



Designation: E 387 – 84 (Reapproved 1995)^{€1}

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

This standard is issued under the fixed designation E 387; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{€1} NOTE—Section 9 was added editorially in November 1995.

1. Scope

1.1 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 pass band transmitted through the monochromator of an absorption spectrophotometer. Test-filter materials are described that discriminate between the desired wavelengths and those which contribute most to SRP for conventional commercial spectrophotometers used in the ultraviolet, the visible, the near infrared, and the alkali halide infrared ranges. These procedures apply to instruments of conventional design, with usual sources, detectors, and optical designs. The vacuum ultraviolet and the far infrared present special problems that are not discussed herein.

NOTE 1—An equivalent test method (1,2)² for use in the ultraviolet that is easier and faster to perform might be preferred, especially when frequent testing is indicated.

NOTE 2—Recent research (3) has shown that particular care must be exercised in testing grating spectrophotometers that use moderately narrow bandpass blocking filters. See 4.2.

1.2 These procedures are neither all-inclusive nor infallible.³ Because of the nature of readily available filter materials, with a few exceptions the procedures are insensitive to SRP of shorter wavelengths in the ultraviolet or visible, or of lower frequencies in the infrared, and they 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.

1.3 The proportion of SRP (that is, SRPR) encountered with a well-designed monochromator, used in a favorable spectral region, is a small fraction of 1 %. With a double monochromator it may easily be less than 1 ppm even with a broad-band continuum source. Under these conditions, it may be difficult to do more than determine that it falls below a certain level. Actual measurement often 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 is frequently true that, owing to the effect of slit width on SRP in a double monochromator, these test procedures tend to give “conservative” results; that is, because larger slit widths than normal must be used to admit enough energy to the monochromator to permit evaluation of the SRP, the stray proportion indicated is greater than would normally be encountered in use.

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 is usually necessary to increase sensitivity in some way during the test in order to evaluate the SRP adequately. This is usually 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 (test) filter. 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.

1.5 Many instruments that use optical attenuators to balance sample absorption make relatively inaccurate measurements below 10 % transmittance, because of poor attenuator linearity. All instruments should be carefully and frequently checked if used below about 1 % transmittance because of the possibility of zero shift due to electrical pickup or other causes. For these reasons, the test procedure specifies that the measurements be made within 100 % and 10 % on the scale. Obviously this is not required if reliable photometric linearity and zero checks are made under the conditions prevailing during the test, and use of the 10 and 1 % range may give lower and more

¹ This method is under the jurisdiction of ASTM Committee E-13 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 method.

³ Currently in preparation by E13.01 are test methods that reduce the potential for error that occurs when the test-filter absorbs an appreciable portion of the SRP.

accurately representative SRP values. In marginal cases this more elaborate test procedure, incorporating accepted ASTM tests for photometric linearity, may be justified.

1.6 High accuracy in SRP measurement is not required. A measurement reliable within 10 or 20 % is always sufficient, but often many readings must be cascaded to obtain the final result, so that painstaking measurements are desirable.

1.7 *This standard does not purport to address the safety problems 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. Summary of Test Method

2.1 The following test procedure is written for transmittance-recording double-beam instruments. Modification for absorbance recording will be obvious. It is readily adapted for point-by-point operation by measuring at enough points to allow reasonably accurate interpolation between the points so as to provide essentially continuous information over the wavelength region covered, or by direct measurement at the desired specific wavelength.

2.2 After establishing that the instrument is adequately free of zero transmittance error, and measuring the baseline (100 %) over the appropriate spectral range, insert a filter into the sample beam and record its transmittance curve, starting in a region where it is nearly transparent and scanning slowly toward increasing absorption. The filter materials are selected for sharp cutoff, freedom from fluorescence, and sufficiently high absorption that their transmittance in the stop band can be neglected. They should be visually clear and free of bubbles and striae. SRP will then set the limit to the minimum transmittance observed, unless an adverse signal-to-noise ratio, a scale limitation of the photometer, or a false electrical zero intervenes.

2.3 These limitations may usually be overcome by increasing the slit width to admit more incident radiant power on the filter. In a double-beam instrument, this may be accomplished by attenuating the reference beam with a screen, mask, or neutral filter. The following procedure assumes the use of etched screens, and measures their transmittance by their effect on the instrument reading.

2.4 The apparent transmittance of the filter is sensitive to spectral bandwidth. Since bandwidth increases with slit width, it is necessary that the transmittance of the screen be measured at a fixed slit width each time. The slits may then be allowed to open for the following steps of the test. The effect of such changes in slit width on the apparent transmittance of the filter becomes insignificant at the end of the test when the SRP becomes the dominant source of signal.

2.5 The scanning is continued, and the reference beam is attenuated further in as many steps as required, until the steeply falling transmittance curve levels off because of SRP. The product of all the reference attenuation fractions times the value of the transmittance reading at the plateau, corrected by the baseline value and the filter reflection loss, is taken as the SRPR.

2.6 The SRPR can in some cases increase with increasing slit width (see Annex A4). Therefore, the smallest practicable

value of slit width should be used at the last step of the reference beam attenuator, as this corresponds most nearly with the normal operating conditions of the spectrophotometer.

2.7 Some instruments scan automatically only in one direction, which may not be the one specified in the test procedure. Manual control or scanning by hand may be necessary. *Particularly note any precautions* called for by the manufacturer's instructions in this case. If, for mechanical reasons, manual scanning is not feasible, the test procedure can be reversed, after making the checks of 100 % line and zero, by going to the desired wavelength within the filter stop band, inserting neutral attenuators in the reference beam until the pen lies between 10 and 100 % transmittance (preferably near 10 %, widening the slits while doing so to restore normal pen response, scanning in reverse until 100 % transmittance is reached, and removing the reference beam attenuators one at a time while measuring their attenuation, until all are out and a region where the filter is transparent is reached.

2.7.1 The only difficulty with this procedure lies in finding the narrower slit width that will give normal pen response after each reference beam attenuator is removed, and finding the transmittance change at that slit width. Several trials may be required.

2.7.2 When done carefully, this procedure gives the same result as the normal one, and in fact affords a way of checking the standard test results whenever both scan directions are permitted.

3. Significance and Use

3.1 Stray radiant power can be a significant source of error in spectrophotometric measurements, and the danger that such error exists is enhanced because its presence is often unsuspected. SRP usually increases with the passage of time; therefore testing should be performed periodically. This test method provides a means of determining the stray radiant power ratio of a spectrophotometer, and so 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 blocking filters.

4. Apparatus and Material

4.1 *Screens⁴ of Etched Nickel*, useful for reference beam attenuators are listed in Table 1 and footnote 4. They may also

⁴ Available in sheet form from Perforated Products, Inc., 68 Harvard St., Brookline, Mass. 02146. Also as cut disks in holders from Varian Instrument Service Center, 670 East Arques Ave., Sunnyvale, CA 94086. These holders fit the Cary spectrophotometer cell blocks for cylindrical cells. They do not fit holders for rectangular cells. The holders are also useful for glass filters for Bouguer's law absorbance linearity tests.

Screen and Holder Part Number	Approximate Mesh	Identification Number	Nominal Absorbance
1404111	30	25 K	0.5
1404112	60	30 R	1.1
1404113	120	40 T	1.5
1404114	270	50 W	2.0

TABLE 1 Perforated Screens

Identification Number ^A	Nominal Transmittance	Nominal Absorbance
20G	0.50	0.30
15H	0.41	0.39
15L	0.29	0.54
10N	0.20	0.70
12½ P	0.14	0.84
10S	0.07	1.20
30T	0.03	1.50
20W	0.01	2.00

^A The identification number is that of Perforated Products, Inc., 68 Harvard St., Brookline, Mass. 02146. Screens from this manufacturer are the only ones so far tested in committee work. Screens may be available from other manufacturers.

be convenient for “quick check” transmittance “standards.” The screens should be placed as far as possible from each other, and preferably at a point along the beam where it is as wide as possible. Usually a 1-cm spacing between screens suffices to allow acceptable reproducibility of results. Their

exact transmittance varies with location in the beam, hence they should be mounted so they can be positioned reproducibly, and mechanical stability of all parts of the spectrometer should be established. The transmittance of two or more screens used in cascade or tandem is rarely equal to the product of their separate transmittances, and may be quite sensitive to lateral displacements with respect to each other, due to the moiré effect.

4.2 *Test Filter Materials*, shown in Table 2, provide an array capable of covering nearly all normal ultraviolet and infrared spectral ranges. The first column shows the approximate spectral range over which remote SRPR determinations can be made. The test wavelength to be used with any given test 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 test filter becomes a negligibly small fraction of the observed transmittance (Note 4 and Note 5). The second

TABLE 2 Filters for Tests for Stray Radiant Power Ratio

Spectral Range ^A	Transmittance, ^B 80 % Wavelength or Wavenumber	Filter ^C	Source ^D	Detector ^E
A. Sharp Cutoff Types				
165 to 173.5 nm	183 nm	0.01 cm H ₂ O ^F	UV	UV
170 to 183.5 nm	195 nm	1.00 cm H ₂ O ^F	UV	UV
175 to 200 nm	214 nm	1.00 cm 12 g/L KCl aqueous ^F	UV	UV
195 to 223 nm	232 nm	100 cm 10 g/L NaBr aqueous ^F	UV	UV
210 to 259 nm	271 nm	1.00 cm 10 g/L NaI aqueous	UV	UV
250 to 320 nm	339 nm	1.00 cm acetone	UV	UV
300 to 385 nm	420 nm	1.00 cm 50 g/L NaNO ₂ aqueous	VIS	UV
2050 to 1200 cm ⁻¹	2800 cm ⁻¹	2.0-mm fused silica ^G (2)	IR	IR
1140 to 800 cm ⁻¹	1760 cm ⁻¹	6 mm LiF	IR	IR
760 to 600 cm ⁻¹	1240 cm ⁻¹	6 mm CaF ₂	IR	IR
630 to 400 cm ⁻¹	1030 cm ⁻¹	6 mm NaF	IR	IR
410 to 250 cm ⁻¹	650 cm ⁻¹	6 mm NaCl	IR	IR
240 to 200 cm ⁻¹	420 cm ⁻¹	6 mm KBr	IR	IR
B. Pass-Band Filters				
600 to 660 nm	...	1.00 cm 0.005 % methylene blue aqueous ^H	VIS	VIS or NIR
1.66 to 1.75 µm	...	5.0 cm CH ₂ Br ₂ ^I	NIR	NIR

^A The shorter wavelength (or lower wavenumber) limits given are nominal. The selection of a test filter should be made in accordance with 4.2. Longer wavelength (or higher 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:

UV—Source is either a deuterium or hydrogen discharge lamp or a xenon short arc.

VIS—Source is a tungsten filament lamp at 2850 to 3300 K. If a xenon arc is substituted, precautions to avoid UV stray should be taken, such as interposition of a Corning No. 7380 or No. 3391 filter, for both test and use of the instrument at wavelengths longer than 410 nm.

NIR—Source is a tungsten filament lamp at 2500 to 3200 K.

IR—Source is a Nernst glower at 1500 to 1800 K, or Globar, or coated Nichrome ribbon, at 1300 to 1500 K. Because the proportion of SRP varies with source temperature, the source current should be set to the value used for analysis.

^E Considerable flexibility in detectors selected is common. The following lists only some of those most frequently employed:

UV—Photomultiplier or diode phototubes with S-5, S-19, or similar spectral response function, such as types 1P28, 7200, or R-106.

VIS—UV types, plus photomultiplier or diode phototubes with S-4, S-5, or S-19 response; extended red threshold types such as 7265 (S-20), or R-136. Photoconductor (PbS) detectors.

NIR—Phototubes with S-1 response to 1.2 µm, photoconductor (PbS, PbSe or PbTe) detectors.

IR—Thermocouples, bolometers, Golay detectors.

^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.

^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 reradiation 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 % methylene blue solution must be made up freshly from a 0.5 % stock solution in 2 % KH₂PO₄, preserved with 1 part of phenylmercuric acetate (Eastman No. P4267 in 50,000 parts of solution).

^I Distillation Products Industries, Eastman Organic Chemicals, No. 1903. 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.