Designation: E 387 – 04

Standard Test Method for Estimating Stray Radiant Power Ratio of Dispersive Spectrophotometers by the Opaque Filter Method[1]

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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 E 275.

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. Painstaking 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]

E 131 Terminology Relating to Molecular Spectroscopy

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers

3. Terminology

3.1 *Definitions*:

3.1.1 For definitions of terms used in this test method, refer to Terminology E 131.

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

[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_2O[F]	UV	UV
183.5 nm	195 nm	1.00 cm H_2O[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 600 to 660 nm	...	1.00 cm 0.005 % (mass fraction) methylene blue aqueous[H]	VIS	VIS or NIR
1.66 to 1.75 mm	...	5.0 cm CH_2Br_2[I]	NIR	NIR

[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 CaF_2 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) KH_2PO_4, 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.

spectrophotometer (or by the spectroscopist) as that at which the SRPR is stated (or measured).

3.2.20 *SRP*—stray radiant power.

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.

[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.

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 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 beam[5]).

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:

Specified Wavelength Method: (5)

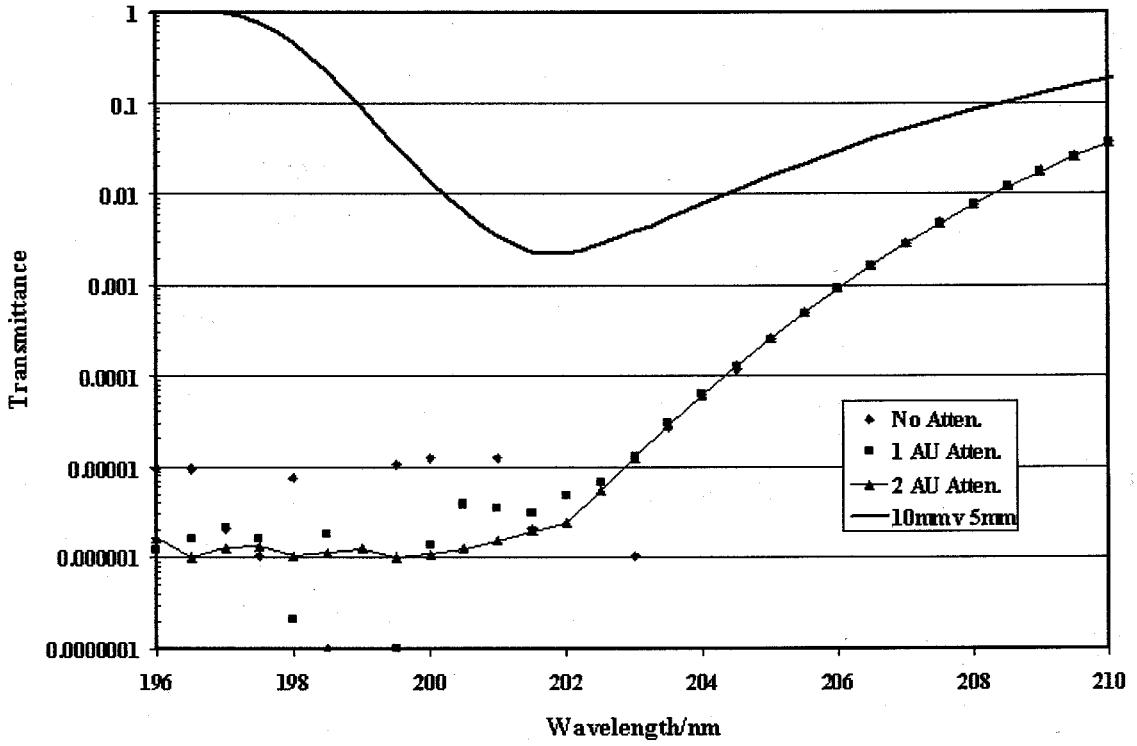
$$SRPR = 1.0 \times 10^{-6} = 1.0 \times 10^{-6}, \text{ at } 200.0 \text{ nm}$$

Solution Filter Ratio Method: (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



Specified Wavelength Method: $SRPR = 1.0\times10^{-6}$ at 200.0 nm
Solution Filter Ratio Method: $SRPR = 1.1\times10^{-6}$ at 201.8 nm

FIG. 1 SRPR Test by the Specified Wavelength Method and by the Solution Filter Ratio Method, Using a Solution of KCl with a Spectrophotometer with Grating Double Monochromator (Perkin-Elmer 900)

ANNEXES

(Mandatory Information)

A1. GENERAL CONCEPTS

A1.1 Stray radiant power ratio in a spectrophotometer is difficult both to define and to measure. It is often defined as the proportion of transmitted radiant power of wavelengths outside the nominal passband of the monochromator to the total power transmitted. However, since only signal-producing radiant power is significant, it is obvious that the relevant measure is the integral of the product of power and detector sensitivity over all wavelengths except the passband, divided by the corresponding total. In practice it is impossible to make the test conform exactly to this definition, so a more empirical definition, based upon an accepted test procedure, such as that described herein, must be used.

A1.2 For absorption spectrophotometers, the definition and measurement problems are difficult. SRP is not uniquely a function of the monochromator itself, but varies with the spectral distribution of the source and of the detector sensitivity, and with other factors discussed below. Also, suitable test materials are scarce. The ideal filter for measuring SRP would have intense absorption over a spectral region of adjustable nominal wavelength and bandwidth, and negligible absorption at other wavelengths. Such absorbers do not exist. One takes advantage of absorption edges such as those seen with alkali halide crystals, certain liquids, and sharp cutoff glass filters, and supplements these by finding a variety of substances having narrow, intense absorption bands. There are spectral regions for which no fully satisfactory filter material has been proposed.

A1.2.1 The tests herein are of limited scope because sharp cutoff filters transparent for the ultraviolet but absorbing in the visible, or transparent in the lower frequency infrared but absorbing higher frequencies, are not in general available. Fortunately, the available filters, from which a recommended set was selected, usually suffice to disclose significant SRP of remote wavelengths. This is because SRP caused by gross scattering arises principally from spectral regions where detector sensitivity and source intensity are high, and such sharp cutoff filters transmit efficiently these regions. If, however, there is any reason to suspect the presence of SRP of wavelengths within the stop band of the filter, for example when a grating is used in second order in the higher frequency

infrared and the stray might be of first order frequency, or if Beer's law departures are observed when preparing calibration curves **(5)**, the following supplemental test should be used:

A1.2.1.1 Obtain a filter that transmits efficiently all wavelengths within the desired monochromator pass band, but rejects the frequencies outside this band that might be causing trouble. Interference filters having suitable characteristics are commercially available for the infrared, visible, and near ultraviolet ranges. Measure the absorbance of samples with and without the filter, setting the zero absorbance level also with and without the filter, respectively. Appreciable differences of measured absorbance, especially at high sample absorbance, indicate trouble from SRP. Samples should then be measured with the narrow band filter in the beam, or filters effective for rejecting the SRP can be employed (see A1.2.7). This test is recommended only as a supplement because of high cost for the array of test filters if it is to be applied for general instrument evaluation, as well as the large amount of testing time required. It is nevertheless strongly recommended for critical applications.

NOTE A1.1—Selected pairings of sharp cutoff shortpass and longpass filters can be combined to make narrow transmission band filters at visible and near infrared wavelengths. Sets of such filters are commercially available.

A1.2.2 Depending on the particular measurement to which the instrument is to be applied, one may be concerned only with SRP of relatively remote wavelengths, or may find so-called "nearby scattering" (sometimes defined as radiant power outside the pass band but within several bandwidths of the nominal wavelength), of significance. For example, measurements of aromatic compounds in the gas phase may impose very strict requirements on scattering of wavelengths adjacent to those absorbed **(6)**. A monochromator entirely suited for liquid-phase measurements on the same compounds might give highly erratic and inaccurate measurements in the gas phase application.

A1.2.3 Because of these considerations, it is not practical to specify SRP in an absorption spectrophotometer in absolute terms. Nevertheless, test procedures have been developed that give definite values: ones that are valid for certifying the suitability of a particular monochromator or spectrophotometer for most of the important applications. SRPR is then defined as the fraction of the total power that is contributed by wavelengths different from those of the spectral band passed by the monochromator, as indicated by the test.

A1.2.4 SRP, if present in significant amounts, is dangerous because it is often unsuspected. With the passage of time, increasing SRP frequently accompanies gradual deterioration of the optics in a spectrophotometer. Thorough testing annually is recommended, with more frequent testing for certain critical applications.

A1.2.5 It is not the intention of this test method to provide for calculating corrections to indicated absorbance values, and to do so using results obtained from this test method is inadvisable. Having a value of SRPR is insufficient: in order to calculate a correction for the absorbance error caused by SRP, one must know the spectral distribution of SRP, the absorption spectrum of the sample, and the spectral response of the detector. Without such full knowledge, even the sign of the error is not known. If, for instance, a sample absorbs more (less) strongly at wavelengths where SRP is large, than it does at the measurement wavelength band, the effect of SRP is to increase (decrease) the indicated absorbance value.

A1.2.6 For situations in which the sample does not absorb in the spectral region over which the SRP is distributed, Slavin **(1)** shows a plot of absorbance error versus absorbance. While it may seem too obvious to mention, it must be realized that the relative error in absorbance is in this case larger than the SRPR. Small relative errors in absorbance (A) are given by the following equation:

$$\Delta A/A = [-0.434(10^{A})s]/A \ldots \quad \text{(A1.1)}$$

where s is the fraction of SRP to power within the nominal pass band (i.e. the SRPR). For example, if the fraction of SRP is 0.001 for a measurement made at an absorbance of 1.5, the relative error in absorbance is - 0.0091, or about nine times the proportion of stray to monochromatic radiant power.

A1.2.7 Optical filters can be used to reduce SRP. Most modern spectrophotometers incorporate "blocking filters" for this purpose, and make filter changes automatically at appropriate wavelengths. Some instruments have filters built-in, but require the operator to make filter changes manually. If desired, the spectroscopist can provide an appropriate SRP-blocking filter. For example, a Schott Glass Type UG-5, 3.0-mm thick polished filter is useful for work between 260 and 380 nm.

A2. TEST MATERIALS

A2.1 Sharp cutoff filters are the most generally available for SRPR evaluation. As indicated in A1.2.1, SRP caused by random scattering within the monochromator is principally of longer wavelengths when instruments are used in the ultraviolet, and of shorter wavelengths when instruments are used in the infrared. Fortunately, sharp cutoff filters having high transmission efficiencies in the wavelength regions principally responsible for SRP, are available in both instances.

NOTE A2.1—This section (A2.1) is not applicable to filter-grating instruments that incorporate SRP-blocking filters.

A2.2 Glass filters for ultraviolet use can be valuable because of their convenience, but they must be used with caution, because most glasses exhibit significant fluorescence **(7)**. Photodetectors used in the ultraviolet and visible regions are generally more sensitive to the fluorescent wavelengths than to the short ultraviolet wavelengths that excite fluorescence efficiently. If the apparent SRPR is found to be increased by locating the filter close to the photodetector, or is decreased

by preceding the glass filter with a solution filter of slightly shorter wavelength cutoff, glass fluorescence may be limiting the SRPR readings. For less exacting applications, and for tests on single monochromators, glass filters are very useful and convenient. Since different batches of glass may exhibit different degrees of fluorescence, glass filters should be tested individually. Moderately sharp cutoff, and a moderately narrow bandpass, glass filters are useful for SRP-reduction in the region from 700 to 1000 nm.

A2.3 Sharp cutoff solution filters have been investigated by several workers **(2,8)**.

A2.4 Filters for reducing mid infrared SRP have been mainly of two types: scatter filters **(8,9)**, including grating filters **(10)**, and thin film interference filters **(11)**.

A2.5 In certain cases, narrow blocking-band absorbers have proved useful for evaluating scattering of both nearby and remote wavelengths. Examples are the most intense bands in the benzene vapor spectrum near 260 nm, hot mercury vapor at 254 nm **(6)**, and polystyrene films at 13.3 and 14.4 mm. Other substances found useful are 1-cm pathlength of 0.005 % (mass fraction) aqueous solution of methylene blue, near 650 nm, and 5-cm pathlength of methylene bromide liquid at 1.43 mm. Of course, the bands used must be well resolved in order to give reproducible results. Because of large variations in resolution between commercial instrument models, no general methods based on such bands can be recommended.

A3. STRAY RADIANT POWER AS AFFECTED BY OPTICAL SYSTEM DESIGN

A3.1 No part of the optical system of a spectrophotometer is completely free of influence on SRP. For example, masks on the source side of the monochromator will reduce SRP if located optically conjugate to the aperture stop of the monochromator and made slightly smaller than the aperture stop image traced by reversed rays. In this way, illumination of the mask that defines the aperture stop inside the monochromator is limited so that diffraction or scattering from mask edges and mask surface imperfections is lessened. Similarly, in the beam between the monochromator and the detector, a mask conjugate with the monochromator aperture stop (if such a position exists) will trap radiant power that may be scattered within the monochromator and that passes through the exit slit from some region other than the area of the aperture stop whence the monochromatic radiant power is intentionally passed to the external optics.

A3.2 Within the monochromator itself, a critical consideration is the freedom from scattering imperfections of the optical elements, and the surface perfection of mirrors, lenses, and dispersing elements. Even with the best techniques for polishing optical surfaces, departures from perfect smoothness occur **(12)**, and in prism monochromators are principally responsible for the small-angle deviations of the emergent beams which are responsible for “nearby scattering,” or tailing off of the slit function of the monochromator.

A3.3 Even if the first optical elements within the monochromator and the entering aperture stop are not overfilled, the process of dispersion causes rays to be deviated in such a way as to illuminate much of the interior of the monochromator with energetic radiation. In a monochromator in which the off-axis angle of a collimator is too small, radiant power can be returned from the collimator to the dispersing element and after again being dispersed can fall by specular paths directly on the exit slit. This is often called “double dispersion” or “secondary dispersion”. The best remedy is to increase the off-axis angle of the collimator, if the resulting aberrations can be tolerated. If not, such specular ray paths may be interrupted by judiciously masking off a part of the aperture stop, often without excessive loss of monochromator transmission efficiency. If this problem is ignored, it can easily turn out that it produces significant SRP only over a narrow spectral region, so that a monochromator that gives excellent tests for SRPR over much of its working region, and possibly in all regions where such tests are easily made, may be seriously deficient over some particular narrow spectral range.

A3.4 An advantage of the Czerny-Turner or Wadsworth-type monochromators over the Littrow monochromator is that only a part of the dispersed radiant power falls on the exit collimator. The flux density on this mirror is therefore less than one half that of the Littrow arrangement, and its scattering imperfections produce a correspondingly reduced amount of trouble.

A3.5 Grating monochromators in general transmit efficiently other orders than the intended order. This source of SRP is troublesome in the infrared, since it leads to relatively efficient transmission of a number of wavelengths at which usual sources emit strongly and detectors are sensitive **(12)**. It is especially troublesome when the grating is operated near the blaze angle, where quite narrow, easily overlooked bands of SRP may arise.

A3.6 The interference filters that are commonly used for SRP reduction in infrared grating monochromators may have “spike” leaks, which can cause very serious narrow band SRP problems. Higher orders of SRP can also be efficiently transmitted by an “order sorting” prism monochromator in tandem with the grating monochromator if the prism monochromator is operated under such low resolution conditions that more than one order falls within its spectral pass band.

A3.7 Another often-overlooked source of SRP in a spectrophotometer is fluorescence from the absorption cell or sample itself. It is entirely possible to set up conditions under which a solution can show apparent negative absorption because of the higher sensitivity of the detector for the fluorescence radiant power generated on absorption of the ultraviolet energy, than for the monochromatic radiant power itself. Glass or solution sharp cutoff filters provide a quick test

for such difficulties when located alternately first ahead of the sample, then following it in the optical train. Also, as noted for glass filters themselves, a shift of apparent sample transmittance with a change of its proximity to the photodetector strongly suggests significant fluorescence, although it can also be caused by scattering, beam deflection, or pathlength change.

A3.8 Another source of SRP may be lack of masking in the sample compartment to confine the beam within the sample cuvette. Even if the beam falls well inside the cell windows when examined by the rules of geometrical optics, diffraction at narrow slit widths, or sample turbidity, can cause it to spread so that appreciable radiation is transmitted through the cell walls or otherwise to the detector. A check for the error caused by diffraction can be made with India ink or a similar "total absorber" in the cell.

A3.9 Similarly, a leak past the shutter used for determining instrument zero, or a leak admitting room light, can give erroneous results.

A3.10 Electrical pickup can cause reading errors very similar to those due to SRP. A check can be made by turning off the slit and source and looking for drifts of the photometric scale reading in a recording spectrophotometer, or following procedures given by the manufacturer.

A4. VARIATION WITH SLIT WIDTH AND HEIGHT

A4.1 If the assumption is made that the scattering process follows the Lambert distribution law, it is possible to state a simple theory for the ideal monochromator which allows prediction of the way in which SRPR varies with monochromator slit width and slit height, and which is at least approximately followed in practice. Several cases occur:

A4.1.1 *Single Monochromator with "White" Continuum Source*—The SRPR does not vary with slit width (when the entrance and exit slits are opened and closed simultaneously). The radiant power within the pass band is proportional to the square of the slit width because it is linearly proportional to the width of the entrance slit, which admits radiation to the monochromator, and also to the spectral bandwidth, which also is proportional to the slit width. The SRP too is proportional to the square of the slit width, because it is linearly proportional to the width of the entrance slit, which controls aperture illumination, and also to the width of the exit slit, which affects the solid angle for the transmission of scattered radiation.

A4.1.1.1 Transmission of monochromatic radiant power varies only linearly with slit height, because slit height has negligible effect on bandwidth, whereas SRP varies with the square of the slit height, just as with slit width. The SRPR therefore increases linearly with slit height. (Actually, experiments to confirm this relationship show that, with gratings, the scattering is predominantly in the direction perpendicular to the grating rulings, and the proportion of scattering varies as a fractional power of the slit height.)

A4.1.2 *Single Monochromator with Pure Narrow Line Source*—Ideally, all of the radiant power in a monochromatic line that is admitted by the entrance slit is transmitted by the exit slit when the monochromator is set at the wavelength of the line; thus the monochromatic radiant power is proportional to the entrance slit width and height. When the monochromator is displaced from the nominal wavelength, the intensity of the scattered radiant power is varied by both entrance and exit slit width and height, and thus is proportional to the square of these parameters. The ratio of SRP at remote wavelengths to monochromatic radiant power at the nominal wavelength is proportional to slit width and height.

A4.1.3 *Double Monochromator with Continuum Source*—In the first monochromator section, as indicated in A4.1.1, the proportion of radiant power of the nominal wavelength is independent of the slit width and varies with the first power of slit height. (It is assumed that all slits, including the intermediate slit, are varied in width by the slit control.) The scattered radiation from the first monochromator that is transmitted into the second monochromator is re-scattered by its optical surfaces. The amount emerging varies with the solid angle subtended by the exit slit as viewed from the scattering surface. Hence, it is proportional to both width and height of the exit slit. Thus, the fraction of stray-to-monochromatic power is very much reduced by the second monochromator, and it varies with the slit width and with the square of the slit height. The sensitivity to slit height makes clear the utility of a slit-height control.

A4.1.4 *Double Monochromator with Line Source*—The same argument as for the double monochromator with continuum source applies, except that the monochromatic power varies only with entrance slit height and width. Therefore, the ratio of stray-to-monochromatic radiant power varies with the square of both the slit width and the slit height.

A4.2 Because of these relationships, it is important that tests for SRPR be made in most cases at slit widths and heights representative of those actually used in the application of the instrument. Unfortunately, many published results on SRPR measurements are made with non-typically narrow slits or with shortened slits, or both. It is often easy to arrange test conditions that give SRPR values substantially different from those that would be found under conditions appropriate to applications. Hence, a SRPR given without specifying test procedure is essentially meaningless.

REFERENCES

(**1**) Slavin, W., "Stray Light in Ultraviolet, Visible and Near-Infrared Spectrophotometry," *Analytical Chemistry*, ANCHA, Vol 35, 1963, p. 561.

(**2**) Paulson, R. E., "Test Methods in Spectrophotometry: Stray Light Determinations," *Applied Optics*, APOPA, Vol 3, 1964, p. 99.

(**3**) Mielenz, K. D., Weidner, V. R., and Burke, R. W., "Heterochromatic Stray Light in U.V. Absorption Spectrometry: a New Test Method," *Applied Optics*, APOPA, Vol 21, 1982, p. 3354.

(**4**) Kaye, W. I., "Stray Light Ratio Measurements," *Analytical Chemistry*, ANCHA, Vol 53, 1981, p. 2201.

(**5**) Hogness, T. R., Zscheile, F. P., Jr., and Sidwell, A. E., Jr., "Photoelectric Spectrophotometry. An Apparatus for the Ultra-Violet and Visible Spectral Regions: Its Construction, Calibration, and Application to Chemical Problems," *Journal of Physical Chemistry*, JPCUA, Vol 41, 1937, p. 379.

(**6**) Tunnicliff, D. D., "Measurement of Nearby Stray Radiation in Ultraviolet Spectrophotometry," *Journal of the Optical Society of America*, JOSAA, Vol 45, 1955, p. 163.

(**7**) Turner, W. H., "Photoluminescence of Color Filter Glasses," *Applied Optics*, APOPA, Vol 12, 1973, p. 480.

(**8**) Pfund, A. H., "Infrared Filters of Controllable Transmission," *Physical Review*, PHRVA, Vol 36, 1930, p. 71.

(**9**) Gorton, A. F., "Reflection From and Transmission Through Rough Surfaces," *Physical Review*, PHRVA, Vol 7, 1916, p. 66.

(**10**) White, J. U., "Gratings as Broad Band Filters for the Infra-Red," *Journal of the Optical Society of America*, JOSAA, Vol 37, 1947, p. 713.

(**11**) Wolfe, W. L., Ed., "Handbook of Military Infrared Technology," Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

(**12**) Koehler, W. F., "Multiple Beam Fringes of Equal Chromatic Order. Part VII. Mechanism of Polishing Glass," *Journal of the Optical Society of America*, JOSAA, Vol 45, 1955, p. 1015.