This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: E958 – 13 (Reapproved 2021)

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 nm 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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 nm 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 nm 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 nm 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.

[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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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 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 ⅛th 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.

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.

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

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 on the spectral

[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.

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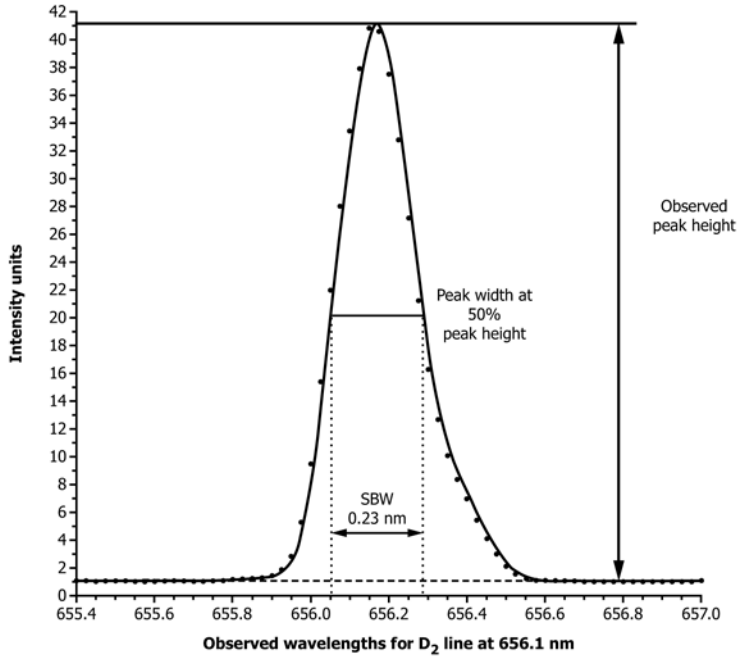

FIG. 1 Resolution Calculation

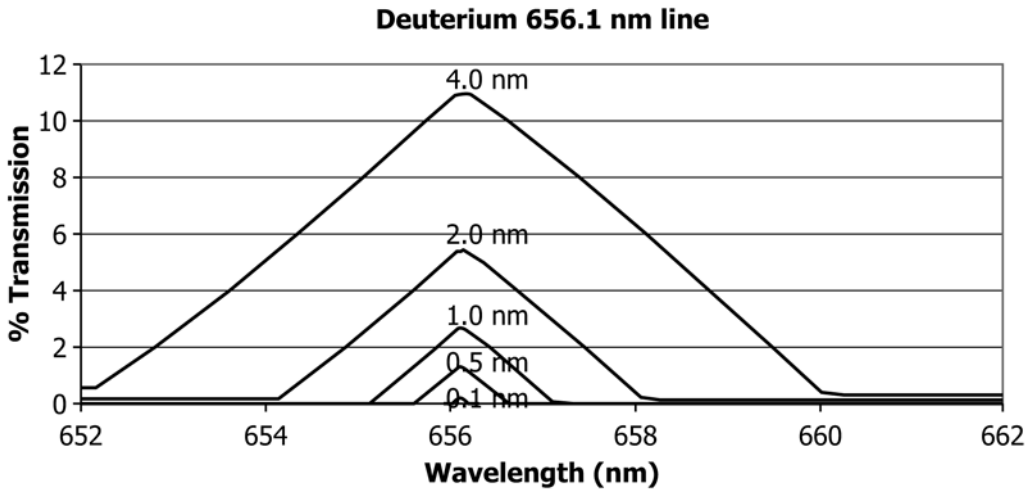

FIG. 2 Effect of Spectral Bandwidth on Line Spectra

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 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 nm 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.

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