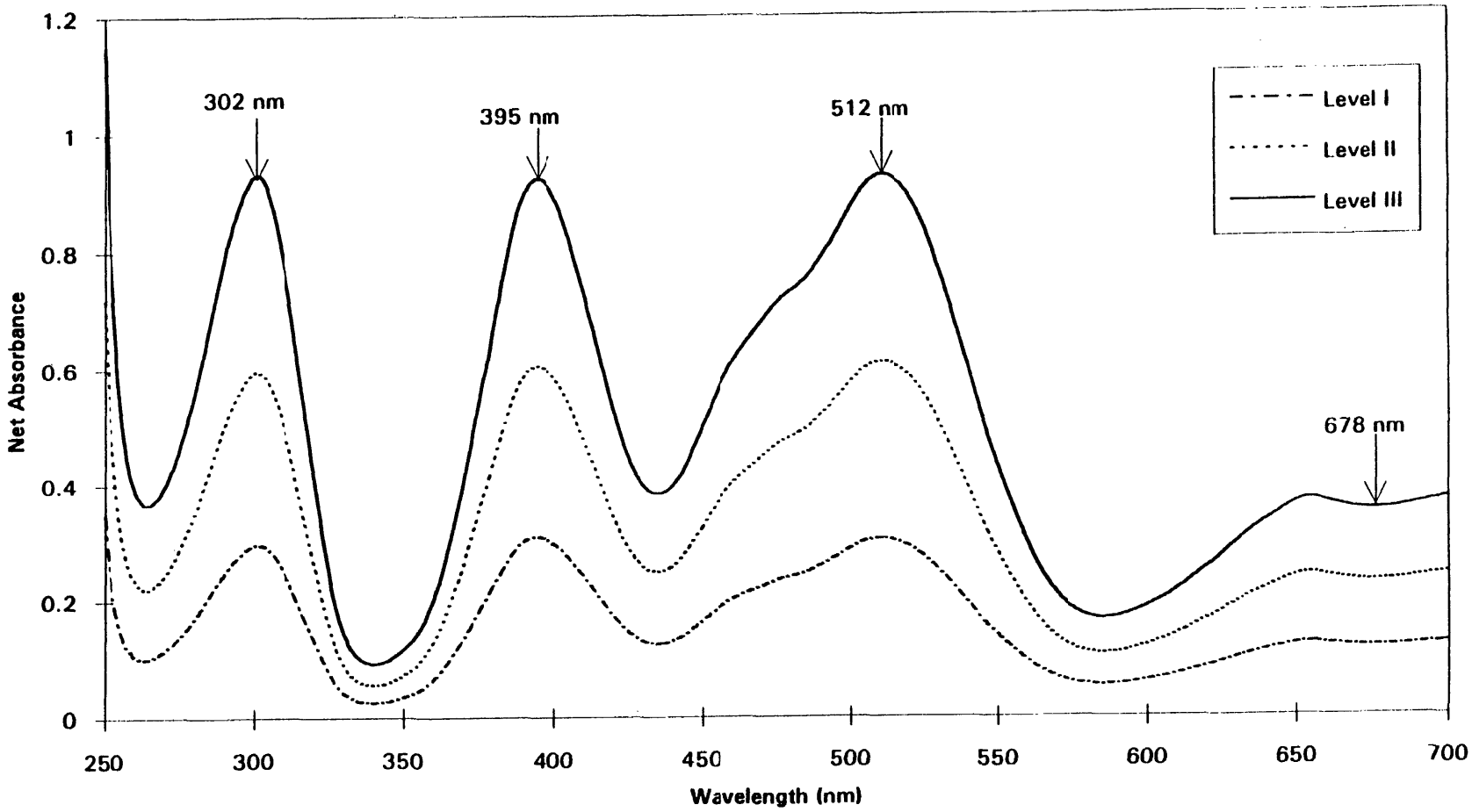

Figure 1. Absorbance Spectrum of SRM 931e

U.S. Department of Commerce
C. William Verity
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 935a

Crystalline Potassium Dichromate for Use as an Ultraviolet Absorbance Standard

This Standard Reference Material (SRM) consists of crystalline potassium dichromate of established purity. Solutions of known concentrations of this SRM in 0.001 N perchloric acid are certified for their apparent* specific absorbances**, ε_a, at 23.5 °C.

This SRM is intended to be used as a reference standard for the verification of the accuracy and linearity of the absorbance scale at 235, 257, 313, 345, and 350 nm of absorption spectrometers that can provide an effective spectral bandpass of 1.6 nm or less. Such verification is accomplished by comparing the measured apparent absorbances, A_a, to the A_a calculated from the certified ε_a values as described under "Instructions for Use."

Table 1 (shown on the next page) gives the certified values of ε_a in $kg \cdot g^{-1} \cdot cm^{-1}$ for ten concentrations of the SRM 935a potassium dichromate in 0.001 N perchloric acid at 23.5 °C and the indicated wavelengths and spectral bandpasses for a 1-cm internal pathlength.

The sample preparations and technical measurements leading to the certification of this SRM were performed by R.W. Burke of the Inorganic Analytical Research Division (now retired).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.L. McKenzie.

*The term "apparent" is used because no corrections have been applied to the data for the effects of internal multiple reflections within the cuvette or for buoyancy, i.e., the weights used to express concentrations have not been corrected to vacuum. These combined corrections do not exceed 0.2 percent. The specific absorbances are given in reference 1.

**The nomenclature used in this certificate is that recommended by K.D. Mielenz, Anal. Chem. 48, 1093-1094 (1976), which is reproduced in the Appendix of NBS Special Publication 260-54.

Gaithersburg, MD 20899
April 25, 1988

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

Table 1. ε_a, Apparent Specific Absorbance, $kg \cdot g^{-1} \cdot cm^{-1}$

Nominal Concentration $g \cdot kg^{-1}$	Wavelength and (Bandpass) nm					
	235.0(1.2)	257.0(0.8)	313.0(0.8)	345.0(0.8)[a]	350.0(0.8)	Uncertainty[b]
0.020	12.260	14.262	4.805	10.604	10.672	± 0.034
0.040	12.304	14.318	4.811	10.603	10.682	± 0.020[c]
0.060	12.347	14.374	4.816	10.602	10.692	± 0.020[c]
0.080	12.390	14.430	4.821	10.601	10.701	± 0.020[c]
0.100	12.434	14.486	4.827	10.600	10.711	± 0.020[c]
	235.0(1.6)[d]	257.0(1.6)[d]	313.0(1.6)[d]	345.0(1.6)[d]	350.0(1.6)[d]	
0.120[e]	12.480	14.541	4.835	10.600	10.722	± 0.04[f]
0.140[e]	12.524	14.605	4.840	10.599	10.731	± 0.04[f]
0.160[e]	12.567	14.658	4.846	10.599	10.742	± 0.04[f]
0.180[e]	12.609	14.711	4.851	10.598	10.751	± 0.04[f]
0.200[e]	12.649	14.763	4.856	10.597	10.759	± 0.04[f]

[a]Wavelength 345.0 nm is near one of the two isosbestic points in $HCrO_4^-/Cr_2O_7^=$ spectra. Because it is on the slope of the composite spectrum, reproduction of the ε_a values is dependent on wavelength accuracy. Measurements at this wavelength should be made only for verification of the linearity of the absorbance scale.

[b]ε_a values are not corrected for the effects of internal multiple reflections within the cuvette, nor have the weights been corrected to vacuum. With these two exceptions, each uncertainty given is the 95 percent confidence interval of the mean and includes all known systematic errors.

[c]At wavelength 313.0 nm, the uncertainty is reduced to ± 0.010.

[d]The increase in spectral bandpass was necessary to obtain an adequate signal. Expected changes in specific absorbance due to this increase do not exceed 1 part in 1,000.

[e]ε_a values are given to the third decimal place to preserve the smooth variation of the data with concentration, although the uncertainties are in the second decimal place.

[f]At wavelength 313.0 nm, the uncertainty is reduced to ± 0.02.

PREPARATION AND CERTIFICATION

The preparation and certification of SRM 935a followed the procedures used for the preparation and certification of SRM 935, which are described in detail in NBS Special Publication 260-54, Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard[2]. This publication should be referred to every time SRM 935a is to be used. Briefly, the transmittances, T, of the solutions prepared from the undried, as received, material were measured with the NBS Institute for Materials Research high accuracy transmission spectrometer[3].

The ε_a values were calculated for each wavelength using the relation:

$$\varepsilon_a = \frac{D_s - D_b}{b \times c} = \frac{A_a}{b \times c} \qquad (1)$$

where: ε_a = apparent specific absorbance
A_a = apparent absorbance
D_s = transmittance density of the sample solution, $-\log_{10} T_s$
D_b = transmittance density of the blank solution, $-\log_{10} T_b$
b = internal cuvette pathlength, cm
c = concentration, by weight, of $K_2Cr_2O_7$ solution, $g \cdot kg^{-1}$

The crystalline potassium dichromate used for SRM 935a is a special lot of analytical reagent grade material obtained from the J.T. Baker Chemical Co., Phillipsburg, N.J.

Assay: A coulometric assay of the purity of the undried material was performed by G. Marinenko of the NBS Center for Analytical Chemistry. The purity was found to be better than 99.97 percent. In addition, the material was examined by optical emission spectrometry for trace elemental impurities by J.A. Norris of the NBS Center for Analytical Chemistry. The only significant impurities detected were sodium and rubidium. Their concentrations were estimated to be in the range of 0.02 and 0.03 weight percent, respectively. Drying at 105 °C for 12 hours showed that the surface moisture of this material was less than 0.01 percent.

Stability: Solutions prepared from SRM 935a in the concentration range indicated in table 1 and made according to the instructions given in NBS SP 260-54 have been found to be stable within the uncertainties given in table 1 for at least six months when stored at room temperature and protected from evaporation and exposure to light.

INSTRUCTIONS FOR USE

The use of SRM 935a as an absorbance standard requires the careful preparation of a series of solutions of known concentrations, c, of the potassium dichromate in 0.001 N perchloric acid. These solutions are transferred sequentially to a quartz cuvette of known pathlength, b, and their apparent absorbances measured at wavelengths 235, 257, 313, and 350 nm, using the spectral bandpass requirements given in table 1. The preparation and measurement of these solutions are described in detail in Section 5 of NBS SP 260-54.

The accuracy of the absorbance scale of the spectrometer being tested is ascertained by comparing the measured apparent absorbances, A_a, of a series of 0.001 N perchloric acid solutions containing 0.020 to 0.200 gram $K_2Cr_2O_7$/kg to the A_a values calculated from the certified ε_a values. Although the ε_a data in table 1 are given for nominal concentrations of 0.020, 0.040, 0.060, 0.080, 0.100, 0.12, 0.14, 0.16, 0.18 and 0.20 g $K_2Cr_2O_7$/kg, the ε_a values for concentrations between these nominal concentrations can be determined by linear interpolation. Using the appropriate ε_a values, the calculated A_a values at 23.5 °C are obtained from the expression:

$$A_a = \varepsilon_a \times b \times c \qquad (2)$$

Calculations:

An example of the calculation of A_a for one concentration of $K_2Cr_2O_7$ under a specified set of conditions is shown below. Calculations of A_a for other concentrations and wavelengths are performed in a similar manner.

Conditions: Wavelength = 350 nm, spectral bandpass 0.8 nm or less
b = 0.9982 cm
c = 0.04375 g·kg^{-1}
t = 23.5 °C

From column 6, table 1, the ε_a for concentrations of 0.040 and 0.060 g·kg^{-1} are 10.682 and 10.692, respectively. The corresponding ε_a for c = 0.04375 g·kg^{-1} is:

$$\varepsilon_a = 10.682 + \frac{0.04375 - 0.040}{0.060 - 0.040}(10.692 - 10.682)$$

$$\varepsilon_a = 10.682 + 0.0019$$

$$\varepsilon_a = 10.684$$

The calculated apparent absorbance, A_a, from equation 2, is:

$$A_a = 10.684 \times 0.9982 \times 0.04375$$

$$A_a = 0.4666$$

The uncertainty, ΔA_a, in the calculated A_a is determined from the combined uncertainties in ε_a, b and c in equation 2, provided no other systematic errors are present. Thus:

$$\Delta A_a = bc|\Delta\varepsilon_a| + \varepsilon_a c|\Delta b| + \varepsilon_a b|\Delta c| \qquad (3)$$

To evaluate ΔA_a, $\Delta\varepsilon_a$ is taken from column 7 of table 1 and the Δb and Δc values must be determined experimentally.

In the experiments performed to obtain the ε_a values in table 1, the uncertainties for b and c did not exceed 1 part in 10^4 and 2 parts in 10^4, respectively.

The solution of equation 3 gives:

$$\Delta A_a = 1(0.044)\ (0.020) + 10.7(0.044)\ (0.0001) + 10.7(1)\ (0.0000088)$$
$$= 0.0010$$

Thus, the uncertainty of A_a, for the above set of conditions, is ±0.0010.

The correction of the absorbance scale of the absorption spectrometer under test is determined by plotting the differences between A_a measured and A_a calculated as a function of absorbance. A typical plot of such a graph is shown in figure 1. The apparent absorbances measured on this instrument at 350 nm are accurate when the indicated correction is subtracted from the corresponding absorbance scale reading, provided that the conditions of wavelength accuracy, spectral bandpass, and absence of stray light are fulfilled as specified in NBS SP 260-54. Correction curves for wavelengths 235, 257, and 313 nm are obtained in a similar manner.

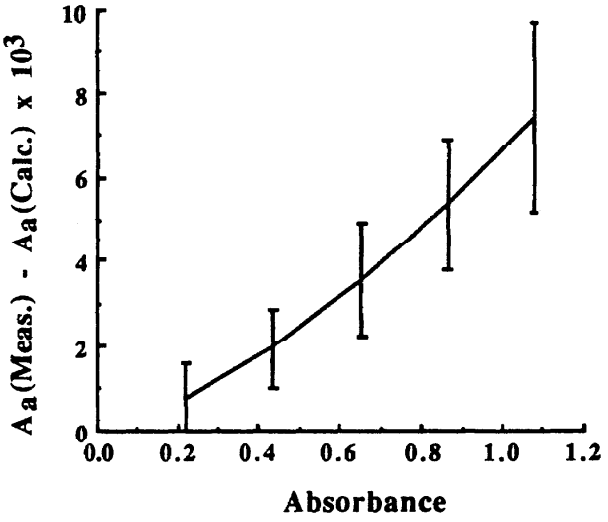

Figure 1. Correction curve for the absorbance scale of a precision spectrometer. The error bars are the sum of the errors arising from the uncertainties in the certified apparent specific absorbances, ε_a, cuvette pathlength, b, and concentration, c.

Temperature Correction:

Although ε_a values in table 1 are certified at 23.5 °C, SRM 935a can be used as an absorbance standard at other temperatures in the range 20 to 30 °C provided corrections are made to the ε_a values. Over this range the apparent specific absorbances decrease linearly with increasing temperature for all the wavelengths given in table 1. The corresponding temperature coefficients, k, for these wavelengths are given in table 2.

Table 2. Variation of ε_a with Temperature Over the Range 20 to 30 °C.

λ, nm	Temperature Coefficient, k Percent per degree Celsius
235	-0.05
257	-0.05
313	-0.02
345	-0.08
350	-0.05

The value of ε_a at any temperature in the range 20 to 30 °C can be calculated from the certified value and the appropriate temperature coefficient using the relation:

$$\varepsilon_a^t = \varepsilon_a^{23.5} \left(1 + \frac{k}{100} (t - 23.5)\right)$$

where: ε_a^t = apparent specific absorbance at temperature t (°C)

$\varepsilon_a^{23.5}$ = apparent specific absorbance certified at 23.5 °C.

k = temperature coefficient, percent per °C.

ACKNOWLEDGEMENTS:

We wish to acknowledge the following contributions to the development of SRM 935, which was the basis of SRM 935a: K.D. Mielenz, NBS Analytical Chemistry Division, for his many valuable discussions and suggestions, and H.H. Ku, NBS Applied Mathematics Division, for his statistical treatment of the data; the cooperation and early support of the National Institute of General Medical Sciences in the research leading to this SRM; and the encouragement of George N. Bowers, Jr., M.D., Hartford Hospital, Hartford, Conn., and Royden N. Rand, Ph.D., Eastman Kodak Co., Research Laboratories, Rochester, N.Y.

REFERENCES:

1. Burke, R.W., and Mavrodineanu, R., Acidic Potassium Dichromate Solutions as Ultraviolet Absorbance Standards, J. Res. Nat. Bur.Stand. (U.S.), 80A (Phys. and Chem.), No. 4, 631-636 (July-Aug. 1976).

2. Burke, R.W., and Mavrodineanu, R., Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard, NBS Spec. Publ. 260-54 (1977). Copies may be obtained from the Office of Standard Reference Materials, National Bureau of Standards, Gaithersburg, MD 20899.

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Appendix 14

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate

Standard Reference Material 2032

Crystalline Potassium Iodide

Heterochromatic Stray Radiant Energy Standard for Ultraviolet Absorption Spectrophotometry

K. D. Mielenz and R. Mavrodineanu

This Standard Reference Material consists of reagent-grade, crystalline potassium iodide (KI) to be used to assess heterochromatic stray radiant energy (stray light) in ultraviolet absorption spectrophotometers in the spectral region below 260 nm. Stray light is assessed by measuring the spectral absorbance of aqueous solutions of SRM 2032 of known pathlengths and concentrations, and comparing the result with the certified values of the specific absorbance, ϵ.

Specific Absorbance[a]

ϵ (L g^{-1} cm^{-1}), vs Wavelength, λ (nm), at 23.5 °C

λ	240	245	250	255	260	265	270	275
ϵ	25.6	10.67	3.66	1.05	0.260	0.0560	0.0121	0.0031

[a]"Specific absorbance" is defined here as absorbance per unit pathlength and unit concentration. The term "absorptivity" has been avoided since it is ambiguously defined. See K. D. Mielenz, Anal. Chem. 48, 1093-1094 (1976).

The estimated uncertainty of these values is ± 5%, which includes the random and systematic errors of the calibration procedure, as well as variations due to possible instability of the KI. (See, Certification Procedure.)

The material used to produce SRM 2032 was obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J., in two bottles, as reagent-grade (99.8% purity) potassium iodide.

SRM 2032 was issued with the technical assistance of J. R. Baldwin, R. W. Burke, A. L. Cummings, B. I. Diamondstone, and G. A. Sleater, and under the overall direction of I. L. Barnes.

The technical and support aspects concerning preparation, certification, and issuance of this SRM were coordinated through the Office of Standard Reference Materials by R. W. Seward.

Washington, D.C. 20234
October 31, 1979

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

Supplementary Information

Material Testing:

Material homogeneity was tested by measuring the absorbance of 1% aqueous solutions of the KI sampled from the top, middle, and bottom of each bottle. These measurements, at 265, 267, and 270 nm, showed no evidence of inhomogeneity. Tests for moisture content (Karl Fischer method) gave an average of 0.007%. This value was sufficiently small that all certified data are based on weighed samples of the undried, as received, material.

Stability of the material to UV and visible light was tested by exposing the KI salt in a low-actinic glass bottle to radiation from a 3 kW xenon-arc lamp at a distance of 25 cm for four days at room temperature. The average absorbances at five wavelengths between 240 and 270 nm of aqueous solutions of the exposed material were 1.1% lower than those of solutions of the unexposed material. In view of the severity of this test, this change was considered minor. Nonetheless, the 1.1% was included in the overall uncertainty of the certified values.

Certification Procedure:

The certified specific absorbances were measured in the NBS Center for Analytical Chemistry high-accuracy spectrophotometer [1, 2], equipped with a deuterium lamp and UV averaging sphere [3, 4]. Thirteen aqueous solutions of KI with concentrations ranging from 0.03 to 30 g L^{-1} were prepared and measured against distilled water, using standard fused-silica cuvettes with pathlengths between 10.001 and 10.009 mm[b]. The absorbance measurements were performed at the temperature, $t = 23.5 \pm 0.5$ °C. A 0.2 nm bandpass was used, and wavelength settings were made with an accuracy of 0.05 nm. The measurements were made on at least three concentrations at each wavelength. These concentrations were chosen so that most absorbance readings fell between 0.1 and 1.0 to minimize stray light and bandwidth errors. The data were found to obey Beer's law.

Thus, the equation,

$$\epsilon = A/c\,\ell \qquad (1)$$

was used to calculate the specific absorbances, ϵ, from the measured absorbances, A, and the known values of concentration, c, and pathlength, ℓ .

Limits to random error (two standard deviations) of these measurements (including the photometric imprecision of the spectrophotometer, errors in the repositioning of cuvettes, concentration errors, pathlength uncertainties, temperature errors, Beer's law uncertainties, and bandwidth errors) were determined to be ± 2.4%. The error due to the 0.05 nm uncertainty of the wavelength calibration of the spectrophotometer is ± 1.1%.

The uncertainty of 5% stated on the face of this certificate represents the sum of these errors and the above mentioned 1.1% uncertainty due to instability of the KI. No corrections were applied for the effects of internal reflections inside the sample and reference cuvettes, nor were the weights corrected to vacuum. These and all other sources of error were considered negligible.

The temperature coefficient at 260 nm was determined to be

$$\frac{1}{\epsilon}\,\frac{d\epsilon}{dt} = 0.031\ °C^{-1}. \qquad (2)$$

For precision measurements, it is recommended that SRM 2032 be used in thermostated cuvettes at 23.5 °C, or that a temperature correction according to Eq. (2) be applied.

[b]Issued by NBS as SRM 932, Quartz Cuvettes for Spectrophotometry.

Instructions for Use

Storage and Preparation:

SRM 2032 should be stored in the original, low-actinic glass bottle and the cardboard container in which it was issued to protect it from unnecessary exposure to light and humidity. When so stored, the expected stability of this material is at least three years. Thus, until additional stability data are obtained, this material should be used within three years of the date of purchase.

All solutions prepared from SRM 2032 should be made in borosilicate glass containers using distilled water and transfer pipettes (Pasteur type) of the same glass and fitted with rubber bulbs[c]. Use clean spectrophotometer cuvettes, free of scratches, made of non-fluorescent fused silica, and fitted with ground-glass or Teflon stoppers to minimize evaporation; or preferably use NBS SRM 932. Mark all cuvettes to assure the same orientation in the spectrophotometer, and place them into their respective holders. Using transfer pipettes of the type mentioned, rinse each cuvette several times with distilled water. Prepare a solution of KI in distilled water (e.g. 1%), fill the sample cuvette with the KI solution and the reference cuvette with distilled water. Measure the absorbance, leaving the cuvettes in their holders, empty them (using the pipettes), and repeat the rinsing and filling operations until constant absorbance readings are obtained. Fresh solutions should be made before every test.

Measurements:

A 1% KI solution ($c = 10\ g\ L^{-1}$) with a 1 cm pathlength exhibits a sharp cutoff in transmittance near 260 nm; i.e., it transmits more than 90% above 273 nm, but less than 0.01% below 258 nm. Therefore, with the monochromator set for a wavelength below 260 nm, any appreciable amount of light detected is heterochromatic stray light, which consists of wavelengths above the cutoff. The amount of stray light in the spectrophotometer at wavelength λ may be determined from the equations:

$$T'(\lambda) = \frac{T(\lambda) + x(\lambda)}{1 + x(\lambda)} \tag{3}$$

$$x(\lambda) = \frac{T'(\lambda) - T(\lambda)}{1 - T'(\lambda)} \tag{4}$$

where:

$x(\lambda)$ is the stray light ratio,

$T'(\lambda)$ is the apparent transmittance,

$T(\lambda)$ is the true transmittance.

The stray light ratio, $x(\lambda)$, is the proportion of heterochromatic stray radiant energy in the spectrophotometer for the wavelength setting λ. Equation (4) forms the theoretical basis for the determination of the stray light ratio by comparing apparent transmittance to true transmittance. For SRM 2032, the true transmittance, $T(\lambda)$, of KI solutions may be calculated as:

$$T(\lambda) = 10^{-\epsilon(\lambda).c\ell}$$

where $\epsilon(\lambda)$ is the certified specific absorbance given on the face of this certificate.

[c]Soft glass containers and pipettes contain residual amounts of UV absorbing material, but can be used after proper cleaning. Several rinses, first with isopropyl alcohol and then with distilled water, are generally adequate.

The apparent transmittances of KI solutions depend not only on the stray light ratio of the spectrophotometer, but also on the wavelength accuracy and the spectral bandwidth, which can significantly affect the results obtained because of the steep slope of the absorbance cutoff of KI. A low-pressure mercury discharge lamp is suggested for verifying the wavelength scale, and a bandwidth as narrow as compatible with adequate signal-to-noise ratios should be used.

Many instruments do not permit the direct measurement of transmittances below certain limits, e.g., 1% or 0.1%. For such instruments, the use of SRM 2032 will only measure stray light ratios above these limits. To measure stray light ratios below these limits, the reference beam of the spectrophotometer must be attenuated to extend the transmittance scale into the low-transmittance region.

References

1. R. Mavrodineanu, J. Res. NBS **76A**, 405-425 (1972).
2. J.F. Barkley, F. C. Ruegg, and R. Mavrodineanu, 29th Pittsburgh Conf., Abstract 452, Cleveland, Ohio, (1978).
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4. K. D. Mielenz, R. Mavrodineanu, and E. D. Cehelnik, Appl. Optics **14**, 1940-1947 (1975).

U. S. Department of Commerce
Philip M. Klutznick
Secretary

National Bureau of Standards
Ernest Ambler, Director

Appendix 15

National Bureau of Standards

Certificate

Standard Reference Material 2033

Crystalline Potassium Iodide with Attenuator Heterochromatic and Isochromatic Stray Radiant Energy Standard for Ultraviolet Absorption Spectrophotometry

K. D. Mielenz and R. Mavrodineanu

This Standard Reference Material consists of reagent-grade crystalline potassium iodide (KI) and a radiation attenuator to be used to assess the heterochromatic stray radiant energy (stray light) in ultraviolet absorption spectrophotometers in the spectral region below 260 nm.. The radiation attenuator consists of two semitransparent evaporated metal-on-fused silica (non-fluorescent) filters, each having a nominal transmittance of 10%. One filter is mounted in a cuvette-style holder that can be inserted into the sample compartment of the spectrophotometer. The other is mounted in one of the two shutters of the holder. The use of this attenuator permits the expansion of the transmittance scale into the low-transmittance region by providing a two-step attenuation of the reference beam of the spectrophotometer to about 1%. The attenuator can also be used to assess isochromatic stray light by following the instructions given in this certificate.

The heterochromatic stray light is assessed by measuring the spectral absorbance of aqueous solutions of SRM 2033 of known pathlengths and concentrations, and comparing the results with the certified values of the specific absorbance, ϵ.

Specific Absorbance[a]

	ϵ (L g^{-1} cm^{-1}), vs Wavelength, λ (nm), at 23.5 °C							
λ	240	245	250	255	260	265	270	275
ϵ	25.6	10.67	3.66	1.05	0.260	0.0560	0.0121	0.0031

[a] "Specific Absorbance" is defined here as absorbance per unit pathlength and unit concentration. The term "absorptivity" has been avoided since it is ambiguously defined. See K. D. Mielenz, Anal. Chem. 48, 1093-1094 (1976).

The estimated uncertainty of these values is ± 5%, which includes the random and systematic errors of the calibration procedure, as well as variations due to possible instability of the KI. (See Certification Procedure.)

The material used to produce SRM 2033 was obtained from the J.T. Baker Chemical Co., Phillipsburg, N.J., in two bottles, as reagent-grade (99.8% purity) potassium iodide.

The transmittance of the filter mounted in the holder at λ255 nm is _____;
the transmittance of both filters at λ255 is _____.

SRM 2033 was issued with the technical assistance of J. R. Baldwin, R. W. Burke, A. L. Cummings, B. I. Diamondstone, and G. A. Sleater, and under the overall direction of E. L. Garner, NBS Inorganic Analytical Research Division.

The technical and support aspects concerning preparation, certification, and issuance of this SRM were coordinated through the Office of Standard Reference Materials by R. W. Seward.

Washington, D.C. 20234
May 9, 1980

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

Potassium Iodide Material Testing:

Material homogeneity was tested by measuring the absorbance of 1% aqueous solutions of the KI sampled from the top, middle, and bottom of each bottle. These measurements, at 265, 267, and 270 nm, showed no evidence of inhomogeneity. Tests for moisture content (Karl Fischer method) gave an average of 0.007%. This value was sufficiently small that all certified data are based on weighed samples of the undried, as received, material.

Stability of the material to UV and visible light was tested by exposing the KI salt in a low-actinic glass bottle to radiation from a 3 kW xenon-arc lamp at a distance of 25 cm for four days at room temperature. The average absorbances at five wavelengths between 240 and 270 nm of aqueous solutions of the exposed material were 1.1% lower than those of solutions of the unexposed material. In view of the severity of this test, this change was considered minor. Nonetheless, the 1.1% was included in the overall uncertainty of the certified values.

Potassium Iodide Certification Procedure:

The certified specific absorbances were measured in the NBS Center for Analytical Chemistry high-accuracy spectrophotometer [1,2], equipped with a deuterium lamp and UV averaging sphere [3,4]. Thirteen aqueous solutions of KI with concentrations ranging from 0.03 to 30 g L^{-1} were prepared and measured against distilled water, using standard fused-silica cuvettes with pathlengths between 10.001 and 10.009 mm[b]. The absorbance measurements were performed at the temperature, t = 23.5 ± 0.5 °C. A 0.2 nm bandpass was used, and wavelength settings were made with an accuracy of 0.05 nm. The measurements were made on at least three concentrations at each wavelength. These concentrations were chosen so that most absorbance readings fell between 0.1 and 1.0 to minimize stray light and bandwidth errors. The data were found to obey Beer's law.

Thus, the equation,

$$\epsilon = A/c\ell \tag{1}$$

was used to calculate the specific absorbances, ϵ, from the measured absorbances, A, and the known values of concentration, c, and pathlength, ℓ .

Limits to random error (two standard deviations) of these measurements (including the photometric imprecision of the spectrophotometer, errors in the repositioning of cuvettes, concentration errors, pathlength uncertainties, temperature errors, Beer's law uncertainties, and bandwidth errors) were determined to be ± 2.4%. The error due to the 0.05 nm uncertainty of the wavelength calibration of the spectrophotometer is ± 1.1%.

The uncertainty of 5% stated on the face of this certificate represents the sum of these errors and the above mentioned 1.1% uncertainty due to instability of the KI. No corrections were applied for the effects of internal reflections inside the sample and reference cuvettes, nor were the weights corrected to vacuum. These and all other sources of error were considered negligible.

The temperature coefficient at 260 nm was determined to be

$$\frac{1}{\epsilon} \cdot \frac{d\epsilon}{dt} = 0.031\ °C^{-1}. \tag{2}$$

For precision measurements, it is recommended that SRM 2033 be used in thermostated cuvettes at 23.5 °C, or that a temperature correction according to Eq. (2) be applied.

[b]Issued by NBS as SRM 932, Quartz Cuvette for Spectrophotometry.

Instructions for Use of Potassium Iodide

Storage and Preparation:

SRM 2033 should be stored in the original, low-actinic glass bottle and the cardboard container in which it was issued to protect it from unnecessary exposure to light and humidity. When so stored, the expected stability of this material is at least three years. Thus, until additional stability data are obtained, this material should be used within three years of the date of purchase.

All solutions prepared from SRM 2033 should be made in borosilicate glass containers using distilled water and transfer pipettes (Pasteur type) of the same glass and fitted with rubber bulbs[c]. Use clean spectrophotometer cuvettes, free of scratches, made of non-fluorescent fused silica, and fitted with ground-glass or Teflon stoppers to minimize evaporation; or preferably use NBS SRM 932. Mark all cuvettes to assure the same orientation in the spectrophotometer, and place them into their respective holders. Using transfer pipettes of the type mentiond, rinse each cuvette several times with distilled water. Prepare a solution of KI in distilled water (e.g., 1%), fill the sample cuvette with the KI solution and the reference cuvette with distilled water. Measure the absorbance, leaving the cuvettes in their holders, empty them (using the pipettes), and repeat the rinsing and filling operations until constant absorbance readings are obtained. Fresh solutions should be made before every test.

Measurements:

A 1% KI solution ($c = 10\ g\ L^{-1}$) with a 1 cm pathlength exhibits a sharp cutoff in transmittance near 260 nm; i.e., it transmits more than 90% above 273 nm, but less than 0.01% below 258 nm. Therefore, with the monochromator set for a wavelength below 260 nm, any appreciable amount of light detected is heterochromatic stray light, which consists of wavelengths above the cutoff. The amount of stray light in the spectrophotometer at wavelength λ may be determined from the equations:

$$T'(\lambda) = \frac{T(\lambda) + x(\lambda)}{1 + x(\lambda)} \tag{3}$$

$$x(\lambda) = \frac{T'(\lambda) - T(\lambda)}{1 - T'(\lambda)} \tag{4}$$

where:

$x(\lambda)$ is the stray light ratio,

$T'(\lambda)$ is the apparent transmittance,

$T(\lambda)$ is the true transmittance.

The stray light ratio, $x(\lambda)$, is the proportion of heterochromatic stray radiant energy in the spectrophotometer for the wavelength setting λ. Equation (4) forms the theoretical basis for the determination of the stray light ratio by comparing apparent transmittance to true transmittance. For SRM 2033, the true transmittance, $T(\lambda)$, of KI solutions may be calculated as:

$$T(\lambda) = 10^{-\epsilon(\lambda)\, c\, \ell}$$

where $\epsilon(\lambda)$ is the certified specific absorbance given on the face of this certificate.

[c] Soft glass containers and pipettes contain residual amounts of UV absorbing material, but can be used after proper cleaning. Several rinses, first with isopropyl alcohol and then with distilled water, are generally adequate.

The apparent transmittances of KI solutions depend not only on the stray light ratio of the spectrophotometer, but also on the wavelength accuracy and the spectral bandwidth, which can significantly affect the results obtained because of the steep slope of the absorbance cutoff of KI. A low-pressure mercury discharge lamp is suggested for verifying the wavelength scale, and a bandwidth as narrow as compatible with adequate signal-to-noise ratios should be used.

Optical Attenuator:

Many instruments do not permit the direct measurement of transmittances below certain limits, e.g., 1% or 0.1%. To measure stray light ratios below these limits, the reference beam of the spectrophotometer must be attenuated to extend the transmittance scale into the low-transmittance region.

As mentioned on the face of this Certificate, the optical attenuator consists of two filters, each of which has a nominal transmittance of 10 percent. One filter is mounted in a metal holder that can be inserted in the sample compartment of the spectrophotometer (5). This holder is provided with a front and rear shutter, one of which has a window in which the second filter is mounted. The holder and shutters are flat black. This unit was produced in the NBS Instrument Shops.

Instructions for Use of the Attenuator

This unit can be used to attenuate the incident radiation in the reference beam of the spectrophotometer in two steps by a total factor of about 100, corresponding to about 1 percent transmittance (6). To attenuate by a factor of 10, the attenuator is inserted in the sample compartment of the spectrophotometer facing the incident beam, with both shutters removed. A further attenuation by a factor of about 10 is obtained when the shutter carrying the second filter is inserted in the holder, in front of the first filter. Under these conditions, and with an instrument that cannot measure transmittances lower than 1 percent, the use of the attenuator will permit heterochromatic stray light to be measured down to about 0.01 percent. This attenuation procedure can be used with spectrophotometers capable of scale expansion.

Isochromatic Stray Light:

The radiation attenuator can be used to assess the isochromatic stray light that results from reflection of the incident radiation at the surface of the sample and various optical components, and reaches the photodetector without passing through the sample. It is implicitly assumed that the sample compartment of the spectrophotometer is light-tight.

The measurement is performed by placing the attenuator in the sample beam of the spectrophotometer, with the opaque shutter placed at the rear of the filter holder. Under these conditions, if a signal is detected, it is caused by reflection at the surface of the filter exposed to the incident radiation. This radiation is scattered from the walls and other components of the sample compartment and reaches the photodetector without passing through the sample (5). This signal is the isochromatic stray light.

Isochromatic stray light, which passes through the sample, is generally caused by interreflections between lenses and/or other sample compartment elements. Tests for this stray light component, which is not detected by the methods described above, are discussed in references 7 and 8.

References:

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3. K. D. Mielenz, R. Mavrodineanu, and E. D. Cehelnik, J. Res. NBS 78A, 631-635 (1974).
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6. Estimating Stray Radiant Energy, ASTM Manual on Recommended Practices in Spectrophotometry, pp. 94-105, 3rd. Edition, 1969, 1916 Race St., Philadelphia, Pa. 19103.
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U. S. Department of Commerce
Malcolm Baldrige
Secretary
National Bureau of Standards
Ernest Ambler, Director

Appendix 16

National Bureau of Standards

Certificate

Standard Reference Material 2009a

Didymium Glass Filter for Checking the Wavelength Scale of Spectrophotometers

SERIAL NO. _____

Kenneth L. Eckerle

This Standard Reference Material (SRM) is a 10 x 30 x 3 mm didymium glass filter. SRM 2009a is intended for use in calibrating the wavelength scale in the visible wavelength region of scanning spectrophotometers having nominal bandwidths in the range 1.5 to 10.5 nm. Depending upon the bandwidth of the spectrophotometer, 12 to 22 wavelength corrections can be determined from 389 to 760 nm. Detailed instructions on the use of this SRM and examples of its use are given in the accompanying NBS Special Publication 260-66. Each didymium glass filter is identified by serial number.

All measurements on these filters were made at 25 °C with a high-accuracy reference spectrophotometer that has a wavelength accuracy of 0.04 nm.

Table 1 gives the wavelengths of the transmittance minima as obtained from measurements on two filters representative of this melt of didymium glass. These values are given for seven equally spaced values of the half-height width of triangular passbands. The minima numbers are shown on Figure 1, which illustrates the spectral transmittance as a function of wavelength.

Table 2 gives the wavelength values of nine points of inflection on the spectral transmittance curve as obtained on two filters. These inflection points are representative of this glass melt and are also shown on Figure 1. These inflection points should only be used with the transmittance minima as described in Sections 2.2 and 2.3 in SP 260-66. Table 2 also indicates the range of the measured wavelengths of the inflection points.

Table 3 gives the estimated random and systematic errors of the transmittance minima given in Table 1 (as obtained from 4 sets of measurements on a single filter).

Table 4 gives the spectral transmittance as a function of wavelength for a filter representative of this melt. These values are not certified but are provided for use as specified in SP 260-66. They should not be used to check the photometric scale of a spectrophotometer.

Trial calibrations made on several instruments, using both minima and inflection points, indicate that wavelength corrections made with these SRM's can be accurate to 0.2 nm. The uncertainty of a calibration, however, will depend upon the stability and other characteristics of a particular instrument.

This filter should be handled only by its edges; when not in use it should be stored in the box provided. If cleaning is necessary, wet the filter with water and rub gently with optical lens tissue soaked with a mild soap solution, rinse with distilled water, rinse with isopropyl alcohol, and rinse again with distilled water. Dry after each rinsing by wiping lightly with optical lens tissue.

July 25, 1984
Gaithersburg, MD 20899

Stanley D. Rasberry, Chief
Office of Standard Reference Material

Figure 1. Spectral transmittance of didymium glass as a function of wavelength. The numbers indentify minima, and the letters identify selected inflection points.

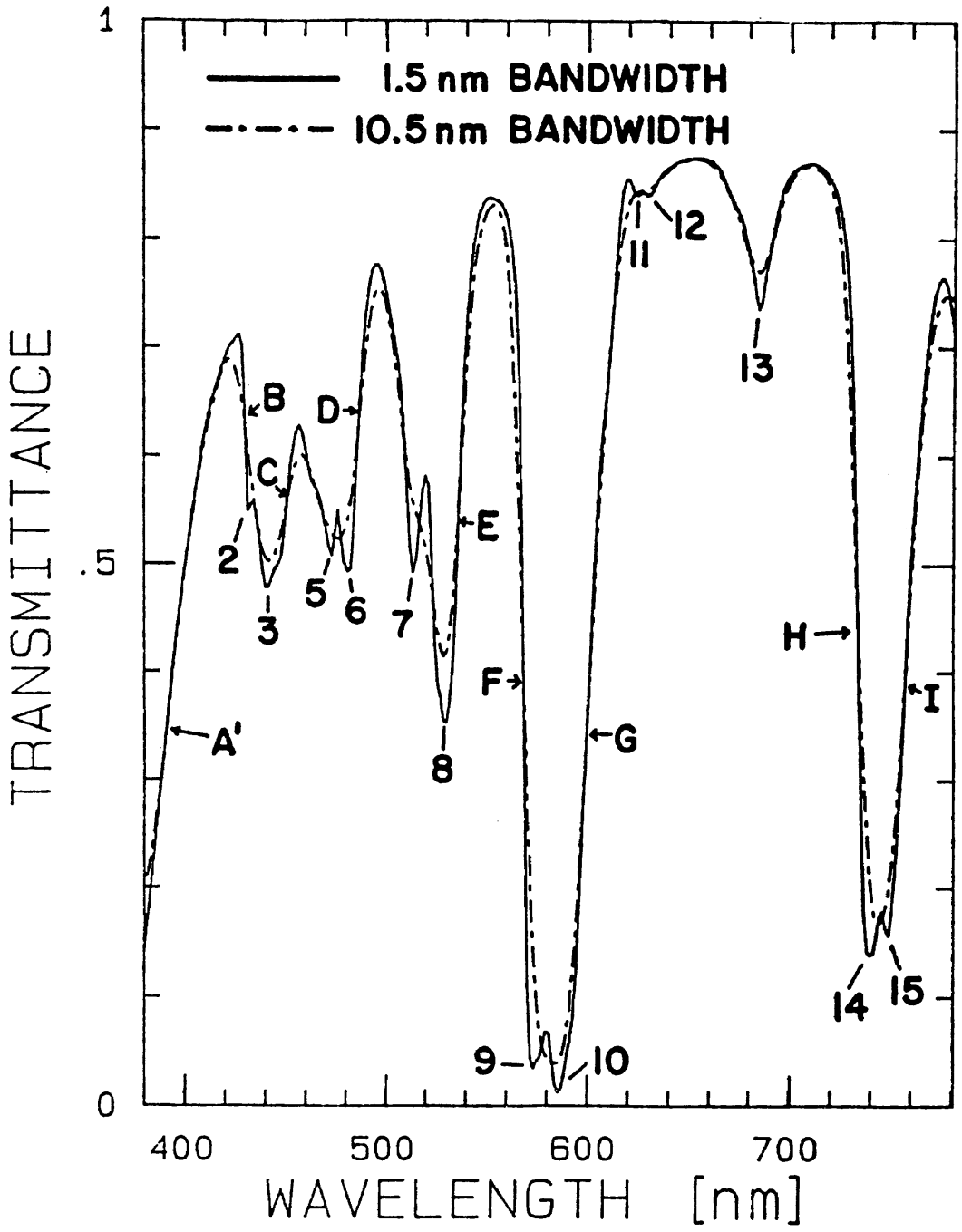

TABLE 1

Certified Wavelengths (nm) of the Transmittance

Minima for the Indicated Bandwidths

Bandwidth Minimum No.	1.5 nm	3.0 nm	4.5 nm	6.0 nm	7.5 nm	9.0 nm	10.5 nm
1	--	--	--	--	--	--	--
2	431.58	--	--	--	--	--	--
3	440.78	440.98	441.41	441.94	442.19	442.17	441.87
4	--	--	--	--	--	--	--
5	472.67	472.43	472.31	--	--	--	--
6	481.20	480.68	480.37	479.67	478.36	477.26	476.18
7	513.66	513.76	513.94	514.25	514.87	--	--
8	529.37	529.47	529.26	529.11	529.08	528.98	528.74
9	573.12	573.88	574.75	575.72	--	--	--
10	585.50	585.68	585.86	586.03	585.91	585.29	584.39
11	623.85	624.42	--	--	--	--	--
12	629.51	629.26	628.17	627.17	627.17	--	--
13	684.71	684.74	684.78	684.80	684.77	684.73	684.65
14	739.61	740.20	740.58	741.33	742.55	743.50	744.16
15	748.64	748.48	--	--	--	--	--

TABLE 2

Wavelengths and Transmittances at Nine Selected

Points of Inflection

Point Identification	Wavelength (nm)	Range* (nm)	Transmittance+
A	388.68	+.02 −.02	0.3027
B	429.67	+.06 −.10	.6268
C	450.21	+.03 −.03	.5569
D	485.75	+.08 −.12	.6210
E	536.39	+.04 −.06	.5597
F	568.40	+.06 −.03	.3969
G	599.57	+.02 −.02	.3375
H	733.55	+.05 −.03	.4493
I	757.22	+.01 −.02	.3959

*The range of wavelengths within which the wavelength for the given transmittance will fall for symmetric triangular passbands with half-height bandwidths from 1.5 to 10.5 nm.

+These values of transmittance are not certified.

TABLE 3

Estimated Random and Systematic Errors of the Transmittance Minima

Band Number	Nominal Wavelength of Minimum Transmittance	Standard Deviation for Indicated Bandwidth						
		1.5 nm	3.0 nm	4.5 nm	6.0 nm	7.5 nm	9.0 nm	10.5 nm
1	402 nm	--	--	--	--	--	--	--
2	431	0.013 nm (0.06)*	0.010 nm	--	--	--	--	--
3	440	0.021 (0.05)	0.013	0.030 nm	0.028 nm	0.009 nm	0.005 nm	0.007 nm (0.25)
4	446	--	--	--	--	--	--	--
5	473	0.011 (0.08)	0.012	0.032	--	--	--	--
6	481	0.015 (0.15)	0.013	0.009	0.009	0.009	0.014	0.017 (0.25)
7	513	0.022 (0.08)	0.016	0.014	0.013	0.010	--	--
8	530	0.012 (0.21)	0.010	0.010	0.011	0.010	0.011	0.010 (0.25)
9	573	0.004 (0.05)	0.010	0.010	0.012	0.014	--	--
10	585	0.007 (0.06)	0.004	0.007	0.008	0.008	0.007	0.007 (0.25)
11	624	0.058 (0.06)	0.061	--	--	--	--	--
12	630	0.210 (0.02)	0.120	0.171	0.133	0.091	--	--
13	685	0.019 (0.05)	0.029	0.024	0.017	0.014	0.014	0.012 (0.25)
14	740	0.009 (0.25)	0.013	0.011	0.010	0.009	0.009	0.010 (0.25)
15	748	0.020 (0.04)	0.016	--	--	--	--	--

* Values in parentheses are estimates of the systematic error. The estimates for the 1.5 nm bandwidth were obtained from the data taken at 1.5 nm intervals as compared to data taken at 0.15 nm intervals. The method of estimating the systematic errors for the 10.5 nm bandwidth is described in Section 3.4 in SP 260-66.

TABLE 4

Transmittance (T) as a function of wavelength from 380 to 780.5 nm for a bandwidth of 1.5 nm. The estimates of random and systematic errors are also provided. These data are not certified.

Wavelength (nm)	T	Δ_T Standard Error	Δ_T Systematic	Wavelength (nm)	T	Δ_T Standard Error	Δ_T Systematic
380.00	.14580	.000027	.00010	381.50	.17003	.000030	.00010
383.00	.19554	.000013	.00010	384.50	.22249	.000015	.00010
386.00	.25140	.000030	.00010	387.50	.28048	.000036	.00010
389.00	.30929	.000054	.00010	390.50	.33718	.000059	.00010
392.00	.36465	.000036	.00010	393.50	.39159	.000027	.00010
395.00	.41903	.000065	.00010	396.50	.44370	.000034	.00010
398.00	.46633	.000062	.00010	399.50	.48705	.000055	.00010
401.00	.50766	.000057	.00010	402.50	.52624	.000068	.00010
404.00	.54799	.000057	.00010	405.50	.56861	.000032	.00010
407.00	.58745	.000094	.00010	408.50	.60604	.000060	.00010
410.00	.62234	.000038	.00010	411.50	.63656	.000068	.00010
413.00	.64951	.000059	.00010	414.50	.66131	.000065	.00010
416.00	.67152	.000046	.00010	417.50	.67987	.000057	.00010
419.00	.68701	.000067	.00010	420.50	.69555	.000103	.00010
422.00	.70151	.000030	.00010	423.50	.70430	.000041	.00010
425.00	.70965	.000033	.00010	426.50	.71287	.000023	.00010
428.00	.70285	.000049	.00010	429.50	.63752	.000022	.00010
431.00	.54947	.000024	.00010	432.50	.55494	.000013	.00010
434.00	.55895	.000046	.00010	435.50	.54368	.000026	.00010
437.00	.52045	.000033	.00010	438.50	.49497	.000054	.00010
440.00	.47901	.000032	.00010	441.50	.47848	.000021	.00010
443.00	.48766	.000036	.00010	444.50	.49576	.000022	.00010
446.00	.49920	.000024	.00010	447.50	.50825	.000046	.00010
449.00	.53230	.000030	.00010	450.50	.56323	.000034	.00010
452.00	.58958	.000041	.00010	453.50	.60902	.000039	.00010
455.00	.62269	.000032	.00010	456.50	.62779	.000015	.00010
458.00	.62218	.000031	.00010	459.50	.60829	.000019	.00010
461.00	.59143	.000041	.00010	462.50	.57854	.000026	.00010
464.00	.57327	.000014	.00010	465.50	.56913	.000036	.00010
467.00	.55998	.000018	.00010	468.50	.54595	.000016	.00010
470.00	.53141	.000028	.00010	471.50	.51638	.000030	.00010
473.00	.50873	.000021	.00010	474.50	.53083	.000021	.00010
476.00	.55022	.000031	.00010	477.50	.52368	.000028	.00010
479.00	.50331	.000028	.00010	480.50	.49395	.000037	.00010
482.00	.49597	.000022	.00010	483.50	.53422	.000031	.00010
485.00	.59664	.000041	.00010	486.50	.65144	.000060	.00010
488.00	.69368	.000055	.00010	489.50	.72897	.000037	.00010
491.00	.75482	.000024	.00010	492.50	.76958	.000047	.00010
494.00	.77582	.000044	.00010	495.50	.77650	.000051	.00010
497.00	.77208	.000054	.00010	498.50	.76286	.000025	.00010

TABLE 4 (Continued)

Transmittance (T) as a function of wavelength from 380 to 780.5 nm for a bandwidth of 1.5 nm. The estimates of random and systematic errors are also provided. These data are not certified.

Wavelength (nm)	T	Δ_T Standard Error	Δ_T Systematic	Wavelength (nm)	T	Δ_T Standard Error	Δ_T Systematic
500.00	.75007	.000038	.00010	501.50	.73534	.000045	.00010
503.00	.71949	.000049	.00010	504.50	.70383	.000045	.00010
506.00	.68654	.000029	.00010	507.50	.66262	.000024	.00010
509.00	.62231	.000040	.00010	510.50	.56707	.000031	.00010
512.00	.51720	.000029	.00010	513.50	.49346	.000056	.00010
515.00	.50708	.000031	.00010	516.50	.53946	.000027	.00010
518.00	.56851	.000043	.00010	519.50	.58209	.000030	.00010
521.00	.57281	.000036	.00010	522.50	.51543	.000052	.00010
524.00	.43289	.000017	.00010	525.50	.39072	.000015	.00010
527.00	.37679	.000020	.00010	528.50	.35483	.000018	.00010
530.00	.35279	.000016	.00010	531.50	.37015	.000025	.00010
533.00	.39916	.000017	.00010	534.50	.45853	.000042	.00010
536.00	.54124	.000035	.00010	537.50	.61975	.000031	.00010
539.00	.68105	.000047	.00010	540.50	.72896	.000044	.00010
542.00	.76653	.000033	.00010	543.50	.79325	.000059	.00010
545.00	.81171	.000029	.00010	546.50	.82444	.000040	.00010
548.00	.83233	.000043	.00010	549.50	.83615	.000081	.00010
551.00	.83719	.000045	.00010	552.50	.83660	.000048	.00010
554.00	.83571	.000022	.00010	555.50	.83426	.000029	.00010
557.00	.83133	.000029	.00010	558.50	.82586	.000025	.00010
560.00	.81679	.000044	.00010	561.50	.80277	.000038	.00010
563.00	.78036	.000034	.00010	564.50	.74242	.000038	.00010
566.00	.67208	.000029	.00010	567.50	.53386	.000026	.00010
569.00	.31171	.000019	.00010	570.50	.11909	.000013	.00010
572.00	.04466	.000020	.00010	573.50	.03514	.000016	.00010
575.00	.04138	.000008	.00010	576.50	.04491	.000012	.00010
578.00	.05465	.000013	.00010	579.50	.06821	.000009	.00010
581.00	.06696	.000015	.00010	582.50	.04148	.000013	.00010
584.00	.01915	.000006	.00010	585.50	.01262	.000006	.00010
587.00	.01731	.000007	.00010	588.50	.03031	.000012	.00010
590.00	.04805	.000019	.00010	591.50	.06187	.000007	.00010
593.00	.08229	.000008	.00010	594.50	.12409	.000025	.00010
596.00	.18771	.000025	.00010	597.50	.25829	.000021	.00010
599.00	.31676	.000014	.00010	600.50	.37306	.000031	.00010
602.00	.43501	.000046	.00010	603.50	.49640	.000049	.00010
605.00	.55363	.000037	.00010	606.50	.59925	.000042	.00010
608.00	.63107	.000066	.00010	609.50	.65692	.000042	.00010
611.00	.68896	.000030	.00010	612.50	.73245	.000043	.00010
614.00	.78043	.000024	.00010	615.50	.82013	.000027	.00010
617.00	.84419	.000022	.00010	618.50	.85409	.000056	.00010

TABLE 4 (Continued)

Transmittance (T) as a function of wavelength from 380 to 780.5 nm for a bandwidth of 1.5 nm. The estimates of random and systematic errors are also provided. These data are not certified.

Wavelength (nm)	T	Δ_T Standard Error	Δ_T Systematic	Wavelength (nm)	T	Δ_T Standard Error	Δ_T Systematic
620.00	.85400	.000056	.00010	621.50	.84757	.000045	.00010
623.00	.84081	.000045	.00010	624.50	.84027	.000029	.00010
626.00	.84212	.000048	.00010	627.50	.84185	.000048	.00010
629.00	.83965	.000035	.00010	630.50	.84039	.000047	.00010
632.00	.84500	.000046	.00010	633.50	.85109	.000062	.00010
635.00	.85677	.000038	.00010	636.50	.86029	.000032	.00010
638.00	.86270	.000045	.00010	639.50	.86501	.000022	.00010
641.00	.86684	.000035	.00010	642.50	.86847	.000026	.00010
644.00	.86991	.000050	.00010	645.50	.87114	.000069	.00010
647.00	.87189	.000053	.00010	648.50	.87232	.000097	.00010
650.00	.87268	.000030	.00010	651.50	.87294	.000108	.00010
653.00	.87322	.000052	.00010	654.50	.87322	.000064	.00010
656.00	.87320	.000078	.00010	657.50	.87276	.000059	.00010
659.00	.87216	.000017	.00010	660.50	.87106	.000029	.00010
662.00	.86924	.000035	.00010	663.50	.86636	.000018	.00010
665.00	.86192	.000120	.00010	666.50	.85616	.000054	.00010
668.00	.84947	.000030	.00010	669.50	.84273	.000043	.00010
671.00	.83688	.000020	.00010	672.50	.83157	.000038	.00010
674.00	.82668	.000032	.00010	675.50	.82088	.000031	.00010
677.00	.81184	.000039	.00010	678.50	.79967	.000058	.00010
680.00	.78648	.000047	.00010	681.50	.77033	.000071	.00010
683.00	.75090	.000047	.00010	684.50	.73735	.000031	.00010
686.00	.74509	.000039	.00010	687.50	.76335	.000040	.00010
689.00	.77874	.000044	.00010	690.50	.79470	.000040	.00010
692.00	.81070	.000036	.00010	693.50	.82509	.000060	.00010
695.00	.83668	.000063	.00010	696.50	.84584	.000038	.00010
698.00	.85296	.000065	.00010	699.50	.85807	.000074	.00010
701.00	.86156	.000057	.00010	702.50	.86388	.000070	.00010
704.00	.86559	.000080	.00010	705.50	.86695	.000087	.00010
707.00	.86777	.000188	.00010	708.50	.86848	.000069	.00010
710.00	.86848	.000063	.00010	711.50	.86809	.000113	.00010
713.00	.86701	.000069	.00010	714.50	.86522	.000073	.00010
716.00	.86278	.000142	.00010	717.50	.85960	.000047	.00010
719.00	.85552	.000123	.00010	720.50	.85002	.000116	.00010
722.00	.84260	.000084	.00010	723.50	.83304	.000031	.00010
725.00	.81990	.000114	.00010	726.50	.80031	.000070	.00010
728.00	.77176	.000077	.00010	729.50	.72617	.000057	.00010
731.00	.65583	.000101	.00010	732.50	.54906	.000059	.00010
734.00	.41047	.000065	.00010	735.50	.27146	.000070	.00010
737.00	.17783	.000032	.00010	738.50	.14350	.000025	.00010

TABLE 4 (Continued)

Transmittance (T) as a function of wavelength from 380 to 780.5 nm for a bandwidth of 1.5 nm. The estimates of random and systematic errors are also provided. These data are not certified.

Wavelength (nm)	T	Δ_T Standard Error	Δ_T Systematic	Wavelength (nm)	T	Δ_T Standard Error	Δ_T Systematic
740.00	.14029	.000039	.00010	741.50	.14205	.000027	.00010
743.00	.15422	.000013	.00010	744.50	.17506	.000027	.00010
746.00	.17950	.000044	.00010	747.50	.16393	.000038	.00010
749.00	.15817	.000026	.00010	750.50	.17714	.000030	.00010
752.00	.21278	.000036	.00010	753.50	.25589	.000065	.00010
755.00	.30634	.000047	.00010	756.50	.36590	.000050	.00010
758.00	.42896	.000027	.00010	759.50	.48660	.000056	.00010
761.00	.53598	.000089	.00010	762.50	.57747	.000099	.00010
764.00	.61508	.000065	.00010	765.50	.65041	.000071	.00010
767.00	.68350	.000108	.00010	768.50	.71193	.000061	.00010
770.00	.73432	.000079	.00010	771.50	.75005	.000086	.00010
773.00	.76019	.000081	.00010	774.50	.76505	.000141	.00010
776.00	.76438	.000145	.00010	777.50	.75658	.000066	.00010
779.00	.74102	.000081	.00010	780.50	.71767	.000142	.00010

National Institute of Standards & Technology

Certificate

Standard Reference Material 2034

Holmium Oxide Solution Wavelength Standard from 240 to 650 nm

Series No. 94

This Standard Reference Material (SRM) is a certified transfer standard intended for the verification and calibration of the wavelength scale of ultraviolet and visible absorption spectrometers having nominal spectral bandwidths not exceeding 3 nm. SRM 2034 is batch-certified for wavelength location of minimum transmittance of 14 bands in the spectral range from 240 to 650 nm for six spectral bandwidths from 0.1 to 3 nm.

SRM 2034 is an aqueous solution prepared to contain 4 percent by weight of holmium oxide (Ho_2O_3) in 10 percent (V/V) perchloric acid ($HClO_4$). The solution is flame-sealed in a non-fluorescent, fused-silica cuvette of optical quality by fusion of the tubular end of the cuvette. The square cuvette has a nominal 10 mm pathlength so that it fits in the sample compartment of most conventional absorption spectrometers (see Note 1 under "Instructions for Use").

Certification: The certified wavelengths are given in Table 1 of this Certificate and apply to Series No. 94 as well as to all preceding series.

Intrinsic Wavelength Stability and Storage: The certified wavelengths listed in Table 1 in this Certificate are expected to be valid as long as the SRM 2034 solution is chemically stable. Wavelength verification measurements have been performed in the NIST Inorganic Analytical Research Division on original SRM 2034 solutions maintained under typical laboratory conditions. The results of these wavelength verification studies indicate that the SRM 2034 solutions are stable for at least 8 years. When not in use, SRM 2034 should be stored in the container provided, and at a temperature between 20 - 30 °C.

CAUTION: SRM 2034 contains perchloric acid as well as holmium oxide which are considered hazardous. Caution should be exercised when handling this SRM (see section on Safety Precautions).

The research, development, and initial production and certification of SRM 2034, including the investigations on the various chemical and physical parameters that might influence the certified measurements and results, were performed by V.R. Weidner, NIST Radiometric Physics Division, and R. Mavrodineanu, NIST Inorganic Analytical Research Division.

The production and certification renewal of SRM 2034 were performed by J.C. Travis, M.V. Smith, and N.K. Winchester, NIST Inorganic Analytical Research Division. The technical leadership for the production and measurements leading to the certification of this SRM was provided by J.C. Travis.

The overall direction and coordination of technical measurements leading to certification was performed in the NIST Inorganic Analytical Research Division by J.C. Travis and R.L. Watters, Jr.

The support aspects involved in the issuance of this SRM were coordinated through the Standard Reference Materials Program by J.C. Colbert.

Gaithersburg, MD 20899
December 2, 1993
(Revision of certificate dated 2-3-92)

Thomas E. Gills, Acting Chief
Standard Reference Materials Program

(over)

Certification Values

The transmittance spectrum of SRM 2034, referenced to air, for a 0.1 nm spectral bandwidth, is illustrated in Figure 1 in this Certificate. The certified wavelengths of minimum transmittance, expressed in nanometers (nm), for 14 bands from 240 to 650 nm and for six spectral bandwidths from 0.1 to 3.0 nm are given below in Table 1. Wavelengths for band No. 10 for the three narrowest spectral bandwidths are not given because this band splits into two transmittance minima for nominal spectral bandwidths less than 1 nm.

Table 1. Certified Wavelengths (nm) of Minimum Transmittance of 14 Bands for SRM 2034 at Six Spectral Bandwidths, Referenced to Air

SRM 2034 Band No.	Spectral Bandwidth (nm)					
	0.1	0.25	0.5	1	2	3
1	240.99	240.97	241.01	241.13	241.08	240.90
2	249.83	249.78	249.79	249.87	249.98	249.92
3	278.15	278.14	278.13	278.10	278.03	278.03
4	287.01	287.00	287.01	287.18	287.47	287.47
5	333.47	333.44	333.43	333.44	333.40	333.32
6	345.55	345.55	345.52	345.47	345.49	345.49
7	361.36	361.35	361.33	361.31	361.16	361.04
8	385.45	385.42	385.50	385.66	385.86	386.01
9	416.07	416.07	416.09	416.28	416.62	416.84
10	------	------	------	451.30	451.30	451.24
11	467.82	467.82	467.80	467.83	467.94	468.07
12	485.28	485.28	485.27	485.29	485.33	485.21
13	536.54	536.53	536.54	536.64	536.97	537.19
14	640.51	640.49	640.49	640.52	640.84	641.05

Certification Uncertainty

The expanded uncertainty (U) for all of the wavelength values given in Table 1 is U = ± 0.1 nm, determined from the root-mean-square combination of component standard uncertainties (i.e., estimated standard deviations) and a "coverage factor" (k) of k=2. The coverage factor is based on the student's t-distribution for >30 effective degrees of freedom, to define an interval within which the unknown value of the band-minimum wavelength can be asserted to lie with a level of confidence of approximately 95%. This uncertainty includes "Type A" components of uncertainty, which are evaluated by statistical methods, and "Type B" components of uncertainty, which are evaluated by other means. Component standard uncertainties for SRM 2034 are u_A = ± 0.025 nm for the calibration of the NIST spectrophotometer wavelength scale against atomic spectral lines, U_{B1} = ± 0.03 for the estimation of absorption band minima, and u_{B2} = ± 0.03 nm for possible wavelength shifts with temperature and concentration of the solution. The methods used to combine standard uncertainties are described in NIST Technical Note 1297.[1]

The certified wavelengths listed in Table 1 in this Certificate are not valid if SRM 2034 is used outside the range of experimental conditions investigated. For example, the wavelengths of minimum transmittance of SRM 2034 for spectral bandwidths greater than 3 nm have not been evaluated.

Production and Certification Procedure

Specific details concerning the materials, instrumentation, and method used in the certification of SRM 2034, are given elsewhere.[2,3] NBS Special Publication 260-102 [2] discusses the influence of temperature as well as the purity and concentration of the holmium oxide solution on the certified wavelengths. The procedures used for the assessment of the wavelengths of minimum transmittance and the establishment of the accuracy of the wavelength scale of the reference spectrometer used for the certification are also described in Special Publication 260-102.

Instructions for Use

To maintain the integrity of SRM 2034, the cuvette should be handled only by the tubular end or by its opposing frosted sides. While not in use, SRM 2034 should be stored in the container provided.

SRM 2034 is to be carefully inserted in the cuvette holder of the sample beam within a lightproof sample compartment of the spectrometer being tested (see **Note 1** below). The desired bands are scanned to measure their locations of minimum transmittance for known spectral bandwidth conditions. The transmittance spectrum is to be acquired at a laboratory temperature of 25 $\pm$ 5 °C, and is referred to air, i.e., no cuvette or blank is to be placed in the reference position. The measured wavelength of the minimum transmittance of a specific band is compared to the certified wavelength in Table 1 for that band; the certified wavelength for the spectral bandwidth that is most representative of the spectral bandwidth of the spectrometer being tested is used as the reference value. Taking into account the certification uncertainty of $\pm$ 0.1 nm for SRM 2034, any significant differences between the measured and the certified wavelengths for the peaks measured may then be used to recalibrate the wavelength scale.

NOTE 1. If the cuvette is too tall for the sample compartment of the absorption spectrometer being tested, a piece of black opaque cloth placed over the sample compartment can be used to provide a temporary lightproof enclosure during the wavelength verification procedure.

Wavelength Verification

Good laboratory practice in the handling and storage of SRM 2034 is highly recommended to help maintain the integrity of the certified wavelength values given in Table 1 in this Certificate. If the user determines at any time that this SRM has been exposed to adverse conditions that could affect the chemical stability of the solution, and perhaps invalidate the certified wavelength values, this SRM may be returned to the NIST Inorganic Analytical Research Division for wavelength verification. Prior to return shipment of this SRM, however, the NIST Inorganic Analytical Research Division should be contacted directly by telephone at (301) 975-4117 to obtain the necessary information regarding recommended shipping instructions and verification measurement fees.

Safety Precautions

SRM 2034 contains perchloric acid as well as holmium oxide in cuvettes that have been individually vacuum-tested for leaks. Should a leak in the cuvette subsequently develop, or if the cuvette is accidentally broken, the general recommendation is to carefully treat the perchloric acid spill immediately with copious amounts of water. [4-6] Specifically, the following remedial action should be taken:

> "Perchloric acid spills should be diluted immediately with water, taken up with swabs (preferably wool), and then washed with generous amounts of water. The swabs should also be washed with water before discarding. Swabs of cotton or other cellulose material contaminated with perchloric acid should be regarded as fire or explosion hazards if not washed thoroughly with large amounts of water."[5]

Acknowledgments

The initial research at NIST concerning the potential use of the Ho_2O_3-$HClO_4$ solution as a wavelength standard was performed by K.D. Mielenz of the NIST Radiometric Physics Division and R.A. Velapoldi of the NIST Surface and Microanalysis Science Division.

The vacuum-testing and flame-sealing of the fused-silica cuvettes for this SRM were performed by J. Anderson, of the NIST Fabrication Technology Division.

REFERENCES

[1] Barry N. Taylor and Chris E. Kuyatt, "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, (1993).

[2] V.R. Weidner, R. Mavrodineanu, K.D. Mielenz, R.A. Velapoldi, K.L. Eckerle, and B. Adams, Holmium Oxide Solution Wavelength Standard from 240 to 640 nm - SRM 2034, NBS Special Publication 260-102, (1986).

[3] V.R. Weidner, R. Mavrodineanu, K.D. Mielenz, R.A. Velapoldi, K.L. Eckerle, and B. Adams, Spectral Transmittance Characteristics of Holmium Oxide in Perchloric Acid, J. Res. Natl. Bur. Stds., Vol. 90, No. 2, 115-125 (1985).

[4] J.C. Schumacher, Ed., Perchlorates: Their Properties, Manufacture and Uses. Reinhold Publishing Corp., New York, NY, p. 180 (1960).

[5] A.A. Schilt, Perchloric Acid and Perchlorates, The G. Frederick Smith Chemical Co., Publisher, Columbus, OH 43223, p. 157 (1979).

[6] GFS Chemicals 90/91 Catalog, GFS Chemicals, Powell, OH 43605, p. 458.

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

Appendix 18

National Bureau of Standards

Certificate

Standard Reference Material 936

Quinine Sulfate Dihydrate

R. A. Velapoldi and K. D. Mielenz

This Standard Reference Material is intended for use in the evaluation of methods and the calibration of fluorescence spectrometers. It is certified for the relative molecular emission spectrum, E(λ), in radiometric units for a solution of 1.28×10^{-6} mol/L quinine sulfate dihydrate in 0.105 mol/L perchloric acid using an excitation wavelength of 347.5 nm. The certified values of the molecular emission spectrum at 5 nm wavelength intervals from 375 to 675 nm are given in table 1. These values have been corrected for instrument and sample parameters, including the spectral responsivity of the detection system, monochromator bandwidth, photomultiplier tube nonlinearity, monochromator wavelength error, solvent refractive index, and cell window transmittance. The relative standard error in E(λ), RSE [E(λ)], is given in table 1. The estimate of the relative systematic error limits in the molecular emission spectrum, RSEL [E(λ)], is also given in table 1 and was determined by the addition of the absolute values of the estimated systematic errors. These relative error limits include uncertainties in the calibration values for the spectral responsivity, the wavelength position of the emission peak maximum, and in the corrections applied for instrument and sample parameters.

From the certified values of E(λ), values may be calculated for the molecular emission spectrum in the various photon, radiometric, wavelength, and wavenumber units using the following equation: [1,2]

$$E(\lambda) = \frac{E_p(\lambda)}{\lambda} = \frac{E(\tilde{\nu})}{\lambda^2} = \frac{E_p(\tilde{\nu})}{\lambda^3}$$

These values have been calculated and are given in NBS Special Publication 260-64.

The technical emission spectrum, $E^T(\lambda)$, i.e., the emission spectrum corrected for instrument parameters only, is also given in SP 260-64. The quinine sulfate dihydrate used for SRM 936 was a special lot of material obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J.

The technical and support aspects concerning the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. W. Mears and R. W. Seward.

Washington, D.C. 20234
April 1, 1979

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

Table 1. The Molecular Emission Spectrum, E(λ), of Quinine Sulfate Dihydrate in 0.105 mol/L $HClO_4$, the Relative Standard Error, RSE, and the Estimated Relative Systematic Error Limits, RSEL, in the E(λ) Values.

λ,nm	E(λ)	RSE [E(λ)]	RSEL [E(λ)]	λ,nm	E(λ)	RSE [E(λ)]	RSEL [E(λ)]
375.0	0.005	0.019	0.087	525.0	0.302	0.001	0.029
380.0	.012	.006	.078	530.0	.264	.003	.029
385.0	.028	.003	.071	535.0	.231	.003	.029
390.0	.057	.003	.064	540.0	.201	.002	.029
395.0	.103	.002	.059	545.0	.175	.002	.029
400.0	.170	.002	.054	550.0	.153	.001	.029
405.0	.257	.003	.049	555.0	.132	.001	.029
410.0	.359	.003	.045	560.0	.116	.001	.029
415.0	.471	.003	.041	565.0	.101	.002	.029
420.0	.586	.003	.037	570.0	.088	.002	.029
425.0	.694	.003	.034	575.0	.076	.003	.029
430.0	.792	.002	.031	580.0	.065	.003	.029
435.0	.874	.002	.028	585.0	.057	.001	.029
440.0	.940	.001	.026	590.0	.050	.003	.030
445.0	.984	.001	.024	595.0	.043	.004	.030
450.0	.999	.001	.023	600.0	.037	.006	.030
455.0	.997	.001	.023	605.0	.032	.002	.030
460.0	.982	.001	.024	610.0	.028	.006	.030
465.0	.947	.001	.024	615.0	.024	.003	.030
470.0	.897	.001	.025	620.0	.021	.011	.030
475.0	.838	.002	.026	625.0	.018	.003	.030
480.0	.782	.002	.027	630.0	.016	.015	.030
485.0	.719	.002	.027	635.0	.014	.014	.030
490.0	.657	.002	.027	640.0	.011	.037	.030
495.0	.595	.003	.027	645.0	.010	.015	.030
500.0	.541	.002	.027	650.0	.009	.027	.030
505.0	.486	.001	.028	655.0	.008	.035	.031
510.0	.434	.003	.028	660.0	.007	.073	.031
515.0	.386	.003	.028	665.0	.006	.046	.032
520.0	.342	.002	.028	670.0	.005	.053	.032
				675.0	.004	.065	.033

SUPPLEMENTARY DATA

The following data for the specific molar absorbances, water content, photon yields, and fluorescence lifetimes are considered to be supplementary and are not to be considered certified values.

The quinine sulfate dihydrate (QSD) used for SRM 936 was found to be homogeneous to better than 0.5% by thin-layer chromatography with development by two solvent systems and the determination of specific molar absorbances, ϵ, at three different wavelengths. The SRM contains approximately 1.7% of an impurity as determined by high performance liquid chromatography using absorbance and fluorescence detection. This impurity is believed to be dihydroquinine sulfate dihydrate, which has optical characteristics that are similar to those of the quinine sulfate dihydrate. The ultraviolet absorption spectrum of SRM 936 in 0.105 mol/L $HClO_4$ exhibits the following absorption maxima:

$$250.0 \text{ nm}, \epsilon_{max} = 56{,}990 \pm 90 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$$
$$347.5 \text{ nm}, \epsilon_{max} = 10{,}810 \pm 20 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$$

and, on the side of a peak:

$$365.0 \text{ nm}, \epsilon_{obs} = 6{,}920 \pm 10 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$$

The water content of this material was measured by two methods. The average of six determinations by the Karl-Fischer method gave a value of (4.74 ± 0.05%), while the average of four determinations by a weight loss procedure gave a value of (4.57 ± 0.04%). The theoretical value for water in quinine sulfate dihydrate is 4.60%.

The photon yield, Q, and the fluorescence lifetime, τ, of SRM 936 were compared to values obtained for a sample of purified quinine sulfate dihydrate and are summarized below:

	Q 0.5 mol/L H_2SO_4	τ, ns 0.5 mol/L H_2SO_4
SRM 936, QSD	0.544 ± 0.03	19.1 ± 0.1
Purified QSD	0.546[a]	19.2 ± 0.1

[a]Melhuish, W. H., J. Phys. Chem. **65**, 229 (1961); *ibid,* New Zealand J. Sci. Tech. **37**, 142 (1955).

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PREPARATION AND USE OF SRM 936

This Standard Reference Material is for "in vitro" diagnostic use as a clinical laboratory standard. A "stock" standard solution containing 0.1 mg/mL of quinine sulfate may be prepared as follows: Weigh 0.100 g of SRM 936 to the nearest one-tenth milligram and quantitatively transfer it to a 1000-mL volumetric flask. Dilute to the calibrated volume with 0.105 mol/L $HClO_4$, to give a solution that is 1.28×10^{-4} mol/L (0.1 mg/mL) in quinine sulfate. Store this solution in the dark in a well-stoppered, glass bottle. A "working" standard solution containing 1 μg/mL may be prepared by transferring 10 mL of the above "stock" standard solution to a 1000-mL volumetric flask and diluting to the calibrated volume with 0.105 mol/L $HClO_4$ to give a solution that is 1.28×10^{-6} mol/L (1 μg/mL) in quinine sulfate. Store this solution in the same manner as the above "stock" standard solution.

Several opinions regarding the stability of quinine sulfate solutions have appeared in the literature [3]. NBS considers the 0.1 mg/mL "stock" standard solution prepared from SRM 936 to be stable for 3 months when stored as specified; and the 1 μg/mL "working" standard solution to be stable for 1 month when so stored.

SRM 936 should be kept in its original bottle and stored in the dark at room temperature (30 °C or less). It should not be subjected to heat or direct sunlight during storage. Experience at NBS indicates that under proper storage this material is stable for at least 3 years. If this material degrades beyond the limits certified, purchasers will be notified by NBS. It is recommended that the material not be used after 3 years from the date of purchase.

References:

[1] Ejder, E. J., J. Opt. Soc. Amer. **59**, 223 (1969).

[2] Melhuish, W. H., J. Res. Nat. Bur. Stand. (U.S.) **76A**, No. 6, 547 (1972).

[3] Melhuish, W. H., J. Phys. Chem. **65**, 229 (1961); Gill, J. E., Photochem. and Photobiol. **9**, 313 (1969); Birks, J. B., J. Res. Nat. Bur. Stand. (U.S.) **80A**, 389 (1976); Heller, C. A., Henry, R. A., McLaughlin, B. A., and Bless, D. E., J. Chem. Eng. Data **19**, 214 (1974); West, M. A., and Kemp, D. R., Int'l. Lab., p. 27 (May/June 1976); and White, J. U., Pittsburgh Conf. Abstracts, Paper 488 (1977).

This Standard Reference Material has been measured and certified at the laboratories of the National Bureau of Standards, Gaithersburg, Maryland. All inquiries should be addressed to:

Office of Standard Reference Materials
Room B311, Chemistry Building
National Bureau of Standards
Washington, D.C. 20234

The date of issuance and certification of SRM 936 was April 1, 1979

Appendix 19

National Institute of Standards & Technology

Certificate

Standard Reference Material 1931

Fluorescence Emission Standards for the Visible Region

This Standard Reference Material (SRM) is intended for use in the evaluation and calibration of the relative spectral response of fluorescence spectrometers. It consists of four fluorescence standards and a "blank" specimen mounted in anodized aluminum cuvette-sized holders. The fluorescence standards are certified for the relative corrected emission spectrum, $E(\lambda)$ in energy/wavelength units. The certified values of the blue, green, yellow and orange emission spectra at 2 nm wavelength intervals are given in Tables I, II, III and IV, respectively. The fluorescence emission standards are:

Fluorescence Emission Standard	Excitation Wavelength, nm*	Emission Wavelength Range, nm*
B (Blue)	340	400 - 550
G (Green)	280	490 - 600
Y (Yellow)	410	490 - 740
O (Orange)	235	530 - 740

*Excitation and emission monochromator bandpass set at 5.3 nm, temperature was 25°C

The fluorescence emission standards are composed of inorganic phosphors (10% by weight) and polytetrafluoroethylene (PTFE) which were pressed into wafers and sintered. The phosphors selected emit in the blue, green, yellow or orange wavelength regions (Figure 1). The PTFE wafer is mounted in an anodized aluminum cuvette-sized holder. The fluorescence excitation beam angle of incidence is 60 degrees from the normal to plane of the sintered wafer. SRM 1931 L and R are oriented for left and right-handed spectrofluorimeters, respectively, as defined by viewing the fluorescent sample along the excitation beam. If the first emission optical component is located to the right of the sample then this orientation is designated R and if it is to the left then it is designated L. The anodized holder is engraved with the first letter of the color of the emission (B, G, Y or O) over the excitation beam aperture. A PTFE blank in a non-engraved holder is also included in the set for diagnostic purposes.

The technical measurements leading to certification of spectral emission were performed by A. Thompson and K.L. Eckerle of the Radiometric Physics Division.

The overall direction and coordination of this project was provided by K.D. Mielenz and J.J. Hsia, NIST Radiometric Physics Division.

The technical and support aspects involved in the issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.L. McKenzie.

Gaithersburg, MD 20899
August 15, 1989

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

CALIBRATION MEASUREMENTS: Calibration measurements were done with s emission polarization (perpendicular to the plane of incidence at the monochromator grating) to minimize polarization errors. Ten spectra were measured for each phosphor standard in the master set, except for the yellow phosphor for which only nine spectra were measured. In an individual emission spectrum, the fluorescence value at each wavelength was the mean net signal from 100 measurements of the fluorescence signal and ten dark measurements. These values have been corrected for the following instrument parameters: spectral responsivity of the detection system, photomultiplier tube nonlinearity, and monochromator wavelength error. The corrected values are used to calculate the relative emission spectrum, $E(\lambda)$, which is presented in Tables I, II, III, and IV. The total standard error , $TSE[E(\lambda)]$, (3 sigma) of $E(\lambda)$ is given in Tables I, II, III, and IV. These error limits include quadrature sums of random and systematic uncertainties for: instrument parameters, the measurement of the emission spectra, and the measurement of the calibration values for the spectral responsivity. In addition to the master set calibration, commercial spectrofluorimeter measurements were carried out on 18 sets out of 50 sets to estimate the uniformity of the SRM 1931 batch preparation. Variation in the standards emission spectra due to: UV instability, long-term stability, sample nonuniformity, sample to sample variation, temperature, excitation wavelength and excitation and emission polarization were estimated and their values will be given in an NIST 260-series Special Publication (currently in preparation). Values for the emission spectra in photon, wavelength and wavenumber units will also be presented in this 260-series Special Publication.

STORAGE AND USE OF SRM 1931: SRM 1931 should be stored in the aluminum container supplied in a location with stable temperature and humidity. The PTFE wafer will readily adsorb tobacco smoke and other organic aerosols. To avoid the adsorption of fluorescent contaminants SRM 1931 should not be exposed to these environments. The left or right-handed orientation of the wafer should not be changed by the user, if reorientation is necessary the standards should be returned to the NIST Radiometric Physics Division (534). The measured corrected emission spectra of SRM 1931 is certified at a bandpass of 5.3 nm. A procedure to correct these spectra for bandpass error is used in the 260-series Special Publication (in preparation) to calculate the emission spectra at zero bandpass.

The measurement of SRM 1931 is a front surface fluorescence measurement. Therefore the proper alignment of the excitation and emission optical paths is essential, otherwise the emission monochromator may view only the fringe of the emission spot or a non-emitting portion of the wafer. The cuvette holders of commercial spectrofluorimeters have a degree of positional uncertainty in the placement of the cuvette. This allows one to place the standard in the holder and to adjust the position of the cuvette in the excitation beam until the fluorescence signal is maximized. Typically this is done with the emission monochromator near the fluorescence maximum. It is also necessary to filter out the excitation light from the emission monochromator. A simple UV glass filter is sufficient for this purpose and prevents first and second order scattered excitation radiation from distorting the emission spectra. This filter must then remain in the instrument for all subsequent fluorescence measurements for which the calibrations generated using these standards are to be used.

The calibration of the yellow master standard required over 80 hours of measurement time. After this long measurement time the standard was observed to have darkened in the region of the excitation spot accompanied by a diminution of the fluorescence signal intensity and a slight change in the shape of the emission spectrum for wavelengths less than 570 nm. Therefore as a conservative precaution, the certified values for the yellow fluorescence standard relative emission spectra encompass the wavelength range from 570 to 740 nm with the values less than 570 nm included for information only. For high accuracy calibrations it is recommended to use the certified values of the green and the orange standards to cover the excluded wavelength region of the yellow fluorescence standard. In typical calibrations the average measurement time will be on the order of several minutes and the small changes observed in the emission spectrum of the yellow master would entail little problems in accuracy. A more detailed treatment of the errors involved will be found in the 260-series Special Publication. For optimum accuracy in the calibration of a spectrofluorimeter, it is recommended to use the standards at wavelengths where the relative emission is greater than 0.10 whenever possible.

Table I. The relative corrected emission spectrum, E(λ), of the blue phosphor, the total standard error in E(λ), TSE[E(λ)] (3 sigma), these error limits include random and systematic uncertainties added in quadrature.

λ, nm	E(λ)	TSE[E(λ)]	λ, nm	E(λ)	TSE[E(λ)]
400	0.04878	0.00123	476	0.67794	0.00506
402	0.05966	0.00127	478	0.64256	0.00477
404	0.07666	0.00146	480	0.60298	0.00446
406	0.09738	0.00092	482	0.56859	0.00455
408	0.12213	0.00092	484	0.53476	0.00486
410	0.15203	0.00098	486	0.49894	0.00408
412	0.18512	0.00112	488	0.46922	0.00440
414	0.22375	0.00122	490	0.43649	0.00373
416	0.26715	0.00194	492	0.40798	0.00370
418	0.31380	0.00125	494	0.38092	0.00403
420	0.36546	0.00143	496	0.35374	0.00372
422	0.41954	0.00226	498	0.32907	0.00324
424	0.47674	0.00202	500	0.30583	0.00330
426	0.53385	0.00206	502	0.28345	0.00332
428	0.59184	0.00144	504	0.26244	0.00235
430	0.65132	0.00149	506	0.24259	0.00229
432	0.70840	0.00170	508	0.22577	0.00215
434	0.76155	0.00164	510	0.20872	0.00209
436	0.81095	0.00212	512	0.19354	0.00206
438	0.85735	0.00261	514	0.17914	0.00189
440	0.89676	0.00169	516	0.16503	0.00173
442	0.93083	0.00266	518	0.15332	0.00174
444	0.95797	0.00248	520	0.14130	0.00155
446	0.97772	0.00250	522	0.13065	0.00141
448	0.99213	0.00318	524	0.12070	0.00133
450	0.99757	0.00215	526	0.11112	0.00115
452	1.00000	0.00242	528	0.10303	0.00108
454	0.99535	0.00378	530	0.09498	0.00102
456	0.98189	0.00356	532	0.08794	0.00098
458	0.96785	0.00471	534	0.08111	0.00093
460	0.94216	0.00347	536	0.07475	0.00084
462	0.91896	0.00475	538	0.06920	0.00082
464	0.88925	0.00378	540	0.06366	0.00069
466	0.85539	0.00433	542	0.05892	0.00069
468	0.82415	0.00435	544	0.05433	0.00064
470	0.78743	0.00421	546	0.04996	0.00055
472	0.75231	0.00490	548	0.04629	0.00054
474	0.71694	0.00511	550	0.04254	0.00051

Table II. The relative corrected emission spectrum, E(λ), of the green phosphor, the total standard error in E(λ), TSE[E(λ)] (3 sigma), these error limits include random and systematic uncertainties added in quadrature.

λ, nm	E(λ)	TSE[E(λ)]	λ, nm	E(λ)	TSE[E(λ)]
490	0.07105	0.00066	546	0.52942	0.00568
492	0.09572	0.00090	548	0.48144	0.00542
494	0.12615	0.00136	550	0.43342	0.00509
496	0.16349	0.00181	552	0.39022	0.00488
498	0.20628	0.00205	554	0.35026	0.00432
500	0.25826	0.00252	556	0.31230	0.00379
502	0.31545	0.00309	558	0.28026	0.00328
504	0.37757	0.00354	560	0.24862	0.00285
506	0.44751	0.00440	562	0.22153	0.00251
508	0.52091	0.00606	564	0.19692	0.00212
510	0.60521	0.00607	566	0.17425	0.00175
512	0.68943	0.00731	568	0.15547	0.00169
514	0.77264	0.00824	570	0.13734	0.00145
516	0.84898	0.00861	572	0.12177	0.00128
518	0.91209	0.01006	574	0.10801	0.00117
520	0.95862	0.01030	576	0.09537	0.00101
522	0.98784	0.01041	578	0.08408	0.00089
524	1.00000	0.01050	580	0.07485	0.00080
526	0.99402	0.01001	582	0.06643	0.00070
528	0.97492	0.00966	584	0.05896	0.00061
530	0.94302	0.00977	586	0.05208	0.00057
532	0.90401	0.00992	588	0.04663	0.00046
534	0.85611	0.00934	590	0.04122	0.00045
536	0.80295	0.00863	592	0.03666	0.00039
538	0.75121	0.00847	594	0.03284	0.00041
540	0.69238	0.00731	596	0.02912	0.00034
542	0.63746	0.00718	598	0.02603	0.00033
544	0.58267	0.00675	600	0.02330	0.00034

Table III. The relative corrected emission spectrum, E(λ), of the yellow phosphor, the total standard error in E(λ), TSE[E(λ)] (3 sigma), these error limits include random and systematic uncertainties added in quadrature. The values in italics (wavenlengths 490 to 568 nm) are not certified, and are presented for purposes of Information Only.

λ, nm	E(λ)	TSE[E(λ)]	λ, nm	E(λ)	TSE[E(λ)]	λ, nm	E(λ)	TSE[E(λ)]
490	*0.05577*	*0.00300*	574	0.99115	0.01089	658	0.19842	0.00291
492	*0.06341*	*0.00276*	576	0.98291	0.01057	660	0.18755	0.00286
494	*0.07398*	*0.00295*	578	0.97375	0.01031	662	0.17766	0.00277
496	*0.08653*	*0.00325*	580	0.96069	0.01005	664	0.16806	0.00238
498	*0.10042*	*0.00341*	582	0.94821	0.00978	666	0.15854	0.00241
500	*0.11699*	*0.00366*	584	0.93378	0.00998	668	0.15042	0.00224
502	*0.13508*	*0.00401*	586	0.91577	0.00980	670	0.14205	0.00216
504	*0.15411*	*0.00422*	588	0.89850	0.00948	672	0.13436	0.00210
506	*0.17543*	*0.00452*	590	0.87739	0.00935	674	0.12702	0.00190
508	*0.19787*	*0.00452*	592	0.85788	0.00869	676	0.12001	0.00175
510	*0.22300*	*0.00461*	594	0.83751	0.00906	678	0.11394	0.00176
512	*0.24977*	*0.00503*	596	0.81368	0.00899	680	0.10745	0.00144
514	*0.27833*	*0.00536*	598	0.79210	0.00839	682	0.10166	0.00145
516	*0.30845*	*0.00528*	600	0.76586	0.00814	684	0.09645	0.00138
518	*0.34007*	*0.00592*	602	0.74265	0.00801	686	0.09115	0.00131
520	*0.37325*	*0.00582*	604	0.72051	0.00795	688	0.08665	0.00129
522	*0.40713*	*0.00599*	606	0.69391	0.00763	690	0.08218	0.00122
524	*0.44221*	*0.00616*	608	0.67077	0.00776	692	0.07789	0.00111
526	*0.47887*	*0.00619*	610	0.64501	0.00762	694	0.07417	0.00105
528	*0.51535*	*0.00644*	612	0.62066	0.00741	696	0.07037	0.00105
530	*0.55208*	*0.00695*	614	0.59752	0.00714	698	0.06704	0.00104
532	*0.58959*	*0.00758*	616	0.57128	0.00685	700	0.06385	0.00094
534	*0.62623*	*0.00774*	618	0.54897	0.00678	702	0.06064	0.00102
536	*0.66228*	*0.00777*	620	0.52502	0.00675	704	0.05762	0.00082
538	*0.69798*	*0.00842*	622	0.50147	0.00639	706	0.05502	0.00075
540	*0.73159*	*0.00823*	624	0.47867	0.00595	708	0.05264	0.00090
542	*0.76552*	*0.00909*	626	0.45644	0.00563	710	0.05011	0.00067
544	*0.79626*	*0.00936*	628	0.43651	0.00550	712	0.04795	0.00074
546	*0.82586*	*0.00920*	630	0.41521	0.00561	714	0.04574	0.00065
548	*0.85557*	*0.00984*	632	0.39552	0.00496	716	0.04369	0.00077
550	*0.88183*	*0.01033*	634	0.37593	0.00475	718	0.04205	0.00064
552	*0.90526*	*0.01129*	636	0.35701	0.00465	720	0.04028	0.00057
554	*0.92653*	*0.01133*	638	0.34006	0.00442	722	0.03854	0.00057
556	*0.94435*	*0.01132*	640	0.32249	0.00424	724	0.03698	0.00062
558	*0.96078*	*0.01106*	642	0.30667	0.00426	726	0.03504	0.00063
560	*0.97309*	*0.01119*	644	0.29031	0.00399	728	0.03372	0.00055
562	*0.98352*	*0.01114*	646	0.27481	0.00381	730	0.03265	0.00049
564	*0.99064*	*0.01060*	648	0.26146	0.00354	732	0.03122	0.00058
566	*0.99277*	*0.00961*	650	0.24707	0.00354	734	0.03003	0.00059
568	*1.00000*	*0.01066*	652	0.23405	0.00330	736	0.02896	0.00049
570	0.99841	0.01034	654	0.22145	0.00319	738	0.02809	0.00062
572	0.99498	0.01055	656	0.20956	0.00317	740	0.02681	0.00053

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