NBS SPECIAL PUBLICATION 260-68

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Standard Reference Materials:

Metal-On-Quartz Filters as a Standard Reference Material for Spectrophotometry—SRM 2031

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Standard Reference Materials:

Metal-On-Quartz Filters as a Standard Reference Material for Spectrophotometry—SRM 2031

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sued April 1980

Library of Congress Catalog Card Number: 79-600192

National Bureau of Standards Special Publication 260-68
Nat. Bur. Stand. (U.S.), Spec. Publ. 260-68, 116 pages (Apr. 1980)
CODEN: XNBSAV

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 1980

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price $4.25

Preface

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards are "well-characterized materials, produced in quantity, that calibrate a measurement system to assure compatibility of measurement in the nation." SRM's are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. In many industries, traceability of their quality control process to the national measurement system is carried out through the mechanism and use of SRM's. 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 NBS in arriving at the certified values of the SRM's produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series is reserved for this purpose.

This 260 Series is dedicated to the dissemination of information on all phases of the preparation, measurement, and certification of NBS-SRM's. In general, much more detail will be found in these papers than is generally allowed, or desirable, 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. It is also hoped that these papers will provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

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

Office of Standard Reference Materials
National Bureau of Standards
Washington, D. C. 20234

George A. Uriano, Chief
Office of Standard Reference Materials

Foreword

A variety of solid and liquid materials which have characteristic optical transmission properties have been used in the past in the analytical laboratories to verify the "proper" functioning of conventional spectrophotometers. During the past few years the optical transmittance of such materials could be measured with an increased accuracy. This is due in large part to the initiation of an extensive program of research and development in the field of standard reference materials for spectrophotometry at the National Measurement Laboratory of the National Bureau of Standards (NBS). As a direct consequence of this program, two high-accuracy spectrophotometers were designed and implemented, one provided with quartz optics, the other with off-axis mirrors. These instruments, which are capable of producing optical transmittance measurements with an accuracy of better than 1×10^{-4} transmittance units, were used to study quantitatively the physical parameters involved in the measurements of optical transmittance. The results from the studies were published in two NBS Special Publications, No. 378 (May 1973) and No. 466 (May 1977).

The NBS high-accuracy spectrophotometers, which constitute the primary optical transmittance standards available in this country was the basis for the selection and certification of several solid and liquid substances having an accurately determined transmittance, which could be used as standard reference materials (SRM's) in spectrophotometry. Those materials which have been issued thus far include SRM 930 and 2030, Glass Filters for Spectrophotometry, SRM 931, Liquid Filters for Spectrophotometry, SRM 932, Quartz Cuvette for Spectrophotometry, and SRM 935, Potassium Dichromate for Spectrophotometry. These materials now make it possible to transfer to the users the accurate transmittance data established at NBS, thus providing reliable means for verifying the accuracy of the transmittance scales of conventional spectrophotometers, as well as monitoring their stability and reproducibility. Such standards also provide an ideal way to establish baselines for intercomparisons of spectrophotometric data between interested laboratories.

The present publication describes in detail the results of a work initiated in 1969 for the production of a new SRM which could be used in the ultraviolet and visible (and possibly the infrared) spectral regions, and would, at the same time, exhibit good optical neutrality. This standard is evaporated metal on fused silica, using chromium metal as the semi-transparent film.

The optical characteristics of this newly issued SRM 2031 are such that it should prove useful in all chemical laboratories where spectrophotometry is used as a measuring tool.

SRM 2031 is but one more of the materials developed by NBS to assist in the standardization of spectrophotometers. The work in this field is continuing and should result in the production of further useful SRM's. In particular, SRM's to measure heterochromatic and isochromatic stray radiant energy are now in the final stage of development, and should be issued in late 1979 as SRM's 2032 and 2033.

By the production of these, and the many other SRM's as well as through the preparation of detailed scientific information on the preparation and utilization of these SRM's in the form of NBS 260 Series Special Publications, the National Bureau of Standards fulfills part of its essential roles designated in the Organic Act which established the Bureau in 1901. It is hoped that this activity will provide a solid foundation for future progress in the field of accurate measurements.

The work reported in this publication was supported in part by the National Institute of General Medical Sciences.

Curt W. Reimann, Acting Director
Center for Analytical Chemistry

OTHER NBS PUBLICATIONS IN THIS SERIES

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Mavrodineanu, R. and Baldwin, J. R., Standard Reference Materials: Metal-On-Quartz Filters as a Standard Reference material for Spectrophotometry-SRM 2031, NBS Spec. Publ. 260-68 (in press).

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Abstract

This publication describes in detail the selection, production, testing, and certification of the semi-transparent evaporated metal-on-fused silica filters as a Standard Reference Material for spectrophotometry. Particular attention is given to various factors that can affect the accuracy of the transmittance values established for these filters, such as: reflections, polarization, angle of incidence, and stability in time. Adequate procedures were devised and are described, for the protection of the exposed metal layer surface using optical contact, and for the protection of the filter aggregate, by the use of metal holders provided with shutters and of metal storage containers.

The data from several interlaboratory tests are also discussed, together with the results obtained on transmittance measurements on 19 sets of chromium-on-fused silica filters, protected by optical contact, which were studied over a period of two years. An Appendix contains the reproduction of several publications relevant to the subject discussed in this work.

Key Words: Filters for spectrophotometry; metal-on-fused silica filters; optical transmittance accuracy; polarization; reflections; spectral bandpass; Standard Reference Materials in Spectrophotometry; stray radiation; transmittance stability.

Disclaimer

1. General

Molecular absorption spectrometry, or spectrophotometry[2], is a measuring technique widely used in science and technology for the determination of a large number of inorganic and organic chemical species in a wide variety of matrices. These determinations are based on measuring the optical transmittance of the samples, and the accurate measurement of this parameter is an essential requirement, especially when used to establish the optical characteristics of the material.

Due to the importance of this parameter and as a result of numerous requests from the users of spectrophotometers, and in particular from the clinical chemists, the National Bureau of Standards (NBS) had initiated in 1969 a project to design and develop means for defining and measuring optical transmittances with a well determined accuracy, and to provide certified materials that can be used to verify the transmittance accuracy of conventional spectrophotometers and to monitor their stability and reproducibility.

As a result of this project, implemented in the Center for Analytical Chemistry at NBS, a special high-accuracy transmittance spectrometer was designed and constructed that measures the optical transmittance of solid or liquid samples with an accuracy of one part in 10^4 transmittance units [2].

This instrument constitutes the primary transmittance standard, and was used to measure and certify the transmittance of a variety of selected solid and liquid materials. These certified materials constitute secondary standards that provide a practical means for transferring to the user accurate optical transmittance values with a well established uncertainty. These, in turn, can be used to verify the accuracy of the transmittance and absorbance scales of conventional spectrophotometers.

The certified materials, known as Standard Reference Materials (SRM's), are produced at NBS and are available to the user. A general discussion of the SRM's for spectrophotometry will be given here. For a more detailed description, the reader is referred to the material reproduced in the Appendix and the publications mentioned in the references at the end of this publication. Some of the publications issued by NBS in the field of high-accuracy spectrophotometry are illustrated in Figure 1. Standard Reference Materials 930 and 2030 are illustrated in Figures 2 and 3, and SRM's 931, 935, and 932 in Figure 4.

1.1 Standard Reference Materials for Spectrophotometry Issued by the National Bureau of Standards

The use of solid materials, in the form of glass or quartz (fused silica), crystals, and of liquids and solutions of inorganic and sometimes organic compounds, to test the correct function of spectrophotometers is a common practice [3]. After a careful review, a number of materials were selected to serve as SRM's and were issued during the last few years. Table 1 gives a general summary of these materials, indicating their use and some of their limitations. Except for SRM's 2009, 2010, 2013, and 2014, they were all certified in the Center for Analytical Chemistry of the National Measurement Laboratory at NBS. From this table it can be concluded that all the SRM's, solid or liquid, issued as transmittance standards require the use of spectrophotometers capable of producing narrow spectral bandpasses from about 0.8 to 6.5 nm throughout the spectral range where the measurements are performed. The use of the glass filters (SRM 930 and SRM 2030) is limited to the visible spectral region due to the intrinsic transmittance properties of this material. SRM 935 can be used only in the ultraviolet and requires the accurate preparation of several solutions together with the use of accurate cuvettes (SRM 932). SRM 931 provides only one certified value in the ultraviolet and requires the use of accurate cuvettes (SRM 932). It is also a "one measurement at a time" type of material. The limitations enumerated above were evident from the early efforts cited to provide SRM's for spectrophotometry. However, at the time of the preparation and issuance of the SRM's described in Table 1, they were the best materials available for use as transfer standards for transmittance.

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[2] Note: The terminology used throughout this publication follows the nomenclature defined by K. D. Mielenz [1][3].

[3] Figures in brackets indicate the literature references at the end of this paper.
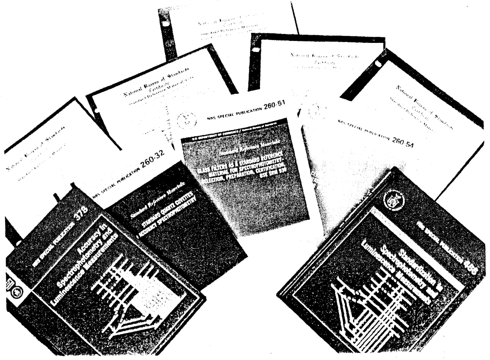
Figure 1. Illustration of several publications issued by NBS in the field of spectrophotometry. The NBS Special Publications can be purchased from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402.

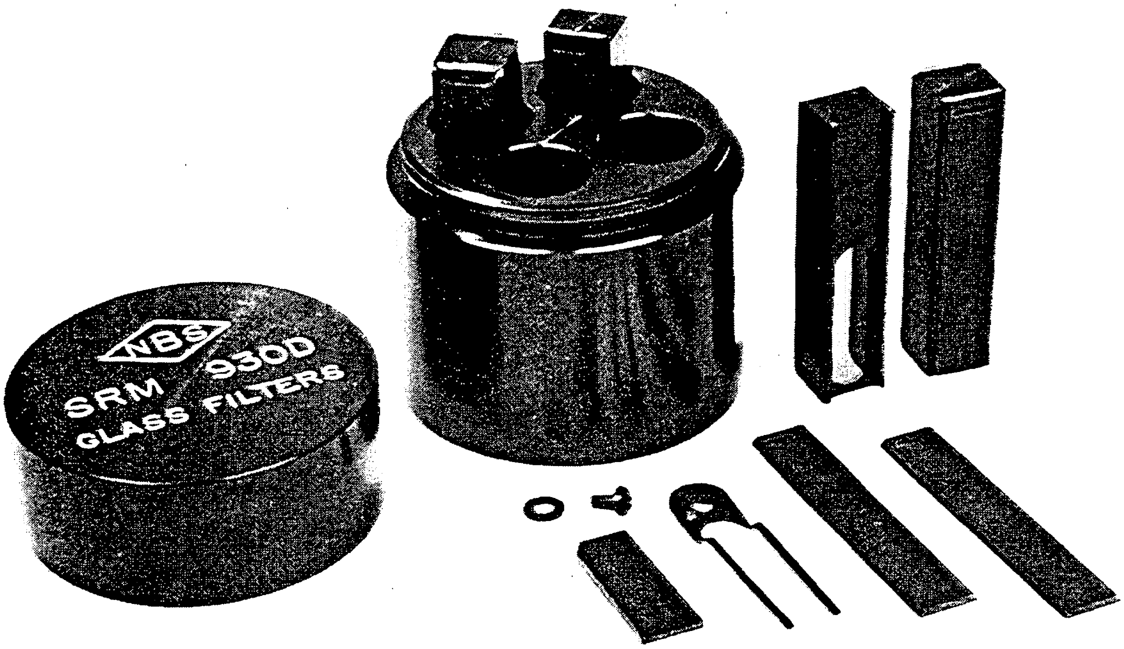

Figure 2. Illustration of SRM 930D, Glass Filters for Spectrophotometry, showing the black-anodized aluminum alloy container for storing three filters in their holders and an empty filter holder. One of the three glass filters, Schott NG4 and NG5, is shown with the retaining spring, nylon screw, washer, and the filter holder with the front and rear shutters.

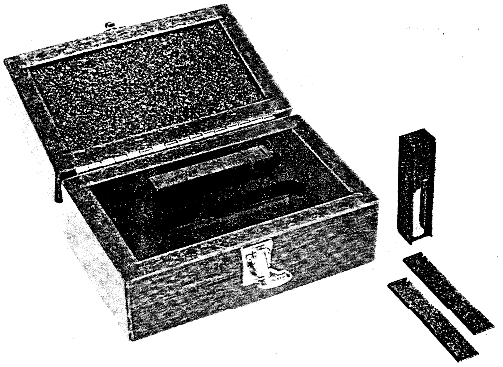

Figure 3. Illustration of SRM 2030, Glass Filter for Spectrophotometry, showing the glass filter, Schott NG4, in its metal holder with front and rear removable shutters. The wood-like plastic box is used to store the glass filter in its holder and an empty filter holder.

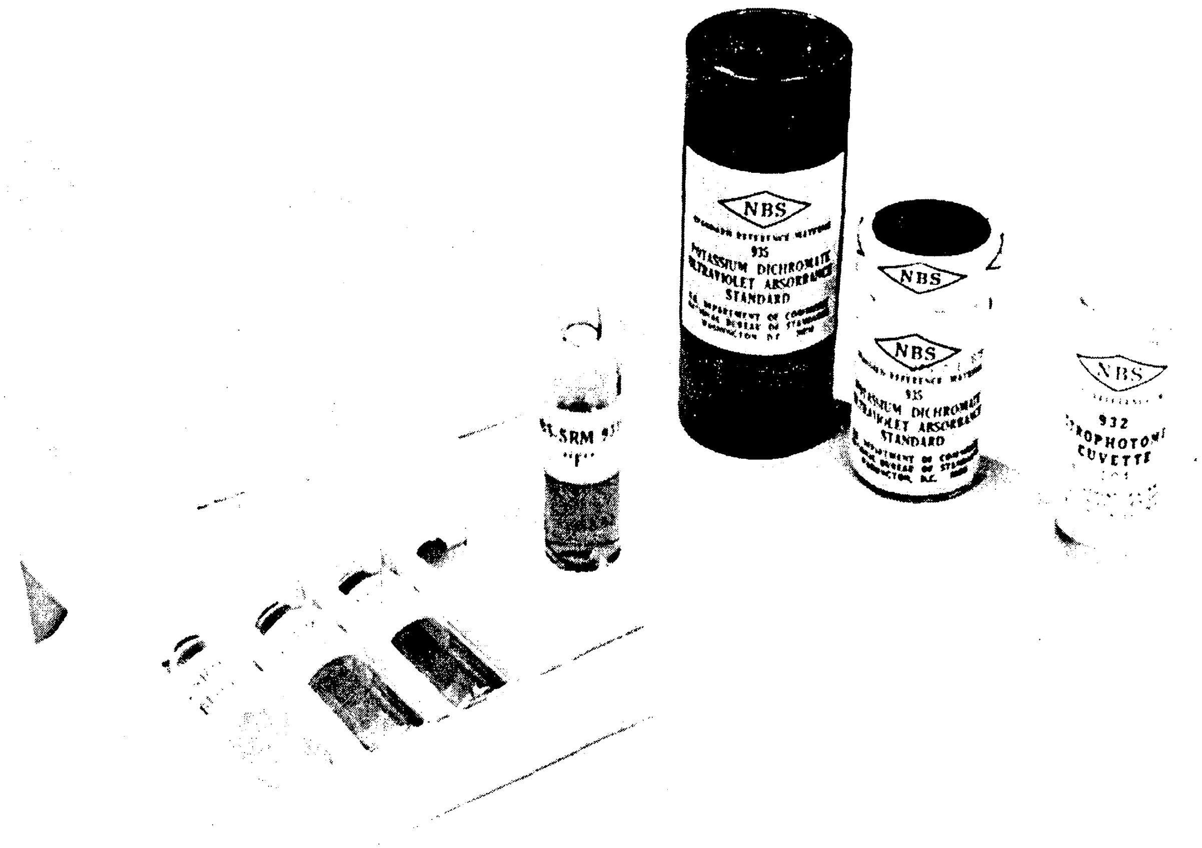

Figure 4. Illustration of SRM 931, Liquid Absorbance Standard for Ultraviolet and Visible Spectrometry SRM 935, Crystalline Potassium Dichromate for Use as an Ultraviolet Absorbance Standard; and SRM 932, Quartz Cuvette for Spectrophotometry.

Table 1. Standard Reference Materials for Spectrophotometry.

SRM Identification \ Description	Material	Composition	Certification	Use	Remarks
930 Glass filters for spectrophotometry	Solid filters made of Schott NG4 and NG5 optically neutral glass.	Three filters with nominal transmittances of 10, 20, 30%. Each filter is mounted in a black anodized aluminum holder provided with front and rear shutters. The filters are stored in a cylindrical aluminum container.	The transmittance of each filter is measured with the high-accuracy spectrophotometer at λ 440, 465, 546.1, 590, 635 nm, using spectral band passes of 2.2, 2.7, 6.5, 5.4, 6.0 nm respectively. The certification is made with an uncertainty of ±0.5%.	This SRM is intended as a reference source for the verification of the transmittance and absorbance scales of conventional spectrophotometers.	The use of this SRM is limited to the visible spectrum and requires narrow spectral bandpasses. For further details consult reference 4 and the Certificate included in the Appendix; see also Figure 2.
2030 Glass filter for transmittance measurements	Same as for SRM 930.	One glass filter with a nominal transmittance of 30% in a black anodized aluminum holder with shutters. The filter is stored in a wood-like plastic box.	The transmittance of the filter is certified as for SRM 930 but only for λ 465 nm and for a nominal transmittance of 30%.	This SRM is intenced as a reference source for one-point verification of the transmittance or absorbance scales of spectrophotometers.	Same as for SRM 930. SRM 2030 is particularly useful in connection with the chemical analysis of spices. A copy of the Certificate is included in the Appendix; see also Figure 3.
931 Liquid absorbance standards for ultraviolet and visible spectrophotometry	Liquid standard made of a solution of Co and Ni metals dissolved in a mixture of nitric-perchloric acids. The pH of the solution is about 1.	Three solutions and a blank are delivered in sealed ampoules and have nominal absorbances of 0.1 to 0.9.	The absorbance of each solution was measured at λ 302, 395, 512, 678 nm using spectral bandpasses of 1.0, 1.7, 2.0, 6.5 nm respectively. The certification is made with an uncertainty of about ±1.0%.	This SRM is primarily intended for the verification of the accuracy of transmittance or absorbance scales of spectrophotometers.	Requires the use of SRM 932 and of narrow spectral bandpasses. Provides only one certified value in the ultraviolet. For further details, consult reference 5 and the Certificate included in the Appendix; see also Figure 4.
932 Quartz cuvette for spectrophotometry	All-quartz cuvette made of non-fluorescent fused silica of optical quality.	Each cuvette is made entirely of fused silica and is provided with a Teflon stopper. The transparent windows are attached to the body of the cuvette by direct fusion. The cuvettes are stress-released by proper annealing. The cuvette is stored in a transparent plastic container.	The nominal inner pathlength is 10 mm and it is certified at 10 points along the height of the transparent windows with an uncertainty of ±0.0005 mm. The cuvettes are 12.5 mm square and 48 mm high.	To be used when accurate transmittance or absorbance measurements are made on liquid samples. Should be used in conjunction with SRM's 931, 935, 2032, and 2033.	For further details, consult reference 6 and the Certificate included in the Appendix; see also Figure 4.
935 Crystalline potassium dichromate for use as an ultraviolet absorbance standard	Crystalline potassium dichromate of established purity.	The crystalline material of reagent grade purity is offered in glass bottles provided with plastic screw caps.	The apparent specific absorbance is certified for 5 concentrations at λ 235, 257, 313, 345, 350 nm using spectral bandpasses of 1.2, 0.8, 0.8, 0.8, 0.8, nm respectively, using SRM 932.	This SRM is intended to be used as a reference standard for the verification of the accuracy and linearity of the absorbance scale of spectrophotometers.	Requires accurate preparation of solutions of potassium dichromate in 0.001N perchloric acid. Requires the use of SRM 932 and of narrow spectral bandpasses. Can be used only in the ultraviolet: for further details, consult reference 7 and the Certificate included in the Appendix; see also Figure 4.

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 transmittances of 10, 30, 90%. Each filter is made from two fused silica plates assembled by optical contact. The 90% filter is made by assembling two clear plates. The 10% and 30% 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 assembly is placed in a metal holder provided with shutters.	The transmittance of each filter is measured with the high-accuracy spectrophotometer at λ 250, 280, 340, 360, 400, 465, 500, 546.1, 590, 635 nm. The certification uncertainty is ±1.0% for the 10% filter and and ±0.5% for the 30% and 90% filters.	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 region.	SRM 2031 has a good optical neutrality and can be used to verify spectrophotometers with wide spectral bandpasses from about 200 to 800 nm (with possible extension to 3 μm). For further details consult this publication.
2032 Potassium iodide for use as a stray light standard	Crystalline potassium iodide of established purity.	These SRMs are in the final stage of certification, and should be available late 1979. An NBS Special Publication in the 260 series is being prepared by K. D. Mielenz, R. W. Burke, and R. Mavrodineanu. For further information on these materials contact K. D. Mielenz or R. W. Burke.			
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 holder provided with shutters.				
2034 Holmium oxide for use as a wavelength standard in spectrophotometry and fluorescence spectrometry.	Holmium oxide of established purity dissolved in perchloric acid.	Holmium oxide is offered in solutions in sealed 10 mm quartz cuvettes.	The wavelengths of maximum absorption of holmium oxide solutions in perchloric acid are determined for various spectral bandpasses at the nominal wavelengths: 279, 288, 338, 361, 386, 418, 453, 536, 637 nm.	This SRM is intended to be used as a reference standard for the verification of the accuracy of the wavelength scale of absorption and fluorescence spectrometers.	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. The use of solutions in conjunction with a diffusing screen (Teflon) placed at 45° in the 10 mm cuvette permits the use of SRM 2034 for the wavelength calibration of fluorescence spectrometers. The issuance of SRM 2034 is projected for the end of 1980.
2009, 2010, 2013, 2014 Didymium glass filters for calibrating the wavelength scale of spectrophotometers		These SRMs are certified in the Radiometric Physics Division, Center for Radiation Research of the National Measurement Laboratory. It is expected that these materials will be available late 1979. An NBS Special Publication in the 260 series is being prepared by W. A. Venable and K. L. Eckerle on this subject. The title is "Didymium Glass Filters for Calibrating the Wavelength Scale of Spectrophotometers". For further information on this material contact K. L. Eckerle.			

1.2 Conditions to be Satisfied by SRM's for Spectrophotometry

A material which can be used as a transmittance standard should satisfy the following major conditions:

- Be transparent over the entire spectral range of interest, usually between 200 nm and 800 nm;
- Have a transmittance independent of wavelength (optically neutral), hence be usable with spectrophotometers having wide spectral bandpasses;
- Be free of optical disturbances such as fluorescence, polarization, reflections;
- Have a transmittance independent of temperature;
- Be stable, homogeneous, and free of strain and scatter;
- Be a solid material with good mechanical stability for the size used (thickness, length, width);
- Be simple for use in conjunction with conventional spectrophotometers currently available in analytical laboratories;
- Be readily available at an acceptable cost.

From the numerous substances examined since 1969, which can be considered as acceptable material, the semi-transparent metal layers deposited by evaporation or sputtering on a fused silica substrate satisfied the conditions cited above.

Indeed, as can be seen from Figure 5, this material satisfies particularly well the conditions of optical transmittance and neutrality throughout the spectral range from 200 nm to 700 nm for which the standard was intended. Furthermore, an extension of this range, especially toward the long wavelengths, and within the transmittance limits of fused silica (about 190 nm to over 3000 nm) seems possible. However, at the time, the problem of protecting the exposed surface of the metal layer from the environmental conditions was a real limitation that could not be solved satisfactorily. The possibility that isochromatic stray light as well as multiple reflections, might be generated at a prohibitive level in the sample compartment of the spectrophotometer, due to reflections at the semi-transparent metal layer, were also considered as potentially disturbing factors.

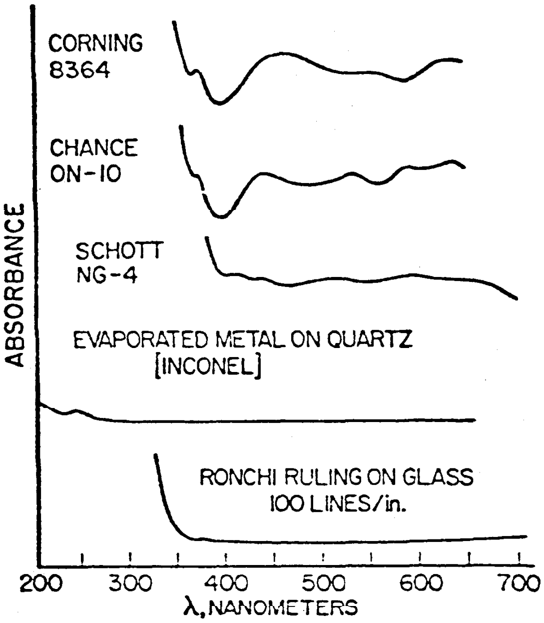

Figure 5. Spectral characteristics for five transparent materials from 200 nm to 700 nm.

Satisfactory solutions have been found, however, during the last several years to these limitations, and, as a result, a new material was developed and it is now being issued as SRM 2031, Metal-on-Quartz-Filters for Spectrophotometry.

The object of this work is to describe in some detail the properties, preparation, and certification of this new standard reference material.

2. Introduction

2.1 Initial Studies

The first studies on the optical characteristics of evaporated metals-on-fused silica substrates were initiated in 1969 [8], when a series of filters were prepared by the Optical Shop of NBS. A number of non-fluorescent fused silica plates of optical quality 10 mm x 25 mm and 1 mm thick were cut and polished to a flatness of two fringes (mercury green, λ546.07 nm) and a parallelism of ±0.02 mm. An inconel alloy was evaporated on the surface to produce nominal transmittances of 25, 50, and 75 percent. The surface carrying the semi-transparent evaporated metal was coated with a thin layer of optical cement Sylgard, made by Dow Chemicals, which has good transmittance to ultraviolet radiation to about λ230 nm. A clear plate of the same material was used to cover and protect the metal layer. Each filter was then marked at one corner to allow positioning of the filter in a black-anodized aluminum alloy holder of conventional size (12.5 mm square x 57 mm) fitting the cuvette holder in the sample compartment of conventional spectrophotometers.

2.2 Characteristics of the Metal-on-Fused Silica Filters

The transmittance characteristics of these filters from λ200 nm to 800 nm were determined with a Cary 14 recording spectrophotometer. Figure 6 illustrates the transmittance of a clear fused silica plate, followed by that of an assembly made of two clear plates assembled with the optical cement, and finally, that of the assembly of a metal-coated plate and a clear plate, cemented together with the Sylgard resin.

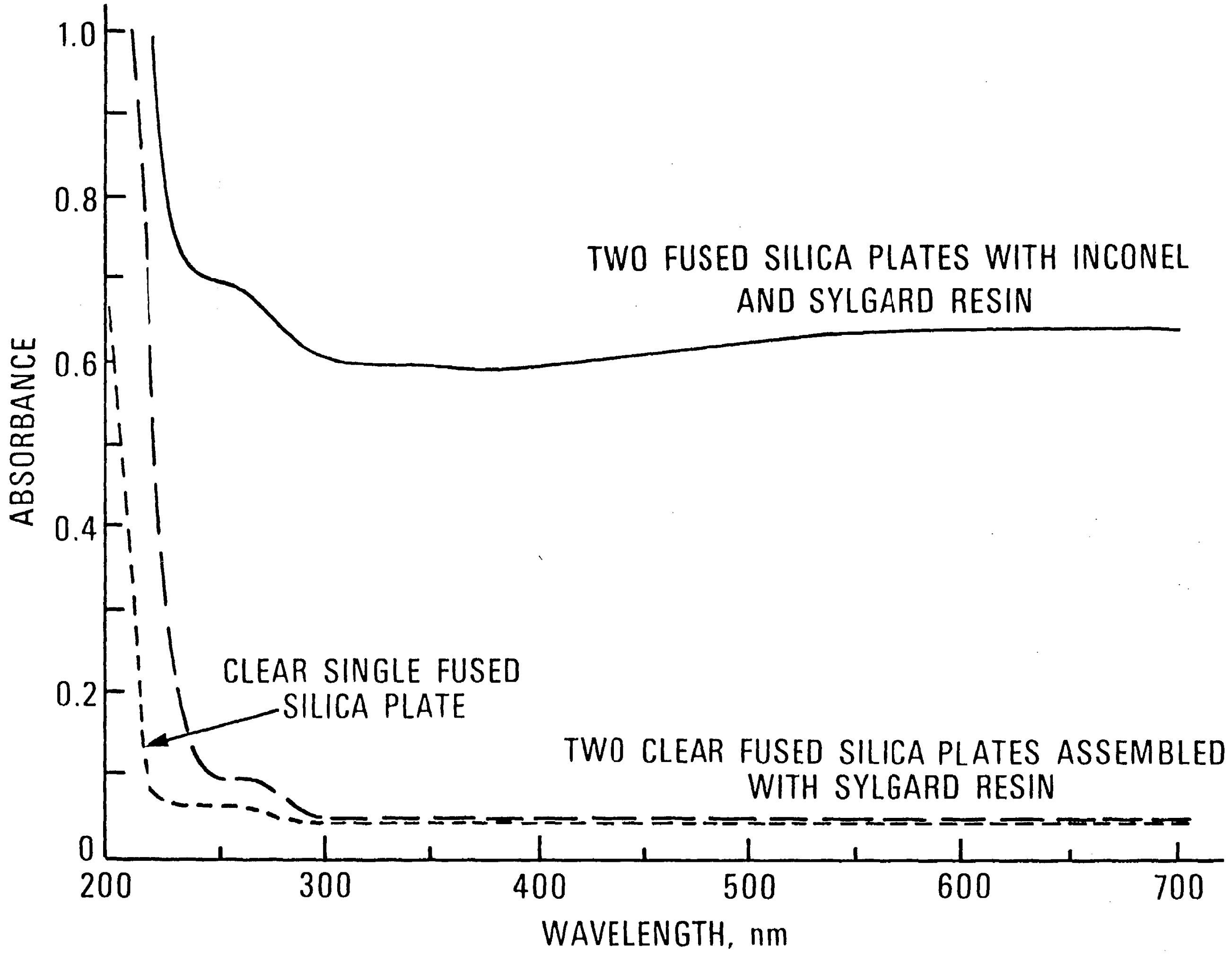

Figure 6. Transmittance of a clear fused silica plate, of two clear fused silica plates assembled with the Sylgard resin, and two fused silica plates coated with a semi-transparent layer of evaporated inconel metal assembled with Sylgard resin.

From these data, it can be seen that the assembled metal-on-fused silica filter exhibits a good transmittance throughout the spectral range from λ240 nm in the ultraviolet to λ800 nm in the visible where the recording was stopped. Furthermore, the dependence of transmittance on wavelength is small over this entire and wide spectral range. Hence, this material satisfies the two major conditions of spectral range coverage and optical neutrality.

The stability of this type of material to radiation was then studied by exposing the metal-on-fused silica filter to an accelerated test in which the radiation had the same spectral distribution as the fluorescent lighting of the laboratory, except that it was 1000 times more intense. The filter was exposed for an equivalent of 36,000 hours of continuous normal laboratory exposure. This test was performed in the Center for Building Technology at NBS. The transmittance of the filter was measured before and after the exposure, using a Cary 16 spectrophotometer. The results are given in Table 2.

Table 2. Stability of an evaporated metal-on-fused silica filter exposed to radiations.

	Transmittance, percent			
Wavelength nm Exposure	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 differences in transmittance observed at λ380, 500, 650 nm, as a result of this severe test, are small, and in the range of the uncertainty of the instrumental measurements. The larger difference observed at λ250 nm is probably due to some radiation instability of the organic resin which absorbs the ultraviolet radiations from this wavelength down.

Due to the severity of the radiation test and to the magnitude of the transmittance differences observed, it was decided to disregard this instability and to resume the study of this material by submitting these filters to a comparative test.

2.3 Comparison of Transmittance Measurements at the National Bureau of Standards and the National Physical Laboratory

Several sets of these filters were made and calibrated at three selected wavelengths: 450 nm, 550 nm, and 650 nm, using the high-accuracy spectrophotometer. The same filters were forwarded to the National Physical Laboratory (NPL), Teddington, Middlesex, U. K. where their transmittance was determined by F. J. J. Clarke using his high-accuracy spectrophotometer. The results are given in Table 3.

The agreement between the measurements performed at NBS and NPL on the nominal 25 and 72 percent filters is good, with the NBS data showing a small negative bias. The average difference of -0.21 percent is close to that found in a similar comparison performed on glass filters (ref. 2, p. 420, Table 9).

The values obtained for the nominal 50 percent transmittance filter indicate, however, larger negative differences. F. J. J. Clarke observed that this particular filter had a flaw in the form of a crack which was at times visible and other times invisible. The larger differences found in the measurements of this filter were attributed to this flaw.

Table 3. *Comparison between the percent transmittance (% T) measured on three metal-on-fused silica filters at NBS and NPL.*

Laboratory / Wavelength nm	NBS, % T	NPL, % T	NBS-NPL, % Difference
450.0	24.87	24.93	-0.24
550.0	23.80	23.86	-0.25
650.0	23.38	23.46	-0.34
450.0	49.34	49.56	-0.45
550.0	47.60	47.81	-0.44
650.0	46.85	47.14	-0.62
450.0	72.18	72.30	-0.17
550.0	72.08	72.20	-0.17
650.0	72.27	72.33	-0.08

This observation prevented the selection of this material as an SRM for spectrophotometry. However, since the evaporated metal-on-fused silica filters possess unique optical qualities, it was decided to continue the investigation of their properties and try to find ways to remedy these limitations.

3. Further Studies

Before discussing the results obtained from further studies concerning the transmittance characteristics of the evaporated metal-on-fused silica filters, it was considered appropriate to describe briefly some of the new instrumental features of the high-accuracy spectrophotometer used to perform these measurements.

3.1 The High-Accuracy Spectrophotometer at the National Bureau of Standards, Center for Analytical Chemistry

Unless otherwise specified, all transmittance measurements discussed in this work were performed with this high-accuracy spectrophotometer that, as mentioned earlier, was designed and constructed in the Center for Analytical Chemistry. A detailed description of this instrument and of its characteristics is given in Reference 2, which is included in the Appendix as a convenience to the reader. During the last few years certain improvements have been made to the initial design. A description will be given here of these changes.

Figure 7 illustrates the optical disposition of the radiation sources used for measurements in the ultraviolet and visible spectral regions. A 1.2 m lathe-bed type optical bench is positioned in front of the 1 m Czerny-Turner grating spectrometer, which is provided with a predisperser. The position of the bench is adjustable through four screws, and is maintained in the proper position by the aluminum angle supports that can be tightened to the top of the vibration isolation table provided with tapped holes. On the optical bench are placed, from the rear to the front: A low-power laser used for alignment and for verifying its stability; a deuterium discharge lamp which is used when transmittance measurements are performed in the spectral range from about λ190 nm to λ400 nm; the power supply for the deuterium lamp; a circular front-face mirror; a quartz circular neutral wedge with its quartz lens; and a rectangular front-face mirror, which reflects the image of the

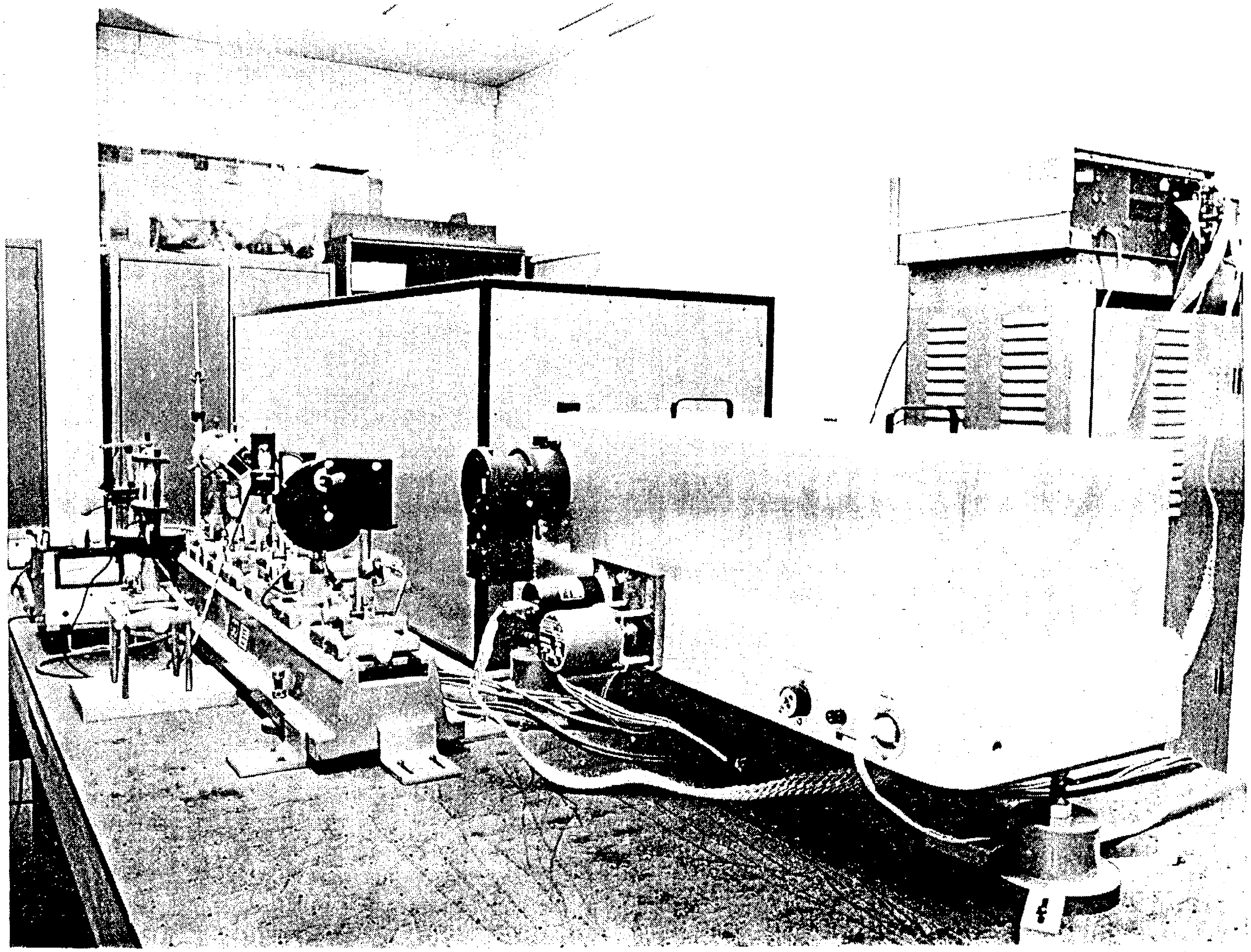

Figure 7. Disposition of the radiation sources used with the high-accuracy spectrophotometer. For further explanation, see text.

light sources on the entrance slit of the predisperser-spectrometer assembly. Left of the optical bench is the tungsten incandescent lamp used when transmittance measurements are performed in the near-ultraviolet and visible spectral region, from about λ360 nm to λ800 nm. Every optical element can be rotated and adjusted in the x-y-z axes. The circular mirror, in front of the deuterium lamp can be moved "in" or "out" of the optical path through a slide moved across the optical axis by a pneumatically operated piston. When the mirror is in the "out" position the radiation from the deuterium arc lamp enters the spectrometer to permit measurements in the ultraviolet. When the mirror is in the "in" position, the radiation from the tungsten incandescent lamp is deflected into the spectrometer for measurements in the visible spectral region. The circular and rectangular mirrors are attached to their main holders through a spring-loaded three-point supporting plate that is used to adjust both mirrors to the desired tilting. The position of the circular neutral wedge can be selected by rotation to provide the desired radiation intensity through an electric slow rotating reversible motor. The wavelength scanning shaft of the spectrometer is provided with a stepping motor and a shaft encoder. This system is interfaced with a microcomputer. The microcomputer can be seen in Figure 8 atop the metal cabinet which contains in addition the power supply of the photomultiplier; the null meter indicator for the potentiometer (partially visible at the right); the amplifier for the photomultiplier; the digital voltmeter, and the computer operation panel. The teletypewriter is visible in front of the cabinet.

A further modification to the circular sample-carrier platform provides for 15 filter or cuvette holders for blanks and samples, instead of the initial seven holders. This modification was made to permit an empty filter holder to be placed in the eight reference beam positions of the spectrophotometer, so that approximately equivalent conditions of stray radiations are achieved for both beams. When measurements are made in the ultraviolet, the usual integrating sphere is replaced by a highly efficient averaging sphere provided with a fluorescent wavelength converter [9].

The spectrophotometer data acquisition and presentation are automated through interface with a microcomputer. The computer system consists of: an Altair 8800A computer with 20K of RAM memory, a Dual North Star Computer floppy disc drive, and an ASR 33 Teletype. The computer is programmed in BASIC with some assembly language subroutines.

The computer can control the following experimental variables:

1. The spectrophotometer wavelength drive position,
2. Position of an incremental sample changer,
3. Light source, either visible or U.V., and
4. A neutral wedge light attenuator.

The computer can sense the following experimental variables:

1. The spectrophotometer wavelength drive position,
2. The position of the sample changer, and
3. The amount of light passing through the spectrometer.

The software written in BASIC performs the following sequence of events to control the experiment:

1. Sets measurement wavelength,
2. Takes measurements of a blank and adjusts the neutral wedge in the light beam to produce a voltmeter reading of 2.000 volts,
3. Advances sample changer to next position and acquires the data for a sample,

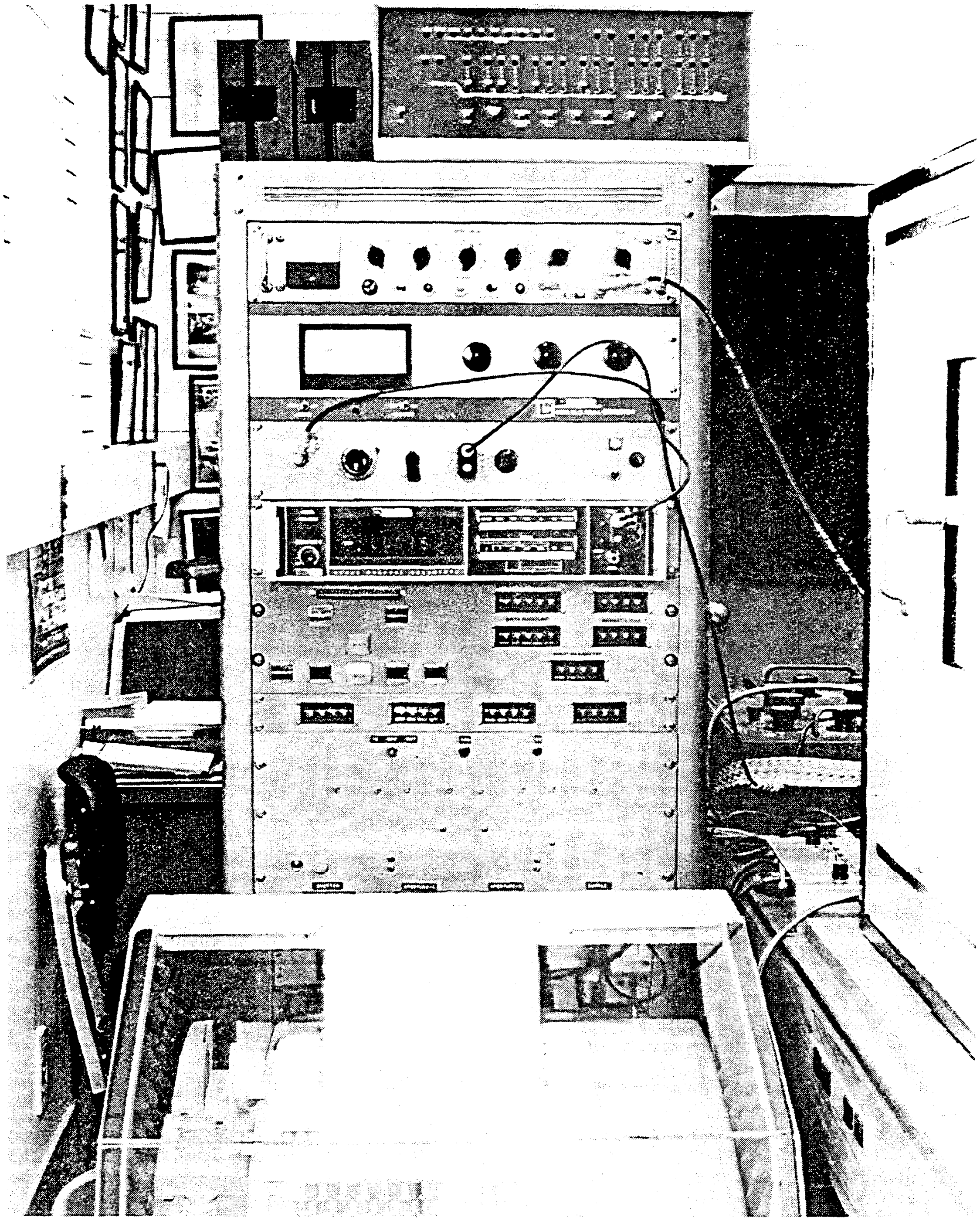

Figure 8. Microcomputer and accessories. For further explanation, see text.

4. Reads blanks and samples alternately, and

5. Changes measurement wavelength and repeats steps (2), (3), and (4).

If the wavelength needed to acquire data extends into the U.V., then the computer can change from the visible to the U.V. light source.

Initial data reduction consists of taking the average and standard deviation of 50 individual measurements of both the sample (I) and reference beam (I_0) intensities. This is followed by computing the ratio of I/I_0, followed by the correction for linearity. Finally, the transmittance density ($-\log_{10}(I/I_0)$) is computed and displayed. A tabular form is provided for final data presentation.

A microcomputer system was selected because of its low cost and its suitability to perform a rather simple function. The programming of the entire system was made by J. F. Barkley and the interfacing of the microcomputer with the high-accuracy spectrophotometer was performed by F. C. Ruegg, both of the Center for Analytical Chemistry at NBS [11].

The high-accuracy spectrophotometer measures the ratio of two radiation intensities: that attenuated by the sample (I) to that passing through air or through a blank sample ($I_{o\ air}$ or $I_{o\ blank}$). In the first case, the measurements produce a transmittance $T = \frac{I}{I_{o\ air}}$ which includes the reflection losses occurring at the surface of the transparent material. The measured transmittance, T, has a corresponding calculated transmittance density, defined as $-\log_{10} T$.

When the measurements are performed against a blank sample in the reference beam, the reflection losses are eliminated, and the parameter measured under these circumstances is the internal transmittance $T_i = \frac{I}{I_{o\ blank}}$. From this parameter, the absorbance, A, is calculated by the expression $A = -\log_{10} T_i$.

Since transmittance is the ratio of two radiant flux intensities, true transmittance values will be produced only when this ratio is measured accurately. These measurements are usually performed by using photodetectors capable of generating signals proportional to the two fluxes. Transmittances are measured accurately when there is a linear relation between the two radiant fluxes and the resulting photoelectric signals. Hence, linear photoelectric measurements result in accurate transmittance values.

The linearity of the photodetector used in the high-accuracy spectrophotometer is established by the radiation addition principle used in conjunction with a double aperture system described in detail in reference 2. This is similar to the double aperture unit developed and used at the National Physical Laboratory for many years to establish the accuracy of their reference spectrophotometers [17]. A critical study of the double aperture device was made recently at NBS by K. D. Mielenz and K. L. Eckerle and is published in reference 6 of the Certificate for SRM 2031 in paragraph 4.6.

An intrinsic property of the evaporated metal-on-fused silica filters is that of attenuating the incident radiation by reflecting part of it, rather than absorbing. As mentioned earlier, the consequence of this property is that this type of filter is susceptible to the generation of isochromatic stray radiations and multiple reflections in the sample compartment of some conventional spectrophotometers, and in particular in those instruments with lens optics. It could also have a position dependence transmittance, and could be sensitive to polarized radiations.

A number of tests were designed to determine the magnitude of these characteristics.

3.2 Description of the Metal-on-Fused Silica Filters Made at the National Bureau of Standards

Several sets of evaporated inconel-on-fused silica were prepared in the NBS Optical Shop, using a single non-protected plate as a support for the semi-transparent metal layer. Each set was composed from three filters and one blank, using non-fluorescent fused silica of optical quality as a substrate on which semi-transparent layers of inconel were deposited by evaporation. Inconel was selected since it has a relatively good optical neutrality in the spectral range from 250 nm to 700 nm. All fused silica filters were ground and polished at the same time and on the same polishing wheel to a parallelism of 0.02 mm and a flatness of less than two fringes (mercury green, λ546.1 nm). The dimensions of these 2 mm thick filters are given in Figure 9 and the nominal transmittances are 1, 20, 30, and 90 percent (clear fused silica plate).

Each filter was mounted in a special black anodized (flat) aluminum alloy holder provided with front and rear sliding shutters as illustrated in Figures 10, 11, 12, and 13. These holders were made in the NBS Instrument Shops and were designed to provide two functions: one to protect the filters from "fingerprinting" and exposure to environmental contamination; and the other to detect and measure the amount of isochromatic stray radiation that could be generated in the sample compartment of the spectrophotometer due to reflections produced at the surface of the semi-transparent metal layer of the filter.

3.3 Measurement of Isochromatic Stray Light

Isochromatic stray light may be assessed as follows: A background signal may be measured when the instrument shutter at the photomultiplier is closed; this represents the dark current of the instrument. Another slightly higher background signal may be detected with the photomultiplier open and with the filter holder placed in the sample compartment with both sliding shutters closed to intercept the incident radiation beam. This signal might be produced by reflections at the black (flat) surface of the shutters. Both of these signals should be very small. A third signal may be detected when the front sliding shutter at the filter holder is removed and the rear sliding shutter is closed. If, under these circumstances, a signal is detected, it is very likely due to the isochromatic stray radiation produced in the sample compartment of the spectrophotometer by reflections at the semi-transparent mirror-like surface of the evaporated metal of the filter. This should also be of low magnitude.

The transmittance of the filter is measured when both sliding shutters of the filter holder are removed.

3.4 Multiple Reflections

The problem of multiple reflections, which may be produced when the filter is inserted in the sample compartment of spectrophotometers, and particularly by those instruments which are equipped with lens optics, was discussed in a previous publication [12]. This phenomenon constitutes a source of systematic bias in transmittance measurements which can be removed by applying a numerical correction obtained from measurements on tilted samples in polarized light. This parameter was determined for the high-accuracy spectrophotometer used in this work and is of the order of one or two 10^{-4} transmittance units, independent of polarization, but slightly dependent of wavelength. It is also, for a given material, instrument dependent. For the evaporated metal-on-fused silica filter, having a transmittance of 0.4 at 474 nm, the value is about -1.4×10^{-3} transmittance difference. This was used to correct the measurement.

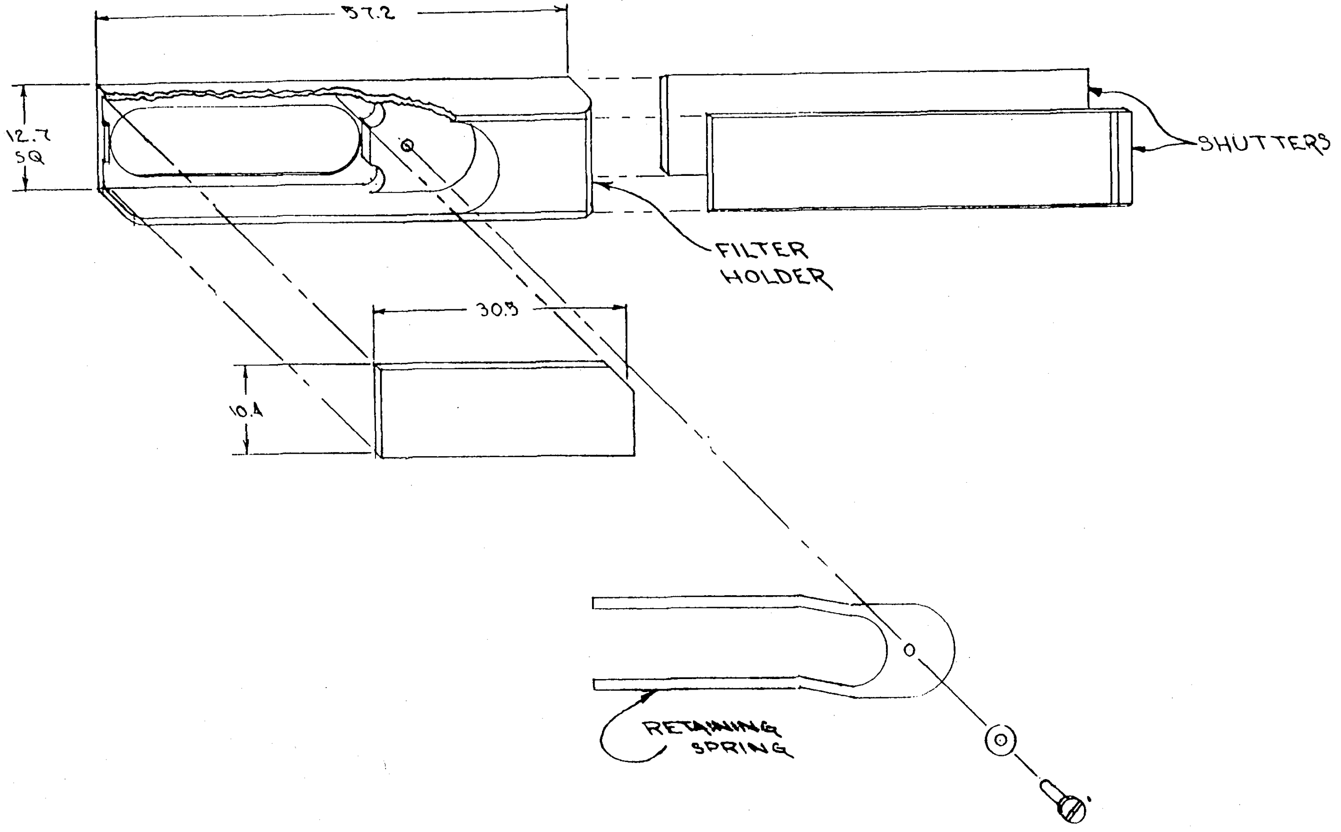

Figure 9. Aluminum alloy holder for the evaporated metal-on-fused silica filters. The retaining spring and the front and rear shutters are illustrated. The same holders were used with the Schott NG4 and 5 glass filters. Dimensions are in mm.

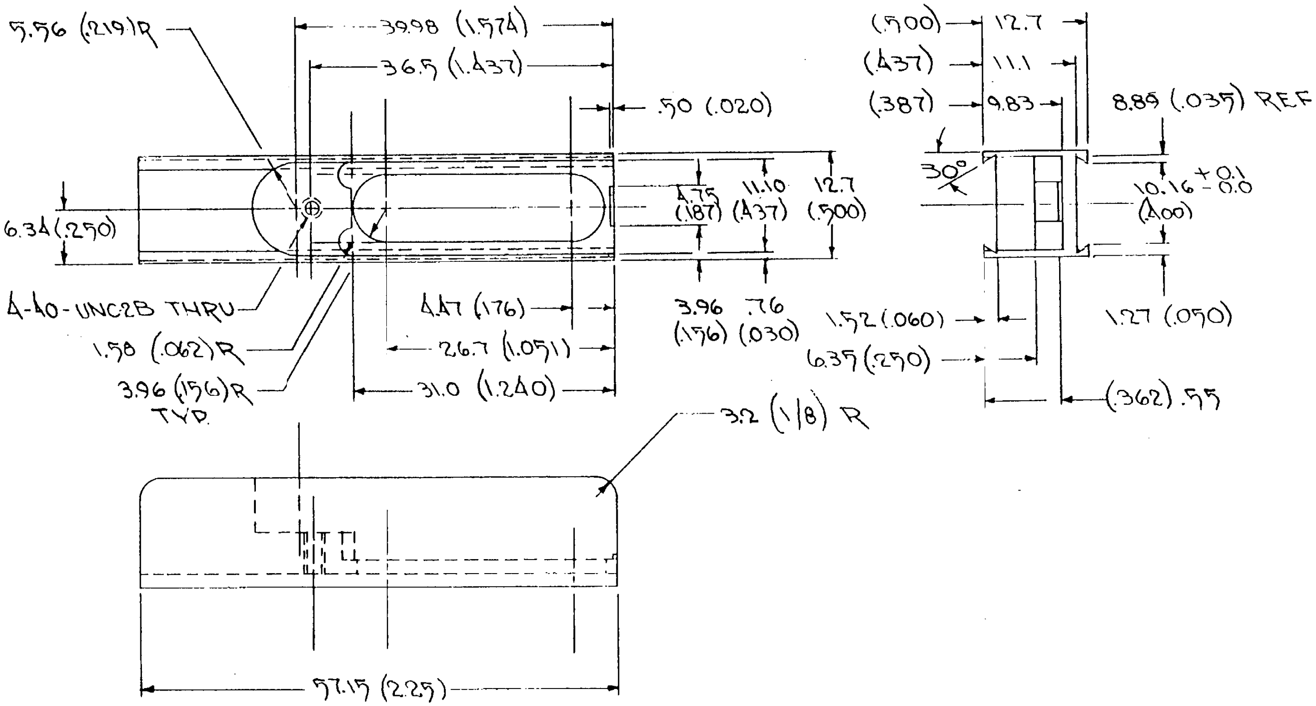

Figure 10. Details of the black anodized aluminum alloy 2024 filter holder body. Dimensions in parentheses are in inches. Dimensions not in parentheses are in mm. Tolerance ±0.1 mm.

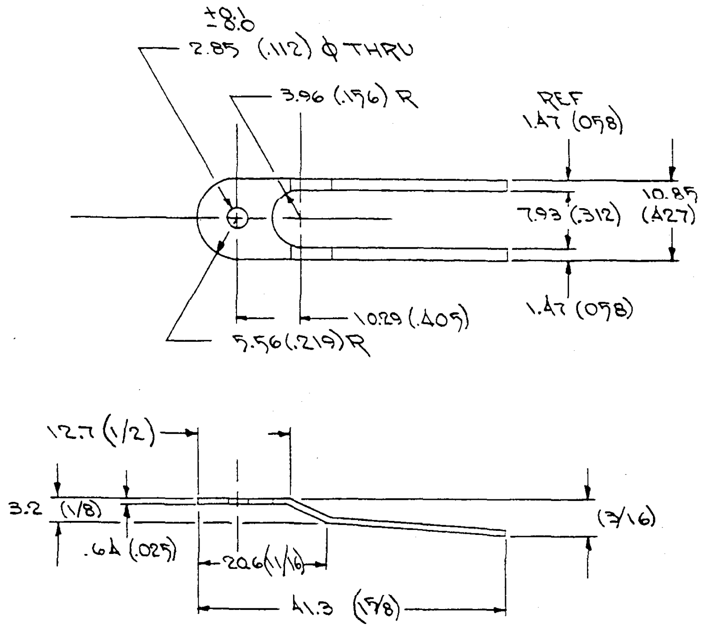

Figure 11. Details of the retaining spring used with the unit from Figure 10. Material: phosphor-bronze or beryllium-copper. Finish: black oxide. Tolerance: ±0.1 mm. Dimensions in parentheses are in inches, all others are in mm.

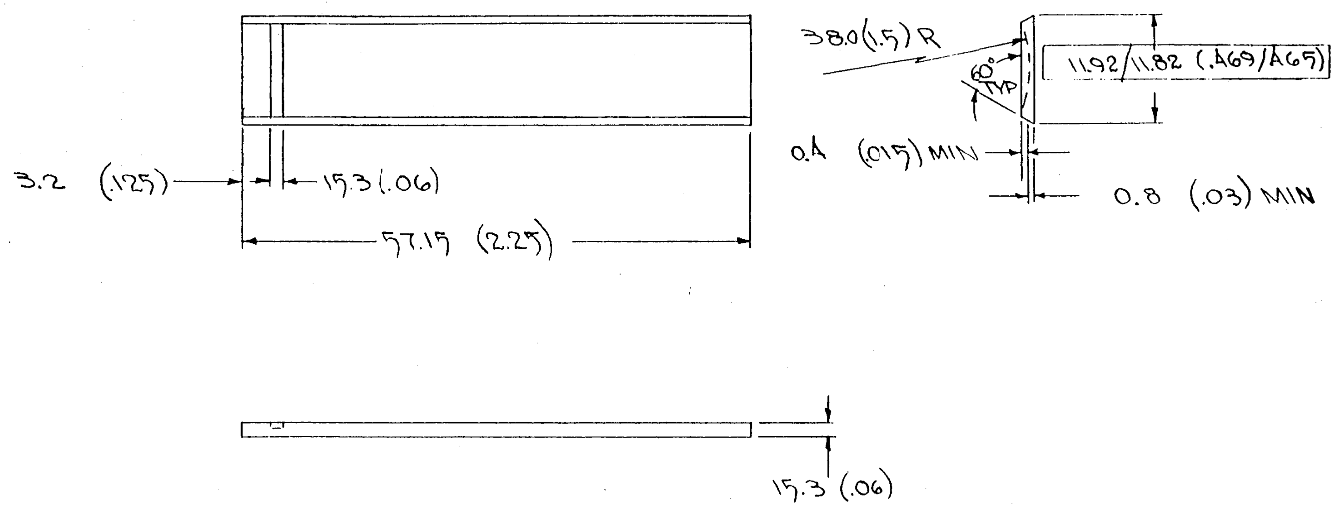

Figure 12. Details of the front and rear shutters used with the unit from figure 10. Material: black Delrin. Finish: flat. Two pieces for every filter holder. Dimensions in parentheses are in inches, all others are in mm. Tolerance: ±0.1 mm except on 38.0 (1.5) R.

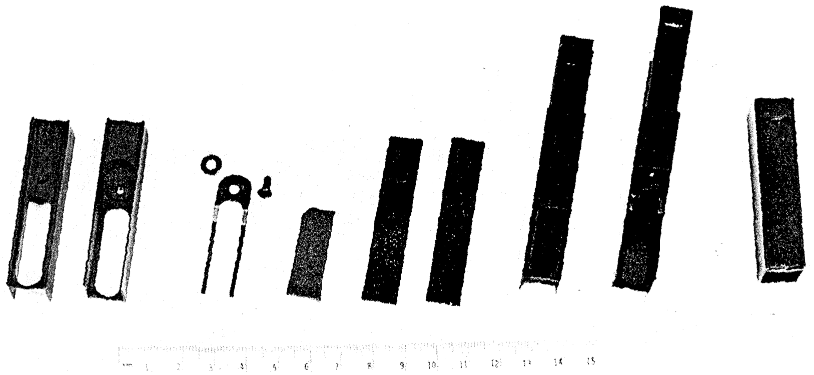

Figure 13. Filter holder with shutters. *From left to right:* front and rear view of the holder body provided with dove-tail grooves; retaining spring with nylon screw and washer; filter; two shutters; front view of the filter holder with front shutter; rear view of the filter with rear shutter; filter holder with both shutters closed. The filter illustrated in this figure is a glass Schott NG4 unit. The metal-on-fused silica filters are not cut-off at the corner.

3.5 Influence of Positioning of the Filters on Transmittances

The transmittance error resulting from positioning the inconel-on-fused silica filter at various angles to the incident radiation beam, was measured by placing the filter 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 (see Ref. 2, Figure 2). 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 4 presents the comparative results for transmittance measurements made at λ590 nm on an inconel-on-fused silica filter and a Schott NG4 neutral glass filter 2 mm thick having a nominal transmittance of 30 percent, for normal incidence and for angles of 3°, 6°, and 9°.

Table 4. Percent transmittance (% T) measured on a Schott neutral glass filter 2 mm thick, and an inconel-on-fused silica filter 2 mm thick at 590 nm, for normal incidence and for angles of 3°, 6°, and 9°.

% T

Filter / Angle	Schott NG4 Glass	Inconel-on-fused silica	
		Front	Back
0°	28.13	29.91	29.87
3°	28.10	29.98	29.87
6°	28.03	29.84	29.82
9°	27.98	29.92	29.90

The inconel filter transmittance was respectively measured with both the metal coated plate (front) facing the incident radiation beam and with the clear fused silica plate (back) facing the beam. 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, the results from Table 4 are valid only for the high-accuracy spectrophotometer used to perform these measurements.

3.6 Intercomparison of Transmittance Measurements at the National Bureau of Standards

The transmittance characteristics of these filters were further studied by performing intercomparison measurements on the high-accuracy spectrophotometer in the Center for Analytical Chemistry (CAC) and on a similar instrument available at NBS in the Center for Radiation Research (CRR) [13,14,15]. The latter measurements were performed by K. L. Eckerle. Table 5 contains the results of the transmittance measurements and includes the differences obtained at the Center for Radiation Research by measuring the transmittances in polarized radiations having the electric vector both horizontal and vertical.

Table 5. Transmittance of some inconel-on-fused *silica filters obtained* using the Center for Analytical Chemistry (CAC) and the Center for Radiation Research (CRR) high-accuracy spectrophotometers. The difference, Δ(CRR), is the difference in transmittance measured by illuminating the filters with polarized radiation having the electric vector in either the horizontal or vertical directions.

	Transmittance									
Wavelength nm / Instrument	250	300	340	400	440	465	500	546.1	590	635
	Nominal 30% Filter									
CAC 9/75	0.2867	0.2989	0.3017	0.2992	0.2963	0.2949	0.2938	0.2936	0.2940	0.2948
CRR 8/76	.2879	.2997	.3025	.3001	.2974	.2960	.2948	.2946	.2950	.2958
CAC 10/76	.2880	.2997	.3026	.3000	.2973	.2958	.2947	.2946	.2950	.2958
Δ(CRR)	0.00013	-0.00002	0.00002	0.00000	0.00005	0.00004	0.00001	0.00010	0.00008	0.00002
	Nominal 20% Filter									
CAC 9/75	0.2127	0.2115	0.2023	0.1884	0.1824	0.1800	0.1781	0.1774	0.1778	0.1787
CRR 8/76	.2129	.2117	.2023	.1885	.1825	.1802	.1782	.1776	.1779	.1788
CAC 10/76	.2131	.2118	.2023	.1885	.1825	.1802	.1784	.1778	.1781	.1790
Δ(CRR)	0.00004	0.00011	0.00002	0.00001	0.00008	0.00002	0.00004	0.00005	0.00007	-0.00002
	Nominal 90% Filter									
CAC 9/75	0.9127	0.9231	0.9265	0.9291	0.9300	0.9305	0.9312	0.9315	0.9320	0.9324
CRR 8/76	.9124	.9225	.9263	.9293	.9303	.9307	.9312	.9318	.9322	.9325
CAC 10/76	.9124	.9224	.9262	.9287	.9298	.9304	.9308	.9314	.9320	.9324
Δ(CRR)	-0.00016	0.00014	0.00002	-0.00016	0.00006	0.00009	0.00014	0.00011	0.00001	-0.00028

The transmittances were measured in the Center for Analytical Chemistry in September 1975 and in October 1976. Those in the Center for Radiation Research were performed in August 1976.

Several observations can be made after examining the data from this table.

- The inconel-on-fused silica filters exhibit good stability over a period of one year.
- Good agreement was obtained between the two high-accuracy spectrophotometers available at NBS, although one instrument uses achromatic lens optics (CAC) while the other uses off-axis mirrors.
- The transmittance values are practically unaffected when measurements are made in polarized radiations with the electric vector horizontal and vertical.

Comparable results were obtained in a similar test performed on three Schott NG4 neutral glasses as seen from Table 6.

Table 6. Transmittance of a set of SRM 930 at two wavelengths obtained using the Center for Analytical Chemistry (CAC) and the Center for Radiation Research (CRR) high-accuracy spectrophotometers. The difference, Δ(CRR), is the difference in transmittance measured by illuminating the filters with polarized radiation having the electric vector in either the horizontal or vertical directions.

Transmittance

	Nominal 30% Filter		Nominal 20% Filter		Nominal 10% Filter	
Wavelength nm / Instrument	465	546	465	546.1	465	546.1
CAC	0.3427	0.3280	0.1980	0.1840	0.1120	0.1014
CRR	0.3430	0.3284	0.1983	0.1844	0.1121	0.1015
Δ(CRR)	-0.00002	-0.00007	-0.00008	-0.00005	-0.00001	-0.00002

3.7 Intercomparison of Transmittance Measurements Performed at the National Bureau of Standards and the Michelson Laboratory of the Naval Weapons Center

The intercomparison study was extended to include the special optical measuring capabilities available at the Michelson Laboratory, Physical Optics Branch of the Naval Weapons Center (NWC), China Lake, California. The transmittance measurements were performed by Harold Bennett and Jean M. Bennett.

Table 7 contains the results of these measurements performed on four inconel-on-fused silica filters having nominal transmittances of 1, 20, 30, and 90 percent.

The agreement between these measurements is excellent, even for the one percent filter.

Table 7. Comparative measurements of transmittance on inconel-on-fused silica filters in the ultraviolet and visible from 250 nm to 635 nm at NBS and at Naval Weapons Center (NWC)

Transmittance, Percent

Filter No.	Lab.	250	300	340	400	440	465	500	546.1	590	635
45	NBS	1.492	1.844	1.899	1.973	2.083	2.171	2.318	2.540	2.750	2.956
	NWC	1.501	1.837	1.884	1.953	2.070	2.158	2.317	2.552	2.755	2.958
46	NBS	21.49	21.39	20.46	19.05	18.45	18.20	18.01	17.94	17.98	18.07
	NWC	21.50	21.37	20.39	19.04	18.38	18.19	18.06	17.99	17.92[a]	18.10
47	NBS	28.73	29.96	30.24	29.99	29.70	29.56	29.44	29.41	29.45	29.55
	NWC	28.80	29.89	30.23	29.95	29.68	29.55	29.45	29.42	29.43	29.48
48	NBS	91.25	92.28	92.64	92.91	93.00	93.04	93.10	93.15	93.19	93.22
	NWC	91.21	92.22	92.59	92.90	92.98	93.01	93.14	93.19	93.21	93.24

[a] Value corrected as indicated in J. M. Bennett communication.

3.8 Scatter, Homogeneity, and Polarization of Inconel-on-Fused Silica Filters and Schott NG4 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 were: freedom of scatter and homogeneity. The presence of pinholes and dust on the metal layer of the inconel-on-fused silica filters could result in scatter and produce apparent inhomogeneity and reduce the usefulness of this material. Hence, a set of three inconel-on-fused silica filters, identified as No. 20 (1, 2, and 3) with nominal transmittances of 10, 30, and 90 percent were subjected to measurements to assess these parameters. They were compared with a set of glass filters subjected to the same measurements.

Scatter and homogeneity measurements in polarized radiation were performed by K. L. Eckerle in the Center for Radiation Research at NBS using the instrument described in reference 15. All measurements were performed at λ546.1 nm and are given in Table 8. 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 λ546.1 nm. Their respective standard errors are $\Delta T_R(0°)$, $\Delta T_R(90°)$, and $\Delta T_R(\mathrm{AVE})$. 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 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. The transmittance measurements to assess the uniformity of the filters were made at a constant angle of 0.0045 steradians.

Table 8. Measurement of scatter, homogeneity, and polarization on three inconel-on-fused silica filters.

(x, y)	Ω	T(0°)	ΔT_R(0°)	T(90°)	ΔT_R(90°)	T(AVE)	ΔT_R(AVE)
			#20 Filter 1				
(+1,0)	0.0045	0.10807	0.000018	--	--	--	--
(-1,0)	0.0045	0.10798	0.000009	--	--	--	--
(0,0)	0.0045	0.10805	0.000013	0.10841	0.000020	0.10823	0.000012
(0,0)	0.0012	0.10801	0.000027	0.10840	0.000020	0.10821	0.000017
(0,0)	0.014	0.10799	0.000010	0.10831	0.000013	0.10815	0.000008
			#20 Filter 2				
(+1,0)	0.0045	0.32089	0.000035	--	--	--	--
(-1,0)	0.0045	0.32050	0.000037	--	--	--	--
(0,0)	0.0045	0.32066	0.000046	0.32092	0.000030	0.32081	0.000027
(0,0)	0.0012	0.32069	0.000039	0.32079	0.000045	0.32073	0.000030
(0,0)	0.0014	0.32045	0.000047	0.32050	0.000057	0.32047	0.000037
			#20 Filter 3				
(+1,0)	0.0045	0.93139	0.000118	--	--	--	--
(-1,0)	0.0045	0.93160	0.000096	--	--	--	--
(0,0)	0.0045	0.93131	0.000067	0.93125	0.000064	0.93128	0.000046
(0,0)	0.0012	0.93107	0.000122	0.93095	0.000039	0.93101	0.000064
(0,0)	0.014	0.93089	0.000041	0.93076	0.000080	0.93083	0.000045

From these data, it can be concluded that within the experimental measuring conditions there is no significant change of transmittance caused by scatter. The material has a good homogeneity, and no significant polarization effect exists. Identical measurements performed on a set of three Schott NG4 neutral glass filters serial number 537 (1, 2, and 3) have produced similar results, as shown in the data in Table 9.

Table 9. Measurement of scatter, homogeneity, and polarization on three Schott NG4 neutral glass filters.

(x, y)	Ω	T(0°)	ΔT_R(0°)	T(90°)	ΔT_R(90°)	T(AVE)	ΔT_R(AVE)
			#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
			#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)	0.0014	0.19237	0.000024	0.19239	0.000027	0.19238	0.000018
			#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

3.9 Further Evaluation of the Metal-on-Fused Silica Filters

A further evaluation of the evaporated metal-on-fused silica filters as a potential SRM in spectrophotometry was initiated by inviting several manufacturers of spectrophotometers to express their opinion on this matter. For this purpose, a number of sets of inconel-on-fused silica filters were distributed to the participating companies and research laboratories listed here in alphabetical order:

Companies

- Bausch and Lomb, Rochester, New York 14625;
- Beckman Instruments Inc., Irvine, California 92664;
- Cary-Varian Instruments, Palo Alto, California 94303;
- Coleman, a Division of Perkin-Elmer Co., Oak Brook, Illinois 60521;
- Gilford Instruments Laboratories, Inc., Oberlin, Ohio 44074;
- McPherson Instruments, Acton, Massachusetts 01720;

Laboratories

- Eastman Kodak Co., Rochester, New York 14650;
- Purdue University, Department of Chemistry, West Lafayette, Indiana 47907;
- Tennessee Eastman Co., Kingsport, Tennessee 37662.

The data from Table 10 were selected to illustrate the results obtained from such an interlaboratory comparison. The transmittance measurements were performed at the Tennessee Eastman Co. by J. H. Lady, using a computerized Cary 14 spectrophotometer.

The general opinions expressed by the participants in these interlaboratory comparisons were favorable to the use of the evaporated metal-on-fused silica filters as a reference standard in spectrophotometry.

Table 10. Transmittance measurements on inconel-on-fused silica filters in the ultraviolet and visible from 250 to 635 nm performed at NBS and at the Tennessee Eastman Co. (TEC).[a]

Wavelength nm / Filter No.		U.V.				Visible							σ^b
		250	300	340	400	400	440	465	500	546.1	590	635	
	NBS	0.01450	0.01808	0.01864	0.01935	0.01935	0.02039	0.02128	0.02273	0.02490	0.02702	0.02904	
41	TEC	0.0146	0.0182	0.0187	0.0194	0.0195	0.0204	0.0213	0.0229	0.0249	0.0271	0.0292	0.0001
	Δ	0.0001	0.0001	0.0001	0.0000	0.0001	0.0000	0.0000	0.0002	0.0000	0.0001	0.0002	
	NBS	0.21386	0.21266	0.20327	0.18933	0.18933	0.18328	0.18086	0.17902	0.17827	0.17861	0.17952	
42	TEC	0.2150	0.2138	0.2042	0.1900	0.1902	0.1840	0.1816	0.1797	0.1789	0.1793	0.1800	0.0001
	Δ	0.0011	0.0011	0.0009	0.0007	0.0009	0.0007	0.0007	0.0007	0.0006	0.0007	0.0005	
	NBS	0.28684	0.29915	0.30198	0.29955	0.29955	0.29695	0.29551	0.29444	0.29435	0.29490	0.29574	
43	TEC	0.2866	0.2986	0.3015	0.2991	0.2989	0.2963	0.2949	0.2939	0.2937	0.2947	0.2951	0.0001
	Δ	-0.0002	-0.0006	-0.0005	-0.0005	-0.0007	-0.0007	-0.0006	-0.0005	-0.0007	-0.0002	-0.0006	
	NBS	0.91422	0.92341	0.92655	0.92899	0.92855	0.93012	0.93050	0.93102	0.93156	0.93194	0.93230	
44	TEC	0.9182	0.9284	0.9320	0.9332	0.9348	0.9352	0.9355	0.9354	0.9353	0.9367	0.9355	0.0002
	Δ	0.0040	0.0050	0.0054	0.0042	0.0062	0.0051	0.0050	0.0044	0.0037	0.0048	0.0032	

[a] Measurements were made on a computerized Cary Model 14 spectrophotometer, 3/1/76.

[b] Estimate of short term repeatability of measurements.

3.10 Metal-on-Fused Silica Filters at the National Physical Laboratory

A discussion concerning the transmission characteristics of metal-on-fused silica filters, using a particular variety of nichrome alloy developed at the National Physical Laboratory (NPL), Teddington, U. K., was given recently by F. J. J. Clarke and associates [16]. The good optical neutrality of this material associated with a good adherence to the fused silica substrate has determined the certification of such filters as transfer standards for transmittance by NPL. The filters consist of single fused silica plates coated on one side with a semi-transparent layer of the nichrome alloy, and each filter is placed in a special holder. The exposed surface of the metallic film is not protected from exposure to environmental conditions and mishandling. Hence, for accurate use, it is recommended that these filters be recalibrated every year to insure that no degradation of the initial calibration has occurred, as indicated by F. J. J. Clarke in a private communication.

A high-accuracy spectrophotometer developed at NPL is used for the certification; its transmittance accuracy is verified with the double aperture system described in reference 17.

3.11 Limitation in the Use of the Metal-on-Fused Silica Filters as SRM's in Spectrophotometry and Removal of this Limitation

The only limitation that has prevented the metal-on-fused silica filters from being issued by NBS as a standard reference material was the fact that the surface of the metallic layer was not protected from exposure to contamination from environmental factors and from careless handling. Under such circumstances, the certified transmittance values could not be expected to retain their integrity for long periods of time.

However, a solution to this problem was found. It consisted of covering the fused silica plate carrying the semi-transparent evaporated metal layer with a clear fused silica plate. This clear plate is about 1.5 mm thick ground and polished in such a manner as to achieve an optical contact with the evaporated semi-transparent metal layer. Both fused silica plates are slightly beveled, and an optical cement is applied to protect the edges from damage. Under these conditions, this assembly behaves optically as if it were a single, solid, semi-transparent plate, and provides full protection to the metal layer. The possibility to achieve an optical contact between an evaporated metal layer and a fused silica plate was suggested as a protective means for the metal-on-fused silica filters by H. E. Bennett, Michelson Laboratory, Naval Weapons Center, China Lake, California, in 1975.

The possibility of producing such filters was explored with H. Peters at the Cosmo Optics, Inc. in Middletown, New York. After a number of experiments with materials prepared at NBS, he achieved the desired optical contact between the metalized surface of a fused silica plate and another clear fused silica plate. Additional experiments indicated that this procedure could be economically used to produce such filters.

4. Semi-Transparent Metal-on-Fused Silica Filters Protected by a Clear Fused Silica Plate Assembled by Optical Contact

The provision of a clear, fused silica plate attached by optical contact to the semi-transparent evaporated metal surface provides a satisfactory solution for the protection of such filters. Also, the method developed for producing such filters proved economical. The use of metal filter holders with removable front and rear shutters, and the use of metal containers for storage of these filters provides added protection against exposure to environmental conditions and mechanical damage. The only parameter that had yet to be assessed was the stability of the transmittance of the filters over a long period of time.

4.1 Preparation of the Chromium-on-Fused Silica Filters

Twenty sets of filters were prepared according to NBS specifications by Cosmo Optics Inc. Each set contained three filters with a nominal transmittance of 10, 30, and 90 percent. The metal used to produce the semi-transparent film was chromium, which was selected for its better adherence to the fused silica substrate than inconel, general resistance to environmental exposure, and acceptable optical neutrality.

Each fused silica plate was 1.5 mm thick and 30.5 mm long and 10.4 mm wide. It was ground and polished to produce the optical contact. The parallelism of each plate was better than 0.01 mm and the fused silica material was of optical quality and non-fluorescent. The semi-transparent chromium layer deposited by evaporation was free of pinholes when examined microscopically under a x30 magnification. The purity of the chromium metal used was 99.998 percent as indicated by its manufacturer, the Atomergic Chemetals Corp., Plainview, NY, and was specially produced by the van Arkel method for the evaporation process. The filters were placed in the holders described in Figures 9-13 as mentioned previously, and each set was kept in the same laboratory as the high-accuracy spectrophotometer at a temperature of 23.5 °C and a humidity of 40 percent.

4.2 Optical Transmittance of the Filters and Spectral Bandpass Dependence

The wavelength dependence of the optical transmittance of the semi-transparent layer of the chromium metal on the fused silica substrate as compared with inconel is illustrated in Figure 14. These measurements were made with a Cary 14 spectrophotometer. The dependence of the transmittance on the spectral bandpass was determined with a Cary 16 spectrophotometer at λ300 nm and λ600 nm. The results are given in Table 11. From these data it can be seen that the material has good optical neutrality. Under these circumstances the accuracy of the wavelength scale of conventional spectrophotometers and their spectral bandpass characteristics are much less critical when using the chromium-on-fused silica filters, than the glass or liquid filters (SRM's 930, 931, and 935), as shown in their certificates and the NBS Special Publications 260-51 [4] and 260-54 [7]. However, for meaningful results it is recommended that SRM 2031 be used in conjunction with spectrophotometers that have an accurate wavelength scale, and adequate spectral bandpass, as shown in Table 11, and for which the heterochromatic and isochromatic stray radiations are at a low level at which they will not affect the measurements (about one order of magnitude lower than the smallest signal measured).

Table 11. Transmittance (T) – spectral bandpass (SBP) dependence of an evaporated chromium metal-on-fused silica filter at two wavelengths (λ).

T, percent

SBP nm λ nm	9.0	7.5	6.0	4.5	3.0	1.5	0.3
300	11.00	11.00	10.95	11.00	11.00	10.95	11.00

SBP nm λ nm	81.0	67.5	54.0	40.5	27.0	13.5	2.7
600	11.42	11.53	11.55	11.65	11.68	11.65	11.60

NOTE: The transmittance measurements were performed with a Cary 16 spectrophotometer.

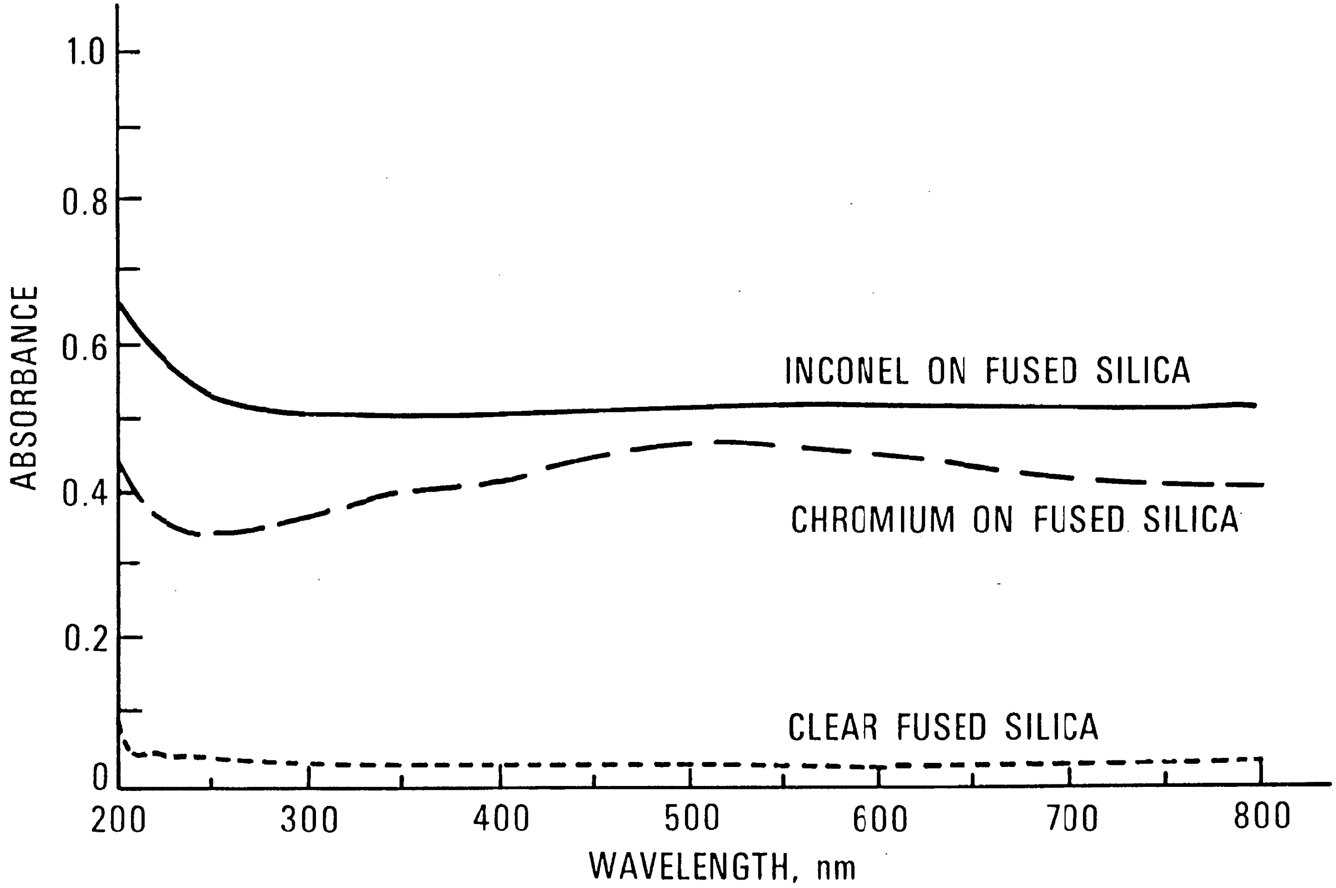

Figure 14. Comparative spectral transmittances of an evaporated inconel-on-fused silica filter and an evaporated chromium-on-fused silica filter.

4.3 Inspection of the Chromium-on-Fused Silica Filters

Each filter was examined visually in monochromatic light to determine that a faultless optical contact was achieved and maintained, using for this purpose the light source illustrated in Figure 15. This source consists of two low-pressure mercury discharge tubes mounted in a desk type lamp replacing the conventional fluorescent tubes. A green filter, made from a colored plastic sheet, contained between two glass plates, was attached to the lamp with springs. The transmittance maximum of the filter permitted the isolation of the green radiation of mercury at λ546.1 nm.

The surfaces of each filter and the quality of the evaporated metal layer were examined with the Bausch and Lomb microscope illustrated in Figure 15. This instrument provides both transmitted and reflected light examination capabilities. Under these conditions the filters were found to be free of visible defects over the period of two years, during which the transmittance stability tests were performed.

4.4 Tests to Determine the Transmittance Stability, in Time, for the Chromium-on-Fused Silica Filters

Stability transmittance tests were made at certain time intervals on 19 sets. The first measurements were made in February 1977, and were repeated in August 1977, December 1977, and July 1978. The last transmittance measurements were performed in March 1979.

Each transmittance value is the average of three repetitive measurements and each measurement consists of determining the ratio $\frac{2I}{I_0' + I_0''} = T$; I being the photodetector signal produced by the attenuated radiation passing through the filter, and I_0' and I_0'' the signals produced by the non-attenuated radiation passing through air and bracketing the I measurements. Each I and I_0 are the average of 50 individual digital voltmeter readings [2]. The transmittance measurements were made at 23.5 °C and a humidity of 40 percent in a room where the particulate matter is controlled through special filters that rates it in the 100,000 class.

The transmittances were measured at three wavelengths in the ultraviolet: λ250, 300, and 340 nm, and at seven wavelengths in the visible spectral regions: λ400, 440, 465, 500, 546.1, 590, and 635 nm.

The spectral bandpass for the ultraviolet measurements was 1.6 nm and 0.3 nm for the measurements performed in the visible.

A tabulation of all measurements performed on the 19 sets would contain 2850 transmittance values, and would take too much space to be all included here. Therefore, two representative examples were selected to illustrate the results obtained in this test. Table 12 shows the transmittances for sets 4 and 6. Each was made from three filters having nominal transmittances of 10, 30, and 90 percent. Set No. 4 was selected as a representative example for filters that have shown a change in transmittance over the two years time period of less than ±0.5 percent. Set No. 6 illustrates the behavior of filters that exhibited a change in transmittance of over ±0.5 percent, but less than ±1.0 percent. The differences, expressed as transmittance percents, are those between the February 1977 measurements and the March 1979 measurements and are referred to the initial measurements performed in February 1977. The corresponding relative transmittance differences obtained for all 19 sets are recorded in Table 13A. The absolute transmittance differences are recorded in Table 13B. A summary of the data from Table 13A is presented in Table 14.

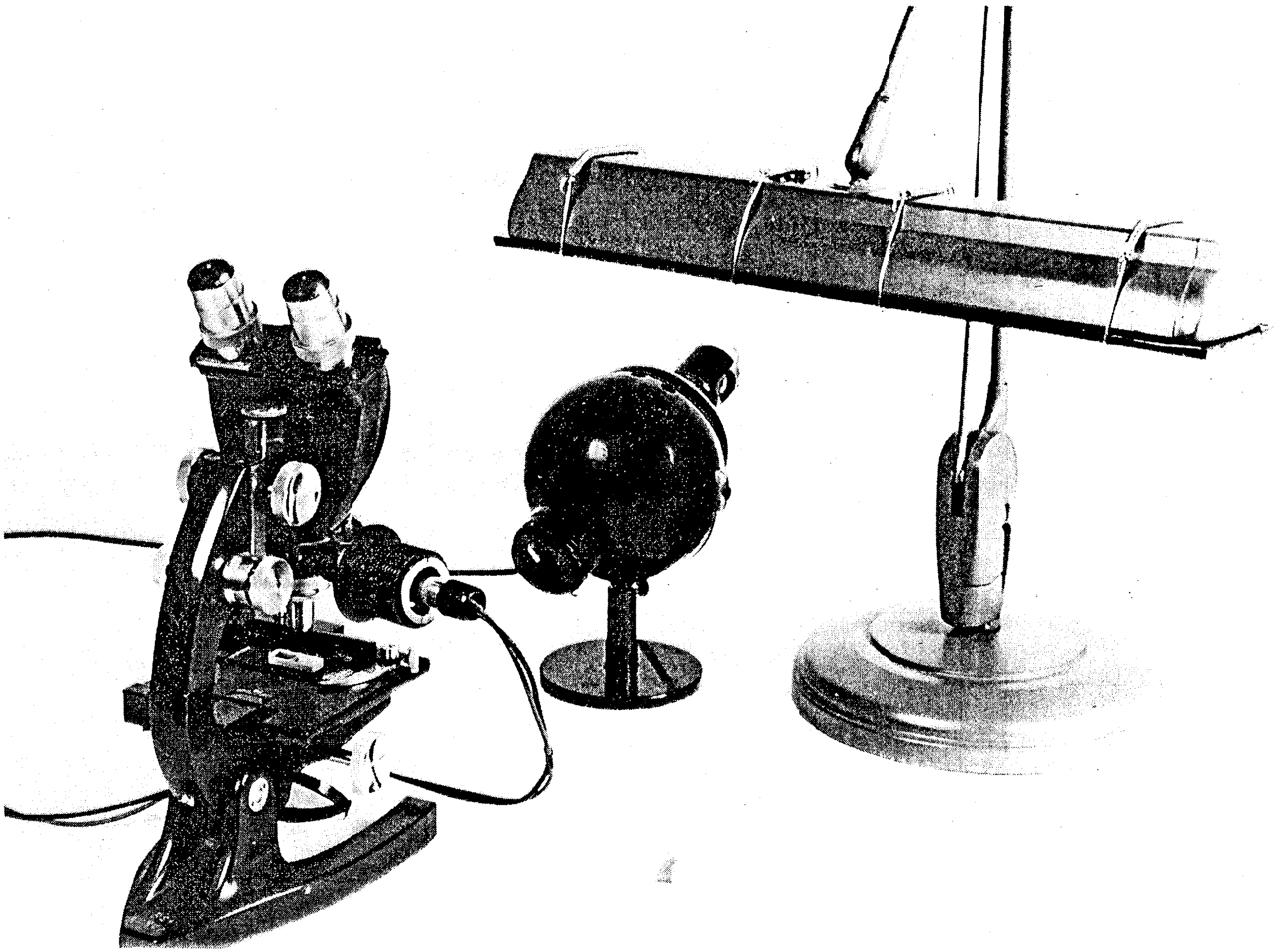

Figure 15. Instrumentation used to examine the chromium-on-fused silica filters. Left: Bausch and Lomb binocular microscope with transmitted and reflected light examination capability. Right: Monochromatic light source isolating the mercury green radiation at λ546.1 nm. It is used to examine the condition of the optical contact between the two fused silica plates assembly.

Table 12. Transmittance of two sets of chromium-on-fused silica filters measured over a period of two years.

Transmittance, percent

Wavelength nm Filter # and Date	250	300	340	400	440	465	500	546.1	590	635
2/77	12.94	11.86	11.29	11.08	10.47	10.27	10.38	11.14	12.11	13.08
4 8/77	12.90	11.86	11.31	11.09	10.51	10.28	10.40	11.17	12.13	13.12
12/77	12.90	11.84	11.29	11.09	10.43	10.24	10.34	11.13	12.10	13.13
10% 7/78	12.92	11.85	11.30	11.09	10.45	10.26	10.35	11.15	12.10	13.11
3/79	12.88	11.82	11.28	11.03	10.45	10.25	10.36	11.15	12.11	13.12
Difference,%T	-0.46	-0.34	-0.09	-0.45	-0.19	-0.19	-0.19	+0.09	0.00	+0.31
2/77	43.59	40.90	38.28	36.39	34.35	33.14	32.38	32.46	33.05	34.39
4 8/77	43.51	40.76	38.46	36.43	34.29	33.05	32.39	32.55	33.02	34.50
12/77	43.62	40.91	38.29	36.38	34.17	33.11	32.12	32.24	33.37	34.35
30% 7/78	43.53	40.83	38.42	36.39	34.34	33.12	32.36	32.50	33.06	34.47
3/79	43.54	40.77	38.41	36.41	34.31	33.18	32.30	32.41	33.17	34.38
Difference,%T	-0.11	-0.32	+0.34	+0.05	-0.12	+0.12	-0.25	-0.15	+0.36	-0.03
2/77	91.49	92.32	92.65	92.93	93.02	93.07	93.14	93.18	93.27	93.27
4 8/77	91.39	92.25	92.61	92.89	93.02	93.04	93.12	93.20	93.23	93.29
12/77	91.63	92.30	92.60	92.89	93.02	93.08	93.14	93.20	93.24	93.32
90% 7/78	91.48	92.40	92.75	93.06	93.20	93.24	93.32	93.37	93.42	93.45
3/79	91.48	92.42	92.73	93.05	93.16	93.21	93.28	93.30	93.37	93.38
Difference,%T	-0.01	+0.11	+0.09	+0.13	+0.15	+0.15	+0.15	+0.13	+0.11	+0.12
2/77	12.54	11.55	11.04	10.88	10.24	10.05	10.21	10.93	11.94	12.89
6 8/77	12.50	11.54	11.03	10.88	10.28	10.09	10.26	11.00	12.02	12.96
12/77	12.56	11.55	11.04	10.88	10.29	10.11	10.22	10.99	11.99	12.96
10% 7/78	12.56	11.56	11.06	10.90	10.30	10.12	10.25	11.00	12.02	12.98
3/79	12.51	11.55	11.04	10.90	10.29	10.12	10.23	11.00	12.01	12.97
Difference,%T	-0.24	0.00	0.00	+0.18	+0.49	+0.70	+0.20	+0.64	+0.59	+0.62
2/77	43.29	40.57	38.21	36.05	33.91	32.85	31.95	32.15	33.25	34.48
6 8/77	43.40	40.68	38.32	36.13	33.99	32.92	32.01	32.27	33.35	34.61
12/77	43.49	40.66	38.28	36.11	34.00	32.90	32.02	32.26	33.30	34.56
30% 7/78	43.41	40.67	38.30	36.10	34.00	32.92	32.03	32.23	33.31	34.56
3/79	43.40	40.68	38.31	36.12	33.99	32.91	32.01	32.27	33.35	34.62
Difference,%T	+0.25	+0.27	+0.26	+0.19	+0.24	+0.18	+0.19	+0.37	+0.30	+0.41
2/77	91.28	92.24	92.64	92.90	93.06	93.08	93.18	93.20	93.21	93.30
6 8/77	91.16	92.18	92.57	92.88	93.03	93.10	93.17	93.21	93.24	93.29
12/77	91.45	92.22	92.59	92.89	93.00	93.04	93.11	93.17	93.23	93.27
90% 7/78	91.31	92.30	92.71	93.06	93.20	93.26	93.33	93.41	93.49	93.49
3/79	91.31	92.31	92.72	93.04	93.13	93.19	93.25	93.33	93.37	93.42
Difference,%T	+0.03	+0.08	+0.09	+0.15	+0.08	+0.12	+0.08	+0.14	+0.17	+0.13

Table 13A. Relative differences in transmittance, ΔT%, observed over the time interval: February 1977 to March 1979 on 19 sets of evaporated chromium-on-fused silica filters. ΔT% is obtained from: $\frac{T\%\ (1977) - T\%\ (1979)}{T\%\ (1977)} \times 100$.

Set Number and Filter Identification		ΔT%									
		Ultraviolet			Visible						
		250	300	340	400	440	465	500	546.1	590	635
2	10	-0.24	-0.17	+0.09	0.00	0.00	0.00	+0.10	+0.18	+0.25	+0.46
	30	-0.39	-0.07	-0.13	+0.36	-0.47	+0.28	-0.47	-0.09	+0.40	-0.09
	90	-0.09	+0.04	+0.03	+0.07	+0.01	-0.02	-0.05	-0.05	0.00	-0.01
3	10	-0.68	-0.57	-0.51	-0.26	-0.37	-0.38	-0.19	-0.17	0.00	+0.15
	30	-0.30	-0.19	-0.05	-0.03	-0.20	-0.15	-0.03	0.00	-0.06	+0.12
	90	+0.12	+0.07	+0.15	+0.14	+0.19	+0.24	+0.16	+0.21	+0.18	+0.25
4	10	-0.46	-0.34	-0.09	-0.45	-0.19	-0.19	-0.19	+0.09	0.00	+0.31
	30	-0.11	-0.32	+0.34	+0.05	-0.12	+0.12	-0.25	-0.15	+0.36	-0.03
	90	-0.01	+0.11	+0.09	+0.13	+0.15	+0.15	+0.15	+0.13	+0.11	+0.12
5	10	-0.47	-0.43	-0.36	-0.09	+0.29	+0.10	0.00	-0.27	+0.17	-0.23
	30	-0.21	-0.02	+0.31	+0.50	+0.94	+1.07	+0.88	-0.93	+0.88	-0.55
	90	+0.15	+0.11	+0.14	+0.10	+0.17	+0.17	+0.16	+0.14	+0.15	+0.16
6	10	-0.24	0.00	0.00	+0.18	+0.49	+0.70	+0.20	+0.64	+0.59	+0.62
	30	+0.25	+0.27	+0.26	+0.19	+0.24	+0.18	+0.19	+0.37	+0.30	+0.41
	90	+0.03	+0.08	+0.09	+0.15	+0.08	+0.12	+0.08	+0.14	+0.17	+0.13
7	10	-0.48	-0.35	-0.09	-0.09	+0.19	-0.39	+0.59	+0.73	+1.17	+0.23
	30	-0.16	+0.07	+0.25	+0.19	+0.11	+0.12	+0.15	+0.24	+0.20	+0.25
	90	+0.09	+0.13	+0.15	+0.16	+0.18	+0.11	+0.17	+0.15	+0.14	+0.13
8	10	-0.55	-0.17	-0.09	+0.19	0.00	-0.20	-0.39	0.00	+0.43	+0.15
	30	-0.28	0.00	0.00	+0.11	+0.18	+0.21	-0.09	-0.37	+0.09	+0.41
	90	+0.01	+0.09	+0.10	+0.10	+0.12	+0.15	+0.07	+0.11	+0.11	+0.11
9	10	-0.88	-0.56	-0.34	-0.17	-0.37	-0.46	-0.46	-0.09	-0.32	-0.22
	30	-0.64	+0.07	+0.10	+0.05	-0.18	+0.58	-0.44	+0.37	+0.57	+0.64
	90	+0.13	+0.10	+0.14	+0.14	+0.22	+0.26	+0.19	+0.24	+0.18	+0.19
10	10	-0.39	-0.08	-0.09	+0.34	+1.68	-0.49	+1.09	+0.55	+1.00	+1.55
	30	-0.30	-0.10	-0.10	+0.11	+0.03	-0.03	+0.03	+0.06	+0.09	+0.23
	90	-0.10	+0.03	+0.11	+0.13	+0.13	+0.08	+0.10	+0.07	+0.06	+0.11
11	10	-0.41	+0.09	+0.19	+0.19	+0.30	+0.92	-0.30	+0.19	+0.77	+0.87
	30	-0.18	+0.12	-0.05	-0.14	-0.38	-0.39	-0.19	+0.19	-0.33	0.00
	90	+0.13	+0.14	+0.11	+0.14	+0.11	+0.17	+0.18	+0.13	+0.20	+0.18
12	10	+0.74	+0.36	+0.66	+0.28	0.00	+0.31	+0.10	+0.28	+0.60	+0.24
	30	-0.20	-0.24	+0.05	+0.08	-0.52	-0.36	-0.71	+0.12	-0.45	+0.67
	90	-0.02	+0.10	+0.11	+0.09	+0.10	+0.13	+0.08	+0.11	+0.15	+0.12
13	10	-0.54	-0.33	-0.53	-0.18	-0.38	-0.77	-0.29	-0.18	+0.16	-0.53
	30	-0.32	+0.05	-0.03	+0.25	0.00	0.00	-0.03	-0.06	-0.06	+0.23
	90	-0.20	-0.09	+0.03	+0.04	+0.13	+0.15	+0.08	+0.17	+0.14	+0.10
14	10	+0.08	+0.17	+0.28	+0.09	+0.20	+0.10	+0.20	+0.19	+0.17	+0.32
	30	-0.29	-0.24	-0.08	+0.03	+0.17	-0.50	0.00	-0.03	+0.12	+0.28
	90	-0.03	0.00	+0.09	+0.10	+0.11	+0.11	+0.11	+0.11	+0.14	+0.11

continued

Table 13A continued.

Set Number and Filter Identification		ΔT%									
		Ultraviolet			Visible						
		250	300	340	400	440	465	500	546.1	590	635
15	10	-0.39	-0.08	+0.18	+0.36	+0.29	+0.29	+0.38	+1.08	-0.08	+0.15
	30	-0.25	+0.05	-0.05	-0.08	-0.03	-0.12	-0.06	+0.24	+0.03	+0.11
	90	+0.16	+0.16	+0.15	+0.06	+0.17	+0.18	+0.12	+0.20	+0.20	+0.16
16	10	-0.48	-0.26	-0.83	-0.09	-0.39	+0.41	-0.19	+0.92	+0.85	+0.94
	30	-0.20	+0.14	+0.05	+0.30	-0.14	0.00	-0.15	+0.06	-0.03	+0.08
	90	-0.01	+0.05	+0.06	+0.07	+0.08	+0.10	+0.12	+0.03	+0.07	+0.07
17	10	-0.49	-0.18	-0.19	+0.47	0.00	-0.20	-0.20	+0.09	-0.34	+1.66
	30	-0.04	+0.10	+0.13	+0.16	+0.06	+0.18	+0.15	+0.28	+0.27	+0.14
	90	+0.14	+0.12	+0.13	+0.12	+0.16	+0.07	+0.22	+0.15	+0.19	+0.16
18	10	0.00	+0.17	+0.37	+0.37	+0.49	+0.30	+0.39	+0.46	+0.46	+0.70
	30	0.00	+0.02	0.00	+0.14	+0.09	+0.03	0.00	+0.06	+0.12	+0.15
	90	+0.12	+0.13	+0.14	+0.11	+0.15	+0.17	+0.13	+0.06	+0.06	+0.13
19	10	-0.75	-0.24	0.00	+0.17	-0.09	+0.19	-1.36	+0.94	+0.08	-1.37
	30	-0.31	+0.38	+1.09	0.00	-0.25	-0.50	-0.71	-0.53	+0.23	+0.31
	90	+0.10	+0.11	+0.09	+0.10	+0.11	+0.15	+0.16	+0.18	+0.15	+0.18
20	10	-0.40	-0.26	-0.18	+0.18	-0.88	-1.20	-0.69	-0.28	-0.59	-0.15
	30	+0.35	+0.45	+0.37	+0.42	+0.24	+0.18	+0.25	+0.16	+0.33	+0.29
	90	-0.10	-0.01	+0.01	+0.15	+0.07	+0.08	+0.04	+0.07	+0.06	+0.04

Table 13B. Absolute differences in transmittance, ΔT, observed over the time interval: February 1977 to March 1979 on 19 sets of evaporated chromium-on-fused silica filters. ΔT is obtained from T% (1977) - T% (1979).

Set Number and Filter Identification		ΔT									
		Ultraviolet			Visible						
		250	300	340	400	440	465	500	546.1	590	635
2	10	-0.03	-0.02	+0.01	0.00	0.00	0.00	+0.01	+0.02	+0.03	+0.06
	30	-0.17	-0.03	-0.05	-0.13	-0.16	+0.09	-0.15	-0.03	+0.13	-0.03
	90	-0.08	+0.04	+0.03	+0.07	+0.01	-0.02	-0.05	-0.05	0.00	-0.01
3	10	-0.09	-0.07	-0.06	-0.03	-0.04	-0.04	-0.02	-0.02	0.00	+0.02
	30	-0.13	-0.08	-0.02	-0.01	-0.07	-0.05	-0.01	0.00	-0.02	+0.04
	90	+0.11	+0.07	+0.14	+0.13	+0.18	+0.22	+0.15	+0.20	+0.17	+0.23
4	10	-0.06	-0.04	-0.01	-0.05	-0.02	-0.02	-0.02	+0.01	0.00	+0.04
	30	-0.05	-0.13	+0.13	+0.02	-0.04	+0.04	-0.08	-0.05	+0.12	-0.01
	90	-0.01	+0.10	+0.08	+0.12	+0.14	+0.14	+0.14	+0.12	+0.10	+0.11
5	10	-0.06	-0.05	-0.04	-0.01	+0.03	+0.01	0.00	-0.03	+0.02	-0.03
	30	-0.09	-0.01	+0.12	+0.18	+0.32	+0.35	+0.28	-0.30	+0.29	-0.19
	90	+0.14	+0.10	+0.13	+0.09	+0.16	+0.16	+0.15	+0.13	+0.14	+0.15
6	10	-0.03	0.00	0.00	+0.02	+0.05	+0.07	+0.02	+0.07	+0.07	+0.08
	30	+0.11	+0.11	+0.10	+0.07	+0.08	+0.06	+0.06	+0.12	+0.10	+0.14
	90	+0.03	+0.07	+0.08	+0.14	+0.07	+0.11	+0.07	+0.13	+0.16	+0.12

continued

Table 13B continued.

Set Number and Filter Identification		ΔT									
		Ultraviolet			Visible						
		250	300	340	400	440	465	500	546.1	590	635
7	10	-0.06	-0.04	-0.01	-0.01	+0.02	-0.04	+0.06	+0.08	+0.14	+0.03
	30	-0.07	+0.07	+0.10	+0.07	+0.04	+0.04	+0.05	+0.08	+0.09	+0.09
	90	+0.08	+0.12	+0.14	+0.15	+0.17	+0.10	+0.16	+0.14	+0.13	+0.12
8	10	-0.07	-0.02	-0.01	+0.02	0.00	-0.02	-0.04	0.00	+0.05	+0.02
	30	-0.12	0.00	0.00	+0.04	+0.06	+0.07	-0.03	-0.12	+0.03	+0.14
	90	+0.01	+0.09	+0.09	+0.09	+0.11	+0.14	+0.07	+0.10	+0.10	+0.10
9	10	-0.12	-0.07	-0.04	-0.02	-0.04	-0.05	-0.05	-0.01	-0.04	-0.03
	30	-0.28	+0.03	+0.04	+0.02	-0.06	+0.19	-0.14	+0.12	+0.19	+0.22
	90	+0.12	+0.09	+0.13	+0.13	+0.21	+0.24	+0.18	+0.22	+0.17	+0.18
10	10	-0.04	-0.01	-0.01	+0.04	+0.17	-0.05	+0.11	+0.06	+0.12	+0.20
	30	-0.13	-0.04	-0.04	+0.04	+0.01	-0.01	+0.01	+0.02	+0.03	+0.08
	90	-0.09	+0.03	+0.10	+0.12	+0.12	+0.08	+0.09	+0.07	+0.06	+0.10
11	10	-0.05	+0.01	+0.02	+0.02	+0.03	+0.09	-0.03	+0.02	+0.09	+0.11
	30	-0.08	+0.05	-0.02	-0.05	-0.13	-0.13	-0.06	+0.06	-0.11	0.00
	90	+0.12	+0.13	+0.10	+0.13	+0.10	+0.16	+0.17	+0.12	+0.19	+0.17
12	10	+0.09	+0.04	+0.07	+0.03	0.00	+0.03	+0.01	+0.03	+0.07	+0.03
	30	-0.09	-0.10	+0.02	+0.03	-0.18	-0.12	-0.23	+0.04	-0.15	+0.23
	90	-0.02	+0.09	+0.10	+0.08	+0.09	+0.12	+0.08	+0.10	+0.14	+0.11
13	10	-0.07	-0.04	-0.06	-0.02	-0.04	-0.08	-0.03	-0.02	+0.02	-0.07
	30	-0.14	+0.02	-0.01	+0.09	0.00	0.00	-0.01	-0.02	-0.02	+0.08
	90	-0.18	-0.08	+0.03	+0.04	+0.12	+0.14	+0.08	+0.16	+0.13	+0.09
14	10	+0.01	+0.02	+0.03	+0.01	+0.02	+0.01	+0.02	+0.02	+0.02	+0.04
	30	-0.13	-0.10	-0.03	+0.01	+0.06	-0.17	0.00	-0.01	+0.04	+0.10
	90	-0.03	0.00	+0.08	+0.09	+0.10	+0.10	+0.10	+0.10	+0.13	+0.10
15	10	-0.05	-0.01	+0.02	+0.04	+0.03	+0.03	+0.04	+0.12	-0.01	+0.02
	30	-0.11	+0.02	-0.02	-0.03	-0.01	-0.04	-0.02	+0.08	+0.01	+0.04
	90	+0.15	+0.15	+0.14	+0.06	+0.16	+0.17	+0.11	+0.19	+0.19	+0.15
16	10	-0.06	-0.03	-0.09	-0.01	-0.04	+0.04	-0.02	+0.10	+0.10	+0.12
	30	-0.09	+0.06	+0.02	+0.11	-0.05	0.00	-0.05	+0.02	-0.01	+0.03
	90	-0.01	+0.05	+0.06	+0.07	+0.08	+0.09	+0.11	+0.03	+0.07	+0.07
17	10	-0.06	-0.02	-0.02	+0.05	0.00	-0.02	-0.02	+0.01	-0.04	+0.21
	30	-0.02	+0.04	+0.05	+0.06	+0.02	+0.06	+0.05	+0.09	+0.09	+0.05
	90	+0.13	+0.11	+0.12	+0.11	+0.15	+0.07	+0.21	+0.14	+0.18	+0.15
18	10	0.00	+0.02	+0.04	+0.04	+0.05	+0.03	+0.04	+0.05	+0.05	+0.09
	30	0.00	+0.01	0.00	+0.05	+0.03	+0.01	0.00	+0.02	+0.04	+0.05
	90	+0.11	+0.12	+0.13	+0.10	+0.14	+0.16	+0.12	+0.06	+0.06	+0.12
19	10	-0.10	-0.03	0.00	+0.02	-0.01	+0.02	-0.15	+0.11	+0.01	-0.19
	30	-0.14	+0.16	+0.43	0.00	-0.09	-0.17	-0.24	-0.18	+0.08	+0.11
	90	+0.09	+0.10	+0.08	+0.09	+0.10	+0.14	+0.15	+0.17	+0.14	+0.17
20	10	-0.05	-0.03	-0.02	+0.03	-0.09	-0.12	-0.07	-0.03	-0.07	-0.02
	30	+0.15	+0.18	+0.14	+0.15	+0.08	+0.06	+0.08	+0.05	+0.11	+0.10
	90	-0.09	-0.01	+0.01	+0.14	+0.07	+0.08	+0.04	+0.07	+0.06	+0.04

Table 14. Summary of the percent transmittance difference, $\Delta T\%$, measured after a time interval of two years on 19 sets of chromium-on-fused silica filters with nominal transmittances (T) of 10, 30, and 90 percent.

Ultraviolet, $\lambda 250$ nm to $\lambda 400$ nm

$\Delta T\%$ / Filters	0.00 - 0.50	0.50 - 1.00	Over 1.00	Increase T	Decrease T	No Change T
10%	12	7	None	12 (21.05%)	41 (71.93%)	4 (7.02%)
30%	17	1	1	26 (45.61%)	27 (47.37%)	4 (7.02%)
90%	19	None	None	46 (80.70%)	10 (17.54%)	1 (1.75%)
Visible, $\lambda 400$ nm to $\lambda 635$ nm						
10%	7	12	7 *	88 (66.16%)	36 (27.07%)	9 (6.77%)
30%	15	4	1 *	80 (60.15%)	45 (33.83%)	8 (6.02%)
90%	19	None	None	127 (95.49%)	5 (3.76%)	1 (0.75%)

*In this case, several filters exhibited transmittance differences between 0.5 and 1.0 and over 1.0 as well. This accounts for a total larger than 19 filters.

NOTE: Each of the 19 sets contains 3 filters (57 filters), and the transmittance of each filter was measured at 3 wavelengths in the ultraviolet (171 measurements) and 7 wavelengths in the visible (399 measurements) for a total of 570 measurements (171 + 399 = 570).

4.5 Conclusions from the Time Stability Tests

From these data it can be inferred that, in general:

- The relative transmittance differences are smaller for the nominal 90 and 30 percent filters (Table 13A), while the opposite is true when the transmittance differences are expressed on an absolute basis (Table 13B).

- The changes in transmittances are larger in the visible region than in the ultraviolet. This was a surprising result because it was believed that the measurements in the ultraviolet would be more likely to be unstable.

- All of the nominal 90 percent filters showed only small changes in transmittance, well below ±0.5 percent, with a tendency toward increasing transmittance, especially in the visible (Table 13A).

- The nominal 30 percent filters (Table 13A) showed good stability in the ultraviolet. Only two measurements indicated a transmittance change greater than ±0.5 percent. The same 30 percent filters exhibited a larger change in the visible. Five measurements showed a transmittance difference of more than ±0.5 percent. About an equal number showed both a decrease and an increase of transmittance in the ultraviolet, while in the visible, the majority of changes are toward an increase of transmittance.

- The nominal 10 percent filters showed a larger change in transmittance (Table 13A). Seven measurements showed a transmittance difference larger than ±0.5 percent in the ultraviolet, nineteen measurements showed in the visible differences in excess of ±0.5 percent. For these filters, the tendency is to show a decrease of transmittance in the ultraviolet. In the visible, the majority of changes show an increase in transmittance.

4.6 Issuance of SRM 2031, Description of the Standard Reference Material, and Certificate

Based on the results just described, it was decided to issue the evaporated chromium-on-fused silica filters as a Standard Reference Material for transmittance measurements in the ultraviolet and visible spectral regions.

Each set will be "aged" in the laboratory for at least six months. The transmittance will be measured at the beginning and end of the aging period. Only those filters that exhibit satisfactory stability will be issued as SRM 2031. The transmittance data will be certified at the time of the measurements with an uncertainty of ±1.0 percent (relative) for the nominal 10 percent filters, and ±0.5 percent (relative) for the nominal 30 percent and 90 percent filters. Because of only two years of experience with this material, it is suggested that SRM 2031 be remeasured on a yearly basis, and more often if the user has a reason to believe that a loss in transmittance integrity has occurred.

In addition it must be also stated that, after two years, none of the filters showed deterioration of the optical contact when stored and used as described in this work.

To reduce further the possibilities of undue changes in the certified transmittance values, accidental "fingerprinting", and mechanical damages, each filter is mounted in an individual filter holder made from black-anodized aluminum alloy provided with removable shutters as illustrated in Figures 9 to 13 and 16 . The same figure also shows the aluminum alloy container with four cylindrical cavities for the three filters in their holders and an empty filter holder. The container is closed with an aluminum alloy screw cap. The empty filter holder is used in the reference beam of the sample compartment of the spectrophotometer to produce an equivalent stray radiation condition.

All aluminum parts of the filter holders are black-anodized to reduce isochromatic stray light during the measurements. The cylindrical container is also anodized black since it was found that the outgassing of this coating over the aluminum alloy is negligible as demonstrated by T. Heslin and R. Hunkeler [18]. They showed that there is little contribution to outgassing from the dyes used to produce the black anodization, and that the evolution of the material which is condensible at 25 °C is minimal.

Under these conditions, little or no chance exists that some volatile products from the filter holders and their container will contaminate the filters. The metallic storage container provides not only protection from mechanical damages, but also minimizes contamination of the filters from particulate matter due to static charges. The cylindrical cavity also prevents any contact between the filter surface and the walls of the storage container.

To prevent damage to the filters during transportation, four flat leaf springs stabilize the filter holders in their cylindrical cavities. These springs should be removed upon receipt of the material. Further information on SRM 2031 can be found in the Certificate for this material which is reproduced at the conclusion of this work.

Figure 16. Illustration of SRM 2031, Metal-on-Quartz Filters for Spectrophotometry. This same figure illustrates the certificate for SRM 2031. See text for details.

NOTE: The filter is shown here with its front surface facing up and the back surface facing down. The filter, in its holder, should be placed in the cuvette compartment of the spectrophotometer with its front surface facing the incident light beam and the back surface facing the photodetector.

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards
Certificate

Standard Reference Material 2031

Metal-on-Quartz Filters for Spectrophotometry

R. Mavrodineanu and J. R. Baldwin

This Standard Reference Material is intended for use in the verification of the transmittance and absorbance scales of spectrophotometers in the ultraviolet and visible spectral regions. It consists of three individual filters in their metal holders and one empty filter holder.

Each filter is made from two non-fluorescent fused silica plates, one of which carries a semi-transparent evaporated chromium metal layer while the other is clear. The two plates comprising the filter are assembled by optical contact. The chromium coating on two of the filters produces nominal transmittances of 10 percent and 30 percent. The third filter is made from assembling two clear fused silica plates by optical contact, and has a nominal transmittance of 90 percent. The metal holders for these filters are provided with shutters to protect the filters when not in use. These shutters must be removed at the time of measurement and be replaced after the measurements have been completed. Each filter bears an identification number.

Filter & Set Ident. Number	TRANSMITTANCE (T)									
	Wavelength, nm									
	250.0	280.0	340.0	360.0	400.0	465.0	500.0	546.1	590.0	635.0

Filter & Set Ident. Number	TRANSMITTANCE DENSITY ($-\log_{10}T$)									
	Wavelength, nm									
	250.0	280.0	340.0	360.0	400.0	465.0	500.0	546.1	590.0	635.0

Date of Certification:

Washington, D.C. 20234
June 1, 1979

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

The transmittance values (T) can be converted to percent transmittance (%T) by multiplying by 100. The transmittance densities are calculated from the measured transmittance (T). The transmittance densities should be indicated by the absorbance scale of the spectrophotometer if the filters are measured against air. The transmittance values given were measured against air at an ambient temperature of 23.5 °C.

The transmittance values for the filter with a nominal transmittance of 10 percent are estimated to be accurate to within ± 1.0 percent at the time of certification. The transmittance values for the filters having a nominal transmittance of 30 percent and 90 percent are estimated to be accurate to within ± 0.5 percent at the time of certification. This uncertainty includes the effects of random and systematic errors of the calibration procedure, as well as possible transmittance changes of the filters during the period of calibration.

Aging of the material may cause some filters to change transmittance with time. Improper storage or accidental touching of the filter surface may also cause changes.

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. In cases where verification is desirable, the filters should be returned to the National Bureau of Standards for cleaning and recalibration. It is advisable to perform the verification on a yearly basis.

The transmittance measurements were made using the high-accuracy spectrophotometer designed and built at the NBS Center for Analytical Chemistry [1]. This instrument represents the primary transmittance standard; its transmittance accuracy was established using the double-aperture method of linearity testing [1,3,5,6]. The estimated standard deviation obtained from a set of 20 measurements of the high-accuracy spectrophotometer used for transmittance measurements on filters of the SRM 2031 type is 5×10^{-5} transmittance units for transmittance between 0.1 and 0.3. The bounds of the systematic error of the instrument are estimated to be $\pm 10^{-4}$ transmittance units.

The transmittance, T, was measured against air in the reference beam; hence it includes the reflection losses that occur at the air-filter interface. Under these circumstances the measured transmittance, T, has a corresponding transmittance density, defined as $-\log_{10} T$. The internal transmittance, T_i, of a material is defined as the transmittance of the material corrected for reflection losses. This is obtained experimentally when the measurements are made against a blank sample in the reference beam. The absorbance, A, of a material is related to this internal transmittance, T_i, by the expression, $A = -\log_{10} T_i$. The transmittance measurements are 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 filter. The filters were measured in the spectrophotometer in a position perpendicular to the incident light beam.

The metal-on-quartz filters which constitute this SRM were produced according to NBS specifications by Cosmo Optics, Inc., Middletown, New York. The quartz plates were produced from non fluorescent fused silica material of optical quality, ground and polished to produce an optical contact. The metal used to produce, by evaporation,the semi-transparent metal coating was chromium, obtained through the van Arkel process, and has an indicated purity of 99.998 percent. It was provided by The Atomergic Chemetals Co., Plainview, New York. The fused silica plates were ground and polished at the same time and on the same grinding wheel, each to the nominal dimensions: 1.5 mm thick, 30.5 mm long, and 10.4 mm wide.

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). 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 transmittance of the filters depends upon the intrinsic properties of the material, wavelength, spectral bandpass, geometry of the optical beam, temperature, and positioning of the filter. A change of ambient temperature of 1 or 2 °C from 23.5 °C will not significantly affect the calibration [5]. Changes in the transmittance may be caused by surface conditions, aging of the material, exposure to a harmful atmosphere, or careless handling [2,3,4,5].

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 through 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.

The filter is shown in the assembled unit with its front surface facing up. The filter, in its filter holder, should be placed in the cuvette compartment of the spectrophotometer with its front surface facing the incident light beam and the rear surface facing the photodetector.

Top: Cylindrical container with its screw cap, both made of black-anodized aluminum alloy. Four filter holders can be stored in the cylindrical container. Bottom (from left to right): Aluminum alloy filter holder, 12.5 mm square and 58 mm high; Metal-on-quartz filter; Retaining spring of beryllium-copper with nylon screw and washer; Assembled unit; and Two Delrin shutters. All metal and plastic parts are flat black.

Prior to certification measurements, each filter was examined for surface defects and the condition of the optical contact [5]. 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 [1,5]. In most cases, where verification or recertification of the transmittance values is desirable, it will be most expeditious to return the filters to the National Bureau of Standards for measurement. Prior to shipment, the NBS Office of Standard Reference Materials should be contacted regarding the conditions and cost of verification and/or recertification.

Further information concerning the selection, preparation and properties of SRM 2031 will be found in reference 5.

This Standard Reference Material was issued with the assistance and advice of K.D. Mielenz and I.L. Barnes.

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.W. Seward.

We wish to acknowledge the cooperation of George N. Bowers, Jr., M.D., of Hartford Hospital, Hartford, Connecticut; Royden N. Rand, Ph.D., of the Eastman Kodak Co. Research Laboratories, Rochester, New York; and Donald S. Young, M.D., Ph.D., of the Mayo Clinic, Rochester, Minnesota.

The contributions of H.E. Bennett and J.M. Bennett of the Michelson Laboratory, Physical Optics Branch, Naval Weapons Center, China Lake, California, who helped in the production of SRM 2031 are also gratefully acknowledged.

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5. Summarizing Remarks

To achieve meaningful measurements by spectrophotometry requires that every step of the chemical processes involved in the analytical procedure, and every parameter of the instrumental spectrophotometric technique be well-known and under the complete control of the analytical chemist. He must assess the importance of these two factors in a quantitative manner, and evaluate their individual contribution to the uncertainty of the final measurement.

Instrumental stability, wavelength accuracy, adequate spectral bandpass, freedom of stray light, and transmittance accuracy are basic parameters that play a determinant role in the accurate transmittance measurements of a transparent material in the spectral range of interest. Without achieving these conditions, no accurate transmittance measurements can be performed. SRM 2031 appears to be the means for achieving instrumental accuracy in the ultraviolet and visible spectral regions with little spectral bandpass limitations.

While the use of SRM 2031 will not solve all the problems in spectrophotometry, its availability should contribute to the production of more accurate and more meaningful measurements in all areas where spectrophotometry is applied.

The production of accurate chemical analytical data, that is, the capability to determine <u>accurately</u> <u>the</u> <u>amount</u> <u>of</u> <u>a</u> <u>particular</u> <u>chemical</u> <u>element</u> <u>in</u> <u>a</u> <u>given</u> <u>matrix</u>, requires spectrophotometric precision, as determined by the instrumental stability and sensitivity. The accuracy of the analytical measurements is determined by the accuracy achieved in the preparation of the analytical samples and in the establishment of the reference curve. These depend on the stability of the chemical reactions involved in the spectrophotometric process, and on the ability to prepare accurate reference solutions that have accurately known concentrations of the chemical element of interest in a matrix identical to that of the analytical sample. Under these conditions, analytical accuracy can be achieved with spectrophotometers that exhibit stability and sensitivity. The wavelength accuracy, the spectral bandpass, and the accuracy of the transmittance or absorbance scale play a secondary role in this analytical application. The lack of accuracy of these parameters can affect the sensitivity and linearity, and in some cases, the specificity of spectrophotochemical analyses, rather than their chemical accuracy.

Standard Reference Material SRM 2031, Metal-on-Quartz Filters for Spectrophotometry, is a transfer standard that is calibrated for transmittance in the spectral range of 250 nm to 635.0 nm, with a high-accuracy spectrophotometer which represents the primary transmittance standard. The transmittance values are certified with an uncertainty of 1.0 and 0.5 percent. The validity of these transmittance values with time will depend on the stability of the material and on the conditions under which this SRM is used. The measurements from Table 12 verify that the stability of the certified transmittance values for set No. 4 are reproducible, within the uncertainty indicated, over a period of two 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 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 be kept in the metal container provided for the purpose. Should the surface of the filters become accidentally contaminated, no attempts should be made to wash them, if the user does not have means to determine whether the cleaning treatment has not altered the properties of the material and degraded the accuracy of the certified transmittance values. Since SRM 2031 is a transfer standard, the only means available for determining its integrity is by remeasuring its transmittance with a primary standard instrument. This can be done only with the high-accuracy spectrophotometer described in this work. Should there be a need to verify the accuracy of the certified transmittance data, SRM 2031 should be returned to NBS for verification, and for cleaning and recalibration, if necessary. As the transmittance stability of SRM 2031 was studied over a time period of two years only, it is recommended that this verification be performed on a yearly basis. Before sending SRM 2031 to NBS, proper arrangements should be made by writing the Office of Standard Reference Materials for instructions.

SRM 2031 is a delicate and costly unit that has required a considerable amount of careful work in its preparation and certification. This material should be handled carefully to insure accurate measurements and long life. This is particularly true when the working conditions require frequent use of SRM 2031. To protect this reference material, it might be desirable to develop "in house" secondary standards based on SRM 2031, and use these secondary standards for daily control of the spectrophotometers. When these standards indicate a significant change in the measurements, only then should SRM 2031 be used as a final verification of the data.

Secondary metal-on-quartz standards can be produced by acquiring the material used at NBS for the production of SRM 2031, cut to size as described in this publication and placed in holders similar to those illustrated in detail in Figures 9, 13, and 16. The transmittance of these filters should be established at the desired wavelengths with the best spectrophotometer available in the laboratory after its transmittance scale is verified with SRM 2031.

The certification of SRM 2031 was performed at 10 predetermined wavelengths: 250, 280, 340, 360, 400, 465, 500, 546.1, 590, and 635 nm. Certification at other wavelengths, within the spectral range of λ200 nm to λ800 nm, can be provided. Requests for additional wavelength certification should be addressed to the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.

The authors gratefully acknowledge the assistance of the following persons and organizations:

- I. L. Barnes, Chief, K. D. Mielenz and R. W. Burke, Inorganic Analytical Research Division; K. L. Eckerle, Radiometric Physics Division; J. F. Barkley and F. C. Ruegg, Instrumentation Development Group, J. R. DeVoe, Leader; R. W. Seward, Office of Standard Reference Materials; E. P. Muth, and R. E. Lach of the Instrument Shops Division, at NBS.
- H. E. and J. M. Bennett of the Michelson Laboratory, Physical Optics Branch, Naval Weapons Center, China Lake, California.
- J. I. Shultz, NBS/ASTM Research Associate, National Bureau of Standards, Washington, D. C.
- F. J. J. Clarke, National Physical Laboratory, Teddington, Middlesex, U. K.
- J. H. Lady, Tennessee Eastman Co., Kingsport, Tennessee.
- R. N. Rand, Eastman Kodak Co., Rochester, New York.
- Bausch and Lomb; Beckman Instruments; Cary-Varian; Coleman, a Division of Perkin-Elmer; Gilford Instruments Labs. and McPherson Instruments.
- The National Institute of General Medical Sciences for supporting, in part, the work reported in this publication.
- The Center for Analytical Chemistry Text Editing Facility for typing the manuscript.

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7. Appendices

These appendices contain reproductions from five publications in the field of high-accuracy spectrophotometry that are considered relevant to the topics discussed in this work. These publications should provide further and more detailed information on specific subjects and are reproduced here as a convenience to the interested reader.

Also reproduced in these appendices are the certificates issued by NBS for the SRM's 930D, 931b, 2030, 932, and 935.

APPENDIX I

Reprinted from **ANALYTICAL CHEMISTRY**, Vol. 48, Page 1093, June 1976

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, $u = \mathrm{d}Q/\mathrm{d}V$. Energy per unit volume.
Flux, $\Phi = \mathrm{d}Q/\mathrm{d}t$. Time rate of energy flow.
Flux density, $W = \mathrm{d}\Phi/\mathrm{d}A$. Flux per unit area.
Intensity, $I = \mathrm{d}\Phi/\mathrm{d}\Omega$. Flux per unit solid angle.
Sterance, $L = \mathrm{d}^2\Phi/\mathrm{d}(A\cos\Theta)\mathrm{d}\Omega$. 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, $u_e[\mathrm{J\ m^{-3}}]$.
Luminous intensity, $I_v[\mathrm{lm\ sr^{-1}}]$.
Photon sterance, $L_p[\mathrm{E\ m^{-2}\ sr^{-1}\ s^{-1}}]$.

(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, $u_{e,\lambda} = \mathrm{d}u_e/\mathrm{d}\lambda\ [\mathrm{J\ m^{-4}}]$.
Radiant energy density per unit wavelength interval.
Spectral photon intensity, $I_{p,\sigma} = \mathrm{d}I_p/\mathrm{d}\sigma\ [E\ \mathrm{sr^{-1}\ s^{-1}\ m}]$.
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*, $\eta_{e,\sigma} = \mathrm{d}\eta_e/\mathrm{d}\sigma$, and *spectral photon yield*, $\eta_{p,\sigma} = \mathrm{d}\eta_p/\mathrm{d}\sigma$, 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 absor*b*ance per unit path length and unit concentration (A/bc), whereas the International Lighting Vocabulary (*2*) defines it as internal absor*pt*ance 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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RECEIVED for review September 26, 1975. Accepted December 23, 1975.

JOURNAL OF RESEARCH of the National Bureau of Standards — A. Physics and Chemistry
Vol. 76A, No. 5, September—October 1972

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

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[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

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

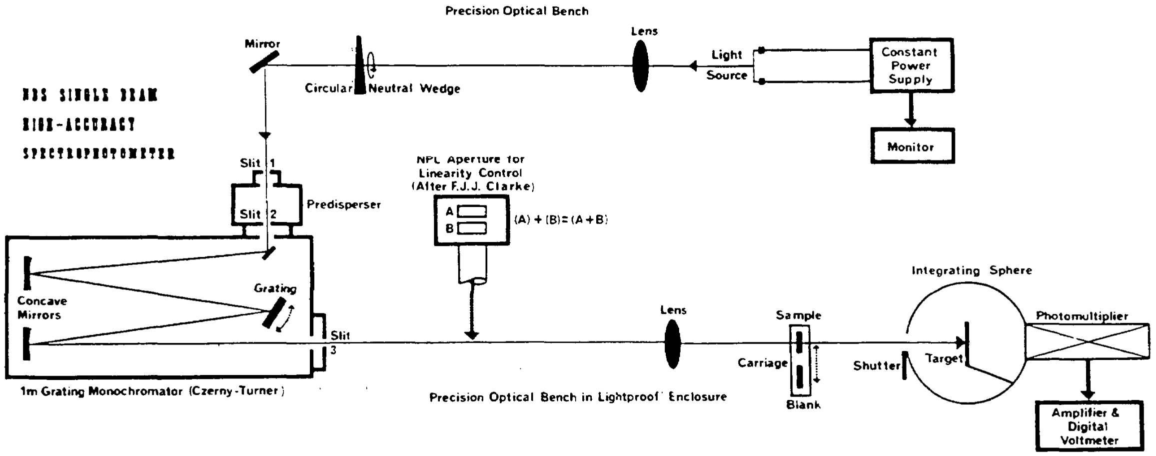

FIGURE 1. Principle of the single beam high accuracy spectrophotometer. The aperture unit is placed on the optical bench only when linearity measurements are performed.

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-

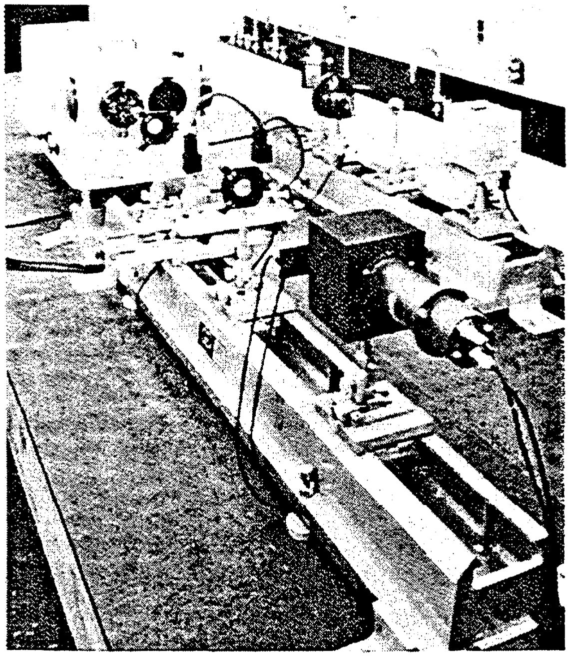

FIGURE 2. General views of the spectrophotometer. Rear: optical bench carrying the tungsten-halogen radiation source used for checking the alignment of optical components, followed by a quartz lens, the circular quartz neutral wedge, and a flat mirror. Left: the 1-m Czerny-Turner grating monochromator (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.

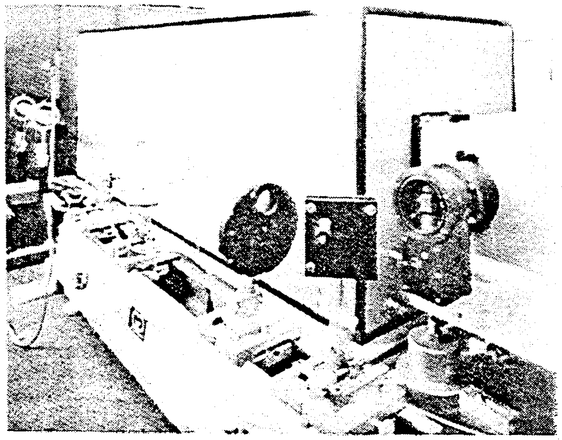

FIGURE 3. Close view of the tungsten ribbon filament lamp on its adjustable holder, followed by the quartz lens—circular neutral wedge assembly, and by the flat mirror in its adjustable holder. The 30° quartz prism Littrow-type predisperser is located at the entrance slit of the 1-m grating monochromator. 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.

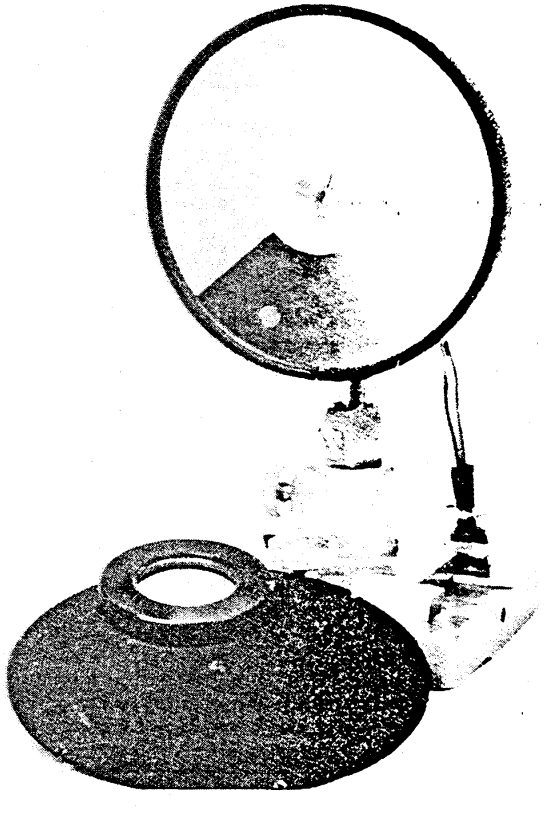

FIGURE 4. Close view of the circular, neutral wedge. The front plate which carries the fused silica lens was removed to show the fused silica disc with the evaporated metal layer.

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 ¾-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 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).

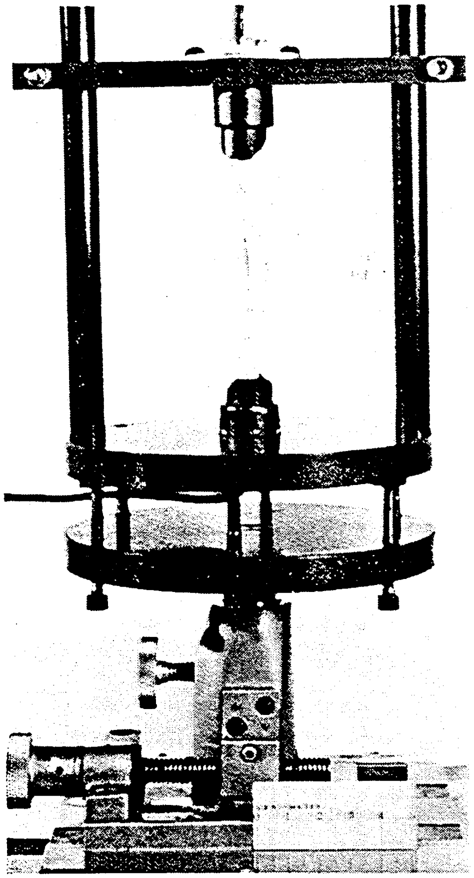

FIGURE 5. Single coil tungsten halogen lamp in the adjustable holder.

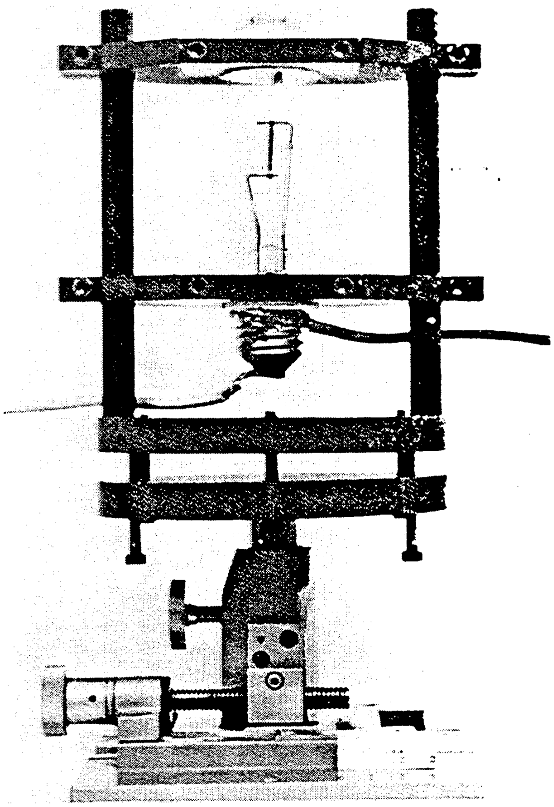

FIGURE 6. The tungsten ribbon filament lamp in the newly designed adjustable holder. The platform which carries the lamp is similar to that described in figure 5 and can be oriented in the horizontal plane through the six screws spaced around the edges of the platform at 60° intervals. Three screws push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

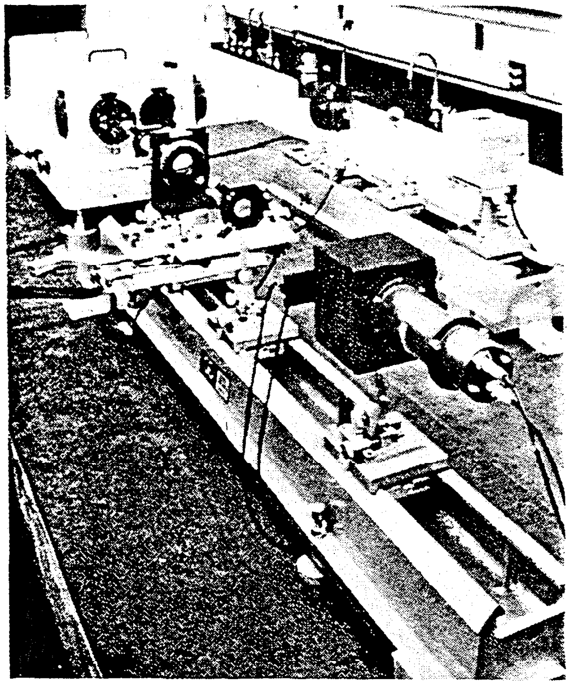

FIGURE 7. Same as figure 2 except for the sample holder which in this case is capable of rotating the sample 360° and to displace it in the x-y direction through the micrometer screws.

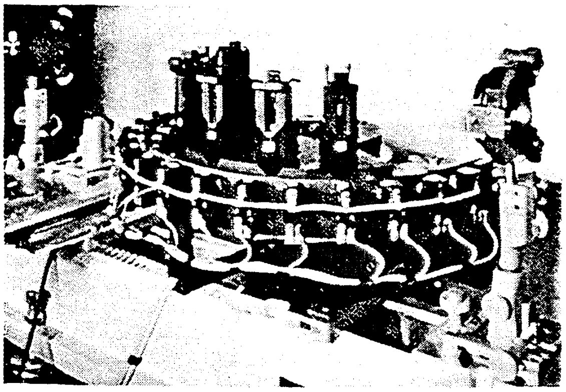

FIGURE 8. Circular platform carrying seven filter holders. The 15 position switches (7 sample positions and 8 blank positions) are visible along with the two quartz lenses. The exit slit of the monochromator is at left.

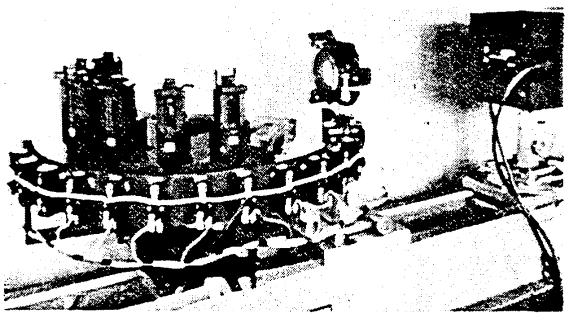

FIGURE 9. Same as figure 8. The pneumatic cylinder which rotates the circular platform through a ratchet mechanism is visible at the rear of the platform. The integrating sphere with its pneumatic shutter is seen at right.

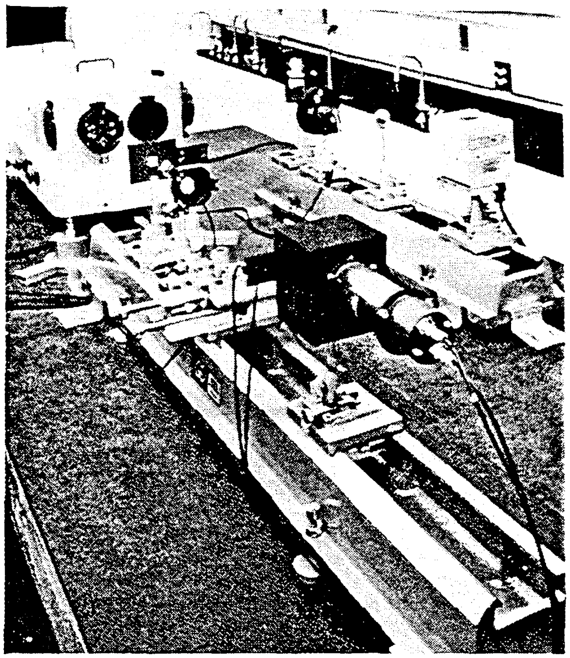

FIGURE 10. Same as figure 2. In this case the dual-aperture unit for linearity control is located on the optical bench after the exit slit of the monochromator.

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 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

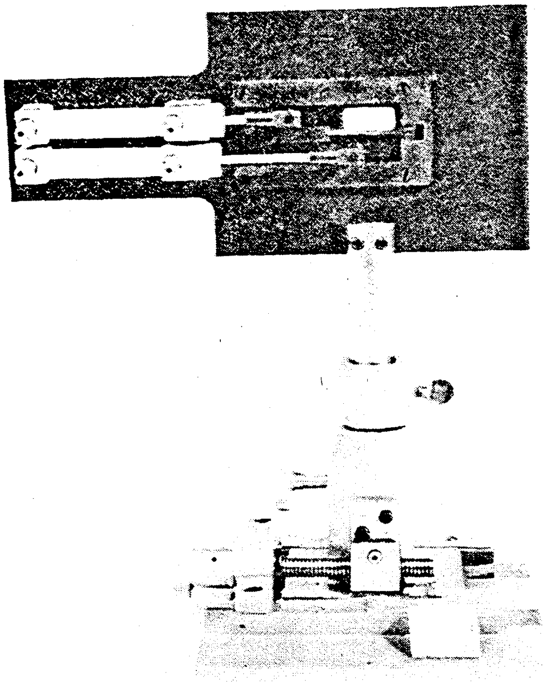

FIGURE 11. Detail of the dual-aperture unit showing its construction and the pneumatic system which operates the two shutters. One aperture is open, the other is closed.

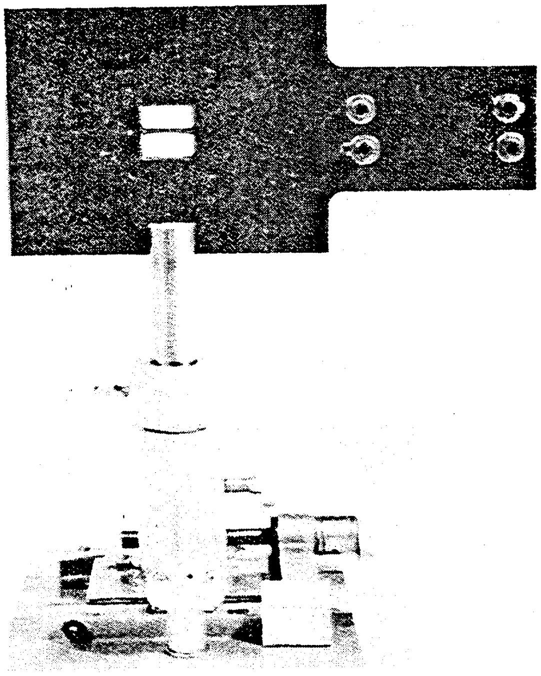

FIGURE 12. Front view of the dual-aperture unit, with both apertures open.

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.

e. **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.

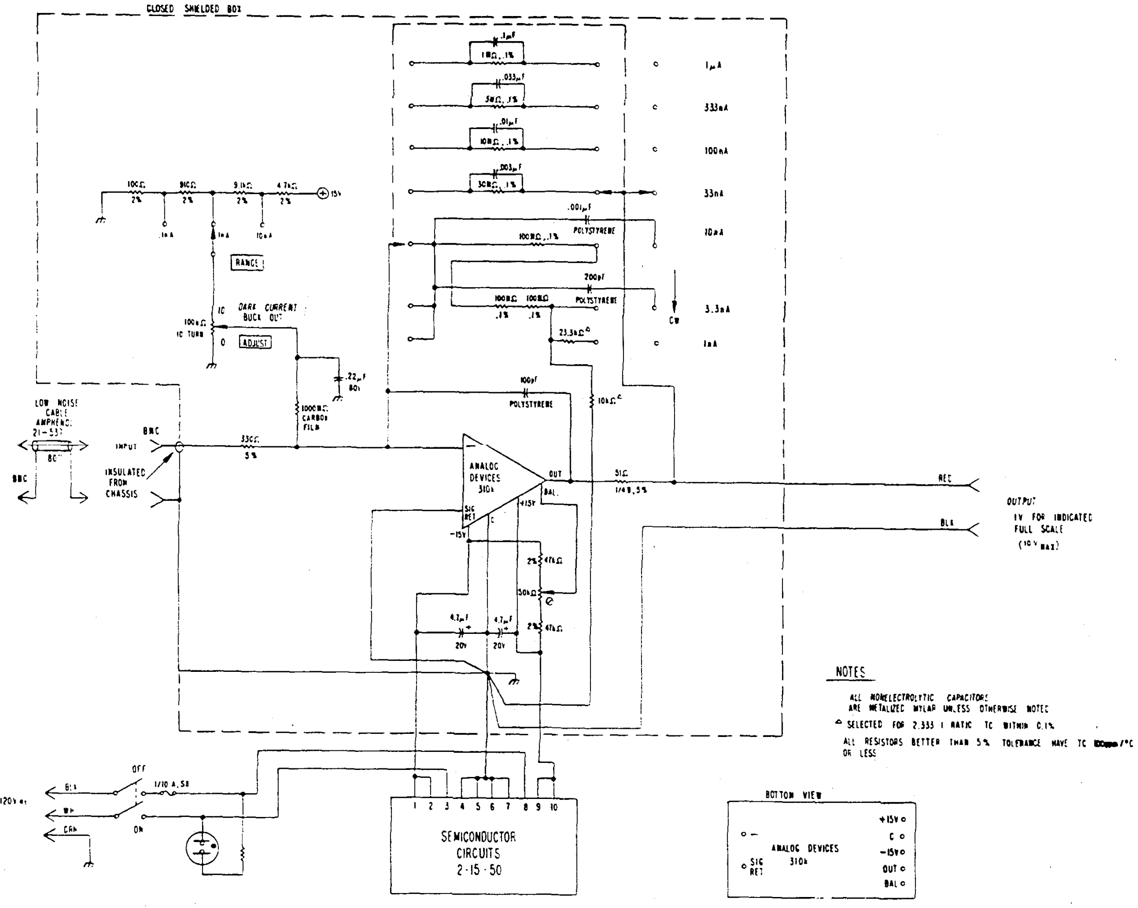

FIGURE 13. Schematic of the current-to-voltage circuitry. Courtesy of K. W. Yee.

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    .2359933E 00    .1886E-03      .7992E-03
 11    .2001634E 01    .4532E-03      .2264E-03        11.790
 12    .6741099E 00    .3418E-03      .5070E-03
 13    .2001589F 01    .6368E-03      .3182F-03        33.676
 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      .1852F-03        32.778
 10    .2358786E 00    .1596E-03      .6767E-03
 11    .2002130E 01    .5036E-03      .2515E-03        11.782
 12    .6740563E 00    .3022E-03      .4484F-03
 13    .2001997E 01    .4545F-03      .2270F-03        33.668
 14    .2388354E 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 individual 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		
Average of replications	1.003535		Second group
Percent standard deviation	0.0015		
Average of replications	1.003545		Third group
Percent standard deviation	0.0010		

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_6
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 NG–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:

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

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_3
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	
Average of replications	2.001517	Second group
Percent standard deviation	0.012	
Average of replications	2.000826	Third group
Percent standard deviation	0.025	
Average of replications	2.001268	Fourth group
Percent standard deviation	0.027	

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.

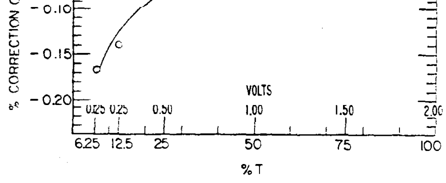

FIGURE 16. Linearity correction curve.

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:

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

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 double aperture method for testing photometric linearity, and have used a curve-fitting procedure for 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

	%T			
Wavelength nm	Produced by spectrophotometer 1	Polarizer, plane of vibration horizontal 2	Polarizer, plane of vibration vertical 3	% Difference %T_1 − %T_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*		NBS, %*T* average	NPL, %*T*	% Diff. NBS to NPL
	1	2			
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,

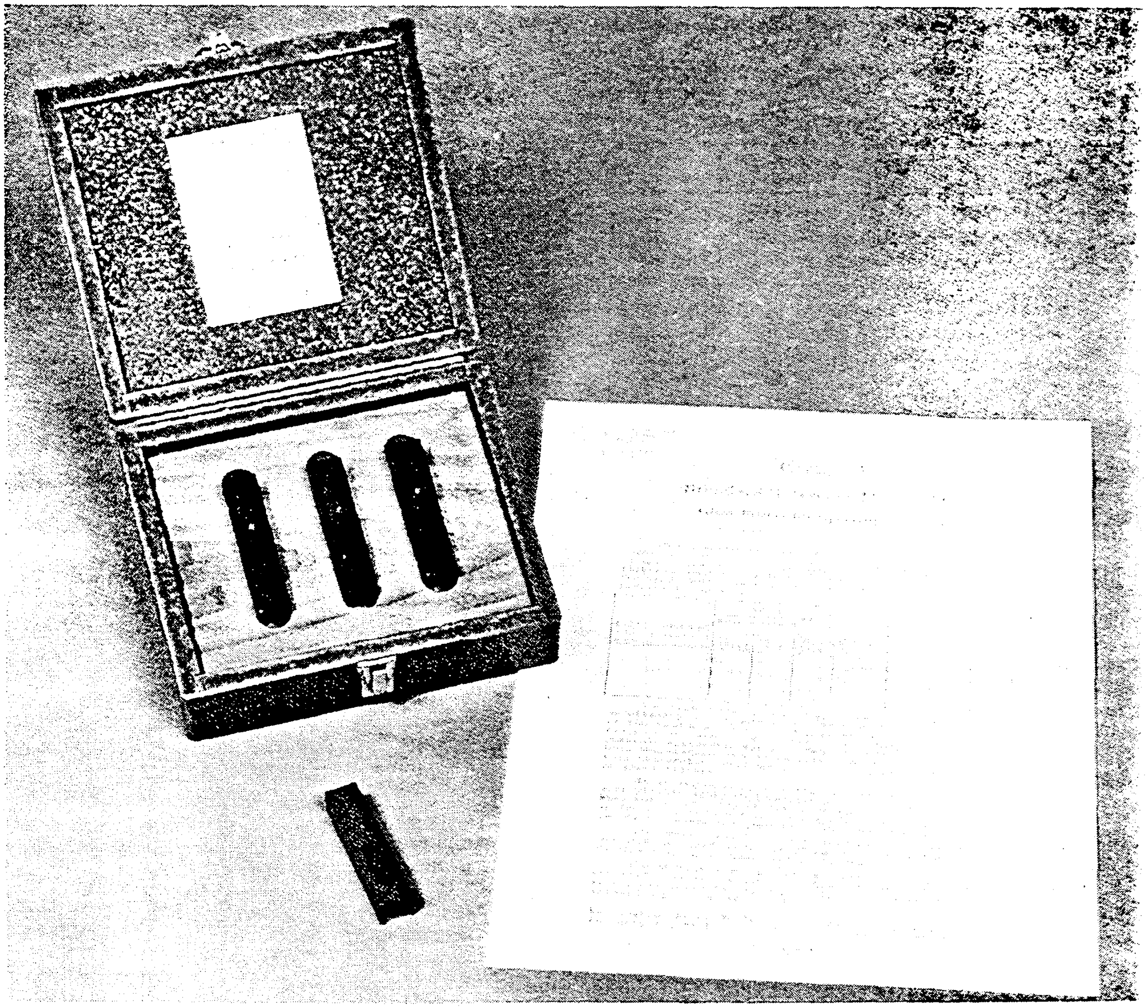

FIGURE 17. NBS Standard Reference Material 930 and calibration certificate.

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.

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.

The author gratefully acknowledges the assistance of the following persons, in addition to those already *mentioned in the text:*

F. J. J. Clarke, for the considerable assistance given through personal discussions on the philosophy and principles of high accuracy spectrophotometry at NPL.

Anne Compton, for advice and help during the experimental work carried-out at the high accuracy spectrophotometer at NPL.

G. E. V. Lambert, for information concerning glass filters (NPL).

K. D. Mielenz (NBS), for constructive discussions on the principles of spectrophotometry and for critically reviewing the manuscript.

W. H. Venable (NBS), for critically reviewing the manuscript.

K. L. Eckerle (NBS), for advice in measuring stray radiations and polarization produced in the monochromator.

C. R. Yokley (NBS), for advice on the radiation stability of incandescent tungsten filament lamps.

W. K. Haller (NBS), for valuable information on the properties of glass surfaces and optical glass filters.

H. H. Ku (NBS), for advice on interpretation of the data discussed in this paper.

NBS Instrument Shop, for constructing the mechanical parts described in this work.

NBS Optical Shop, for grinding the quartz lens used in this work.

D. S. Bright (NBS guest worker), for the programs written at various times during the initial phase of this work.

V. E. Gray (NBS), for assistance in performing the accelerated radiation tests.

H. J. Höfert and A. Reule (C. Zeiss, Oberkochen, Germany), for valuable information on linearity of photodetectors and for demonstration of the radiation addition method.

R. J. Carpenter (NBS), for constructive discussions on electronic circuitry and photodetectors.

L. Marzetta (NBS), for advice and assistance in assessing various functioning parameters of photomultiplier tubes.

O. Menis, Section Chief, Analytical Coordination Chemistry (NBS), for approving and encouraging the work reported in this paper.

J. I. Shultz, Assistant Section Chief, Analytical Coordination Chemistry (NBS), for critically reviewing the manuscript.

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(Paper 76A5–729)

JOURNAL OF RESEARCH of the National Bureau of Standards — A. Physics and Chemistry
Vol. 78A, No. 5, September–October 1974

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.

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*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.

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.

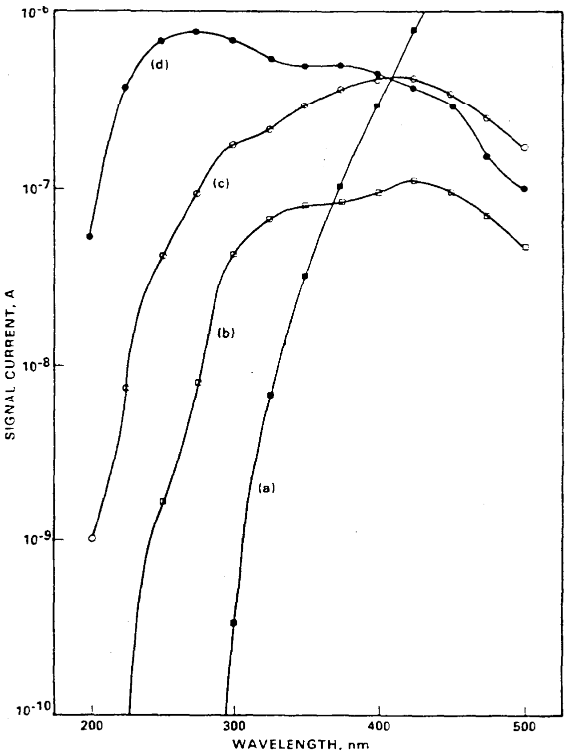

FIGURE 1. *Successive improvement of clear-space signal level of original spectrophotometer (curve a) obtained by: (b) deuterium arc lamp, (c) improved averaging sphere, and (d) new grating.*

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

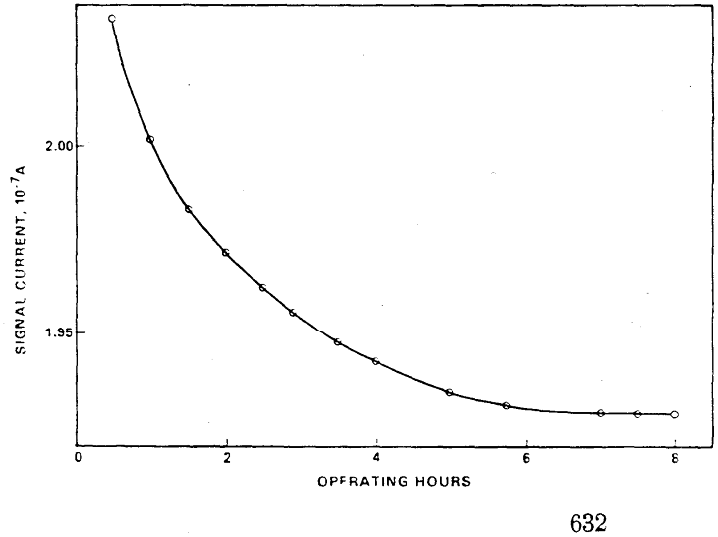

FIGURE 2. *Long-term signal drift observed with deuterium lamp.*

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].

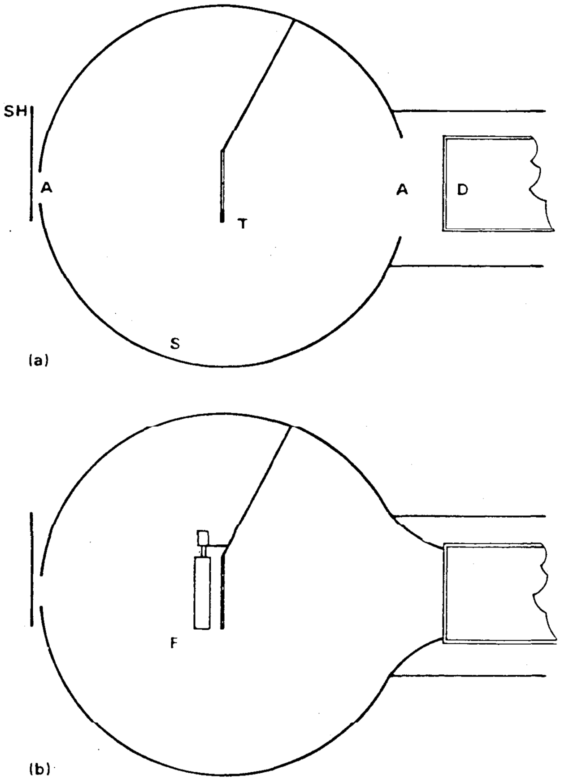

FIGURE 3. *Geometry of (a) original averaging sphere and (b) improved sphere.*

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 $(1\text{-}e/d)$, 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 fluorescent 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

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

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

[1] Mavrodineanu, R., J. Res. Nat. Bur. Stand. (U.S.), **76A** (Phys. and Chem.), No. 5, 405–425 (Sept.–Oct. 1972).

[2] Mielenz, K. D., Eckerle, K. L., Madden, R. P., and Reader, J., Appl. Optics **12**, 1630–1641 (1973); Mielenz, K. D., and Eckerle, K. L., Nat. Bur. Stand. (U.S.), Tech. Note 729, 60 pages (June 1972).

[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 IV

JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 80A, No. 4, July-August 1976

Considerations for the Use of Semi-Transparent Metallic Thin Films as Potential Transmittance Standards in Spectrophotometry*

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(May 20, 1976)

Various characteristics of evaporated metal-on-fused silica filters are discussed in relation to their optical transmission properties. Special metal holders provided with shutters were designed to be used with these filters, and are described in detail. Transmittance measurements, performed in various conditions, are reported and indicate that the evaporated metal-on-fused silica filters might present an acceptable material as transfer standards in spectrophotometry.

Key words: Evaporated metal-on-quartz; filters, transmittance; neutral filters; standard reference materials; transmittance characteristics; ultraviolet-visible filters.

The use of solid materials, in the form of glass filters and of solutions of inorganic and sometime organic compounds, to test the correct functioning of spectrophotometers is a common practice [1].[1] A variety of materials are available from the National Bureau of Standards (NBS) which can be used as transfer standards to verify the accuracy of the transmittance scale and the short and long term stabilities of conventional spectrophotometers. Two Standard Reference Materials (SRM's) have been issued by NBS for the verification of the accuracy of the transmittance scale; these are SRM 930 and SRM 931.

SRM 930 is a solid material which consists of a set of three glass filters having nominal transmittance of 10; 20; and 30 percent. They are certified for transmittance in the visible spectral range from 400 nm to 635 nm. A detailed description of this SRM is given in NBS Special Publication 260-51 [2]. SRM 931 is a liquid standard which consists of a solution of cobalt and nickel in dilute perchloric acid contained in glass ampoules [3]. The transmittance of these solutions is certified from 302 nm to 678 nm and should be used in conjunction with curvettes having a known light path; such curvettes are available from NBS as SRM 932 [4].

Both SRM's 930 (the glass filters) and 931 (the liquids) are limited in their spectral transmittance range and require the use of spectral bandpasses, from 2.2 nm to 6.5 nm for the glass filters and from 1.0 nm to 6.5 nm for the liquid filters depending of wavelength, when accurate transmittance values are sought.

The need to provide similar transfer standards, but with expanded spectral range to the ultraviolet and with less stringent spectral bandpass requirements, has resulted in an investigation to find adequate materials for this purpose. 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 nonfluorescent; (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. Thus, various solid materials were examined and the final choice was the evaporated metal-on-(non-fluorescent) fused silica type filter.

The transmission characteristics of such filters are illustrated in figure 1 and are compared with that of three glass filters and Ronchi ruling on glass.

The major limitation of the evaporated metal-on-quartz filters results from their intrinsic property of attenuating the incident radiation by reflecting rather than absorbing part of it. As a consequence of this property, this type of filter could generate stray radiations in the sample compartment of conventional spectrophotometers and is susceptible to produce interreflections when used with instruments equipped with lenses.

To determine the practical value of such filters as a transfer transmittance standard, comparative meas-

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*This work was supported in part by the National Institute of General Medical Sciences.

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

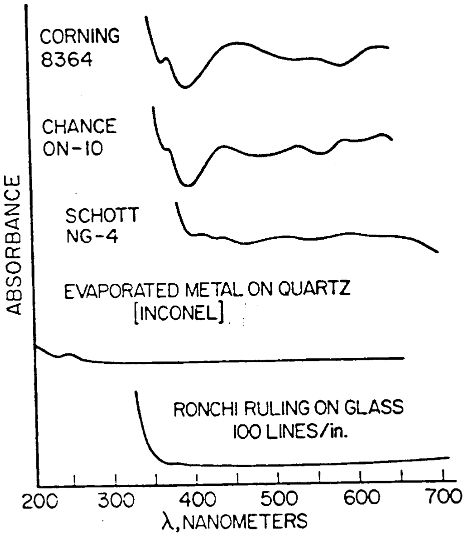

FIGURE 1. *Spectral characteristics for five transparent materials from 200 nm to 700 nm.*

urements were performed with the National Physical Laboratory in England (NPL), and the results are given in table I. In this case the inconel-on-fused silica filter was protected by a clean fused silica plate held in place with an organic cement. Except for a filter which showed some mechanical flaws in its structure, the reproducibility of transmittance measurements was as good as that obtained for the absorbing glass filters (table II). The error which would result from positioning the inconel-on-fused silica was measured by rotating from 0° angle to 3°—6°—and 9°. From the results obtained (table III) it can be concluded that in the case of the high-accuracy spectrophotometer used at NBS a positioning error within 3° can be tolerated.

The interreflection error affecting the measurements when a filter is inserted in the radiation path between the two lenses of a spectrophotometer was examined in detail [5]. The measured error for a glass filter established for the high-accuracy spectrophotometer was one or two 10^{-4} transmittance units; a value which is about four times larger was found for an evaporated metal-on-fused silica filter. It should be mentioned here that both the positioning and interreflection errors are, for a given material, instrument dependent.

As a result of these considerations a decision was made to produce a limited number of sets of evaporated inconel-on-fused silica and to test these filters in actual measurements performed on the conventional spectrophotometers manufactured in the United States.

One of the filters from a set is shown in figure 2. From left to right one can see the main body of the filter holder made from an aluminum alloy anodized black. This body is provided with dove-tail grooves which can accept a front and rear shutter made

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

Wavelength nm	NBS, %T		NBS, %T average	NPL, %T
	1	2		
450.0	24.87	24.88	24.87_5	24.93
550.0	23.78	23.82	23.80	23.86
650.0	23.38	23.39	23.38_5	23.46
450.0	49.35	49.33	49.34	[a] 49.56
550.0	47.60	47.60	47.60	47.81
650.0	46.85	46.85	46.85	47.14
450.0	72.17	72.20	72.18_5	72.30
550.0	72.05	72.11	72.08	72.20
650.0	72.20	72.34	72.27	72.33

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

[a] 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.

TABLE II. *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
440.0	12.92	12.91	12.91_5	12.93
465.0	14.96_5	14.98	14.97_3	15.01
590.0	11.70	11.64	11.67	11.67
635.0	12.72	12.68	12.70	12.72
440.0	19.62_5	19.58	19.60_3	19.62
465.0	22.38_5	22.35	22.36_7	22.43
590.0	19.06	18.95	19.00_5	19.01
635.0	20.45_5	20.37	20.41_3	20.47
440.0	32.89	32.86	32.87_5	32.98
465.0	35.52	35.54	35.53	35.66
590.0	31.16_5	31.10	31.13_3	31.21
635.0	32.56_5	32.52	32.54_3	32.62

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

TABLE III. *Percent transmittance (%T) measured on a Schott neutral glass filter 2 mm thick, and an inconel-on-fused silica filter 2 mm thick at 590 nm, for normal incidence and for the angle of 3°; 6°; and 9°*

%T

Filter / Angle	Schott NG-4 Glass	Inconel-on-fused silica	
		Front	Back
0°	28.13	29.91	29.87
3°	28.10	29.98	29.87
6°	28.03	29.84	29.82
9°	27.98	29.92	29.90

FIGURE 2. *Filter holder with 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; 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.

from a black plastic (Delrin [2]). The last three units illustrate the holder with these shutters on. A more detailed dimensional drawing of the filter holder is shown in figure 3. The shutters provide two functions: one is to protect the filter from contamination, the other to detect if stray radiant energy (SRE) is produced in the spectrophotometer compartment as a result of reflections generated by the incident beam on the semi-transparent metal layer. The determination of stray radiant energy generated in the sample compartment of the spectrophotometer, due to the reflecting propreties of these filters, may be assessed as follows: A background signal may be measurable when the instrument shutter at the photomultiplier tube is closed. Another slightly higher background signal may be detectable with the instrument shutter open and with the filter placed in the beam, in the sample compartment, with both sliding shutters closed. Both of these signals should be very small. A third signal may be detected when the front sliding shutter at the filter holder is removed and the rear sliding shutter is closed. If under these circumstances a signal is detected, it is very likely due to SRE produced by reflections resulting from the semi-transparent mirror which scatter from the walls of the cell compartment. This should also be low in magnitude. The transmittance of the filter is measured where both sliding shutters at the filter holder are removed.

Under these circumstances a source of systematic error can be from multiple reflections between the lenses in the instrument and the filter surfaces [5]. An indication of the existence and magnitude of such interreflection phenomena can be obtained by comparing the differences between the transmittance measurements and the certified values for SRM 930 and 931 to the corresponding differences for the inconel-on-fused silica filters.

Each set is made from three filters and one blank placed in individual metal holders which are provided with the front and rear sliding shutters. The selection of inconel as the semi-transparent metal layer was made on the basis of its relatively good optical neutrality in the spectral range from 250 nm to 700 nm. The fused silica substrate is of optical quality and non-fluorescent. All the silica filters, including the blank, were ground and polished at the same time and together to a parallelism of 0.02 mm and a flatness of less than 2 fringes (mercury 546.1 nm). The nominal dimensions are 30.5 mm by 10.4 mm by 2 mm thick, and the nominal transmittances of these filters are 1 percent; 20 percent; 30 percent; and 90 percent.[3] The transmittances of each set were measured at 250 nm, 300 nm, 340 nm, 400 nm, 440 nm, 465 nm, 500 nm, 546.1 nm, 590 nm, and 635 nm. Sets of these filters were sent to the manufacturers of spectrophotometers for evaluation and tests on the individual instruments. The results of these

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[2] In order to describe materials and experimental procedures adequately, it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Bureau of Standards, nor does it imply that the particular product or equipment is necessarily the best available for that purpose.

[3] The filter holders and the evaporated inconel-on-fused silica filters were made in the NBS Instrument Shops.

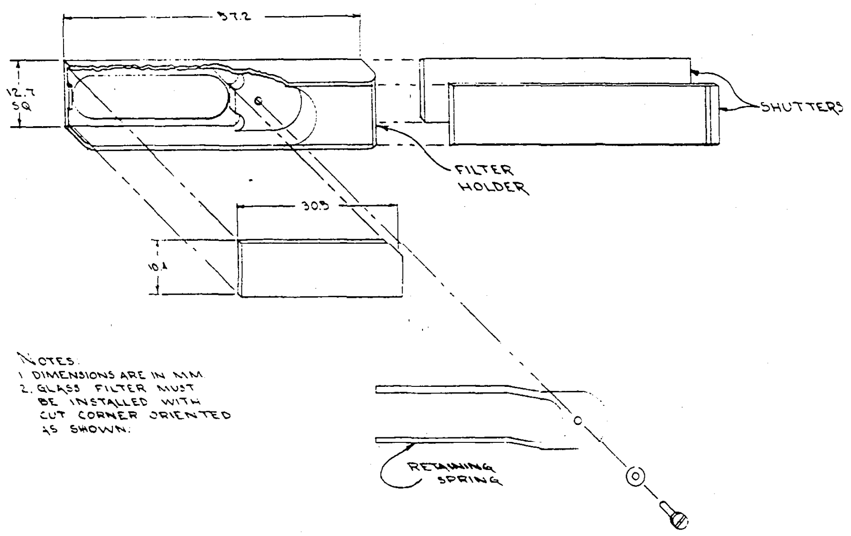

FIGURE 3. *Details of the filter holder with shutters.*

Nominal dimensions are in millimeters.

TABLE IV. *Percent transmittance (%T) measured on four inconel-on-fused silica filters at 10 wavelengths and on the NBS-IMR high-accuracy spectrophotometer and on two conventional instruments A and B*

%T

Wavelength nm / Instrument	250	300	340	400	440	465	500	546	590	635
NBS-IMR High-accuracy Spectrophotometer	1. 45 21. 39 28. 68 91. 42	1. 81 21. 27 29. 92 92. 34	1. 86 20. 33 30. 20 92. 66	1. 94 18. 93 29. 96 92. 90	2. 04 18. 33 29. 70 93. 01	2. 13 18. 09 29. 55 93. 05	2. 27 17. 90 29. 44 93. 11	2. 49 17. 83 29. 44 93. 16	2. 70 17. 86 29. 49 93. 19	2. 90 17. 95 29. 57 93. 23
Spectrophotometer A	1. 53 21. 37 28. 67 91. 59	1. 84 21. 24 29. 87 92. 60	1. 93 20. 31 30. 19 93. 32	2. 00 18. 91 29. 95 93. 20	2. 12 18. 29 29. 70 93. 30	2. 20 18. 07 29. 58 93. 30	2. 34 17. 89 29. 49 93. 42	2. 55 17. 82 29. 46 93. 46	2. 75 17. 84 29. 52 93. 50	2. 95 17. 92 29. 60 93. 58
Spectrophotometer B	1. 49 21. 6 28. 8 91. 4	1. 85 21. 5 30. 0 92. 6	1. 90 20. 5 30. 2 92. 6	1. 97 19. 1 30. 0 93. 1	2. 07 18. 5 29. 9 93. 3	2. 16 18. 3 29. 7 93. 3	2. 31 18. 1 29. 5 93. 3	2. 53 18. 0 29. 5 93. 3	2. 83 18. 3 29. 9 93. 9	3. 06 18. 5 30. 0 93. 9

tests will permit to establish the usefulness of these filters as SRM's in spectrophotometry.

In the mean time comparative measurements were performed on two conventional spectrophotometers available at NBS, and the results are assembled in table IV. These results are preliminary measurements and should be considered with caution. The data seem to indicate, however, that the evaporated metal-on-fused silica filters may be an acceptable material for use as transfer standards in spectrophotometry.

NOTE.—The semi-transparent metallic surface of the filters described in this paper is not protected from environmental exposure and careless handling. A solution to this problem was found recently. It consists in placing on top of the fused silica plate carrying the semi-transparent evaporated metal layer a clear fused silica plate, about 1.5 mm thick, adequately ground and polished, to achieve an *optical contact* with the evaporated semi-transparent metal layer surface. The two fused silica plates are slightly beveled, and an optical cement is applied to protect the edges. Under these conditions the two fused silica plate assembly, with the semi-transparent evaporated metal layer in between, behaves optically as if it were a single semi-transparent plate, and provides full protection of the metal layer. Several sets of these new filters were made for evaluation in actual working conditions.

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(Paper 80A4-909)

APPENDIX V

JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 77A, No. 6, November–December 1973

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

$$\tau = T_M + \Delta T. \tag{1}$$

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.

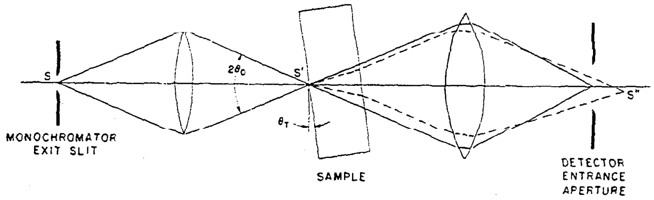

FIGURE 1. *Sample-compartment optics of a focused-beam spectrophotometer.*

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

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

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

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

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

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

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

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

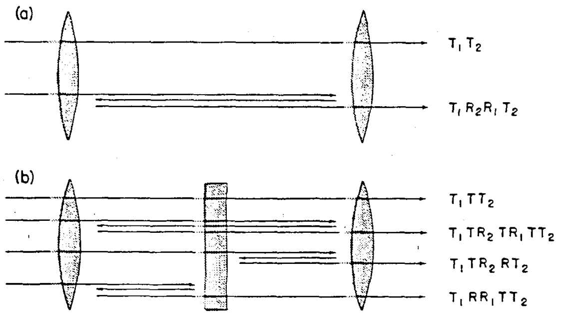

FIGURE 2. *Reflected beams in a spectrophotometer with lenses.*

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

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

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

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

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.

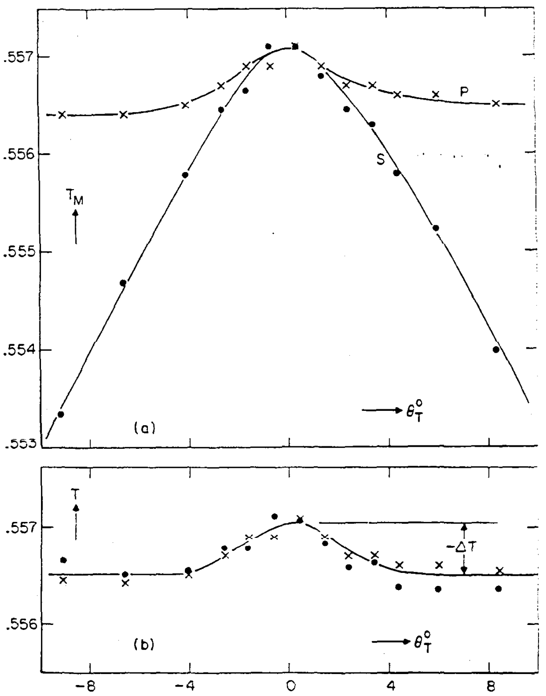

FIGURE 3. *(a) Measured transmittance* T_M *versus tilt angle* θ_T *for 55 percent filter in* S *and* P *polarized light at* $\lambda = 574$ *nm.*
(b) The same data after application of tilt correction.

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

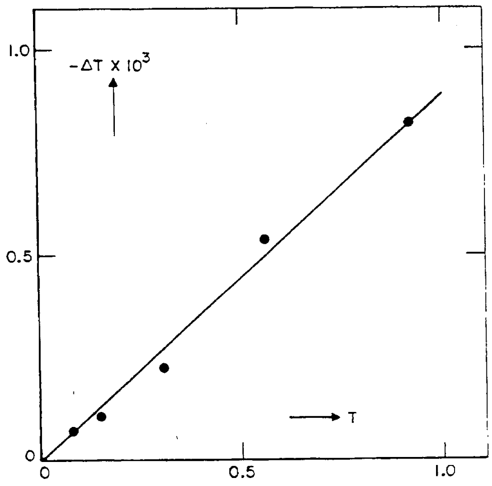

FIGURE 4. *Reflection correction* ΔT *versus* T *for* $\lambda = 574$ *nm.*

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 ± 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

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

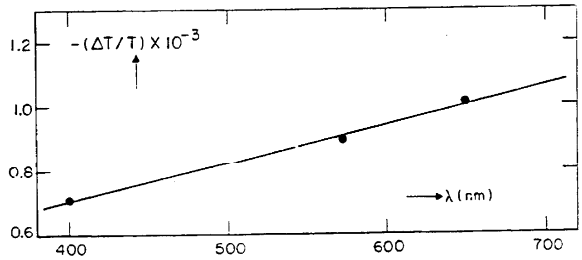

FIGURE 5. *Reflection correction* ΔT *versus* λ *for* T = *0.92*

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

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

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)

U.S. Department of Commerce
Juanita M. Kreps
Secretary
National Bureau of Standards
Ernest Ambler, Acting Director

APPENDIX VI

National Bureau of Standards
Certificate
Standard Reference Material 930D
Glass Filters for Spectrophotometry

R. Mavrodineanu and J. R. Baldwin

This Standard Reference Material is intended as a reference source for the verification of the transmittance and absorbance scales of spectrophotometers. It consists of three individual glass filters in their metal holders and one empty filter holder. The holders are provided with shutters to protect the glass filters when not in use. These shutters must be removed at the time of measurements and be replaced after the measurements have been completed. Each filter bears an identification number, and the upper left corner has been removed to indicate correct placing in the metal holder.

Filter & Set Ident. Number	TRANSMITTANCE (T)					TRANSMISSION DENSITY ($-\log_{10}T$)				
	Wavelength and (Bandpass) nm					Wavelength and (Bandpass) nm				
	440.0 (2.2)	465.0 (2.7)	546.1 (6.5)	590.0 (5.4)	635.0 (6.0)	440.00 (2.2)	465.0 (2.7)	546.1 (6.5)	590.0 (5.4)	635.0 (6.0)

Date of Certification:

The transmittance values (T) can be converted to percent transmittance (%T) by multiplying by 100. The transmission densities are calculated from the measured transmittance (T). These values should be indicated by the absorbance scale of the spectrophotometer if the filters are measured against air. The transmittance values given were measured against air at an ambient temperature of 23.5 °C.

The transmittance values are estimated to be accurate to within ±0.5 percent at the time of certification. This uncertainty includes the effects of the random and systematic errors of the calibration procedure, as well as possible transmittance changes of the filters during the period of calibration.

Aging of the glass may cause some filters to change transmittance by about ±1 percent over a period of approximately one year from the date of calibration. Improper storage or handling of the filters may also cause changes [5]. 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. In cases where verification is desirable, the filters should be returned to the National Bureau of Standards for cleaning and recalibration.

This Standard Reference Material was issued with the assistance and advice of K. D. Mielenz and J. R. DeVoe.

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 T. W. Mears and R. W. Seward.

Washington, D.C. 20234
August 1, 1977

(over)

J. Paul Cali, Chief
Office of Standard Reference Materials

The transmittance measurements were made using the high-accuracy spectrophotometer designed and built at the NBS Institute for Materials Research [1]. This instrument represents the primary transmittance standard; its transmittance accuracy was established using the double-aperture method of linearity testing [1,3,5,6]. The estimated standard deviation obtained from a set of 20 measurements of the high-accuracy spectrometer used for transmittance measurements on glass filters of the SRM 930 type is 5×10^{-5} transmittance units for transmittance between 0.1 and 0.3. The bounds of the systematic error of the instrument are estimated to be $\pm 10^{-4}$ transmittance units.

The neutral glasses for the filters were provided by Schott of Mainz, Germany, and are designated as "Jena Color and Filter Glass." The glass material was prepared by the manufacturer especially for SRM 930. It was fine-annealed and was selected for best homogeneity and minimum of inclusions and striae. The glass filters were aged at NBS for about one year prior to certification. They are of the type NG-4 and NG-5, and their nominal transmittances are 10, 20, and 30 percent [2,5]. The glasses were selected to provide a means to verify the transmittance scale of conventional spectrophotometers at three levels. 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). The empty filter holder is provided to be used in the reference beam of the spectrophotometer so that approximately equivalent conditions of stray radiations are achieved for both beams.

The transmittance of the filters depends upon the intrinsic properties of the material, wavelength, spectral bandpass, geometry of the optical beam, temperature, and positioning of the filter. A change of ambient temperature of 1 or 2 °C from 23.5 °C will not significantly affect the calibration [5]. Changes in the transmittance may be caused by surface conditions, aging of the glass, exposure to a harmful atmosphere, or careless handling as indicated on the face of this certificate [2,3,4,5]. The effective spectral bandpasses used to determine the certified values are given on the face of the certificate and the transmittance measurements are made by producting 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 glass filter. The filters were measured in the spectrophotometer in a position perpendicular to the incident light beam as shown in the attached figure.

SRM 930D 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 glass filter surface with particulate matter due to static charges is minimized through the metallic nature of the 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.

Prior to certification measurements, each filter was examined for surface defects and thorougly cleaned [5]. 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 degraded the accuracy of the certified values. As the Standard Reference Material is a transfer standard, the only means available to verify its integrity is remeasuring its transmittance with a primary standard instrument similar to that used in this certification [1,4,5]. In most cases where verification, or recertification, of the transmittance values is desirable, it will be most expeditious to return the filters to the National Bureau of Standards for measurement. Prior to shipment, the NBS Office of Standard Reference Materials should be contacted regarding the conditions and cost of verification and/or recertification.

We wish to acknowledge the cooperation of George N. Bowers, Jr., M.D., of Hartford Hospital, Hartford, Connecticut; Royden N. Rand, Ph.D., of the Eastman Kodak Co. Research Laboratories, Rochester, New York; and Donald S. Young, M.D., Ph.D., of the National Institutes of Health, Bethesda, Maryland.

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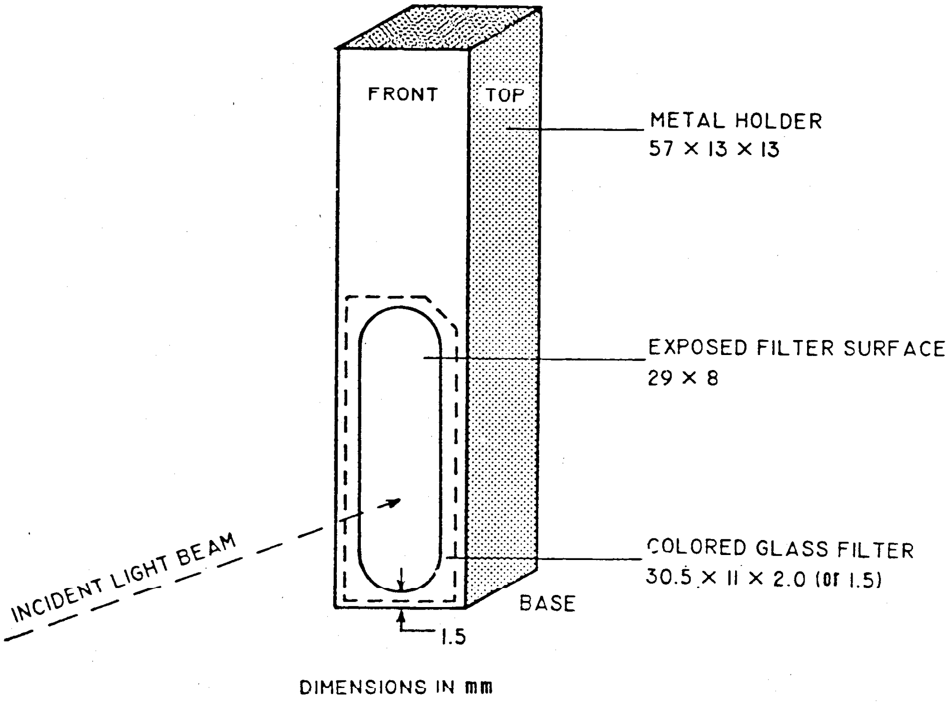
3. K. S. Gibson, Spectrophotometry, NBS Circ. 484 (Sept. 1949).

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

5. R. Mavrodineanu and J. R. Baldwin, Glass Filters as a Standard Reference Material for Spectrophotometry-Selection, Preparation, Certification, Use, SRM 930, NBS Special Publication 260-51, U.S. Government Printing Office, Washington, D.C. 20402, 1975.

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

METAL HOLDER FOR THE COLORED GLASS FILTERS*



*Shutters not illustrated.

U.S. Department of Commerce
Elliot L. Richardson,
Secretary

National Bureau of Standards
Ernest Ambler, Acting Director

National Bureau of Standards
Certificate

Standard Reference Material 2030

Glass Filter for Transmittance Measurement

R. Mavrodineanu and J. R. Baldwin

This Standard Reference Material is intended as a reference source for one-point verification of the transmittance and absorbance scales of spectrophotometers at the given wavelength and measured transmittance. It consists of one glass filter in its holder and one empty filter holder. The filter bears an identification number. For protection, the metal holder is provided with two shutters that should be removed during measurements.

The transmittance, T, at λ 465.0 nm and for a spectral bandpass of 2.7 nm is: ________________. The corresponding transmission density, $-\log_{10}T$, is: ________________.

Date of Certification: ________________________________.

The transmittance value (T) can be converted to percent transmittance (%T) by multiplying by 100. The transmission density is calculated from the measured transmittance (T). This value should be indicated by the absorbance scale of the spectrophotometer if the filter is measured against air.

The transmittance value given was measured against air at an ambient temperature of 23.5 °C, and is estimated to be accurate to within ±0.5 percent at the time of certification. This uncertainty includes the random and systematic errors of the calibration procedure, as well as transmittance changes of the filter during the period of calibration.

It is possible that aging of the glass may cause some filters to change transmittance by about ±1 percent over a period of approximately 1 year from the date of calibration. Improper storage or handling of the filter may also cause changes [5]. In cases where verification is desirable, the filter should be returned to the National Bureau of Standards for cleaning and recalibration.

It is recommended that the filter in the holder be handled only by the edges and with soft plastic (polyethylene) gloves and optical lens tissue. When not in use, it should be stored in its holder, with the shutters on, and in the box provided for this purpose. Extended exposure to laboratory atmosphere and dusty surroundings should be avoided.

This Standard Reference Material was issued with the assistance and advice of K. D. Mielenz and J. R. DeVoe.

The technical and support aspect involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. W. Seward.

Washington, D.C. 20234
September 23, 1976

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

The transmittance measurements were made using the high-accuracy spectrophotometer designed and built at the Institute for Materials Research, National Bureau of Standards [1]. This instrument represents the primary transmittance standard; its transmittance accuracy was established using the double-aperture method of linearity testing [1,3,5,6]. The reproducibility (relative standard deviation obtained from a set of 20 measurements) of this high-accuracy spectrometer for transmittance measurements on glass filters similar to the one used to produce this SRM, is approximately 0.02 percent.

The combined uncorrected systematic error of the instrument is estimated to be not more than $\pm 10^{-4}$ transmittance units.

As indicated on the face of this certificate, SRM 2030 is intended to be used as a one-point verification of the transmittance (absorbance) scales of spectrophotometers. If these scales require verification at other wavelengths and transmittances, "Glass Filters for Spectrophotometry," SRM 930c or subsequent issues, should be used.

The neutral glass for the filter was provided by Schott of Mainz, Germany, and is designated as "Jena Color and Filter Glass " [2,5].

The exposed surface of the glass is approximately 29 × 8 mm, measuring from a point 1.5 mm above the base of the filter holder (see figure). The empty filter holder is provided to be used in the reference beam of the spectrophotometer so that approximately equivalent conditions of stray radiations are achieved for both beams.

The transmittance of the filter depends upon the intrinsic properties of the material, spectral bandpass, wavelength, geometry of the optical beam, temperature, and positioning of the filter. A change of ambient temperature of 1 or 2 °C from 23.5 °C will not significantly affect the calibration [5].Changes in the transmittance may be caused by surface conditions, aging of the glass, exposure to a harmful atmosphere, or careless handling as indicated on the face of this certificate [2,3,4,5]. The effective spectral bandpass used to determine the certified value is given on the face of the certificate and the transmittance measurements are 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 glass filter. The filter was measured in the spectrophotometer in a position perpendicular to the incident light beam as shown in the attached figure.

Prior to certification measurements, the filter was examined for surface defects and thoroughly cleaned [5]. 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 degraded the accuracy of the certified value. Because the Standard Reference Material is a transfer standard, the only means available to verify its integrity is remeasuring its transmittance with a primary standard instrument similar to that used in this certification [1,4,5]. In most cases where verification, or recertification, of the transmittance value is desirable, it will be most expeditious to return the filter to the National Bureau of Standards for measurement. Prior to shipment the NBS Office of Standard Reference Materials should be contacted regarding the conditions and cost of verification and/or recertification.

REFERENCES

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

[2] R. Mavrodineanu, Solid Materials to Check the Photometric Scale of Spectrophotometers, NBS Tech. Note 544, O. Menis and J. I. Shultz, ed., pp 6-17, U.S. Government Printing Office, Washington, D.C. 20402 (Sept. 1970), ibid NBS Tech. Note 584, pp 2-21 (December 1971).

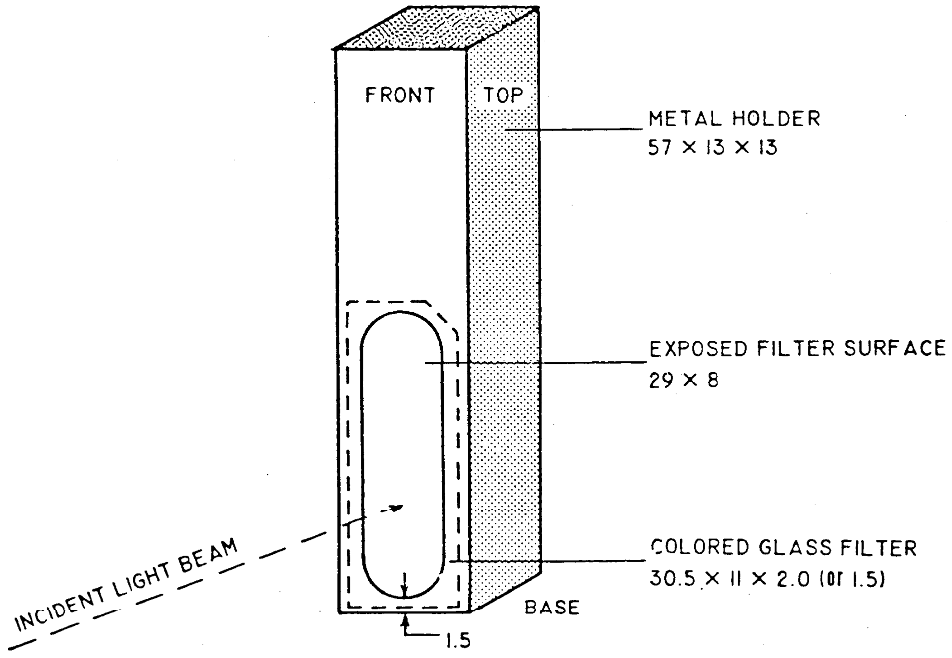
[3] K. S. Gibson, Spectrophotometry, NBS Circ. 484 (Sept. 1949).

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

[5] R. Mavrodineanu and J. R. Baldwin, Glass Filters as a Standard Reference Material for Spectrophotometry-Selection, Preparation, Certification, Use SRM 930, NBS Special Publication *260-51*, U.S. Government Printing Office, Washington, D.C. 20402, (1975).

[6] K. D. Mielenz and K. L. Eckerle, Spectrophotometric Linearity Testing Using Double-Beam-Aperture Method, Appl. Optics, **11**, 2294-2303 (1972).

METAL HOLDER FOR THE COLORED GLASS FILTERS



DIMENSIONS IN mm

U.S. Department of Commerce
Juanita M. Kreps
Secretary
National Bureau of Standards
Ernest Ambler, Acting Director

National Bureau of Standards
Certificate
Standard Reference Material 931b
Liquid Absorbance Standards for Ultraviolet and Visible Spectrophotometry

R. W. Burke and E. R. Deardorff

This Standard Reference Material is certified as solutions of known net absorbance at specific spectral wavelengths. It is intended primarily for use in the calibration and checking of accuracy of the photometric scale of narrow bandpass spectrophotometers employed in clincial analysis and for routine critical evaluation of daily working standards used in clinical spectrophotometry. This Standard Reference Material is applicable for calibrating those instruments that provide an effective spectral bandpass of 1.5 nm or less at 302 nm, 2.0 nm or less at 395 nm, 3.3 nm or less at 512 nm and 8.5 nm or less at 678 nm [1].

Net Absorbance[a]

	Wavelength and (Bandpass), nm			
Filter	302(1.0)	395(1.7)	512(2.0)	678(6.5)
"I" - "Blank"	0.306 ± 0.003	0.302 ± 0.003	0.300 ± 0.003	0.115 ± 0.002
"II" - "Blank"	.607 ± .004	.605 ± .004	.602 ± .004	.230 ± .003
"III" - "Blank"	.891 ± .005	.902 ± .005	.899 ± .005	.342 ± .003

[a] Net absorbances ("I" - "Blank", "II" - "Blank", and "III" - "Blank") were determined using 10.00 mm cuvettes (SRM 932) at 25 °C. See Instructions for Use.

Absorbance measurements were performed on a high precision double-beam spectrophotometer equipped with a double monochromator. The accuracy of the photometric scale of this instrument was established with the NBS high-accuracy spectrophotometer described by Mavrodineanu [2]. The uncertainties of the certified values include all known sources of possible systematic error and the 95 percent confidence level for the mean.

While no long-term stability studies have been made on this lot (931b), studies on previous lots (931 and 931a) over a three-year period showed no degradation of the material when stored in the original sealed ampoules. Nevertheless, until additional information is forthcoming, it is recommended that this material not be used after three years from the date of purchase.

The overall direction and coordination of technical measurements leading to certification were performed under the chairmanship of I. L. Barnes.

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 W. P. Reed.

Washington, D.C. 20234
November 10, 1977

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

Temperature Dependence

Absorbances at various temperatures (17 to 35 °C) may be calculated using the equation

$$A_t = A_{25}[1+C_A(t-25)],$$

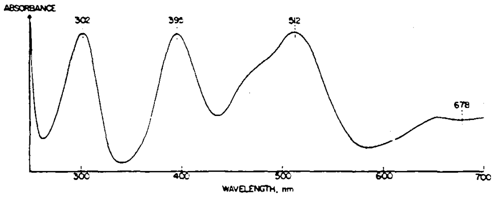
where: A_t = Absorbance at temperature t (°C)
A_{25} = Absorbance certified at 25.0 °C
C_A = Fractional change in absorbance per °C

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

Preparation of Filters

The filters were prepared by dissolving high-purity cobalt and nickel in a mixture of nitric and perchloric acids. The absorbance spectrum of the resulting solution is shown in the following figure. The maxima 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 $Ni(H_2O)_6^{++}$. The pH of these solutions is about 1.



Warning

This Standard Reference Material is intended for "in vitro" diagnostic use only.

Instructions for Use

This material is for use as a spectrophotometric absorbance standard.

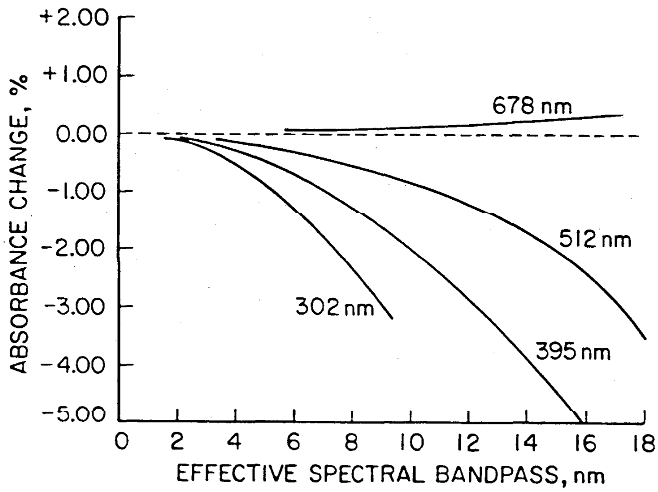
1. Select two clean 10.00 mm cuvettes free of scratches. At least one should be fitted with a ground glass or Teflon stopper to minimize evaporation. Reserve it for all sample measurements.
2. Mark each of the cuvettes to assure the same orientation in the spectrophotometer.
3. Place the cuvettes in their respective holders 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 optical mismatch of the cuvettes at 302, 395, 512, and 678 nm, using the spectral bandpass limitations given on the face of the certificate.
5. Empty the cuvettes by suction without removing them from their holders, refill with distilled water and measure the absorbances again at each of the above wavelengths.

6. Repeat the emptying and refilling operation until constant absorbance readings are obtained.
7. Using the liquid filters provided, measure, in turn, the absorbance of the "Blank", "I", "II", and "III" against distilled water. Shake each ampoule before opening to remix any condensate which may have collected in the neck. (The ampoules have been prescored directly below the gold band to facilitate opening.)
8. Subtract the appropriate "Blank" reading from the absorbances obtained for "I", "II", and "III". These net absorbances should agree with the certified values within the uncertainties specified. Consult the manufacturer of the instrument if they do not.

The above instructions are for use with the standard 10-mm rectangular cuvette. For calibration of the several spectrophotometric systems used in various automated instruments, the user is referred to the instruction manual for the particular instrument.

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. 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 insure that the measured absorbances are not significantly different from the certified values, the following restrictions are placed on the size of the spectral bandpass selected: To obtain ±0.1 percent of the true value, 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. For ±0.2 percent, the respective bandpasses should not exceed 2.2, 2.9, 4.8, and 12.3 nm. Additional information on the effect of spectral bandpass on the absorbances of these filters is given in the figure below. These curves are not to be used, however, to correct the measured absorbances.



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. In addition, it is recommended that this Standard Reference Material not be used after three years from the purchase date.

References

[1] R. W. Burke, E. R. Deardorff, and O. Menis, J. Research, Nat. Bur. Stand. **76A**, 469-482 (1972).

[2] R. Mavrodineanu, J. Research, Nat. Bur. Stand. **76A**, 405-425 (1972).

Note: The above papers 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. Government Printing Office, Washington, D.C. 20402, 1973.

APPENDIX IX

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards
Certificate

Standard Reference Material 932

Quartz Cuvette for Spectrophotometry

R. Mavrodineanu and J. W. Lazar

This Standard Reference Material consists of a single, accurately calibrated cuvette that is issued for use in the production of accurate spectrophotometric data on liquids. The design and nominal dimensions of the all-quartz cuvette are shown in Figure 1. The pathlength of the cuvette is defined by the distances between the two optically transparent windows taken at several heights within the cuvette. Cuvettes issued as Standard Reference Material 932 have a nominal pathlength of 10 mm. The pathlength and parallelism are certified with an uncertainty of ±0.0005 mm as determined by measurements (at 20°C) taken at the positions indicated below.

Cuvette number is issued with this certificate. For this cuvette the following measurements were obtained.

Height mm	Pathlength mm

The cuvette must be handled with great care and should be held only by the frosted-quartz side windows. When not in use, it should be stored in the container provided for this purpose. Extended exposure to laboratory atmosphere and dusty surroundings is to be avoided.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of O. Menis and J. A. Simpson.

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 T. W. Mears.

Washington, D.C. 20234
August 2, 1978
(Revision of certificates
dated 11-5-73 and 6-16-77)

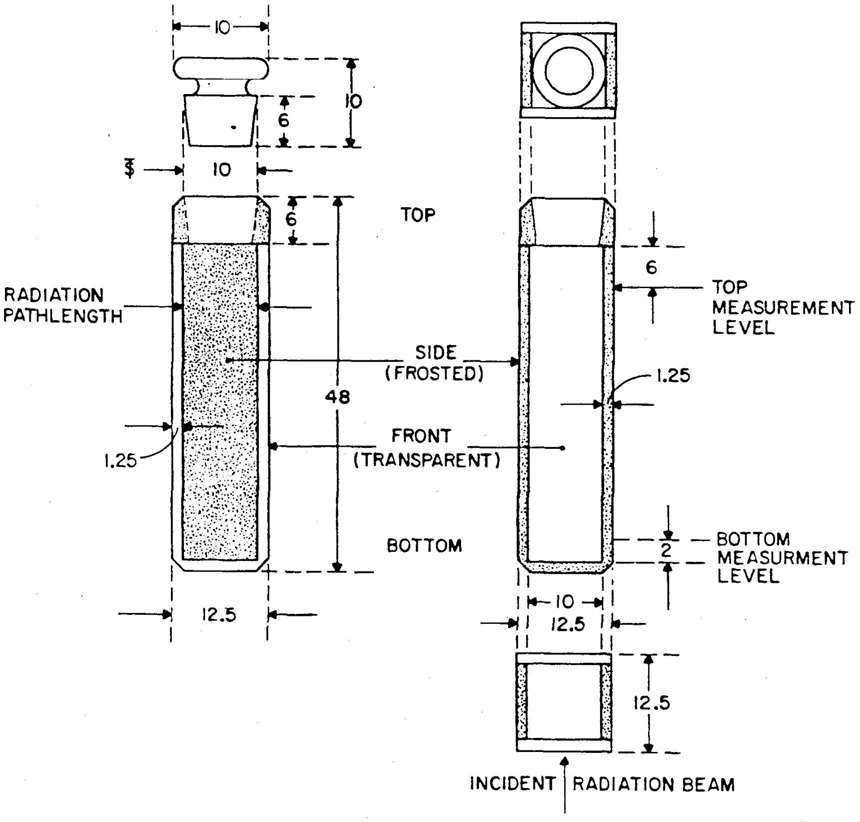
J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

The original cuvettes were designed and produced at the National Bureau of Standards using special techniques and non-fluorescent optical-quality fused silica as described in NBS SP 260-32 [1]. The transparent windows are attached to the body of the cuvette by direct fusion, and the unit was stress-relieved by annealing. The overall flatness of each surface of a transparent window is within two fringes (546 nm Hg line). The radiation pathlength measurements of the cuvette were performed using electronic feeler-gauge type instruments capable of a resolution of 5 parts in 10^6. The development and production of SRM 932 is a result of the combined efforts of the Center for Analytical Chemistry, the Center for Mechanical Engineering and Process Technology, and the Instrument Shops Division. E. P. Muth and E. I. Klein designed and assembled the cuvettes, respectively. Since January 1977, the cuvettes issued as SRM 932 have been prepared by Starna, Ltd., Dayenham, Essex, U. K., in accordance with NBS techniques and specifications described in NBS SP 260-32. The radiation pathlength measurements of all of these cuvettes, regardless of manufacturer, have been performed by E. G. Erber of the Mechanical Processes Division.

Reference:

[1] Mavrodineanu, R., and Lazar, J. W., Standard Reference Materials: Standard Quartz Cuvettes for High Accuracy Spectrophotometry, Nat. Bur. Stand. (U.S.), Spec. Publ. 260-32 (December 1973). Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, 55 cents.



APPENDIX X

U.S. Department of Commerce
Juanita M. Kreps
Secretary
National Bureau of Standards
Ernest Ambler, Acting Director

National Bureau of Standards
Certificate

Standard Reference Material 935
Crystalline Potassium Dichromate
for Use as an Ultraviolet Absorbance Standard

R. W. Burke and R. Mavrodineanu

This Standard Reference Material 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 of absorption spectrometers that can provide an effective spectral bandpass of 1.2 nm or less at 235 nm, and 0.8 nm or less at 257, 313, 345, and 350 nm. 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 gives the certified values of ϵ_a in $kg{\cdot}g^{-1}{\cdot}cm^{-1}$ for five concentrations of the SRM 935 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.

Table 1. ϵ_a, Apparent Specific Absorbance,[a] $kg{\cdot}g^{-1}{\cdot}cm^{-1}$

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)[b]	350.0(0.8)	Uncertainty[c]
0.020	12.260	14.262	4.805	10.604	10.672	± 0.034
.040	12.304	14.318	4.811	10.603	10.682	± .020[d]
.060	12.347	14.374	4.816	10.602	10.692	± .020[d]
.080	12.390	14.430	4.821	10.601	10.701	± .020[d]
.100	12.434	14.486	4.827	10.600	10.711	± .020[d]

[a] 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.

[b] 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.

[c] 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, the uncertainties given include all known systematic errors and the 95 percent confidence interval of the mean.

[d] At wavelength 313.0 nm, the uncertainty is reduced to ±0.010.

*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.

Washington, D.C. 20234
June 1, 1977

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

The overall direction and coordination of the technical measurements leading to this certificate were performed under the joint chairmanship of I. L. Barnes and J. R. DeVoe.

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. W. Seward.

We wish to acknowledge: The contributions of 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.

PREPARATION AND CERTIFICATION

The details of the preparation and certification of SRM 935 are provided 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 935 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:

$$\epsilon_a = \frac{D_s - D_b}{b \times c} = \frac{A_a}{b \times c} \qquad (1)$$

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 935 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 Analytical Chemistry Division. The purity of SRM 935, expressed as an oxidant, was found to be 99.972 ± 0.005 percent where the uncertainty figure represents the 95 percent confidence interval for the mean based on 11 degrees of freedom. In addition, the material was examind by optical emission spectrometry for trace elemental impurities by J. A. Norris of the NBS Analytical Chemistry Division. The only significant impurities detected were sodium and rubidium. Their concentrations were estimated to be in the range of 0.02 and 0.03 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 935 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 935 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 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 0.100 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, and 0.100 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:

$$A_a = \epsilon_a \times b \times c \tag{2}$$

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
$c = 0.04375\ g{\cdot}kg^{-1}$
$t = 23.5$ °C

From column 6, table 1, the ϵ_a for concentrations of 0.040 and 0.060 $g{\cdot}kg^{-1}$ are 10.682 and 10.692, respectively. The corresponding ϵ_a for $c = 0.04375\ g{\cdot}kg^{-1}$ is:

$$\epsilon_a = 10.682 + \frac{0.04375 - 0.040}{0.060 \quad 0.040}(10.692 - 10.682)$$

$$\epsilon_a = 10.682 + 0.0019$$

$$\epsilon_a = 10.684$$

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:

$$\Delta A_a = bc\left|\Delta\epsilon_a\right| + \epsilon_a c\left|\Delta b\right| + \epsilon_a b\left|\Delta c\right| \tag{3}$$

To evaluate ΔA_a, $\Delta\epsilon_a$ 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:

$$\Delta A_a = 1(0.044)\ (0.020) + 10.7(0.044)\ (0.0001) + 10.7(1)\ (0.0000088)$$
$$\doteq 0.0010$$

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.

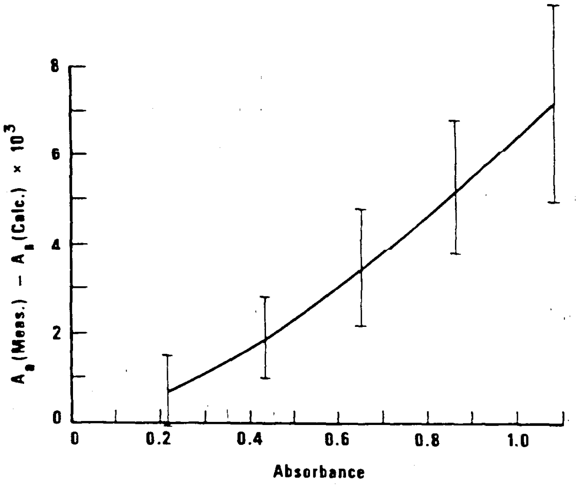


Figure 1. Correction curve for the absorbance scale of a precision spectrometer. The error bars are the sum of the errors arising from the uncertainties in the certified apparent specific absorbances, ϵ_a, cuvette pathlength, b, and concentration, c.

Temperature Correction:

Although ϵ_a values in table 1 are certified at 23.5 °C, SRM 935 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:

$$\epsilon_a^t = \epsilon_a^{23.5}\left[1 + \frac{k}{100}(t - 23.5)\right]$$

where: ϵ_a^t = apparent specific absorbance at temperature t (°C)

$\epsilon_a^{23.5}$ = apparent specific absorbance certified at 23.5 °C.

k = temperature coefficient, percent per °C.

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).
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3. Mavrodineanu, R., An Accurate Spectrophotometer for Measuring the Transmittance of Solid and Liquid Materials, J. Res. Nat. Bur. Stand. (U.S.), **76A** (Phys. and Chem.), No. 5, 405-425 (1972).