Designation: E958 – 13

Standard Practice for Estimation of the Spectral Bandwidth of Ultraviolet-Visible Spectrophotometers[1]

This standard is issued under the fixed designation E958; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice describes procedures for estimating the spectral bandwidth of a spectrophotometer in the wavelength region of 185 to 820 nm.

1.2 These practices are applicable to all modern spectrophotometer designs utilizing computer control and data handling. This includes conventional optical designs, where the sample is irradiated by monochromatic light, and 'reverse' optic designs coupled to photodiode arrays, where the light is separated by a polychromator after passing through the sample. For spectrophotometers that utilize servo-operated slits and maintain a constant period and a constant signal-to-noise ratio as the wavelength is automatically scanned, and/or utilize fixed slits and maintain a constant servo loop gain by automatically varying gain or dynode voltage, refer to the procedure described in Annex A1. This procedure is identical to that described in earlier versions of this practice.

1.3 This practice does not cover the measurement of limiting spectral bandwidth, defined as the minimum spectral bandwidth achievable under optimum experimental conditions.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Terminology

2.1 *Definitions:*

2.1.1 *spectral bandwidth, n*—the wavelength interval of radiation leaving the exit slit of a monochromator measured at half the peak detected radiant power.

3. Summary of Practice

3.1 The following test procedures are written for all spectrophotometer designs that have provision for recording (that is, collecting and storing) spectral data digitally. Processing may be by built-in programs or in a separate computer. Data may be collected in either the transmittance or the absorbance mode, although for the Liquid Ratio procedure, the peak and trough values must be measured in absorbance.

3.2 *Line Emission Source Procedure*—The continuum source is replaced with a line emission source, such as a mercury lamp, and the apparent half-intensity bandwidth of an emission line occurring in the wavelength region of interest is measured using the slit width, or indicated spectral bandwidth required to be estimated. This procedure can be used for instrumentation having spectral bandwidths in the range 0.1 to 10 nm.

NOTE 1—In photodiode array instrumentation, the array spacing between the diode elements may invalidate this procedure.

3.3 *Liquid Ratio Procedure*—The calculated spectral peak to trough ratio of a defined small percentage of toluene in hexane will vary with the spectral bandwidth of the spectrophotometer when scanned in the UV region. This procedure can be used for all instrumentation having spectral bandwidths in the range 0.5 to 3.0 nm.

3.4 *Benzene Vapor Procedure*—The characteristics of a spectrum of benzene vapor in the UV region will vary significantly with the spectral bandwidth of the spectrophotometer. This procedure can be used for instrumentation having spectral bandwidths in the range 0.1 to 0.5 nm.

4. Significance and Use

4.1 These practices should be used by a person who develops an analytical method to ensure that the spectral bandwidths cited in the practice are actually the ones used.

NOTE 2—The method developer should establish the spectral bandwidths that can be used to obtain satisfactory results.

4.2 These practices should be used to determine whether a spectral bandwidth specified in a method can be realized with a given spectrophotometer and thus whether the instrument is suitable for use in this application. If accurate absorbance

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.01 on Ultra-Violet, Visible, and Luminescence Spectroscopy.

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measurements are to be made on compounds with sharp absorption bands (natural half band widths of less than 15 nm) the spectral bandwidth of the spectrometer used should be better than 1/8th of the natural half band width of the compound's absorption.

4.3 These practices allow the user of a spectrophotometer to estimate the actual spectral bandwidth of the instrument under a given set of conditions and to compare the result to the spectral bandwidth calculated from data given in the manufacturer's literature or indicated by the instrument.

5. Test Materials and Apparatus

5.1 *Line Emission Source Procedure:*

5.1.1 Table 1 lists reference emission lines that may be used for measuring the spectral bandwidth of ultraviolet/visible instruments at the levels of resolution encountered in most commercial instruments. All of the lines listed have widths less than 0.02 nm, suitable for measuring spectral bandwidths of greater than 0.2 nm.

TABLE 1 Emission Lines Useful for Measuring Spectral Bandwidth

Reference Line, nm	Emitter
194.16	Hg
205.29	Hg
237.83	Hg
226.22	Hg
253.65	Hg
275.28	Hg
289.36	Hg
296.73	Hg
312.57	Hg
318.77	He
334.15	Hg
314.79	Ne
359.35	Ne
365.02	Hg
388.87	He
404.66	Hg
427.40	Kr
435.83	Hg
447.15	He
471.31	He
486.00	D_2
486.13	H_2
501.57	He
541.92	Xe
546.08	Hg
557.03	Kr
576.96	Hg
579.07	Hg
587.56	He
603.00	Ne
614.31	Ne
626.65	Ne
640.23	Ne
656.10	D_2
656.28	H_2
667.82	He
692.95	Ne
703.24	Ne
724.52	Ne
743.89	Ne
750.39	Hg
785.48	Kr
811.53	Ar
819.01	Kr

5.1.2 The second column in Table 1 lists the emitter gas of various sources. Only sources operating at low pressure should be used, as line broadening can introduce errors. The lamps used to obtain these data are either the instrument source lamps or "pencil-lamp" types.[2]

5.2 *Liquid Ratio Procedure*—This procedure uses a 0.02 % v/v solution of toluene in hexane[3] in a 10-mm far UV quartz cuvette measured against a similar hexane filled cuvette.

5.3 *Benzene Vapor Procedure*—This procedure uses a sealed far UV 10-mm path length cuvette containing benzene vapor.[3]

NOTE 3—A suitable vapor filled cell can be produced by placing a 10 µl drop of liquid benzene in the cuvette and sealing.

6. Procedure

6.1 *Line Emission Source Procedure:*

6.1.1 Measure the spectral bandwidth of the instrument as follows:

6.1.1.1 Position the appropriate line source so that it illuminates the entrance slit of the monochromator (Note 4). The positioning is not critical if sufficient light enters the monochromator.

NOTE 4—The continuum source is turned off unless one of its lines is used to measure the spectral bandwidth.

6.1.1.2 Select the "single-beam" or "energy" mode of operation, or the manufacturers approved operating protocol.

6.1.1.3 Slowly scan through the region of the line to locate the wavelength of maximum emission.

6.1.1.4 Scan to longer wavelengths until the signal returns to a level close to 0 % *T* and remains relatively constant over a few nanometre range.

6.1.1.5 Estimate the baseline level by establishing reference points on either side of the band, by 'drawing' a background line between the flat regions on each side of the band. Locate the point midway between this reference level and the maximum signal and measure the width of the band at this point. This value, expressed in nanometres, is the spectral bandwidth that will be realized at this wavelength when the instrument is operated with a continuum source. This is shown graphically in Fig. 1.

6.1.1.6 Repeat 6.1.1.1-6.1.1.5 for as many of the lines shown in Table 1 as are of interest.

6.1.2 Although the spectral bandwidth at a single slit setting may be sufficient to characterize the routine performance of an instrument, it is recommended that the bandwidths be determined at each of the discrete slit widths available or at several points if the slits are continuously variable. This procedure in effect calibrates the bandwidth settings of the instrument. Fig. 2 shows the measured spectral bandwidth plotted versus the spectral bandwidth setting of a modern grating spectrophotometer. Although there appears to be a slight deviation from linearity at each end of the plot, the agreement between the

[2] These alternative source lamps are often available as an accessory for a given spectrophotometer from the instrument vendor, or commercially available.

[3] Given the hazardous nature of materials, permanently sealed reference cells are commercial available.

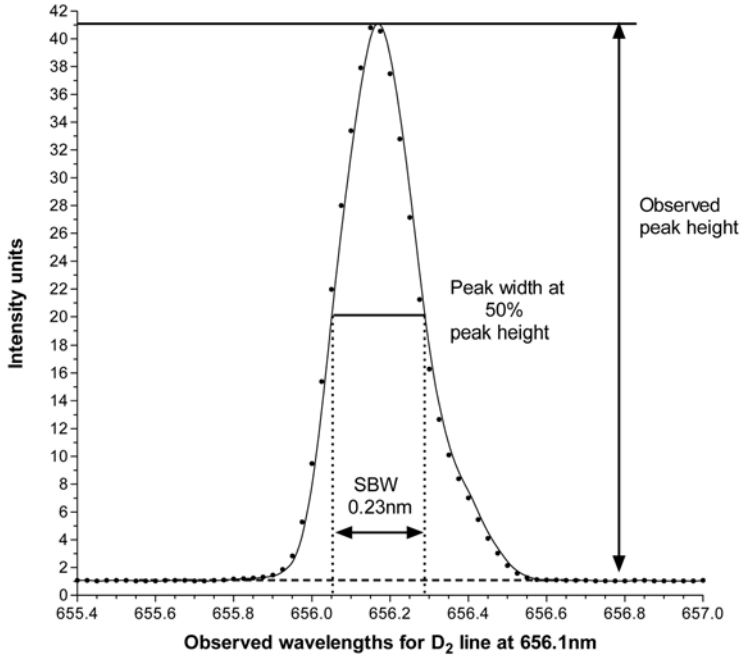

FIG. 1 Resolution Calculation

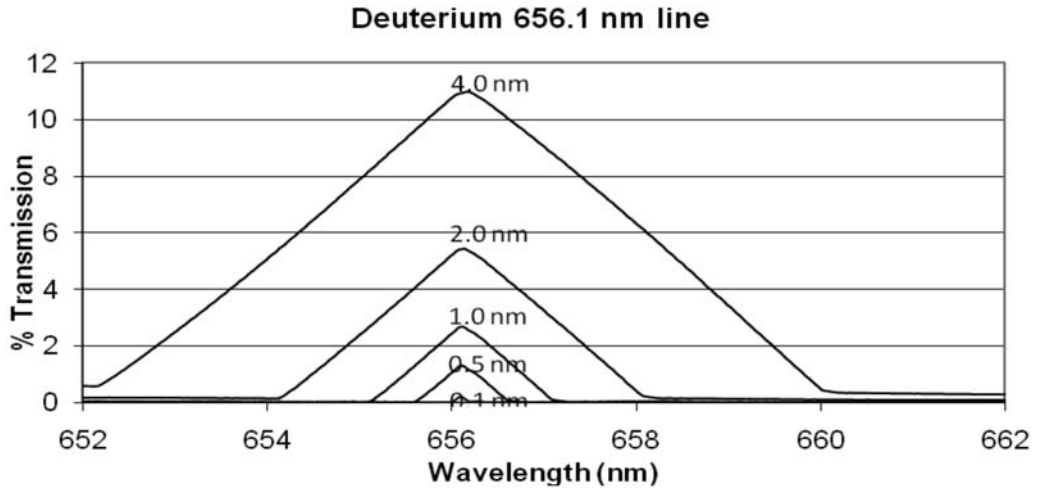

FIG. 2 Effect of Spectral Bandwidth on Line Spectra

indicated and measured values is good. Thus, the set value can be used with a high degree of confidence.

6.2 *Liquid Ratio Procedure:*

6.2.1 With no cells or references in the sample area, zero the spectrophotometer over the wavelength range 265 to 270 nm.

NOTE 5—In many instrument/software systems, this process is often referred to as 'baselining' or '...running a baseline on' the instrument.

6.2.2 Establish a hexane reference spectrum over the wavelength range 265 to 270 nm. This can either be achieved by placing the 10-mm path length far UV cuvette filled with hexane in the sample position and digitally storing the spectrum, or by placing the hexane reference in the reference beam of a double-beam spectrophotometer at the same time as recording the scan of the toluene in hexane reference.

6.2.3 If in 'single-beam' mode, replace the hexane reference with the toluene in hexane cuvette and repeat the scan to obtain the toluene in hexane spectrum. Fig. 3 shows the spectra obtained as the spectral bandwidth is varied.

6.2.4 Using the peak maximum absorbance value at approximately 269 nm, and the trough minimum value at approximately 267 nm, calculate the ratio according to the equation:

$$\text{Ratio}(R) = \text{Peak}_{269}/\text{Trough}_{267} \quad (1)$$

NOTE 6—As shown in Fig. 3, the absolute position, that is, wavelength values of the peak and trough will vary with the spectral bandwidth of the instrument.

6.2.5 Table 2 shows the expected ratio values for a range of spectral bandwidths.

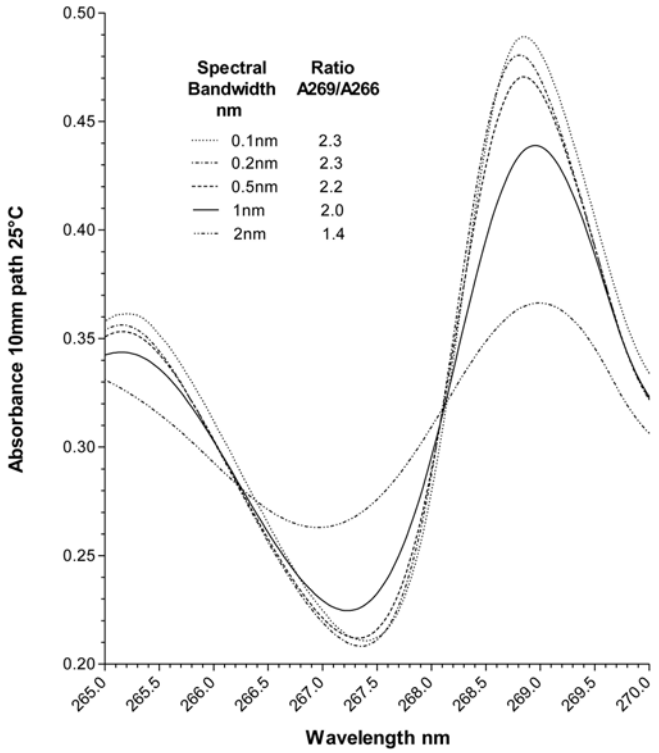

FIG. 3 Effect of Spectral Bandwidth on Toluene in Hexane Spectrum

TABLE 2 Ratio Values Versus Spectral Bandwidth for Toluene in Hexane

	Spectral Bandwidth				
Temperature of Measurement	0.5 nm ±0.1 nm	1.0 nm ±0.1 nm	1.5 nm ±0.1 nm	2.0 nm ±0.2 nm	3.0 nm ±0.2 nm
20 ± 1°C	2.4 – 2.5	2.0 – 2.1	1.6 – 1.7	1.3 – 1.4	1.0 – 1.1
25 ± 1°C	2.3 – 2.4	1.9 – 2.0	1.6 – 1.7	1.3 – 1.4	1.0 – 1.1
30 ± 1°C	2.1 – 2.2	1.8 – 1.9	1.5 – 1.6	1.3 – 1.4	1.0 – 1.1

6.3 *Benzene Vapor Procedure:*

6.3.1 Baseline the spectrophotometer over the wavelength range 250 to 270 nm, with no cells or references in the sample area.

6.3.2 Establish a benzene vapor spectrum over the above wavelength range.

6.3.3 Fig. 4 shows the spectra obtained at 0.1, 0.2, 0.5, 1.0 and 2.0 nm respectively (offset for clarity).

6.3.4 Match the spectral characteristics of the scanned spectra to the above reference spectra to obtain an estimation of the spectral bandwidth, at or below 0.5 nm.

7. Documentation and Reporting

7.1 The amount of spectral bandwidth data that should be included in an analytical method depends upon the complexity of the method and the type of instrument being used. For a single-component analysis at a single wavelength, only the spectral bandwidth at the analytical wavelength is needed. For single-component analyses with a background point or line and for multi-component analyses with or without background points, spectral bandwidth requirements at all wavelengths of interest should be specified. For simplicity, however, one may choose to specify a single relatively large spectral bandwidth and state that this value or a smaller one is adequate for use at two or more wavelengths. In fact, with constant resolution grating instruments, a single value may serve for a multi-wavelength analysis.

8. Keywords

8.1 molecular spectroscopy; ultraviolet-visible spectrophotometers; spectral bandwidth

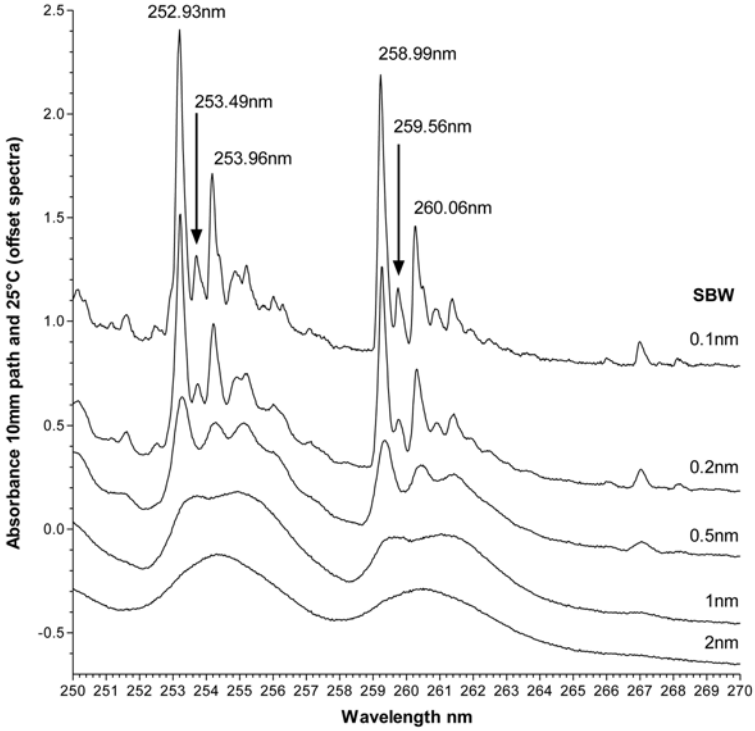

FIG. 4 Effect of Spectral Bandwidth on Benzene Spectrum

ANNEX

(Mandatory Information)

A1. ADDITIONAL INFORMATION

A1.1 General Concepts

A1.1.1 This practice describes a procedure for measuring the practical spectral bandwidth of a manual spectrophotometer in the wavelength region of 185 to 820 nm. Practical spectral bandwidth is the spectral bandwidth of an instrument operated at a given integration period and a given signal-to-noise ratio.

A1.1.2 This practice is applicable to instruments that utilize servo-operated slits and maintain a constant period and a constant signal-to-noise ratio as the wavelength is automatically scanned. It is also applicable to instruments that utilize fixed slits and maintain a constant servo loop gain by automatically varying gain or dynode voltage. In this latter case, the signal-to-noise ratio varies with wavelength. It can also be used on instruments that utilize some combination of the two designs, as well as on those that vary the period during the scan.

A1.1.3 This practice does not cover the measurement of limiting spectral bandwidth, defined as the minimum spectral bandwidth achievable under optimum experimental conditions.

A1.2 Terminology

A1.2.1 *Definitions:*

A1.2.1.1 *integration period, n*—the time, in seconds, required for the pen or other indicator to move 98.6 % of its maximum travel in response to a step function.

A1.2.1.2 *practical spectral bandwidth, n*—designated by the symbol:

$$(\Delta\lambda)^{\pi}{}_{S/N}$$

where:

$\Delta\lambda$ = spectral bandwidth,
π = integration period, and
S/N = signal-to-noise ratio measured at or near 100 % *T*.

A1.2.1.3 *signal-to-noise ratio, n*—the ratio of the signal, S, to the noise, N, as indicated by the readout indicator. The recommended measure of noise is the maximum peak-to-peak excursion of the indicator averaged over a series of five successive intervals, each of duration ten times the integration period. (This measure of noise is about five times the root-mean-square noise.)

A1.3 Summary of Practices

A1.3.1 The pen period and signal-to-noise ratio are set at the desired values when the instrument is operated with its normal light source and adjusted to read close to 100 % *T*. The

mechanical slit width, or the indicated spectral bandwidth, required to give the desired signal-to-noise ratio is recorded. The continuum source is replaced with a line emission source, such as a mercury lamp, and the apparent half-intensity bandwidth of an emission line occurring in the wavelength region of interest is measured using the same slit width, or indicated spectral bandwidth, as was used to establish the signal-to-noise ratio with the continuum source.

A1.4 Significance and Use

A1.4.1 This practice should be used by a person who develops an analytical method to ensure that the spectral bandwidths cited in the practice are actually the ones used.

NOTE A1.1—The method developer should establish the spectral bandwidths that can be used to obtain satisfactory results.

A1.4.2 This practice should be used to determine whether a spectral bandwidth specified in a method can be realized with a given spectrophotometer and thus whether the instrument is suitable for use in this application.

A1.4.3 This practice allows the user of a spectrophotometer to determine the actual spectral bandwidth of the instrument under a given set of conditions and to compare the result to the spectral bandwidth calculated from data given in the manufacturer's literature or indicated by the instrument.

A1.4.4 Instrument manufacturers can use this practice to measure and describe the practical spectral bandwidth of an instrument over its entire wavelength operating range. This practice is highly preferred to the general practice of stating the limiting or the theoretical spectral bandwidth at a single wavelength.

A1.5 Test Materials and Apparatus

A1.5.1 Table A1.1 lists reference emission lines that may be used for measuring the spectral bandwidth of ultraviolet/visible instruments at the levels of resolution encountered in most commercial instruments. All of the lines listed have widths less than 0.02 nm, suitable for measuring spectral bandwidths of greater than 0.2 nm. The wavelengths of these lines in nanometres are listed in the first column. Values refer to measurements in standard air (760 nm, 15°C) except for the two lines below 200 nm. The wavelengths for these lines refer to a nitrogen atmosphere at 760 nm and 15°C.

A1.5.1.1 The second column in Table A1.1 lists the emitter gas of six sources. Only sources operating at low pressure should be used, as line broadening can introduce errors. The hydrogen, deuterium, and mercury lamps used to obtain these data were Beckman lamps operated on Beckman spectrophotometer power supplies. The other lamps are all of the

TABLE A1.1 Emission Lines Useful for Measuring Spectral Bandwidth

Reference Line, nm	Emitter	Intensity	Nearest Neighbor, nm	Separation, nm	$I_{Neighbor}/I_{Reference}$	Weak Neighbor, nm
184.91	Hg	8	194.17	9.26	0.13	
194.17	Hg	8	184.91	9.26	0.13	197.33
205.29	Hg	4	202.70	2.59	0.08	
226.22	Hg	5	237.83	11.61	0.06	226.03
253.65	Hg	10	...	...	...	253.48
275.28	Hg	5	280.35	5.07	0.08	
289.36	Hg	6	296.73	7.37	0.42	
296.73	Hg	8	302.15	5.42	0.04	
318.77	He	5	294.51	24.26	0.06	
334.15	Hg	7	313.18	20.97	0.70	
341.79	Ne	5	344.77	2.98	0.20	
359.35	Ne	5	352.05	7.30	0.14	360.02
388.87	He	7	447.15	58.28	0.04	
404.66	Hg	8	407.78	3.12	0.04	
427.40	Kr	5	431.96	4.56	0.28	428.30
435.95	Hg	9	407.78	28.17	0.02	435.75
447.15	He	5	471.31	24.16	0.04	
471.31	He	4	492.19	20.88	0.25	
486.0	D_2	...	...	...	...	
486.13	H_2	6	492.87	6.74	0.03	485.66
501.57	He	5	492.19	9.38	0.06	
546.07	Hg	8	577.12	31.05	0.04	
557.03	Kr	3	587.09	30.06	0.30	556.22
587.56	He	7	706.52	118.96	0.03	667.82
603.00	Ne	5	607.43	4.43	0.54	
614.31	Ne	7	616.36	2.05	0.04	
626.65	Ne	6	630.48	3.83	0.07	
640.23	Ne	7	638.30	1.93	0.11	
656.1	D_2	...	...	...	...	
656.28	H_2	7	...	...	...	656.99
667.82	He	5	706.52	38.70	0.50	
692.95	Ne	6	703.24	10.29	0.45	
703.24	Ne	7	692.95	10.29	0.06	702.41
724.52	Ne	5	703.24	21.28	0.02	717.39
743.89	Ne	4	724.52	19.37	1.4	748.89
785.48	Kr	3	769.45	16.03	0.7	
819.01	Kr	2	811.29	7.72	3.1	

"pencil-lamp" type.[4] A mercury vapor Pen-Ray lamp[5] was used to obtain the data shown in Fig. A1.1. In many applications the mercury and hydrogen (or deuterium) lines suffice.

A1.5.1.2 Relative intensity data for the reference lines are given in the third column of Table A1.1. The data refer to measurements made with a double prism-grating spectrophotometer equipped with a silica window S-20 photomultiplier (RCA-C70109E). These intensities will be different when using detectors of different spectral sensitivity. They may also vary somewhat among sources. All of the lines are intense ones, but all may not always be sufficiently intense to allow the spectrophotometer to be operated with very narrow slit widths.

A1.5.1.3 Information on nearest neighbors of appreciable intensity is needed in order to set an upper limit on the measurable spectral bandwidth. If the resolution of the instrument in question is so poor that two lines or bands of the test source or sample overlap, the measured half bandwidth will not indicate the spectral bandwidth of the instrument. Very few of the lines listed in Table A1.1 are so well isolated from other lines of appreciable intensity that they could always be used without interference or overlap. The atomic hydrogen (deuterium) line at 656 nm and the very intense mercury resonance line at 253 nm fall in a category of "isolation," but in all other cases interfering lines are nearby. The nearest neighboring lines having an intensity more than 15 % of the reference lines are given in the fourth column of Table A1.1. The separation in nanometres between the reference and nearest neighbor lines is listed in the fifth column. In general, lines cannot be used for a spectral bandwidth test when the spectral bandwidth exceeds one half the separation between reference and nearest neighbor lines.

A1.5.1.4 To some extent this rule can be modified by the relative intensities of neighbor to reference lines. This ratio, $I_{neighbor}$ /$I_{reference}$, is listed in Column 6. Neighboring lines having an intensity less than 15 % of the reference lines will not seriously distort bandwidth measurements. However, to accommodate the possible situation of sources with intensity relationships different from that encountered in this study, neighboring lines weaker than 15 % are tabulated in the seventh column under the heading "weak neighbor."

A1.6 Procedure

A1.6.1 *Instruments with Servo-Operated Slits*—These instruments maintain a constant period and signal-to-noise ratio as wavelength is automatically scanned. The determination of practical spectral bandwidth requires a preliminary determination of the mechanical slit width necessary to yield a given signal-to-noise at a given integration period. This is best accomplished by first establishing the desired period. Next determine the slit widths required to yield a given signal-to-noise ratio throughout the region of interest using the standard continuum source of the instrument. Then use appropriate line sources to illuminate the monochromator, and record the spectral bandwidths obtained at the appropriate mechanical slit widths for the wavelengths in question.

A1.6.1.1 Although the integration period may be indicated on the instrument or in the manufacturer's literature, check the value as follows:

(1) For recording instruments, set the wavelength at any convenient position and adjust the 0 and 100 % *T* controls for normal recorder presentation. Using 100 % *T* as the base line, block the sample beam and measure the time required for the pen to reach the 2 % *T* level (Note A1.2).

[4] Suitable lamps are available from laboratory supply houses as well as manufacturers.

[5] The sole source of supply of the apparatus known to the committee at this time is UVP, Inc., 5100 Walnut Grove Ave., P.O. Box 1501, San Gabriel, CA 91778-1501. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

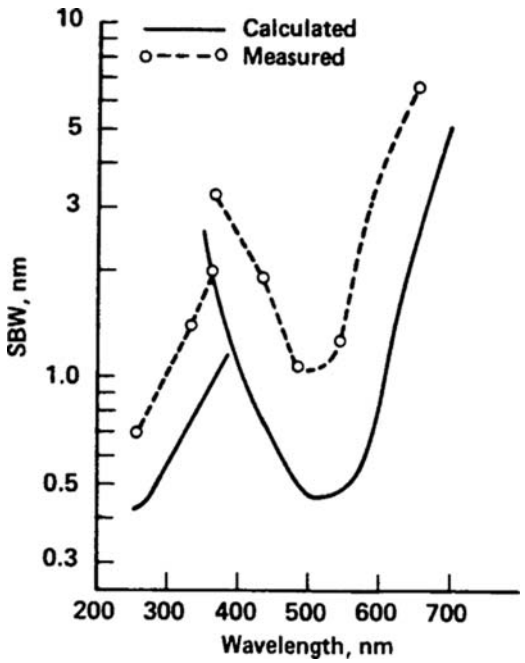

FIG. A1.1 Comparison of Measured and Calculated Spectral Bandwidths

NOTE A1.2—The time may be measured with a stopwatch or from the distance the chart moves, if a fast chart speed recorder is being used. Integration periods of 1 s or less can only be estimated by either technique, but generally this estimate is adequate to determine if the indicated period is approximately correct.

(2) For instruments that can be operated only in the absorbance mode, follow the same procedure, with the exception that 0 *A* replaces 100 % *T* and 1.7 *A* replaces 2 % *T*.

A1.6.1.2 The signal-to-noise ratio is measured as follows:

(1) Set the instrument at a convenient wavelength and adjust the pen to read either 100 % *T* or 0 *A*. For low-noise levels use an expanded scale, if available.

(2) Adjust the slit width either to its normal value or to a value that gives the desired signal-to-noise ratio.

(3) Disengage the wavelength drive, start the chart drive, and allow the pen to record for at least 2 min or 50 integration periods, whichever is longer.

(4) Divide the recording into five approximately equal segments and determine the maximum peak-to-peak excursion in each segment (Note A1.3).

NOTE A1.3—Care should be taken that the noise level is not partially obscured by a detectable recorder dead zone.

(5) Average the five readings to obtain the noise, *N*.

(6) If a % *T* recording is being used, divide 100 by *N* to obtain the signal-to-noise ratio, *S/N*. If an absorbance recording is being used, divide 0.43 by *N* to determine *S/N*.

(7) The signal-to-noise ratio should be independent of wavelength for a given source and detector combination, but it is advisable to check this point experimentally. For example, many instruments are operated with different slit programs in the ultraviolet and visible regions and thus exhibit different signal-to-noise ratios in the two regions.

A1.6.1.3 Set the period and signal-to-noise ratio to the values used in A1.6.1.1 and A1.6.1.2 , scan to the wavelength of interest (see Table 1), and record the resulting mechanical slit widths or spectral bandwidth (Note A1.4).

NOTE A1.4—It may be desirable to scan the entire wavelength range of the instrument and record the slit width at suitable intervals so that a curve of slit width versus wavelength may be constructed (usually 25 and 50-nm intervals are satisfactory for the ultraviolet and visible regions, respectively).

A1.6.1.4 Measure the spectral bandwidth of the instrument as follows:

(1) Position the appropriate line source so that it illuminates the entrance slit of the monochromator (Note A1.5). The positioning is not critical if sufficient light enters the monochromator.

NOTE A1.5—The continuum source is turned off unless one of its lines is used to measure the spectral bandwidth.

(2) Select the "single-beam" or "energy" mode of operation, and set the slit width to the value recorded in A1.6.1.3.

(3) Slowly scan through the region of the line to locate the wavelength of maximum emission, adjusting the gain or dynode voltage as necessary to keep the signal on scale but still as large as possible.

(4) Scan to longer wavelengths until the signal returns to a level close to 0 % *T* and remains relatively constant over a few nanometre range. Reverse the scan and slowly scan through the line, continuing until the signal returns close to 0 % *T* and remains relatively constant.

NOTE A1.6—For instruments that normally scan toward longer wavelengths while recording: first scan to a shorter wavelength until the signal remains near 0 % *T*, then reverse the scan and slowly scan through the line.

(5) Draw a background line joining the flat regions on each side of the band. Locate the point midway between the background line and the maximum signal and measure the width of the band at this point (Note A1.7 and Note A1.8). This value, expressed in nanometres, is the spectral bandwidth that will be realized at this wavelength when the instrument is operated with a continuum source and the signal-to-noise and integration period previously determined in 6.1.1 and 6.1.2 (Note A1.9).

NOTE A1.7—If an absorbance slide wire is used instead of a % *T* slide wire, the point at which the signal is at half of its maximum value is determined as follows: (*a*) convert the apparent absorbance at maximum signal to % *T*, (*T*1); (*b*) convert the apparent absorbance of the background line at the wavelength of maximum signal to % *T* (*T*2); (*c*) subtract *T*2 from *T*1 and divide the result by 2 to obtain *T*3; (*d*) add *T*3 to *T*2 to yield *T*4; and (*e*) convert *T*4 to absorbance and locate this value on each side of the recorded line profile.

NOTE A1.8—If the slit width is too wide, neighboring lines may interfere with the spectral bandwidth measurement. Fig. A1.2 illustrates this problem. This figure consists of three superimposed and normalized spectra of a low-pressure mercury lamp in the region 293–307 nm. The spectra differ in mechanical slit width. The half bandwidths of the 296-nm line are indicated by arrows. Note that they are not at the same elevation because of the background level. This background arises from a weak continuum emitted by this lamp in this region. As slits are widened the continuum signal increases with the square of the slit width, while the peak line signal increases linearly with slit width.

The neighboring 302-nm line is clearly evident. It introduces a small error into the measured spectral bandwidth when the spectral slit width exceeds half the separation (5.42 nm) between the two lines. If the 302-nm line were absent the slit function of the 296-nm line would presumably follow the dotted line. Actually the slit functions are not perfectly triangular in this illustration at wide slits because of the variable dispersion of the quartz prism used. This is discernible in the curvature of the left side of the 296-nm line.

If the mechanical slit at maximum gain is so wide that line breadths cannot be measured without excessive interferences from neighboring lines, the calculated spectral slit width may be substituted for spectral bandwidth (the ratio of spectral bandwidth to spectral slit width will always approach unity at wide slits if the instrument is in proper adjustment). Of course, if a very low resolution instrument is under test, interference from neighboring lines might occur even for narrow slits where the ratio is not unity.

NOTE A1.9—The signal-to-noise ratio for the line width measurement will probably be different from the one measured with the continuum source. The difference is of no consequence, however, because the spectral bandwidth of the line is measured with the slit width that corresponds to the signal-to-noise ratio measured in A1.6.1.2 with a continuum source.

(6) Repeat A1.6.1.4(*1*)–A1.6.1.4(*5*) for as many of the lines shown in Table 1 as are of interest.

A1.6.2 *Instruments with Fixed Slits*—Many instruments with grating monochromators maintain fixed slits over an extended wavelength range and vary the gain or dynode voltage automatically to maintain a constant servo loop gain. Consequently, the spectral bandwidth is independent of wavelength but the signal-to-noise ratio changes. In principle, one needs to measure spectral bandwidth at only one wavelength and then determine the signal-to-noise ratio throughout the wavelength range of the instrument. It is recommended,

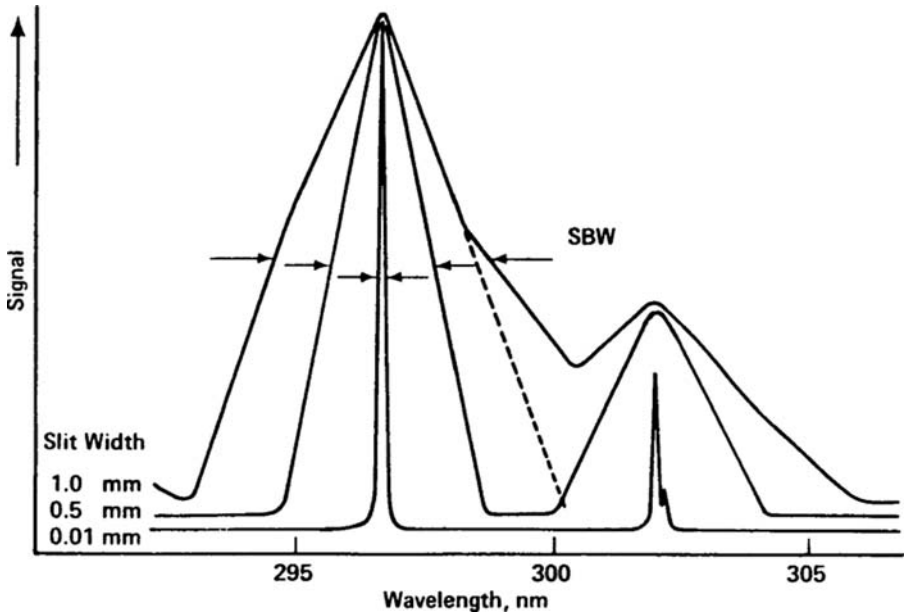

FIG. A1.2 Slit Function of Beckman DK-U Prism Monochromator

however, that the bandwidth be measured at wavelengths near the middle and the two extremes of the operating range. If the bandwidth is found to be constant, the value can be used with confidence at the intermediate wavelengths.

A1.6.2.1 As with the variable slit instruments, determine the practical spectral bandwidth of fixed slit instruments by first establishing the desired integration period. Measure the period using the procedure in A1.6.1.1. Next choose the slit width, or the nominal spectral bandwidth, to give the desired signal-to-noise ratio when the instrument is operated with the continuum source (Note A1.10). Measure the signal-to-noise ratio at the wavelength of interest using the procedure in A1.6.1.2. Measure the spectral bandwidth using the appropriate narrow line source and the procedure in A1.6.1.4.

NOTE A1.10—The slit widths on some instruments are identified by arbitrary designations or letters, but on other instruments they are identified by nominal spectral bandwidths, usually expressed in nanometres. Some instruments have one or more discrete slit settings, while others have continuously variable slits.

A1.6.2.2 Although the spectral bandwidth at a single slit setting may be sufficient to characterize the routine performance of an instrument, it is recommended that the bandwidths be determined at each of the discrete slits' widths available or at several points if the slits are continuously variable. This procedure in effect calibrates the slit width indicator (Note A1.11). Fig. A1.3 shows the measured spectral bandwidth plotted versus the spectral bandwidth dial reading of a modern grating spectrophotometer. Although there appears to be a slight deviation from linearity at each end of the plot, the agreement between the indicated and measured values is good. Thus, the dial readings can be used with a high degree of confidence.

NOTE A1.11—The signal-to-noise ratio will vary significantly as the slit width is changed, and it may be necessary to change the period to obtain a suitable noise level. The changes have no bearing on the calibration of the slit width indicator, but values for the signal-to-noise ratio and the period must be given if spectral bandwidth is used to describe instrument performance.

A1.7 Documentation and Reporting

A1.7.1 The amount of spectral bandwidth data that should be included in an analytical method depends upon the complexity of the method and the type of instrument being used. For a single-component analysis at a single wavelength, only the spectral bandwidth at the analytical wavelength is needed. For single-component analyses with a background point or line and for multi-component analyses with or without background points, spectral bandwidth requirements at all wavelengths of interest should be specified. For simplicity, however, one may choose to specify a single relatively large spectral bandwidth and state that this value or a smaller one is adequate for use at two or more wavelengths. In fact, with constant resolution grating instruments, a single value may serve for a multi-wavelength analysis.

A1.7.2 Spectral bandwidths given in an analytical method do not require integration period and signal-to-noise ratio descriptors. The user can adjust these parameters, along with scan speed, to obtain the desired results as long as an adequate spectral bandwidth is maintained.

A1.7.3 When practical spectral bandwidth is used to describe the performance of an instrument, the period and signal-to-noise ratio should always be given. The symbol used is:

$$(\Delta\lambda)^{\pi}{}_{S/N} \tag{A1.1}$$

where:

$\Delta\lambda$ = spectral bandwidth,
π = integration period, s, and
S/N = signal-to-noise ratio.

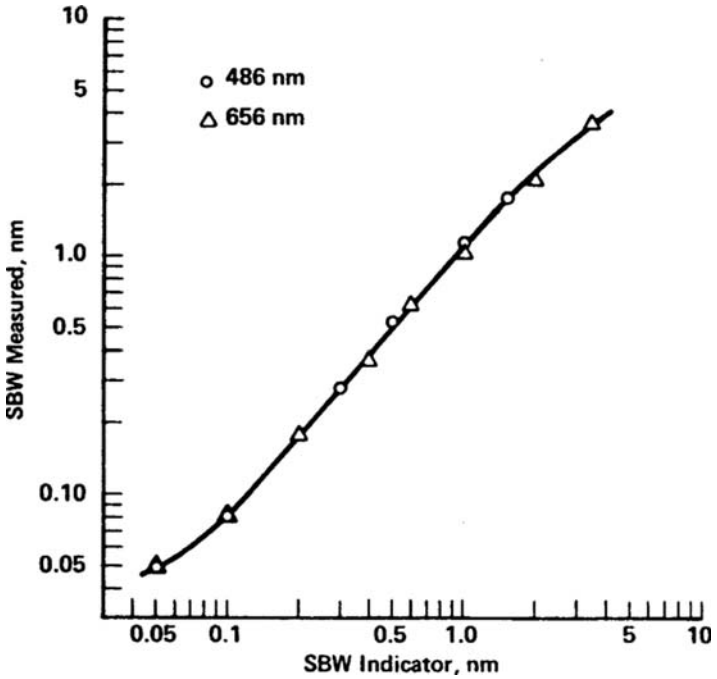

FIG. A1.3 Calibration of Spectral Bandwidth Indicator

A1.7.3.1 For instruments with servo-operated slits, a wavelength should be given with each spectral bandwidth value. The preferred practice is to present a plot of practical spectral bandwidth versus wavelength. Fig. A1.1 shows a plot of this type for an old, double-prism monochromator instrument. Also shown are the calculated spectral bandwidth curves for this instrument (the calculated values were obtained by calculating the spectral slit width and adding corrections for slit curvature and Rayleigh diffraction). The measured spectral bandwidths are approximately twice as large as the calculated ones.

A1.7.3.2 For instruments with fixed slits and variable gain, a plot of *S/N* versus wavelength at a specified spectral bandwidth and period is very informative. A simpler but still useful practice is to plot gain versus wavelength and to specify signal-to-noise ratio at one wavelength. Since signal-to-noise ratio is directly related to gain, variable gain, a plot of *S/N* at any wavelength is easily calculated.

RELATED MATERIAL

ASTM E131 Terminology Relating to Molecular Spectoscopy

ASTM E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers