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Standard Reference Materials:

GLASS FILTERS AS A STANDARD REFERENCE MATERIAL FOR SPECTROPHOTOMETRY-- SELECTION, PREPARATION, CERTIFICATION, USE SRM 930

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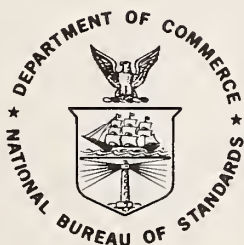
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Standard Reference Materials:

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

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

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

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

1. GENERAL

Among the measuring techniques available to the analyst for the detection and determination of a large number of chemical species in a large variety of matrices, spectrophotometry constitutes a valuable tool of major significance. This is due largely to the inherent characteristics of high sensitivity and good specificity of the method, associated with the need for only relatively simple instrumentation and straightforward sample preparation methodology. For these reasons spectrophotometric procedures are used in practically all fields of science, where chemical analytical measurements are required. As mentioned by Rand (1) of 147 analytical procedures used in clinical chemistry laboratories, 84 require the use of spectrophotometry, and of 450,000 analyses per year, performed only in one hospital, 300,000 required measurements by spectrophotometric procedures. In such a laboratory, 800 to 1,000 determinations are made daily by spectrophotometry.

From the information given by Rand in 1972 (1), a conservative estimate of analyses made by spectrophotometry indicates that more than 1,000,000 such tests are performed daily in the clinical laboratories in this country, and this figure increases by approximately 15 percent per year.

These considerations refer to clinical laboratories alone, and to these one should add the numerous other areas such as the general field of scientific research, industry, agriculture, environmental sciences, etc., where spectrophotometry represents a major analytical technique.

In spite of this wide use of spectrophotometry, no suitable standards were available to verify the stability of the spectrophotometer, and no adequate reference material was available to verify the accuracy of the transmittance or absorbance scale of the instrument. This situation is even more surprising when one considers the wide discrepancies obtained in interlaboratory comparisons of spectrophotometric data (2,3,4,5,6,7). Under these circumstances a program was initiated at the National Bureau of Standards (NBS) in the Analytical Chemistry Division of the Institute for Materials Research in July 1969, with the objective to provide the analytical chemist with means to verify that his spectrophotometer functions properly and that it produces reliable and meaningful data. This decision was taken in response to the requests received from scientists using spectrophotometry in all areas of science, and more specifically from the analytical chemists who use spectrophotometry in clinical and pathological laboratories (8).

The planned program was implemented in 1970 through the design and construction, in the Analytical Chemistry Division, of a high-accuracy spectrophotometer (8,10) which was used to produce two Standard Reference Materials (SRM's), SRM 930 (a and b), Glass Filters for Spectrophotometry, and SRM 931, Liquid Filters for Spectrophotometry. These SRM's were issued in 1971. A third SRM 932, Quartz Cuvettes for Spectrophotometry, was added in 1973 and was produced in association with the Optical Physics Division of the Institute for Basic Standards at NBS. SRM 932 was intended to be used in association with SRM 931 and for all measurements requiring accuracy in the determination of transmittance in solutions. A detailed description of this SRM and of the techniques developed at NBS for its production and certification is given in reference 9 which is reproduced in the NBS Special Publication 260-32, issued in December 1973. This publication is available from the U. S. Government Printing Office, Washington, D.C. 20402, under SD Catalog No. C13.10:260-32, price 55 cents.*

SRM 930 (a,b) consists of a set of three glass filters having nominal transmittances of 10, 20, and 30 percent from 440 nm to 635 nm. These glasses are calibrated and certified for optical transmittance at 440.0 nm; 465.0 nm; 590.0 nm; and 635.0 nm. These wavelengths were selected in accordance with the transmission characteristics of the glass. An additional certification at 546.1 nm, corresponding to the mercury green radiation, was provided with the more recent SRM 930b. SRM 930 is a transfer standard reference material which can be used to determine and monitor the short and long term stability of a spectrophotometer and to verify the accuracy of its transmittance and absorbance scales.

This publication is intended as a practical guide for the proper calibration of spectrophotometers and the use of SRM 930 and contains data presented in a simple and straightforward manner. The reader interested in the more fundamental problems associated with high-accuracy spectrophotometry and luminescence measurements is advised to consult the publications listed in reference 10 together with the papers mentioned in those publications. Reprints from several papers closely related to the subject discussed in this publication are reproduced here in the Appendix Section as a convenience to the reader.

* See Appendix 1 for NBS-SRM ordering information.

2. INTRODUCTION

Factors Affecting the Proper Functioning of a Spectrophotometer

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

a. The short and long term stability.

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

b. The wavelength accuracy.

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

c. The spectral bandpass of a spectrophotometer.

This is the spectral interval $\Delta\lambda$ in wavelength which emerges through the exit slit w of the instrument: $\Delta\lambda = w \frac{d\lambda}{dx}$, where $\frac{d\lambda}{dx}$ is the linear dispersion of the spectrophotometer.

It is a parameter which depends on the optical design and of the associated elements: grating, prism, or filters used in the instrument. The magnitude of the spectral bandpass for a specific spectrophotometer over the whole spectral range of the instrument is important information that is provided by the manufacturers of the particular instrument.

d. The accuracy of the transmittance or absorbance scales.

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

e. Stray radiations.

They can originate in the spectrometer and in the sample compartment. The stray radiation produced in the spectrometer is the radiant energy at wavelengths different from those of the nominal spectral bandpass transmitted through the instrument at a particular wavelength. The stray radiation in the sample compartment is the radiant energy which falls on the photosensitive detector without passing through the absorbing sample.

f. Conditions associated with the stability of the analytical sample (color reaction) and its homogeneity.

Dissociation and association reactions, radiation scatter inside the sample, polarization, fluorescence, temperature, particulate matter, and surface conditions can affect, in a significant manner, the accuracy of the measurements.

These conditions are characteristics of the analytical sample and of the chemical reactions involved in the spectrophotometric process and are to a large extent independent of the spectrophotometer used for the measurements. However, since these factors can affect the precision and accuracy of the measurement, they are mentioned here to remind the analytical chemist that he must be aware of their existence, and that he must evaluate their magnitude in the particular analytical process considered before proceeding with the actual measurement. As a result of his knowledge, he must be able to select the most adequate analytical procedure for the matrix and chemical species under consideration, and to establish ways to eliminate, minimize, or compensate for these causes of errors.

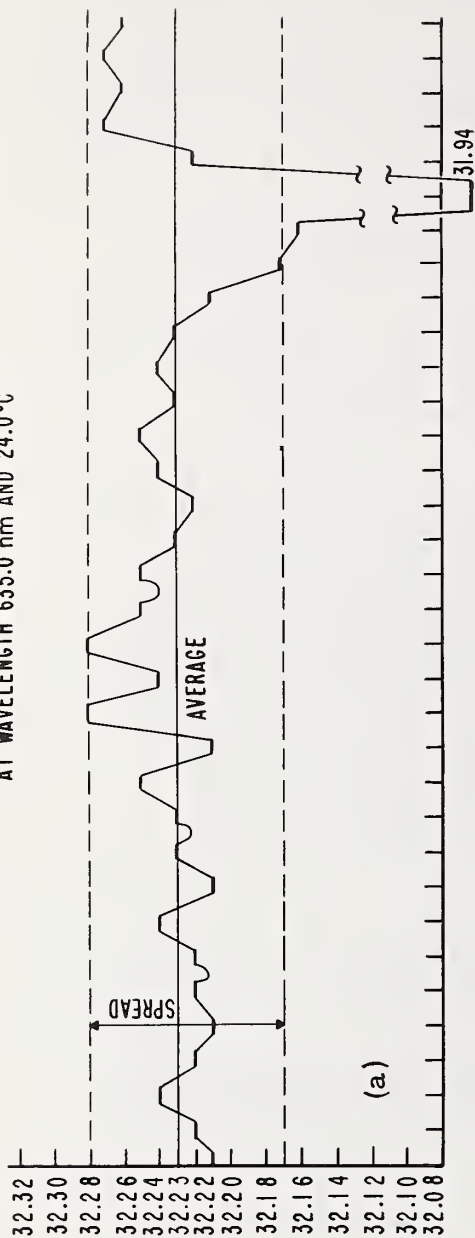
From the factors mentioned above, those which are relevant to the subject discussed in this publication will be examined in more detail.

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

3.1 Short and Long Term Stability

The short and long term stability of a spectrophotometer can be verified and monitored by using glass filters specially selected for this purpose. Stable radiation sources, such as tritium-activated luminescent materials, could be considered for the same purpose (11). The use of such a source, however, is not always possible due mainly to problems associated with the design and operation of the instrument.

AT WAVELENGTH 635.0 nm AND 24.0°C



AT WAVELENGTH 590.0 nm

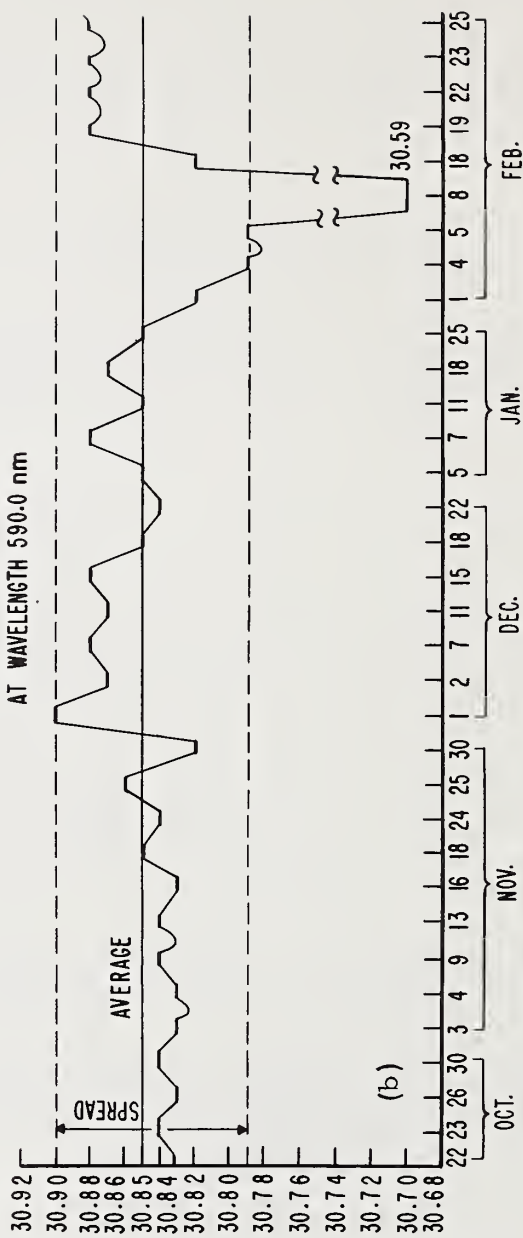


Figure 1. Control chart for a spectrophotometer showing the variation of transmittance as a function of time for a neutral glass filter at 635.0 nm (a) and 590.0 nm (b) and 24.0 °C.

From the several kinds of glass filters which can be used, those constituting SRM 930 (a or b) are most suitable. The optical characteristics of these glass filters are discussed in Section 4; however, since the stability of a spectrophotometer is the first test which should be carried out, we will describe their use now.

As a general rule, it is desirable to place the spectrophotometer in a clean laboratory and in an area where the temperature is as constant and reproducible as possible, protected from direct sunlight, sudden changes of temperature, corrosive atmosphere, dust, and vibration.

The tests should be carried out after the instrument was verified by the manufacturer, and was found to perform well and to meet all the required specifications. After an initial warming-up period, the "0" and "100" reading on the scale is verified, following the procedure described by the manufacturer of the particular instrument, the wavelength dial is set at a selected value, usually the one at which the transmittance of the analytical sample will be determined, e.g. 635.0 nm, and one of the glass filters in its metal holder having the nominal transmittance of 30 percent is inserted in the sample compartment. The reference compartment or "blank" is left empty. The transmittance of the glass filter is measured following the method specified by the manufacturer, and the results recorded. This procedure is repeated at all wavelengths at which the analytical samples will be measured. Similar transmittance measurements are performed using the glass filters having a nominal transmittance of 20 percent and 10 percent. The temperature at which these measurements are made should also be recorded. In this manner, the performance of the instrument is determined over the working spectral range for a transmittance interval and at a temperature which covers most of the conditions of analytical determinations under consideration.

The values obtained are then displayed in a graphical form, by plotting the transmittance found for every wavelength on the ordinate, and on the abscissa the date at which these measurements were made. An example of such a graph is given in figures 1a and b for only two wavelengths: 635.0 nm and 590.0 nm. Similar graphs should be made for the wavelengths of interest and for the 10 percent, 20 percent, and the 30 percent nominal transmittance filters. Since the laboratory in which the measurements shown in figure 1 were made is provided with controls which maintain the surrounding temperature at $24.0\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$, this was recorded on the graphs as a common value for all measurements. When solutions are used, the temperature of the liquid in the cuvette should be determined. Where the temperature changes from measurement

to measurement, its value should be recorded and written on the graph under the corresponding transmittance value. The procedure described above should be performed every time the spectrophotometer is used, before, and preferably after, the analytical work is carried out.

The data plotted in figures 1a and 1b were obtained with a commercial spectrophotometer provided with a quartz prism double spectrometer, and a transmittance scale divided in 1000 units between 0 and 100 transmittance readings. The size of each division and the stability and reproducibility of the instrument is such that it permits visual interpolation between each division, to fractions of a division; hence, the ordinate scale on the graphs (figs. 1a and b) was selected to reflect this resolution.

An examination of the data shows that the stability of the instrument as expressed by the transmittance value, operated at 24.0 °C, and from October 22 to February 5, varied from 32.17 percent T to 32.28 percent T with an average of 32.23 T percent at 635.0 nm. At 590.0 nm the equivalent values were 30.79 percent T and 30.90 percent T with an average of 30.85 percent T. The spread is in both cases 0.11 percent of T. This spread results from the inherent instability of the instrument and of the glass filters used. This situation changed markedly on February 8 when a transmittance of 31.94 percent and 30.59 was found at 635.0 nm and 590.0 nm respectively. Since these values largely exceeded the specified spread established for this particular instrument by the manufacturer, a field engineer from the manufacturer was called in. An examination of the spectrophotometer revealed that a potentiometer was malfunctioning. After replacement of this faulty part the instrument was tested again on February 18, and the transmittance values, measured on the same glass filters, were within the established spread of the instrument, as seen in figures 1a and 1b, indicating that the spectrophotometer was again performing according to its specifications. This example illustrates the usefulness of the short and long term stability tests described in this paragraph since this permits detection and diagnosis of possible malfunctions in an instrument before such malfunctions would affect the validity of measurements. It is obvious that similar control charts can be prepared using absorbance values.

The periodic verification of the stability of spectrophotometers as described above and illustrated in figures 1a and 1b, is used in these laboratories routinely. This procedure is highly recommended to all users of such instruments, and is performed, as has already been mentioned, with the help of specially selected glass filters. It should be added here that the precision of such tests, however, cannot exceed the

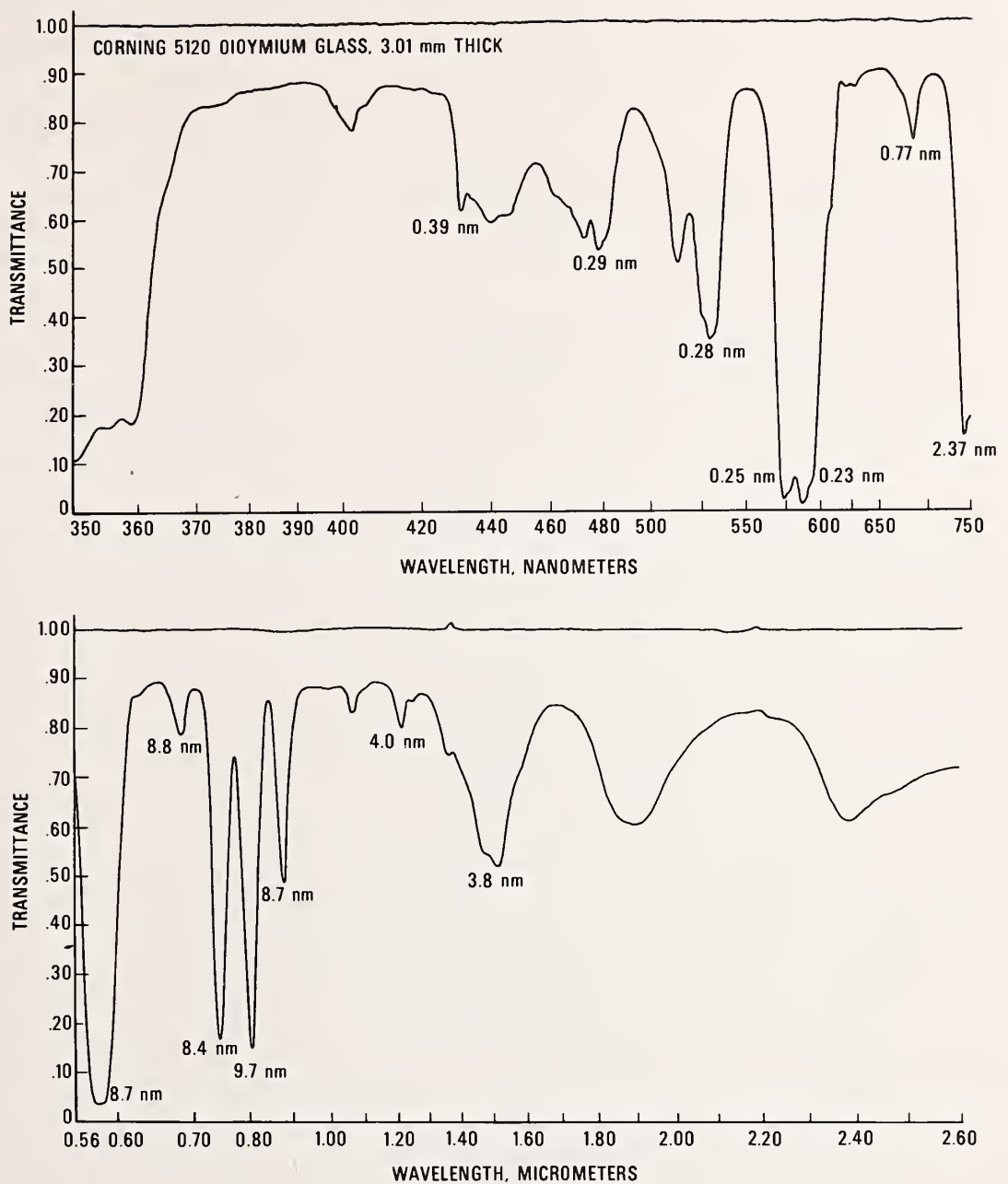


Figure 2. Transmittance of a didymium glass filter. The spectral bandpass used is marked at the corresponding transmittance minimum. Courtesy Corning Glass Works.

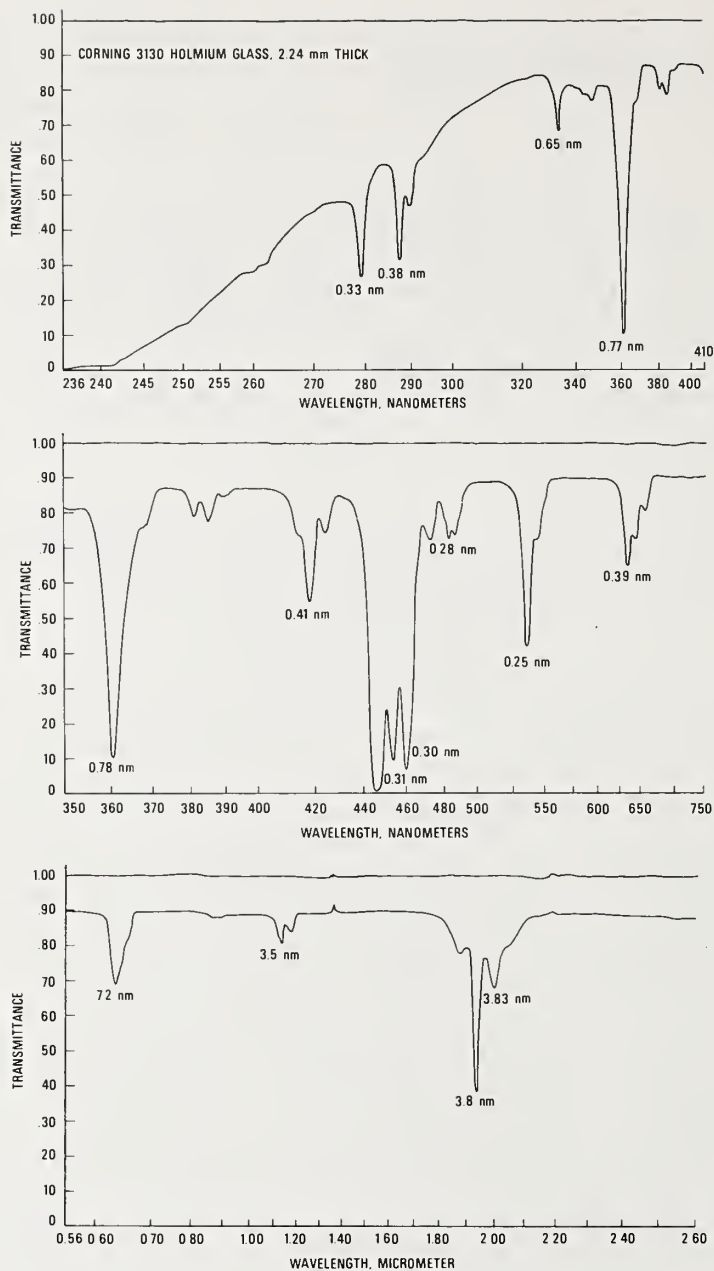


Figure 3. Transmittance of a holmium oxide glass filter. The spectral bandpass used is marked at the corresponding transmittance minimum. Courtesy Corning Glass Works.

stability of the glass filters; this parameter will be discussed in Section 5.1 for the material used in this work.

3.2 Wavelength Accuracy

Although the test discussed in paragraph 3.1, may show that a spectrophotometer exhibits a good stability, large errors in the accuracy of its wavelength scale may produce unreliable measurements.

The wavelength accuracy of a spectrophotometer can be verified by the use of (a) an emission source capable of producing discrete radiations of suitable intensity and adequately spaced throughout the spectral range of interest, e.g., 200 to 800 nm, or (b) by using glass filters with sharp absorption bands.

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

(b) Wavelength calibrations can be made by using a glass filter having a number of strong and narrow absorption or transmission bands suitably spaced over the spectral range of interest. Two materials have been used or suggested for this purpose: glasses containing rare-earth oxides, such as didymium glasses and holmium oxide glasses. They have been used for many years at the National Bureau of Standards. The transmission characteristics of these two glasses are illustrated in figures 2 and 3.

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

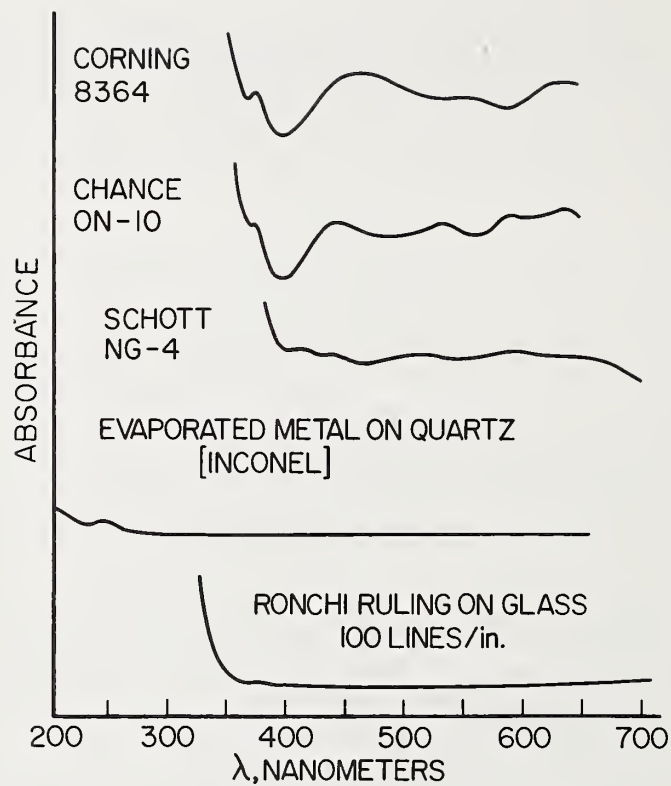


Figure 4. Spectral characteristics for five transparent materials from 200 nm to 700 nm (8).

The Bureau is in the process of certifying as Standard Reference Materials didymium and holmium oxide glasses. These SRM's will have increased wavelength accuracy in comparison to and will replace the didymium and holmium oxide glasses offered by NBS through the Office of Measurement Services. For those who wish further information on this subject, the reader should consult W. H. Venable of the Institute for Basic Standards at NBS.

3.3 Spectral Bandpass

As mentioned in Section 2, the spectral bandpass over the entire spectral range for various slit widths is an instrumental parameter which should be provided by the manufacturer. For spectrophotometers with prisms or gratings, the spectral bandpass ($\Delta\lambda$) is related to reciprocal linear dispersion ($d\lambda/dx$) and slit width (w) by $\Delta\lambda = w \ d\lambda/dx$. For example, for an instrument with a reciprocal dispersion of 15 nm/mm and a slit width of 0.2 mm, the bandpass is 3.0 nm. For prism instruments, the reciprocal dispersion and therefore the bandpass vary with wavelength. The following discussion will be limited to the influence of this often neglected and important parameter on the measurements of transmittance for the glass filters discussed in this publication.

Two types of filters were used having a transmittance which varies only moderately with wavelength: the Chance* ON-10 and Schott NG-4 optically neutral glasses. A neutral glass #8364 produced by Corning was also included in this study. However since this filter produced results similar to those found for the Chance ON-10 glass it will be discussed together with the later glass filter.

The transmission characteristics of these glasses as a function of wavelength in the spectral interval of 350 nm to 700 nm were obtained using a Cary 14 spectrophotometer and an adequate instrumental bandpass. The results are illustrated in figure 4, where it can be seen that the Corning 8364 and Chance ON-10 glasses exhibit similar characteristics. Figure 4 also shows that these glasses have an absorbance, or transmittance, more dependent on wavelength than the Schott NG-4 glass. The transmittance of these last two glasses was then

* The identification of commercial instruments and products is given only to permit reproduction of the work described in this publication. 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.

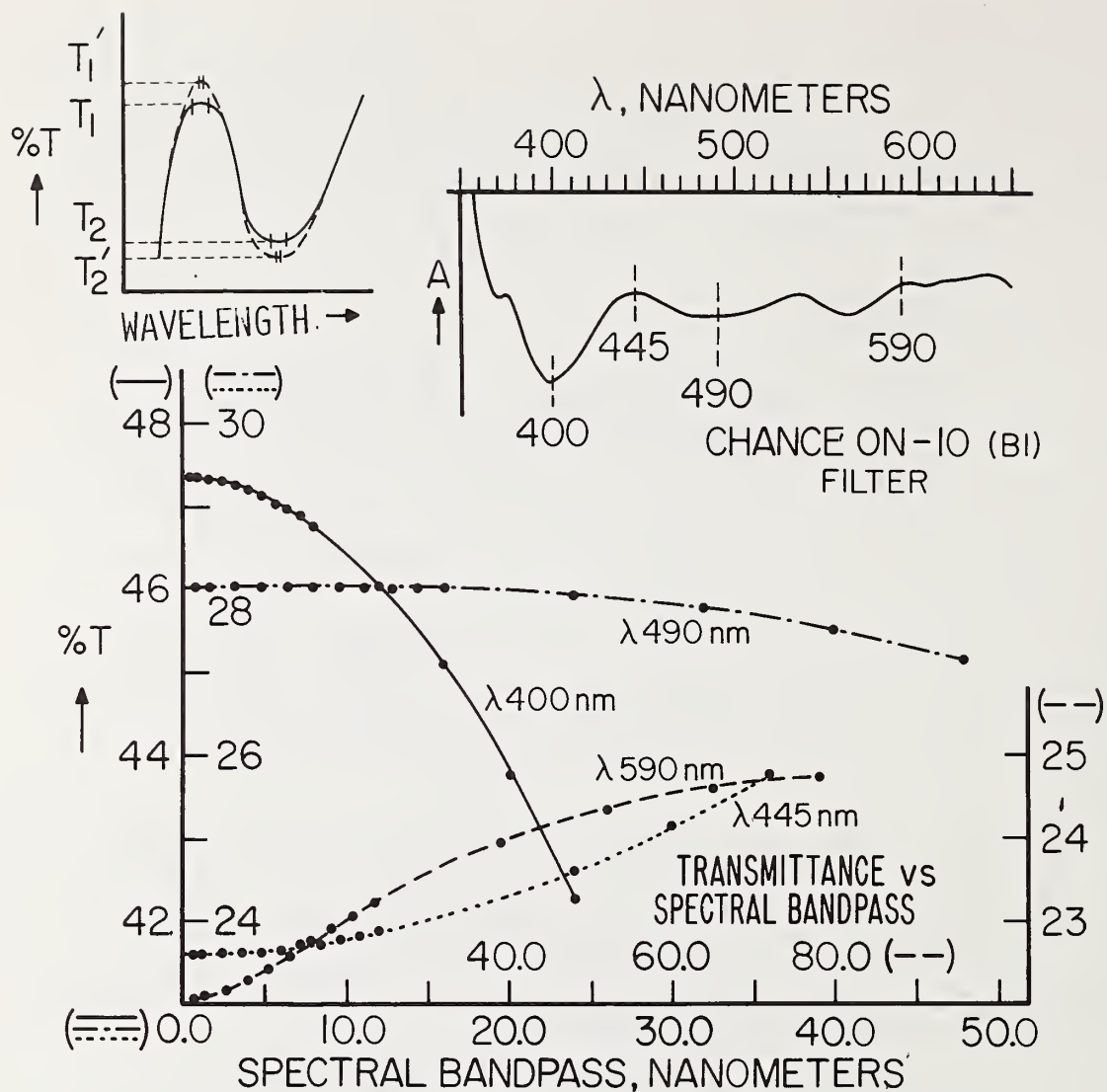
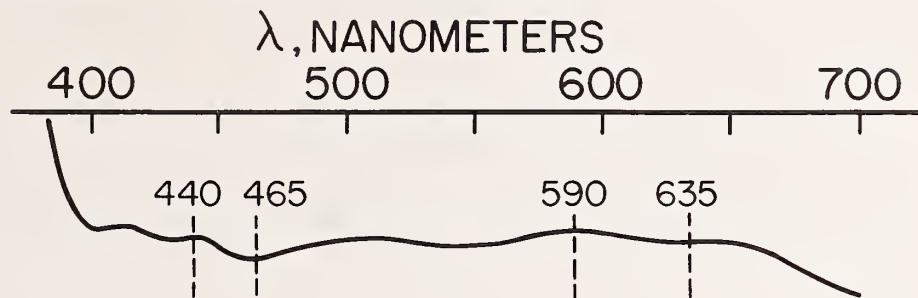


Figure 5. Influence of spectral bandpass on the transmittance of a Chance ON-10 glass filter measured at 400 nm; 445 nm; 490 nm; and 590 nm. The graph at left, upper corner, describes in general the relation between spectral transmittance and spectral bandpass. Measurements made with a smaller bandpass || are susceptible to provide accurate T values when compared with those made with a larger spectral bandpass | | (8).

SCHOTT GLASS FILTER NG-4



OPTICAL TRANSMITTANCE VERSUS SPECTRAL BANDPASS FOR A SCHOTT GLASS FILTER NG-4

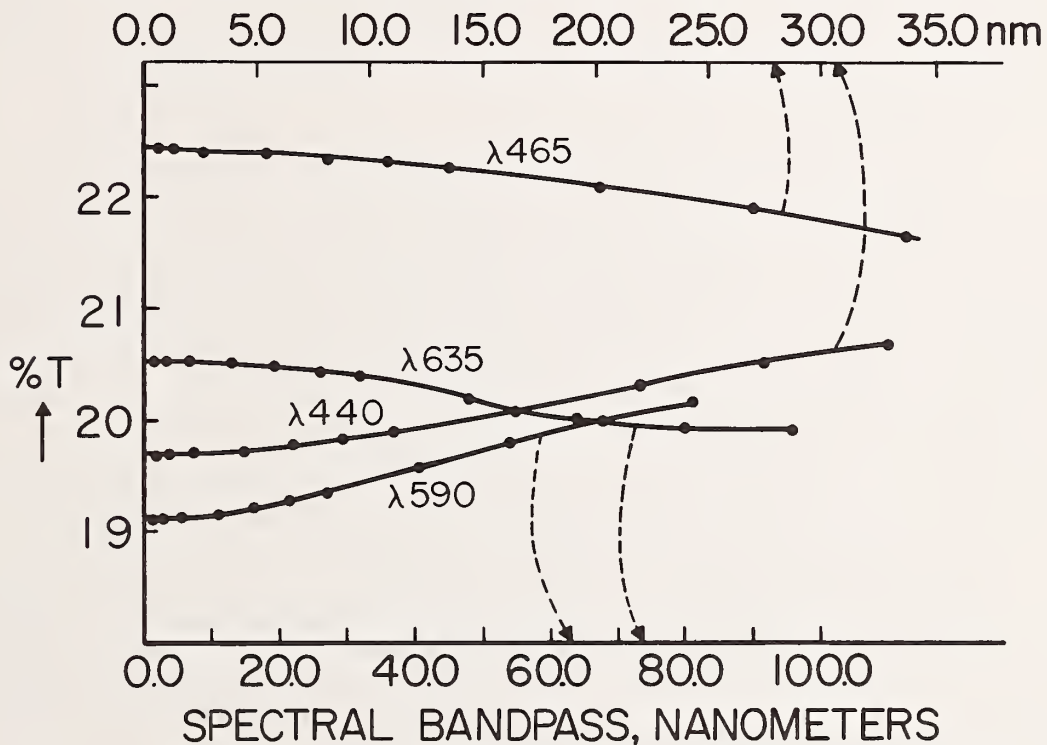


Figure 6. Influence of spectral bandpass on the transmittance of a Schott NG-4 glass filter measured at 440 nm; 465 nm; 590 nm; and 635 nm (8).

measured at four wavelengths as indicated in figure 5 and 6, using this time variable slit widths, and consequently various spectral bandpasses, from 0.5 nm to 100.0 nm, using a Cary 16 spectrophotometer.

Figure 5 illustrates the dependence of the transmittance for the Chance ON-10 (and Corning 8364) on the spectral bandpass at 400.0; 445.0; 490.0; and 590.0 nm. It can be seen that the transmittance varies with the bandpass, and that this dependence is stronger at the wavelengths where the glass has a stronger and sharper absorption band. For instance, at 400.0 nm a rather narrow spectral bandpass of 0.5 nm will be required for this type of glass to obtain an accurate transmittance value, everything else being equal and in particular the wavelength and photometric scale accuracy, while at 490.0 nm a spectral bandpass of 15 nm would be adequate. The same dependence, but to a smaller extent, is illustrated in figure 6 for a Schott NG-4 glass, and here it can be seen that larger spectral bandpasses could be used to produce accurate transmittance values.

This transmittance-spectral bandpass dependence is summarized in the graph from figure 5 at the upper left corner, where it can be seen that the use of wider spectral bandpasses will produce the inaccurate T_1 and T_2 values when compared with T_1' and T_2' , which are theoretically the correct values. As a general rule the value of the spectral bandpass required to produce accurate transmittance measurements with an uncertainty not greater than 0.1 percent, should be $\frac{1}{20}$ of the symmetrical natural spectral bandwidth, at half intensity, of the material to be analyzed and at the wavelength at which the measurement is performed. When this information is not available, it can be determined by measuring the transmittance (or absorbance) of the material at the wavelength of interest, using various spectral bandpasses (or slit widths) as illustrated in figures 5 and 6. The largest bandpass or slit width which can be used is given by the value found at the end of the horizontal portion of the transmittance-spectral bandpass curve.

The selection and use of adequate spectral bandpass is one of the indispensable conditions which must be fulfilled to obtain true transmittance values.

3.4 Stray Radiations

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 Standard Method (13), which is reprinted in the Appendix, reprint 7. The procedure recommended in this work should be used to determine this parameter in the spectral range of interest.

The stray radiation generated inside the photometric system is defined as the radiant energy which falls on the photosensitive detector without passing through the absorbing sample. This stray radiation 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 photodetector. The measurements can be performed using a maximum slit opening and 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. In this way, a maximum stray radiation condition will be generated in the spectrophotometer. The measurements should be performed at the wavelength of interest by determining the dark current of the photomultiplier with the shutter in the closed position at the photodetector. The mirror is then placed at the sample position, the shutter is opened and measurements should be made again. The differences between the two measurements are an indication for the presence and amount of stray radiation generated under these circumstances in the sample compartment of the spectrophotometer.

3.5 Accuracy of the Transmittance or Absorbance Scales

This is an essential condition which must be fulfilled by a spectrophotometer for production of accurate transmittance or absorbance values.

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. In this discussion the optical transmittance T of a solid material includes the reflection losses which occur at the air-solid interface. The internal transmittance T_i is defined

as the transmittance of the material corrected for reflection losses. This internal transmittance can be calculated in principle from the transmittance by using the well-known Fresnel equations as shown in reprint 4 in the Appendix. The internal transmittance is obtained experimentally when the measurements are made using a blank sample in the reference beam of the spectrophotometer. When a blank is not available, as in the case of SRM 930, the measurements are made against air in the reference beam. Under these circumstances the resulting transmittance value includes the reflection losses (which are about 8 percent for a glass filter having an index refraction of 1.5). A discussion of this subject by Mielenz is given in reference 10. The absorbance A of a material is related to the internal transmittance T_i by the expression $A = -\log_{10} T_i$ while the optical density D is related to the transmittance T by the expression $D = -\log_{10} T$.

Transmittance is the ratio of two radiant fluxes. It is therefore necessary that the transmittance scale of the spectrophotometer be accurate. The transmittance of a particular material is also a function of wavelength; hence the wavelength scale of the monochromator should also be accurate, and appropriate spectral bandpasses should be used. These conditions were examined in the previous paragraphs. The measurements should be made using collimated radiation. 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 (See Appendix, reprints 4 and 5). Other important factors, already mentioned, 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.

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 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

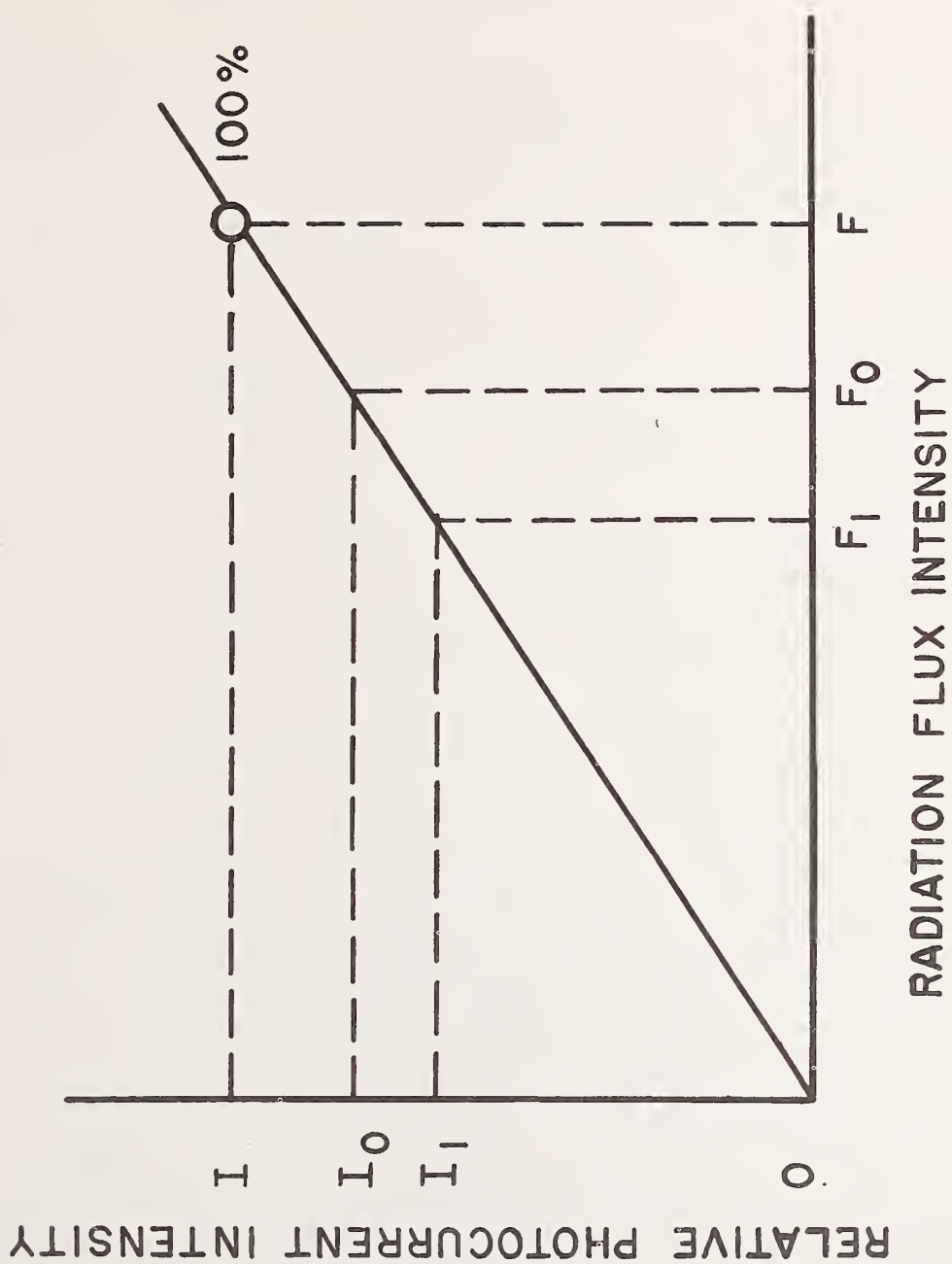


Figure 7. Illustration of the relation between radiation flux intensities F and corresponding photocurrent I in an ideal case.

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

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

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

Since transmittance is the ratio of two radiant fluxes 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. This is illustrated in the simple graph (fig. 7) on which the abscissa represents arbitrary radiation flux intensities F with the relative intensities I on the ordinate. In an ideal case, when $F=0$, $I=0$; for a certain value of F , called here arbitrarily 100 percent, there corresponds a maximum value of the photocurrent, I . These determine two fixed points on the graph, and any measurement of radiant flux intensity will be accurate if it falls on the straight line which connects the origin 0 with the 100 percent point.

Photodetector linearity can be measured by various methods (11), but of these only the use of the inverse square law and the radiation addition principle using a plurality of sources or multiple apertures will be mentioned here. This last method was selected and used in conjunction with a spectrophotometer designed and built in the Analytical

Chemistry Division at NBS (14). This instrument is described in detail in the Appendix (reprint 4). Its adaptation for work in the ultraviolet is described in reprint 6 of the Appendix.

Using this high-accuracy spectrophotometer, a series of glass filters was developed as Standard Reference Materials and were issued as SRM 930. SRM 930 consists of three neutral glass filters having transmittances of approximately 10, 20, and 30 percent. Each filter is individually calibrated and certified for transmittance over a spectral wavelength range from 440 to 635 nm. These filters are intended to verify the accuracy of the transmittance or absorbance scales of spectrophotometers as well as their short and long term stability and to provide a means for interlaboratory comparisons of data. A further purpose of these filters is to assure that systematic errors due to a particular characteristic or condition of an instrument can be recognized.

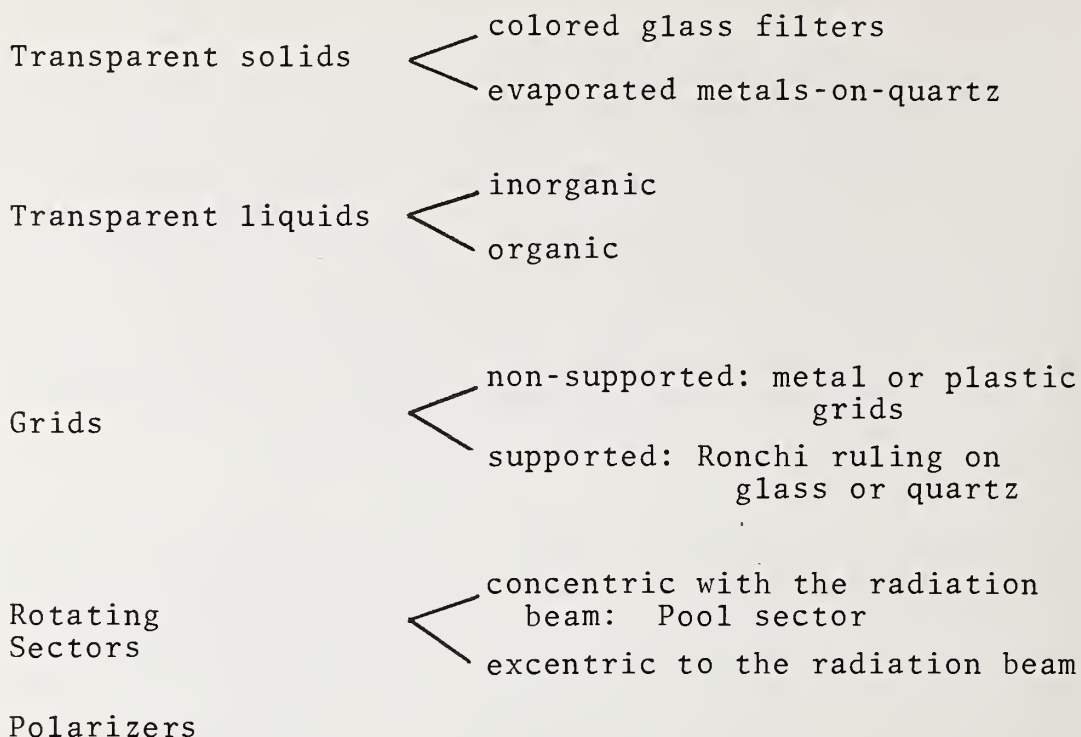
SRM 930 (a and b) should be valuable in checking the calibration of instruments used to obtain accurate physico-chemical constants such as molar absorptivity and equilibrium constants. For example, current interest in molar absorptivity values, as an index of the purity of biological clinical materials, requires greater accuracy of measurement. Also, as discussed earlier in this section, the accuracy in the determination of equilibrium constants of chemical reactions in solutions is dependent on true values of their molar absorptivities.

4. STANDARD REFERENCE MATERIALS FOR TRANSMITTANCE IN SPECTROPHOTOMETRY.

4.1 Selection and Preparation of Materials Which Can Be Used as Standard Reference Material in Spectrophotometry.

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

These conditions are fulfilled to a smaller or larger extent by the following materials:



From these materials, the colored glass filters, mentioned in the first group, most nearly satisfied the required conditions and constitute the most acceptable compromise when compared with the other materials mentioned above.

Several colored glasses were examined, and from these the Corning 8364, the Chance ON-10, and the Schott NG-4 were initially selected. The spectral transmittance of these glasses is illustrated in figure 4 in comparison with an evaporated metal-on-quartz filter (non-fluorescent fused silica of optical quality) and a Ronchi ruling on a glass substrate. The transmittance of these two last materials exhibits the least dependence of wavelength from 200 nm to over 700 nm (the Ronchi ruling transmittance below 350 nm is limited only by the transmittance of the glass substrate and not by the nature of the ruling itself). However, since the attenuation of radiations is produced by the evaporated metal-on-quartz, through reflection rather than absorption, this material was not selected for the purpose considered here, since there is a possibility that reflected radiation is generated in conventional spectrophotometers. The Ronchi ruling was rejected since it is subjected, by its nature, to



Figure 8. Instrumentation to examine, clean, and mount the glass filters used to produce SRM 930, a, b. The entire equipment is placed and used in an all-polypropylene hood provided with a vertical clean air flow.

diffraction phenomena. From the remaining glasses, the Schott NG-4 type was finally selected since this material exhibits the best optical neutrality, and, excluding its limited spectral transmittance range to the visible and near-infrared spectral domain, it is the best material which satisfies the other conditions enumerated above.

A number of procedures were developed and used for the preparation of SRM 930 (a and b) and were tested in a variety of conditions. From these, only those which were finally selected and are used currently for the preparation of this SRM will be described here.

The optically neutral NG-4 and NG-5 glasses for the filters were produced by Schott of Mainz, Germany, and are designated as "Jena Colored and Filter Glass." The NG-5 glass is similar to the NG-4 glass in its spectral transmittance but is less absorbing. This permits the use of a thicker glass (1.5 mm) for the nominal 30 percent filter. These glasses are provided by the Fish-Schurman Corp., 70 Portman Road, New Rochelle, New York, 10802, in the form of rectangular pieces 30.5 mm long, 10.4 mm wide and 2.0 mm and 1.5 mm thick for the NG-4 glass and 1.5 mm thick for the NG-5 glass. Corresponding to these thicknesses are nominal transmittances of 10, 20, and 30 percent, respectively. These transmittances were selected to provide a means to verify the short and long term stability of the instrument, and the accuracy of its transmittance or absorbance scale at the three different levels of transmittance at which most spectrochemical analyses are performed. A further specification for these filters is freedom of visible defects such as inhomogeneity, stains, inclusions and scratches. The parallelism should be within 0.02 mm and flatness should not exceed three fringes (mercury 546.1 nm radiation) over the entire glass surface.

4.2 Preparation of the Glass Filters

The glass filters are received from the supplier wrapped individually in lens paper and contained in small individual envelopes to avoid damage during transportation. Each glass filter is submitted to a preliminary manual cleaning, with distilled water using a piece of lens paper. This is followed by a preliminary examination for defects using a stereomicroscope with a magnification X12. This examination as well as the following cleaning procedures are performed in an all-polypropylene hood provided with a vertical laminar flow of filtered air, illustrated in figure 8.



Figure 9. Stainless steel holders for six 50 mm by 50 mm, and twelve 30 mm by 10 mm glass filters.

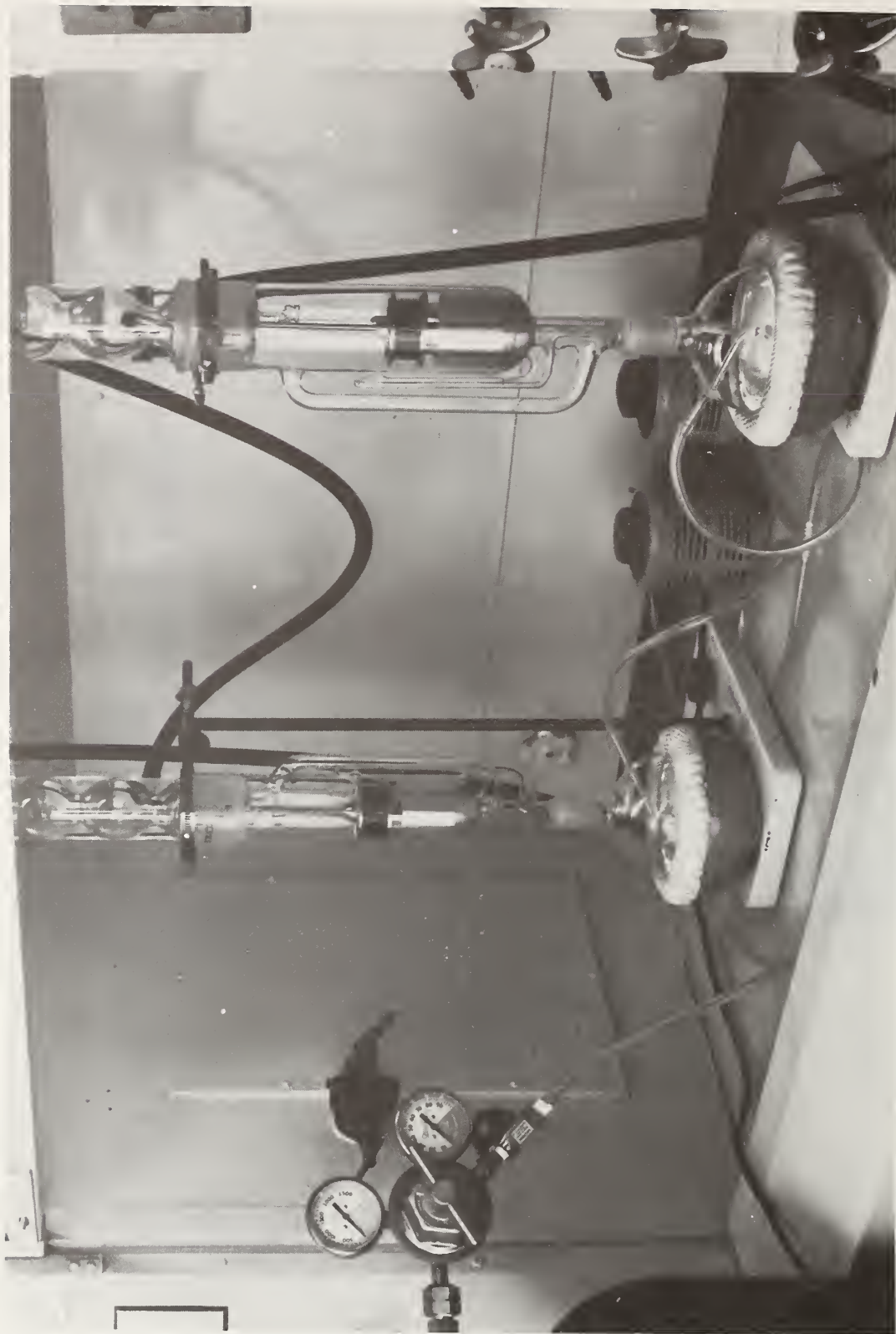


Figure 10. Soxhlet extractors used for the final cleaning of the 50 mm by 50 mm, and 30 mm by 10 mm glass filters, using isopropyl alcohol (electronic grade).

Each glass filter which has passed this initial examination is engraved at its upper end with a serial number using a diamond scribe and is placed in a stainless steel holder. Two types of such holders were developed and are illustrated in figure 8, at left and lower right for twelve 30 mm by 10 mm units and at rear right for six 50 mm by 50 mm glass filters. These filter holders are shown in more detail in figure 9, at left for the 50 mm by 50 mm and at right for the 30 mm by 10 mm glass filters. The holder is placed, in a borosilicate beaker which is then placed in an ultrasonic bath (80 w) containing distilled water (shown at right in the figure (fig. 8)). Isopropyl alcohol of electronic grade is added to the beaker to cover the filters and the unit is operated for 5 min. This operation eliminates all the glass particles produced by the engraving which could damage the glass surface of the filter during the subsequent cleaning operations. Each glass filter is then washed manually with a diluted aqueous solution of a nonionic detergent such as the alkyl phenoxy polyethoxy ethanol (Triton X-100, Rohm and Haas), rinsed with distilled water, and dried in air.

Each glass filter is then re-examined carefully under the stereomicroscope, and those which pass this final inspection are transferred in the 12 unit stainless steel holder and placed in a Soxhlet extractor illustrated in figure 10. An aluminum slug is inserted at the bottom of each extraction flask to reduce the volume of solvent required for the functioning of the extractor and to shorten the syphoning time. To avoid bumpy boiling, followed sometimes by an undesirable overflow of the isopropyl alcohol from the boiling flask into the extraction vessel, a side tube provided at the bottom with a coarse glass frit is inserted through the side of each flask. A steady stream of clean air from a compressed gas cylinder equipped with a gas regulator and needle valve, is passed through the tube to produce a continuous and gentle bubbling. The glass filters are then washed for 3 hours, at a rate of three syphoning per hour, using isopropyl alcohol of electronic grade. After this period the glass filters are dried in air in the laminar flow hood, placed individually in the special aluminum alloy holder designed in collaboration with L. Monostori and made at NBS in the Instrument Shops. This operation is performed by using the tools illustrated in figure 8, which includes an antistatic brush and plastic-tipped tweezers. The mounted filters, placed in a covered plexiglass box, are aged for at least two weeks in the laminar flow hood where they are exposed continuously to the radiation of the three fluorescent lamps provided at the top (total 120 w, arbitrarily chosen). Since the individual glass filter metal holder contributes significantly to the usefulness of the filters, it will be described below.

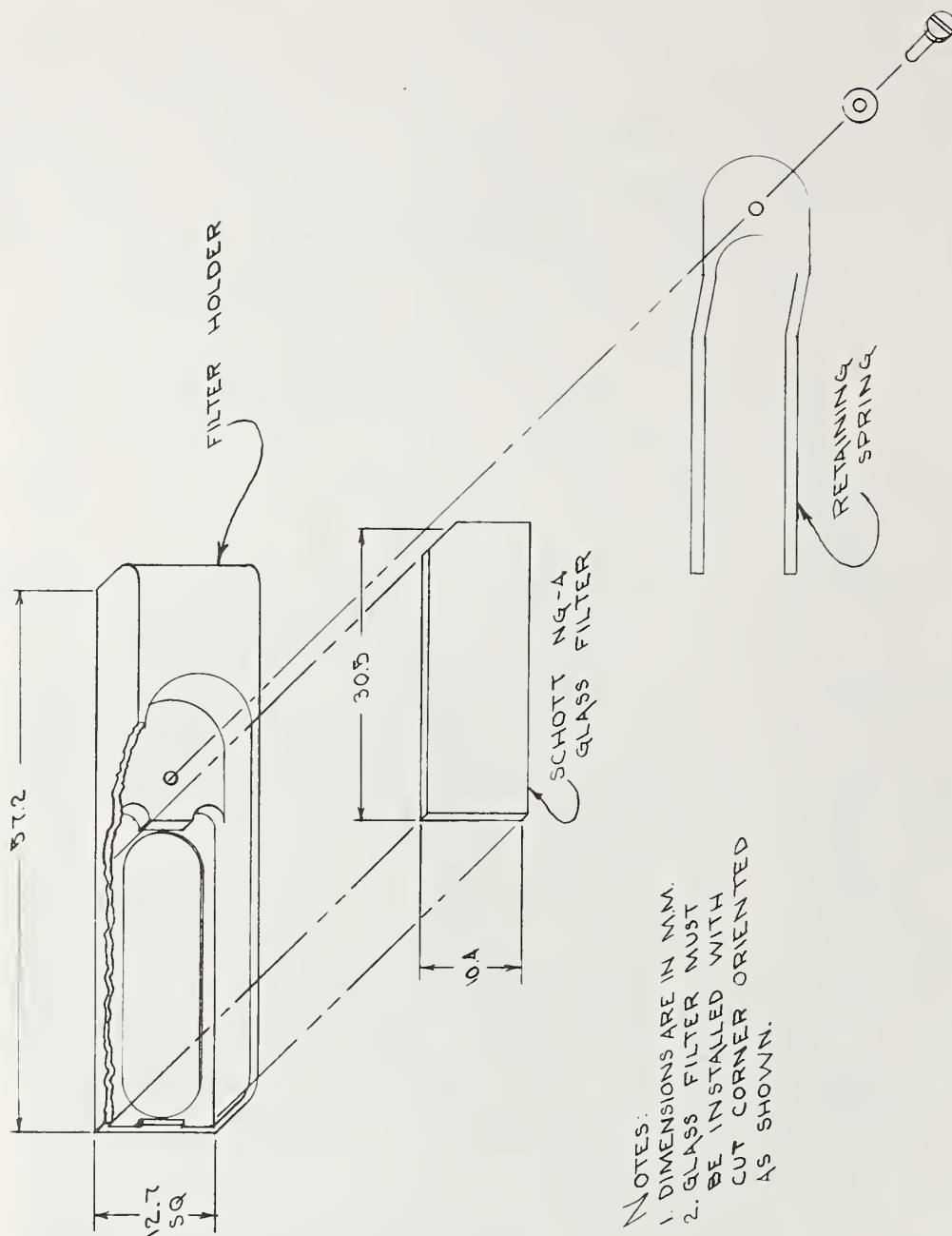


Figure 11. Schematic description of the aluminum alloy holder with its bronze retaining spring used to hold the glass filters.

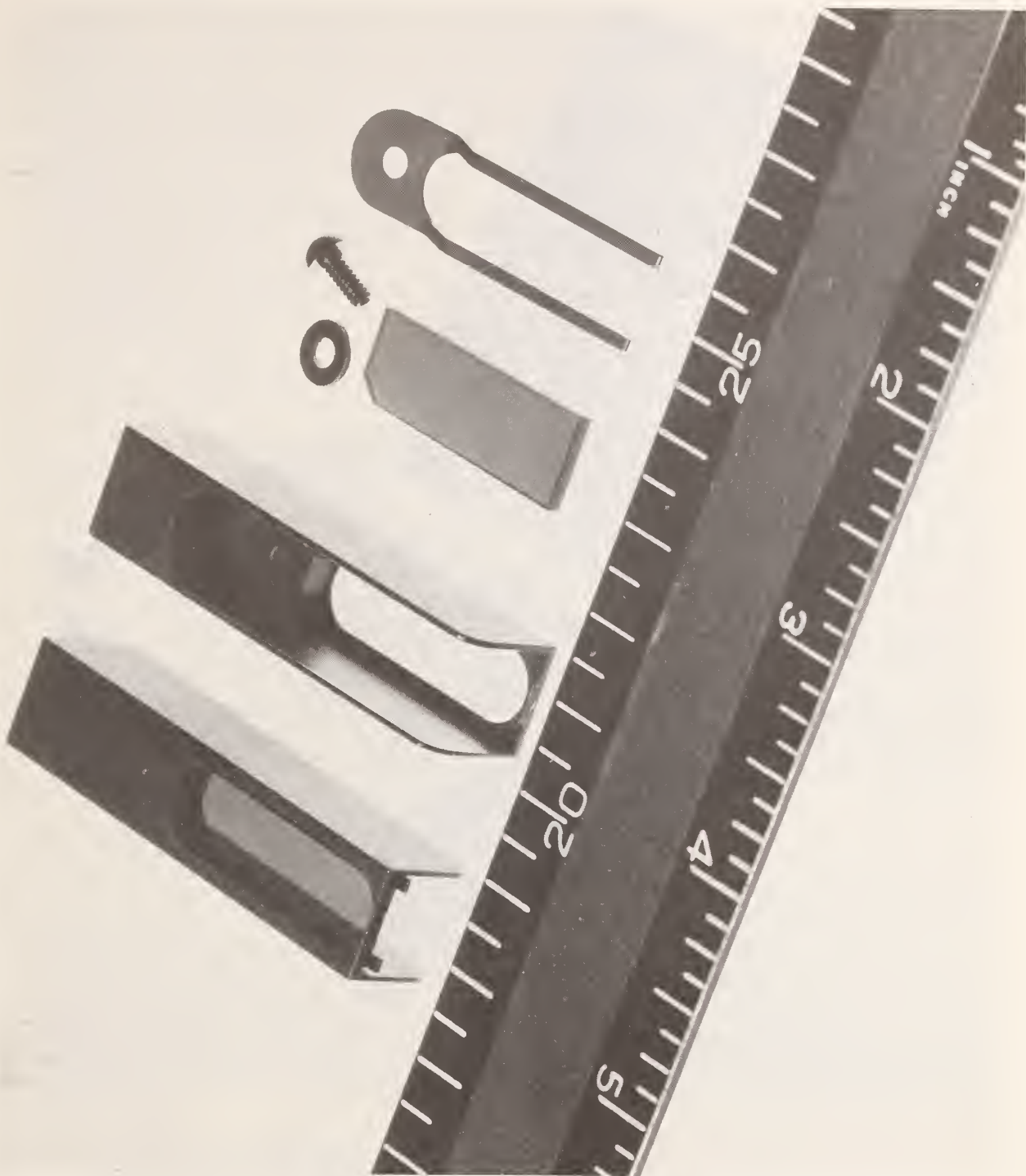


Figure 12. View of the assembled and unassembled glass filter holder.



Figure 13. Plastic box for SRM 930b containing the three glass filters in their holders. A fourth empty holder is provided for use in the reference beam. The grooved insert is made of polypropylene.

The shape and dimensions of these metal holders are given in figures 11 and 12. They were established in conformance to the dimensions of the rectangular sample compartments of most conventional spectrophotometers, and were designed to hold the glass filters without producing mechanical strains in the material, as indicated by a polariscope examination. The metal used for the holder is an aluminum alloy 2024 (4.5% Cu; 1.5% Mg; 0.6% Mn); the retaining two-pronged spring is made of phosphor bronze, and both parts are anodized black (flat). The spring is secured by a screw and washer made of nylon (black). The dimensions and shape of the window were selected to avoid vignetting even for spectrophotometers having a low pass radiation beam.

4.3 Packaging of the Glass Filters

Each set, consisting of three glass filters in their metal holder and having a nominal transmittance of 10, 20, and 30 percent, is placed in a plastic box similar to that shown in figure 13. The insert is made of polypropylene and the glass filters are placed in the metal holder described in figures 11 and 12; this constitutes SRM 930b.

This SRM is produced currently, and replaces SRM's 930 and 930a. It differs from SRM 930 and 930a by an additional metal holder without glass filters. This empty filter holder should be placed in the reference beam when performing measurements. SRM's 930 and 930a were certified at 440.0 nm; 465.0 nm; 590.0 nm; and 635.0 nm. An additional measurement at 546.1 nm was included for SRM 930b.

5. RESULTS

The transmittance measurements used in the certification of the glass filters discussed previously as well as those measurements which were made to assess the various characteristics of this material, together with interlaboratory comparative transmittance measurements, were made with the high-accuracy spectrophotometer described in Appendix 4, except the data from table 6. Some of the measurements relevant to the topic covered in this publication will be given here.

5.1 Stability of SRM 930

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.

Table 1. Influence of temperature on the transmittance (T) of seven Schott NG-4 glass filters at five wavelengths (nm).

		T % at					
		25.5 °C			20.5 °C		
Wavelength \ Date	1-14	1-15	1-17	1-23	1-22	1-24	Average Difference
440.0	9.30	9.29	9.30	9.32	9.32	9.32	+0.02
	18.70	18.69	18.70	18.73	18.72	18.73	+0.03
	29.08	29.07	29.09	29.11	29.10	29.11	+0.03
	32.95	32.96	32.95	32.96	32.95	32.96	+0.01
	9.89	9.89	9.89	9.91	9.91	9.91	+0.02
	18.53	18.53	18.53	18.54	18.54	18.54	+0.01
	29.15	29.15	29.17	29.20	29.20	29.20	+0.04
465.0	11.03	11.04	11.04	11.05	11.05	11.06	+0.01
	21.06	21.08	21.08	21.09	21.10	21.09	+0.02
	32.20	32.21	32.22	32.24	32.25	32.24	+0.03
	35.62	35.61	35.61	35.61	35.61	35.61	0.0
	11.69	11.69	11.69	11.70	11.70	11.70	+0.01
	20.92	20.91	20.92	20.93	20.92	20.92	0.0
	32.27	32.27	32.30	32.32	32.33	32.33	+0.05
546.1	9.94	9.95	9.95	9.93	9.93	9.93	-0.02
	19.59	19.60	19.61	19.57	19.58	19.57	-0.03
	30.69	30.69	30.70	30.67	30.68	30.67	-0.02
	33.76	33.76	33.76	33.70	33.71	33.71	-0.05
	10.55	10.57	10.57	10.54	10.53	10.54	-0.02
	19.43	19.47	19.48	19.43	19.43	19.44	-0.03
	30.74	30.76	30.78	30.75	30.73	30.75	-0.02
590.0	8.82	8.82	8.83	8.79	8.80	8.80	-0.02
	18.02	18.04	18.04	18.00	18.00	18.00	-0.03
	27.62	27.65	27.65	27.62	27.62	27.62	-0.02
	31.20	31.22	31.22	31.14	31.14	31.14	-0.07
	9.37	9.38	9.38	9.34	9.35	9.35	-0.03
	17.89	17.90	17.90	17.86	17.86	17.86	-0.04
	27.69	27.70	27.71	27.68	27.67	27.68	-0.02
635.0	9.85	9.86	9.86	9.83	9.83	9.83	-0.03
	19.47	19.48	19.49	19.45	19.44	19.45	-0.03
	27.74	27.74	27.76	27.72	27.71	27.73	-0.03
	32.65	32.67	32.66	32.59	32.60	32.60	-0.06
	10.44	10.44	10.44	10.40	10.41	10.42	-0.03
	19.34	19.35	19.35	19.30	19.31	19.31	-0.04
	27.78	27.80	27.80	27.77	27.77	27.78	-0.02

Table 2. Percent transmittance of three Schott NG-4 neutral glass filters before and after exposures to accelerated radiation tests. Filters were exposed twice for 21 hours to a high intensity radiation source similar in spectral distribution to the fluorescent light tubes but 1000 times stronger.

Exposure Sample		440.0 nm				465.0 nm			
		BEFORE	DIFF. %	AFTER	DIFF. %	BEFORE	DIFF. %	AFTER	DIFF. %
1		12.96	0	12.96	0.08	12.97	0	15.22	0.07
2		20.53	0	20.53	0	20.52	0	23.23	0.04
3		34.45	0.06	34.45	0.03	37.34	0.05	37.32	0.03

Exposure Sample		590.0 nm				635.0 nm			
		BEFORE	DIFF. %	AFTER	DIFF. %	BEFORE	DIFF. %	AFTER	DIFF. %
1		12.19	0	12.19	0.25	12.20	0	13.36	0.15
2		19.61	0.05	19.60	0.10	19.59	0	21.03	0.14
3		33.44	0.06	33.42	0.09	35.02	0.11	34.98	0.09

Seven glass filters were placed in the sample holder of the high-accuracy spectrophotometer and measured in six replications. The results are given in table 5 (see Appendix 4) and show that these measurements can be reproduced with a pooled relative standard deviation of 0.010 percent.

The temperature dependence of the transmittance was measured for the same type of glass by determining this value at a room temperature of 20.5 °C and 25.5 °C and at 440.0 nm; 465.0 nm; 546.1 nm; 590.0 nm; and 635.0 nm; and table 1 gives the results.

From these data it can be concluded that the transmittance dependence on temperature over the tested temperature range, in the spectral interval from 440.0 nm to 635.0 nm, for the type of glass used is insignificant at the .95 confidence level. For a variation of ± 1 °C to 2 °C the dependance is minimal and averaged less than 0.2 percent of the measured transmittance values.

The stability of the Schott NG type of glass to visible radiations was tested by exposing three filters having a nominal transmittance of 10, 20, and 30 percent to the high intensity radiation of a source with a spectral distribution similar to the conventional fluorescent lamps used for illumination of laboratories. Each high intensity exposure lasted 21 hours and was equivalent to 21,000 hours of normal exposure. The transmittance measurements assembled in table 2 were made before and after each of the two exposures. Column 2 gives the transmittance of the glass filters at 440.0 nm before the exposure; column 4 gives the same measurements after the 21 hours of accelerated exposure. The difference between these two measurements is given in column 3. The same filters were exposed again for another 21 hours, and column 5 contains the transmittance values before this exposure, while column 7 gives these values after this second 21 hours exposure. The difference between these data (columns 5 and 7) is given in column 6. Measurements were also made at 465.0 nm, 590.0 nm, and 635.0 nm. From these data it can be concluded that the type of glass tested exhibits an acceptable stability when exposed to the visible radiation experiment described. Similar stability tests performed on other neutral glasses have indicated that these glasses were less stable by a factor of four when compared with the Schott NG-4 glass, and consequently this latter material was selected for SRM 930 (a and b).

Table 3. Stability of transmittance (T) as a function of time, measured on SRM 930.

Wavelength nm	%T			
	1	2	3	DATE
440.0	32.87	19.80	11.59	5-18-71
	32.88	19.83	11.62	7-12-72
	32.91	19.81	11.59	8-30-73
	32.96	19.84	11.61	11-16-73
	32.98	19.84	11.62	1- 9-74
	32.94	19.84	11.61	8- 1-74
	32.95	19.84	11.62	1-13-75
465.0	35.53	22.59	13.56	5-18-71
	35.54	22.62	13.59	7-12-72
	35.54	22.62	13.59	8-30-73
	35.62	22.62	13.58	11-16-73
	35.63	22.63	13.58	1- 9-74
	35.60	22.62	13.57	8- 1-74
	35.60	22.62	13.58	1-13-75
590.0	31.13	19.16	10.37	5-18-71
	31.14	19.20	10.41	7-12-72
	31.14	19.20	10.41	8-30-73
	31.21	19.19	10.40	11-16-73
	31.21	19.20	10.41	1- 9-74
	31.18	19.20	10.40	8- 1-74
	31.19	19.20	10.41	1-13-75
635.0	32.55	20.60	11.37	5-18-71
	32.59	20.65	11.39	7-12-72
	32.59	20.65	11.39	8-30-73
	32.66	20.65	11.40	11-16-73
	32.68	20.67	11.41	1- 9-74
	32.63	20.66	11.41	8- 1-74
	32.64	20.66	11.40	1-13-75

Table 4. Comparison of percent transmittance (%T) measurements performed on a set of three Schott NG-4 glass filters over a period of two years.

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

The variation of transmittance as a function of time for the Schott NG type glasses (NG-4 and NG-5) was determined by using three filters which constitute our own reference set, and measuring them over a period of 4 years. Table 3 presents the results obtained at 440.0 nm, 465.0 nm, 590.0 nm, and 635.0 nm. The largest difference observed after 4 years of use did not exceed about 3 parts in 1000. The measurements also seem to indicate a trend toward an increase of the transmittance of these glass filters which are in accordance with the known property of glass surfaces to produce a layer of SiO₂ at its surface when exposed to atmospheric conditions. This phenomena is called "blooming" of the glass, and the thin SiO₂ deposit which is formed acts as an antireflection layer which results in an apparent increase of the transmittance of the glass. Similar measurements were made on another set of three glass filters over a period of two years; table 4 contains the resulting transmittances, which confirm the previous data.

5.2 Interlaboratory Transmittance Measurements on SRM 930

A set of SRM 930 was measured at NBS and at the National Physical Laboratory (NPL) in England by F. J. J. Clarke and his associates using their high-accuracy instrument. These 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 of about 8 mm by 0.5 mm was used for the transmittance measurements. The results given in table 5 indicate that an average difference of about 0.20 percent of the measured values was obtained between the measurements carried out at NPL and at NBS. Agreement to within the instrumental accuracy of about 1 part in 10⁴ was also obtained in comparative measurements, using another high-accuracy spectrophotometer built at NBS (See Mielenz in reference 10). The average reproducibility of these measurements performed in 1971 and repeated in 1973 and 1975 was within this value.

Table 5. Comparison between the percent transmittances (%T) measured on three Schott NG-4 glass filters at NPL and NBS in 1971, 1973, and 1975.

Wavelength nm	NBS, %T 1971	NPL, %T 1971	NBS, %T 1973	1975
440.0	12.91	12.93	12.91	12.90
465.0	14.97	15.01	14.98	14.97
590.0	11.67	11.67	11.65	11.62
635.0	12.70	12.72	12.71	12.69
440.0	19.60	19.62	19.60	19.56
465.0	22.37	22.43	22.39	22.34
590.0	19.00	19.01	19.00	18.94
635.0	20.41	20.47	20.46	20.40
440.0	32.87	32.98	32.86	32.87
465.0	35.53	35.66	35.52	35.51
590.0	31.13	31.21	31.11	31.07
635.0	32.54	32.62	32.57	32.53

Another comparative study was performed to include three clinical laboratories to determine the reproducibility of transmittance measurements on the Schott NG-4 neutral glass filters. Again three filters having nominal transmittances of 10, 20, and 30 percent were measured at four wavelengths on a conventional spectrophotometer at the NBS. This instrument included a double monochromator with quartz prisms used in a double beam mode, and a transmittance scale with 1000 divisions between 0 and 100 percent transmittance. The transmittance accuracy of this scale was established with SRM 930. The same filters were then sent to laboratories A, B and C describing the technique to be used in measuring their transmittances. The results obtained are summarized in table 6 and include the percent transmittance (%T) values, the standard deviation (S. D.), the percent standard deviation (% S. D.), and the percent difference (% difference). This difference was calculated using the NBS data as a reference.

Table 6. Comparative transmittance measurements performed by four laboratories on three Schott NG-4 colored glass filters.

Laboratory		A			
Measurement		% T			
No.		440 nm	465 nm	590 nm	635 nm
1	Ave.	12.91	14.99	11.68	12.71
	S.D.	0.0063	0.004	0.008	0.005
	% S.D.	.049	.027	.070	.041
	Diff. %	- .4	- .07	- .6	- .5
2	Ave.	19.61	22.37	19.06	20.50
	S.D.	0.004	0.010	0.004	-
	% S.D.	.021	.046	.022	-
	Diff. %	- .5	- .3	- .3	-0.1
3	Ave.	32.81	35.44	31.12	32.58
	S.D.	0.0080	0.0080	0.0050	0.0050
	% S.D.	.023	.023	.017	.016
	Diff. %	+ .3	+ .3	+ .1	+ .2

Laboratory		B			
Measurement		% T			
No.		440 nm	465 nm	590 nm	635 nm
1	Ave.	12.91	14.87	11.56	12.59
	S.D.	-	0.041	0.041	-
	% S.D.	-	.276	.36	-
	Diff. %	-0.4	- .9	-1.6	-1.4
2	Ave.	19.59	22.39	18.90	20.51
	S.D.	-	-	0.053	-
	% S.D.	-	-	.281	-
	Diff. %	-0.6	-0.2	-1.1	-0.05
3	Ave.	32.58	35.23	30.90	32.36
	S.D.	-	0.093	-	-
	% S.D.	-	.264	-	-
	Diff. %	-0.4	- .3	-0.6	-0.4

Table 6 (Cont'd)

Laboratory		C			
Measurement		% T			
No.		440 nm	465 nm	590 nm	635 nm
1	Ave.	12.88	14.96	11.66	12.65
	S.D.	-	0.014	0.011	0.018
	% S.D.	-	.09	.09	.15
	Diff. %	-0.6	- .3	- .8	- .9
2	Ave.	19.54	22.34	19.12	20.37
	S.D.	-	-	0.024	-
	% S.D.	-	-	.13	-
	Diff. %	-0.9	-0.4	+ .05	-0.7
3	Ave.	32.88	35.40	30.97	32.43
	S.D.	-	-	-	-
	% S.D.	-	-	-	-
	Diff. %	+0.5	+0.1	-0.4	-0.2

Laboratory		NBS			
Measurement		% T			
No.		440 nm	465 nm	590 nm	635 nm
1	Ave.	12.96	15.00	11.75	12.77
	S.D.	0.0053	0.0037	0.0048	0.0057
	% S.D.	.041	.025	.041	.045
	Diff. %	-	-	-	-
2	Ave.	19.71	22.44	19.11	20.52
	S.D.	0.0049	0.0052	0.0038	0.0049
	% S.D.	.025	.023	.020	.024
	Diff. %	-	-	-	-
3	Ave.	32.72	35.35	31.09	32.50
	S.D.	0.0045	0.0056	0.0040	0.0043
	% S.D.	.014	.016	.013	.013
	Diff. %	-	-	-	-

In this study, the cooperation of George N. Bowers, Jr., M. D., of Hartford Hospital, Hartford, Connecticut, Royden N. Rand, Ph.D., of the Hospital of the University of Pennsylvania, Philadelphia, Pennsylvania*, and Donald S. Young, M. D., Ph.D., of the National Institutes of Health, Bethesda, Maryland, is gratefully acknowledged.

This study demonstrates that transmittance data can be reproduced in actual laboratory conditions with a general uncertainty of less than one percent. From the total of 36 transmittance measurements only 3 exceed this value, and this was due probably to limitations in the spectral band-pass of the particular spectrophotometer used.

The transmittances of several sets of SRM 930 were determined, after several years of use in routine laboratory conditions, to assess the effect of time and handling on this parameter. Table 7 presents the results obtained on set no. 106 certified in 1972. The column marked 1 contains the transmittance values as certified in November 29, 1972. This set was measured again in February 27, 1974, in an "as received" condition, and the transmittance values obtained are given in the column marked 2. The difference between these measurements is given in the column marked 3. As it can be seen, the transmittance of these glass filters, after about two years of use in a laboratory, is lower than the certified values, suggesting a possible contamination of the glass surface. This supposition was verified by submitting the filters to the cleaning procedure described previously. The filters were remeasured, and the data obtained are given in the column marked 4, which present the average of four series of measurements carried out over a period of three days. These results, which indicate this time a positive difference, given in the column marked 5, confirm the hypothesis of a surface contamination of the glass during their use, and verify the tendency of the glass to cover itself with a layer of SiO_2 as was already discussed. The results of this phenomenon is an apparent increase of the transmission of the material.

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Table 7. Transmittance of SRM 930, set 106, after two years of use in a laboratory.

		Percent Transmittance				
Set No.	Conditions	1	2	3	4	5
	Wavelength, nm	As certified in Nov. 29, 1972	Measured as "received" in Feb. 27, 1974	ΔT [1-2]	Cleaned and remeasured	ΔT [4-1]
1-106	440.0	9.23	9.23	0.0	9.27	+0.04
	465.0	10.95	10.92	-0.03	10.99	+0.04
	590.0	8.77	8.74	-0.03	8.78	+0.01
2-106	635.0	9.83	9.80	-0.03	9.84	+0.01
	440.0	16.53	16.51	-0.02	16.58	+0.05
	465.0	18.78	18.73	-0.05	18.82	+0.04
3-106	590.0	15.90	15.84	-0.06	15.92	+0.02
	635.0	17.33	17.25	-0.08	17.33	0.0
	440.0	30.02	29.98	-0.04	30.12	+0.10
	465.0	33.37	33.29	-0.08	33.47	+0.10
	590.0	29.91	29.81	-0.10	29.94	+0.03
	635.0	30.90	30.78	-0.12	30.90	0.0

In another series of tests, a set of SRM 930 was used to verify and correct the transmittance scale of a conventional spectrophotometer, by measuring the transmittance of the certified glass filters on the tested instrument, and by comparing the results with the certified values, and Table 8 presents these results.

Table 8. Comparison of % T measurements performed on a Schott NG-4 filter using the NBS high-accuracy instrument and a conventional spectrophotometer.

Wavelength nm	NBS Instrument	Conventional Instrument	Diff.	Relative % Diff.	Average Relative % Diff.
440.0	32.82	32.75	+0.07	+0.21	
465.0	35.51	35.40	+ .11	+ .31	+0.22
590.0	30.98	30.93	+ .05	+ .16	
635.0	32.38	32.32	+ .06	+ .19	

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

The glass which is used to produce SRM 930 has a spectral transmittance limited to the visible range from about 400 nm to 800 nm, as illustrated in figures 4 and 6, and this obviously limits the usefulness of this standard reference material. Appreciable efforts have been made at NBS in the past and are continuing now, to find a transparent material which could extend this spectral range to the ultraviolet. At the present time, however, only one material has been found which satisfies these required characteristics; this material is the evaporated metal-on-quartz filter which was already discussed (figure 4). The evaporated metal-on-quartz filter meets the

requirements for spectral neutrality and good stability and is not susceptible to the production of an SiO layer. When chromium is used to produce the evaporated metal layer, the filter exhibits a good resistance to abrasion. The only limitation of the evaporated metal-on-quartz results from its intrinsic property of attenuating the incident radiation by reflecting part of it rather than by absorbing it. Although interlaboratory tests between NBS and NPL, in which evaporated metal-on-quartz filters have been used, have produced results similar to those obtained with the glass filters used in SRM 930, it should be noted that these results were obtained with specially designed high-accuracy spectrophotometers. The use of such filters in conjunction with the large variety of conventional instruments is now being studied to determine to what extent and under what circumstances the metal-on-quartz filters could be used as standard reference material in spectrophotometry.

6. SUMMARIZING REMARKS

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

While the use of SRM 930a and b does not solve all problems in spectrophotometry, its availability should contribute appreciably to the production of more accurate and therefore more meaningful measurements in all fields where spectrophotometry is applied.

Instrumental stability, wavelength accuracy, adequate spectral bandpass, and transmittance accuracy are basic parameters which play a determinant role in the production of accurate transmittance measurements of a transparent material

in the spectral range of interest. Without the fulfillment of these conditions no accurate transmittance measurements could be performed. SRM 930 seems to be a useful means to assume that the measurements are accurate.

The production of accurate chemical analytical data, that is the capability to determine accurately the amount of a particular chemical element in a given matrix, requires, on the other hand, only spectrophotometric precision, as determined by the instrumental stability and sensitivity. The accuracy of the analytical measurements is determined in this case solely by the accuracy achieved in the preparation of the analytical samples and in the establishment of the reference curve. These in turn depend on the stability of the chemical reactions involved in the spectrophotometric process, and on the ability to prepare adequate reference solutions having accurately known concentrations of the chemical element of interest in a matrix identical to that of the analytical sample. Under these circumstances, analytical accuracy can be achieved using spectrophotometers which exhibit good stability and sensitivity. The wavelength accuracy, the spectral bandpass, and the accuracy of the transmittance or absorbance scale play a secondary role in this analytical application. The lack of accuracy of these parameters could affect the sensitivity and linearity, and in some cases, the specificity of spectrophotocchemical analyses, rather than their chemical accuracy.

Standard Reference Material, "SRM 930, a and b, Glass Filters for Spectrophotometry," is a transfer standard which was calibrated for transmittance in the spectral range of 440.0 nm to 635.0 nm, with a high-accuracy spectrophotometer which represents the primary transmittance standard. The transmittance values were certified with an uncertainty of 0.5 percent. The validity of these transmittance values with time will depend on the stability of the glass and the conditions under which it is used. The measurements from table 3 prove that the stability of the certified transmittance values are reproducible, within the uncertainty indicated, over a length of time exceeding 4 years. This assumes that the filters have been used with proper care, following the instructions given in the certificate. Deviations from these instructions could result in degradation or loss of accuracy. In particular, the glass surface should never be touched with the fingers, the filters should not be exposed to dust or corrosive reagents, and when not in use they should be kept always in the box provided for this purpose. Should the glass surface of the filters become accidentally contaminated, no attempts should be made to wash it, since the user does not have means to determine if this cleaning treatment has not altered the properties of

the glass surface and degraded the accuracy of the certified transmittance values. Since SRM 930 is a transfer standard, the only means available to determine its integrity is by remeasuring its transmittance with a primary standard instrument, and 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, the glass filters should be returned to NBS for verification of the transmittance data assigned to that particular set, and for cleaning and recalibration if necessary. It is recommended that before sending the glass filters, proper arrangements be made by writing the Office of Standard Reference Materials at NBS to establish the best conditions in which such a verification can be made.

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

Secondary glass standards could be produced by purchasing the optically neutral glass used for the production of SRM 930, cut to size as described in this publication and placed in holders similar to those illustrated in detail in figures 11 and 12. The transmittance of these filters should be established at the desired wavelengths with the best spectrophotometer available in the laboratory after its transmittance scale was verified with SRM 930 (a or b).

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14. Mavrodineanu, R., in ref. 10.

8. APPENDICES

These appendices contain a reproduction of the notice introducing the Standard Reference Material 930, and the calibration certificate issued for SRM 930b. It differs from SRM 930 and 930a by the addition of an empty filter holder and an additional transmittance certification at 546.1 nm. Also included are reprints from five publications which should provide further and more detailed information on the subject discussed in this publication.

9. ACKNOWLEDGEMENT

The authors gratefully acknowledge the assistance of the following persons:

- J. R. DeVoe, Chief, Special Analytical Instrumentation Section; R. W. Burke, Research Chemist; K. D. Mielenz, Analytical Chemistry Division, NBS; T. W. Mears, Standards Coordinator, Office of Standard Reference Materials, NBS; and R. N. Rand of Eastman Kodak, Research Laboratories, and President Elect, American Association of Clinical Chemists, for reviewing the manuscript and for making many valuable comments and constructive suggestions.

- H. L. Hoover, Corning Glass Works, for providing the transmittance information of the didymium and holmium oxide glass filters.

- American Society for Testing and Materials for permission to reproduce "Standard Method of Estimating Stray Radiant Energy" reprint for Appendix 7.



NBS STANDARD REFERENCE MATERIALS



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

March 26, 1971

Standard Reference Material 930 Glass Filters for Spectrophotometry

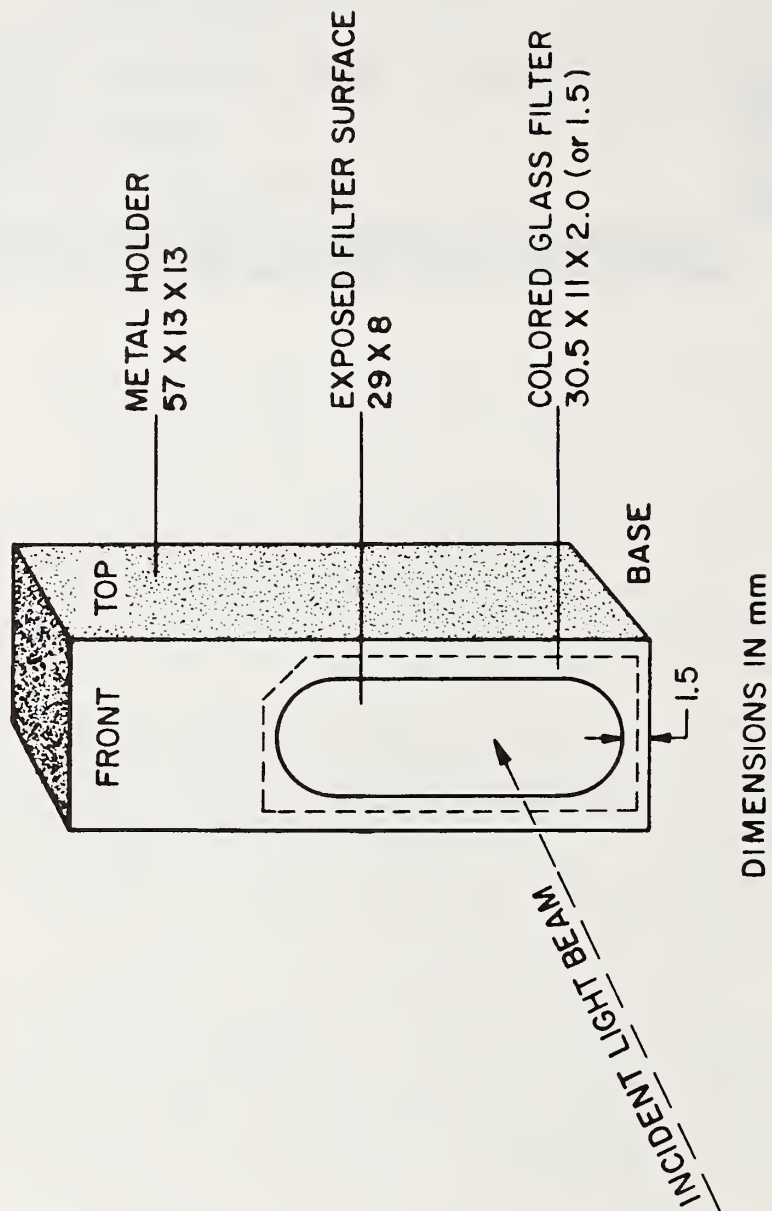
The Office of Standard Reference Materials announces the availability of Standard Reference Material 930, Glass Filters for Spectrophotometry. This SRM consists of three glass filters having transmittances of approximately 10, 20, and 30 percent. Each filter is individually calibrated and certified for absorbance and transmittance over a spectral wavelength range from 440 to 635 nanometers.

These filters are intended to check the accuracy of the photometric scale of spectrophotometers, and to provide a means of interlaboratory comparisons of spectrophotometric data. It is probable that in the field of clinical chemistry a large amount of data are being obtained on precise instruments whose accuracy is unknown. To make these data more meaningful and universally applicable, the biases between instruments must be eliminated or at least determined. A major purpose of these filters will be to assure that systematic errors due to a particular characteristic or condition of an instrument can be recognized.

This SRM should be valuable in the calibration of instruments used to obtain accurate physico-chemical constants such as molar absorptivity and equilibrium constants. For example, current interest in molar absorptivity values, as an index of the purity of biological clinical materials, requires greater accuracy of measurement. Also, the accuracy in the determination of equilibrium constants of chemical reactions in solutions, is dependent on true values of their molar absorptivities.

Standard Reference Material 930 is available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. 20234. The price is \$ 395 for a unit of three filters.

METAL HOLDER FOR THE COLORED GLASS FILTERS



U. S. Department of Commerce
Frederick B. Dent
Secretary

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards Certificate

Standard Reference Material 930b

Glass Filters for Spectrophotometry

R. Mavrodineanu and J. R. Baldwin

This Standard Reference Material is intended as a reference source for the calibration of the photometric scale of spectrophotometers. It consists of three individual filters and one empty filter holder. 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	ABSORBANCE (A)					TRANSMITTANCE (%T)				
	Wavelength and (Bandpass)					Wavelength and (Bandpass)				
	nm					nm				
	440.0 (2.2)	465.0 (2.7)	546.1 (6.5)	590.0 (5.4)	635.0 (6.0)	440.0 (2.2)	465.0 (2.7)	546.1 (6.5)	590.0 (5.4)	635.0 (6.0)

The transmittance values given are certified with a relative uncertainty of ± 0.5 percent (example: a nominal value of absorbance of 0.500 ± 0.0022). This uncertainty is the sum of the random error of ± 0.1 percent (2SD limit) and of estimated biases which are ± 0.4 percent. These biases are due to possible systematic errors. Measurements were made at 25 °C. Room temperature variations within several degrees Celsius of this temperature will not significantly affect the calibration of these filters.

It is recommended that the filters be handled only by the edges and with soft plastic (polyethylene) gloves and optical lens tissue. When not in use they should be stored in their holders and in the box provided for this purpose. Extended exposure to laboratory atmosphere and dusty surroundings should be avoided.

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

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
February 24, 1975

(over)

J. Paul Cali, Chief
Office of Standard Reference Materials

The transmittance measurements were made with the high-accuracy spectrophotometer designed and constructed at the National Bureau of Standards [1]. The accuracy of this instrument was established by light-addition measurements.

The neutral NG-4 and NG-5 glasses for the filters were provided by Schott of Mainz, Germany, and are 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 [2].

The filter holder is black anodized aluminum alloy and has the following nominal dimensions: height: 57 mm, width: 13 mm, depth: 13 mm. This holder and the size and shape of the filters were selected to conform to the dimensions of the sample compartment of most conventional spectrophotometers. The filters are approximately 30.5 mm long, 11 mm wide, and 2.0 mm and 1.5 mm thick for the NG-4 glass and 1.5 mm thick for the NG-5 glass. Corresponding to these thicknesses are nominal transmittances of 10, 20, and 30 percent, respectively. These thicknesses were selected to provide a means for calibrating the photometric scale at three different levels. The exposed surface of the glass filter is approximately 29 mm by 8 mm, starting from a distance of 1.5 mm from the filter holder base (see figure).

The transmittance of filters depends on the intrinsic properties of the material. Spectral band-pass, wavelength [2.3.5], geometry of the optical beam, surface conditions, and positioning of the filter also affect the transmittance values, and can lead to further biases. The certified data will be reproduced when transmittance measurements are made under similar conditions. 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 producing the vertical image of the slit (about 8 mm by 0.5 mm), using a convergent beam geometry with an opening of f:10, in the middle of the entrance face of the glass filter. (The filter should be positioned in the spectrophotometer as shown in the figure, to obtain correct values.)

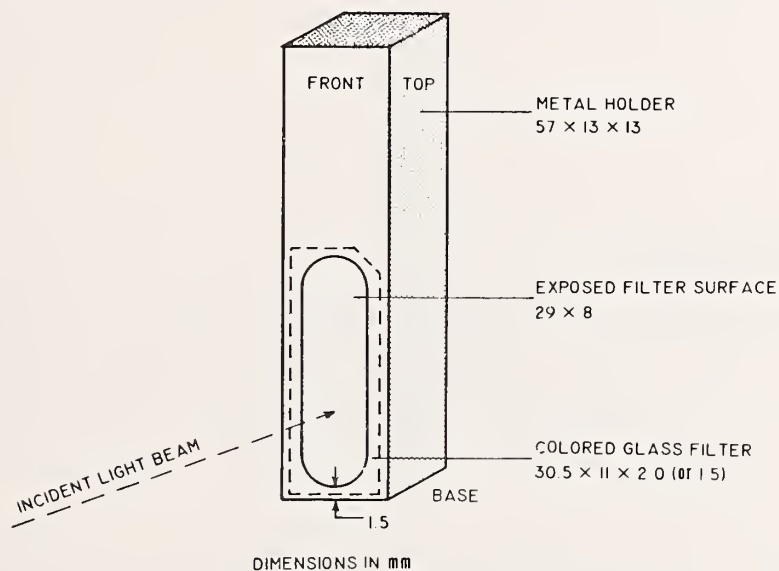
Prior to the certification measurements, each filter was examined for surface defects and then thoroughly cleaned. If, through handling, the surface of the filter becomes contaminated with dust, it may be cleaned with a small soft brush attached to a rubber tube connected to a vacuum source [2.4]. If the surface becomes contaminated with fingerprints, they must be eliminated 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 replaced in its proper position in its holder. To remove and replace the filter in the metal holder, the spring-loaded plate should be removed with care to prevent damage to the filter. As little handling as possible is recommended.

NOTE: The check of the calibration of photometric scales defines only one of the parameters required for obtaining accurate transmittance values and molar absorptivities. Other factors that also must be established are wavelength accuracy, stray light, cell parameters, fluorescence, polarization, reflection, and temperature coefficient. Some of these variables are discussed in NBS publications [1.2.5]. It is planned to summarize various aspects of accurate spectrophotometric measurements in an NBS-260 Special Publication that would provide additional data on specific Standard Reference Materials. In the interim, SRM 930b, should be used as described in the certificate. Consult the manufacturer of the instrument if differences are obtained that exceed those specified by the manufacturer.

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 Hospital of the University of Pennsylvania, Philadelphia, Pennsylvania; and Donald S. Young, M.B., Ph.D., of the National Institutes of Health, Bethesda, Maryland.

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METAL HOLDER FOR THE COLORED GLASS FILTERS



January
1955

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

Letter
Circular
LC-1017

Re-issued
January 1967

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

Contents

1. Introduction.
2. Checking the wavelength scale.
 - 2.1 Non-recording spectrophotometers.
 - 2.2 Recording spectrophotometers.
 - 2.2.1 General Electric recording spectrophotometers.
 - 2.2.2 Cary Model 14 recording spectrophotometers.

References.

1. Introduction.

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

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

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

2. Checking the Wavelength Scale.

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

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

*Numbers in parentheses refer to the References.

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

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

<u>Wavelength</u> (nm)	<u>Note</u>	<u>Wavelength</u> (nm)	<u>Note</u>	<u>Wavelength</u> (nm)	<u>Note</u>	<u>Wavelength</u> (nm)	<u>Note</u>
Mercury Arc in Quartz (Same wavelengths in glass above 300 nm)							
205.29		253.48	3*	296.73	*	398.40	
222.47		253.65		302.15		400.63	
223.41		257.63		302.35	6*	404.66	*
225.88		260.32		302.56		407.78	*
230.21		265.20		302.75		435.83	*
232.32		265.37	4*	312.57	*	491.60	
135.25		265.51		313.15		546.07	*
237.83	*	269.95		313.18	7*	576.96	
239.94	1*	275.28	*	334.15	*	579.07	9*
239.97		275.97		349.28		623.44	
244.69		280.35		365.01		671.62	
246.41		280.45	5*	365.48		690.72	
248.20		284.78		366.29	8*	1014.0	*
248.27	2*	289.36	*	366.33		1128.7	
248.38		292.54		390.64			

Helium Discharge Tube in Glass

318.77		396.47		447.15	*	667.81	*
361.36		402.62		471.31	*	706.52	*
363.42		412.08		492.19		728.13	
370.50		414.38		501.57	*	1083.0	*
381.96		438.79		504.77			
388.86	*	443.75		587.56	*		

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

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

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

Neon Discharge Tube		Aluminum Spark in Air	Hydrogen Arc
<u>Wave- length</u> (nm)	<u>Relative Intensity</u>	<u>Wavelength</u> (nm)	<u>Wavelength</u> (nm)
585.25	5	216.88	434.05
588.19	4	217.40	486.13
594.48	8	220.46	656.28
597.55	2	221.00	
603.00	2	226.35	
607.43	8	226.91	
609.62	13	236.71	Sodium Arc
614.31	25	237.21	<u>Wavelength</u>
616.36	6	237.31	(nm)
621.73	4	237.34	589.00
626.65	11	237.84	589.59
630.48	4	256.80	
633.44	20	257.51	Cesium Arc
638.30	23	257.54	<u>Wavelength</u>
640.22	100	263.16	(nm)
650.65	39	265.25	852.11
653.29	8	266.04	894.35
659.90	12	281.62	
667.83	23	308.22	
671.70	14	309.27	
692.95	23	358.69	
702.41	2	394.40	
703.24	45	396.15	
705.91	--		
717.39	5		
724.52	17		
743.89	4		
748.89	--		
753.89	--		
754.40	--		

2.1 Non-Recording Spectrophotometers.

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

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

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

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

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

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

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

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

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

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

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

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

2.2 Recording Spectrophotometers.

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

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

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

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

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

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

2.2.1. General Electric Recording Spectrophotometer.

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

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

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

<u>Wavelength of Maximum Absorption (nm)</u>	<u>Approximate Spectrum Interval Transmitted by Slits (nm)</u>
441.0	10
475.0	10
528.5	10
585.7	10
684.0	10
743.8	10
745.5	20
808.	20
883.	20
1067.	20

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

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

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

2.2.2. Cary Model 14 recording spectrophotometer.

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

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

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

Useful wavelengths
between 240 and 370 nm

241.5
279.3
287.6
333.8
360.8

Useful wavelengths
between 360 and 650 nm

360.8
385.8
418.5
453.4
459.9
536.4
637.5

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

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

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

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

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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

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_λ 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 $R^\perp = R^\parallel = R$.

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 handpasses 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

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 10⁴ 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 Instrument³

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

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

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

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

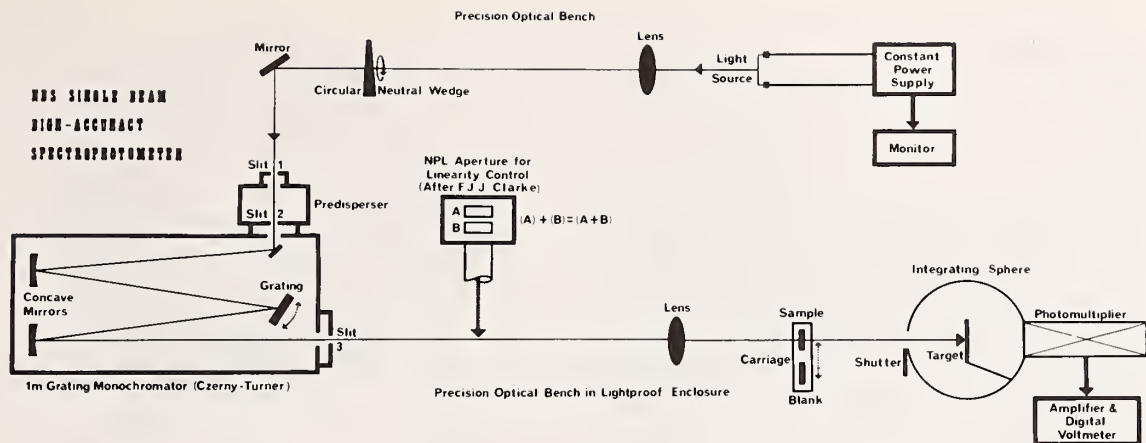


FIGURE 1. Principle of the single beam high accuracy spectrophotometer. The aperture unit is placed on the optical bench only when linearity measurements are performed.

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

The demagnified (2 to 1) image of the ribbon filament is projected on the entrance slit of the predisperser by a fused quartz (nonfluorescent SiO₂) 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-

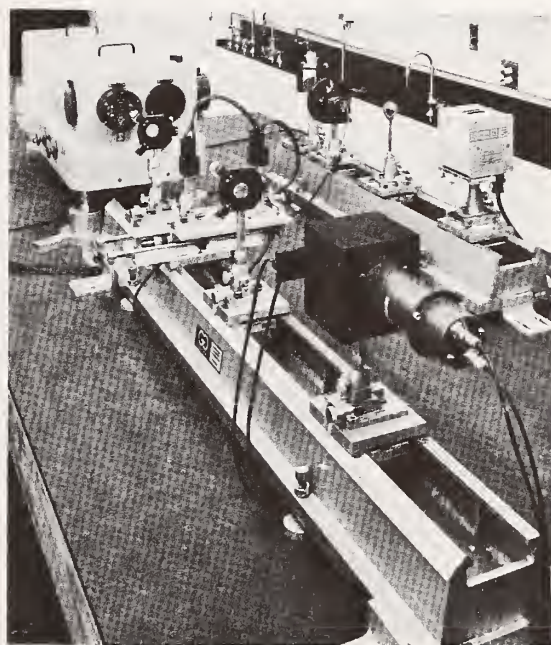


FIGURE 2. General views of the spectrophotometer. Rear: optical bench carrying the tungsten-halogen radiation source used for checking the alignment of optical components, followed by a quartz lens, the circular quartz neutral wedge, and a flat mirror. Left: the 1-m Czerny-Turner grating monochromator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

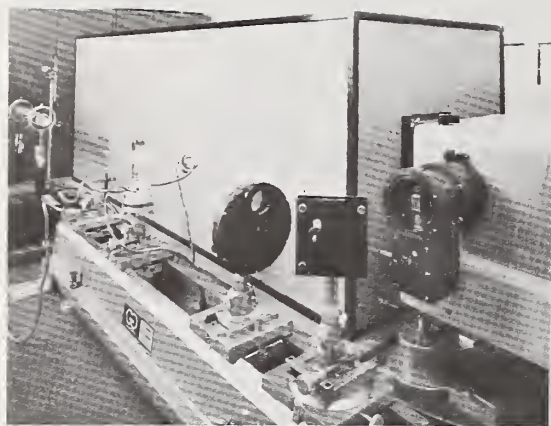


FIGURE 3. Close view of the tungsten ribbon filament lamp on its adjustable holder, followed by the quartz lens—circular neutral wedge assembly, and by the flat mirror in its adjustable holder. The 30° quartz prism Littrow-type predisperser is located at the entrance slit of the 1-m grating monochromator.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

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

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

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

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

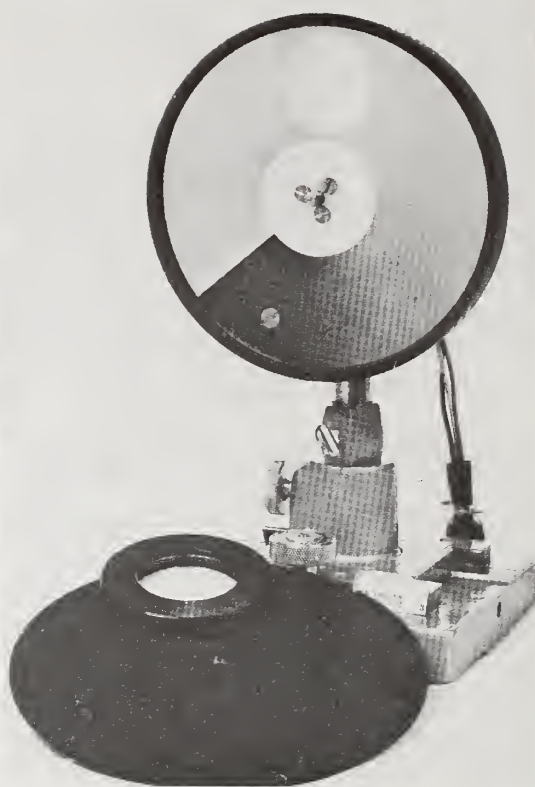


FIGURE 4. Close view of the circular, neutral wedge. The front plate which carries the fused silica lens was removed to show the fused silica disc with the evaporated metal layer.

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

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



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

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

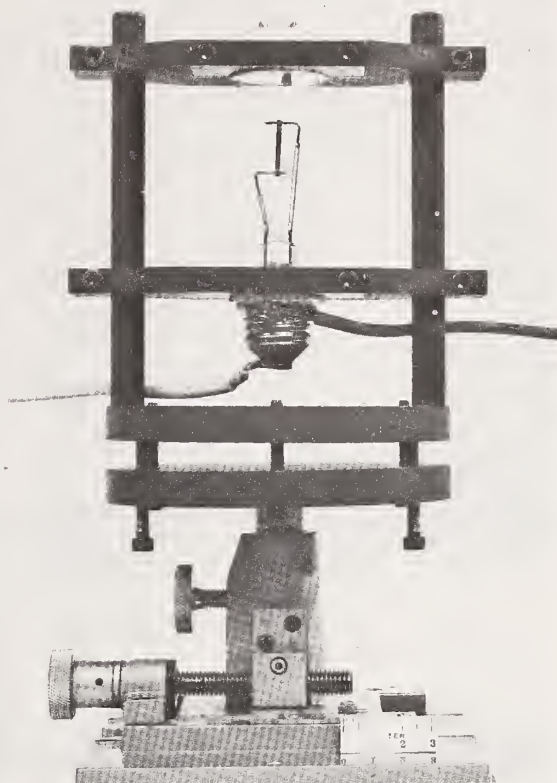


FIGURE 6. The tungsten ribbon filament lamp in the newly designed adjustable holder. The platform which carries the lamp is similar to that described in figure 5 and can be oriented in the horizontal plane through the six screws spaced around the edges of the platform at 60° intervals. Three screws push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

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

photometric measurements was described by O. C. Jones and F. J. J. Clarke [24, 29] and by F. Desvignes and J. Ohnet [32]. A critical discussion of some aspects of accurate spectrophotometry will be found in an NBS manuscript by Gibson and associates [22]. The radiation addition principle, using two apertures with one source of radiation, was chosen for our work. The aperture method for checking the linearity of photometric data was in use at the National Physical Laboratory from about 1930 onwards, and one form of it was described by Preston and Cuckow [11] in conjunction with a single beam spectrophotometer, using a five aperture screen. One year later, Buchmüller and König [12] described and used a two aperture unit. At NBS, Barbrow [14] used a 10 aperture arrangement, while Harding [16] and Cordle and Habell [25] at NPL described a two aperture system. Multiapertures were used by Hoppmann [21], Bischoff [23], Sanders [26] and Nonaka and Kashima [27]. Finally, Clarke [30]

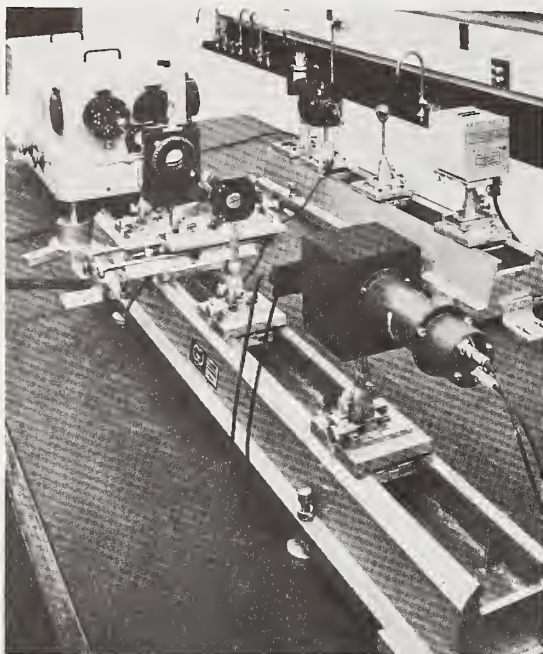


FIGURE 7. Same as figure 2 except for the sample holder which in this case is capable of rotating the sample 360° and to displace it in the x-y direction through the micrometer screws.

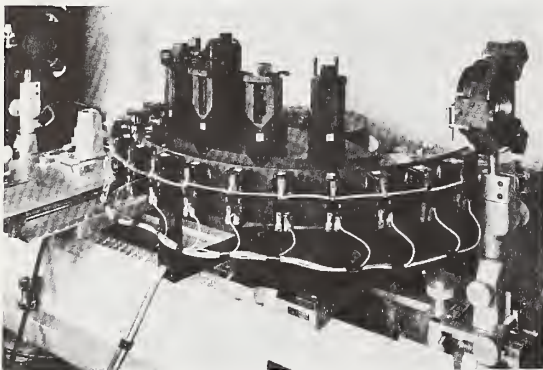


FIGURE 8. Circular platform carrying seven filter holders. The 15 position switches (7 sample positions and 8 blank positions) are visible along with the two quartz lenses. The exit slit of the monochromator is at left.

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

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

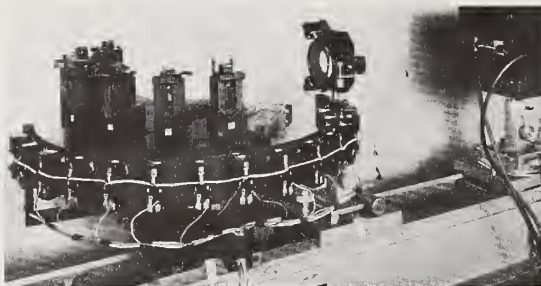


FIGURE 9. Same as figure 8. The pneumatic cylinder which rotates the circular platform through a ratchet mechanism is visible at the rear of the platform. The integrating sphere with its pneumatic shutter is seen at right.

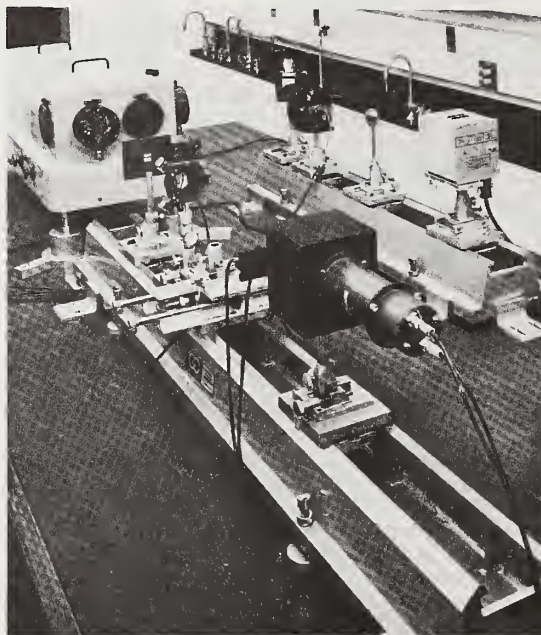


FIGURE 10. Same as figure 2. In this case the dual-aperture unit for linearity control is located on the optical bench after the exit slit of the monochromator.

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

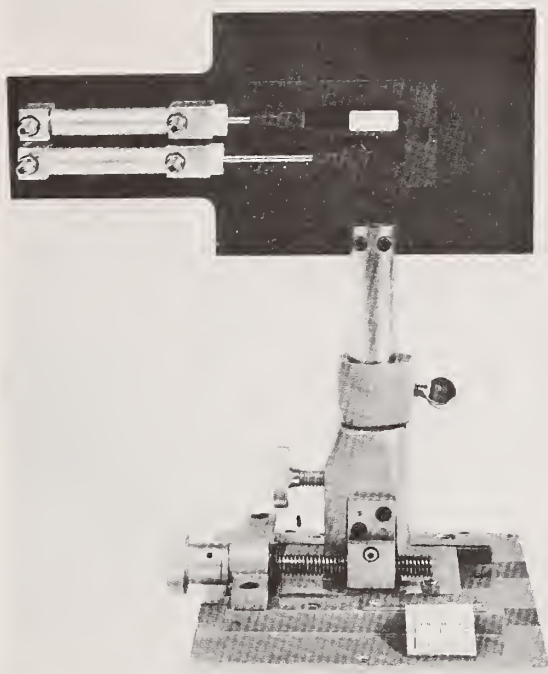


FIGURE 11. Detail of the dual-aperture unit showing its construction and the pneumatic system which operates the two shutters. One aperture is open, the other is closed.

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

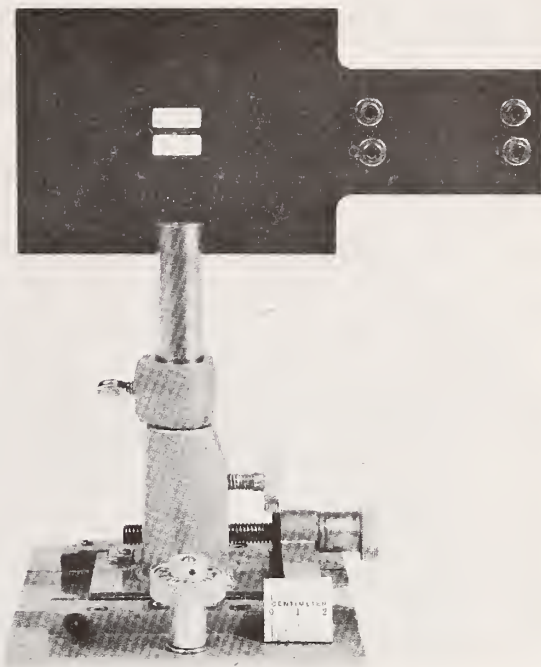
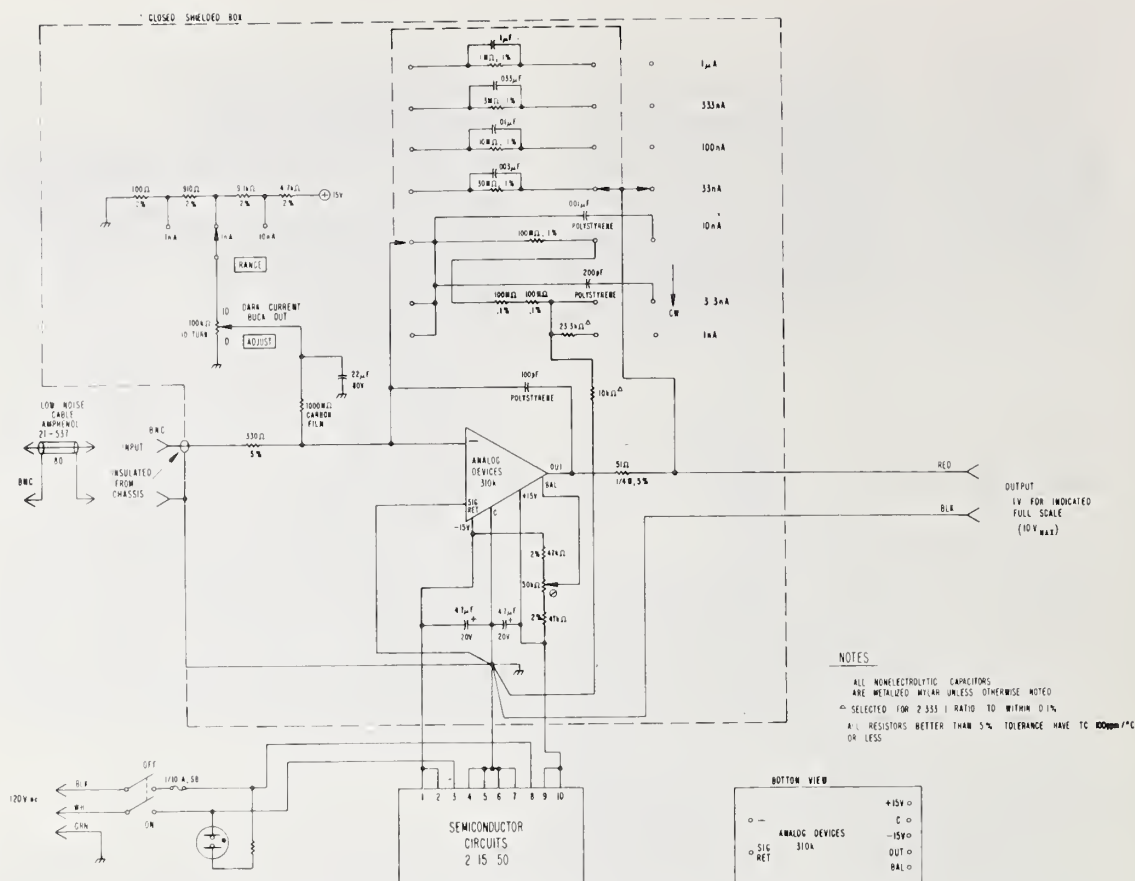


FIGURE 12. Front view of the dual-aperture unit, with both apertures open.

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.



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

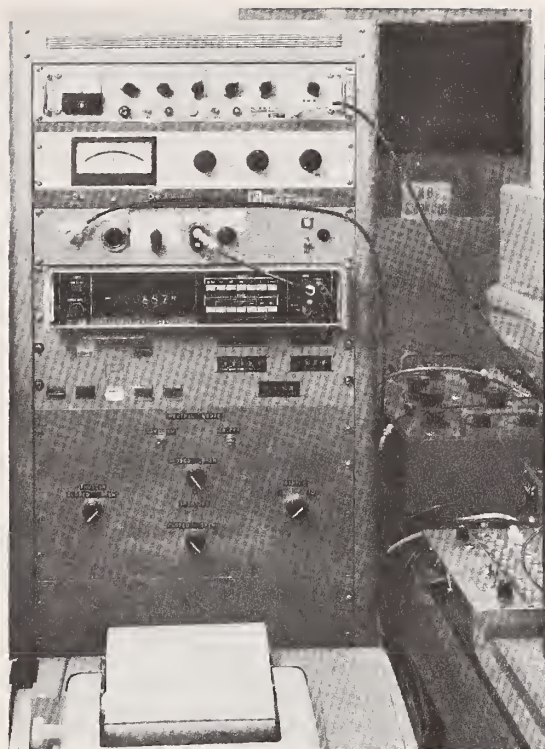


FIGURE 14. Console containing the power supply for the photomultiplier tube, the dc null detector, the current-to-voltage converter, the digital voltmeter, the command panel for computer operation, and the command panel for the pneumatic operation of the shutter, aperture system, and single sample carriage. 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.

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.

CALIBRATION OF SRM930 AT 440 NM
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	.4388F-03	.2192F-03	
2	.6413441E 00	.3256E-03	.5077F-03	
3	.2001230E 01	.4320F-03	.2159F-03	32.044
4	.6528346E 00	.4804F-03	.7359F-03	
5	.2001040E 01	.4254F-03	.2126F-03	32.623
6	.4221110F 00	.2293E-03	.5432E-03	
7	.2000905F 01	.3041E-03	.1520F-03	21.095
8	.6560142F 00	.3189F-03	.4861F-03	
9	.2001402F 01	.4476E-03	.2234F-03	32.781
10	.2358762F 00	.1425F-03	.6039F-03	
11	.2001539E 01	.4114F-03	.2055F-03	11.785
12	.6739426F 00	.2848F-03	.4266F-03	
13	.2001205F 01	.4678F-03	.2338F-03	33.674
14	.2366761E 00	.1064E-03	.4456E-03	
15	.2001101E 01	.4150E-03	.2074F-03	11.927
1	.2001622F 01	.3187E-03	.1592F-03	
2	.6412963E 00	.1321E-03	.2060F-03	
3	.2002043E 01	.6139F-03	.3067F-03	32.036
4	.6526482E 00	.2474E-03	.3790F-03	
5	.2001551E 01	.4756E-03	.2376F-03	32.603
6	.4222282F 00	.2174E-03	.5149F-03	
7	.2001507F 01	.4355F-03	.2176F-03	21.095
8	.6562004E 00	.3344F-03	.5095F-03	
9	.2001529F 01	.5337E-03	.2667F-03	32.785
10	.2359933E 00	.1886F-03	.7992F-03	
11	.2001634E 01	.4532F-03	.2244F-03	11.790
12	.6741099F 00	.3418F-03	.5070F-03	
13	.2001589F 01	.6368F-03	.3182F-03	33.678
14	.2386828F 00	.1604E-03	.6720F-03	
15	.2001829F 01	.3388F-03	.1693F-03	11.924
1	.2002214F 01	.2826E-03	.1412F-03	
2	.6413472F 00	.3518F-03	.5486F-03	
3	.2001882F 01	.3882F-03	.1939F-03	32.035
4	.6526177F 00	.2513F-03	.3851F-03	
5	.2001761F 01	.3841F-03	.1919F-03	32.601
6	.4223418F 00	.2957F-03	.7000F-03	
7	.2002075F 01	.4892F-03	.2443F-03	21.097
8	.6562083F 00	.1365F-03	.2081E-03	
9	.2001871F 01	.3708F-03	.1852F-03	32.777
10	.2358786F 00	.1596F-03	.6767F-03	
11	.2002130F 01	.5036F-03	.2515F-03	11.782
12	.6740563F 00	.3022F-03	.4484F-03	
13	.2001997F 01	.4545F-03	.2270F-03	33.668
14	.2368354F 00	.1704E-03	.7133F-03	
15	.2002478F 01	.2975F-03	.1485F-03	11.928

FIGURE 15. Computer data presentation.

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

III. Stability of the Electronic System

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

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

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

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

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

a. **Stability of the Current-to-Voltage Converter.** A constant voltage was supplied to the converter using the dark current compensation provided on the unit. Fifty individual measurements were taken every 5 seconds and the average value was printed along with its percent standard deviation. The measurements were then repeated 15 times and an average

of the 15 values was calculated along with the corresponding percent standard deviation. These measurements were then repeated three times. The results are summarized in table 1. This table also presents the values for the first group and the average values and corresponding percent standard deviation for the two consecutive groups. It can be seen from the stability of the current-to-voltage unit that measurements can be performed with a reproducibility of about 0.0012 (at the 67% confidence level) expressed as percent standard deviation for a single determination. The time interval between the first and last group of measurements was 15 min.

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

Replication	Average of 50 individual measurements; volts	Percent standard deviation
1	1.003494	0.0013 ₆
2	1.003496	0.0012 ₉
3	1.003482	0.0014 ₆
4	1.003507	0.0011 ₁
5	1.003515	0.0013 ₄
6	1.003508	0.0013 ₆
7	1.003497	0.0011 ₈
8	1.003498	0.0013 ₃
9	1.003505	0.0011 ₀
10	1.003510	0.0014 ₂
11	1.003518	0.0013 ₃
12	1.003521	0.0012 ₀
13	1.003522	0.0013 ₁
14	1.003507	0.0012 ₆
15	1.003527	0.0013 ₇
<hr/>		
Average of replications	1.003507	} First group
Percent standard deviation	0.0012	
<hr/>		
Average of replications	1.003535	} Second group
Percent standard deviation	0.0015	
<hr/>		
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 0.022₅ for single measurements with 2.00 V at the photomultiplier tube anode.

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

Replication	Average of 50 individual measurements; volts	Percent standard deviation
1	1.012329	0.027 ₁
2	1.012342	0.048 ₈
3	1.012322	0.027 ₂
4	1.012320	0.033 ₈
5	1.012394	0.043 ₅
6	1.012421	0.015 ₃
7	1.012404	0.018 ₄
8	1.012406	0.029 ₆
9	1.012365	0.019 ₆
10	1.012402	0.019 ₁
11	1.012465	0.025 ₂
12	1.012412	0.061 ₅
13	1.012451	0.023 ₅
14	1.012417	0.029 ₈
15	1.012481	0.024 ₈
<hr/>		
Average of replications	1.012395	} First group
Percent standard deviation	0.0050	
<hr/>		
Average of replications	1.012467	} Second group
Percent standard deviation	0.0033	
<hr/>		
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 M Ω 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:

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

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 \AA stroms. 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
<hr/>		
Average of replications	1.536122	} First group
Percent standard deviation	0.0082	
<hr/>		
Average of replications	1.535768	} Second group
Percent standard deviation	0.0095	
<hr/>		
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 pro-

cedure 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
<hr/>		
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 NC-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
<hr/>							
Average	33.32	21.710	12.238	50.987	33.378	20.902	13.472
<hr/>							
Percent σ	0.0080	0.0051	0.0150	0.0072	0.0083	0.0108	0.0141
<hr/>							
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 10^6 [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 M Ω 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:

<i>Step 1</i>	(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		

<i>Step 2</i>	(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		

<i>Step 3</i>	(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

<i>Step 4</i>	(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.

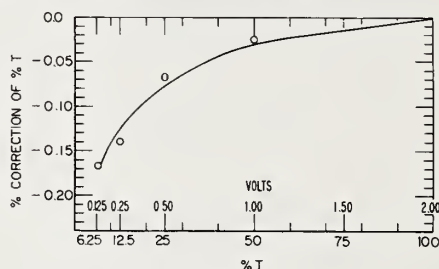


FIGURE 16. Linearity correction curve.

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 $I_0 = 2.00228$ V and $I = 0.54220$ V, then percent T is:

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

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

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

Mielenz and Eckerle have studied recently the 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
I St.							
I No.	2	4	6	8	10	12	14
II %T	27.07	16.40	46.39	26.11	15.21	37.34	23.23
II St.							
II No.	14	2	4	6	8	10	12
III %T	27.08	16.43	46.39	26.11	15.21	37.33	23.23
III St.							
III 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 pre-disperser-monochromator unit, and by projecting the image of the exit slit (8 by 0.5 mm) at the entrance face of the filter with a convergent beam geometry corresponding to an f:10 opening. The glass filter was checked prior to measurements with a polariscope for freedom of internal tensions. Column one of table 8 shows the results obtained when transmittance measurements were made using the radiations produced by the spectrophotometer. Column two shows the results

obtained when a polarizing sheet, with the vibration plane horizontal, was placed in front of the glass filter. The measurements obtained with the vibration plane in vertical position, are given in column three.

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

XI. Comparison of Transmittance Measurements

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

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

Wavelength nm	% <i>T</i>			% Difference $\%T_1 - \%T_3$
	Produced by spectro- photometer	Polarizer, plane of vibration horizontal	Polarizer, plane of vibration vertical	
	1	2	3	
440.0	19.81 ₈	19.80 ₀	19.78 ₈	- 0.15
465.0	22.59 ₇	22.60 ₀	22.56 ₉	- 0.12
590.0	19.17 ₈	19.17 ₀	19.09 ₉	- 0.41
635.0	20.61 ₁	20.60 ₂	20.54 ₇	- 0.31

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

The results given in table 9 indicate that an average difference of -0.19 percent of the values was obtained between the measurements carried out at NPL and at NBS. An average difference of -0.30 percent of the value was found when similar measurements were

performed on the inconel-on-quartz filters, as shown in table 10.

X. Standard Reference Materials for Spectrophotometry

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

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

Wavelength nm	NBS, % <i>T</i> March 12, 1971	NBS, % <i>T</i> May 18, 1971	NBS, % <i>T</i> average	NPL, % <i>T</i> 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 ₃	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.

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

Wavelength nm	NBS, % <i>T</i>		NBS, % <i>T</i> average	NPL, % <i>T</i>	% 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,

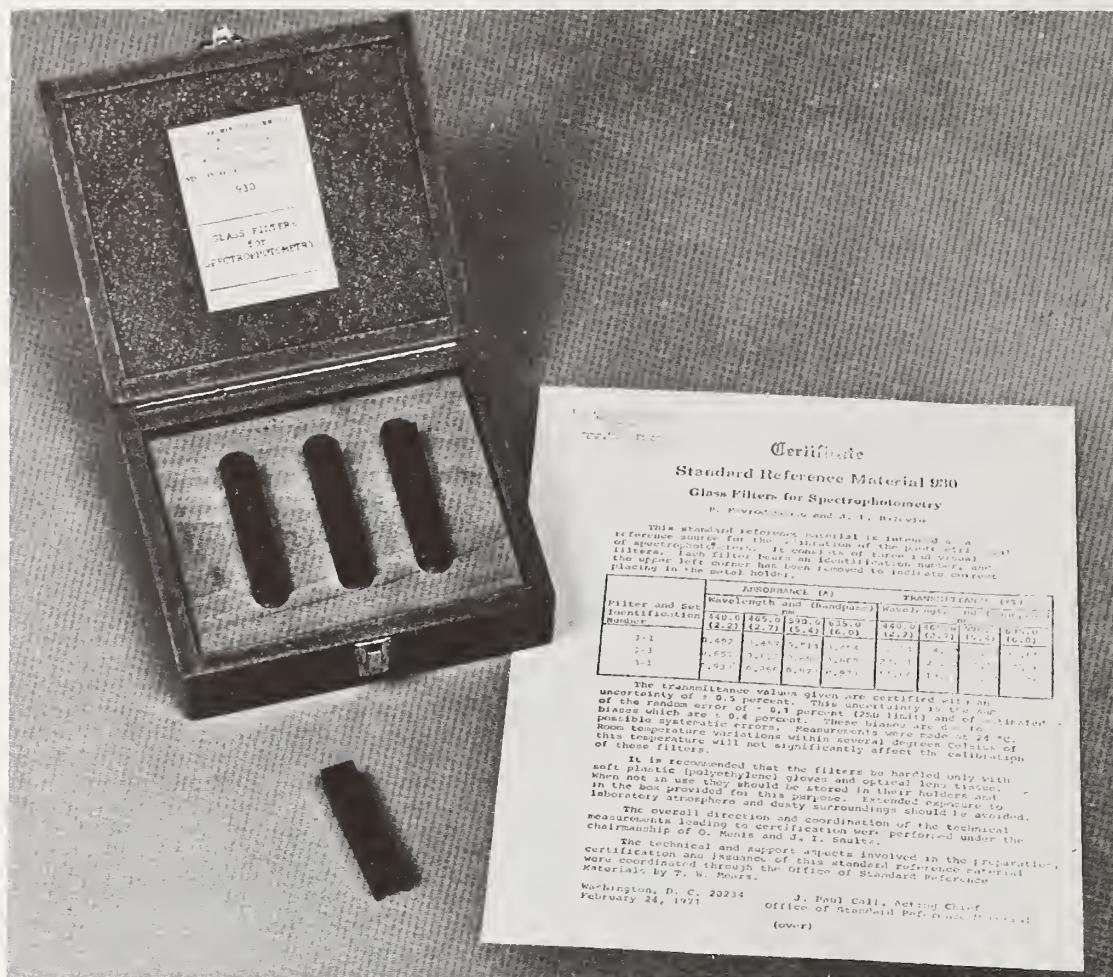


FIGURE 17. NBS Standard Reference Material 930 and calibration certificate.

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_2 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 \times 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 \times 13 \times 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:

Wavelength, nm	Transmittance, percent			
	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 BaSO₄ 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: Oriol Optics Corp., 1 Market Street, Stamford, Connecticut 06902.

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

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

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Reflection Correction for High-Accuracy Transmittance Measurements on Filter Glasses

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

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

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

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

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

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

2. Theoretical Background

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

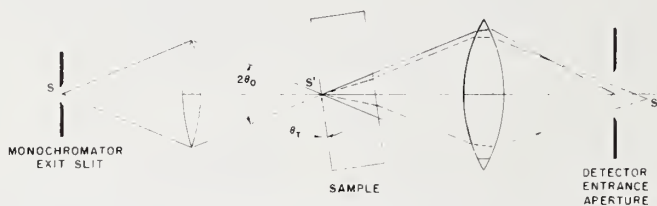


FIGURE 1. Sample-compartment optics of a focused-beam spectrophotometer.

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

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

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

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

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

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

$$\phi_0 = T_1 T_2 (1 + R_1 R_2 + \dots), \quad (3a)$$

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

$$\phi = T_1 T T_2 (1 + R_1 R_2 T^2 + R R_2 + R_1 R + \dots), \quad (3b)$$

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

$$T_M = \phi/\phi_0 = T[1 + (R_1 + R_2)R - R_1 R_2(1 - T^2)]. \quad (3c)$$

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

$$T - T_M = \Delta T + \Delta T', \quad (4a)$$

where

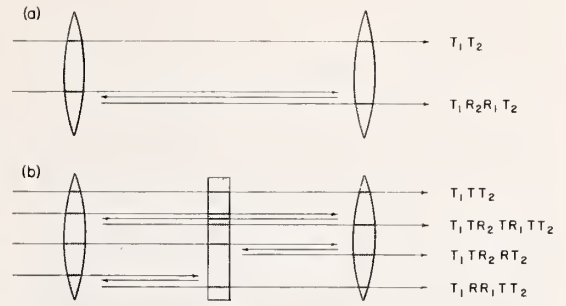


FIGURE 2. Reflected beams in a spectrophotometer with lenses.

$$\Delta T = -(R_1 + R_2)RT, \quad (4b)$$

$$\Delta T' = R_1 R_2 T(1 - T^2). \quad (4c)$$

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

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

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

$$T = \tau[1 + (1/2n^2)(\ln \tau_i)(\theta_7^2 + \frac{2}{3}\theta_0^2) \pm (4r/n)\theta_7^2 + \dots], \quad (5)$$

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 under-filled 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.

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

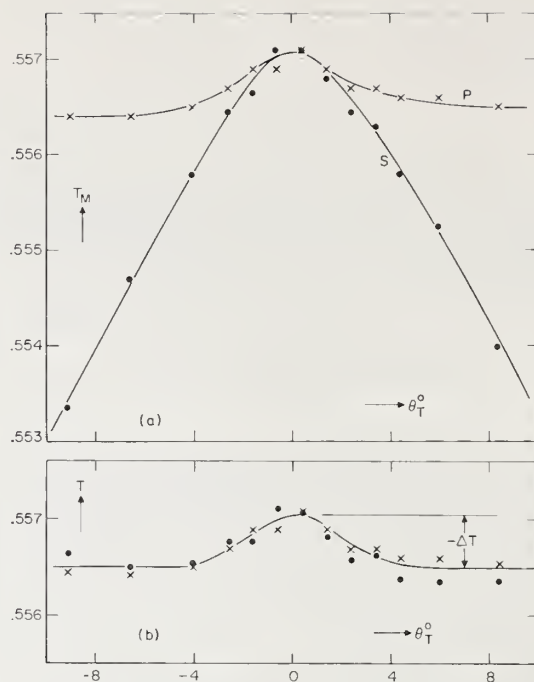


FIGURE 3. (a) Measured transmittance T_M versus tilt angle θ_T for 55 percent filter in S and P polarized light at $\lambda = 574$ nm. (b) The same data after application of tilt correction.

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 \times 50 mm \times 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

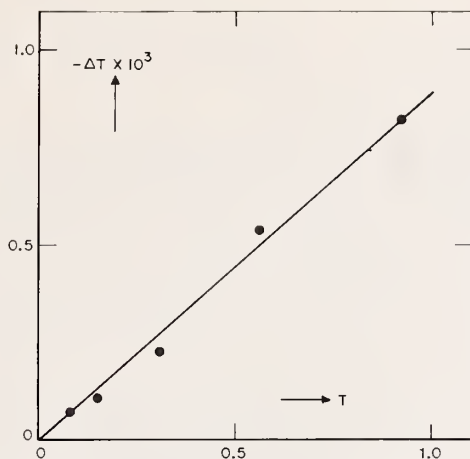


FIGURE 4. Reflection correction ΔT versus T for $\lambda = 574$ nm.

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 pre-disperser-monochromator aggregate of the spectrophotometer between the circular neutral wedge and the flat front-surface mirror (see ref. [4], fig. 3). This placement of the polarizer on the source side of the spectrophotometer avoids the additional reflection errors which would occur if the polarizer were put in the sample compartment of the spectrophotometer, but requires that the monochromator does not significantly depolarize the incident radiation or rotate its plane of polarization. This was ascertained by testing the monochromator between crossed polarizers at the wavelengths at which the measurements were performed.

Each transmittance measurement was performed in S and P polarized radiation and for tilt angles varying by $\pm 10^\circ$ 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,

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

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

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

These results were then combined into the final empirical expression.

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

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,

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

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

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

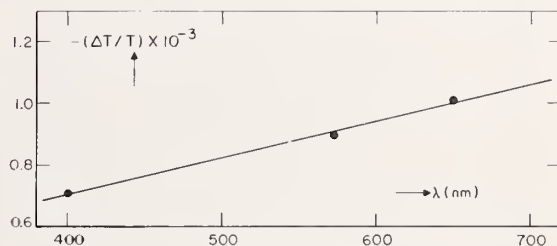


FIGURE 5. Reflection correction ΔT versus λ for $T = 0.92$

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

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

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)

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],[†] 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, BaSO₄-coated averaging sphere as the signal detector. The tungsten lamp is imaged on the predisperser entrance slit by a fused-silica lens. Two additional fused-silica lenses are used in the sample compartment to focus the monochromator exit slit at the sample, and to refocus it into the averaging sphere [3]. The photomultiplier signal is measured by means of a current-to-voltage converter and a digital voltmeter, interfaced with a computer.

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

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

[†] 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 attrib-

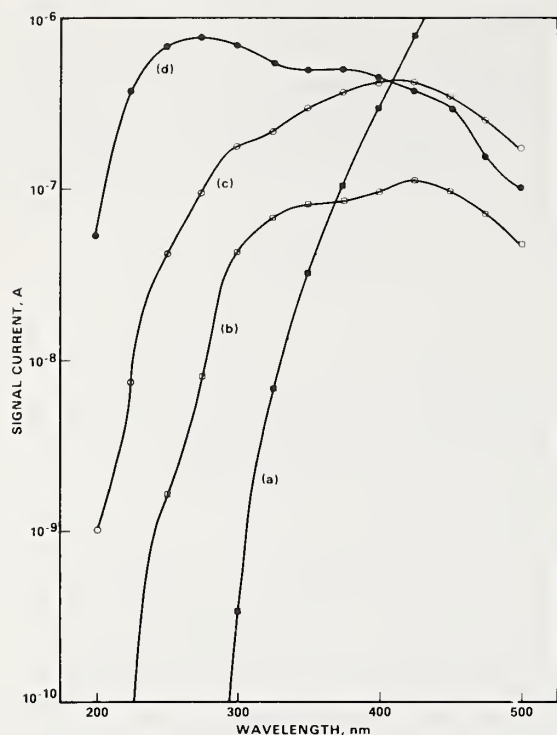


FIGURE 1. Successive improvement of clear-space signal level of original spectrophotometer (curve a) obtained by: (b) deuterium arc lamp, (c) improved averaging sphere, and (d) new grating.

utable 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.

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

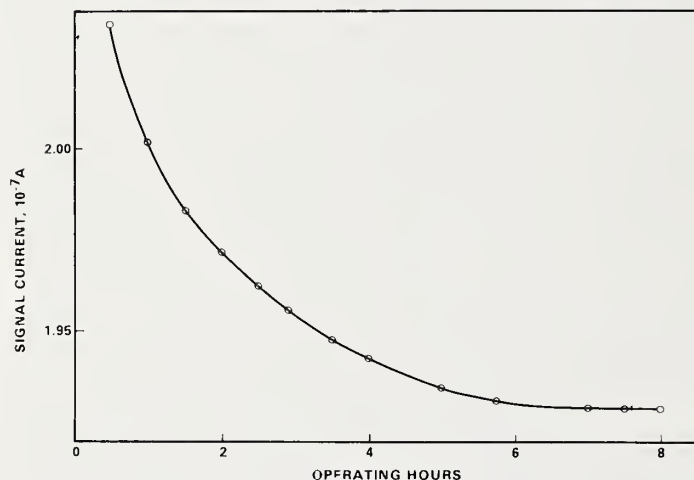


FIGURE 2. Long-term signal drift observed with deuterium lamp.

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].

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

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

where

ϕ = radiant flux into sphere,

ϕ_D = flux reaching detector,

r = wall reflectance (assumed close to, but not equal to unity),

s = sphere radius,

d = radius of sensitive area of detector (assumed equal to radius of exit-port)

e = distance between exit port and detector.

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

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

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

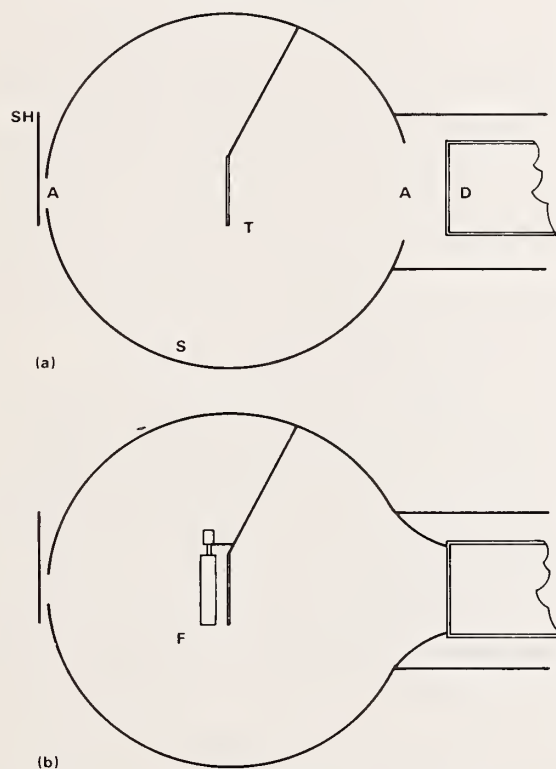


FIGURE 3. Geometry of (a) original averaging sphere and (b) improved sphere.

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

cent material selected was a 0.923 g/l solution of 2,5-diphenyloxazole (PPO) in *n*-hexane in a $10 \times 10 \times 2$ 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

$$I_e = QI_a, \quad (2a)$$

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

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

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_o , the diameter of the blur circle in the sample plane for a wavelength $\lambda < \lambda_o$ can easily be shown to be equal to

$$\delta = D[2f(\lambda_o)/f(\lambda) - 1], \quad (3)$$

where f is the focal length and D is the effective diameter of the focusing lens. For the particular lenses of the original spectrophotometer [$f(200 \text{ nm}) = 168 \text{ mm}$, $f(500 \text{ nm}) = 200 \text{ mm}$, $D = 38 \text{ mm}$], and assuming that the focusing was done at 500 nm, the computed blur-circle diameter at 200 nm 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.

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- [4] K. D. Mielenz, *J. Res. Nat. Bur. Stand. (U.S.)*, **76A** (Phys. and Chem.), No. 5, 455-467 (Sept.-Oct. 1972).
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- [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.
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(Paper 78A5-838)



Designation: E 387 - 72

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Standard Method of ESTIMATING STRAY RADIANT ENERGY¹

This Standard is issued under the fixed designation E 387; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 Stray energy (SRE) can be a significant source of error in spectrophotometric measurements. The danger of significant error is enhanced since its presence is often unsuspected. Also, SRE frequently increases with passage of time. Therefore, thorough periodic testing is highly important.

1.2 This method affords an estimate of radiant energy at wavelengths remote from those of the nominal pass band transmitted through the monochromator of an absorption spectrophotometer. Test-filter materials are described that discriminate between the desired wavelengths and those which contribute most to SRE for conventional commercial spectrophotometers used in the ultraviolet, the visible, the near infrared, and the alkali halide infrared ranges. These procedures apply to instruments of conventional design, with usual sources, detectors, and optical designs. The vacuum ultraviolet and the far infrared present special problems that are not discussed herein.

1.3 These procedures are neither all-inclusive nor infallible. Because of the nature of readily available filter materials, with a few exceptions the procedures are insensitive to SRE of shorter wavelengths in the ultraviolet or visible, or of lower frequencies in the infrared, and they are not necessarily valid for "spike" SRE nor for "nearby SRE." (See Appendixes for general discussion and definitions of these terms.) However, they are adequate in most cases and for typical applications. They do cover instruments using prisms or gratings, in either single or double monochromators.

1.4 The proportion of SRE encountered with

a well-designed monochromator, used in a favorable spectral region, is a small fraction of 1 percent. With a double monochromator it may easily be less than 1 ppm even with a broad-band continuum source. Under these conditions, it may be difficult to do more than determine that it falls below a certain level. Actual measurement often requires special techniques and instrument operating conditions that are not typical of those occurring during use. When absorption measurements with continuum sources are being made, it is frequently true that, owing to the effect of slit width on SRE in a double monochromator, these test procedures tend to give "conservative" results; that is, because larger slit widths than normal must be used to admit enough energy to the monochromator to permit evaluation of the SRE, the stray proportion indicated is greater than would normally be encountered in use.

1.5 The principal reason for a test procedure that is not exactly representative of normal operation is that the effects of SRE are "magnified" in sample measurements at high absorbance. It is usually necessary to increase sensitivity in some way during the test in order to evaluate the SRE adequately. This is usually accomplished by increasing slit width and so obtaining sufficient energy to allow meaningful measurement of the SRE after the monochromatic energy has been removed by the SRE filter. A further reason for increasing energy or sensitivity can be that

¹ This method is under the jurisdiction of ASTM Committee E-13 on Molecular Spectroscopy.

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many instruments have only absorbance scales, which obviously do not extend to zero transmittance. Even a SRE proportion as large as 1 percent may fall outside the measurement range.

1.6 Many instruments that use optical attenuators to balance sample absorption make relatively inaccurate measurements below 10 percent transmittance, because of poor attenuator linearity. All instruments should be carefully and frequently checked if used below about 1 percent transmittance because of the possibility of zero shift due to electrical pickup or other causes. For these reasons, the test procedure specifies that the measurements be made within 100 percent and 10 percent on the scale. Obviously this is not required if reliable photometric linearity and zero checks are made under the conditions prevailing during the test, and use of the 10 and 1 percent range may give lower and more accurately representative SRE values. In marginal cases this more elaborate test procedure, incorporating accepted ASTM tests for photometric linearity, may be justified.

1.7 High accuracy in SRE measurement is not required. A measurement reliable within 10 or 20 percent is always sufficient, but often many readings must be cascaded to obtain the final result, so that painstaking measurements are desirable.

2. Summary of Method

2.1 The following test procedure is written for transmittance-recording double-beam instruments. Modification for absorbance recording will be obvious. It is readily adapted for point-by-point operation by measuring at enough points to allow reasonably accurate interpolation between the points so as to provide essentially continuous information over the wavelength region covered, or by direct measurement at the desired specific wavelength.

2.2 After establishing that the instrument is adequately free of zero transmittance error, and measuring the baseline (100 percent) over the appropriate spectral range, a filter is inserted into the sample beam and its transmittance curve is recorded, starting in a region where it is nearly transparent and scanning

slowly toward increasing absorption. The filter materials are selected for sharp cutoff, freedom from fluorescence, and sufficiently high absorption that their transmittance in the stop band can be neglected. They should be visually clear and free of bubbles and striae. SRE will then set the limit to the minimum transmittance observed, unless an adverse signal-to-noise ratio, a scale limitation of the photometer, or a false electrical zero intervenes.

2.3 These limitations may usually be overcome by increasing the slit width to admit more incident radiant energy on the filter. In a double-beam instrument, this may be accomplished by attenuating the reference beam with a screen, mask, or neutral filter. The following procedure assumes the use of etched screens, and measures their transmittance by their effect on the instrument reading.

2.4 The apparent transmittance of the filter is sensitive to spectral bandwidth. Since bandwidth increases with slit width, it is necessary that the transmittance of the screen be measured at a fixed slit width each time. The slits may then be allowed to open for the following steps of the test. The effect of such changes in slit width on the apparent transmittance of the filter becomes insignificant at the end of the test when the SRE becomes the dominant source of signal.

2.5 The scanning is continued, and the reference beam is attenuated further in as many steps as required, until the steeply falling transmittance curve levels off because of SRE. The product of all the reference attenuation fractions times the value of the transmittance reading at the plateau, corrected by the baseline value and the filter reflection loss, is taken as the proportion of SRE.

2.6 The proportion of SRE can in some cases increase with increasing slit width (see Appendix A4). Therefore, the smallest practical value of slit width should be used at the last step of the reference beam attenuator, as this corresponds most nearly with the normal operating conditions of the spectrophotometer.

2.7 Some instruments scan automatically only in one direction, which may not be the one specified in the test procedure. Manual

control or scanning by hand may be necessary. *Particularly note any precautions* called for by the manufacturer's instructions in this case. If, for mechanical reasons, manual scanning is not feasible, the test procedure can be reversed, after making the checks of 100 percent line and zero, by going to the desired wavelength within the filter stop band, inserting neutral attenuators in the reference beam until the pen lies between 10 and 100 percent transmittance (preferably near 10 percent, widening the slits while doing so to restore normal pen response, scanning in reverse until 100 percent transmittance is reached, and removing the reference beam attenuators one at a time while measuring their attenuation, until all are out and a region where the filter is transparent is reached.

2.7.1 The only difficulty with this procedure lies in finding the narrower slit width that will give normal pen response after each reference beam attenuator is removed, and finding the transmittance change at that slit width. Several trials may be required.

2.7.2 When done carefully, this procedure gives the same result as the normal one, and in fact affords a way of checking the standard test results whenever both scan directions are permitted.

3. Apparatus and Material

3.1 *Screens² of Etched Nickel*, useful for reference beam attenuators are listed in Table 1 and footnote 2. They may also be convenient for "quick check" transmittance "standards." The screens should be placed as far as possible from each other, and preferably at a point along the beam where it is as wide as possible. Usually a 1-cm spacing between screens suffices to allow acceptable reproducibility of results. Their exact transmittance varies with location in the beam, hence they should be mounted so they can be positioned reproducibly, and mechanical stability of all parts of the spectrometer should be established. The transmittance of two or more screens used in cascade or tandem is rarely equal to the product of their separate transmittances, and may be quite sensitive to lateral displacements with respect to each other, due to the moiré effect.

3.2 *Test Filter Materials*, shown in Table 2, provide an array capable of satisfactorily covering nearly all normal ultraviolet and infrared spectral ranges. The first column shows the spectral range over which critical remote SRE measurements can be made. The second column shows the approximate 80 percent transmittance wavelength or wavenumber. Scanning for the following procedure should always begin at this point, or at one more remote from the test spectral range.

3.2.1 Filter diameters are not specified. They should be large enough to cover the entire beam with substantial safety margin. Because of the danger that radiant energy outside the nominal beam may bypass the filter and be scattered back into the beam it is advisable to mount them against a cell compartment window or in a much larger metal holder so as to block any such paths. If in doubt, test with an opaque object of the same size as the filter.

3.2.2 If there is any possibility that fluorescence of windows, cells, or sample solvents may be contributing to SRE in the ultraviolet range, locate the test filter immediately following the sample position in the beam, and test in the presence of such cell or solvent. Note that fluorescence of optical elements between the sample and the detector merely modifies the detector sensitivity. It does not constitute an effective source of SRE, since this fluorescent emission is not differentially absorbed or transmitted by the sample.

3.2.3 The useful spectral range of the sharp cutoff filters can be extended toward considerably more remote wavelengths, but if this is

² Available in sheet form from Perforated Products, Inc., 68 Harvard St., Brookline, Mass. 02146. Also as cut disks in holders from Cary Instruments, Monrovia, Calif. These holders fit the Cary cell blocks for cylindrical cells. They do not fit holders for rectangular cells. The holders are also useful for glass filters for Bouguer's law absorbance linearity tests.

Screen and Holder Part Number	Approximate Mesh	Identification Number	Nominal Absorbance
1404111	30	25 K	0.5
1404112	60	30 R	1.1
1404113	120	40 T	1.5
1404114	270	50 W	2.0

done, it must be recognized that the measurement becomes progressively less significant. The apparent proportion of SRE may be reduced in such regions because the filter absorbs energy at wavelengths contributing significantly to SRE.

3.2.4 *Plates of Alkali Halide*, about 6 mm thick for absorption cell windows are commonly on hand in analytical laboratories, and the 80 percent transmittance points are specified for this thickness. However, other thicknesses, over a range from about 4 to 15 mm, can be substituted without invalidating the test.

3.2.5 *Fused Silica*,³ in the form of cell windows, is commonly available and useful over a thickness of 1 to 5 or 6 mm. Crystal quartz is less desirable because of its birefringence, which may cause apparent cyclical transmittance variations with wavelength.

4. Procedure

4.1 Verify that pen response is "normal," that is, that normal damping (preferably slight underdamping) and designated response time and low (less than 1/2 percent) dead zone exist. Follow the manufacturer's instructions, or test by moving a mask a small distance into and out of first the sample, then the reference beam.

4.2 Check the zero transmittance error with an opaque shutter or sample. Adjust the zero control or note the indicated zero and subtract it from subsequent readings.

4.2.1 In some infrared instruments the radiant energy from a rotating beam modulator can be compensated by an adjustable electrical signal. The amount of compensation required varies with wavelength and slit width. Make frequent zero checks during the SRE tests. It is desirable to interpose the opaque shutter ahead of the filter, and only briefly, so that radiation from the filter is self-compensated. A shutter made of thick insulating board, such as Celotex,⁴ or several thicknesses of cardboard separated by air spaces, is recommended, preferably brought to instrument temperature by being stored in the sample compartment.

4.3 Record a 100 percent line over the de-

sired wavelength range for a single filter. If the slit system is controlled by a servo system to maintain a constant reference signal, leave this control on; otherwise put the slits under manual control or leave off (immobile). In the latter cases, check pen response frequently during the scan, and change the slit width if and when pen response becomes sluggish or markedly underdamped. Check by quickly inserting and removing an opaque object in the sample beam. At each change point, record the wavelength and new slit width, so that they can be reproduced in step 4.5.

4.3.1 If the spectrophotometer is provided with a single beam mode in which the sample signal is compared with a fixed electrical reference signal, use this provision to check and readjust slit width instead of the less reliable pen response test.

4.4 Insert the filter in the sample beam.

4.5 Scan slowly from high transmittance to low. When about 10 percent transmittance is reached, stop the scan but leave the pen on and the chart running, recording the pen position for several full pen periods (multiples of five times the time constant for an exponential response function).

4.6 Insert in the reference beam a "neutral" beam attenuator, such as a screen selected from the list shown in Table I, and having about 12 to 20 percent transmittance.

4.7 Record the resulting increased apparent transmittance for at least 20 times the nominal response period of the instrument. (The lengthened time is required because the reduced reference beam energy results in sluggish pen response.) If possible, displace the optical attenuator, or the pen, or both, by hand first in one direction, then the other, and allow to recover to make sure that the photometric system still functions.

4.8 Note on the record the ratio of transmittance values, or "setback," that corresponds to the displacement at fixed slit width.

³ Corning 7940 glass, General Electric Type 151 glass, Heraeus Suprasil, Ultrasil, or Thermal American Spectrosil have been found satisfactory.

⁴ Celotex® is a trademark of the Celotex Corp.

4.9 Turn on the slits or otherwise adjust them to give normal reference signal levels.

NOTE 1—As indicated in Appendix A4, the change in slit width may sometimes change the value of SRE. The displacement resulting from slit width change may be due in small part to this, or to possible shift of zero resulting from the change in illumination conditions resulting from the slit width change, but is mainly due to the accompanying change of spectral bandwidth.

4.10 Continue scanning in the direction toward decreasing transmittance of the filter until the indicated transmittance again falls to about 10 percent.

4.11 Repeat steps 4.5 through 4.9, replacing the reference beam attenuator of step 4.6 by another with about 12 percent of the transmittance of the previously used filter, or about 0.9 absorbance more; or add a second attenuator, spaced from the first and having about the same transmittance as the first.

4.12 Again measure and note the new transmittance change resulting from the reference beam attenuation at fixed slit width.

4.13 Repeat steps 4.11 and 4.12 with a succession of additional reference beam attenuators until the indicated transmittance reaches a minimum, or until the slits reach their maximum value (Note 2). If the indicated transmittance does reach a minimum, select the reference beam attenuator for the last setback such that the scale reading is about 10 percent (or even less, if the zero point is verified). If necessary, after selecting the attenuator for the last setback, return to the preceding attenuator and recording conditions before measuring the final setback.

NOTE 2—To qualify the instrument for a particular application, it is usually only required that the SRE fall below a given proportion. It is then of course not necessary to continue adding reference attenuators beyond the point required to demonstrate compliance.

5. Calculation

5.1 Calculate the SRE proportion as the product of all the "setbacks" times the final transmittance fraction at the desired wavelength, divided by the transmittance fraction of the 100 percent line at this wavelength, measured in step 4.3, and divided by the filter transmittance in the pass band, due to reflection loss, of about 0.90.

NOTE 3—Since the instrument SRE often increases with increasing slit width, the value obtained will ordinarily indicate a greater proportion of SRE than is normally encountered in use. If the final slit width corresponds to a normal use value, the SRE proportion will be correct for that value. Such a condition may sometimes be obtained by starting the series of measurements at unusually high values of amplification or at high photomultiplier dynode voltage, accepting more than normal noise on the records of the SRE test. If this is done, it is doubly important to be sure that the photometer scale still reads correctly near zero transmittance under the higher gain condition.

6. Illustrative Example

6.1 A stray radiant energy test was done on a Cary Model 15 Spectrophotometer following the procedure described in Section 4. The resulting recording is shown as Fig. 1. The chart reads from right to left. The steps of the procedure are marked by the corresponding numbers of the paragraphs in Section 4. Step 4.1 was performed but was omitted on the chart. However, it is evident from the pen test shown in step 4.7 that the pen dead zone is small and its response sufficiently fast even with a reduction of total radiant energy to less than $1/9$ of normal.

6.2 Calculate in accordance with Section 5 as follows:

$$\begin{aligned} \text{SRE} &= 0.108 \times 0.118 \times 0.111 \times 0.151 \times 0.183 \\ &\quad \times \frac{0.0128}{0.996} \times \frac{1}{0.885} \\ &= 5.67 \times 10^{-7} \text{ or } 0.000057 \text{ percent} \end{aligned}$$

APPENDICES

A1. GENERAL CONCEPTS

A1.1 Stray radiant energy in a spectrophotometer is difficult both to define and to measure. It is often defined as the proportion of transmitted radi-

ant energy of wavelengths outside the nominal pass band of the monochromator to the total energy transmitted. However, since only signal-producing

radiant energy is significant, it is obvious that the relevant measure is the integral of the product of energy and detector sensitivity over all wavelengths except the pass band, divided by the corresponding total. In practice it is impossible to make the test conform exactly to this definition, so a more empirical definition, based upon an accepted test procedure, such as that described herein, must be used.

A1.2 Only for a Raman spectrophotometer is SRE measurement relatively straightforward. Here, it is possible to employ a very narrow, very intense band of frequencies. The SRE is determined by the "slit function" normalized to unity peak height; that is, by the intensity of this monochromatic radiant energy which is transmitted by the monochromator, over the spectral interval of interest. The intensity of frequency-shifted radiant energy is so feeble that it does not itself constitute a significant source of SRE.

A1.2.1 Yet even in this case problems are encountered. It is not legitimate, for example, to beam a laser directly into the monochromator for the measurement, because in so doing only a small fraction of the aperture is illuminated, and the slit is coherently illuminated, so that neither typical scattering nor typical aberrations are produced. The test illumination and the monochromator control settings must fairly reproduce the conditions during use. But if the exciting energy is scattered into the entrance optical train, the scattering medium must itself be free of appreciable fluorescence and Raman scattering. Very few substances are suitable, if a well designed double monochromator is being evaluated.

A1.2.2 For a Raman spectrophotometer, in common with most emission instruments, values of SRE observed are usually small compared with absorption instruments, because they arise only from the single line, or a few isolated lines, rather than from the integrated effect of all the wavelengths of a continuum source.

A1.3 For absorption spectrophotometers, the definition and measurement problems are much more difficult. SRE is not uniquely a function of the monochromator itself, but varies with the spectral distribution of the source and of the detector sensitivity, and with other factors discussed below. Also, suitable test materials are scarce. The ideal filter for measuring SRE should have intense absorption over a spectral region of adjustable nominal wavelength and bandwidth, and negligible absorption at other wavelengths. Such absorbers do not exist. One takes advantage of absorption edges such as those seen with alkali halide crystals, certain liquids, and sharp cutoff glass filters, and supplements these by finding a variety of substances having narrow, intense absorption bands. There are spectral regions for which no fully satisfactory filter material has been proposed.

A1.3.1 The tests herein are of limited scope because sharp cutoff filters transparent for the ultraviolet but absorbing in the visible, or transparent in the lower frequency infrared but absorbing higher frequencies, are not in general available. Fortu-

nately, the available filters, from which a recommended set was selected, usually suffice to disclose significant SRE of remote wavelengths. This is because SRE caused by gross scattering arises principally from spectral regions where detector sensitivity and source intensity is high, and such sharp cutoff filters transmit efficiently these regions. If, however, there is any reason to suspect the presence of SRE of wavelengths within the stop band of the filter, for example when a grating is used in second order in the higher frequency infrared and the stray might be of first order frequency, or if Beer's law departures are observed when preparing calibration curves (1),⁵ the following supplemental test should be used:

A1.3.1.1 Obtain a filter that transmits efficiently all wavelengths within the desired monochromator pass band, but rejects the frequencies outside this band that might be causing trouble. Interference filters having suitable characteristics are commercially available for the infrared, visible, and near ultraviolet ranges. Measure the absorbance of samples with and without the filter, setting the zero absorbance level also with and without the filter, respectively. Appreciable differences of measured absorbance, especially at high sample absorbance, indicate trouble from SRE. Samples should then be measured with the narrow band filter in the beam, or filters effective for rejecting the SRE can be employed (see A1.3.7). This test is recommended only as a supplement because of high cost for the array of test filters if it is to be applied for general instrument evaluation, as well as the large amount of testing time required. It is nevertheless strongly recommended for critical applications.

A1.3.2 Depending on the particular measurement to which the instrument is to be applied, one may be concerned only with SRE of relatively remote wavelengths, or may find so-called "nearby scattering" (sometimes defined as radiant energy outside the pass band but within several bandwidths of the nominal wavelength), of significance. For example, measurements of aromatic compounds in the gas phase may impose very strict requirements on scattering of wavelengths adjacent to those absorbed (2). A monochromator, entirely suited for liquid-phase measurements on the same compounds might give highly erratic and inaccurate measurements in the gas phase application.

A1.3.3 Because of these considerations, it is not practical to specify SRE in an absorption spectrophotometer in absolute terms. Nevertheless, test procedures have been developed that give definite values; ones that are valid for certifying the suitability of a particular monochromator or spectrophotometer for most of the important applications, and that additionally allow instruments to be compared when similar detectors and sources are used. SRE is then defined as the fraction of the total energy that is contributed by wavelengths different

⁵ The boldface numbers in parentheses refer to the list of references at the end of this method.

from those of the spectral band passed by the monochromator, *as indicated by the test*.

A1.3.4 SRE if present in significant amounts is dangerous because it is often unsuspected. With the passage of time, increasing SRE frequently accompanies gradual deterioration of the optics in a spectrophotometer. Thorough testing annually is recommended, with more frequent tests for certain critical applications.

A1.3.5 It might be assumed that it is only necessary to know the magnitude of SRE in order to make corrections on indicated absorbance values. A little reflection, however, will demonstrate the hazard of attempting such corrections except in special circumstances. Samples may absorb even more strongly in spectral regions where SRE is intense than they do in the region being measured. Under such circumstances, the effect of SRE will be to increase rather than to decrease indicated absorbance values. An accurate correction for SRE would require a detailed knowledge of the sample absorption spectrum and of the spectral distribution of SRE and detector spectral response, and is rarely feasible.

A1.3.6 For situations in which the sample does not absorb in the spectral region over which the SRE is distributed, Slavin (3) shows a plot of absorbance error versus absorbance. While it may seem too obvious to mention, it must be realized that the relative error in absorbance is in this case larger than the proportion of SRE. Small relative errors in absorbance (A) are given by the following equation:

$$\Delta A/A = [-0.434(10^4)s]/A \quad (1)$$

where s is the fraction of SRE to energy within the nominal pass band. For example, if the fraction of SRE is 0.001 for a measurement made at an absorbance of 1.5, the relative error in absorbance is -0.0091 , or about nine times the proportion of stray to monochromatic radiant energy.

A1.3.7 While the data obtained with optical filters do not allow one to correct for SRE, their use to *reduce* SRE can be very valuable in improving performance, particularly of single monochromator instruments. An example is the use of the Corning No. 9863 (7-54) red-purple Corex filter for work between 260 and 380 nm (4). In general, the same tests for SRE that serve to measure the performance of the monochromator alone give correct values for a monochromator-filter combination.

A1.3.8 It is also possible to use sharp cutoff filters to provide a kind of automatic SRE correction by substituting the sharp cutoff filter for an opaque shutter when establishing the zero transmittance point of a spectrophotometer (5). If this is done with the sample in place, it also automatically corrects for errors due to sample absorption at other wavelengths, provided they fall outside the rejection band of the filter. This technique is especially useful in infrared measurements, using alkali halide crystal plates as the absorption filters. Allowance is made for the reflection losses of the filter, for instance, by using a transparent plate of matching reflection loss to transmit the desired wavelengths.

A2. TEST MATERIALS

A2.1 Sharp cutoff filters are the most generally available for SRE evaluation. As noted in A1.3, SRE caused by random scattering within the monochromator is principally of longer wavelengths when instruments are used in the ultraviolet, and of shorter wavelengths when instruments are used in the infrared. Fortunately, sharp cutoff filters having high transmission efficiencies in the wavelength regions principally responsible for SRE are available in both instances.

A2.2 Glass filters for ultraviolet use can be valuable, but must be regarded with suspicion, because most glasses exhibit significant fluorescence (6). Unfortunately phototubes are frequently more sensitive to the fluorescent wavelengths than to the short ultraviolet wavelengths that excite fluorescence efficiently. If the apparent SRE is found to be increased by locating the filter close to the phototube, or is decreased by preceding the glass filter with a solution filter of slightly shorter wavelength cutoff, glass fluorescence may be limiting the SRE readings. For less exacting applications, and for tests on single monochromators, glass filters are very useful and convenient. Since differ-

ent batches of glass may exhibit different degrees of fluorescence, caution with the use of glass filters is indicated.

A2.3 Sharp cutoff solution filters have been investigated by several workers (7,8,9), as have crystal filters for the infrared (10).

A2.4 Filters for reducing infrared SRE have been mainly of two types: scatter filters (11,9), including grating filters (12), and thin film interference filters (13,14,15).

A2.5 In certain cases, narrow pass band absorbers have proved useful for evaluating scattering of both nearby and remote wavelengths. Examples are the most intense bands in the benzene vapor spectrum near 260 nm (16), hot mercury vapor at 254 nm (2), and polystyrene films at 13.3 and 14.4 μm (17). Other substances found useful are 1 cm of 0.05 percent aqueous solution of methylene blue, near 650 nm, and 5 cm of methylene bromide liquid at 1.43 μm (18). Of course the hands used must be well resolved in order to give reproducible results. Because of large variations in resolution between commercial instrument models, no general methods based on such bands can be recommended.

A3. STRAY RADIANT ENERGY AS AFFECTED BY OPTICAL SYSTEM DESIGN

A3.1 No part of the optical system of a spectrophotometer is completely free of influence on SRE. For example, masks on the source side of the monochromator will reduce SRE if located optically conjugate to the aperture stop of the monochromator and made slightly smaller than the aperture stop image traced by reversed rays. In this way illumination of the mask that defines the aperture stop inside the monochromator is limited so that diffraction or scattering from mask edges and mask surface imperfections is lessened. Similarly, in the beam between the monochromator and the detector, a mask conjugate with the monochromator aperture stop (if such a position exists) will trap radiant energy that may be scattered within the monochromator and that passes through the exit slit from some region other than the area of the aperture stop whence the monochromatic radiant energy is intentionally passed to the external optics.

A3.2 Within the monochromator itself, a critical consideration is the freedom from scattering imperfections of the optical elements, and the surface perfection of mirrors, lenses, and dispersing elements. Even with the best techniques for polishing optical surfaces, departures from perfect smoothness occur (19), and in prism monochromators are principally responsible for the small-angle deviations of the emergent beams which are responsible for "nearby scattering," or tailing off of the slit function of the monochromator.

A3.3 Even if the first optical elements within the monochromator and the entering aperture stop are not overhilled, the process of dispersion causes rays to be deviated in such a way as to illuminate much of the interior of the monochromator with energetic radiation. In a monochromator in which the off-axis angle of a collimator is too small, energy can be returned from the collimator to the dispersing element and after again being dispersed can fall by specular paths directly on the exit slit. This is often called "double dispersion", or "secondary dispersion." The best remedy is to increase the off-axis angle of the collimator, if the resulting aberrations can be tolerated. If not, such specular ray paths may be interrupted by judiciously masking off a part of the aperture stop, often without excessive loss of monochromator transmission efficiency. If this problem is ignored, it can easily turn out that it produces significant SRE only over a narrow spectral region, so that a monochromator that gives excellent tests for SRE over much of its working region, and possible in all regions where such tests are easily made, may be seriously deficient over some particular narrow spectral range.

A3.4 An advantage of the Czerny-Turner or Wadsworth-type monochromators over the Littrow monochromator is that only a part of the dispersed energy falls on the exit collimator. The flux density on this mirror is therefore less than one half that of the Littrow arrangement, and its scattering im-

perfections produce a correspondingly reduced amount of trouble.

A3.5 Grating monochromators in general transmit efficiently other orders than the intended order. This source of SRE is troublesome in the infrared, since it leads to relatively efficient transmission of a number of wavelengths at which usual sources emit strongly and detectors are sensitive (20). It is especially troublesome when the grating is operated near the blaze angle, where quite narrow, easily overlooked bands of stray energy may arise.

A3.6 As Keahl et al (20) have shown, the interference filters that are commonly used for SRE reduction in infrared grating monochromators may have "spike" leaks which can cause very serious narrow band SRE problems. The same authors further note that higher orders of SRE can also be efficiently transmitted by an "order sorting" prism monochromator in tandem with the grating monochromator, if the prism monochromator is operated under such low resolution conditions that more than one order falls within its spectral pass band.

A3.7 Another often overlooked source of SRE in a spectrophotometer is fluorescence from the absorption cell or sample itself. It is entirely possible to set up conditions under which a solution can show apparent negative absorption because of the higher sensitivity of the detector for the fluorescence radiant energy generated on absorption of the ultraviolet energy, than for the monochromatic radiant energy itself. Glass or solution sharp cutoff filters provide a quick test for such difficulties when located alternately first ahead of the sample then following it in the optical train. Also, as noted for glass filters themselves, a shift of apparent sample transmittance with a change of its proximity to the phototube strongly suggests significant fluorescence, although it can also be caused by scattering, beam deflection, or pathlength change.

A3.8 Another source of SRE may be lack of masking in the sample compartment to confine the beam within the sample cuvette. Even if the beam falls well inside the cell windows when examined by the rules of geometrical optics, diffraction at narrow slit widths, or sample turbidity, can cause it to spread so that appreciable energy is transmitted through the cell walls or otherwise to the detector. A check for the error caused by diffraction can be made with India ink or a similar "total absorber" in the cell.

A3.9 Similarly, a leak past the shutter used for determining instrument zero, or a leak admitting room light, can give erroneous results.

A3.10 Electrical pickup can cause reading errors very similar to those due to SRE. A check can be made by turning off the slit and source and looking for drifts of the pen in a recording spectrophotometer, or following procedures given by the manufacturer.

A4. VARIATION WITH SLIT WIDTH AND HEIGHT

A4.1 If the assumption is made that the scattering process follows the Lambert distribution law, it is possible to state a simple theory for the ideal monochromator which allows prediction of the way in which the proportion of SRE varies with monochromator slit width and slit height, and which is at least approximately followed in practice. Several cases occur:

A4.1.1 *Single Monochromator with "White" Continuum Source*—The proportion of SRE does not vary with slit width (when the entrance and exit slits are opened and closed simultaneously). The energy within the pass band is proportional to the square of the slit width because it is linearly proportional to the width of the entrance slit, which admits energy to the monochromator, and also to the spectral bandwidth, is proportional to the slit width. The SRE also is proportional to the square of the slit width, because it is linearly proportional to the width of the entrance slit, which controls aperture illumination, and also to the width of the exit slit, which affects the solid angle for the transmission of scattered energy.

A4.1.1.1 Transmission of monochromatic energy varies only linearly with slit height, because slit height has negligible effect on bandwidth; whereas SRE varies with the square of the slit height, just as with slit width. The proportion of SRE therefore increases linearly with slit height. (Actually, experiments to confirm this relationship show that, with gratings, the scattering is predominantly in the direction perpendicular to the grating rulings, and the proportion of scattering varies as a fractional power of the slit height.)

A4.1.2 *Single Monochromator with Pure Narrow Line Source*—Ideally, all of the energy in a monochromatic line that is admitted by the entrance slit is transmitted by the exit slit when the monochromator is set at the wavelength of the line; thus the monochromatic energy is proportional to the entrance slit width and height. When the monochromator is displaced from the nominal wavelength, the intensity of the scattered energy is varied by both entrance and exit slit width and height, and

thus is proportional to the square of these parameters. The proportion of SRE at remote wavelengths to monochromatic energy at the nominal wavelength is proportional to slit width and height.

A4.1.3 *Double Monochromator with Continuum Source*—In the first monochromator section, as indicated in A4.1.1, the proportion of energy of the nominal wavelength is independent of the slit width and varies with the first power of slit height. (It is assumed that all slits, including the intermediate slit, are varied in width by the slit control.) The scattered energy from the first monochromator that is transmitted into the second monochromator is re-scattered by its optical surfaces. The amount emerging varies with the solid angle subtended by the exit slit as viewed from the scattering surface. Hence, it is proportional to both width and height of the exit slit. Thus, the fraction of stray-to-monochromatic energy is very much reduced by the second monochromator, and it varies with the slit width and with the square of the slit height. The sensitivity to slit height makes clear the utility of a slit-height control.

A4.1.4 *Double Monochromator with Line Source*—The same argument as for the double monochromator with continuum source applies, except that the monochromatic energy varies only with entrance slit height and width. Therefore, the proportion of stray-to-monochromatic radiant energy varies with the square of both the slit width and the slit height.

A4.2 Because of these relationships, it is important that tests for SRE be made in most cases at slit widths and heights representative of those actually used in the application of the instrument. Unfortunately many published results on SRE measurements are made with nontypically narrow slits or with shortened slits, or both. It is often easy to arrange test conditions that give SRE proportions substantially different from those which would be found under conditions appropriate to applications. Hence, a SRE proportion given without specifying test procedure is essentially meaningless.

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TABLE 1 Perforated Screens

Identification Number ^a	Nominal Transmittance	Nominal Absorbance
20G	0.50	0.30
15H	0.41	0.39
15L	0.29	0.54
10N	0.20	0.70
12½P	0.14	0.84
10S	0.07	1.20
30T	0.03	1.50
20W	0.01	2.00

^a The identification number is that of Perforated Products, Inc., 68 Harvard St., Brookline, Mass. 02146. Screens from this manufacturer are the only ones so far tested in committee work. Screens may be available from other manufacturers.

TABLE 2 Filters for Tests of Stray Radiant Energy

Spectral Range ^a	Transmittance, ^b 80 Percent Wavelength or Wavenumber	Filter ^c	Source ^d	Detector ^e
A. Sharp Cutoff Types				
165 to 173.5 nm	183 nm	0.01 cm H ₂ O ^f	UV	UV
170 to 183.5 nm	195 nm	1.00 cm H ₂ O ^f	UV	UV
175 to 200 nm	214 nm	1.00 cm 12 g/liter KCl aqueous ^g	UV	UV
195 to 223 nm	232 nm	1.00 cm 10 g/liter NaBr aqueous ^g	UV	UV
210 to 259 nm	271 nm	1.00 cm 10 g/liter NaI aqueous	UV	UV
250 to 320 nm	339 nm	1.00 cm acetone	UV	UV
300 to 385 nm	420 nm	1.00 cm 50 g/liter NaNO ₂ aqueous	VIS	UV
2050 to 1200 cm ⁻¹	2800 cm ⁻¹	2.0-mm fused silica ^h (2)	IR	IR
1140 to 800 cm ⁻¹	1760 cm ⁻¹	6 mm LiF	IR	IR
760 to 600 cm ⁻¹	1240 cm ⁻¹	6 mm CaF ₂	IR	IR
630 to 400 cm ⁻¹	1030 cm ⁻¹	6 mm NaF	IR	IR
410 to 250 cm ⁻¹	650 cm ⁻¹	6 mm NaCl	IR	IR
240 to 200 cm ⁻¹	420 cm ⁻¹	6 mm KBr	IR	IR
B. Pass-Band Filters				
600 to 660 nm	—	1.00 cm 0.005 percent methylene blue aqueous ^h	VIS	VIS or NIR
1.66 to 1.75 μm	—	5.0 cm CH ₂ Br ₂ ⁱ	NIR	NIR

^a Longer wavelength (or higher wavenumber, for infrared range) gives 10⁻⁴ transmittance point.

^b Transmittance value not corrected for reflection loss.

^c Solution filters should be placed in sample cuvettes appropriate to the range covered. Solid filters are best retained in metal holders.

^d Under "source" is tabulated the usual and appropriate source for each spectral range:

UV—Source is either a deuterium or hydrogen discharge lamp or a xenon short arc.

VIS—Source is a tungsten filament lamp at 2850 to 3300 K. If a xenon arc is substituted, precautions to avoid UV stray should be taken, such as interposition of a Corning No. 7380 or No. 3391 filter, for both test and use of the instrument at wavelengths longer than 410 nm.

NIR—Source is a tungsten filament lamp at 2500 to 3200 K.

IR—Source is a Nernst glower at 1500 to 1800 K, or Globar, or coated Nichrome ribbon, at 1300 to 1500 K. Because the proportion of SRE varies with source temperature, the source current should be set to the value used for analysis.

^e Considerable flexibility in detectors selected is common. The following lists only some of those most frequently employed:

UV—Photomultiplier or diode phototubes with S-5, S-19, or similar spectral response function, such as types 1P28, 7200, or R-106.

VIS—UV types, plus photomultiplier or diode phototubes with S-4, S-5, or S-19 response; extended red threshold types such as 7265 (S-20), or R-136. Photoconductor (PbS) detectors.

NIR—Phototubes with S-1 response to 1.2 μm, photoconductor (PbS, PbSe or PbTe) detectors.

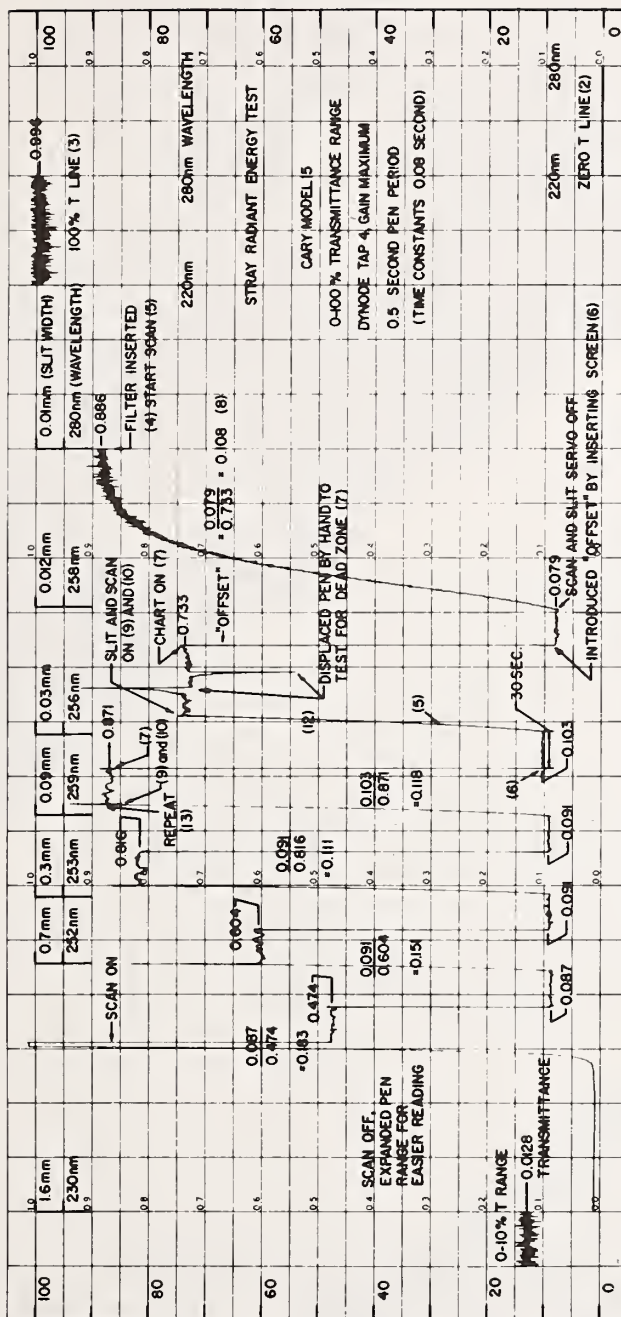
IR—Thermocouples, bolometers, Golay detectors.

^f Apparent absorbance is strongly affected by dissolved oxygen. Bubble pure nitrogen through liquid for several minutes immediately before use. Use only recently distilled (not demineralized) water.

^g Filters such as these, which absorb over a wide range in the infrared, may be warmed sufficiently by the source beam to reradiate, and so produce significant zero shifts which vary with wavelength and with time of exposure to the beam. This effect is greatly reduced by using two filters, separated by at least 1 cm along the beam axis. The reradiation from the first is then mostly absorbed by the second. A slightly less effective alternative is to use a LiF disc for the first filter. If zero shift is troublesome with the LiF filter, a CaF₂ disk can be used ahead of the LiF filter.

^h Passes blue to yellow light efficiently. The 0.005 percent methylene blue solution must be made up freshly from a 0.5 percent stock solution in 2 percent KH₂PO₄, preserved with 1 part of phenylmercuric acetate (Eastman No. P4267 in 50,000 parts of solution).


ⁱ Distillation Products Industries, Eastman Organic Chemicals, No. 1903. Passes from ultraviolet to 1.5 μm radiant energy efficiently, except for a narrow, intense band at 1.4 μm, which is suitable for "nearby stray" evaluation in NIR grating monochromators.



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