NBS SPECIAL PUBLICATION 260-66

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

Standard Reference Materials:

Didymium Glass Filters for Calibrating the Wavelength Scale of Spectrophotometers – SRM 2009, 2010, 2013, and 2014

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Standard Reference Materials:

Didymium Glass Filters for Calibrating the Wavelength Scale of Spectrophotometers – SRM 2009, 2010, 2013, and 2014

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DIDYMIUM GLASS FILTERS FOR CALIBRATING THE WAVELENGTH SCALE OF SPECTROPHOTOMETERS - SRM 2009, 2010, 2013, and 2014

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This publication describes the use of didymium glass filters as wavelength standards. These filters are supplied as Standard Reference Materials (SRM). The Standard Reference Materials are labeled 2009, 2010, 2013 and 2014 depending on size and method of calibration. The certification and uncertainties are also discussed. An appendix with background material and terminology is included. Wavelengths of minimum transmittance and inflection points in the transmittance curve are given. They provide a convenient basis for calibrating the passband centroid of spectrophotometers with bandwidths between 1.5 and 10.5 nm.

Key Words: Bandwidth; didymium glass filter; passband centroid; spectrophotometer; transmittance; wavelength standard.

1. INTRODUCTION

1.1 Description of Materials

Standard Reference Materials SRM 2009, 2010, 2013 and 2014 are optical glass filters containing rare earth oxides which have distinct absorption bands. These filters are intended to be used in setting the wavelength scale of a spectrophotometer which is capable of continuous scan in wavelength and which has a bandwidth* from 1.5 to 10.5 nanometers. Wavelength data for this purpose are supplied for points of minimum transmittance and for points of inflection in the transmittance curve in the wavelength range 400 nm to 750 nm. As an aid to interpreting the wavelength data, transmittance data are also supplied in the wavelength range 380 to 780.5 nm. However, since the transmittance of the filters depends to some extent upon the condition of the filter surfaces and upon the thickness of the filter, these filters should not be used as standards of transmittance.

The principal differences between these Standard Reference Materials are the size and the measurements made on the specific filter. All of the filters are approximately 3 mm thick. SRM 2009 and 2013 are approximately 1 cm wide by 3 cm high and are supplied in a holder which fits in the place of a standard analytical cuvette. SRM 2010 and 2014 are in the form of squares approximately 5.1 cm by 5.1 cm. The SRM 2009 and 2010 come from a set of filters all made to common specifications from the same melt of glass. These filters are not measured individually, but data in tables supplied separately with these filters give the average of measurements made on two representative samples from the set. Each of the SRM 2013 and 2014 filters is supplied with data which were obtained from measurements of that specific filter. Thus the data provide a more accurate representation of the optical properties of the individual filter, but the main advantage which is gained is in terms of more concrete assurance that the filter's performance does not depart significantly from that indicated in the data. It is recommended that SRM 2013 and 2014 be purchased only in cases in which assurance in the evaluation of an instrument's wavelength scale is highly critical. SRM 2009 and 2010 are recommended for most applications.

1.2 The General Approach to Calibrating Wavelength

The wavelength scale of an instrument is calibrated by using one or both of two sets of characteristic points on the spectral transmittance curve of the filter -- points of minimum transmittance and points of inflection. At each point, a correction factor can be established consisting of the difference between what the instrument wavelength scale should read and what it actually reads. A curve can be fitted to these discrete correction factors which will provide wavelength scale correction data at any wavelength. In choosing the type of curve which is fitted to the data, one should take into account the way the wavelength drive mechanism works in the instrument being calibrated.

1.3 Extending Use to Reflectance Spectrophotometers and Densitometers

In addition to being used to calibrate the wavelength scales of transmittance spectrophotometers, these SRM filters can be used to calibrate the wavelength scale of spectrophotometers designed to measure reflectance and of spectrophotometers with output in terms of optical density (negative logarithm of transmittance). To calibrate a reflectance spectrophotometer, a spectrally neutral reflecting sample is placed in the sample position and the SRM filter is placed at some point in the path of the beam of radiation incident on

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*See Appendix, Sec. A.4.1.

the sample from the monochromator or coming from the sample through the monochromator depending respectively upon whether or not the sample illumination is monochromatic. In the case of double beam instruments, one must always be sure that the filter is placed in the sample beam of radiation at a point where the sample and reference beams are separate. From this point on, the wavelength calibration procedures for the reflectance and transmittance instruments are identical. In the case of instruments with output in terms of optical density, it is recommended that the optical density values be changed to transmittance values by an appropriate mathematical transformation and then that the same procedure be used as for an instrument which reads transmittance directly.

1.4 Illustrative Examples Using the General Electric Recording Spectrophotometer

Throughout this Special Publication, the Procedures being discussed will be applied by way of illustration to calibrating the wavelength scale of a 1934 General Electric Recording Spectrophotometer[1]. That instrument was chosen because the technology of its day produced more noticeable departures from idealized performance than will be found in a very high quality modern instrument. As a result, many of the points being illustrated are more obvious. The caption "ILLUSTRATION" will appear at the top of all figures and tables which apply to this illustration in order to distinguish them from figures and tables which apply to the filters in general.

2. USING SRM DIDYMIUM GLASS FILTERS

This section provides an illustrated set of instructions for using the SRM didymium glass filters to calibrate the wavelength scale of a spectrophotometer. Subsection 2.1 describes the process for determining discrete corrections to the wavelength scale using points of minimum transmittance and Subsection 2.2 contains a similar description for the points of inflection. Procedures for fitting these correction data to obtain a continuous wavelength scale correction curve are discussed in Subsection 2.3.

2.1 Discrete Wavelength Corrections from Transmittance Minima

Using transmittance minima for wavelength calibration is very straightforward in principle. The spectral transmitance of the filter is measured and the wavelengths on the instrument scale are noted. The difference obtained by subtracting the wavelength at minimum transmittance as observed on the instrument scale from the "correct" value for the corresponding wavelength provides an additive wavelength correction. The difficulty in this approach, as can be seen in Section 2.1.2, is that the "correct" value for the wavelength of a transmittance measurement depends upon the nature of the instrument passband function*, a quantity whose values are usually not well known. However, the procedure is simple to apply and provides adequate wavelength calibration data for many applications. A method is described in Section 2.3 by means of which some adjustment for lack of knowledge of the instrument passband can be made during the fitting of the final correction curve.

2.1.1 Locating the Wavelengths of Minimum Transmittance on the Instrument Scale

The transmittance of the filters as a function of wavelength is shown in Figure 1. for two different instrument bandwidths representing the extremes for which data are supplied. For the 1.5 nm bandpass there are fifteen distinct points at which the transmittance is locally at a minimum. These minima, indicated by arrows in the figure, have been numbered consecutively from shorter to longer wavelengths for convenience. For an instrument which has a larger bandwidth than 1.5 nm, the lack of resolution may obscure some of these minima. At 10.5 nm bandpass, the number of distinct minima is reduced to six.

Transmittance data near the points of minimum transmittance should be obtained by using the procedure for measuring transmittance which is normally prescribed for the particular instrument. In any procedure for gathering data to locate the wavelength scale reading at minimum transmittance in which a continuous scan of the wavelength is used, the rate of scan must be slow enough so that the data do not depend upon the rate of scan. A

*See Appendix. Sec. A.3

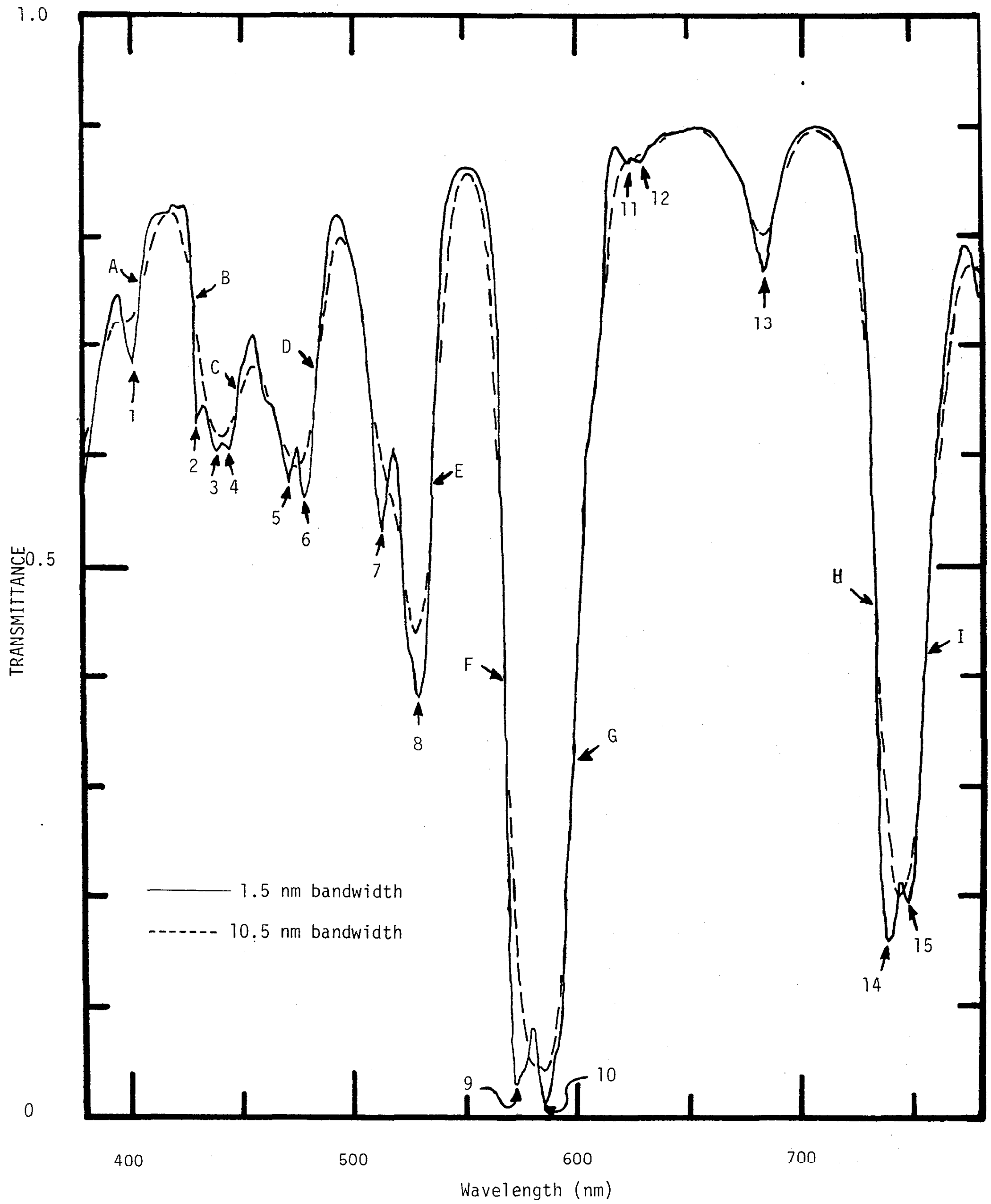

Figure 1: Spectral transmittance of a typical didymium glass filter. Numbers indicate the principal points of minimum transmittance and letters indicate the principal points of inflection.

mechanical or electronic lag in the instrument response can cause a shift of the measured wavelength at minimum transmittance in the direction of scan. For example if the scan is from shorter to longer wavelength, an overly high scan rate will cause a shift in the measured wavelength at minimum transmittance toward longer wavelengths. The extent of this shift will depend upon the shape of the transmittance minimum being examined, the speed of scan and the temporal response of the instrument. It is not the purpose of these SRM filters either to provide a way to evaluate these factors or to provide a means to correct them.

In the following three sections are given three commonly used methods for locating the point on the wavelength scale at which the minimum transmittance occurs. Before one performs a complete calibration, it is advisable to make several repeated independent experimental determinations of the wavelength of minimum transmittance at one of the minimum points. This will provide an estimate of the uncertainty in locating these wavelengths of minimum transmittance for the instrument under consideration and may prevent the forming of unwarranted conclusions about the accuracy of calibration.

2.1.1.1 Direct Search

If the instrument readout is sufficiently steady, one can simply set and reset the wavelength scale until the minimum transmittance is located. During such a search, the wavelength setting should always be approached from the same direction on the scale as when scanning in normal use in order to avoid errors due to backlash in the wavelength-setting mechanism. A systematic means of locating the minimum-transmittance point by direct search is illustrated in Table I and Figure 2 using data from the General Electric spectrophotometer. In this procedure, the transmittance is measured at four wavelengths spaced at equal intervals over a range which is chosen just large enough to certainly include the wavelength of minimum transmittance. If the wavelength interval chosen contains a single minimum, the lowest measured transmittance of the four will occur at either the second or third wavelength in the sequence. The two wavelengths flanking the wavelength at which the transmittance was the lowest are then taken as the end points of a second interval and the transmittance at two additional wavelengths equally spaced in that interval can be measured to provide a new sequence of four wavelengths which are equally spaced over an interval which includes the wavelength of minimum transmittance and which is only 2/3 the extent of the original interval. Each repetition of this process allows the interval containing the wavelength of minimum transmittance to be reduced by a factor of 2/3 or less with at most only two additional measurements of transmittance, and the process can be repeated until noise or lack of resolution in the data makes further reduction of the interval impossible.

2.1.1.2 Graphical Extrapolation

For instruments in which the output is in the form of a chart recording, interpolation to the wavelength of minimum transmittance can be made from a graph which is made with high resolution both with respect to wavelength and transmittance. This method can also be used with digital data which has been graphed and through which a representative curve has been drawn as will be done in the illustration, but the results depend to some extent upon the choice of the representative curve. A series of lines of constant transmittance are drawn through the curve and the segment of each of these lines which is bounded by the two intersections with the curve is bisected. A smooth curve is then drawn through the center points of the line segments and extrapolated downward to pass through the transmittance data curve. The intersection of these two curves is assumed to occur at the wavelength of minimum transmittance. This procedure is illustrated in Figure 3 and Table II using the same data as in Figure 2. It is based on the hypothesis that a small enough section of curve containing the minimum point of that curve can be approximated by a parabola, which is symmetric about the minimum point. A disadvantage of this procedure as compared to the direct method is that it does not provide a good estimate of the uncertainty of the wavelength-at-minimum value which is obtained.

2.1.1.3 Curve Fitting

When data of measured transmittance of the filter as a function of wavelength scale

ILLUSTRATION

Table I. Systematic Direct Search for Wavelength of Minimum Transmittance in the following table and Figure 2, the first five steps of a systematic search for the wavelength of minimum transmittance are illustrated. Notice how the convergence rate has been made less than 2/3 per step by careful attention to the data.

Comments	Data: Wavelength	Data: Transmittance
First step - Interval of wavelengths from 513 to 540 nm chosen arbitrarily	513	.569
	522	.496
	531	.419
	540	.733
Second step - Interval of wavelengths from 522 to 540 nm includes lowest transmittance measured so far at 531	522	.496 (measured in first step)
	528	.397
	534	.499
	540	.733 (measured in first step)
Third step - Interval of wavelengths from 522 to 531 nm includes lowest transmittance measured so far at 528. Only one measurement needed	522	.496 (measured in first step)
	525	.434
	528	.397 (measured in second step)
	531	.419 (measured in first step)
Fourth step - Interval of wavelengths from 525 to 531 includes lowest transmittance measured so far at 528	525	.434 (measured in third step)
	527	.404
	529	.397
	531	.419 (measured in first step)
Fifth step - Interval of wavelengths from 528 to 529 is bounded by the two lowest transmittances measured so far.	528	.397 (measured in second step)
	528.33	.396
	528.67	.396
	529	.397 (measured in fourth step)

The next interval would logically be chosed to extend from 528.33 to 528.67 nm. However, in this region, there is no change in the measured transmittance. Therefore one would assign the value 528.5 $\pm$0.2 nm to the wavelength at minimum transmittance obtained in this manner.

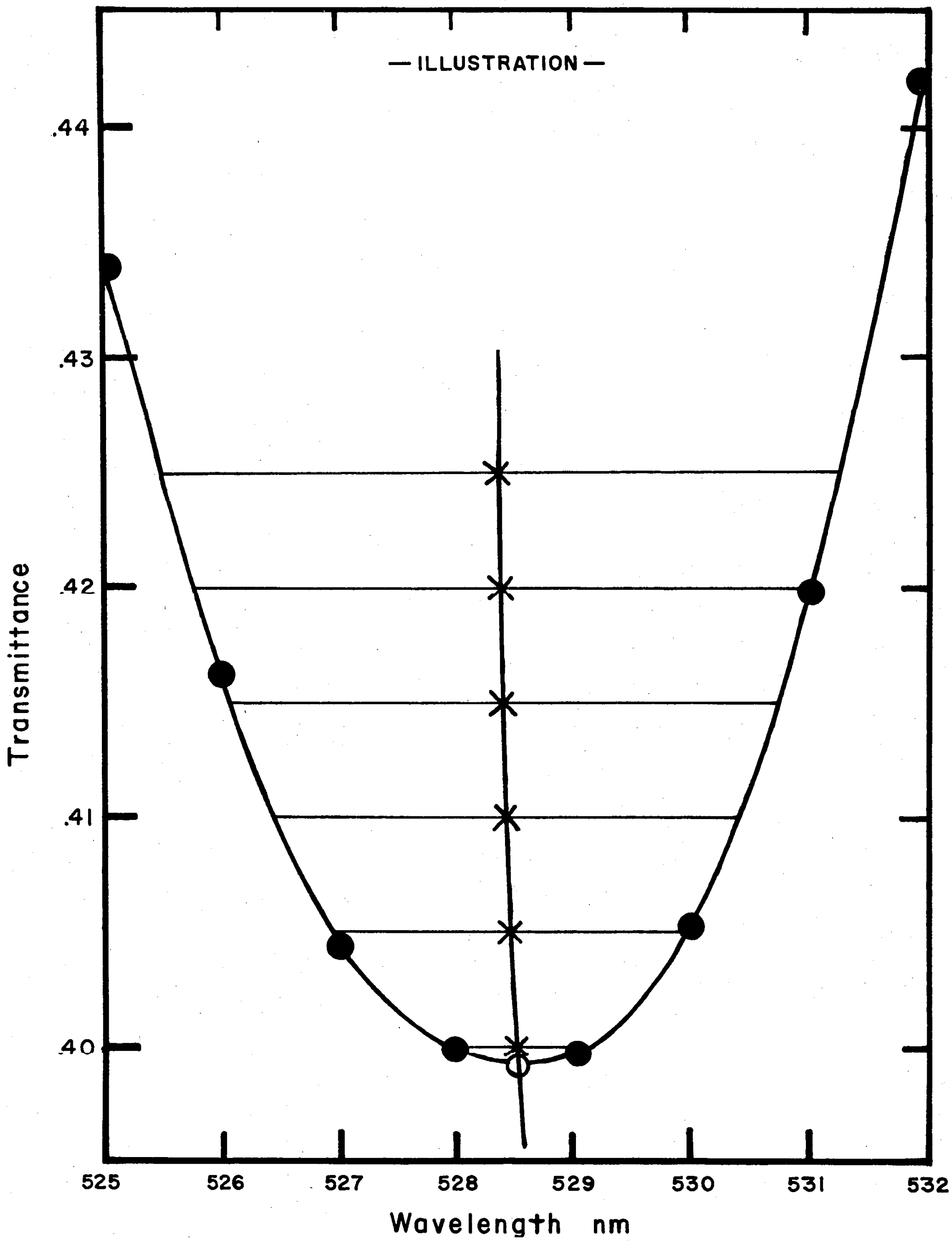

Figure 3: Graphical extrapolation to wavelength of minimum transmittance.

readings can be taken in digital form, the wavelength at minimum can be found by fitting a curve to the data and determining the minimum point of the curve. If a number of data are taken over a small wavelength range including the minimum transmittance point, a reasonable fitting function for the measured transmittance $\tau_m(\lambda_s)$ is a parabola of the form:

$$\tau_m(\lambda_s) = a + b\lambda_s + c\lambda_s^2 \quad (1)$$

where λ_s is the wavelength scale reading

Once the fitting coefficients a, b, and c have been obtained, the wavelength at minimun λ_{sm} can be determined as

$$\lambda_{sm} = -b/2c \quad (2)$$

If the data must be taken over a range so great that it cannot be reasonably fitted by a quadratic of the form given in (1) above, then functions in higher powers of λ_s must be used to fit the data. The choice of the degree of the fitting function must be made sensibly in terms of the number of data points, the noise in the data, and the resolution of the wavelength and transmittance readouts. The higher order fitting procedure used to determine the values of the data supplied with the filters is discussed in Section 3.2. The wavelength at minimum transmittance as determined by curve fitting for each of the six applicable minima are listed for the General Electric Recording Spectrophotometer in the second column of Table IV.

2.1.2 Obtaining Correct Wavelengths for the Transmittance Minima

The wavelength at which the centroid of the instrument passband is located for each minimum transmittance depends upon the shape and width of the passband. Table V gives the wavelength at which the minimum transmittance of Master Filter D-1 will occur for triangular passbands with width at half-height which are even multiples of 0.3 nm. (Master Filter D-1 is a selected filter which has optical properties falling near the center of the range for the measured set of Standard Reference Material didymium filters.) Interpolation to obtain data for a triangular passband with a half-height bandwidth falling anywhere in the range 1.5 to 10.5 nm can be obtained by interpolating in Table V, using the curves in Figure 4a-h as a guide for interpolation. The triangular passband occurs in the case of a well-focussed prism or grating monochromator in which the exit slit and the image of the entrance slit at the exit slit are both the same width, a common arrangement for the monochromators used in spectrophotometers. These data can also be applied to other passband shapes through the use of the equivalent triangular bandwidth concept defined in Section A.4.2, or the wavelength at minimum transmittance can be calculated by means of the procedure given in Section 3.2.4 specifically for the particular passband being used. The General Electric Recording Spectrophotometer is commonly assumed to have a triangular passband width of 10 nm[2]. By interpolating in Table V, the wavelength at minimum transmittance for a 10-nm triangular passband was obtained for each of the six applicable minima as given in the third column of Table IV.

ILLUSTRATION

Table III

The following data were fitted with a parabola by using a least squares fitting routine on a digital computer.

Wavelength	Transmittance
527	0.404
528	.397
529	.397
530	.405

From this fitting, the coefficients in equation (1) were determined to be:

Coefficient	Value
a	1047.26
b	-3.96194
c	3.74857×10^{-3}

The wavelength of minimum transmittance given by equation (2) in this case is:

$$\lambda_{sm} = 528.46$$

ILLUSTRATION

Table IV

Determination of wavelength corrections for General Electric Spectrophotometer from wavelengths at transmittance minima.

Minimum Number	Instrument Wavelength at Minimum* (nm)	Correct Wavelength at Minimum # (nm)	Additive Correction† (nm)
3	440.66	441.43	0.77
6	475.07	475.94	0.87
8	528.42	529.02	0.60
10	594.85	584.78	-0.07
13	683.78	684.66	0.88
14	740.67	743.43	2.76

*Obtained from a 4th degree polynomial fitting of seven data points at 1-nm intervals. (Sec. 2.1.1.3)

Based on the assumption of a triangular passband of 10-nm bandwidth. (Sec. 2.1.2)

† See Section 2.1.3

TABLE V

Wavelengths at minimum transmittance, λ_{MIN}, for Master D-1 at the indicated bandwidths

Minimum No. \ Bandwidth	1.5 nm	1.8 nm	2.1 nm	2.4 nm	2.7 nm	3.0 nm	3.3 nm	3.6 nm	3.9 nm
1	402.36	402.28	402.17	402.03	401.86	401.67	401.61	401.56	401.52
2	431.49	431.58	431.69	431.88	432.16	432.45	--	--	--
3	440.17	440.21	440.25	440.29	440.33	440.39	440.48	440.61	440.80
4	445.58	445.51	445.44	445.37	445.27	445.15	--	--	--
5	472.71	472.69	472.67	472.65	472.61	472.57	472.58	472.61	472.65
6	478.77	478.88	478.99	479.08	479.17	479.25	479.26	479.26	479.25
7	513.44	513.47	513.50	513.55	513.58	513.60	513.64	513.69	513.75
8	529.67	529.76	529.85	529.95	530.04	530.12	530.12	530.11	530.08
9	572.67	572.80	572.93	573.04	573.15	573.25	573.46	573.67	573.89
10	585.33	585.39	585.44	585.48	585.52	585.55	585.59	585.63	585.68
11	623.62	623.68	623.74	623.82	623.90	624.00	--	--	--
12	629.62	629.58	629.56	629.52	629.49	629.44	629.35	629.24	629.09
13	684.70	684.71	684.71	684.72	684.72	684.73	684.74	684.73	684.74
14	739.91	739.94	739.96	739.97	739.98	739.98	740.04	740.10	740.16
15	748.34	748.31	748.27	748.24	748.20	748.15	--	--	--

Minimum No. \ Bandwidth	4.2 nm	4.5 nm	4.8 nm	5.1 nm	5.4 nm	5.7 nm	6.0 nm	6.3 nm	6.6 nm
1	401.50	401.48	401.45	401.42	401.40	401.38	401.36	401.31	401.25
2	--	--	--	--	--	--	--	--	--
3	441.10	441.58	441.95	442.19	442.31	442.36	442.38	442.38	442.36
4	--	--	--	--	--	--	--	--	--
5	472.74	472.94	--	--	--	--	--	--	--
6	479.23	479.20	479.10	478.96	478.76	478.52	478.26	478.05	477.86
7	513.81	513.88	513.95	514.03	514.11	514.20	514.31	514.42	514.56
8	530.04	530.00	529.92	529.83	529.73	529.63	529.54	529.48	529.43
9	574.05	574.18	574.35	574.53	574.71	574.89	575.07	575.28	575.52
10	585.73	585.78	585.82	585.86	585.91	585.97	586.03	586.06	586.08
11	--	--	--	--	--	--	--	--	--
12	628.88	628.55	628.15	627.61	627.09	627.01	626.99	626.97	626.97
13	684.75	684.76	684.76	684.77	684.77	684.77	684.77	684.77	684.77
14	740.21	740.27	740.36	740.47	740.60	740.75	740.92	741.11	741.31
15	--	--	--	--	--	--	--	--	--

Minimum No. \ Bandwidth	6.9 nm	7.2 nm	7.5 nm	7.8 nm	8.1 nm	8.4 nm	8.7 nm	9.0 nm	9.3 nm
1	401.18	401.09	400.98	400.87	400.75	400.59	400.43	400.24	--
2	--	--	--	--	--	--	--	--	--
3	442.32	442.28	442.23	442.18	442.12	442.06	441.98	441.90	441.79
4	--	--	--	--	--	--	--	--	--
5	--	--	--	--	--	--	--	--	--
6	477.68	477.51	477.35	477.19	477.04	476.90	476.71	476.52	476.34
7	514.73	514.97	515.39	--	--	--	--	--	--
8	529.38	529.35	529.32	529.29	529.26	529.23	529.20	529.17	529.13
9	575.80	576.14	576.52	--	--	--	--	--	--
10	586.07	586.05	586.01	585.93	585.83	585.69	585.54	585.37	585.20
11	--	--	--	--	--	--	--	--	--
12	626.97	626.98	626.99	626.97	626.94	--	--	--	--
13	684.77	684.76	684.75	684.75	684.74	684.73	684.72	684.71	684.69
14	741.54	741.77	742.01	742.23	742.43	742.62	742.80	742.96	743.11
15	--	--	--	--	--	--	--	--	--

TABLE V (Continued)

Bandwidth	9.6nm	9.9nm	10.2nm	10.5nm
Minimum No.				
1	--	--	--	--
2	--	--	--	--
3	441.66	441.49	441.28	441.04
4	--	--	--	--
5	--	--	--	--
6	476.17	476.00	475.83	475.66
7	--	--	--	--
8	529.08	529.04	528.98	528.92
9	--	--	--	--
10	585.03	584.84	584.65	584.45
11	--	--	--	--
12	--	--	--	--
13	684.68	684.66	684.65	684.63
14	743.25	743.39	743.52	743.64
15	--	--	--	--

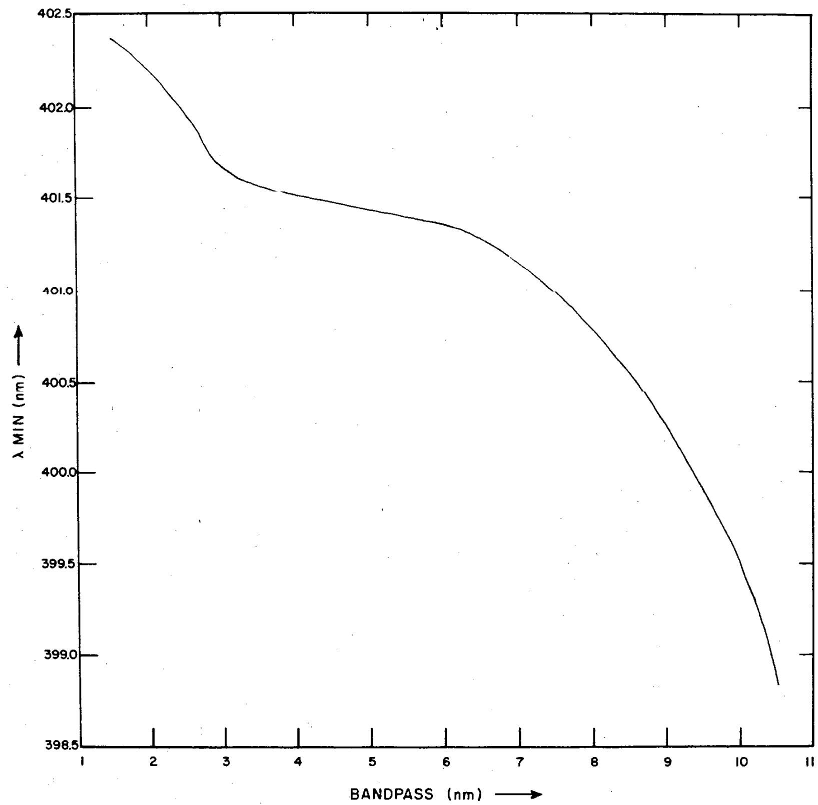

Figure 4a: Transmittance Minima, λ_{MIN}, as a function of bandwidth

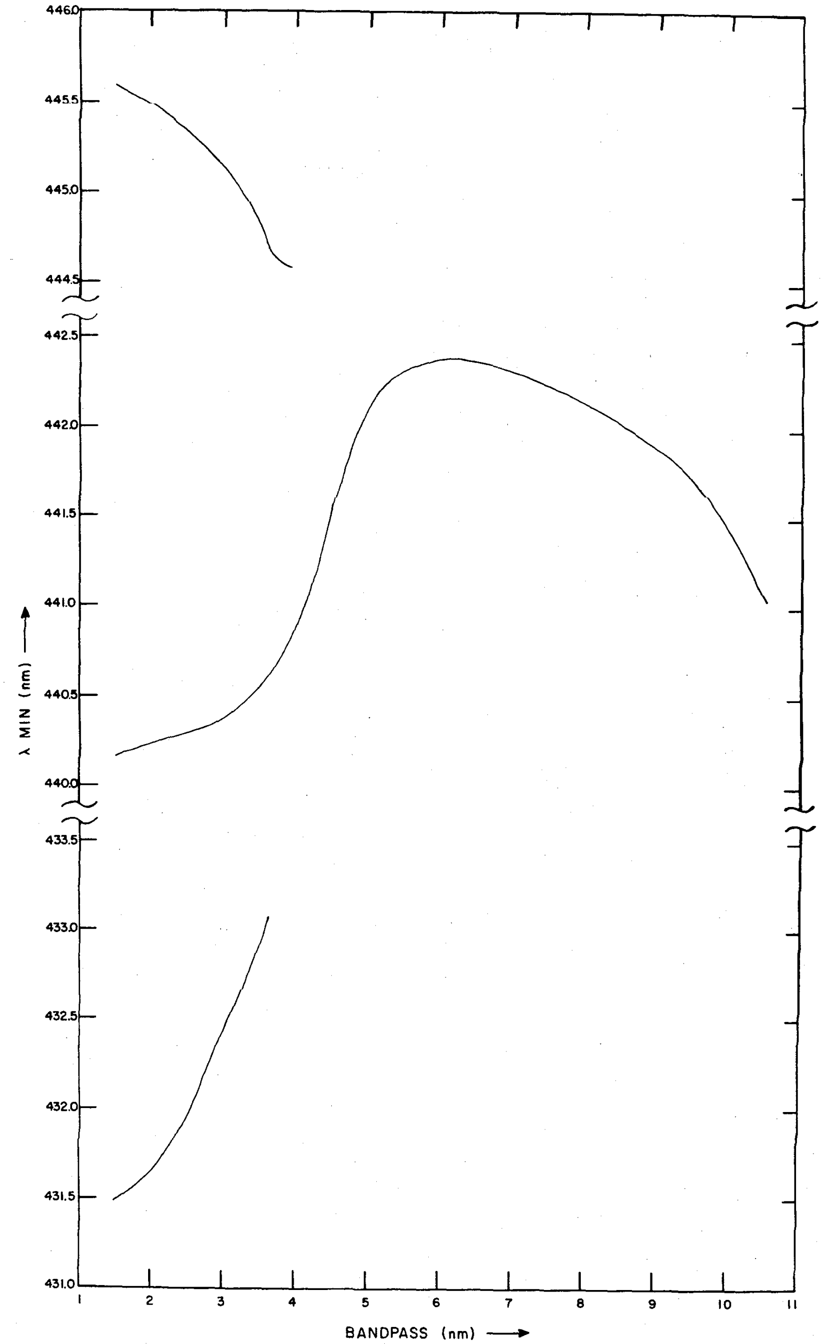

Figure 4b: Transmittance Minima, λ_{MIN}, as a function of bandwidth

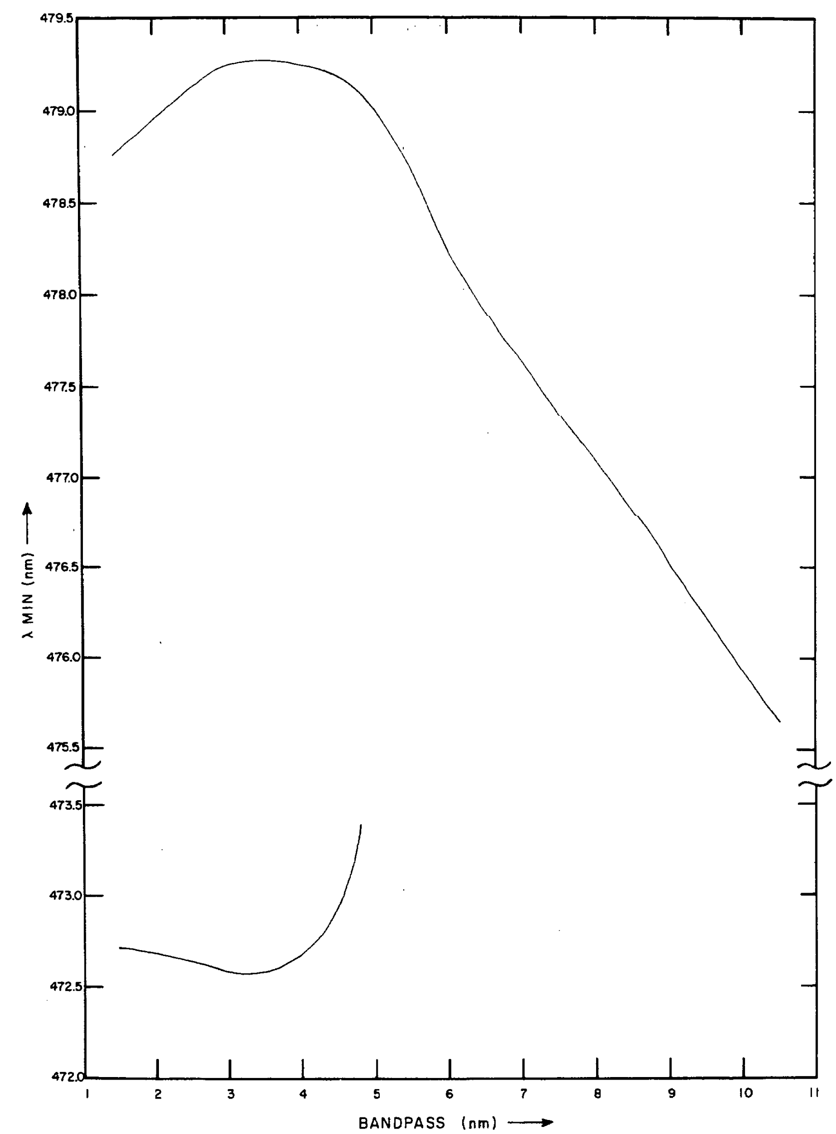

Figure 4c: Transmittance Minima, λ_{MIN}, as a function of bandwidth

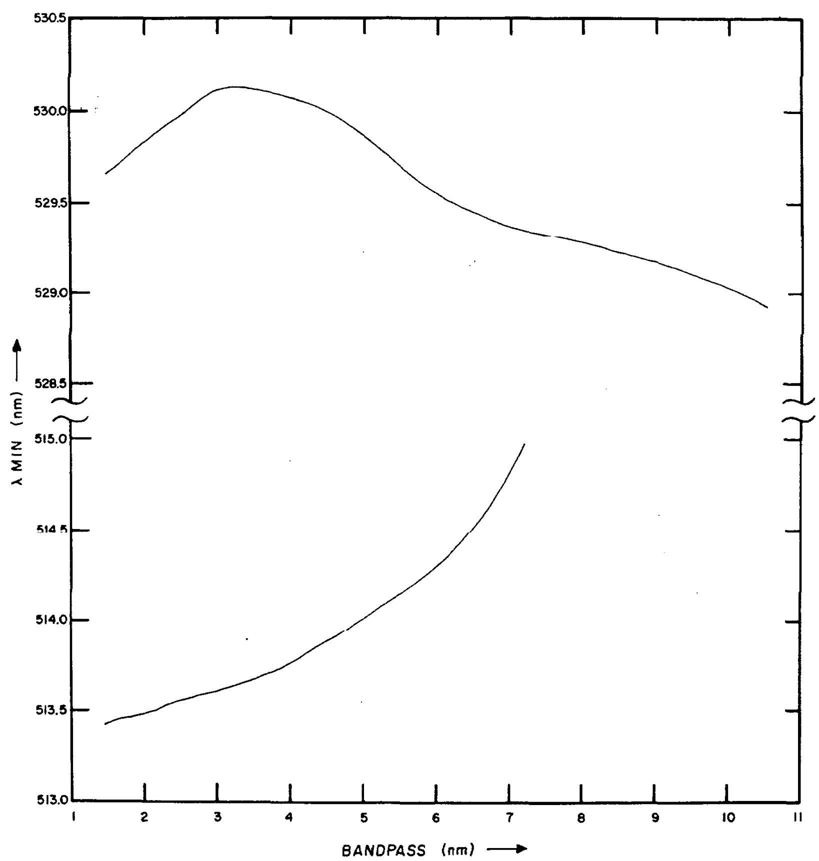

Figure 4d: Transmittance Minima, λ_{MIN}, as a function of bandwidth

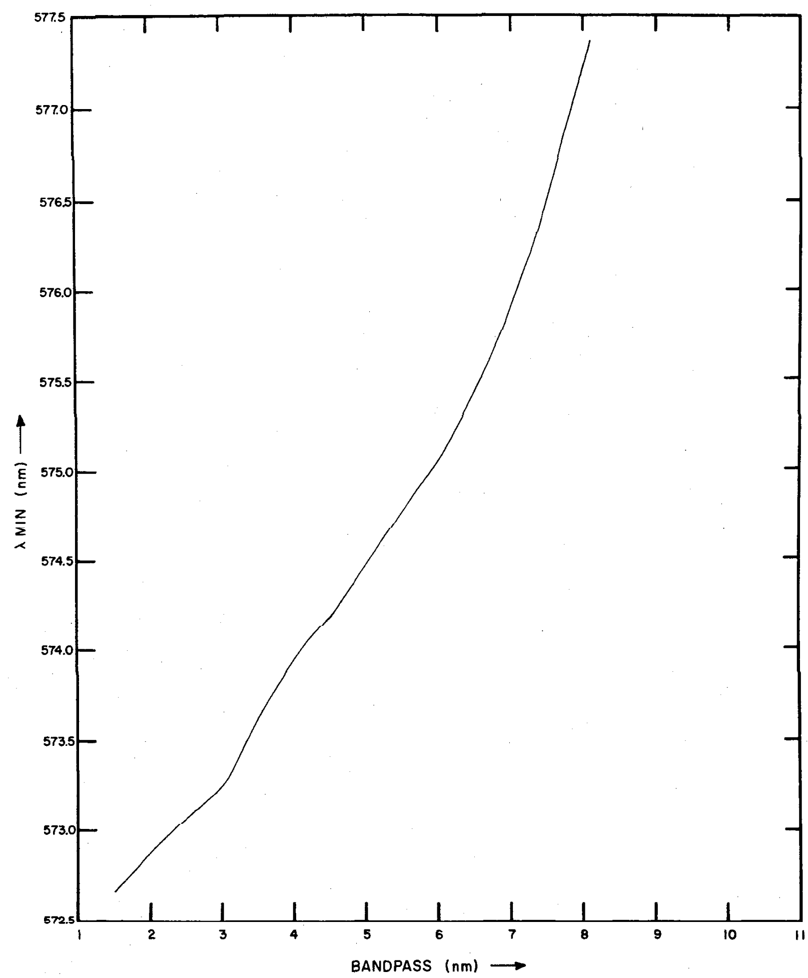

Figure 4e: Transmittance Minima, λ_{MIN}, as a function of bandwidth

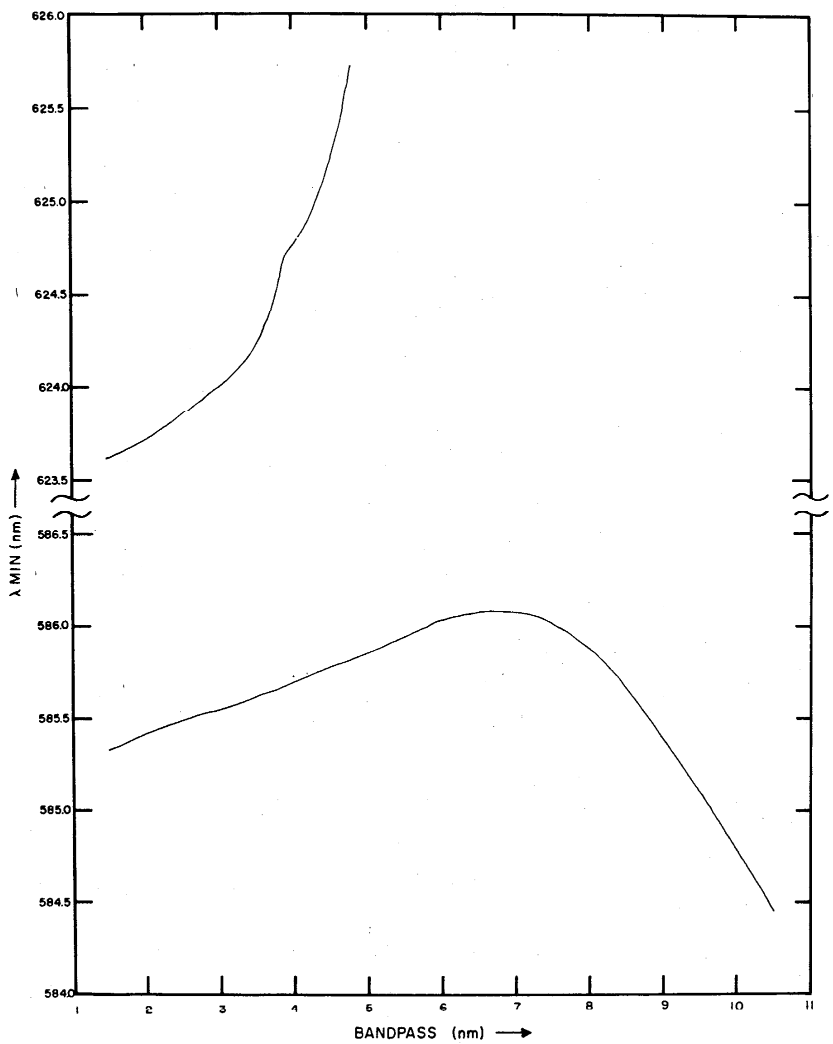

Figure 4f: Transmittance Minima, λ_{MIN}, as a function of bandwidth

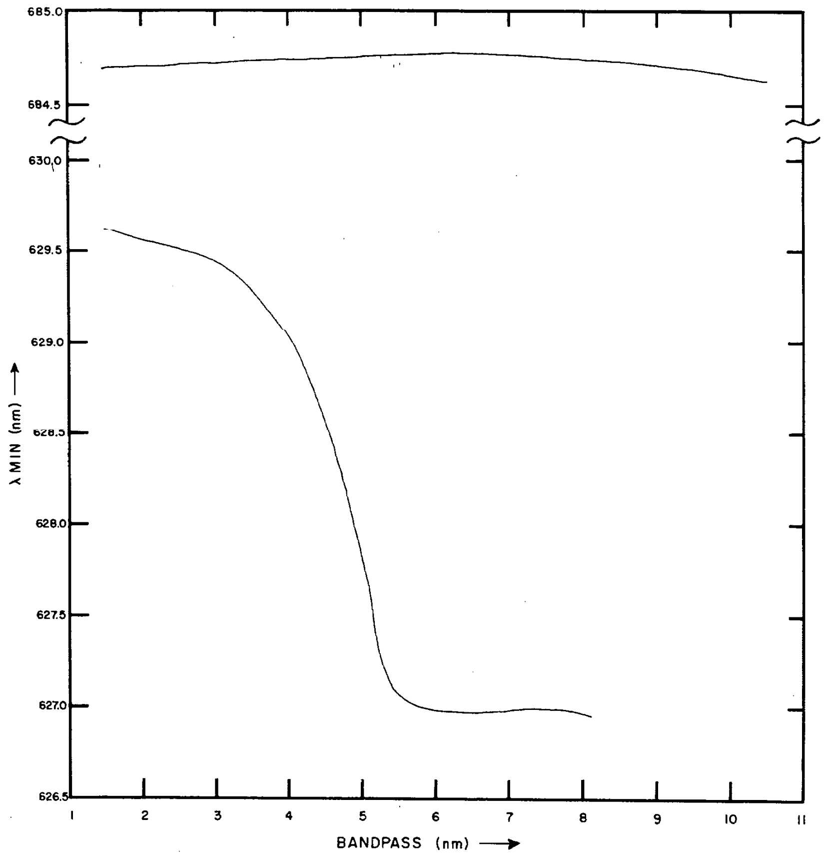

Figure 4g: Transmittance Minima, λ_{MIN}, as a function of bandwidth

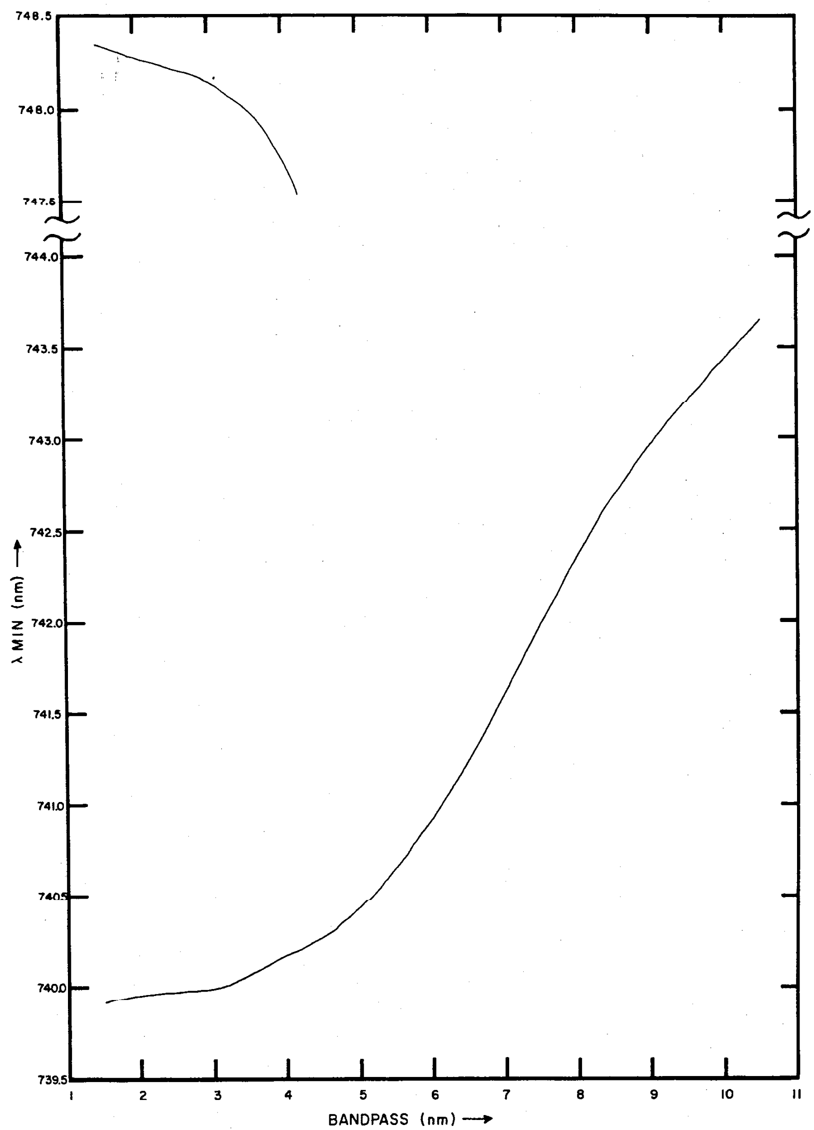

Figure 4h: Transmittance Minima, λ_{MIN}, as a function of bandwidth

2.1.3 Determining the Additive Correction

Once the point on the instrument wavelength scale at which a minimum occurs and the wavelength at which that same minimum should occur are both known, an additive correction $\delta\lambda$ can be calculated straightforwardly as:

$$\delta\lambda = \lambda_c - \lambda_s \tag{3}$$

where

λ_c is the wavelength at which the minimum transmittance should occur and

λ_s is the wavelength reading on the instrument scale at which the minimum transmittance is found.

These corrections are used as the basis for determining an overall wavelength correction as described in Section 2.3. The additive correction values for our General Electric Recording Spectrophotometer as determined from the wavelengths at minimum transmittance are listed in the fourth column of Table IV.

2.2 Discrete Wavelength Corrections from Transmittance Inflection Points

A second set of characteristic points on the spectral transmittance curve which can be used to provide wavelength calibration data are the inflection points. Not all inflection points are satisfactory for this purpose. What is desired is that the transmittance curve should be nearly linear over a range comparable to the width of the largest passband for which the wavelength calibration is to be used. If the transmittance curve is completely asymmetric about the inflection point, it follows that all instruments with symmetric passbands will measure the same transmittance value at the point of inflection regardless of bandwidth or passband shape. Nine points on the didymium filter spectral transmittance curve which very nearly have this property have been selected, and these are denoted by letters in Figure 1.

2.2.1 Locating Wavelengths of the Points of Inflection on the Instrument Scale

Before the points of inflection can be located, one must have the instrument approximately within calibration in order to be sure that the correct part of the transmittance curve is being measured. This can be done by producing a spectral transmittance curve with the instrument and comparing it with Figure 1 or by locating the wavelengths of minimum transmittance as described in Section 2.1. Once a wavelength can be approximately selected, one refers to Table VI for the wavelength-transmittance pairs corresponding to each of the selected points of inflection. The setting on the instrument wavelength scale at which the given transmittance occurs is then determined. Since the transmittance curve is very nearly a straight line at these points, linear interpolation is an adequate way to locate the wavelength. This is illustrated with data from the General Electric Recording Spectrophotometer in Figure 5. In this figure, a graph was made of the measured spectral transmittance near point of inflection A. The transmittance at point of inflection A was found from Table VI to be .7562, and the wavelength at which this transmittance occurs on the instrument wavelength scale was found from the curve in Figure 5 to occur at 404.25 nm. The second column of Table VII lists the wavelengths so determined for each of the nine selected inflection points.

2.2.2 Obtaining the Correct Wavelengths for Inflection Points

The wavelengths listed in Table VI are independent of the instrument or filter. However, this does not mean that the wavelength calibration will be free of error. The spectral transmittance curve has a large but finite slope at each of the points of inflection. Therefore, since there may be an error in the transmittance measurement due to instrument non-linearity or to dirt or some other surface film on the filter, and since the transmittance of a particular filter probably differs from Master Filter D-1 because of a difference in thickness or in concentration of didymium, the transmittance value given in Table IV is approximate for a specific filter. Consequently, the wavelength of the point of inflection on the instrument

Table VI

Wavelengths and Transmittances at Nine Selected Points of Inflection for Master Filter D-1

Point Identification	Transmittance	Wavelength (nm)
A	.7562	406.38
B	.7293	429.42
C	.6514	449.45
D	.6743	484.77
E	.5801	536.52
F	.4008	568.16
G	.3346	598.99
H	.4730	733.45
I	.4215	756.48

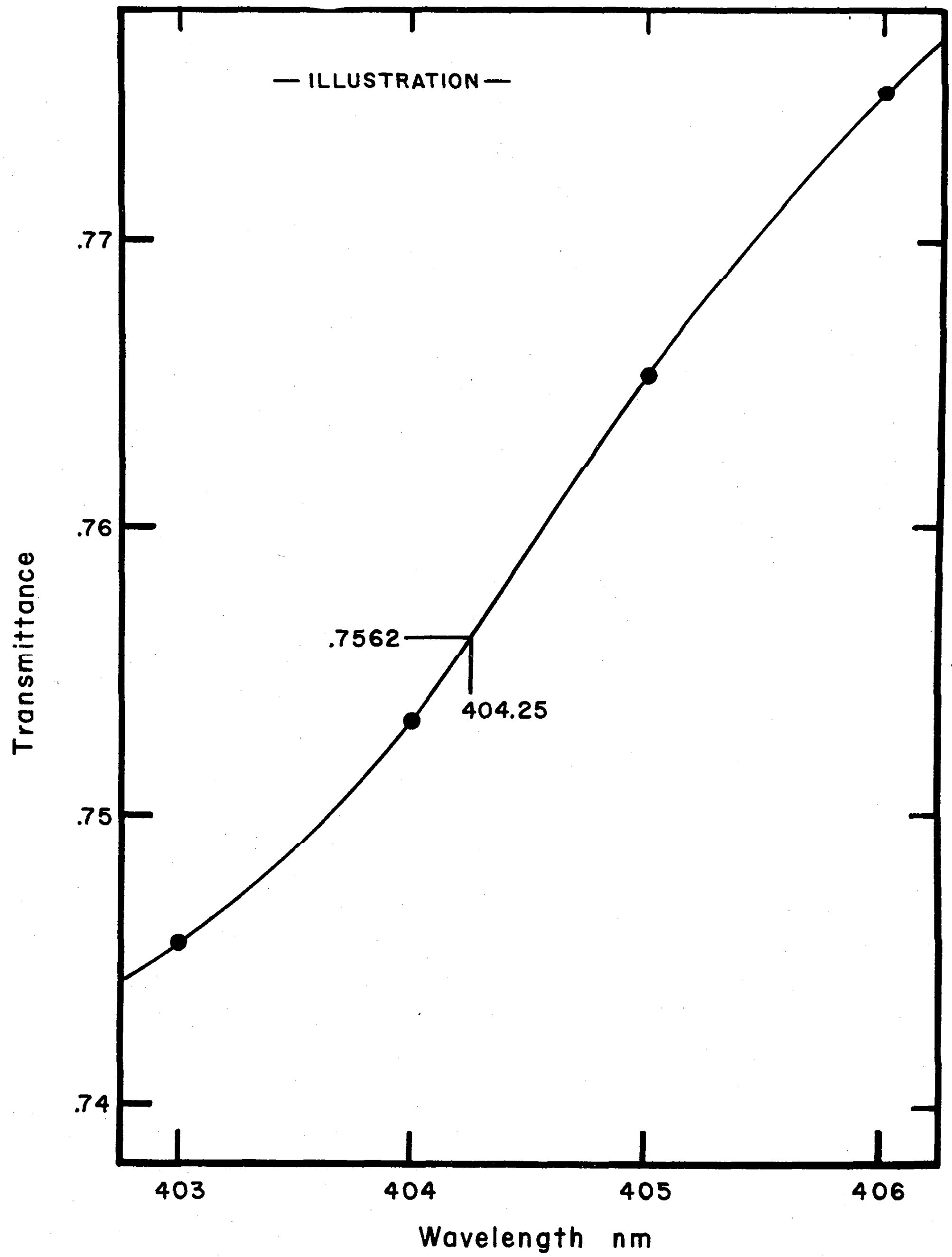

Figure 5: Interpolating to find the wavelength λ_s for point of inflection A

ILLUSTRATION

Table VII

Wavelength corrections for the General Electric Spectrophotometer from inflection points on the spectral transmittance curve

Point ID	Instrument Wavelength	Correct Wavelength	Additive Correction	Slope of Curve
A	404.25	406.38	2.13	.012
B	427.62	429.42	1.80	-.019
C	447.42	449.45	2.03	.009
D	483.16	484.77	1.61	.022
E	535.52	536.52	1.00	.042
F	567.23	568.16	0.93	-.078
G	597.59	598.99	1.40	.044
H	731.46	733.45	1.99	-.065
I	Off Scale			

scale as determined in Section 2.2.1 will approximate. Fortunately, the wavelength error introduced in this way is small, and also a very effective correction can be made for them if they are introduced by errors in transmittance measurements if one carries out the fitting procedure for the calibration curve. This procedure is described in Section 2.3.

2.2.3 Determining the Additive Correction

The additive correction $\delta\lambda$ is determined from the inflection point data in exactly the same way as it is obtained from the minimum point data as described in Section 2.1.2. These corrections for the General Electric Recording Spectrophotometer appear in the fourth column of Table VII. Comparing these additive corrections with those obtained from transmittance minima (See Table IV) shows differences which can be reconciled by the curve fitting procedures described in Section 2.3.

2.3 Producing a Wavelength Calibration Curve

The additive wavelength corrections obtained by the procedures in Sections 2.1 and 2.2 contain information on which a spectral wavelength correction can be based. However, these data also contain both systematic and random errors. The systematic errors in the corrections derived from the minimum transmittance data arise mainly from the lack of knowledge about the instrument passband. From Figure 4, it can be seen that an error in determining the bandwidth will produce different errors in the wavelength assigned to each of the transmittance minima, but the relative magnitude of these errors is quite predictable. Thus, these errors should be considered as systematic. Similarly, an error in measured transmittance will produce a set of errors of various sizes in the correction factors determined from the points of inflection, but the relative magnitudes of these errors are predictable from the transmittance curves. In addition, there are random errors in the additive correction data just as in any other experimental data. These errors arise both from random errors in the transmittance measurements, and possibly from some randomness in the performance of the wavelength scanning mechanism itself. The goal of the wavelength calibration is usually to obtain a correction curve which is a relatively simple function of wavelength based on reasonable assumptions concerning possible causes of systematic error in the wavelength-scale setting of the instrument. For this reason, it is desirable to make a rational approach to fitting the correction data rather than making wavelength corrections by simple linear interpolation. In the following parts of this section, methods for fitting curves will be given by which one can take advantage of what is known about the systematic errors in order to obtain a reliable correction function.

2.3.1 Choosing a Fitting Function

As in any curve-fitting effort, it is best to choose the simplest fitting function which is consistent with the physical system being described. If the mathematical equations governing the motion of the wavelength drive can be expressed in terms of parameters representing settings of the various adjustments in the instrument wavelength drive mechanism, there can be a distinct advantage in using such an equation. Not only will the fit obtained be more representative of the instrument's actual performance, but also clues may be provided as to how to adjust the wavelength mechanism to correct for the wavelength error. In lieu of such equations, a linear or quadratic power series expansion in wavelength is usually sufficient to provide an empirical fit to the data which will be as accurate as the random errors in the data will permit. A fitting function involving more than three parameters is probably too complicated and will tend to follow excursions in the data which do not represent real systematic wavelength setting errors. For the purposes of the general discussion which follows, the function used to represent the wavelength correction will be denoted by $C(a,b,c;\lambda)$ where a, b, and c represent three fitting parameters and λ represents the wavelength. When the data from the General Electric Recording Spectrophotometer are treated in illustration, a simple quadratic function of wavelength will be used since it is readily followed in calculations. Thus, for these illustrations we will use as a correction function

$$C(a,b,c;\lambda) = a + b\lambda + c\lambda^2 \qquad (4)$$

2.3.2 Fitting with no Correction for Systematic Errors

One can make the assumption that the bandwidth has been properly estimated and that there is no transmittance error introduced either because of instrument nonlinearity or by differences between the filters. If this assumption is made, the correction function $C(a,b,c;\lambda)$ can simply be fitted to the additive correction data. This has been done for the data obtained from the General Electric Recording Spectrophotometer and the results of least squares fitting are shown in Figure 6. The fit of the curve representing all of the data is not very satisfactory, and the separate fits of the data from the transmittance minima and the data from the points of inflection appear to indicate two separate but similar families of data. Therefore, it is reasonable to assume that there may be a systematic error in the transmittance, in the bandwidth estimate, or in both and that perhaps a better fit can be obtained if the possibility of such systematic errors is taken into account.

2.3.3 Fitting with Correction for Systematic Errors

The fitting process used in Section 2.3.2 above can be represented symbolically in terms of a set of simultaneous equations having the general form

$$\delta\lambda_i = C(a,b,c;\lambda_i) \qquad (5)$$

or, in the case of the illustration, the specific quadratic form

$$\delta\lambda_i = a + b\lambda_i + c\lambda_i^2 \qquad (6)$$

The index i is used to denote a particular point (either minimum or inflection point), $\delta\lambda_i$ denotes the additive correction corresponding to that point, and λ_i the wavelength of that point as it appears on the instrument wavelength scale. (Note that in this type of expression in which a small error in a variable is expressed as a function of the variable itself, either the corrected or uncorrected value of the variable can be used equally well. In this case, λ_i might just as well be the "correct" wavelength.) The object of the fitting procedure, whether it is done graphically or by calculations is to select values for the parameters a, b, and c such that the fit to the data is most satisfactory. When the fitting is done by calculation, the most satisfactory fitting is usually taken to be the one for which the sum of the squares of the deviations from the correction curve $C(a,b,c;\lambda)$ of the additive correction data is minimum, i.e. a "least squares fit" is obtained. In order to take possible systematic errors into account, one needs simply to add two more terms to each of the simultaneous equations represented in (4) to obtain the expressions:

$$\delta\lambda_i = C(a,b,c;\lambda) + d\cdot\Delta\lambda_i/\Delta W + e\cdot\Delta\lambda_i/\Delta\tau \qquad (7)$$

In this expression $(\Delta\lambda_i/\Delta W)$ represents rate at which the "correct" wavelength changes with respect to triangular bandwidth at point i. This can be obtained from Figure 4 for the points of minimum transmittance and is assumed to be zero for the points of inflection, since these points are supposed to occur at the same wavelength regardless of bandwidth. The value of the new fitting parameter d which is obtained through the fitting process will be the systematic error in the estimation of the equivalent triangular bandwidth. The quantity $\Delta\lambda_i/\Delta\tau$ is the rate at which the wavelength measured for the characteristic point changes with measured transmittance. This quantity can be evaluated from the experimental transmittance data at the point of inflection and is zero at the points of minimum transmittance. The value of the parameter e which is obtained through the fitting process will be the systematic error in the transmittance measurement. Notice that since the transmittances at the inflection points are all of roughly the same magnitude, the cause of the transmittance error is not important. To a first order of correction, representing the error in transmittance by a constant is satisfactory.

2.3.3.1 Correcting for Systematic Errors by Graphical Fitting

In order to illustrate the fitting procedure, the data from our General Electric Recording Spectrophotometer will be used again. First, the fitting will be done graphically in order to help promote a feeling for what is being done in the fitting procedure and then

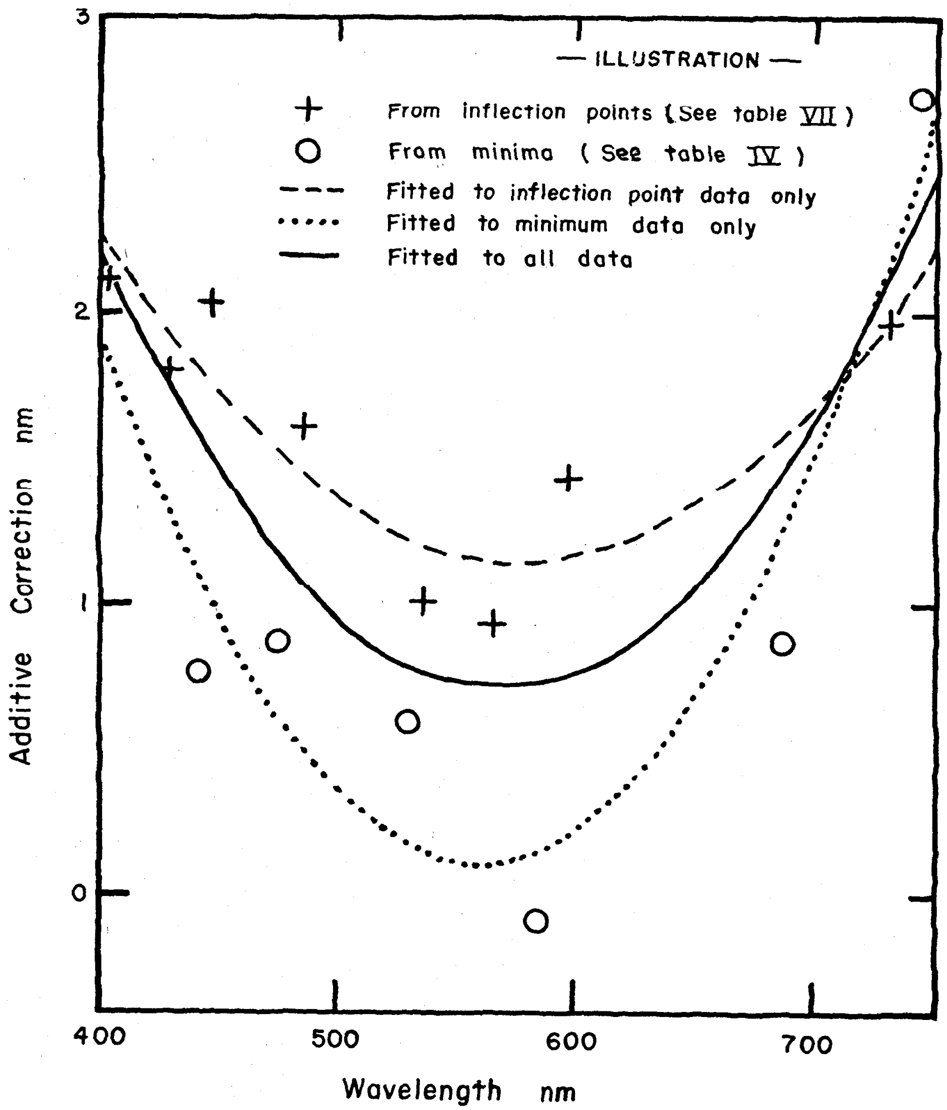

Figure 6: Fitting additive corrections with no corrections for systematic errors in the data.

the fitting will be done analytically using a least squares fitting done with the aid of a computer. In this illustration, we are not seeking to fit any particular form of $C(a,b,c;\lambda)$, but will simply try to find a "satisfactory" curve which passes through two sets of data, one representing wavelength at minimum data taken with a particular effective triangular passband and the other representing data taken with a constant correction of the measured transmittance. The different sets of additive corrections for the wavelengths of minimum transmittance are obtained in exactly the manner described in Section 2.1.3 with various assumptions being made about the bandwidth. The different sets of additive corrections for the wavelengths at the points of inflection are obtained by assuming a certain error in the measured transmittance and adjusting the instrument wavelength values to "correct" for that error in measured transmittance. The amount of correction required at each inflection point is calculated from the slope of the spectral transmittance curve at that inflection point. The goal of the fitting is to find a pair of sets of points, one set for transmittance minima and one set for inflection points through which a curve can be passed in a satisfying manner. This type of fitting is illustrated for the General Electric Recording Spectrophotometer in Figure 7. In the figure, the additive correction data for the wavelengths at minimum transmittance are shown as squares, with the triangular bandwidth shown as a number inside the square. The additive correction data for the inflection points are shown as circles. The circles with a negative sign indicate the additive corrections which would be needed if the transmittance scale reads too low and the circles with the positive sign indicate the additive corrections which would be needed if the transmittance scale reads 0.005 too high. By visual estimation, it was determined that a good fit could be obtained by assuming that the effective triangular bandwidth was 8.5 nm and that the transmittance scale was reading approximately 0.001 too high. These conclusions about the bandwidth and transmittance are confirmed by independent evidence, as will be shown in the next section. The corresponding additive corrections are shown on Figure 7 as solid dots, and the curve was drawn by visual estimation through these points. It should be pointed out that in this visual fitting, more weight was given to the additive corrections obtained from the points of inflection than to those obtained from the minima since the uncertainties in the wavelengths of minimum transmittance due to uncertainties in the shape of the passband are considerably greater than the corresponding uncertainties in the wavelengths of the points of inflection. Similar account should be taken in fitting the data by calculation.

2.3.3.2 Correcting for Systematic Errors by Calculation

If, in the example of the General Electric Recording Spectrophotometer, we use the quadratic form for the fitting function, we can write equation (7) as

$$\delta\lambda_i = a + b\lambda_i + c\lambda_i^2 + d(\Delta\lambda_i/\Delta W) + e(\Delta\lambda_i/\Delta\tau) \tag{8}$$

The value of λ_i can be taken either as the nominal wavelength of the characteristic point or as the wavelength of the characteristic point as read on the instrument scale. Values for the average slope over the range of bandwidths from 8 to 10 nm was obtained from the curves in Figure 4 and used as $\Delta\lambda_i/\Delta W$. The value of $\Delta\lambda_i/\Delta\tau$ at each wavelength was taken from the transmittance data and is the inverse of the slope of the transmittance curve as given in the fifth column of Table VII. A computer least-squares-fitting program was used to produce a least-squares best-fit solution to the set of simultaneous equations represented by expression (8). The results, appearing in Figure 8, were very similar to those obtained graphically in the preceding section, and the scatter of the data is consistent with what would be expected from the three-slit cam-operated wavelength mechanism used in the monochromator of the General Electric Spectrophotometer. In this illustration, fitting by calculation was very straightforward, but this may not always be the case. It is always a good idea to roughly fit the data graphically in order to see what range of correction for bandwidth and transmittance seems reasonable. The bandwidth and transmittance adjustments should never be allowed to be larger than is consistent with what is known about the instrument. In the case of the General Electric Spectrophotometer, it was assumed that the transmittance error had to be small since the instrument transmittance scale had recently been very carefully calibrated and the filter which was measured was the same one from which the transmittance data in Table VI were taken. It was also known from the line source experiments described in Appendix A that the passband was trapezoidal

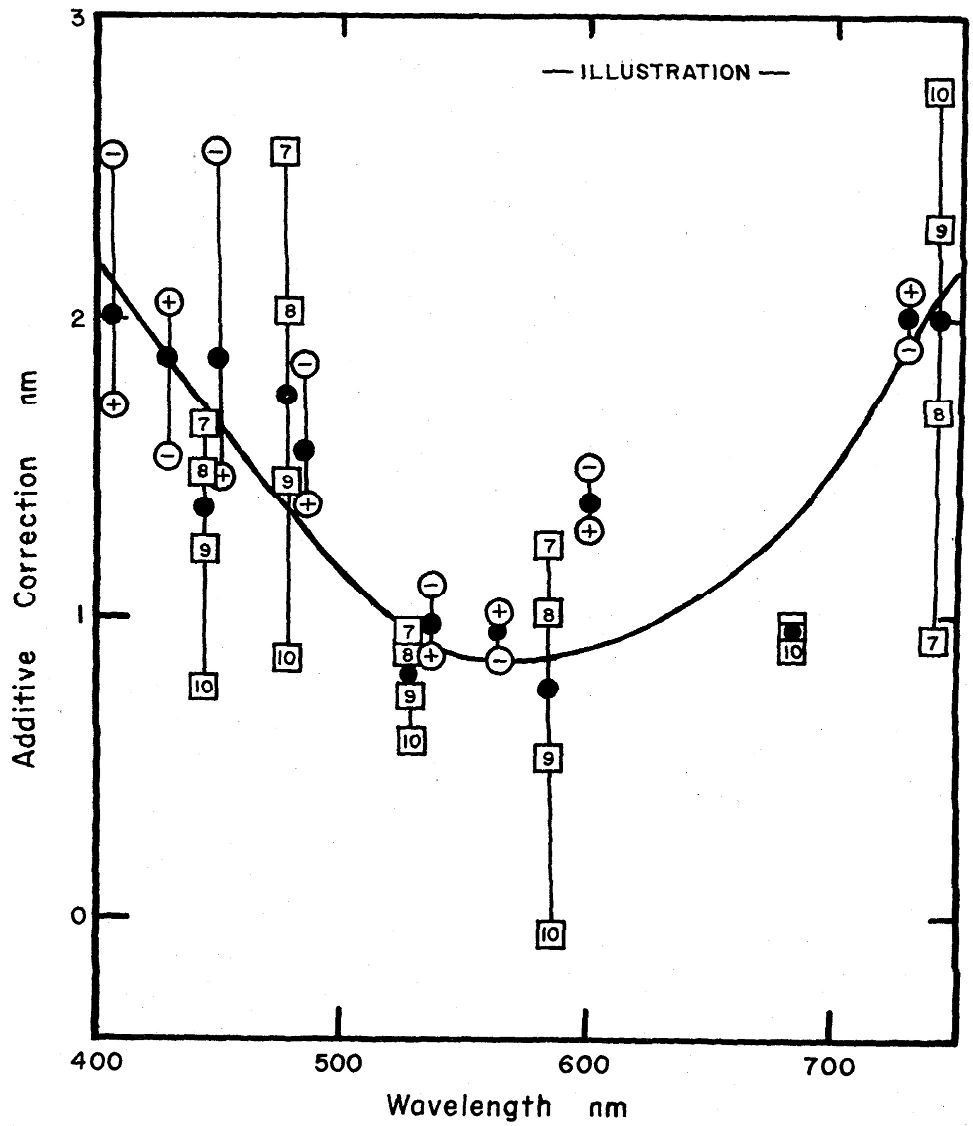

Figure 7: Graphical fitting of additive correction data with corrections for systematic errors in bandwidth and transmittance.

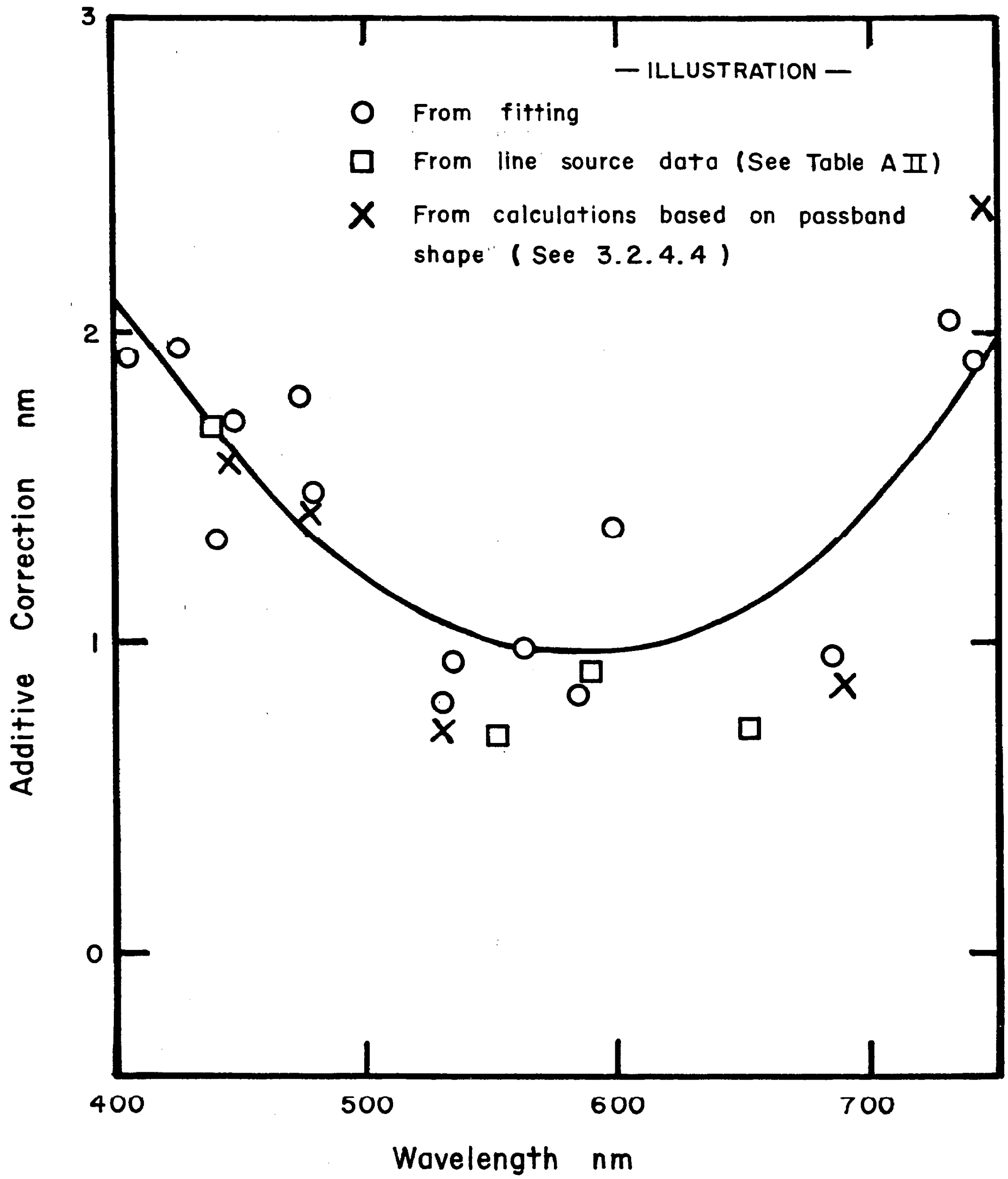

Figure 8: Least squares fitting results using equation 10. (The line-source and passband calculated data were not included in the fitting.)

rather than triangular, and the effective triangular bandwidth for that trapezoidal-shaped passband is, as described in Appendix A, expected to be approximately 8.5 nm, somewhat narrower than the actual half-height bandwidth of the trapezoid. The results shown in Figure 8 are consistent with this knowledge, since the fitting indicated an effective triangular bandwidth of 8.4 nm and a transmittance error of only 0.0025. Notice the good agreement of the data resulting from this fitting with the data which were obtained independently from line sources (square points in Figure 8) and with the data which were obtained from wavelengths of minimum transmittance curves generated from the reference instrument data using the measured passband shapes for the General Electric Recording Spectrophotometer (cross points in Figure 8).

3. Certification and Measurement Uncertainties

3.1 Introduction

As early as 1938, Jena BG-11 didymium filters were used at the National Bureau of Standards for in-house calibrations of the General Electric Recording Spectrophotometer[3] which was the predecessor of the one used as an illustration in this special publication. At that time, an uncertainty of 0.2 to 0.3 nm was placed on the wavelength calibration being obtained for that instrument. In the February 1941 meeting of the optical Society of America, it was announced that Corning 5120 didymium glass filters were available from NBS for calibrating the wavelength scale of spectrophotometers.[4] In a later presentation to the Optical Society of America[5] a single wavelength at each transmittance minimum was given which was to be used with 4, 8, and 10 nm bandwidths. From Figure 4, it is apparent that there is a systematic shift of any given wavelength of transmittance with bandwidth, so that the rather large error limits of ± 1 nm may have been assigned to cover that shift. However, no written evidence has survived the intervening 34 years to confirm that viewpoint. The filters were issued during those 34 years "for use with recording spectrophotometers with 10 nm bandwidth" and the wavelength uncertainty was given as ± 1 nm. They have provided a stable, reliable, and moderately accurate means of wavelength calibration over that period of time.

In 1971 a reference spectrophotometer was constructed at NBS which made available a highly accurate transmittance measurement capability.[6] After the initial demand for measurements on the new instrument was satisfied, it was decided to upgrade the measurements on the didymium filters as much as could reasonably be used and to offer them as Standard Reference Materials. Through the use of the new instrument and the application of high-speed digital computation to the analysis of the data, it has been possible to provide the data and techniques given in this Special Publication. Using these data and techniques, wavelength scale of a high quality spectrophotometer with bandwidth in the range 1.5 nm to 10.5 nm can be calibrated.

3.2. Uncertainties in the NBS Measurements

There are uncertainties associated with calibrating and operating the NBS instruments as well as uncertainties associated with the data analysis used to provide the numerical tables which appear in this Special Publication and in the data sheets which go with each filter. The user is in no position to reduce these uncertainties, and therefore they will determine a lower limit on the uncertainty which he can achieve in his calibration. To provide an understanding of these uncertainties, the calibrations, measurement procedures, and computations used to provide the NBS data for these filters are described in the remaining part of Section 3.2.

3.2.1. Wavelength Calibration of the Reference Spectrophotometer.

The wavelength scale of the reference spectrophotometer on which the filters were measured was calibrated using line sources as described in Section A.3. One of the difficulties encountered in this type of calibration is that the presence within the passband of weaker neighboring lines tends to make determining the centroid wavelength for a particular line very difficult. Therefore, the wavelength calibration of the reference spectrophotometer was carried out in two steps. First, calibration was made at high resolution, for which a large number of lines could be used, in order to determine the general shape of the wavelength calibration curve for fitting purposes. Then, with the spectrophotometer set for a larger bandwidth, a calibration was made using a smaller number of lines and fitting with the same type of curve. For the high resolution determination, .25 mm diameter entrance and exit ports were used in the monochromator for a half-height bandwidth of approximately 0.38 nm. The centroid values were obtained from measurements made at intervals of 0.2 nm. The sources and line wavelengths used for this determination are listed in Part a. of Table VIII and the corresponding additive corrections are shown in Figure 9. From these data it was concluded that a straight line would provide an adequate fit within the scatter of the points. Next, the entrance and exit ports which were to be used for measuring the didymium filters were installed. These ports were 1 mm in diameter and yielded a half-height bandwidth of approximately 1.5 nm. A wavelength calibration was again carried out using the spectral lines listed in Part b. of Table VIII. In these determinations, the location of the centroid was calculated from measurements made at 0.04 nm intervals. The additive corrections for this calibration and the final wavelength calibration curve are also shown in Figure 9. The uncertainty in wavelength setting associated with this calibration curve is estimated to be a random 0.02 nm uncertainty associated with the wavelength drive mechanism superimposed upon a 0.02 nm systematic uncertainty associated with obtaining the calibration curve.

3.2.2 The Effects of the Sensitivity Function of the Reference Spectrophotometer

The sensitivity function of the reference spectrophotometer is not a constant, but has the form illustrated in Figure 10. The general trend of the curve as determined by the detector sensitivity and the source spectral power distribution is approximately that shown for the 90° polarization (electric vector parallel to grating grooves). In the 0° polarization configuration, Wood's anomalies introduced by the monochromator grating produce additional complexities in the curve. The effect of the sensitivity function on the centroid of the bandpass of the reference instrument, as determined by the method described in Section A.4.2.1, is shown in Figure 11. Since the bandwidth is relatively narrow, the centroid shift due to the slope of the sensitivity function is quite small and was not included as a correction to the wavelength data in this Special Publication or in the wavelength data supplied with the filters. For applications in which a wavelength error of this magnitude is important, a direct calibration using line sources as described in Section A.3 should be carried out rather than using the SRM filters.

3.2.3 Transmittance Measurements

Transmittance measurements were made with the reference spectrophotometer using procedures similar to those described in reference 6. Measurements were made at two levels (high and low) of precision. High precision measurements were made on three selected filters which will be called the "master filters". The data from these filters, which are from the same melt as the 2013 and 2014 filters, were used in the analysis from which the procedures for using the filters were derived. Two master filters from the melt used for 2009 and 2010 filters were also measured with high precision, and the average of the data from these two filters are supplied as representative data for the melt. In addition, special sets of high precision measurements were used to explore for relatively small effects on the filter caused by outside influences such as temperature changes and cleaning of the filter surfaces. Measurements of a slightly lower precision which could be made in a significantly shorter time were used to supply the individual sets of data which are issued with each SRM 2013 and 2014.

3.2.3.1 High Precision Transmittance Measurements

The high precision measurements were made on sets of three filters as follows: The filters were mounted in a filter wheel which positioned them in the instrument beam automatically and the following time-symmetric measurement sequence was used at each wavelength:

0-1-2-3-0-3-2-1-0-1-2-3-0-3-2-1-0

where 0 represents measurement of a signal for the beam with no filter in place and 1, 2, and 3 represent the signals obtained with each of the three filters in place. Between each measurement, a reading was made of the background signal with a light trap inserted in the

Table VIII

The elements and wavelengths of the atomic lines used for the wavelength calibration

a. Lines used with the .25 mm aperture.

Element	Wavelength (nm)	Element	Wavelength (nm)
Cs	455.536	He	388.865
	459.318		501.568
			587.562
			667.815
Rb	420.185		
	421.556		
	780.023	Ne	640.225
	794.760		692.947
			724.517
Hg	275.278		
	296.728	Cd	467.816
	334.148		479.992
	404.657		508.582
	407.784		643.847
	435.834		
	491.604		
	546.075	Zn	213.856
	576.960		
	579.066		

b. Lines used with the 1 mm apertures

Element	Wavelength
Zn	213.856
He	388.865
Hg	546.075
Rl	780.023

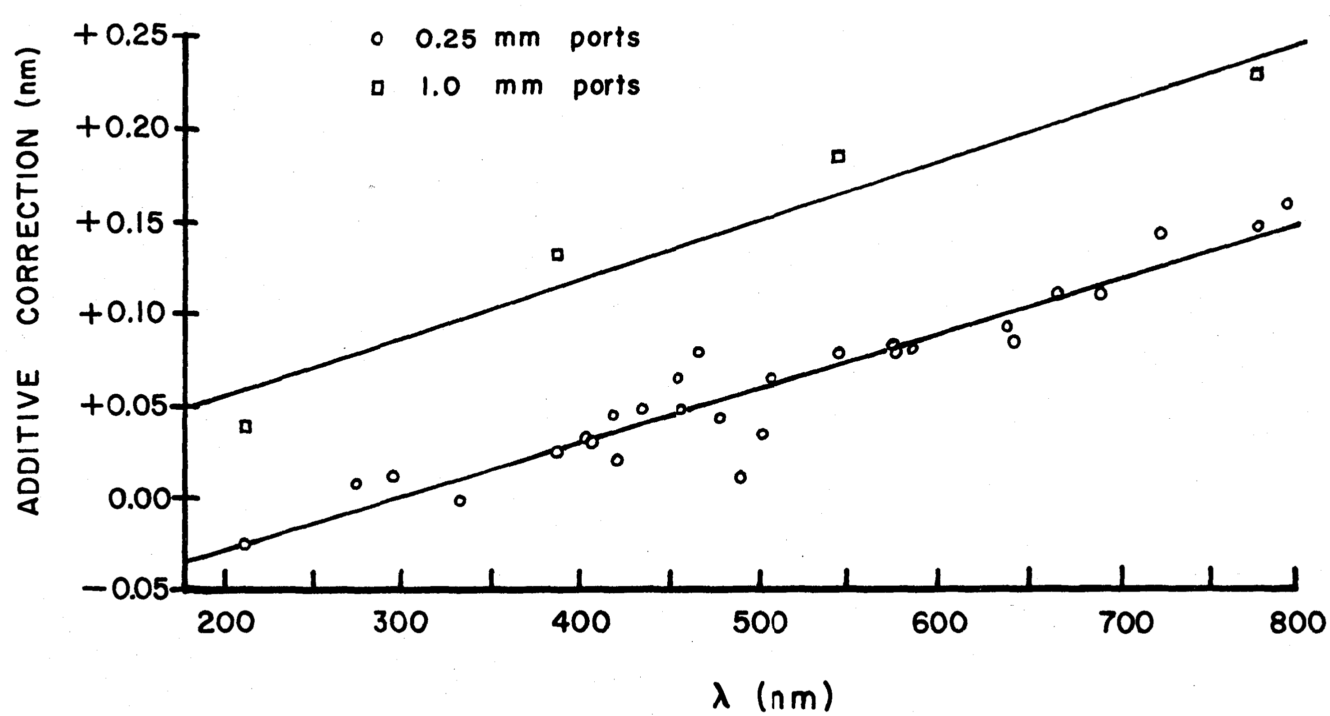

Figure 9: Wavelength calibration curves for reference spectrophotometer

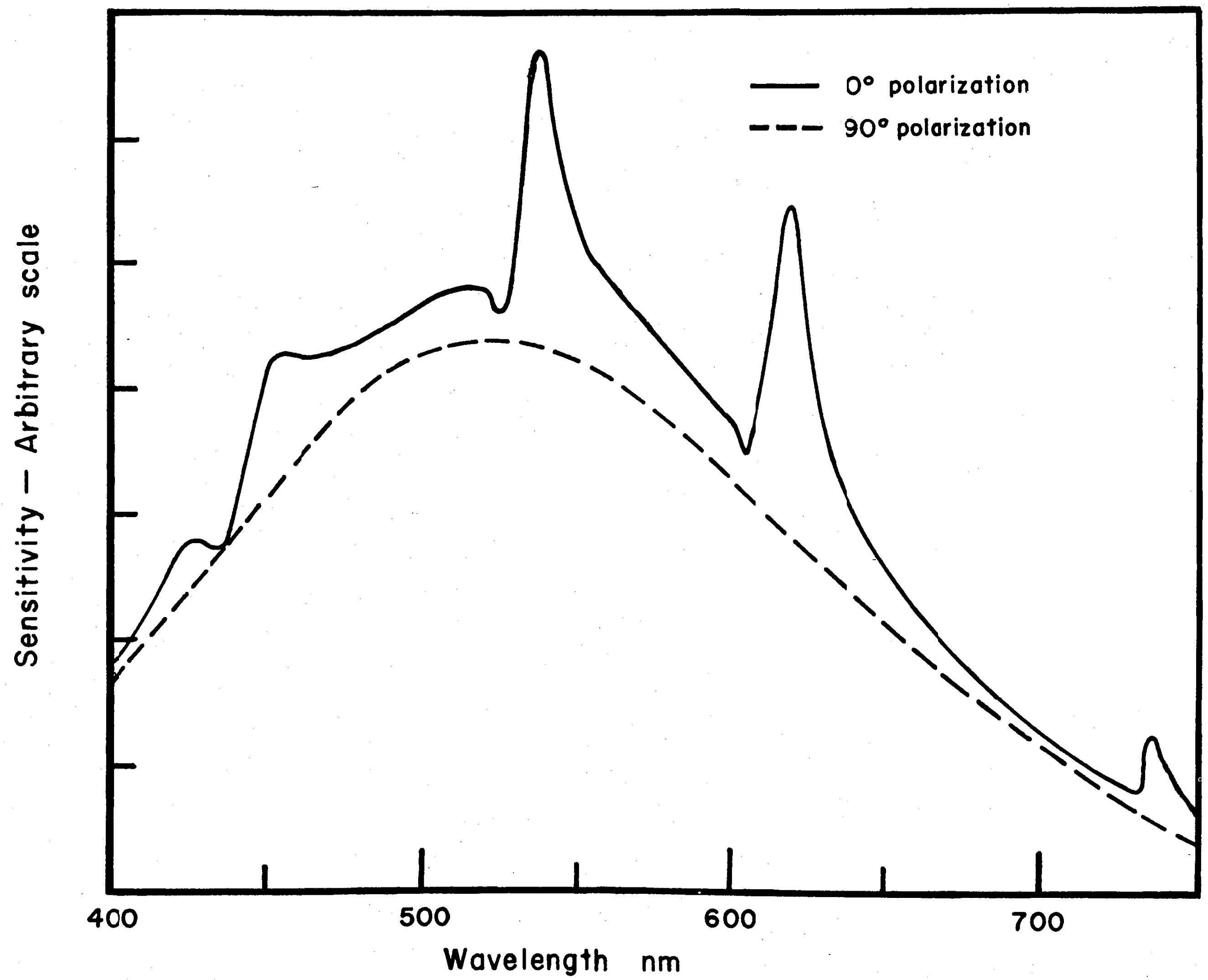

Figure 10: Spectral sensitivity function of the NBS reference spectrophotometer

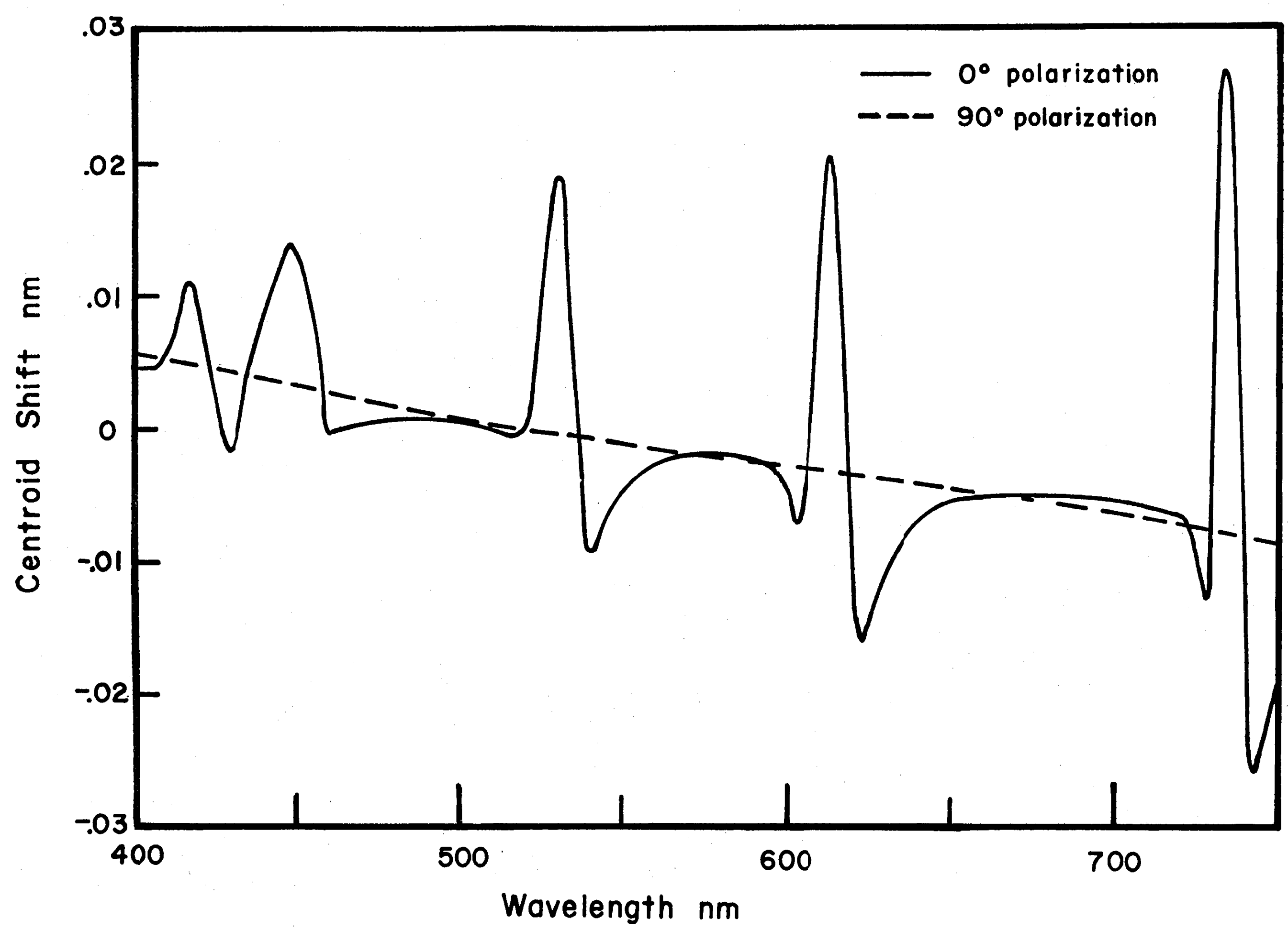

Figure 11: Shift of passband centroid, $\lambda_c-\lambda_g$, due to the slope of the sensitivity function for the NBS reference spectrophotometer

beam just ahead of the detector unit. Each measurement was made by integration of the output current over a ten-second period, and a ten-second settling time was allowed before the measurement of each signal except for the background where only a brief wait was found to be needed. The background signal from the photomultiplier was subtracted from each of the other signal values and the resulting values were then corrected for a very slight instrument non-linearity. The resulting data were fitted to straight lines with respect to time by means of a least-squares fitting routine in which it was assumed that the time drift in a signal was due to a drift in gain and, therefore, that the slope of each of the fitted lines was proportional to the average signal. The ratio of the appropriate signals represented by the lines at any one time are taken to be the transmittance values. A typical value of the random uncertainty associated with a 95% level of confidence for these transmittance measurements was 0.0002 for $\tau \simeq .9$. Transmittance data taken at 1.5 nm intervals on one of the master filters are given in Table IX. The high precision measurements described above required approximately 20 minutes measuring time per wavelength for a set of three filters.

3.2.3.2 Lower Precision Transmittance Measurements

Since measurements are made at each of 268 different wavelengths, it was not economically feasible to use that procedure on all of the replica filters. Therefore a shortened measurement sequence of the form

0-0-1-1-2-2-3-3-0-0

was used. This required much less motion of the filter wheel as well as having fewer total readings. A background reading was taken only at the beginning and the end of the sequence, the "settling" time was reduced from 10 seconds to 2.5 seconds, and the current integration time was reduced from 10 seconds to 1 second. Using this sequence, the measurement time was reduced to 90 seconds per wavelength for a set of three filters. The uncertainty in transmittance associated with a 95% level of confidence for these measurements was found to be 0.0009 for $\tau \simeq .9$.

3.2.4 Synthesizing Data for Other Passbands

In the mode used for measuring these filters, the reference spectrophotometer was equipped with circular apertures rather than the usual slits. Consequently, the geometrical passband (see Section A.3) is not quite triangular although, as can be seen from Figure 12, it very closely resembles a triangular passband with a bandwidth of 1.5 nm. Therefore, the transmittance data in Table IX and the corresponding transmittance data supplied for each particular SRM can, for most practical purposes, be regarded as being from a triangular passband of 1.5 nm bandwidth and will be so treated in the remainder of this section. The transmittance which would be measured for other passbands that can be constructed as the weighted sum of 1.5 nm triangular passbands can be calculated from a table of transmittance data such as Table IX by using a series of weighting factors' B_i which are related to the shape of a passband of bandwidth greater than 1.5 nm that is sampled at 1.5 nm intervals (see Sections 3.2.4.1, ff). The measured transmittance τ can be calculated by taking the weighted average of a series of transmittance values from Table IX using the B_i as weighting factors

$$\tau_j = \frac{\sum_{i=0}^{2(N-1)} B_i \cdot \lambda(j+1)}{\sum_{i=0}^{2(N-1)} B_i} \qquad (9)$$

The centroid wavelength for the transmittance measurement so represented is

$$\lambda = \lambda_j + \Delta\lambda \qquad (10)$$

where λ_j is the wavelength at which τ_j was measured and $\Delta\lambda$ is the distance from λ_j of the passband centroid which can be calculated as

Table IX

Transmittance of Master Filter D-1 measured with the reference spectrophotometer. The bandwidth was approximately 1.5 nm. A typical passband is shown in Figure 12.

CAUTION: THESE TRANSMITTANCE VALUES ARE GIVEN ONLY TO ILLUSTRATE A TYPICAL SET OF TRANSMITTANCE DATA. THESE SRM FILTERS SHOULD NOT BE USED AS TRANSMITTANCE STANDARDS.

Wavelength	Transmittance	Wavelength	Transmittance	Wavelength	Transmittance
380.00	0.5660	458.00	0.6973	536.00	0.5565
381.50	0.5898	459.50	0.6759	537.50	0.6419
383.00	0.6161	461.00	0.6575	539.00	0.7046
384.50	0.6396	462.50	0.6490	540.50	0.7544
386.00	0.6606	464.00	0.6480	542.00	0.7935
387.50	0.6806	465.50	0.6433	543.50	0.8206
389.00	0.6996	467.00	0.6314	545.00	0.8386
390.50	0.7153	468.50	0.6170	546.50	0.8508
392.00	0.7300	470.00	0.6026	548.00	0.8586
393.50	0.7409	471.50	0.5849	549.50	0.8623
395.00	0.7482	473.00	0.5752	551.00	0.8628
396.50	0.7458	474.50	0.5965	552.50	0.8623
398.00	0.7280	476.00	0.6061	554.00	0.8619
399.50	0.7059	477.50	0.5710	555.50	0.8609
401.00	0.6944	479.00	0.5618	557.00	0.8575
402.50	0.6826	480.50	0.5702	558.50	0.8511
404.00	0.7233	482.00	0.5870	560.00	0.8409
405.50	0.7453	483.50	0.6317	561.50	0.8246
407.00	0.7638	485.00	0.6864	563.00	0.7983
408.50	0.7921	486.50	0.7270	564.50	0.7550
410.00	0.8079	488.00	0.7579	566.00	0.6744
411.50	0.8142	489.50	0.7849	567.50	0.5176
413.00	0.8178	491.00	0.8059	569.00	0.2723
414.50	0.8205	492.50	0.8171	570.50	0.0868
416.00	0.8208	494.00	0.8204	572.00	0.0308
417.50	0.8214	495.50	0.8186	573.50	0.0305
419.00	0.8228	497.00	0.8123	575.00	0.0411
420.50	0.8290	498.50	0.8019	576.50	0.0459
422.00	0.8283	500.00	0.7886	578.00	0.0603
423.50	0.8254	501.50	0.7733	579.50	0.0808
425.00	0.8274	503.00	0.7582	581.00	0.0803
426.50	0.8269	504.50	0.7438	582.50	0.0470
428.00	0.8105	506.00	0.7279	584.00	0.0197
429.50	0.7279	507.50	0.7037	585.50	0.0133
431.00	0.6281	509.00	0.6607	587.00	0.0200
432.50	0.6404	510.50	0.6014	588.50	0.0364
434.00	0.6474	512.00	0.5529	590.00	0.0559
435.50	0.6408	513.50	0.5332	591.50	0.0672
437.00	0.6270	515.00	0.5503	593.00	0.0870
438.50	0.6112	516.50	0.5793	594.50	0.1331
440.00	0.6035	518.00	0.5978	596.00	0.2078
441.50	0.6072	519.50	0.6082	597.50	0.2860
443.00	0.6128	521.00	0.5920	599.00	0.3429
444.50	0.6077	522.50	0.5297	600.50	0.3997
446.00	0.6051	524.00	0.4546	602.00	0.4635
447.50	0.6194	525.50	0.4261	603.50	0.5256
449.00	0.6461	527.00	0.4165	605.00	0.5781
450.50	0.6723	528.50	0.3872	606.50	0.6133
452.00	0.6877	530.00	0.3805	608.00	0.6331
453.50	0.6982	531.50	0.3894	609.50	0.6519
455.00	0.7084	533.00	0.4054	611.00	0.6860
456.50	0.7097	534.50	0.4648	612.50	0.7390

Table IX (Continued)

Wavelength	Transmittance	Wavelength	Transmittance
614.00	0.7986	702.50	0.8939
615.50	0.8445	704.00	0.8955
617.00	0.8717	705.50	0.8967
618.50	0.8814	707.00	0.8975
620.00	0.8811	708.50	0.8982
621.50	0.8744	710.00	0.8981
623.00	0.8685	711.50	0.8974
624.50	0.8688	713.00	0.8966
626.00	0.8713	714.50	0.8945
627.50	0.8710	716.00	0.8922
629.00	0.8683	717.50	0.8889
630.50	0.8687	719.00	0.8846
632.00	0.8733	720.50	0.8784
633.50	0.8795	722.00	0.8712
635.00	0.8851	723.50	0.8614
636.50	0.8879	725.00	0.8473
638.00	0.8896	726.50	0.8274
639.50	0.8918	728.00	0.7978
641.00	0.8936	729.50	0.7508
642.50	0.8951	731.00	0.6784
644.00	0.8961	732.50	0.5701
645.50	0.8968	734.00	0.4264
647.00	0.8972	735.50	0.2891
648.50	0.8971	737.00	0.1983
650.00	0.8968	738.50	0.1661
651.50	0.8970	740.00	0.1617
653.00	0.8980	741.50	0.1663
654.50	0.8988	743.00	0.1881
656.00	0.8987	744.50	0.2135
657.50	0.8985	746.00	0.2144
659.00	0.8979	747.50	0.1977
660.50	0.8970	749.00	0.1965
662.00	0.8956	750.50	0.2225
663.50	0.8927	752.00	0.2640
665.00	0.8882	753.50	0.3124
666.50	0.8823	755.00	0.3673
668.00	0.8757	756.50	0.4274
669.50	0.8696	758.00	0.4871
671.00	0.8652	759.50	0.5410
672.50	0.8613	761.00	0.5863
674.00	0.8579	762.50	0.6242
675.50	0.8530	764.00	0.6592
677.00	0.8444	765.50	0.6924
678.50	0.8323	767.00	0.7225
680.00	0.8180	768.50	0.7479
681.50	0.8011	770.00	0.7674
683.00	0.7821	771.50	0.7807
684.50	0.7680	773.00	0.7885
686.00	0.7764	774.50	0.7919
687.50	0.7949	776.00	0.7897
689.00	0.8108	777.50	0.7801
690.50	0.8274	779.00	0.7623
692.00	0.8434	780.50	0.7370
693.50	0.8579		
695.00	0.8692		
696.50	0.8779		
698.00	0.8845		
699.50	0.8892		
701.00	0.8920		

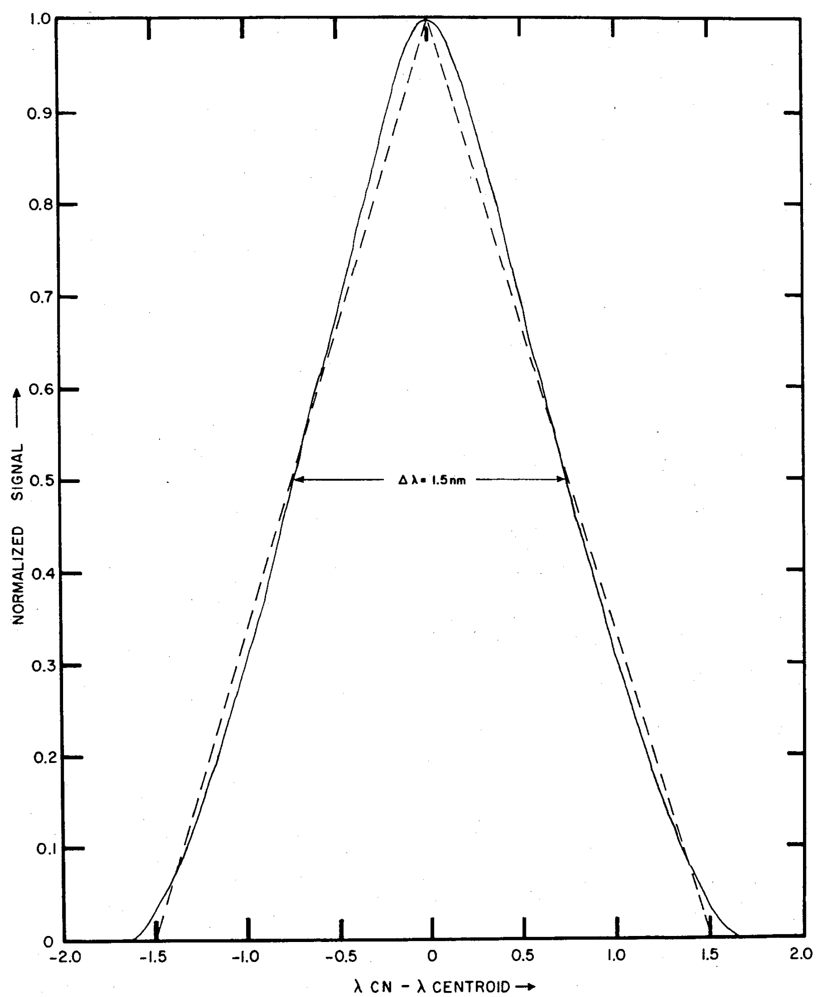

Figure 12: Typical Normalized geometrical passband $G(\lambda_s,\lambda)$ for the NBS reference spectrophotometer used to evaluate these SRM

$$\Delta\lambda = 1.5 \frac{\Sigma\, i \cdot B_i}{\Sigma\, B_i}\ [nm] \qquad (11)$$

The synthesizing of such data for particular passband shapes which were used in the development of the procedures given in this Special Publication will be discussed briefly in the following subsections.

3.2.4.1 Symmetrical Triangular Passbands

Triangular passband functions having a bandwidth which is an even multiple of 1.5 nm were constructed exactly from the weighted sum of 1.5 nm bandwidth triangular functions spaced at 1.5 nm intervals. To construct such a triangular passband of width 1.5N, the summation index i must range from 0 to 2(N-1). The B_i are evaluated as

$$B_i = i + 1 \text{ for } i < N \qquad (12a)$$

and

$$B_i = (2N-1)-i \text{ for } N \le i \le 2(N-1) \qquad (12b)$$

For example, for a 4.5 nm bandwidth, N = 3 and we have $B_0 = 1$, $B_1 = 2$, $B_2 = 3$, $B_3 = 2$, and $B_4 = 1$. From inspection or from the use of (11) it can be seen that the centroid wavelength is 3 nm higher than λ_j, i.e. at the wavelength for which B_2 is the multiplier. The data for the bandwidths, 1.5, 3, 4.5, 6, 7.5, 9 and 10.5 nm given in Table V were obtained from this type of exact triangular construction. The interpolation used to obtain the curves in Figure 4 and the remaining data in Table V was done by using approximations of triangular passbands which were not exact multiples of 1.5 nm. The approximation which was used is illustrated in Figure 13 for bandwidth 1.5Y where 6<Y<7. In this case, the largest i is 2(N-1) where N is the next integer larger than Y. The value of each B_i is proportional to the corresponding height on the triangle and multiplies the corresponding transmittance value as before except for the end points corresponding to B_0 and B_{12} in this case. At these points, the height of the triangle B_0' or B_{12}') is reduced by the fraction of the triangle which falls outside the passband being constructed (shaded areas) and is multiplied by the transmittance value linearly interpolated to the wavelength corresponding to the centroid (point a or point b) of the unshaded portion of the triangle contained in the passband being approximated.

3.2.4.2 A Family of Trapezoidal Passbands

A set of transmittance data were obtained for a family of trapezoidal passbands with bandwidths an odd multiple of 1.5 nm by making B_0 through B_{N-1} equal for odd N. The characteristic shape of these trapezoids is that the upper base is 3 nm shorter than the lower base. Data were calculated for such trapezoids having bandwidths from 1.5 to 19.5 nm. These data were used in evaluating the effect of passband shape on the wavelength calibrations obtained from points of inflection.

3.2.4.3 A Family of Asymmetrical Triangular Passbands

A set of asymmetrical passbands were constructed for further extreme-case evaluation of the use of the inflection points for wavelength calibration. These were designed so that they could be exactly constructed from 1.5 nm triangles at 1.5 nm spacing and so that their centroids fell at one of the measured wavelengths. The B_i values and the i corresponding to the centroid are listed in Table X.

3.2.4.4 Data Constructed from Real Passbands

A set of B_i values can be constructed to represent an approximation to a real passband which would be obtained by adding 1.5 nm triangles. This approximation corresponds to choosing points on the passband curve at 1.5 nm intervals and connecting them with straight lines as illustrated for the passband of the General Electric Recording Spectrophotometer in Figure 14. With the B_i so obtained, equation (11) can be used to calculate the transmittance which would be measured with such an instrument and therefore to obtain the correct

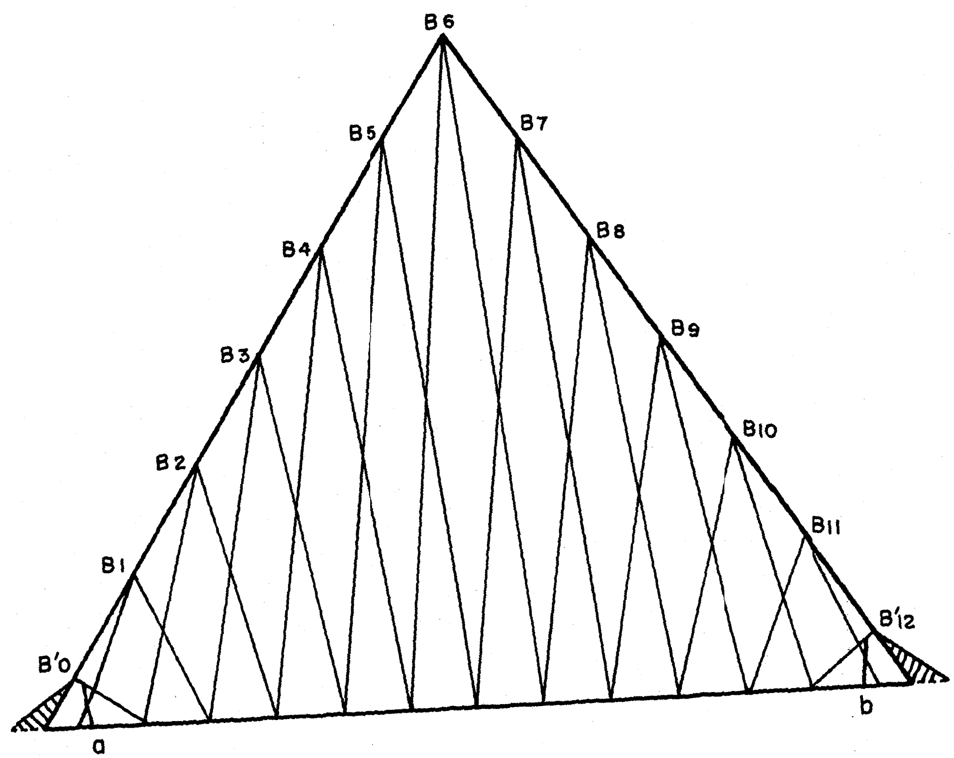

Figure 13: Illustration of the approximate construction of a symmetric triangular passband between 9 and 10.6 nm ir bandwidth.

Table X

Weighting factors used to construct asymmetrical triangular passband functions from a sum of 1.5-nm symmetrical passbands (See Section 3.2.4.3)

Weighting Factor B_i	Passband Number 1	2	3	4	5	6
B_0	1	4	1	7	1	10
B1	2	3	2	6	2	9
B_2	3	2	3	5	3	8
B_3	4	1	4	4	4	7
B_4			5	3	5	6
B_5			6	2	6	5
B_6			7	1	7	4
B_7					8	3
B_8					9	2
B_9					10	1
Centroid i	2	1	4	2	6	3

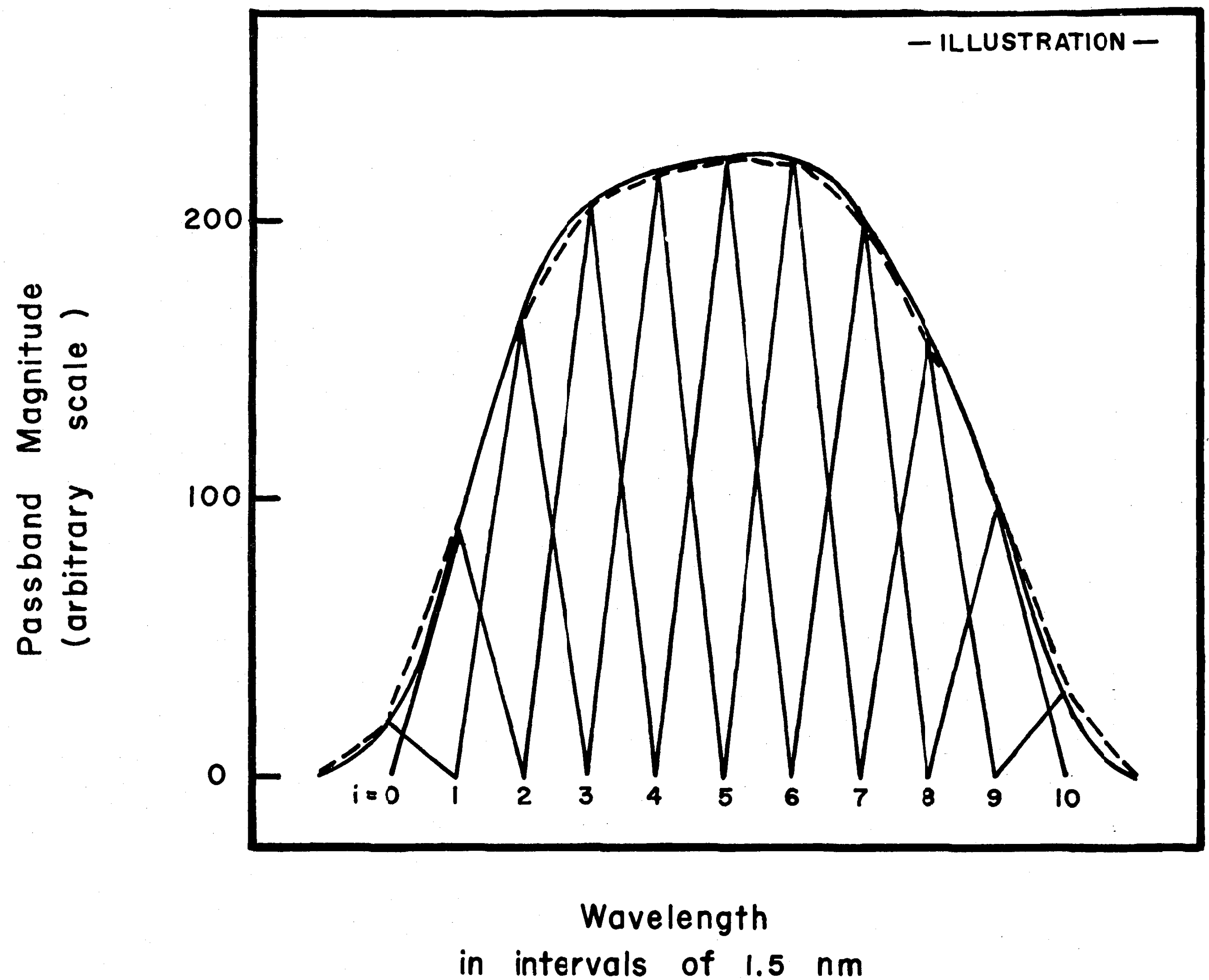

Figure 14: Construction of approximation of General Electric Recording Spectrophotometer passband from sum of 1.5 nm triangular passbands. This construction was arranged so that the centroid corresponds to i = 5.

wavelength at minimum for that instrument. The correct wavelengths at the minima and the corresponding additive corrections which were obtained by this method are listed in Table XI and the additive corrections are plotted in Figure 8.

3.2.5 Locating Minima by Polynomial Fit

Since the transmittance data were obtained at discrete wavelengths taken at intervals of 1.5 nm, polynomial fitting was used to estimate the location of the point of minimum transmittance to a higher degree of precision than 1.5 nm. Polynomials of various degrees from 2 to 6 in wavelength were fitted to various numbers of data points surrounding each of the transmittance minima for each of the three master filters in order to test for consistency between the various fitting approximations. The transmittance near the wavelength minima of each master filter was also measured at intervals of 0.15 nm and the minima were found by fitting these data with a fourth degree polynomial in wavelength. From comparing these results, it appeared that a sixth degree polynomial fitted to seven points at 1.5 nm intervals gave the most consistent data. The comparison between the wavelengths at minimum which were found from sixth degree polynomial fitting to those which were obtained from the data taken at 0.15 nm intervals is made in Table XII. From this table the uncertainty in locating the wavelength of minimum transmittance due to the curve-fitting procedure can be estimated. This uncertainty is the largest uncertainty of all of the uncertainties which are attributable completely to the NBS measurements.

3.2.6 Random Noise in Wavelength-at-Minimum Data

In order to test the effects of random noise in the transmittance measurements on the determination of the wavelengths of minimum transmittance, four independent sets of measurements were made on master filter D-1 using the lower precision sequence of measurements described in Section 3.2.3.3. For each set of transmittance data, the wavelength of minimum transmittance was calculated for each of seven different triangular passbands at each recognizable point of minimum transmittance. From the four independent wavelength-at-minimum values, a standard deviation in the wavelength of minimum transmittance was calculated for each minimum at each bandwidth. These values are shown in Table XIII and indicate that in general the contribution to the wavelength uncertainty from this type of noise is less than the uncertainty introduced by the polynomial fitting process. (It should be noted when comparing Tables XII and XIII that the values in Table XII were calculated from data obtained with the high precision measurement sequence.)

3.2.7 Obtaining the Wavelengths of the Inflection Points

Transmittance data for each of seven different symmetric triangular passbands with bandwidths ranging from 1.5 nm to 10.5 nm were constructed as described in Section 3.2.4.1. In principle, the transmittance measured at an inflection point should be independent of the bandwidth, and linear interpolation should be very accurate at an inflection point. Therefore, linear interpolation was used to determine the transmittance for each of the seven passbands at any wavelength in the vicinity of a point of inflection. The point of inflection was found by a computer search routine which sought out the wavelength at which the sum of the squares of the deviations of the seven transmittances from their mean value was a minimum. The wavelength and transmittance values at the inflection points given in Table VI and in the corresponding data table accompanying each filter were found in this manner.

3.2.8 Sensitivity of Inflection Determination to Passband

The wavelengths of minimum transmittance depend fairly strongly on the second moment of the passband function and to some extent on other characteristics of the passband shape. By their very nature, the wavelength determinations at the inflection points are not supposed to depend strongly upon passband shape or width. This was tested by developing transmittance data for each of 19 different passbands (7 symmetric triangles, 6 trapezoids, and 6 skew triangles) and determining for each inflection point the wavelength corresponding to the appropriate inflection point transmittance from Table VI. The fitting procedure from section 2.3.3.2 was then applied to the data to produce a calibration curve. The fitting was done for a constant, for a line, and for a quadratic function. Since the data for the various passbands was generated from the same data used to obtain Table VI, it follows that

Table XI

Determination of wavelength corrections for General Electric Spectrophotometer from wavelength at transmittance minima

Minimum Number	Instrument Wavelength at Minimum* (nm)	Correct Wavelength at Minimum# (nm)	Additive Correction (nm)
3	440.66	442.30	1.64
6	475.07	476.54	1.47
8	528.42	529.19	.77
10	584.85	585.71	.86
13	683.78	684.63	.85
14	740.67	743.08	2.41

* Obtained from a 4th degree polynomial fitting of seven data points at 1 nm intervals.

Based on transmittance values calculated from measured bandpass function approximation as described in Section 3.2.4.4.

Table XII

Comparison of wavelength at minimum transmittance obtained by fitting polynomial of degree 6 to 7 transmittance values measured at 1.5 nm intervals to the wavelength at minimum transmittance obtained by fitting a polynomial of degree 4 to the indicated number of transmittance values measured at 0.15 nm intervals. All measurements were made of master filter D-1 with 1.5 nm bandwidth.

Minimum Number	Number of Data Points (0.15 nm)	Minimum Wavelength of Transmittance		Difference
		λ_{min}(.15 nm)	λ_{min}(1.5 nm)	λ_{min}(1.5 nm)- λ_{min}(.15 nm)
1	5	402.43	402.36	-0.07
2	5	431.43	431.49	0.06
3	10	440.22	440.17	-0.05
4	9	445.52	445.58	0.06
5	8	472.79	472.71	-0.08
6	8	478.62	478.77	0.15
7	7	513.52	513.44	-0.08
8	7	529.46	529.67	0.21
9	5	572.72	572.67	-0.05
10	5	585.39	585.33	-0.06
11	8	623.67	623.61	-0.06
12	7	629.64	629.62	-0.02
13	9	684.75	684.70	-0.05
14	9	740.16	739.91	-0.25
15	8	748.30	748.34	0.04

Table XIII

Random uncertainty for certified values as obtained from four sets of measurements on Master D-1 using the lower-precision measurement sequence.

Band Number	Mean Wavelength of Minimum Transmittance 1.5 nm Bandwidth	Standard Deviation for Indicated Bandwidth						
		1.5	3.0	4.5	6.0	7.5	9.0	10.5
1	402.38	0.015	0.018	0.020	0.021	0.025	0.029	--
2	431.50	0.013	0.010	--	--	--	--	--
3	440.18	0.021	0.013	0.050	0.028	0.009	0.005	0.007
4	445.61	0.023	0.029	--	--	--	--	--
5	472.73	0.011	0.012	0.032	--	--	--	--
6	478.79	0.015	0.013	0.009	0.009	0.009	0.014	0.017
7	573.46	0.022	0.016	0.014	0.013	0.010	--	--
8	529.67	0.012	0.010	0.010	0.011	0.010	0.011	0.010
9	572.66	0.004	0.010	0.010	0.012	0.014	--	--
10	555.34	0.007	0.004	0.007	0.008	0.008	0.007	0.007
11	623.68	0.058	0.061	--	--	--	--	--
12	629.65	0.210	0.120	0.171	0.133	0.091	--	--
13	684.82	0.019	0.029	0.024	0.017	0.014	0.014	0.012
14	739.91	0.009	0.013	0.011	0.010	0.009	0.009	0.010
15	748.26	0.020	0.016	--	--	--	--	--

if there were no passband effects the fitting should result in a constant value of zero for the correction curve. The maximum departure of the fitted wavelength correction curve from zero is given in Table XIV for each class of passband shape and for each degree of polynomial. It can be seen that the errors become larger as the passbands depart from the symmetric triangles from which Table VI was derived and when more freedom is allowed in the fitting function.

3.2.9 Temperature Effects

Most of the measurements described in this Special Publication were made at an ambient temperature of 25 ± 0.5 C. In order to determine the effect of changes in temperature of the filter upon the wavelength at minimum transmittance, we mounted one of the master filters (Master #3) in a special filter holder in which the temperature of the filter and the surrounding air could be set with an accuracy of ±0.2 C and held constant to within 0.1 C for the duration of an entire set of measurements. Measurements were made at 18.3 C, 25.0 C, and 32.0 C with data taken at 1.5 nm intervals using the high precision measurement sequence described in Section 3.2.3.1. Transmittance values were calculated for seven different symmetrical triangular passbands, and the wavelength at minimum transmittance was determined by fitting a polynomial of degree 6 to 7 transmittance values closest to the wavelength at minimum. The wavelengths at minimum transmittance obtained in each case are reported in Table XV. A repeat of the measurement at 32.0 C showed these data to be repeatable to the point that the last figures appear significant. However, none of the differences due to changes in temperature can be assumed to be significant in view of the uncertainty in locating the wavelength at minimum transmittance as described in Section 3.2.5.

3.2.10 Effects due to Filter Thickness

The three master filters, D-1, D-2, and Master #3, covered the full range of filter thicknesses from 2.84 mm to 3.00 mm. In no case did the wavelength of minimum transmittance differ from filter to filter by more than 0.02 nm and in most cases the difference was less than 0.01 nm. It is probable that the observed differences were due to the uncertainty in locating the minimum by polynomial fitting. Differences in filter thickness produced no observable effect on the wavelength of the inflection points.

3.2.11 Effects due to Polarization of Incident Radiation

No significant differences in the transmittance data from high precision measurements were observed under a 90° rotation of the plane of polarization of the incident light.

3.2.12 Effects due to Changes in the Condition of the Filter Surface.

The transmittance of the didymium filters change slightly in time even in a reasonably controlled environment such as an air conditioned laboratory. This is due to a change in the surface of the filter. For example, over a period of approximately six months after its surfaces were cleaned, one of the master filters was observed to decrease in transmittance by 1% at 400 nm and by 0.2% at 775 nm. After the filter was cleaned, transmittance returned to its original value. This change in transmittance does not affect the use of the filter for wavelength calibrations, since the change in transmittance causes no significant change in the wavelengths of minimum transmittance and is taken into account in the fitting procedure used in connection with the points of inflection (see Section 2.3.3). If the filters are kept free from obvious contamination, they probably will not need cleaning. However, if cleaning becomes necessary, it is recommended that they be wetted with water, cleaned with lens tissue wetted with a solution of mild soap, rinsed with distilled water, rinsed with isopropyl alcohol, and rinsed again with distilled water.

3.3 Uncertainties Introduced by the User

The uncertainties discussed in the preceding section are those introduced in the calibration of the NBS instruments, in the measurements made with them, and in the subsequent data analysis. By identifying these sources of uncertainty and by placing an upper limit on them, it is possible to provide a certification of the values assigned to the filters and to the data supplied in the tables in this special publication. However, if the user is to calibrate the wavelength scale of his instrument, he must also make a number of

Table XIV

Maximum departure of fitted wavelength correction curve from correct (constant at zero) wavelength correction curve for various correction curve fitting functions and passbands.

	Magnitude of Maximum Wavelength Error (nm)		
	Fitting Function		
Passband	Constant	Linear	Quadratic
symmetric triangle bandwidth (nm) (see 3.2.4.1)			
1.5	.0	.01	.08
3	.02	.03	.04
4.5	.01	.01	.02
6	.0	.02	.05
7.5	.02	.04	.06
9	.02	.03	.04
10.5	.01	.04	.07
symmetric trapezoid bandwidth (nm) (see 3.2.4.2)			
4.5	.03	.05	.11
7.5	.01	.02	.06
10.5	.03	.10	.18
13.5	.05	.09	.18
16.5	.03	.03	.14
19.5	.07	.32	.77
asymmetric triangles passband number from Table BIV (see 3.2.4.3)			
1	.09	.16	.27
2	.06	.10	.14
3	.20	.30	.46
4	.20	.34	.40
5	.34	.49	.72
6	.37	.67	.84

Table XV

Measured values for wavelength at minimum transmittance for filter D-1 for three different temperatures.

Band Number	Temperature (Celsius)	BANDPASS 1.5 nm	3.0 nm	4.5 nm	6.0 nm	7.5 nm	9.0 nm	10.5 nm
1	18.3	402.41	401.71	401.51	401.40	401.04	400.34	
	25	402.37	401.67	401.48	401.35	400.98	400.23	
	32	402.39	401.68	401.48	401.35	400.95	400.17	
2	18.3	431.51	432.44					
	25	431.50	432.45					
	32	431.53	432.49					
3	18.3	440.15	440.45	441.50	442.34	442.20	441.87	441.00
	25	440.15	440.38	441.56	442.37	442.22	441.89	441.02
	32	440.20	440.42	441.62	442.40	442.23	441.90	441.04
4	18.3	445.58	445.15					
	25	445.58	445.14					
	32	445.58	445.14					
5	18.3	472.73	472.58	472.91				
	25	472.72	472.58	472.95				
	32	472.74	472.61	472.98				
6	18.3	478.75	479.25	479.21	478.27	477.37	476.52	475.65
	25	478.78	479.25	479.20	478.26	477.35	476.51	475.66
	32	478.80	479.27	479.21	478.26	477.36	476.53	475.68
7	18.3	513.43	513.58	513.85	514.26	515.24		
	25	513.44	513.60	513.88	514.31	515.40		
	32	513.48	513.64	513.93	514.37	515.58		
8	18.3	529.56	530.06	529.95	529.50	529.29	529.14	528.89
	25	529.67	530.12	530.00	529.54	529.32	529.16	528.92
	32	529.64	530.15	530.02	529.56	529.34	529.18	528.94
9	18.3	572.66	573.22	574.16	575.04	576.49		
	25	572.67	573.25	574.19	575.08	576.53		
	32	572.68	573.25	574.20	575.11	576.58		
10	18.3	585.31	585.51	585.74	586.00	585.97	585.33	584.38
	25	585.33	585.55	585.78	586.04	586.01	585.37	584.44
	32	585.35	585.55	585.78	586.04	586.03	585.40	584.48
11	18.3	623.63	624.03					
	25	623.60	624.01					
	32	623.67	624.02					
12	18.3	629.64	629.44	628.51	626.98	627.00		
	25	629.64	629.45	628.58	627.03	627.01		
	32	629.65	629.46	628.57	627.04	627.00		
13	18.3	684.68	684.70	684.72	684.73	684.71	684.66	684.57
	25	684.71	684.73	684.76	684.77	684.75	684.71	684.63
	32	684.71	684.74	684.78	684.80	684.78	684.74	684.66
14	18.3	739.81	739.93	740.21	740.85	741.92	742.88	743.57
	25	739.91	739.98	740.27	740.92	742.01	742.97	743.65
	32	739.99	740.01	740.29	740.95	742.05	743.00	743.68
15	18.3	748.28	748.10					
	25	748.34	748.15					
	32	748.30	748.12					

measurements as described in Section 2 of this special publication, and in so doing he introduces additional uncertainties into the calibration process. Many of these sources of uncertainty have already been discussed in connection with the various measurements or are similar to those for the NBS measurements as described in Section 3.2. In the remainder of this section, the uncertainties introduced in the use of these standard reference filters will be listed and ways to estimate them will be discussed.

3.3.1 Effects of Instrument Sensitivity Function*

If there is a substantial rate of change of the instrument sensitivity function with wavelength, the effect would be to cause the actual passband centroid to be shifted away from the centroid of the geometrical passband. In most instruments, the wavelength setting mechanism is not designed to take this factor into account, and therefore a wavelength calibration error is introduced. However, a calibration made with an SRM filter calibrates the instrument completely with respect to the centroid of passband, including the effects of the instrument sensitivity function. For this reason, one need know nothing about the instrument sensitivity function to obtain a correct calibration at each of the calibration points. If the instrument sensitivity is a smooth function of wavelength as, for example, in the 90° polarization curve in Figure 10 or the sensitivity curve in Figure A2, a smooth curve fitted to these exact calibration points would be a correct calibration curve for the whole instrument. If, on the other hand, the sensitivity curve is not smooth, as, for example, in the 0° polarization curve in Figure 10, a smooth curve through correct calibration points might not be a good representation of the general calibration curve if the calibration points fell on parts of the sensitivity curve which did not represent its general trend. This effect is illustrated in Figure 11 and in the accompanying discussion. If the sensitivity function is unknown, one must assume that the calibration curve derived from the use of the filters is representative. If something is known about the sensitivity curve, an estimate can be made of the amount of shift of the centroid due to the slope of the sensitivity curve. In particular, for a triangular geometrical passband the displacement $d\lambda$ of the passband centroid from the center of the geometrical passband is given by

$$d\lambda = \frac{aw^2}{6} \qquad (13)$$

where a is the slope of the sensitivity curve normalized at the center of the triangle and w is the width at half-height of the geometrical passband. If the slope and the effective triangular bandwidth are both known, equation (13) can be used to provide a very good estimate of the magnitude of the centroid shift due to slope in the sensitivity curve.

3.3.2 Effects of Passband Shape and Width

In the case of the calibrations by points of inflection, the passband shape and width have little effect upon the wavelength calibration which is obtained. The values given in the tables of transmittances and wavelengths for the inflection points were obtained from the average of seven triangular passbands ranging from 1.5 to 10.5 nanometers in width as described in Section 3.2.7. The magnitude of the wavelength error which results from assuming the average value to be correct for a given bandwidth is given in Table XIV for several shapes and widths of passbands. It can be seen that except for the very wide and very asymmetric passbands, the maximum error in the resulting calibration curves is rather small. The effects of passband width and shape on the wavelength of minimum transmittance, on the other hand, is quite large. Errors due to this can be minimized in a case in which the bandpass shape is known by generating transmittance data from the known passband shape and then finding the wavelengths at minimum transmittance corresponding to that transmittance data. This procedure is described in Section 3.2.4.4. Advantage can be taken of the stability of the inflection point data to make use of the minimum transmittance points even when the bandwidth is only approximately known. This is done through the curve fitting procedure symbolized by equation (7) and discussed in Section 2.3.3. In this equation, the only assumption made about the bandwidth is that it is constant. Determining the effective bandwidth (d in equation 7) consumes a portion of the information contained in the measured

*The instrument sensitivity function is sometimes called the responsivity factor.

wavelength of minimum transmittance data, but the net result of fitting in this manner is to improve the calibration curve. This improvement depends, of course, on the extent to which the bandwidth is actually constant.

3.3.3 Uncertainties Connected with Transmittance

An error in measured transmittance can occur for any number of reasons. The instrument which is to have its wavelength scale calibrated may be off calibration on its transmittance scale because of an improper gain setting, an improper zero setting, or a non-linearity in the detection system. Such an error is usually constant with respect to wavelength and will make no difference at all in the wavelength of minimum transmittance. If the constant error is small, the wavelengths determined from the inflection points will only be slightly in error, and this error will be reduced further by the fitting procedure described in Section 2.3.3. This also holds true for wavelength errors which are introduced because the actual transmittance of the filters has changed by a constant amount at all wavelengths. If the transmittance errors are not constant with respect to wavelength, the fitting procedure in Section 2.3.3 will not reduce the error much. Such non-constant wavelength errors can be introduced through stray radiation of another wavelength in the user's instrument or through contamination of the filter, which is usually more effective at the short wavelength end of the spectrum than at the long wavelength end. Additional terms could be put into the fitting expression, equation (7), but this is not recommended. If a non-constant error in transmittance measurements is suspected because of difficulties in obtaining a good fit with expression (7), the filters should be cleaned and the instrument should be checked for stray light.

3.3.4 Other Causes of Systematic Uncertainty

Two other parameters are potentially causes of systematic uncertainties in the measurement. One of them, polarization, either of the incident radiation or in the instrument's detection system, has a negligible effect. The other, temperature, produces no noticeable effect on the wavelength at minimum transmittance. The wavelength and transmittance at the inflection point is measurably affected by changes in temperature, but the effect does not follow a regular pattern. In most cases, the effect of temperature is small, however, with a change in inflection point wavelength of less than 0.1 nm over the temperature range 18 °C to 32 °C.

3.3.5 The Effect of Random Measurement Errors

The most reliable way to determine the effect upon the wavelength calibration of random errors introduced in using the filters is to make several repeated calibrations and to look for differences in the results. Evaluating the random error in each of the measurement parameters and calculating the net effect upon the wavelength calibration would be time consuming and subject to error. However, if the random error in the calibration is found to be too large, the latter procedure is useful for locating the principle causes of random uncertainty.

3.4 Illustrated Summary of Uncertainty Estimations

The systematic uncertainty was experimentally evaluated for the 1.5 nm bandpass data as discussed in Section 3.2. It was also possible to experimentally evaluate the uncertainty for 10 nm triangular bandpass data using the NBS Reference Spectrophotometer for Diffuse Reflectance and Transmittance.[7] This instrument has a 10 nm triangular bandpass defined by the dispersion of the grating and the entrance and exit apertures in the monochromator. The instrument was calibrated by the method discussed below in Section A.3.1 and using 6 atomic lines and also taking account of the instrument sensitivity functions as described in Section A.3.2. The atomic lines used were Hg 435.834 nm, Hg 546.075 nm, He 587.562 nm, He 667.815 nm, Cd 508.582 nm, and Cd 643.847 nm. A linear least squares fit through the data for the 6 atomic lines was corrected by the instrument sensitivity function to obtain a calibration curve.

Then, the instrument was calibrated using the didymium glass filter Master 3. It was found that the corrections obtained from the 6 didymium minima with 10 nm bandpass never differed from the calibration curve by more than 0.25 nm, and the corrections obtained from the points of inflection never differ by more than 0.2 nm from the calibration curve. We list these as indications for the uncertainty at 10 nm bandpass. However, it is possible to use techniques to improve the results obtained from the didymium glass filter as described in the following paragraph.

The results of fitting the additive correction data under three assumptions are shown in Figure 15. In the first case, equation (8) was used with a least squares fitting to obtain the curve shown as a dashed line. A second curve, shown as a dotted line, was obtained by adding an extra term in λ^3 to equation (8). In both of these cases, it was assumed that nothing was known about possible causes of instrument wavelength error. The difference between the two curves was simply in terms of the complexity of the fitting function. Actually, information was available which could be used to produce a better calibration curve. The instrument sensitivity function had been measured, and so it was possible through the use of equation (13) to determine the contribution of this function to the additive correction. This additive correction, shown as the lower alternate dot-dash curve in Figure 15, was subtracted from each piece of experimental additive correction data and the resulting points were fitted with equation (8) with the constraint that c = 0, i.e. a corrected linear fit since gratings have a linear dispersion. The sensitivity function correction was then added back to this line to give the solid curve in Figure 15. This curve is essentially the sensitivity correction curve shifted by 0.45 nm in the positive direction. Although any one of the three calibration curves is reasonable in light of the random noise in the data, the solid curve is to be preferred since it was based on a great deal of additional information. The agreement with the calibration curve obtained from the atomic lines was always within the 0.1 nm.

The uncertainties for bandpasses between 1.5 and 10.5 nm have not been explored by comparisons with atomic lines. Although the authors believe that they are probably not much different from the other uncertainties since the fitted polynomials did not oscillate near the minima, we have not mathematically proven it and to measure each minimum at each bandpass is not economically feasible. It was pointed out to us by an NBS mathematician that spline fitting yields itself to numerical error analysis*, and if further work is done, this avenue will be explored.

4. Making Use of the Calibration Curve

If the additive corrections which are determined in the calibration process turn out to be approximately the same size as or smaller than the uncertainties in the calibration, then it is usually advisable to simply assume the instrument wavelength scale to be accurate enough. If the additive corrections are significant, the proper course of action depends strongly upon the particular instrument being calibrated. One of two approaches is often taken in making wavelength corrections. The first approach is to make physical adjustments on the instrument to correct its wavelength scale reading. After each such adjustment, the filter should be remeasured to determine that the wavelength shift is in the right direction and by the right amount. The second approach is to leave the instrument alone and to simply calculate the correct instrument wavelength scale setting from the correction curve. As can be seen from equation (3) the correct wavelength scale setting λ_s to obtain a desired centroid wavelength λ_c is given by subtracting the additive correction $\delta\lambda$ from λ_c. This procedure is convenient when the wavelength setting is done by hand or under the direct control of a computer. If transmittance measurements are made at regular wavelength intervals and the transmittance is a slowly varying function of wavelength, the additive correction can be used to calculate the transmittance value τ_n at the nth correct wavelength value from the measured transmittance values by means of linear interpolation:

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*Dr. Walter Liggett, Private Communication

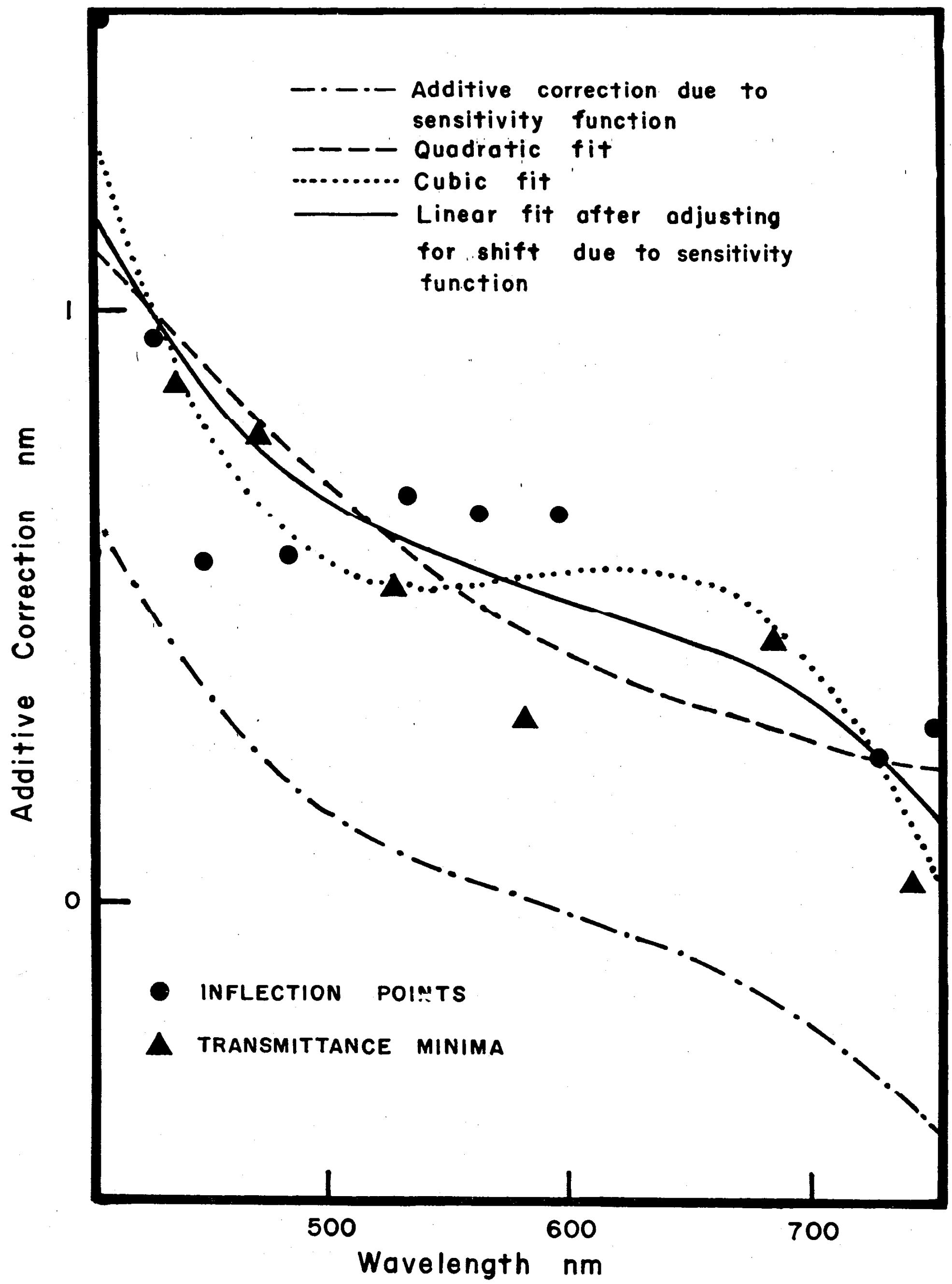

Figure 15: Wavelength Calibration of NBS Reference Spectrophotometer for Diffuse Transmittance and Reflectance.

$$\tau_n = \tau'_n - \delta\lambda(\lambda'_{n+1} - \tau'_{n-1})/(\lambda_{n+1} - \lambda_{n-1}) \quad (14)$$

where λ_i is the wavelength scale value at which measurement number i in the series was made and τ'_i is the corresponding measured value of the transmittance.

APPENDIX A

Background and Terminology

A.1 Introduction

In the main body of this Special Publication, the way in which the didymium glass SRM filters are to be used to calibrate the wavelength scale of a spectrophotometer is described in detail. Although a satisfactory calibration can usually be obtained by simply following the procedure as described, a more complete understanding of the problem of wavelength calibrations will enable one to make better use of the information which can be obtained from the filters. For this reason, a more detailed discussion of principles underlying wavelength calibration is presented in this appendix and, where possible, these principles are also illustrated with data from the General Electric Recording Spectrophotometer which was used to illustrate the main text.

A.2 Spectral Transmittance

Since the filters are used by making measurements of their spectral transmittance this quantity should first be carefully discussed. In principle, the spectral transmittance $\tau(\lambda)$ at a given wavelength λ incident on the filter which is transmitted by it. If one were to experimentally measure this quantity using very nearly monochromatic radiation such as that from a laser, one would find that the measured spectral transmittance curve is shaped by interference effects arising from reflections from the filter's surfaces as well as from absorption of radiation by the rare earths within the glass. Since the interference effects can depend strongly upon the way the instrument projects the radiation upon the filter and can also depend strongly upon the minute details of the thickness and surface shape of the filter, spectral transmittance so defined would not be a satisfactory quantity upon which to base wavelength calibrations. Instead, we will first define measured spectral transmittance $\tau(\lambda)$ as the fraction of radiation from a band of radiation centered at λ which is transmitted by the filter, where the band of radiation is sufficiently broad that interference effects are averaged out. The spectral transmittance $\tau(\lambda)$ can then be defined as the extrapolation to zero bandwidth of measured transmittances made with narrower and narrower bandwidths. Under this definition, the dominating property shaping the spectral transmittance curve would be the absorption of the radiation in the rare earth oxide in the glass, and it could be correctly considered to be a property of the glass. In calibrating an instrument, one would like to adjust the instrument so that over a large variety of randomly selected measurements the rms deviation between measured spectral transmittance and spectral transmittance would be minimized. Once this is done, one would also like to know to what other instruments a particular instrument is equivalent, that is to say, what other instruments would consistently give the same differences between the measured spectral transmittance and the spectral transmittance. Both of these aspects of calibration will be considered here.

A.3 The Spectral Passband* (Function) of Wavelength

The instruments with which these SRM filters are intended to be used made measurements using a mixture radiation from a finite range of wavelengths. We define a function $B(\lambda_s,\lambda)$, which we will call the spectral passband (function), to describe, as a function of wavelength λ, the way the mixture of radiation is effectively used when the instrument measures transmittance with its wavelength scale set at λ_s. It is convenient to think of the passband as being made up of the product of two functions $S(\lambda)$ and $G(\lambda_s,\lambda)$ which represent two measurable aspects of the passband.

$$B(\lambda_s,\lambda) = G(\lambda_s,\lambda)\, S(\lambda) \qquad \text{(A1)}$$

The function $S(\lambda)$, which we will call the instrument sensitivity, indicates the relative efficiency of the measurement with respect to wavelength and results from the combined

*Not to be confused with the bandwidth $\Delta\lambda = \lambda_2 - \lambda_1$ (of the passband).

relative wavelength dependency of the light emitted from the source, of the amount of light absorbed or scattered as it passes through the monochromator along a path for which it is expected to be transmitted, and of the sensitivity of the detector. The function $G(\lambda_s,\lambda)$, which we will call the geometrical passband, describes the way in which, by specific dispersion or absorption, the monochromator limits the radiation it passes to a small range around λ_s. It is interesting to note that $B(\lambda_s,\lambda)$ can be very precisely defined in terms of its rôle in relating measured spectral transmittance to actual spectral transmittance, but it is nearly impossible to measure directly. However, $S(\lambda)$ and $G(\lambda_s,\lambda)$, which are not very precisely defined, can be measured rather directly in a way in which their product will provide a representation of $B(\lambda_s,\lambda)$ which is sufficiently good for the purposes of wavelength calibration. Therefore, before we show how $B(\lambda_s,\lambda)$ is involved in describing the measured transmittance, we will show how $S(\lambda)$ and $G(\lambda_s,\lambda)$ can be experimentally determined.

A.3.1 Determining the Geometrical Passband Experimentally

This experimental method of determining the geometrical passband is based on the assumption that the geometrical passband does not change its shape very rapidly with changing λ_s, so that, over a range of λ_s equal in magnitude to the range over which $B(\lambda_s,\lambda)$ is non-zero for a fixed λ_s, the curve $G(\lambda_s,\lambda)$ can be regarded as shifting its position along the wavelength axis without changing shape. In mathematical terms this can be represented as

$$G(\lambda_1,\lambda_1+\Delta\lambda) = G(\lambda_1-\Delta\lambda,\lambda_1) \tag{A2}$$

where λ_1 is a specific wavelength and $\Delta\lambda$ represents a specific displacement in wavelength. To make use of this result to determine $G(\lambda_s,\lambda)$ experimentally, the usual light source is removed from the monochromator and replaced by a stable source of monochromatic radiation such as low pressure gaseous discharge lamp. Under these conditions, the instrument sensitivity is held constant and when the wavelength scale is scanned with no sample in the instrument, the instrument produces a signal which is proportional to $G(\lambda_s,\lambda)$ for fixed λ. As an illustration, the results are shown in Figure A1a for a measurement made with the General Electric Spectrophotometer using the mercury line at 435.8 nm. Equation (A2) above can be used to produce the curve of $G(\lambda_s,\lambda)$ for fixed λ_s shown in Figure A1b. Note that the correct wavelength scale on the instrument and true physical wavelength can be tied together at the wavelength of the line source, since at this point both should have the same numerical value. It might be pointed out that for this determination, a different detector than the one in the instrument can be used if it is more convenient, since all the measurements are made with radiation at one wavelength. However, care should be taken that the line source and the substitute detector, if one is used, bear the same geometrical relationships to the monochromator as the operating source and detector. For example, the radiation from the line source should fill the monochromator entrance optics in the same way as the operating source. Otherwise a change in $G(\lambda_s,\lambda)$ from that for ordinary use may be caused by the change in geometry.

A.3.2 Determining the Instrument Sensitivity Experimentally

To determine $S(\lambda)$ experimentally, one can observe the detector output as the instrument is scanned over its full wavelength range using its normal source and detector and with no sample in the measuring position. The detector output must be measured in such a way that a linear relationship between the detector output and the amount of radiation striking it at a given wavelength is obtained. In a dual beam spectrophotometer such as the General Electric instrument it is generally not possible to use the instrument output scale for obtaining the detector output, since what is usually shown on the output scale of such an instrument is a number proportional to the ratio of the signals from the two beams rather than the signals themselves. For this determination, we stopped the chopping mechanism at the point where a maximum amount of radiation was in the sample beam, disconnected the detector from the instrument electronics, and read the detector current directly with a picoameter. The resulting plot of detector current as a function of wavelength scale reading λ_s is shown in Figure A2a.

To establish the relationship between this function and $S(\lambda)$, one must take into account the particular monochromator which is being used. In the case of the General

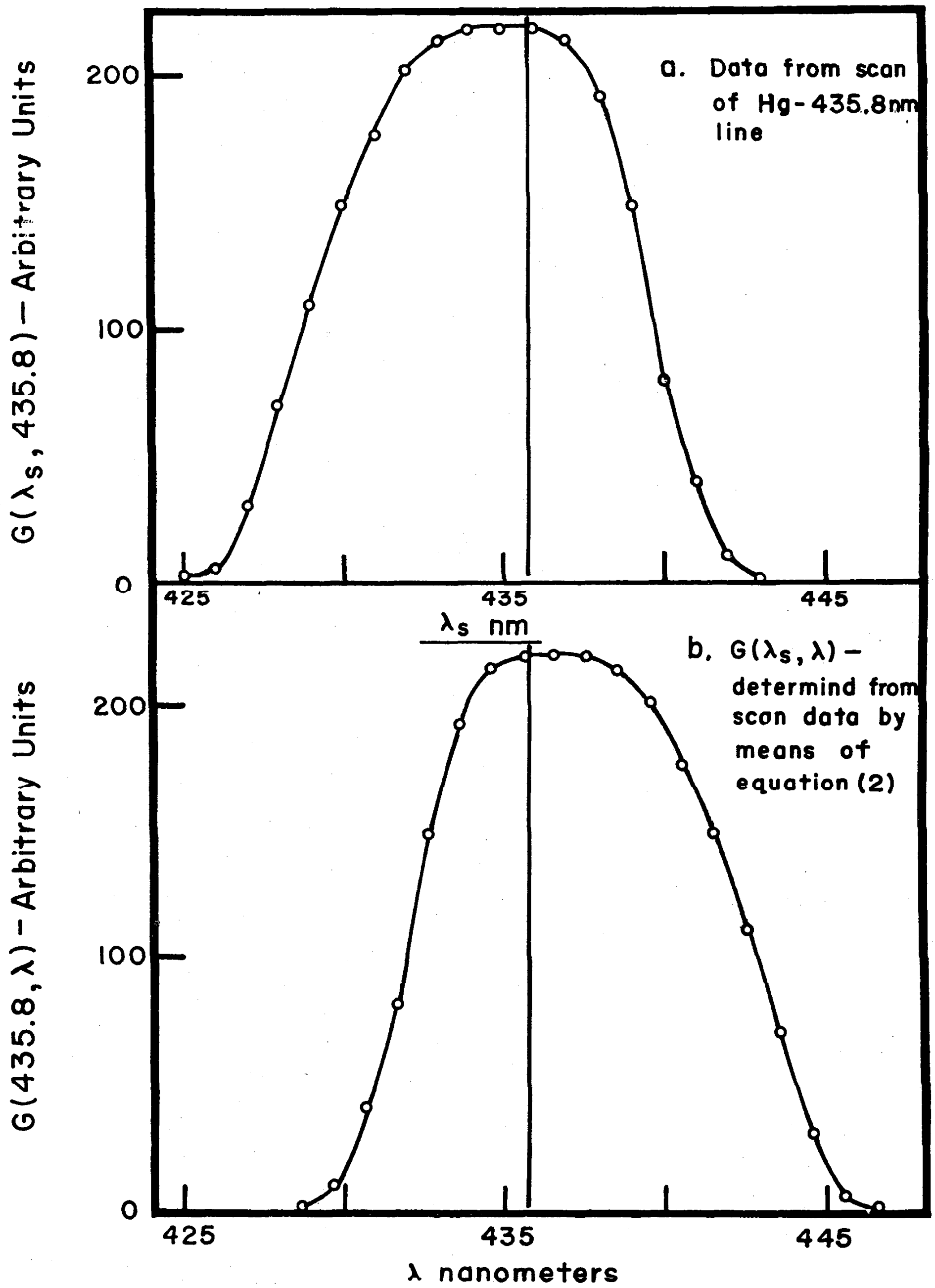

Figure A1: Experimental evaluation of $G(\lambda_s,\lambda)$ near λ_s = 435 nm

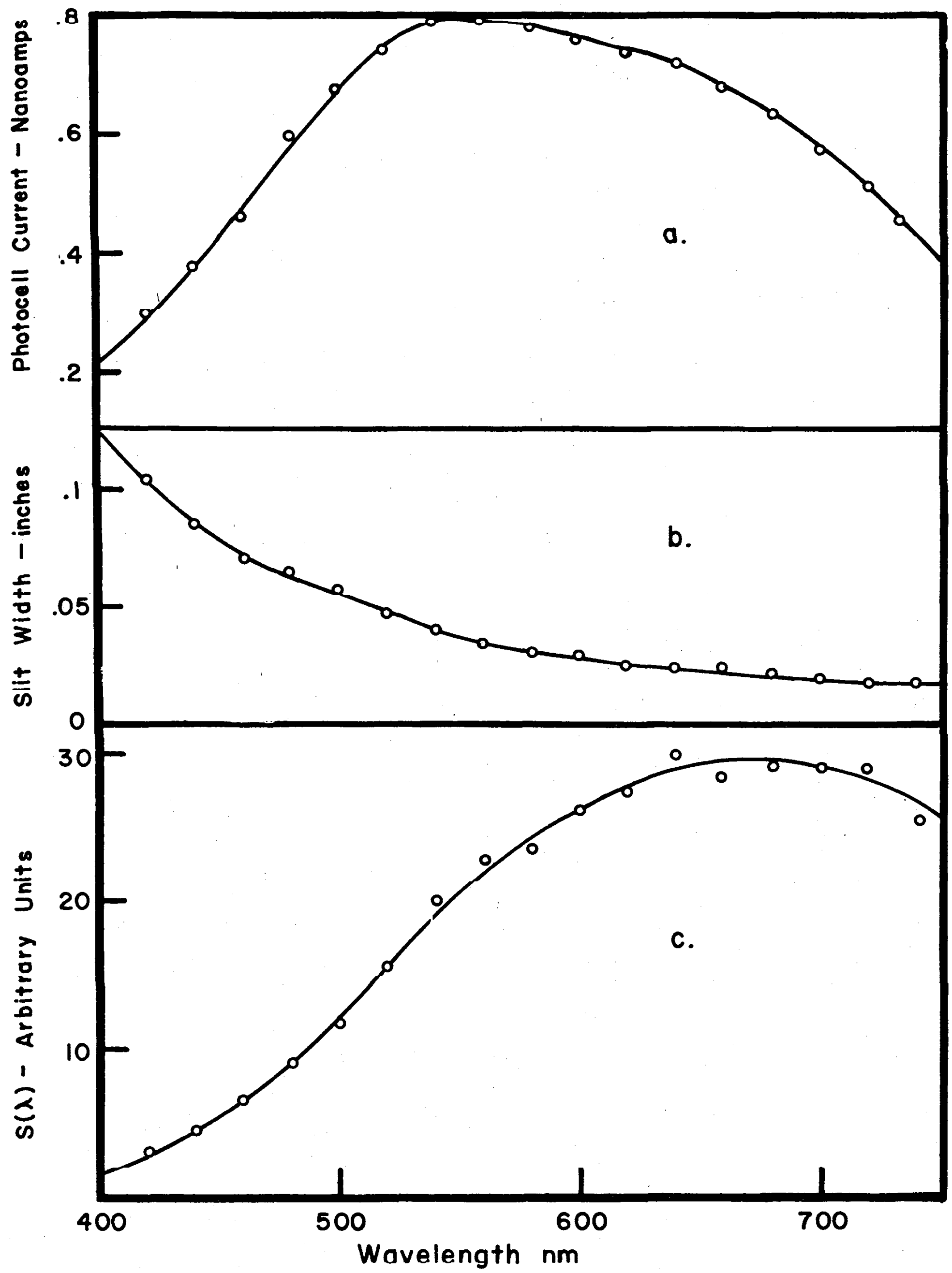

Figure A2: Experimental Evaluation of S(λ)

Electric instrument, the monochromator uses prisms for the dispersive elements and has the widths of the entrance and exit slits automatically adjusted in constant proportion to each other by means of cams to maintain a $G(\lambda_s,\lambda)$ nearly constant both in width and shape. Under these circumstances, the detector signal at λ_s is proportional to the product $S(\lambda)$ times the slit width at that wavelength scale setting. That is to say, if $S(\lambda)$ were constant, one would expect the function shown in Figure A2a to be proportional to the slit width. Therefore, if the function in Figure A2a is divided by the instrument slit width at each wavelength, shown in Figure A2b, the resulting function will be the approximation to $S(\lambda)$ shown in Figure A2c. This approximation of $S(\lambda)$ is crude both because of the noise and lack of resolution of the data in Figure A2a and because of the approximations used in deriving the relationship between the data and $S(\lambda)$. However, the influence of the $S(\lambda)$ curve on the wavelength calibration is small and thus the uncertainties in wavelength calibration induced by the uncertainties in $S(\lambda)$ will be very small.

A.3.3 Calculation of the Spectral Passband (Function) from Experimental Data

With experimental functions proportional to $G(\lambda_s,\lambda)$ and $S(\lambda)$ available, a function proportional to $B(\lambda_s,\lambda)$ can be constructed by multiplying $G(\lambda_s,\lambda)$ by $S(\lambda)$ at each wavelength λ. In Figure A3, a section of the $S(\lambda)$ curve in the region of 435.8 nm is shown normalized to 1 at 435.8 nm, the passband $B(\lambda_s,\lambda)$ obtained by multiplying this portion of the $S(\lambda)$ curve by the $G(\lambda_s,\lambda)$ curve shown in Figure A1b. The $G(\lambda_s,\lambda)$ curve is shown in the same figure to show how the shape of the geometrical passband is modified by the sensitivity function to produce the passband. In the course of this determination of the passband, the results of all measurements have been placed on an arbitrary scale and no effort has been made to define or determine an associated constant of proportionality.

The reason for this is that the constant of proportionality cancels in the expression for measured transmittance. The aspect of the passband in which we are most interested from the wavelength calibration standpoint is the shape of the passband as a function of wavelength at each setting of the instrument wavelength λ_s.

A.4 Wavelength Calibration

In general terms a wavelength calibration is an effort to relate the wavelength scale on an instrument to a wavelength representative of the passband. There are any number of possible choices for the wavelength to represent the passband. One common choice of a representative wavelength, for example, is the wavelength at which the geometric passband reaches its peak value. This choice is not unreasonable, and this wavelength can be readily determined for a number of points λ_s on the wavelength scale with the aid of line sources by the method described in Section A.3.1. However, the analysis of the way the instrument is used to measure transmittance which is to be presented in this section reveals that the wavelength of the centroid of the passband is a better representative point. In this Special Publication, therefore, a wavelength calibration is by definition the relationship between an instrument wavelength scale reading and the wavelength of the corresponding passband centroid. Since an understanding of the reasoning behind this definition is fundamental both to the understanding of the meaning of a transmittance measurement as well as to the use of these SRM filters, we will give a brief discussion of the nature of transmittance measurements and the reason for choosing the centroid wavelength as the wavelength to represent the passband.

A.4.1 Measuring Spectral Transmittance

The goal of a transmittance measurement is to determine the spectral transmittance $\tau(\lambda)$ of an object as described in Section A.1. For the preponderance of practical applications, however, it is not advisable to measure spectral transmittance using highly monochromatic radiation. The interference effects which pose a problem in interpreting the measurements have already been discussed in A.1. In a wide variety of applications such as measuring color, luminous transmittance, or effective radiant energy transfer for solar energy applications, for example, one is interested in integrated effects over a large range of wavelengths. In order to be assured that the entire wavelength range is covered with no gaps, the wavelengths at which measurements are made should be spaced closely enough so that the passbands overlap at the half-height points. In this way, the entire spectral transmittance curve receives nearly equal weighting when the integrals are taken. In order to produce this kind of uniform coverage with nearly monochromatic radiation, much more data would have to be taken than can usually be justified from the detailed shape of the spectral transmittance curve, and, because of the lower total amount of radiation involved in each measurement at narrow bands, the corresponding noise level of each measured transmittance would be higher.

Even though the spectral transmittance measurements may not be done with monochromatic radiation, it is convenient to represent the limiting ratio in terms of an imaginary interference-free measurement done with monochromatic radiation in which the radiation incident on the detector without a filter in place produces a signal $I_o(\lambda)$ and the same radiation passing through the filter produces a signal $I_t(\lambda)$. For such an idealized experiment, the spectral transmittance $\tau(\lambda)$ would be the ratio of the two signals

$$\tau(\lambda) = I_t(\lambda)/I_o(\lambda) \tag{A3}$$

(It should be mentioned that here as in the other portions of this special publication, we have deliberately avoided discussing the geometrical parameters of the measurement. These are, of course, important to an accurate measurement, but it will be assumed that they are properly handled and we will concentrate on the wavelength-related aspects of the measurement.)

We can now relate the measured spectral transmittance $\tau_m(\lambda)$ for a given instrument to the actual spectral transmittance $\tau(\lambda)$ through the use of an equation similar to (A3) above. In this case, however, the signals are proportional to integrals related to the passband.

$$I_o(\lambda_s) = k\int B(\lambda_s,\lambda)d\lambda \tag{A4}$$

and

$$I_t(\lambda_s) = k\int B(\lambda_s,\lambda)\tau(\lambda)d\lambda \tag{A5}$$

where the constant of proportionality k is the same in both expressions and the integrals are taken over the entire range for which $B(\lambda_s,\lambda)$ is non-zero. The measured transmittance is, therefore

$$\tau_m(\lambda_s) = \frac{\int B(\lambda_s,\lambda)\tau(\lambda)d\lambda}{\int B(\lambda_s,\lambda)d\lambda} \tag{A6}$$

Notice that the constant of proportionality cancels in this definition so that it is not important to determine it or to normalize the expression for $B(\lambda_s,\lambda)$ for the purposes of this discussion. The measured transmittance is seen to be a weighted average of the idealized spectral transmittance in which the instrument's passband is the weighting function. In addition to being a definition of measured transmittance, equation (A6) forms the basis for a very exact definition of the passband of a given instrument. By definition the passband $B(\lambda_s,\lambda)$ is the weighting function which correctly related the measured spectral transmittance to the actual spectral transmittance for all arbitrarily chosen $\tau(\lambda)$.

A.4.2 The Passband Centroid Wavelength

We have chosen to represent the wavelength of the passband by its centroid wavelength or first moment wavelength, as it is sometimes called. The centroid wavelength $\lambda_c(\lambda_s)$ of the passband, when the wavelength scale is set at λ_s, can be defined in terms of the passband function as:

$$\lambda_c(\lambda_s) = \frac{\int B(\lambda_s,\lambda)\lambda d\lambda}{\int B(\lambda_s,\lambda)d\lambda} \tag{A7}$$

Since the passband represents the effective contribution of radiation at wavelength λ to the transmittance measurement, the centroid wavelength can in a very real sense be thought of as the wavelength of the effective center of the passband. As an example of how the centroid can be located from data obtained from a real instrument, consider the passband illustrated in Figure A3. The values of B(435.8,λ) can be read from the curve at uniform intervals and the integrals in equation (A7) approximated by the appropriate sums. The results of such a calculation made with intervals of 1 nm are summarized in Table AI. In that calculation, the centroid wavelength was found to be at approximately 437.5 nm, which is 1.7 nm greater than the 435.8 nm indicated by the wavelength scale. Therefore, in this region of the spectrum, we must add 1.7 nm to the wavelength indicated by the instrument scale in reporting the wavelength of spectral transmittance data measured with the General Electric Spectrophotometer. A similar calibration was made for each of three other line sources, with the results shown in Table AII. Notice that we have calibrated the instrument directly from the measurements reported in Section A.2 and did not need to use the SRM filters at all. However, a similar calibration can be obtained from transmittance measurements on the SRM filters without the inconvenience of having to switch sources in the instrument and make special measurements of the detector output. It is their convenience which makes the SRM wavelength filters a valuable tool for calibrating the wavelength scale.

A.4.2.1 Centroid Shift due to Instrument Sensitivity

Quite often it is the case that the sensitivity function does not change greatly over the region for which the geometrical passband is not zero, and therefore, the shape of the passband resembles the shape of the geometrical passband. This is true, for example in the illustration in Figure A3. In this case, a computational tool can be developed which is useful in locating the centroid wavelength when the centroid of the geometrical passband is known, as it would be, for example in the case of a symmetric triangular passband. If the instrument function is sufficiently smooth to be well represented by a straight line in the region of the passband, then the sensitivity factor, normalized at the centroid of the geometrical passband can be represented as:

$$S = 1 + a(\lambda-\lambda_g) \tag{A7a}$$

where a is the slope of the curve so normalized and λ_g is the centroid wavelength of the geometrical passband. The centroid wavelength corresponding to the passband is obtained by using equations (A1) and (A7a) in (A7) to obtain an expression for the centroid wavelength

$$\lambda_c(\lambda_s) = \frac{\int G(\lambda_s,\lambda)[1+a(\lambda-\lambda_g)]\lambda d\lambda}{\int G(\lambda_s,\lambda)[1+a(\lambda-\lambda_g)]\lambda d\lambda} \tag{A7b}$$

By making use of the fact that $\int G(\lambda_s,\lambda)\cdot[\lambda-\lambda_g]d\lambda$ is zero by definition of the centroid wavelength λ_g of the geometrical passband, one can reduce expression (A7b) to the following form:

$$\lambda_c(\lambda_s) = \lambda_g(\lambda_s) + a\int G(\lambda_s,\lambda)(\lambda-\lambda_g)^2 d\lambda / \int G(\lambda_s,\lambda)d\lambda \tag{A7c}$$

In words, this expression says that the centroid wavelength of the passband (function) is the centroid wavelength of the geometrical passband plus the product of the slope of the normalized instrument sensitivity with the second moment of the geometrical passband taken about its own centroid. For a symmetric triangular geometric passband, the second moment about its centroid, which is the center in this case, is $W^2/6$ as is indicated in equation (15) in the main text. Therefore for example, if one knows that he has a triangular geometrical passband with a bandwidth of W nm and knows from experimental measurement of the instrument sensitivity function that the slope of the normalized instrument sensitivity function is a per nm, he knows that the centroid of the passband lies a $W^2/6$ from the peak of the geometrical passband as might be determined from scanning line sources. This can sometimes be a useful calculation shortcut.

A.4.3 The Significance of the Passband Centroid Wavelength

The main objective in calibrating the instrument wavelength scale would be to minimize the difference between $\tau_m(\lambda_s)$ and $\tau(\lambda)$ to the greatest possible extent commensurate with a given passband. A second and related objective would be to minimize the difference between

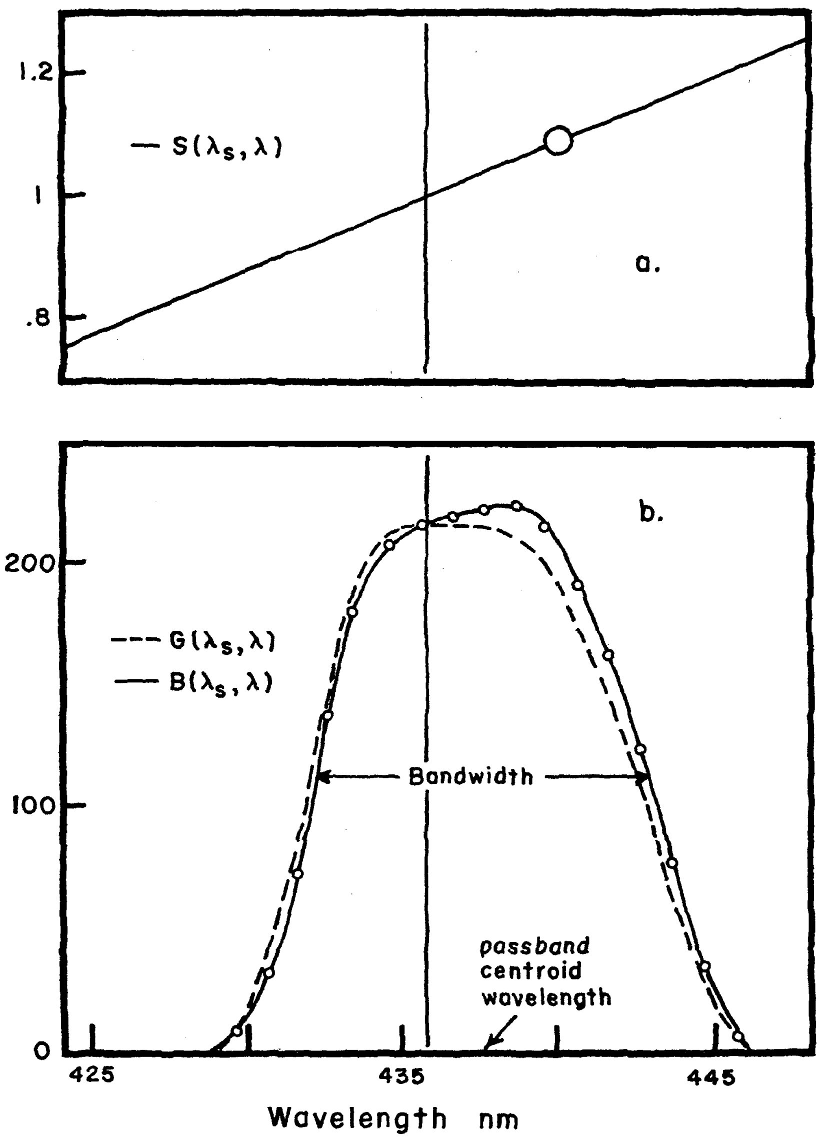

Figure A3: Passband as determined experimentally for λ_s = 435.8 nm

Table AI

Calculation of Centroid Wavelength $\lambda_c(\lambda_s)$

$\lambda_s = 435.8$

Wavelength λ	Passband $B(435.8,\lambda)$	Product $B(435.8,\lambda)\cdot\lambda$
446.6	1.7	737
445.6	3.5	1570
444.6	34.1	15145
443.6	77	34173
442.6	123.7	54759
441.6	163	71971
440.6	191.1	84202
439.6	215.5	94729
438.6	224.2	98314
437.6	222.5	97378
436.6	219	95631
435.6	214.7	93513
434.6	208.4	90570
433.6	181.5	78688
432.6	137.1	59312
431.6	71.7	30964
430.6	34	14639
429.6	7.5	3237
Sums	2330.2	1019525

$$\lambda_c(435.8) = \frac{\int B(435.8,\lambda)\cdot\lambda\cdot d\lambda}{\int B(435.8,\lambda)d\lambda} \simeq \frac{1019525}{2330.2}$$

$\lambda_c(435.8) = 437.5$

Table AII

Additive Wavelength Corrections and Effective Bandwidths Determined for the General Electric Recording Spectrophotometer from Line Source Data

Lamp Gas	Line Wavelength (nm)	Additive Correction (nm)	Effective Bandwidth (nm)	Equivalent Triangular Bandwidth*(nm)
Hg	435.8	1.7	3.4	8.4
Hg	546.1	.7	3.4	8.4
He	587.6	.9	3.2	7.8
Cd	643.8	.7	3.5	8.6

*Half-height bandwidth of triangular bandpass which has the same effective bandwidth as is given in the preceding column.

the $\tau_m(\lambda_s)$ measured by two instruments having approximately the same passband. A wavelength calibration in which the reported value of the instrument wavelength scale is corrected so that it is given in terms of the passband centroid wavelength is correct to the greatest extent possible for measurements made on arbitrarily selected samples, i.e.for arbitrary $\tau(\lambda)$. This can be demonstrated by considering the instrument to be set at wavelength λ_s and expressing $\tau(\lambda)$ in terms of the centroid wavelength $\lambda_c(\lambda_s)$. This can be shown by expressing the spectral transmittance on a new scale as $\tau(L)$ where

$$L = \lambda - \lambda_c(\lambda_s) \tag{A8}$$

The transmittance can be expressed as a power series in the new wavelength, generated by Taylor's series expansion or by some other means, as

$$\tau(L) = \tau_0 + \tau_1 L + \tau_2 L^2 + \tau_3 L^3 + \ldots (9)$$

which can be expressed in summation notation as

$$\tau(L) = \sum_{i=0}^{\infty} \tau_i \cdot L^i \tag{A9}$$

For the well-behaved spectral transmittance functions usually encountered with real materials, the magnitude of the coefficients τ_i will decrease rather rapidly for increasing i. If equation (A6) is rewritten using the new wavelength scale and the expansion for the spectral transmittance given in equation (A9), the measured transmittance can be shown to be

$$\tau_m(\lambda_s) = \tau_0 + \sum_{i=2}^{\infty} \tau_i \frac{\int B(\lambda_s, L) L^i dL}{\int B(\lambda_s, L) dL} \tag{A10}$$

The term for i = 0 is just τ_0, which from equation (A9) can be seen to be the spectral transmittance for L = 0, that is, the spectral transmittance at the passband centroid wavelength. The term for i = 1 is identically zero because the multiplier of τ_1 defines the centroid wavelength, which on the L scale is zero by definition, i.e. L = 0 when $\lambda = \lambda_c(\lambda_s)$ according to equation (A8). The magnitude and sign of the sum of the remaining terms in equation (A10) depends upon the functional form of the particular spectral transmittance function $\tau(\lambda)$ which is being considered. The important things which can be seen from this expansion at this point in the discussion are that if the wavelength scale is calibrated with respect to the passband centroid wavelength, the dominant term in the measured transmittance is the spectral transmittance at the scale wavelength, and there will be no error introduced by the slope of the spectral transmittance curve. Put in other words, to the extent that the portion of the spectral transmittance function falling within the passband is a straight line, any instrument with its wavelength scale calibrated to its passband centroid wavelength will measure the correct spectral transmittance. By placing other restrictions on the instrument with regard to its bandwidth and passband shape, it is possible to further control the magnitude of the summation of terms at the right side of equation (A10) and obtain better instrument-to-instrument agreement.

It should be pointed out that if the passband is symmetric around its centroid its central peak value (if it has one) will fall at the centroid wavelength. In this case, calibration to the peak wavelength and calibration to the centroid wavelength would be identical and equation (A10) would apply in both cases. However, if the peak wavelength is not at the centroid, calibration to the peak wavelength will result in contribution to the measured transmittance at each point at which the slope of the spectral transmittance curve is not zero.

The results of this section could be summarized from the point of view of the series expansion of the transmittance in terms of increasingly complex spectral transmittance functions as follows:

1) if the spectral transmittance is constant in a given region, any wavelength calibration

can be used,

2) if the spectral transmittance is linear in a given region, calibration with respect to the centroid wavelength will produce an exact measurement of the spectral transmittance and therefore will produce inter-instrument agreement, and

3) if the transmittance function is more complex than linear, there will be certain passband-related differences between the spectral transmittance and the measured spectral transmittance which cannot be resolved by wavelength calibration.

For further improvement in inter-instrument agreement beyond that which can be achieved by wavelength calibration, the shape and width of the passband must be taken into account. This aspect of the measurement will be discussed briefly in the remainder of this appendix.

A.5 Characterizing the Passband

For any instrument, the passband is completely characterized by the function $B(\lambda_s,\lambda)$ introduced in Section A.3. However, it would be more convenient if there were one number which could be used to characterize the passband which would relate significantly to the measurement of spectral transmittance in such a way as to promote inter-instrument agreement. The concept of bandwidth, and especially of effective bandwidth, provides such a characterizing parameter.

A.5.1 Bandwidth

In an instrument for spectral measurements, the passband will usually be non-zero over only a limited range of wavelengths. It is convenient to have a concise way to describe just how large this non-zero range is, and therefore the concept of "half-height bandwidth" or, for simplicity, "bandwidth" is customarily introduced. This is defined as the difference between the shortest wavelength at which $B(\lambda_s,\lambda)$ is at half its maximum value and the longest wavelength at which $B(\lambda_s,\lambda)$ is at half its maximum value. In the case of the passband illustrated in Figure A3, the passband is half its maximum value at 432 nm and at 443 nm. Therefore, the bandwidth in this case is defined to be 11 nm. It is this bandwidth which should govern the spacing of data points in a set of measurements in which one is planning to perform an integration and therefore wants a nearly uniform weighting of the spectral transmittance over the entire spectrum.

A.5.2 Effective Bandwidth

Another concept of bandwidth can be introduced which is more significant than half-height bandwidth in terms of inter-instrument agreement for spectral transmittance measurements. This bandwidth, which will be called "effective bandwidth", is defined as the square root of the second moment of the passband with respect to wavelength taken about the centroid wavelength, i.e.

$$W_{eq} = M_2 \tag{A11}$$

where

$$M_2 = \frac{B(\lambda_s,L)L^2dL}{B(\lambda_s,L)dL} \tag{A12}$$

The symbols in equation (A12) are defined in the discussion connected with equation (A10), and it is from equation (A10) that the significance of the effective bandwidth can be seen. This is the instrument-dependent portion of the first, and usually the largest, of the terms which are summed to obtain the departure of the measured transmittance from the idealized spectral transmittance. As a matter of fact, in a very large number of practical cases in which the transmittance is not an extremely rapidly varying function of wavelength, this term completely dominates the summation. Therefore, two instruments which have the same effective bandwidth and which are properly calibrated for wavelength with respect to the centroid wavelength will produce measured spectral transmittance values which are in agreement. Thus, the first, and generally the only, additional step which needs to be taken in principle to assure inter-instrument agreement is to require that all instruments in a given group have the same effective bandwidth. In Table AII, the effective bandwidth of the General Electric Spectrophotometer was calculated for each of the four spectral lines for which passband data were obtained as described in Section A.3. In the final column of the table is given the half-height bandwidth of a triangular passband which would have the same effective bandwidth. It can be seen that these data confirm the results of Section 2.3.3 in which it was found that the best wavelength calibration curve fit for the General Electric Spectrophotometer was obtained from the triangular bandpass data by using the data for 8.4 nm half-height bandwidth.

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