



Designation: E 387 – 84 (Reapproved 1995)^{e1}

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.

^{e1} 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.

column (Table 2) 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 3—Once the test wavelength has been established for a test filter and an instrument of any given design, the test is applicable to all instruments of the same design.

NOTE 4—The true transmittance of a test filter can be determined by measuring the spectrum of a dilute solution or a thin specimen of the test filter material and using Beer's law to extrapolate the transmittance to the concentration or thickness employed in the test for SRPR.

NOTE 5—For testing grating spectrophotometers that use moderately narrow bandpass blocking filters, use a test filter that cuts off sharply at a wavelength as near as possible to the edge of the passband of the blocking filter that is normally in the beam at the designated test wavelength. The test wavelength itself should be as close as possible to the transmission cutoff of the test filter to minimize absorption of SRP by the test filter.

4.2.1 Filter diameters are not specified. They should be large enough to cover the entire beam with substantial safety margin. Because of the danger that radiant energy outside the nominal beam may bypass the filter and be scattered back into the beam, it is advisable to mount them against a cell compartment window or in a much larger metal holder so as to block any such paths. If in doubt, test with an opaque object of the same size as the filter.

4.2.2 If there is any possibility that fluorescence of windows, cells, or sample solvents may be contributing to SRP in the ultraviolet range, locate the test 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.

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

4.2.4 *Fused Silica*,⁵ in the form of cell windows, is commonly available and useful over a thickness of 1 to 5 or 6 mm. Crystal quartz is less desirable because of its birefringence, which may cause apparent cyclical transmittance variations with wavelength.

5. Procedure

5.1 Verify that pen response is "normal," that is, that normal damping (preferably slight underdamping) and designated response time and low (less than ½ %) dead zone exist. Follow the manufacturer's instructions, or test by moving a mask a small distance into and out of first the sample, then the reference beam.

5.2 Check the zero transmittance error with an opaque shutter or sample. Adjust the zero control, or note the indicated zero and subtract it from subsequent readings.

5.2.1 In some infrared instruments the radiant power from a rotating beam modulator can be compensated by an adjustable electrical signal. The amount of compensation required varies with wavelength and slit width. Make frequent zero checks during the SRP tests. It is desirable to interpose the opaque shutter ahead of the filter, and only briefly, so that radiation from the filter is self-compensated. A shutter made of thick insulating board, such as Celotex,⁶ or several thicknesses of cardboard separated by air spaces, is recommended, preferably brought to instrument temperature by being stored in the sample compartment.

5.3 Record a 100 % line over the desired wavelength range for a single filter. If the slit system is controlled by a servo system to maintain a constant reference signal, leave this control on; otherwise put the slits under manual control or leave off (immobile). In the latter cases, check pen response frequently during the scan, and change the slit width if and when pen response becomes either sluggish or markedly underdamped. Check by quickly inserting and removing an opaque object in the sample beam. At each change point, record the wavelength and new slit width, so that they can be reproduced in step 5.5.

5.3.1 If the spectrophotometer is provided with a single beam mode in which the sample signal is compared with a fixed electrical reference signal, use this provision to check and readjust slit width instead of the less reliable pen response test.

5.4 Insert the filter in the sample beam.

5.5 Scan slowly from high transmittance to low. When about 10 % transmittance is reached, stop the scan and turn the slit servo off, but leave the pen on and the chart running, recording the pen position for several full pen periods (multiples of five times the time constant for an exponential response function).

5.6 Insert in the reference beam a "neutral" beam attenuator, such as a screen selected from the list shown in Table 1, and having about 12 to 20 % transmittance.

5.7 Record the resulting increased apparent transmittance for at least 20 times the nominal response period of the instrument. (The lengthened time is required because the reduced reference beam energy results in sluggish pen response.) If possible, displace the optical attenuator, or the pen, or both, by hand first in one direction, then the other, and allow to recover to make sure that the photometric system still functions.

5.8 Note on the record the ratio of transmittance values, or "setback," that corresponds to the displacement at fixed slit width.

5.9 Turn on the slits or otherwise adjust them to give normal reference signal levels.

NOTE 6—As indicated in Annex A4, the change in slit width may sometimes change the value of SRP. The displacement resulting from slit width change may be due in small part to this, or to possible shift of zero resulting from the change in illumination conditions resulting from the slit width change, but is mainly due to the accompanying change of spectral bandwidth.

⁵ Corning 7940 glass, General Electric Type 151 glass, Hereaus Suprasil, Ultrasil, or Thermal American Spectrosil have been found satisfactory.

⁶ Celotex® is a trademark of the Celotex Corp.

5.10 Continue scanning in the direction toward decreasing transmittance of the filter until the indicated transmittance again falls to about 10 %.

5.11 Repeat steps 5.5-5.9, replacing the reference beam attenuator of step 5.6 by another with about 12 % of the transmittance of the previously used filter (about 0.9 absorbance more); or add a second attenuator, spaced from the first and having about the same transmittance as the first.

5.12 Again measure and note the new transmittance change resulting from the reference beam attenuation at fixed slit width.

5.13 Repeat steps 5.11 and 5.12 with a succession of additional reference beam attenuators until the indicated transmittance reaches a minimum, or until the slits reach their maximum value (Note 7). If the indicated transmittance does reach a minimum, select the reference beam attenuator for the last setback such that the scale reading is about 10 % (or even less, if the zero point is verified). If necessary, after selecting the attenuator for the last setback, return to the preceding attenuator and recording conditions before measuring the final setback.

NOTE 7—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 continue adding reference attenuators beyond the point required to demonstrate compliance.

6. Calculation

6.1 Calculate the SRPR as the product of all the “setbacks” times the final transmittance fraction at the desired wavelength, divided by the transmittance fraction of the 100 % line at this wavelength, measured in step 5.3, and divided by the filter transmittance in its pass band (about 0.90, resulting from surface reflection losses).

NOTE 8—Since the instrument SRPR often increases with increasing slit width, the value obtained will ordinarily indicate a greater SRPR than

is normally encountered in use. If the final slit width corresponds to a normal use value, the SRPR will be correct for that value. Such a condition may sometimes be obtained by starting the series of measurements at unusually high values of amplification or at high photomultiplier dynode voltage, accepting more than normal noise on the records of the SRPR test. If this is done, it is doubly important to be sure that the photometer scale still reads correctly near zero transmittance under the higher gain condition.

7. Precision and Bias

7.1 High accuracy is not required for SRPR determinations, and no estimate of the precision that is achieved in using this test method is needed or useful. 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.

8. Illustrative Example

8.1 A stray radiant power ratio test was done on a Cary Model 15 Spectrophotometer following the procedure described in Section 5. The resulting recording is shown as Fig. 1. The chart reads from right to left. The steps of the procedure are marked by the corresponding numbers of the paragraphs in Section 5. Step 5.1 was performed but was omitted on the chart. However, it is evident from the pen test shown in step 5.7 that the pen dead zone is small and its response sufficiently fast even with a reduction of total radiant power to less than 1/4 of normal.

8.2 Calculate in accordance with Section 6 as follows:

$$SRPR = 0.108 \times 0.118 \times 0.111 \times 0.151 \times 0.183 \times \frac{0.0128}{0.996} \times \frac{1}{0.885}$$

$$= 5.67 \times 10^{-7} \text{ or } 0.000057\% \quad (1)$$

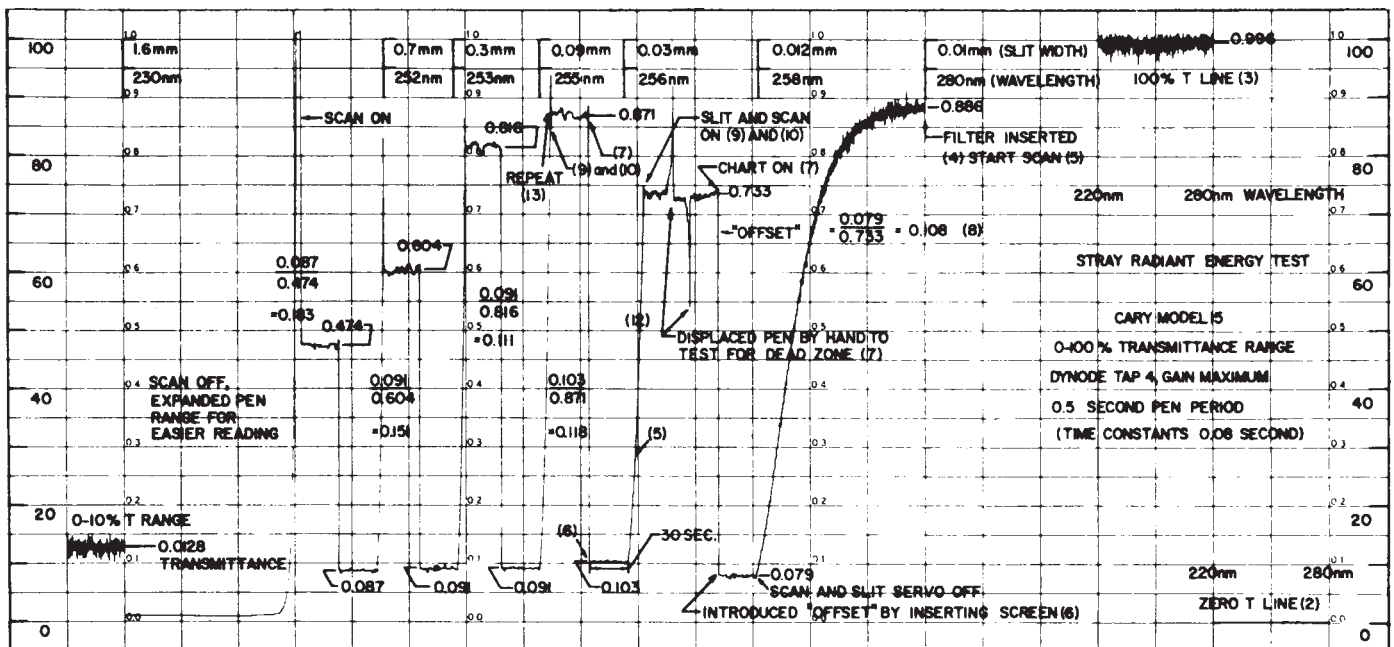


FIG. 1 SRPR Test of Spectrophotometer with Silica Prism Double Monochromator

9. Keywords

9.1 molecular spectroscopy

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 pass band 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 pass band, 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 should 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 is 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 (4),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.

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 (5). 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, and that additionally allow instruments to be compared when similar detectors and sources are used. 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 tests 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