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Standard Practice for Monitoring the Calibration of Ultraviolet-Visible Spectrophotometers whose Spectral Slit Width Bandwidth does not Exceed 2 nm¹

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INTRODUCTION

In the application of spectrophotometric methods of analysis it is the responsibility of the analyst to verify and validate that the instrument is functioning properly and is capable of providing acceptable analytical results. It is preferable that the verification of instrument performance be accomplished through the use of reference materials whose properties have been accurately determined. Such materials are readily available, and their use in the tests and measurements described in this practice is satisfactory for evaluating the performance of spectrophotometers whose spectral slit width bandwidth does not exceed the value for which the intrinsic or certified properties are valid. A compromise maximum permissible spectral slit width bandwidth of 2 nm is recommended for the reference materials and error tolerances recommended here.

This practice covers some of the essential instrumental parameters that should be evaluated to ensure the acceptability of the analytical data routinely obtained on the instrument. These parameters include the accuracy of the wavelength and absorbance scales and stray radiant power levels.

The accuracy of the wavelength scale in both the ultraviolet (UV) and visible regions is determined using the sharp absorption bands of a holmium oxide glass or solution filter. The absorbance scale accuracy in the UV region (235–350 nm) is determined using acidic solutions of potassium dichromate. In the visible region (440–635 nm) the absorbance accuracy is determined using individually certified neutral density glass filters. The use of these reference materials provides a valid and relatively simple means to test the errors in the wavelength and absorbance scales of small spectral slit width bandwidth spectrophotometers in the spectral ranges indicated. A simplified version of the opaque filter method is provided as a test for excessive stray radiant energy.

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1. Scope

1.1 This practice covers the parameters of spectrophotometric performance that are critical for testing the adequacy of instrumentation for most routine tests and methods² within the wavelength range of 200 to 700 nm and the absorbance range of 0 to 2. The recommended tests provide a measurement of the important parameters controlling results in spectrophotometric methods, but it is specifically not to be inferred that all factors in instrument performance are measured.

1.2 This practice may be used as a significant test of the performance of instruments for which the spectral slit width bandwidth does not exceed 2 nm and for which the manufacturer's specifications for wavelength and absorbance accuracy do not exceed the performance tolerances employed here. This practice employs an illustrative tolerance of $\pm 1\%$ relative for the error of the absorbance scale over the range of 0.2 to 2.0, and of ± 1.0 nm for the error of the wavelength scale. A suggested maximum stray radiant power ratio of 4×10^{-4} yields $<1\%$ absorbance bias at an absorbance of 2. These tolerances are chosen to be compatible with many chemical applications while comfortably exceeding the uncertainty of the certified values for the reference materials and typical manufacturer's specifications for error in the wavelength and absorbance scales of the instrument under test. The user is encouraged to develop and use tolerance values more appropriate to the requirements of the end use application. This procedure

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 Ultraviolet and Visible Spectroscopy.

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² Routine tests are defined as those in which absorbance data obtained on a sample are compared to those of a standard sample preparation.

is designed to verify quantitative performance on an ongoing basis and to compare one instrument's performance with that of other similar units. Refer to Practice E275 to extensively evaluate the performance of an instrument.

1.3 This practice should be performed on a periodic basis, the frequency of which depends on the physical environment within which the instrumentation is used. Thus, units handled roughly or used under adverse conditions (exposed to dust, chemical vapors, vibrations, or combinations thereof) should be tested more frequently than those not exposed to such conditions. This practice should also be performed after any significant repairs are made on a unit, such as those involving the optics, detector, or radiant energy source.

1.4

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. Referenced Documents

2.1 ASTM Standards:³

E131 Terminology Relating to Molecular Spectroscopy

E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis

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

E387 Test Method for Estimating Stray Radiant Power Ratio of Dispersive Spectrophotometers by the Opaque Filter Method

E1866 Guide for Establishing Spectrophotometer Performance Tests

2.2 Other Publications: NIST Publications:⁴

NBS Special Publication 260-54: NIST Special Publication 260-54 Certification and Use of Acidic Potassium Dichromate Solutions As An Ultraviolet Absorbance Standard

NBIST Special Publication 260-102: Holmium Oxide Solution Wavelength Standard from 240 to 640 nm—SRM 2034

NIST Special Publication 260-116: Glass Filters as a Standard Reference Material for Spectrophotometry—Selection, Preparation, Certification, and Use of SRM 930 and SRM 1930

NIST Special Publication 260-140: Technical Specifications for Certification of Spectrophotometric NTRMs⁴

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³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards Vol 03.06 volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ Available from the National Technical Information Service, Port Royal Road, Springfield, VA 22161.

⁴ Available from National Technical Information Service (NTIS), 5285 Port Royal Rd., Springfield, VA 22161, <http://www.ntis.gov>.

2.3 ISO Publications:⁵**ISO 17025 General Requirements for the Competence of Testing and Calibration Laboratories****ISO Guide 34 General Requirements for the Competence of Reference Material Producers****3. Terminology****3.1 Definitions:**

3.1.1 For the definitions of terms used in this practice, refer to Terminology E131.

3.1.2 For a description of the instrumental parameters evaluated in this practice, refer to Practice E275.

3.1.3 For a description of quantitative ultraviolet spectrophotometric techniques, refer to Practice E169.

4. Significance and Use

4.1 This practice permits an analyst to compare the performance of an instrument to the manufacturer's supplied performance specifications and to verify its suitability for continued routine use. It also provides generation of calibration monitoring data on a periodic basis, forming a base from which any changes in the performance of the instrument will be evident.

5. Reference to this Calibration-Monitoring Procedure

5.1 Reference to this practice in any spectrophotometric calibration-monitoring scheme shall constitute due notification that the adequacy of the spectrophotometer performance has been evaluated by means of this practice. Performance is considered to be adequate when the data obtained are within the stated tolerances from the true values.

6. Instrument Operation

6.1 In obtaining spectrophotometric calibration data the analyst must select the proper instrumental operating conditions to realize satisfactory instrument performance. Operating conditions for individual instruments are best obtained from the manufacturer's literature because of variations in instrument design.

6.2 When using reference materials, all the components of the spectrophotometer must be functioning properly. In addition, the temperature of the specimen compartment should be between 20 and 25°C. Matched solution cells should be used for calibration purposes.

6.3 Each of the above factors in instrument operation is important in the determination of wavelength and absorbance accuracy.

7. Determination of Wavelength Accuracy in the Ultraviolet and Visible Spectral Regions

7.1 *Discussion*—The holmium oxide glass filter (1, 2) or solution standard (NBS Special Publication 260-102) may be used for evaluating wavelength accuracy. The glass and solution standards are both widely available commercially in the cuvette format (a cuvette-shaped metal holder is used for the glass), as well as from NIST for high-accuracy needs. Holmium glass filters for wavelength calibration checks are available from several distributors of glass color filters and possibly from different glass manufacturers. A purchaser should require certification by the supplier that the wavelengths of the absorption bands are within 0.2 nm of the values given in Reference⁶ or solution standard (NIST Special Publication 260-102) may be used for evaluating wavelength accuracy. The glass and solution standards are both available commercially from reference material producers, in the sealed cuvette format (a cuvette-shaped metal holder is used for the glass) or as a bottled solution, prepared from high purity Holmium Oxide (> 99.99 %), where value assignment is by self assertion (Note 1). A purchaser should require certification by the supplier that the wavelengths of the absorption bands are within 0.2 nm of the values given in Ref. (2), and reported below. The NIST Calibration Services program provides individually verified glass wavelength standards through Service ID No. 38050C. The appropriate solution standard is 4% (mass fraction) holmium oxide in 10% (volume fraction) perchloric acid, contained in a 10-mm pathlength cuvette. Band positions for the solution reference material were determined as locations of the transmittance minima of specified bands in the transmittance spectrum of the material in the original certification of NIST SRM 2034. Absorbance maxima or transmittance minima must be located within ± 1 nm of the wavelengths given below, and reported below. The appropriate solution standard is 4% (mass fraction) holmium oxide in 10% (volume fraction) perchloric acid, contained in a 10-mm path length cuvette. For this material, the transmittance minima of 18 absorption bands have been certified by a multi-laboratory inter-comparison, at the highest level, allowing the peak value assignments as an intrinsic wavelength standard (3). Absorbance maxima or transmittance minima must be located within ± 1 nm of the wavelengths given below:

Glass Filter^A241.5 nm^C

...

279.3 nm

287.6 nm

Dilute Acidic Solution^B

241.1 nm

249.9 nm

278.1 nm

287.2 nm

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

⁶ Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, <http://www.iso.ch>.

^C The boldface numbers in parentheses refer to a list of references at the end of this standard.

Glass Filter ^A	Dilute Acidic Solution ^B
333.8	<u>333.5 nm</u>
nm <u>333.4 nm</u>	
... 345.5	
nm	
360.8 nm	<u>345.4 nm</u>
385.8	361.3 nm
nm <u>385.7 nm</u>	
418.5 nm	<u>385.6 nm</u>
453.4 nm	416.3 nm
459.9 nm	...
...	467.8 nm
536.4 nm	485.3 nm
637.5 nm	536.6 nm
	640.5 nm

^A Wavelengths taken from Reference Ref. (2) for Corning Glass Works Code 3130 glass, superceded by Corning Glass Works Code 3131 glass and Kopp Glass Code 3131 glass, for which the wavelengths are also valid.

^B Wavelengths rounded to 0.1 nm from the results given in NBS SP-260-102 for a 1-nm spectral slit width. Wavelengths rounded to 0.1 nm for a 1-nm spectral bandwidth taken from Ref. (3).

^C May not be usable, depending on the base glass of the filter.

^D Peak omitted because it resolves into a doublet at spectral slit width values less than 1 nm.

7.1.1 If the observed absorption bands of the holmium oxide glass or solution deviate by more than ± 1 nm from the values stated, then corrective service must be performed on the instrument by a qualified service person. If the user performs this service, the manufacturer's recommended procedure should be followed carefully.

7.1.2 The wavelength accuracy is dependent on the spectral slit width and thus on the physical slit width. Spectral slit widths may be determined from the manufacturer's specifications.

7.1.3 Computer based peak location algorithms that may be used to assign absorbance maxima or transmittance minima are discussed in section 7.6 of Guide Peak omitted because it resolves into a doublet at spectral bandwidth values less than 1 nm.

NOTE 1—‘Self assertion’ may take the form of value assignment and certification in many forms. Some specific examples are:

(1) By a national metrology institute (NMI),

(2) By an ISO 17025 and ISO Guide 34 accredited Reference Material producer, and

(3) By a laboratory claiming ‘traceability’ to an NMI.

In all cases, the user should be satisfied that the quality of the value assignment data meets the laboratory requirements.

7.1.1 If the observed absorption bands of the holmium oxide glass or solution deviate by more than ± 1 nm from the values stated, then corrective service must be performed on the instrument by qualified personnel. If the user performs this service, the manufacturer's recommended procedure should be followed carefully.

7.1.2 The wavelength accuracy is dependent on the spectral bandwidth and thus on the physical bandwidth. Spectral bandwidths may be determined from the manufacturer's specifications.

7.1.3 Computer based peak location algorithms that may be used to assign absorbance maxima or transmittance minima are discussed in 7.6 of Guide E1866. It should be noted that peak asymmetries in the holmium oxide reference materials are such that digital filter widths should be smaller than the full-width-half-maximum recommendation of that Guide—guide.

7.1.4 In the absence of drift or slippage in the wavelength drive train, repeatability of the band positions should be on the order of ± 0.1 nm for a given instrument, especially with the use of a computer based peak location algorithm.

7.2 Procedure:

7.2.1 Examine the holmium oxide reference material and remove any surface contamination using a soft brush or lens paper:lint-free cloth. Measure the temperature of the sample compartment by placing an appropriate sensor into the cell compartment of a stabilized instrument and replacing the compartment cover securely. Place the sensor as close as possible to the actual position that will be occupied by the standard. After a suitable period of time record the temperature reading, remove the sensor, and resume normal operations.

7.2.2 Record the blank absorbance or transmittance (air versus air) spectrum at the desired resolution and at the appropriate wavelength intervals and scan speeds, in order to perform any necessary baseline adjustments. The wavelength intervals should be no greater than the spectral slit width—bandwidth used. Acquire the appropriate spectrum of the holmium oxide reference material with respect to air and baseline correct if necessary using the blank spectrum. Record the wavelengths of the positions of the relevant bands, and compare these values to the expected values. If large discrepancies (>1 nm) exist between the true and measured wavelengths, repeat the procedure at a slower scan speed and smaller spectral slit width,bandwidth, if possible, to verify the nonconformity.

7.2.3 Report the wavelength calibration data in the manner of Table 1, given as an example for the holmium oxide glass reference material.

8. Evaluation of Stray Radiant Power Ratio (SRPR)

8.1 Discussion—A portion of the unwanted stray radiant power detected by the photodetector can be measured using the following sharp cut-off solution filters in 1-cm cells: