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Standard Test Method for Estimating Stray Radiant Power Ratio of Dispersive Spectrophotometers by the Opaque Filter Method¹

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1. Scope

1.1 Stray radiant power (SRP) can be a significant source of error in spectrophotometric measurements, and the danger that such error exists is enhanced because its presence often is not suspected (1-4).² This test method affords an estimate of the relative radiant power, that is, the Stray Radiant Power Ratio (SRPR), at wavelengths remote from those of the nominal bandpass transmitted through the monochromator of an absorption spectrophotometer. Test-filter materials are described that discriminate between the desired wavelengths and those that contribute most to SRP for conventional commercial spectrophotometers used in the ultraviolet, the visible, the near infrared, and the mid-infrared ranges. These procedures apply to instruments of conventional design, with usual sources, detectors, including array detectors, and optical arrangements. The vacuum ultraviolet and the far infrared present special problems that are not discussed herein.

NOTE 1—Research (3) has shown that particular care must be exercised in testing grating spectrophotometers that use moderately narrow bandpass SRP-blocking filters. Accurate calibration of the wavelength scale is critical when testing such instruments. Refer to Practice E275.

1.2 These procedures are neither all-inclusive nor infallible. Because of the nature of readily available filter materials, with a few exceptions, the procedures are insensitive to SRP of very short wavelengths in the ultraviolet, or of lower frequencies in the infrared. Sharp cutoff longpass filters are available for testing for shorter wavelength SRP in the visible and the near infrared, and sharp cutoff shortpass filters are available for testing at longer visible wavelengths. The procedures are not necessarily valid for “spike” SRP nor for “nearby SRP.” (See Annexes for general discussion and definitions of these terms.) However, they are adequate in most cases and for typical applications. They do cover instruments using prisms or

gratings in either single or double monochromators, and with single and double beam instruments.

NOTE 2—Instruments with array detectors are inherently prone to having higher levels of SRP. See Annexes for the use of filters to reduce SRP.

1.3 The proportion of SRP (that is, SRPR) encountered with a well-designed monochromator, used in a favorable spectral region, typically is 0.1 % transmittance or better, and with a double monochromator it can be less than 1×10^{-6} , even with a broadband continuum source. Under these conditions, it may be difficult to do more than determine that it falls below a certain level. Because SRP test filters always absorb some of the SRP, and may absorb an appreciable amount if the specified measurement wavelength is not very close to the cutoff wavelength of the SRP filter, this test method underestimates the true SRPR. However, actual measurement sometimes requires special techniques and instrument operating conditions that are not typical of those occurring during use. When absorption measurements with continuum sources are being made, it can be that, owing to the effect of slit width on SRP in a double monochromator, these test procedures may offset in some degree the effect of absorption by the SRP filter; that is, because larger slit widths than normal might be used to admit enough energy to the monochromator to permit evaluation of the SRP, the stray proportion indicated could be greater than would normally be encountered in use (but the net effect is still more likely to be an underestimation of the true SRPR). Whether the indicated SRPR equals or differs from the normal-use value depends on how much the SRP is increased with the wider slits and on how much of the SRP is absorbed by the SRP filter. What must be accepted is that the numerical value obtained for the SRPR is a characteristic of the particular test conditions as well as of the performance of the instrument in normal use. It is an indication of whether high absorbance measurements of a sample are more or less likely to be biased by SRP in the neighborhood of the analytical wavelength where the sample test determination is made.

1.4 The principal reason for a test procedure that is not exactly representative of normal operation is that the effects of SRP are “magnified” in sample measurements at high absorbance. It might be necessary to increase sensitivity in some

¹ This method is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.01 on Ultraviolet and Visible Spectroscopy.

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² The boldface numbers in parentheses refer to the list of references at the end of this standard.

way during the test in order to evaluate the SRP adequately. This can be accomplished by increasing slit width and so obtaining sufficient energy to allow meaningful measurement of the SRP after the monochromatic energy has been removed by the SRP filter. However, some instruments automatically increase sensitivity by increasing dynode voltages of the photomultiplier detector. This is particularly true of high-end double monochromator instruments in their ultraviolet and visible ranges. A further reason for increasing energy or sensitivity can be that many instruments have only absorbance scales, which obviously do not extend to zero transmittance. Even a SRP-proportion as large as 1 % may fall outside the measurement range.

NOTE 3—Instruments that have built-in optical attenuators to balance sample absorption may make relatively inaccurate measurements below 10 % transmittance, because of poor attenuator linearity. The spectrophotometer manufacturer should be consulted on how to calibrate transmittance of the attenuator at such lower level of transmittance.

1.5 High accuracy in SRP measurement is not always required; a measurement reliable within 10 or 20 % may be sufficient. However, regulatory requirements, or the needs of a particular analysis, may require much higher accuracy. Pains-taking measurements are always desirable.

1.6 *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

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

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology **E131**.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *absorption edge*—of a sharp cutoff filter: the wavelength interval over which the transmittance changes rapidly from high to very low (that is, less than 0.01 %).

3.2.1.1 *Discussion*—The bandpass transmittance filters used in some spectrophotometers to reduce SRP within their bandpass are considered to have both a short wavelength and a long wavelength absorption edge. The rate of change of transmittance in the absorption edge may not be as fast as for sharp cutoff filters.

3.2.2 *blocked-beam spectrum*—a spectrum recorded with an opaque (that is, transmittance less than 0.001 %) object in the sample beam; the level of opacity must exist over the range of wavelengths where the photodetector is sensitive.

3.2.3 *corrected spectrum*—the transmittance (absorbance) spectrum of a SRP filter after the measured spectrum has been adjusted for the offset of the open-beam spectrum and (transmittance mode) of the blocked-beam spectrum.

3.2.4 *cutoff wavelength (wavenumber)*—the wavelength (wavenumber) at which the transmittance of a sharp cutoff filter is 0.01 %.

3.2.5 *filter, longpass*—an optical filter having high transmittance at wavelengths longer than its absorption edge.

3.2.6 *filter, moderately narrow bandpass SRP-blocking*—a filter used to reduce remote SRP by transmitting efficiently over a limited band of wavelengths within a nominal wavelength range of a spectrophotometer.

3.2.7 *filter, narrow blocking-band*—an optical filter having high transmittance at shorter and at longer wavelengths than a narrow band within which the transmittance is very low (that is, less than 0.001 %).

3.2.8 *filter, narrow transmission band*—an optical filter having very low transmittance at shorter and longer wavelengths than those of a narrow band within which some transmittances exceed 10 %.

3.2.9 *filter, neutral (also, neutral density: ND)*—a filter that attenuates the radiant power reaching the detector by the same factor at all wavelengths within a prescribed wavelength region.

3.2.10 *filter, opaque*—an optical filter that has transmittances less than 0.01 % over a specified band of wavelengths.

3.2.11 *filter, sharp cutoff*—an optical filter that has a very rapid transition in wavelengths (wavenumbers) from a state of high transmittance to a state of very low transmittance (that is, less than 0.001 %) and that continues in that low transmittance state to at least the end of the spectral region that is being tested.

3.2.12 *filter, shortpass*—a sharp cutoff filter having a high transmittance at wavelengths shorter than its absorption edge.

3.2.13 *filter, SRP*—a test filter for determining SRPR.

3.2.14 *limiting transmittance (absorbance)*—the minimum transmittance (maximum absorbance) of the SRP filter that is observed in the SRPR test; the transmittance (absorbance) indicated when the spectral curve levels off or starts to increase (decrease).

3.2.15 *near SRP*—stray radiant power of wavelengths (wavenumbers) within several spectral bandwidths from the spectral position of the spectrophotometer (**3**).

3.2.16 *open-beam spectrum*—the spectrum recorded with no attenuating medium in the sample beam.

3.2.17 *passband—of a monochromator*, the band of wavelengths around the spectral position of the monochromator that are preferentially transmitted; *of a sharp cutoff filter*: the wavelength region of high transmittance of the filter.

3.2.18 *remote SRP*—stray radiant power of wavelengths (wavenumbers) more than several spectral bandwidths from the spectral position of the spectrophotometer (**3**).

3.2.19 *specified wavelength (wavenumber)*—the wavelength (wavenumber) specified by the manufacturer of a spectrophotometer (or by the spectroscopist) as that at which the SRPR is stated (or measured).

3.2.20 *SRP*—stray radiant power.

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* volume information, refer to the standard's Document Summary page on the ASTM website.

TABLE 1 Filters for Tests for Stray Radiant Power Ratio

Cutoff Wavelength, Wavenumber ^A	Transmittance, ^B 80 % Wavelength or Wavenumber	Filter ^C	Source ^D	Detector ^E
A. Sharp Cutoff Types				
173.5 nm	183 nm	0.01 cm H ₂ O ^F	UV	UV
183.5 nm	195 nm	1.00 cm H ₂ O ^F	UV	UV
200 nm	214 nm	1.00 cm 12 g/L KCl aqueous ^F	UV	UV
223 nm	232 nm	1.00 cm 10 g/L NaBr aqueous ^F	UV	UV
259 nm	271 nm	1.00 cm 10 g/L NaI aqueous	UV	UV
259 nm	271 nm	1.00 cm 10 g/L KI aqueous	UV	UV
325 nm	339 nm	1.00 cm acetone	UV	UV
385 nm	420 nm	1.00 cm 50 g/L NaNO ₂ aqueous	VIS	UV
1200 cm ⁻¹	2800 cm ⁻¹	2.0-mm fused silica ^G (2)	IR	IR
800 cm ⁻¹	1760 cm ⁻¹	6 mm LiF	IR	IR
600 cm ⁻¹	1240 cm ⁻¹	6 mm CaF ₂	IR	IR
400 cm ⁻¹	1030 cm ⁻¹	6 mm NaF	IR	IR
250 cm ⁻¹	650 cm ⁻¹	6 mm NaCl	IR	IR
200 cm ⁻¹	420 cm ⁻¹	6 mm KBr	IR	IR
B. Passband Filters				
Approximate Stop Band	...	1.00 cm 0.005 % (mass fraction) methylene blue aqueous ^H	VIS	VIS or NIR
600 to 660 nm	...	5.0 cm CH ₂ Br ₂ ^I	NIR	NIR
1.66 to 1.75 μm	...			

^A The wavelength (or wavenumber, for infrared range) gives 10⁻⁴ transmittance point.

^B Transmittance value not corrected for reflection loss.

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

^D Under "source" is tabulated the usual and appropriate source for each spectral range.

^E Considerable flexibility in detectors selected is common.

^F Apparent absorbance is strongly affected by dissolved oxygen. Bubble pure nitrogen through liquid for several minutes immediately before use. Use only recently distilled (not demineralized) water. Alternatively, use commercially available solution-in-sealed-cuvette filters.

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

^H Passes blue to yellow light efficiently. The 0.005 % (mass fraction) methylene blue solution must be made up freshly from a 0.5 % (mass fraction) stock solution in 2 % (mass fraction) KH₂PO₄, preserved with 0.002 % (mass fraction) phenylmercuric acetate solution. User should test performance, which may vary with source of the chemicals.

^I Passes from ultraviolet to 1.5 μm radiant power efficiently, except for a narrow, intense band at 1.4 μm, which is suitable for "nearby stray" evaluation in NIR grating monochromators. Users should test performance, which may vary with source of the chemicals.

3.2.21 SRPR—stray radiant power ratio.

3.2.22 *stray light*—the term used in much technical and manufacturer's literature to represent either SRP or SRPR.

4. Summary of Test Method

4.1 The following test procedures are written for spectrophotometers that have provision for recording (that is, for 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. The data sets to be collected are: (1) open-beam spectrum: 100 % transmittance or zero absorbance; (2) blocked-beam spectrum: 0 %T, transmittance mode only; and (3) SRP filter spectra. Filter spectra are assumed to have been corrected in the following discussion.

NOTE 4—For instruments that lack digital recording capability, traditional methods of correcting open-beam and blocked-beam spectra must be applied.

4.2 Specified Wavelength Method:

4.2.1 Manufacturers typically specify stray light, meaning SRPR, at one or more wavelengths. Where sharp cutoff SRP filters are used, the specified wavelengths should be near, but a little toward the lower transmittance side, of the cutoff wavelength of the chosen SRP filter. Other wavelengths can be specified by the spectroscopist, according to the need of particular analyses, using sharp cutoff filters listed in Table 1 or

sharp cutoff filters that are now available from various manufacturers and distributors.⁴ Cutoff wavelengths of some solution filters for the ultraviolet and cutoff wavenumbers of some solid filters for the mid-infrared are given in Table 1. Where narrow blocking-band filters are used, the filters themselves define the specified wavelength.

NOTE 5—In some cases, manufacturers state SRPR at a wavelength well removed from the cutoff wavelength of the cited SRP filter. This can result in an appreciable underestimate of the true SRPR at the specified wavelength. Users are cautioned to note carefully the specific information provided about the test used to determine the stated SRPR.

4.2.2 The SRP filter materials are selected for sharp cutoff, freedom from fluorescence, and sufficiently high absorption that their transmittance in the stop band can be neglected. Liquid (solution) filters should be visually clear and free of bubbles; cuvette windows should be free of striae. SRP will then set the limit to the minimum transmittance (maximum

⁴ Sources of solution filters in sealed cuvettes, interference filters, glass filters, neutral density filters, and materials for mid-infrared filters can be found in Annual Buyers Guides of several scientific organizations, in advertisements in trade journals that serve optical and spectroscopic disciplines, in catalogs of suppliers of optical and spectroscopic materials, and by searching the Internet, using concatenations of selected terms: filter, optical, stray light, color, absorbing, solution (or liquid) cuvette, spectrophotometer cell, interference, cutoff, sharp cut, longpass, shortpass, bandpass, neutral density; for mid infrared materials: infrared cells, infrared crystals, infrared accessories, fused silica.

absorbance) observed, unless an adverse signal-to-noise ratio or limiting dynamic range of the spectrophotometer intervenes.

4.2.3 Open-beam, blocked-beam (zero % transmittance), and SRP filter spectra are recorded over the nominal wavelength range of the spectrophotometer in which the specified wavelength lies, and the filter spectrum is corrected (automatically, in the case of some instruments). The limiting transmittance (absorbance), indicated by the leveling off or increase (decrease) of the transmittance (absorbance) spectrum, is adjusted for the transmittance of the SRP filter in its high transmittance passband. This result is the estimated SRPR. (If SRP is small enough that the limiting transmittance (absorbance) is not observed, see 4.2.4.)

NOTE 6—For a single monochromator instrument, inspection of the spectral curve may show, by where the transmittance (absorbance) levels off or starts to rise (fall), the wavelength limit of reliable use of the instrument. That limit might be set by SRP or by other instrumental limitations (for example, dynamic range).

4.2.4 SRP in double monochromator instruments is too small for the limiting transmittance to be observed without using increased reference attenuation. This is accomplished by inserting a calibrated neutral filter into the reference beam of a double beam spectrophotometer and recording the spectrum of the SRP filter. It might be necessary to increase slit width in order to obtain an acceptable signal-to-noise ratio (S/N). For a single beam spectrophotometer, the spectrum of the neutral filter is recorded and used as a divisor of the corrected test filter spectrum (this will succeed only if the dynamic range of instrument is adequate).

NOTE 7—Electronic scale expansion may be used, provided that the S/N is acceptable.

4.3 Solution Filter Ratio Method:

4.3.1 This method (4) uses a solution filter from Table 1, Part A, and so is intended for testing only in the ultraviolet range of a spectrophotometer. The sample beam filter is a 10-mm pathlength cuvette containing the solution, and the reference beam filter is a 5-mm pathlength cuvette containing the same solution. Alternatively, the reference beam filter can be a 10-mm pathlength cuvette containing the solution diluted to one-half concentration. This test can be performed with a single beam instrument by recording the two solution filter spectra sequentially and calculating their ratio. However, this will not provide the benefit of reducing the needed dynamic range of the instrument that is gained by the double beam measurement.

5. Significance and Use

5.1 Stray radiant power can be a significant source of error in spectrophotometric measurements. SRP usually increases with the passage of time; therefore, testing should be performed periodically. Moreover, the SRPR test is an excellent indicator of the overall condition of a spectrophotometer. A control-chart record of the results of routinely performed SRPR tests can be a useful indicator of need for corrective action or, at least, of the changing reliability of critical measurements.

5.2 This test method provides a means of determining the stray radiant power ratio of a spectrophotometer at selected wavelengths in a spectral range, as determined by the SRP filter

used, thereby revealing those wavelength regions where significant photometric errors might occur. It does not provide a means of calculating corrections to indicated absorbance (or transmittance) values. The test method must be used with care and understanding, as erroneous results can occur, especially with respect to some modern grating instruments that incorporate moderately narrow bandpass SRP-blocking filters. This test method does not provide a basis for comparing the performance of different spectrophotometers.

NOTE 8—Kaye (3) discusses correction methods of measured transmittances (absorbances) that sometimes can be used if sufficient information on the properties and performance of the instrument can be acquired. See also A1.2.5.

5.3 This test method describes the performance of a spectrophotometer in terms of the specific test parameters used. When an analytical sample is measured, absorption by the sample of radiation outside of the nominal bandpass at the analytical wavelength can cause a photometric error, underestimating the transmittance or overestimating the absorbance, and correspondingly underestimating the SRPR.

5.4 The SRPR indicated by this test method using SRP filters is almost always an underestimation of the true value (see 1.3). A value cited in a manufacturer's literature represents the performance of a new instrument, tested exactly in accordance with the manufacturer's specification. The implication is that the manufacturer's stated SRPR can serve as a benchmark for future performance, provided that the user performs the manufacturer's specified test. It is recommended that users test new instruments promptly, thereby establishing a comparative benchmark in terms of their own testing facilities. The solution filter ratio method (4.3) is a convenient method for control-charting SRPR. Mielenz, et al., (4) show that its results tend to correlate well with those of the specified wavelength method, but for critical comparison with the manufacturer's specification, the method used by the manufacturer must be used. Because some instruments reduce SRP by incorporating moderately narrow bandpass SRP-blocking filters that are changed as the wavelength range is scanned, it is possible for SRPR determinations to be highly inaccurate if the cutoff wavelength of the SRP filter falls too close to the absorption edge of an instrument's SRP-reducing filter (3).

6. Apparatus and Materials

6.1 Liquid cells for the ultraviolet should have low fluorescing fused silica windows; those for the visible and near infrared may be of less expensive glass. Neutral filters must be approximately constant in transmittance over the full wavelength range of the photodetector's sensitivity; that is, for ultraviolet and visible testing, from the shortest usable wavelength in the ultraviolet to the long wavelength end of the visible range. Recommended neutral (neutral density, ND) filters are the "metal-on-quartz" type, that is, evaporated metal on fused silica substrate. Recommended optical densities are 1.0, 2.0, and 3.0. It should not be necessary to stack neutral filters to have optical densities greater than 3.0. If stacking must be done, separate these highly reflecting filters and tilt them slightly to avoid multiple reflection into the beam path.

6.2 *SRP Filter Materials*, such as shown in **Table 1**, provide an array capable of covering nearly all normal ultraviolet and infrared spectral ranges. The first column shows the cutoff wavelength (wavenumber). The test wavelength to be used with any given SRP filter will depend on the design and performance of the instrument under test, and so must be determined empirically (**Note 3**). The test wavelength shall be that at which the true transmittance of the SRP filter becomes a negligibly small fraction of the observed transmittance (**Notes 5 and 6**). The second column (**Table 1**) shows the approximate 80 % transmittance wavelength or wavenumber. Scanning for the following procedure should always begin at this point, or at one more remote from the test spectral range.

NOTE 9—Once the test wavelength has been established for a SRP filter and an instrument of any given design, the test is applicable to all instruments of the same design.

NOTE 10—The true transmittance of a SRP filter can be determined by measuring the spectrum of a dilute solution or a thin specimen of the SRP filter material and using Beer’s law to extrapolate the transmittance to the concentration or thickness employed in the test for SRPR.

NOTE 11—For testing grating spectrophotometers that use moderately narrow bandpass SRP-blocking filters, use a SRP filter that cuts off sharply at a wavelength as near as possible to the edge of the bandpass of the instrument’s SRP-blocking filter that is normally in the beam at the designated wavelength, if known. If necessary, consult the manufacturer, or test in accordance with the manufacturer’s stated method. In any case, it is strongly recommended that the test wavelength itself be as close as possible to the transmission cutoff of the SRP filter in order to minimize absorption of SRP by the test filter.

6.2.1 SRP filters (and analytical samples) should be large enough to cover the entire cross-sectional area of the optical beam with a substantial safety margin. Radiation scattered in the sample compartment can sometimes bypass the SRP filter (analytical sample), re-enter the optical beam, and reach the photodetector. If the determined SRPR appears to be large enough to bias a measurement significantly, use an opaque mask in the sample compartment that intercepts any bypassing radiation, to test for this source of SRP.

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

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

6.2.4 *Fused Silica*, in the form of cell windows, is commonly available and is useful over a range of thickness of 1-mm to 6-mm. Crystal quartz should not be used because of its birefringence, which may cause apparent cyclical transmittance variations with wavelength.

7. Hazards

7.1 Narrow blocking-band filters, referenced for use in **A1.2.2**, using benzene and, as described by Tunnicliff (**6**), hot mercury vapor, should be handled with proper precaution.

8. Procedure

8.1 *Specified Wavelength Method:*

8.1.1 Record an open-beam (100 % transmittance or zero absorbance) and a blocked-beam (0 % transmittance spectrum in the transmittance mode) over the nominal wavelength range of the spectrophotometer that includes the specified wavelength.

8.1.2 Insert the SRP filter into the sample beam (and, optionally, a blank solution in the reference beam⁵).

8.1.3 For a single monochromator instrument, record the SRP filter spectrum. Correct it with stored open-beam and zero transmittance spectra. Inspect the spectral curve for indication of a limiting transmittance (absorbance). If such be present, calculate the SRPR. Otherwise, proceed per **8.1.4**.

8.1.4 For a double monochromator instrument (and a very low SRP single monochromator instrument), insert into the reference beam a “neutral” beam attenuator, that is, a neutral filter (or a built-in optical attenuator, for example, a perforated metal screen) of which the transmittance at or near the specified wavelength of the test is known. Record the spectrum of the SRP filter and correct it. If necessary to have adequate S/N, increase the slit width and repeat the measurement.

NOTE 12—As indicated in **Annex A4**, the change in slit width may change the value of SRP.

8.2 *Solution Filter Ratio Method:*

8.2.1 Record the open-beam and blocked-beam (0 % transmittance) spectra per **8.1.1**.

8.2.2 Select a solution from **Table 1** that has a cutoff wavelength at or near the desired wavelength for the test.

8.2.3 Insert into the sample beam of the spectrophotometer a 10-mm pathlength cuvette filled with the solution. Insert into the reference beam a 5-mm pathlength cuvette filled with the same solution. (Alternatively, use in the reference beam a 10-mm pathlength cuvette filled with the solution diluted to one-half concentration.)

8.2.4 Record the solution filter ratio spectrum and correct it.

8.3 *Mid-Infrared Testing:*

8.3.1 Proceed as per **8.1** for the specified wavelength method, using SRP filters from **Table 1** for the mid infrared range.

NOTE 13—To qualify the instrument for a particular application, it is usually only required that the SRPR fall below a given value. It is then, of course, not necessary to use greater reference beam attenuation beyond the point required to demonstrate compliance.

9. Calculation

9.1 For the Specified Wavelength Method, calculate the SRPR as the product of the limiting transmittance at the desired wavelength times the transmittance of the reference beam

⁵ A paired set of sealed cuvettes, viz., KI solution per **Table 1** as the SRP filter, and a water blank for the reference beam, is available commercially.

attenuation, divided by the transmittance of the SRP filter in its high transmittance wavelength band (about 0.90, resulting from surface reflection losses). Calculate SRPR with the observed limiting transmittance (absorbance), the transmittance (absorbance) of the reference beam attenuation, the transmittance (absorbance) of the SRP filter's high transmittance band, and incorporate the corrections with the open beam and blocked beam spectra (Eq 1 and 2).

$$SRPR = [(T_L - T_{BB})(T_{RA} / T_{High})] / [T_{OB} - T_{BB}] \quad (1)$$

$$SRPR = \text{Antilog}_{10} [(-)(A_L + A_{RA} - A_{High} - A_{OB})] \quad (2)$$

where:

$T_L (A_L)$ = observed limiting transmittance (absorbance),

$T_{RA} (A_{RA})$ = transmittance (absorbance) of the reference beam attenuation,

$T_{High} (A_{High})$ = transmittance (absorbance) of the SRP filter in its high transmittance band. (If a blank solution is used in the reference beam, set $T_{High} = 1$; $A_{High} = 0$),

$T_{OB} (A_{OB})$ = open-beam transmittance (absorbance), and

$T_{BB} (A_{BB})$ = blocked-beam transmittance (absorbance).

9.2 For the Solution Filter Ratio Method:

$$SRPR = 0.25 T_i^2 [(T_L - T_{BB}) / (T_{OB} - T_{BB})]^2 \quad (3)$$

$$SRPR = 0.25 T_i^2 \text{Antilog}_{10} [-2 (A_L - A_{OB})] \quad (4)$$

where:

T_L = observed minimum transmittance, and A_L is the observed maximum absorbance, and

T_i = net transmittance through the cuvette interfaces (two silica-air, and two silica-solution).

9.2.1 Eq 3 and 4 differ from their prototypes in (4) because, (a) account is not taken there of possible need for T_{OB} and T_{BB} corrections, and (b) it is assumed that the transmittance of the solution filter in the reference beam is exactly equal to the square root of the that of the solution filter in the sample beam. This is the case for the transmittances of the solutions, themselves, but account must also be taken of the fact that there are reflectance losses at each of the four interfaces of the two cell windows, as is done in Eq 3 and 4.

9.2.2 Suitable values for T_i^2 are 0.83 (200 nm – 250 nm), 0.84 (250 – 300 nm), 0.85 (300 nm – 350 nm), and 0.86 ($\lambda > 350$ nm).

10. Report

10.1 Report the identification of the spectrophotometer, the date of the SRPR test, the SRPR test used, the SRP filter used, the reference beam attenuator(s) used and the net transmittance

(absorbance) of reference beam attenuation, the observed limiting transmittance (absorbance), the wavelength at which the SRPR was determined, and the value of the SRPR obtained.

11. Precision and Bias

11.1 High accuracy is not always required for SRPR determinations, and no estimate of the precision that is achieved in using this test method ordinarily is needed or useful. However, where regulatory or Quality Assurance requirements demand the formal establishment of an Uncertainty Budget for the procedure, the spectroscopist must determine precision by the usual method of multiple replications of the SRPR measurements, considering all of the relevant operational variables. These variables may include temperature, filter rotation, etc. Although bias can be appreciable, figures on it can't be given, as bias will vary greatly with such things as the design of the instrument, the wavelengths chosen for testing, the materials available for use in performing the test, and the care expended in performing the test. These problems are treated at various places in the text and in the references (1-3). Where high accuracy is mandated, only a research grade double monochromator instrument should be relied upon. A control-chart record showing the initial comparison with the manufacturer's specification and the results of periodic re-testing should be of great value toward minimizing the uncertainty of bias.

12. Illustrative Examples

12.1 Fig. 1 shows transmittance spectra recorded for the Specified Wavelength Method and for the Solution Filter Ratio Method. The SRP filter is KCl in aqueous solution (see Table 1). The spectrophotometer used is a Perkin-Elmer Lambda 900, which automatically calculates and displays spectra corrected for open-beam and blocked-beam offsets. It also adjusts automatically for the transmittance of the SRP filter in its high transmittance band (Specified Wavelength Method). This spectrophotometer has a built-in optical attenuator for the reference beam. A displayed transmittance spectrum has the reference beam attenuation automatically incorporated into the indicated transmittance values. Because the spectra shown in Fig. 1 are fully corrected:

$$\text{Specified Wavelength Method:} \quad (5)$$

$$SRPR = 1.0 \times 10^{-6} = 1.0 \times 10^{-6}, \text{ at } 200.0 \text{ nm}$$

$$\text{Solution Filter Ratio Method:} \quad (6)$$

$$SRPR = 0.25 \times 0.83 (2.3 \times 10^{-3})^2 = 1.1 \times 10^{-6}, \text{ at } 201.8 \text{ nm}$$

13. Keywords

13.1 molecular spectroscopy; spectrophotometry; stray light; stray radiant power; SRP; stray radiant power ratio; SRPR