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Standard Test Method for Determination of Weight-Average Molecular Weight of Polymers By Light Scattering[1]

This standard is issued under the fixed designation D4001; 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. Scope*

1.1 This test method describes the test procedures for determining the weight-average molecular weight M_w of polymers by light scattering. It is applicable to all nonionic homopolymers (linear or branched) that dissolve completely without reaction or degradation to form stable solutions. Copolymers and polyelectrolytes are not within its scope. The procedure also allows the determination of the second virial coefficient, A_2, which is a measure of polymer-solvent interactions, and the root-mean-square radius of gyration $(s^2)^{1/2}$, which is a measure of the dimensions of the polymer chain.

1.2 The molecular-weight range for light scattering is, to some extent, determined by the size of the dissolved polymer molecules and the refractive indices of solvent and polymer. A range frequently stated is 10,000 to 10,000,000, is often extended in either direction with suitable systems and by the use of special techniques.

1.2.1 The lower limit to molecular weight results from low levels of excess solution scattering over that of the solvent. The greater the specific refractive increment d*n*/d*c* (difference in refractive indices of solution and solvent per unit concentration), the greater the level of solution scattering and the lower the molecular weight that shall be determined with a given precision.

1.2.2 The upper limit to molecular weight results from the angular dependence of the solution scattering, which is determined by the molecular size. For sufficiently large molecules, measurements must be made at small scattering angles, which are ultimately outside the range of the photometer used.

1.3 The values stated in SI units are to be regarded as standard.

1.4 *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.*

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

IEEE/ASTM SI-10 American National Standard for Use of the International System of Units (SI): The Modern Metric System

3. Terminology

3.1 *Definitions*—Units, symbols, and abbreviations are in accordance with IEEE/ASTM SI-10.

4. Significance and Use

4.1 The weight-average molecular weight is a fundamental structure parameter of polymers, which is related to many physical properties of the bulk material, such as its rheological behavior. In addition, knowledge of the weight-average molecular weight, together with knowledge of the number-average molecular weight from osmometry, provides a useful measure of the breadth of the molecular-weight distribution.

4.2 Other important uses of information on the weight-average molecular weight are correlation with dilute-solution or melt-viscosity measurements and calibration of molecular-weight standards for use in liquid-exclusion (gel-permeation) chromatography.

4.3 To the extent that the light-scattering photometer is appropriately calibrated, light scattering is an absolute method and is therefore be applied to nonionic homopolymers that have not previously been synthesized or studied.

5. Apparatus

5.1 *Volumetric Flasks,* 100-mL, or other convenient size.

5.2 *Transfer Pipets.*

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.70.05).

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[2] 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.

***A Summary of Changes section appears at the end of this standard**

5.3 *Photometer,* whose major components, described in Appendix X1, are a light source, a projection optical system, a sample-cell area, a receiver optical system, a detector system, and a recording system. Typical photometers are described and summarized (**1**)[3] in the literature.

5.4 *Differential Refractometer,* with sensitivity of approximately 3×10^{-6} refractive-index units, capable of measuring the specific refractive increment d*n*/d*c* at the wavelength and temperature of the scattering measurements (**2**).

NOTE 2—Specific refractive increments are tabulated (**2**,**3**) for many polymer-solvent systems.

5.5 *Refractometer,* Abbé type or equivalent, capable of measuring the refractive indices of solvents and solutions at the wavelength and temperature of the scattering measurements.

5.6 *Spectrophotometer,* capable of measuring the absorbance of solutions at the wavelength of the scattering measurements.

5.7 *Laminar-Flow Clean-Air Station,* to provide a dust-free area for preparing and cleaning solutions and filling the scattering cell.

5.8 *Filters and Filter Holders,* for cleaning solvents and solutions. Membrane filters with pore sizes from 0.10 to 0.45 µm, used in glass or plastic filter holders, are recommended.

5.8.1 For water and aqueous solutions, and for organic solvents that do not attack the material, the use of polycarbonate (Nucleopore) filters is recommended. These filters have the advantages of high flow rate without the use of gas pressure, minimal retention of solute on the filter, and efficient cleaning action. For other solvents, the use of cellulosic filters (Millipore or equivalent) is recommended.

NOTE 3—Sintered-glass filters is sometimes used, but these are relatively expensive and difficult to clean between uses. Centrifugation is sometimes used, but this step requires special care and techniques, or special scattering cell design, to be satisfactory.

6. Reagents and Materials

6.1 *Solvents,* as required. Since d*n*/d*c* is a function of composition, solvents shall be of high purity. Significant errors in molecular weight, which depends on the square of d *n*/d*c*, will be incurred if literature values of d*n*/d*c* are employed and the actual value of this quantity is different because of impurities in the solvent.

6.2 *12-Tungstosilicic Acid,* as standard for calibration of photometer.

7. Sample

7.1 The sample must be homogeneous, and must be thoroughly free of all foreign impurities. If at all possible, samples to be used for light-scattering measurements must be specially treated from synthesis on to minimize exposure to or contamination with particulate impurities. Gels that consist of very high-molecular-weight particles, are sometimes formed during synthesis and will interfere with the analysis. All such particulate matter must be removed, sometimes with considerable difficulty. It should be understood that when this is done, the remaining sample is no longer truly representative of the entire polymer. The extent of the difference from the original sample will depend on the removal techniques employed.

NOTE 4—Reduction of sample particle size in a clean Spex or Wiley mill speeds solution and, with slow-dissolving materials, is essential if the measurements are to be made in a reasonable time. Overheating with consequent sample degradation must be avoided during the milling process. Hard, tough samples or those with low melting points are handled by mixing with clean dry ice, milling the mixture, and then allowing the dry ice to sublime. Clean dry ice may be obtained by opening a tank of carbon dioxide to the atmosphere. Commercial dry ice has often been shown to be contaminated.

8. Preparation of Dust-Free Cell and Contents

8.1 Clean all glassware, including the scattering cell, with a suitable detergent to remove grease and other contaminants. Use of an ultrasonic cleaning bath is recommended. Rinse glassware at least four times with distilled water to remove all traces of detergent, and dry in a clean, dust-free drying oven.

NOTE 5—A laminar-flow clean-air station is recommended for providing a dust-free area for solution preparation and filtration. If a clean-air station is not used, a closed area in a location free of drafts and of sufficient size to hold the filter unit, scattering cell, and other glassware shall be used.

8.2 Filter solvent directly into the scattering cell. First rinse the cell several times with 5 to 10 mL of filtered solvent each, to remove dust particles. Upper surfaces of the interior of the cell shall be well washed down. Close the cell with a cap similarly rinsed with filtered solvent. After rinsing, fill the cell with the minimum amount of solvent required to bring the liquid level above the point where the light beam in the photometer passes through the cell.

NOTE 6—Use of a small filter holder fitting between a hypodermic syringe and needle is convenient where only small quantities of liquids are filtered. A cell cap, with a hole just large enough to insert the needle, is used.

8.3 Place the scattering cell in the photometer, or in an equivalent strong light beam, and examine it in the dark, viewing at small scattering angles. Bright specks of dust must not be visible; if they are, the cell was not rinsed completely or the filtration procedure is inadequate.

8.4 Subsequent use of the clean cell for adding increments of filtered solution or for replacing solvent with solution requires no further rinsing, except to ensure that residual solvent remaining, after the cell is emptied, is removed and replaced with solution.

9. Procedure

9.1 Calibrate the light-scattering photometer. This calibration is required to convert measurements of scattered light intensity from arbitrary to absolute values, an essential step in the calculation of molecular weight. The calibration procedure, which is lengthy and requires great care to obtain accurate results, is given in Appendix X2. The calibration constant of most photometers remains stable for long periods of time, however, so making the calibration procedure infrequent.

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[3] The boldface numbers in parentheses refer to the list of references at the end of this test method.

9.2 Prepare a stock solution of polymer, noting the precautions of Sections 7 and 8, at a concentration estimated as follows: For a polymer of $M_w = 100,000$ in a solvent such that d*n*/d *c* ≈ 0.2 mL/g (for example, polystyrene in 2-butanone), the stock solution shall be in the range from 10 to 20 g/L. Since scattered intensity is proportional to M_w and to the square of d*n*/d*c*, estimates of the stock-solution concentration required for other samples and systems is made. Prepare no more stock solution than is required by the following procedure.

9.3 Select one of the following measurement schemes:

9.3.1 Where the volume of liquid required for measurement in the photometer is varied by at least a factor of two, it is recommended that the scattering from the minimum volume of solvent be measured first, followed by measurement of solutions prepared in the cell by the addition of weighed or volumetrically measured aliquots of filtered stock solution. From four to six such solutions shall be measured, the most concentrated consisting of approximately equal volumes of solvent and stock solution if its concentration is selected in accordance with 9.2, and the least concentrated being about one fourth this concentration. A specific example is given in Appendix X3.

9.3.2 If the volume of liquid in the scattering cell cannot be varied as in 9.3.1, it is necessary to prepare and filter into the cell from four to six separate solutions covering the range suggested in 9.3.1.

9.3.3 A further alternative is to measure the most concentrated solution first (for this purpose, the stock solution concentration estimated in 9.3.1 shall be reduced by a factor of two), followed by successive dilutions with solvent. The scattering from the pure solvent must be measured in a separate step. If necessary, start dilution sequences at two or more concentration levels to obtain the range specified in 9.3.1.

9.4 Measure the scattering of the pure solvent, filtered into the cell as described in Section 8, and of each of the series of filtered solutions described in 9.3, following the instructions provided with the photometer or in the literature **(4)**, being sure that the following steps are included. (This procedure is based on the scheme of 9.3.1.)

9.4.1 *Instrument Check*—See that the photometer is prepared for measurement, with the lamp lit, high voltage supplied to the photomultiplier detector, and all components fully warmed up and stabilized.

9.4.2 *Solvent Preparation*—Fill the cleaned scattering cell with filtered solvent as described in Section 8, insert it in the instrument, and align it as required.

9.4.3 *Intensity Level*—Select the wavelength-isolating filter to be used. Turn the detector to the specified angle and set the level of high voltage, or adjust the slit openings, as called for to provide an appropriate solvent reading. In subsequent steps, do not readjust these variables, but change amplifier gain by known factors or insert neutral filters of known transmittance as required to maintain readings on scale.

9.4.4 *Solvent Measurement*—After the cell has remained undisturbed in the photometer for 10 to 15 min to allow residual dust to settle out, read and record the scattered intensity at angles of 30°, 90°, 150°, and at least three pairs between, symmetrically placed with respect to 90°, as available on the photometer used.

9.4.5 *Reference*—Turn the phototube to the specified reference angle, adjust amplifier gain or insert neutral filters as required, insert the reference standard, and read and record the indicated reference intensity.

9.4.6 *Solution Measurement*—Prepare and filter into the cell the solutions required in 9.3. Mix thoroughly, allow a few minutes for residual dust to settle out, and measure each solution as in 9.4.4.

9.5 Determine solution concentrations. Since filtration through membrane filters has been known to result in retention of some polymer on the filter, it is necessary to determine the solution concentrations after filtration.

9.5.1 If successive concentrations are generated in the cell from a stock solution filtered under constant conditions, only the concentration of the filtered stock solution need be determined; otherwise, the concentration of each solution measured must be determined.

9.5.2 Determine the concentrations of solutions, as required, by one of the following methods. Use standard analytical techniques where applicable.

9.5.2.1 Evaporate a portion of the solution to constant weight. It is necessary to do this at high temperatures, namely, above the glass transition temperature and under vacuum, to remove tightly bound solvent. Because solvent is sometimes very difficult to remove, such a procedure for determining concentration must be verified by other techniques before being adopted.

9.5.2.2 Determine the ultraviolet absorbance of the solution at a suitable wavelength.

9.5.2.3 Determine the difference in refractive index between solution and solvent, using a differential refractometer, for cases where the specific refractive increment is known.

9.5.3 For cases where a series of solutions is produced in the cell, calculate the actual solution concentrations from that of the stock solution by standard volumetric or gravimetric analytical methods.

9.6 If the specific refractive increment d*n*/d*c* is not known, determine it using solutions of known concentrations; the same solutions used for light scattering measurements shall be utilized. The specific refractive increment is the slope of the straight line relating solution-solvent refractive-index difference, Δn, to solution concentration, *c*. Since the relation is linear, determination of Δn for one value of *c* suffices, but multiple determinations are recommended to reduce the uncertainty of the value of d*n*/d*c*. For use and calibration of the differential refractometer, follow the instructions supplied with the instrument.

9.7 If the refractive index of the solvent is not known for the wavelength and temperature of the measurements, determine it using a conventional refractometer. If the refractive indices of the polymer solutions used differ significantly from that of the solvent, determine them also.

9.8 If the polymer absorbs light, or is suspected of absorbing light, at the wavelength of the scattering measurement, an absorption correction (Appendix X4) must be applied.

9.9 If the polymer or solvent fluoresces, or is suspected of doing so, the possibility of fluorescence must be eliminated.

9.9.1 Fluorescence is detected by placing in the detector optical system a sharp-cutting short-wavelength-cutoff filter that absorbs completely at the wavelength of the incident light. The scattered-light reading will drop to zero if there is no fluorescence, but will remain finite if fluorescence is present.

9.9.2 If fluorescence is present, place a narrow-bandpass interference filter transmitting at the wavelength of the incident light in the detector optical system. Alternatively, but with less certainty of success, place in the detector optical system an absorbing filter that absorbs at wavelengths longer than that of the incident light. (Such filters are not usually sharp-cutting, and hence are less efficient than the use of an interference filter.)

10. Calculation

10.1 *Calculate Correction Factors*—Using the methods of Appendix X4, calculate the following correction factors, as required.

10.1.1 Factors that must be considered for each data point: amplification, filter, and reflection factors.

10.1.2 Factors to be applied at each concentration: absorption and depolarization factors.

10.1.3 Factors to be applied at each angle: polarization and volume factors.

10.1.4 Factor to be applied to calibration constant: refraction correction.

10.2 *Calculate the Calibration Constant*— Following the procedure of Appendix X2, calculate the calibration constant for converting light-scattering intensities into Rayleigh ratios.

10.3 *Calculate Rayleigh Ratios*—Apply the necessary correction factors and otherwise treat the data of 9.4 and 9.5 as follows. Typical data are shown in Appendix X3.

10.3.1 Obtain original data from recorder chart, galvanometer, or other readout device, at each concentration and angle utilized. Correct for zero-signal level as required. Apply amplification and filter factors, if any, to obtain a self-consistent set of data. Tabulate as in Table X3.1, Section A.

10.3.2 Apply the volume correction factor determined from Appendix X4 to the data of 10.3.1. Typical data are shown in Table X3.1, Section B.

10.3.3 Correct the data of 10.3.2 for the reference by dividing by the reference intensity. Typical data are shown in Table X3.1, Section C.

10.3.4 Subtract the solvent readings from 10.3.3 from the corresponding data for each concentration of polymer. Typical data are shown in Table X3.1, Section D.

10.3.5 As required, apply absorption, depolarization, polarization, and reflection factors to the data of 10.3.4.

10.3.6 By use of the calibration constant determined in 10.2, convert the data of 10.3.5 (or 10.3.4 if no additional factors were applied in 10.3.5) to values of the Rayleigh ratio ΔR_θ. Typical data are shown in Table X3.1, Section E.

10.4 Prepare data for graphical treatment by the Zimm-plot method.

NOTE 7—An alternative method, known as the dissymmetry method, is used when the angular dependence of the Rayleigh ratio is small (for example $\Delta R_{45°} < 2\ \Delta R_{135°}$). The method is less general in application than the Zimm-plot method, however, and is not recommended. Further details of the dissymmetry method is found in the literature (**5**).

10.4.1 Divide each polymer concentration by the corresponding values of ΔR_θ from step 10.3.5 to obtain the quantities $c/\Delta R_\theta$. Typical data are given in Table X3.1, Section F.

10.4.2 Select an appropriate value of the quantity k in the expression $\sin^2(\theta/2) + kc$, such that for the highest value of c utilized, kc is in the range from 0.2 to 0.4. Tabulate the quantity $\sin^2(\theta/2) + kc$. Typical data are shown in Table X3.1, Section G.

10.5 Plot the data of steps 10.4.1 and 10.4.2 to yield the Zimm plot. A typical Zimm plot is shown in Fig. X3.1.

10.5.1 Plot, on graph paper with scales suitably selected, corresponding values of $c/\Delta R_\theta$ and $\sin^2(\theta/2) + kc$.

10.5.2 For each angle θ, connect points at various values of c to form (if possible) a straight line. Extrapolate this line to the point corresponding to $c = 0$, that is, to the value of $\sin^2(\theta/2)$ for that angle.

10.5.3 For each concentration c, connect points at various values of θ to form (if possible) a straight line. Extrapolate this line to the point corresponding to $\theta = 0$, that is, to the value of kc for that concentration.

10.5.4 Connect points at $c = 0$ to form (if possible) a straight line. Connect points at $\theta = 0$ to form (if possible) another straight line. Extrapolate these lines to the ordinate axis (where $c = 0$ and $\theta = 0$), where they must meet at a single point, denoted the intercept.

NOTE 8—It is possible to produce the plots of 10.5.2, 10.5.3, and the two lines of 10.5.4 on separate graphs, using the variables $\sin^2(\theta/2)$ and kc separately as required instead of together, but when the principles of the Zimm plot have been mastered, plot the combined data on a single graph as indicated.

10.6 Assess the quality of the Zimm plot.

10.6.1 If the families of lines in 10.5.2 and 10.5.3 are all straight and reasonably parallel, and if the lines in 10.5.4 are straight and meet at a point on the ordinate axis, the quality of the Zimm plot is satisfactory and 10.7 shall be carried out.

10.6.2 If the data of 10.5.1 cannot be made to fit straight lines, due to scatter or systematic deviations, the quality of the Zimm plot is *not* satisfactory, and conclusions must be drawn from the experiment only with extreme caution. The recommended action is to repeat the experiment, paying more careful attention to sample preparation and solution filtration, since dust or other unwanted scattering material is the most probable cause of the difficulty. Reference to the literature (**6**) is recommended. In some cases, a microgel component, which is really part of the distribution of polymer, has been known to cause severely distorted Zimm plots (**7**), and few valid conclusions are drawn from the data.

10.6.3 If the data of 10.5.2 fall on straight, reasonably parallel lines, and the data of 10.5.3 fall on gently curved but still parallel lines, the distortion results from large molecules or a broad distribution of molecular sizes, and conclusions drawn have been shown valid if data at small enough angles are included in the analysis (**8**).

10.7 Calculate the molecular parameters.

10.7.1 Calculate the Debye constant, K, as follows:

$$K = 2\pi^2 n^2 (dn/dc)^2 / N_o \lambda^4$$

where:

n = the refractive index from 9.8 or tables (**2,3**),
dn/dc = the specific refractive increment from 9.6 or tables (**2,3**),
N_o = Avogadro's number, and
λ = the wavelength of the incident light as measured in air.

NOTE 9—This treatment assumes that the refractive index n is essentially the same (within 0.01) for the solvent and all polymer solutions. If not, separate values of K must be calculated for each polymer concentration, and applied to the corresponding data in 10.4.1 rather than at this stage.

10.7.2 Calculate the weight-average molecular weight $\bar{M}_w$ as follows:

$$\bar{M}_w = \left[K(C/\Delta R_\theta)_{c=0,\ \theta=0}\right]^{-1}$$

where:

K is the calibration constant of 10.7.1 and $(c/\Delta R_\theta)_{c = 0,\ \theta = 0}$ is the intercept of the Zimm plot from 10.5.4.

10.7.3 Calculate the second virial coefficient A_2 as follows:

$$A_2 = 1/2\ K[(c/\Delta R_\theta)_{c2} - (c/\Delta R_\theta)_{c1}]/(c_2 - c_1)$$

where the quantities have the same meanings as before and c_1 and c_2 are two concentrations, at the high and low ends of the range encompassed, respectively.

NOTE 10—Since A_2 has been known to vary slightly with the angle θ, calculate it from the data extrapolated to $\theta = 0$.

10.7.4 Calculate the radius of gyration $(s^2)^{1/2}$ as the square root of the mean square radius of gyration obtained from the following equation:

$$\bar{s}^2 = (3\lambda^2/16\pi^2 n^2) \times (\text{slope/intercept})$$

where:

$\bar{s}^2$ = the mean square radius of gyration,
λ = the wavelength of incident light measured in air, and
n = the refractive index. "Slope" refers to the initial slope of the line of $c = 0$ points in the Zimm plot (10.5.2) and "intercept" is the value of $(c/\Delta R_\theta)_{c = 0,\ \theta = 0}$ determined from 10.5.4.

NOTE 11—The derivations of the equations in 10.7, and typical data, are given in Appendix X3.

11. Report

11.1 Report the following information:

11.1.1 Identification of the sample.

11.1.2 Conditioning of the sample, if any.

11.1.3 Solvent, temperature, and instrument used.

11.1.4 Filtration technique.

11.1.5 Basic data, including wavelength, d n/dc, n, vertically polarized or unpolarized light, nature of reference, and calibration constant.

11.1.6 Correction factors and any basic data (absorbance, depolarization) used in deriving them.

11.1.7 Results, including K, $\bar{M}_w$, and (optionally) A_2 and $(\bar{s}^2)^{1/2}$. Unless otherwise agreed, $\bar{M}_w$ shall be reported to three significant figures, and A_2 and $(s^2)^{1/2}$ to two significant figures.

11.1.8 If agreed, a table of data similar to Table X3.1, and the Zimm plot.

12. Precision and Bias

12.1 For most polymer-solvent systems where the solutions are reasonably free of dust or other extraneous scattering material, the weight-average molecular weight will be determined with a standard deviation for reproducibility of about 5 % of its value. A typical statistical analysis is given in the literature (**9**). Bias in the strict sense are seldom estimated because of the lack of absolute standards in the molecular weight ranges involved. No round-robin data have been obtained.

12.2 In accordance with 12.1, "absolute standards" means polymers for which $\bar{M}_w$is accurately determined by methods other than light-scattering. There are few such polymers capable of being used interchangeably with the synthetic polymers to which this practice is directed. Relative standards do exist, in the form of well-characterized polystyrene samples (**10,11**), and it is recommended that one of these be measured at periodic intervals to ensure that the results obtained are consistent with the body of experience elsewhere (**12,13**).

13. Keywords

13.1 light scattering; polymers; weight-average molecular weight

APPENDIXES

(Nonmandatory Information)

X1. PHOTOMETERS

X1.1 Typical Photometers

X1.1.1 Typical photometers have as major components, a light source, a projection optical system, a sample cell area, an optical receiver system, a detector system, and a recording system. They are surveyed (**1**) and described (**14-18**) in the literature.

X1.2 Light-Source System

X1.2.1 A powerful and stable source is required because of the low level of scattering from typical polymer solutions. Mercury arc lamps have been the most commonly used source. The mercury lines at 435 nm (blue) and 546 nm (green) are the most commonly used.

X1.2.2 Absorbing filter combinations have often been used to isolate the mercury line used. Such filters typically have halfband widths of 2550 nm and often transmit no more than 20 % of their peak wavelength. Interference filters, which have halfband widths as low as 0.51 nm and typically transmit over 80 % at their peak wavelength, are recommended to replace the older filters.

X1.2.3 TEM-00 lasers, such as He-Ne (632.8 nm) or He-Cd (441.6 nm), are optionally used as sources. They provide stable, powerful, monochromatic, fully polarized sources, but because of their different wavelengths, the large body of values of n and dn/dc in the literature cannot be directly used. Argon-ion lasers can be obtained with a tunable dye attachment and adjusted to operate at the same wavelengths as the mercury lines.

X1.2.4 Neutral-density filters are normally required to aid in keeping the intensity of scattered light in the range of the detector system. Typically, four filters transmitting approximately 50, 25, 12, and 6 % are used.

X1.3 Projection Optical System

X1.3.1 The function of the projection optical system is to provide, by the use of lenses and slits, a sharply defined uniform beam passing through the cell compartment with a minimum of stray light. Lasers, when used, require no projection optical system. A polarizer, capable of being set accurately to pass either vertically or horizontally polarized light, or removed from the system entirely, is also normally included.

X1.4 Sample-Cell Area

X1.4.1 Several different types of sample cells have been used, including those with rectangular, octagonal, and cylindrical cross section. For use with the Zimm-plot method in conventional photometers, use of a cylindrical cell with flat entrance and exit windows is recommended.

X1.4.2 Reflection or scattering from the air-glass interfaces of the sample cell is one source of stray light. Care must be taken to keep such surfaces clean, and proper design of the cell and the detector optical system is important to minimize the problem. In some photometers, the cell is immersed in a container of liquid having the same refractive index as the glass of the cell, with the container walls out of the field of view of the detector system.

X1.4.3 The sample-cell compartment is usually placed in a light-tight box to shield the detector system from extraneous light. Such a box should be amply large. The cell should be reproducibly and rigidly mountable with its center on the optic axis of rotation of the detector system and its entrance face precisely perpendicular to the optic axis of the incident beam, but easily removable for cleaning and filling.

X1.4.4 Provision must be made for replacing the scattering cell with a stable, reproducible scatterer or diffuser, which can serve as a constant arbitrary reference for periodic measurement. Scattered intensities from solutions and solvent are adjusted to correspond to constant intensity from the reference in order to correct for fluctuations or drifts in source output, photomultiplier responsivity, or other system variables. Opal-glass diffusers, from which transmitted light is measured at $\theta = 0$, are commonly used as references, but other materials and geometric arrangements are also satisfactory.

X1.4.5 The cell compartment is typically thermostatically controlled. Since the scattered intensity from most polymer solutions changes less than 0.5 %/°C, the requirements for temperature control are not severe.

X1.5 Detector Optical System

X1.5.1 The typical configuration has the detector and its optical system mounted on an arm rotating about the center of the cell to provide selection of the angle of observation. Lenses and slits are used to define the field of view of the detector and minimize its sensitivity to stray light. For calibration purposes (Appendix X4); an arrangement in which the detector does not view outside the edges of the illuminated portion of the cell volume is preferred. A polarizer that is capable of being set accurately to pass vertically or horizontally polarized light or removed entirely from the system is normally included.

X1.6 Detector System

X1.6.1 Because of their high responsivity, photomultiplier tubes are universally used in light-scattering photometers. Highly stabilized, high-voltage power supplies are required and are readily available.

X1.6.2 The photomultiplier tube base and resistor network must be protected from moisture. The optical system shall provide a constant image on the photocathode, which sometimes varies in sensitivity over its surface.

X1.7 Recording System

X1.7.1 The use of an amplifier to monitor the direct-current output of the photomultiplier tube is recommended. The current range of the amplifier should be about 10^{-4} to 10^{-8} A. A 5-mV recorder is adequate to record the output of the amplifier. Inexpensive instruments are currently available which contain, in one package, the photomultiplier high-voltage supply, the amplifier, circuitry for canceling the photomultiplier dark current, a meter to display voltage or current, and output to a recorder.

X1.7.2 Earlier practice was often to feed the output of the photomultiplier tube to a galvanometer, typically with a sensitivity of about 0.0015 µA/mm of scale deflection.

X1.7.3 A more modern and highly sensitive technique is to utilize photon counting to register the output of the photomultiplier. The technique has the advantages that a discriminator is used to reject noise and that counting can be done for fixed times to obtain very high precision. For this approach a photomultiplier that is linear up to about 5×10^6 pulses per second is required.

X2. CALIBRATION

X2.1 Purpose and Method

X2.1.1 To make light scattering an absolute method for measuring polymer-molecular weights, it is necessary to calibrate the photometer to obtain absolute values of the ratio of scattered to incident light intensity. In principle, this can be done through knowledge of the geometry, dimensions, and optical parameters of the photometer. In practice, however, this information is difficult to obtain with the required accuracy, and the photometer is calibrated with a material of known scattering power. Many materials have been used to effect this calibration, with varying success, including the perfect reflecting diffuser, pure liquids of high scattering power such as benzene, and so-called "standard" polymer samples (which provide only a secondary calibration) (**19**). This test method uses a chemical compound whose molecular weight is established by classical methods, 12-tungstosilicic acid (hereafter abbreviated 12-TSA), $H_4 SiW_{12} O_{40}$, $M = 2879$, in aqueous salt solution to provide absolute calibration of the photometer (**8, 20-23**).

X2.1.2 The calibration of the photometer is carried out by establishing the relation between (in radiometric terms) the scattered radiance L_θ (λ) at the scattering angle θ per unit irradiated volume, V, observed at a distance r from the point of scattering, to the incident irradiance $M(\lambda)$. The above terms form the definition of the Rayleigh ratio:

$$R_\theta(\lambda) = L_\theta(\lambda) r^2 / M(\lambda) V \text{ cm}^{-1} \text{ sr}^{-1}$$

Here λ serves as a reminder that the indicated terms depend upon the wavelength and the dimension sr^{-1} (where sr is the steradian, the unit of solid angle) is conventionally disregarded. The Rayleigh ratio is related to the observed ratio of scattered light (strictly, radiance) from the scattering solution to that from the reference by a calibration constant k_w, where the subscript indicates that the calibration was carried out in an aqueous (salt) solution.

X2.2 Purification of 12-TSA

X2.2.1 Purify 12-TSA prior to use for calibration by adding 1 + 1 hydrochloric acid to a saturated aqueous solution of 12-TSA. Extract with ether and discard the aqueous phase. Remove the ether by careful evaporation, redissolve the 12-TSA in water, recrystallize it, and dry it in vacuum over P_2O_5 at room temperature.

NOTE X2.1—12-TSA is reactive and must never be allowed to come in contact with metal, either dry or in solution.

X2.2.2 Test the purity of the recrystallized 12-TSA by preparing a small amount of a solution of 0.5 g 12-TSA/mL of 3 *M* aqueous NaCl. (Note that the recrystallized material is the hydrate, (approximately) $SiO_2 \cdot 12\ WO_3 \cdot 26\ H_2O$, $M = 3311$.) The solution must not be visibly turbid or colored, and must show no absorbance when measured against the solvent in 1-cm cells in a visible-range spectrophotometer (400 to 700 nm).

X2.3 Measurements

X2.3.1 Prepare four to six solutions (250 mL each) of 12-TSA in 3 *M* aqueous NaCl, ranging in concentration from 0.05 to 0.5 g/mL, for use in steps X2.3.2 – X2.3.5.

X2.3.2 Following the procedures of Sections 8 and 9, filter (preferably by the use of Nucleopore polycarbonate filters with plastic holders) the solvent and the several solutions of X2.3.1 into the light-scattering cell and measure scattered and reference intensities at 30°, 90°, and 150°. Make at least three repeat measurements, which shall differ by less than ±1.5 %, and average them.

NOTE X2.2—There must be no dissymmetry from clean solutions of 12-TSA, and the primary purpose of measuring at 30° and 150° as well as 90° is to ensure that all solutions used are satisfactory in this respect. After application of the volume correction factor, readings at the three angles shall differ by less than ±1.5 %.

X2.3.3 For each solution, measure at 90° the horizontally and vertically polarized components of the scattered light, using vertically polarized incident light, for use in the calculation of the depolarization factor.

X2.3.4 Determine the concentration of each 12-TSA solution, after filtration, by the following procedure.

X2.3.4.1 Transfer two 25-mL aliquots of each solution by pipet to tared evaporating dishes and evaporate to dryness overnight at 65°C. Increase the temperature to 230°C and maintain for 24 h to remove all water of crystallization. Cool and weigh, avoiding excess exposure to moisture. This provides total solids as $NaCl + H_4\ SiW_{12}O_{40}$.

X2.3.4.2 Transfer two 25-mL aliquots of each solution by pipet to suitable containers and determine their content of NaCl by standard procedures (**24**) for the gravimetric analysis of chloride ion by quantitative precipitation with $AgNO_3$.

X2.3.4.3 Obtain the concentration of 12-TSA in each solution by difference from the results of X2.3.4.1 and X2.3.4.2.

X2.3.5 Determine the specific refractive increment d*n*/d*c* for each solution by the following procedure. Note that, because of the high concentrations of 12-TSA used, the solution refractive indices are sufficiently different from that of the solvent that a standard refractometer is appropriately used instead of a differential refractometer.

X2.3.5.1 Determine the refractive indices of the solvent and each 12-TSA solution at the wavelength and temperature of the calibration measurements. Take three repeat measurements, which shall differ by less than ±0.0002, and average them.

X2.3.5.2 Calculate d*n*/d*c* for each solution as $(n - n_0)/c$, where n_0 is the solvent refractive index. (Values of d*n*/d*c* are typically near 0.09 mL/g.)

X2.4 Calculation

X2.4.1 Following the procedure of Section 10 through step 10.3.5, calculate, for the 90° data at each concentration, the ratio of scattered to reference readings, with solvent readings subtracted and all pertinent corrections (including that for depolarization) applied. Divide solution concentrations by these ratios to obtain the quantities, $c/\Delta(L_s/L_r)$.

X2.4.2 Calculate the Debye constant *K* separately for each solution concentration, using the appropriate values of *n* and d*n*/d*c* from X2.3. Form the products $Kc/\Delta(L_s/L_r)$ and extrapolate a plot of this quantity versus *c* to zero concentration.

X2.4.3 Calculate the calibration constant k_w as follows:

$$k_w = M[Kc/\Delta(L_s/L_r)]_{c=0}\ \mathrm{cm}^{-1}$$

where $M = 2879$, the molecular weight of 12-TSA.

X3. TYPICAL DATA

X3.1 The data used in this section refer to a sample of poly(methyl methacrylate) measured in 2-butanone at room temperature using a Baum-Billmeyer photometer (**9, 25**).

X3.2 *Data Obtained at Selected Concentrations and Angles*—The scattered intensities and reference intensities, after correction for zero-signal readings and application of amplification and filter factors, are given in Table X3.1, Section A. The data after manipulation as described in 10.3 and 10.4 are given in the remaining sections of the table.

X3.3 *Zimm Plot*—The Zimm plot prepared from the data in Table X3.1 is given in Fig. X3.1.

X3.4 *Equations for Calculations*—The basic equation for light scattering is the Debye equation:

$$Kc/\Delta R_\theta = 1/\bar{M}_w P(\theta) + 2A_2c$$

where the symbols have been introduced previously except for *P*(θ), which is a particle-scattering factor (**5**) describing the angular dependence of the scattered light. Although the exact form of *P*(θ) is required to be known in the dissymmetry method (Note 7), it is not required in the Zimm-plot method. It is shown that for small θ,

$$1/P(\theta) = 1 + (16\pi^2 n^2/3\lambda^2)\,\bar{s}^2\ \sin^2(\theta/2)$$

so that measurement of the initial slope of the zero-concentration curve of the Zimm plot allows calculation of the radius of gyration.

X3.5 *Calculation of the Rayleigh Ratio from Scattered and Reference Intensities* —The primary calibration of the photometer was carried out with an aqueous standard, and yielded (as described in Appendix X2) a calibration constant for aqueous solutions $k_w = 0.869 \times 10^{-4}\ \mathrm{cm}^{-1}$. A refractive correction (Appendix X4) must be applied. The refractive index of 2-butanone at the temperature (25°C) and wavelength (546 nm) used in the experiment is $n_s = 1.3856$; the refractive index of the calibration solvent under the (same) conditions of calibration is $n_w = 1.3343$. The Rayleigh ratio is as follows:

$$\begin{aligned} R_\theta &= k_w\,(n_s/n_w)^2\,(L_s/L_r) \\ &= 0.869 \times 10^{-4}\,(1.3856/1.3343)^2\,(L_s/L_r) \\ &= 0.936 \times 10^{-4}\,(L_s/L_r),\ \mathrm{cm}^{-1} \end{aligned}$$

where L_s/L_r is the ratio of scattering to reference readings. Thus each figure in Section D of Table X3.1 is converted to the corresponding Rayleigh ratio in Section E by multiplying by 0.936×10^{-4}.

X3.6 *Calculation of the Debye Constant* (10.7.1)—The Debye constant *K* requires knowledge of the refractive index *n* from 9.8 or tables (here $n = n_s = 1.3856$), the specific refractive increment $\mathrm{d}n/\mathrm{d}c = 0.112\ \mathrm{cm}^3/\mathrm{g}$), Avogadro's number $N_0 = 6.023 \times 10^{23}\ \mathrm{mol}^{-1}$), and the wavelength (here $\lambda = 546$ nm $= 5.46 \times 10^{-5}$ cm).

$$\begin{aligned} K &= 2\pi^2 n^2 (\mathrm{d}n/dc)^2/N_0\lambda^4 \\ &= 2\pi^2\,(1.3856)^2\ {}^2/(6.023 \times 10^{23})\,(5.46 \times 10^{-5})^4 \\ &= 0.925 \times 10^{-7}\ \mathrm{mol\cdot cm^2/g^2} \end{aligned}$$

X3.7 *Calculation of the Weight Average Molecular Weight*—The intercept from the Zimm plot is read as $(c/\Delta R_\theta)_{c=0,\theta=0} = 4.05\ \mathrm{g/cm^2}$.

$$\begin{aligned} \bar{M}_w &= 1/K(c/\Delta R\upsilon_\theta)_{c=0,\ \theta=0} \\ &= 1/(0.925 \times 10^{-7})\,(4.05) \\ &= 2\ 600\ 000\ \mathrm{g/mol} \end{aligned}$$

X3.8 *Calculation of the Second Virial Coefficient*—At θ = 0, take $c_2 = 0.00208\ \mathrm{g/cm^3}$ and $c_1 = 0$. Then $(c/\Delta R_\theta)_{c2}$ is read from the Zimm plot as $11.07\ \mathrm{g/cm^2}$ and, as in X3.7, $(c/\Delta R_\theta)_{c1} = 4.05\ \mathrm{g/cm^2}$.

$$\begin{aligned} A_2 &= \tfrac{1}{2} K[(c/\Delta R_\theta)_{c2} - (c/\Delta R_\theta)_{c1}]/(c_2 - c_1) \\ &= \tfrac{1}{2}\,(0.925 \times 10^{-7})\,[11.07 - 4.05]/(0.00208 - 0) \\ &= 1.56 \times 10^{-4}\ \mathrm{cm^3 \cdot mol/g^2} \end{aligned}$$

X3.9 *Calculation of the Radius of Gyration*—Since the $c = 0$ line on the Zimm plot is here a straight line, extend it to $\sin^2(\theta/2) = 1.00$ and read $c/\Delta R_\theta = 14.00$. Then the slope is $(14.00 - 4.05)/(1.00 - 0) = 9.95$, and the intercept is, as before, 4.05. The value of *K* and the units cancel. The mean square

TABLE X3.1 Typical Data from Light Scattering

Concentration *c*, g/mL	Scattering Angle θ, deg				Reference Intensity
	30	60	90	120	
A. Observed Intensities, Recorder Chart Divisions					
0	38	16	13.4	14.0	218
0.00060	456	205	140	134	220
0.00108	646	300	213	208	221
0.00147	770	370	266	261	220
0.00180	820	405	290	294	220
0.00208	910	450	333	339	230
B. Intensities Corrected for Scattering Volume					
0	19	14.1	13.4	12.1	218
0.00060	228	177.5	140	116	220
0.00108	323	260	213	180	221
0.00147	385	320	266	226	220
0.00180	410	350	290	254	220
0.00208	455	390	333	293	230
C. Scattered Intensity Divided by Reference Intensity					
0	0.087	0.065	0.062	0.056	
0.00060	1.038	0.807	0.636	0.528	
0.00108	1.460	1.175	0.964	0.815	
0.00147	1.750	1.453	1.200	1.029	
0.00180	1.865	1.590	1.319	1.155	
0.00208	1.978	1.695	1.447	1.273	
D. Intensity Ratio Less Solvent Reading					
0.00060	0.951	0.742	0.574	0.472	
0.00108	1.383	1.110	0.902	0.759	
0.00147	1.663	1.388	1.138	0.973	
0.00180	1.778	1.525	1.257	1.099	
0.00208	1.891	1.630	1.385	1.217	
E. $\Delta R\theta \times 10^4$					
0.00060	0.890	0.695	0.537	0.443	
0.00108	1.295	1.040	0.845	0.710	
0.00147	1.555	1.300	1.065	0.911	
0.00180	1.665	1.427	1.177	1.029	
0.00208	1.770	1.525	1.295	1.138	
F. $c/\Delta R\theta$					
0.00060	6.75	8.63	11.17	13.55	
0.00108	8.33	10.38	12.77	15.19	
0.00147	9.47	11.30	13.80	16.12	
0.00180	10.80	12.60	15.30	17.48	
0.00208	11.75	13.65	16.05	18.28	
G. $\sin^2(\theta/2) + 100\,c$					
0.00060	0.127	0.310	0.560	0.810	
0.00108	0.175	0.358	0.608	0.858	
0.00147	0.214	0.397	0.647	0.897	
0.00180	0.247	0.430	0.680	0.930	
0.00208	0.275	0.458	0.708	0.958	

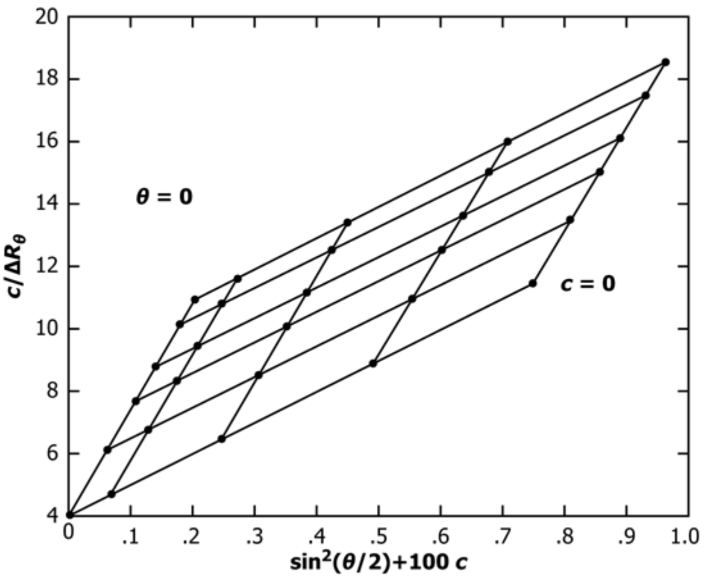

FIG. X3.1 Zimm Plot for the Data of Table X3.1

radius of gyration is as follows:

$$\bar{s}^2 = 3\lambda^2/16\pi^2 n^2 \times (\text{slope/intercept})$$
$$= (3)\,(546)^2/16\pi^2\,(1.3856)^2 \times (9.95/4.05)\ \text{nm}^2$$
$$= 7247\ \text{nm}^2$$
$$(\bar{s}^2)^{1/2} = 85\ \text{nm}$$

Note that the radius of gyration and the wavelength must be in consistent units.

NOTE X3.1—In the data considered, vertically polarized light was used, so there is no polarization correction; a circular cell was used, so the volume correction factor was sin θ; and there was no absorption, fluorescence, or depolarization, so use of these correction factors was not required.

X4. CORRECTION FACTORS

X4.1 Introduction

X4.1.1 The following correction factors (**19**), discussed in alphabetical order, must be calculated for the particular polymer, solvent, and photometer used, and applied to light-scattering data as described in Section 8.

X4.2 Absorption Factor

X4.2.1 The correction factor for absorption, C_a, must be applied to all scattering data when the scattering medium absorbs light at the wavelength of the incident beam. Its function is to restore the scattered intensity to the value it would have had if no absorption had been present.

X4.2.2 If a cylindrical scattering cell is used, and if the design of the photometer permits, measure the internal transmittance, T_i, of scattering solution at $\theta = 0$, as the ratio of the reading with the solution in the cell to that when the same cell is filled with a nonabsorbing solvent. This is normally attributed to the scattering solvent, or a pure nonabsorbing liquid of approximately the same refractive index. The value of C_a under these conditions is $1/T_i$.

X4.2.3 Alternatively, the internal transmittance T_i of the scattering solution is measured relative to that of a nonabsorbing liquid in a cell of length l', in a spectrophotometer at the wavelength of interest, and T_i calculated for the scattering-cell length l by the application of Lambert's law:

$$\log T_i = (l/l')\log T_i'$$

X4.2.4 For other cell shapes, l is not typically independent of angle, and the analysis becomes somewhat more complex (**23**).

X4.3 Amplification Factor

X4.3.1 Whenever the amplification of the amplifier is varied to keep the scattered-light readings within the range of the recorder system, the amplifier attenuation factor must be applied to all data. In order that this factor be reproducible, it is recommended that only stepwise, rather than continuously variable, attenuators be used, and that the attenuation factors be determined with the same photometer system used for the measurements.

X4.4 Depolarization Factor

X4.4.1 When the scattering particles are anisotropic, the scattered radiation is depolarized, and the depolarization or Cabannes factor C_d must be applied. To compute C_d, the intensities of horizontally (H) and vertically (V) polarized light must be measured at $\theta = 90°$, by use of a polarizer in the detector optical system.

NOTE X4.1—The responsivity of the photomultiplier tube has been shown to be sensitive to the state of polarization of the light incident on it. This sensitivity must be determined, for example by measurement of the reference diffuser with unpolarized incident light and the use of the polarizer in the detector optical system, and applied as a correction to measurements of H and V.

X4.4.2 The ratio H/V is the depolarization,ρ . It is concentration-dependent, and the excess depolarization of the solution over that of the solvent must be extrapolated to zero concentration. In practice, $\rho < 0.01$ for polymers and decreases with increasing molecular weight; C_d is then <1.05 and is often ignored. In any case, $V >> H$, and use of a neutral filter or amplifier attenuation to reduce V to the same magnitude as H has been found to be convenient.

X4.4.3 For unpolarized (subscript u) and vertically polarized (v) incident light, respectively,

$$C_{d,u} = (6+6\rho_u)/(6-7\rho_u)$$
$$C_{d,v} = (3+3\rho_v)/(3-4\rho_v)$$

C_d is applied as a correction factor to $(c/\Delta R_\theta)_{c=0,\theta=0}$.

NOTE X4.2—C_d is much more complicated (**23**) when measurement must be made at an angle other than 90°.

X4.5 Filter Factor

X4.5.1 Whenever neutral filters are used to keep the scattered-light readings within the range of the recorder system, the filter attenuation factor must be applied to all data. It is important that these factors be determined, for each filter or combination of filters used, with the same photometer system used for the measurements. The factor for a combination of two or more filters must not be calculated from the factors for the individual filters because of the effects of inter-reflections among the filters.

X4.6 Polarization Factor

X4.6.1 When unpolarized incident light is used, the excess Rayleigh ratio ΔR_θ must be corrected by C_p, a polarization factor:

$$C_p = 1/(1+\cos^2\theta)$$

When vertically polarized incident light is used, as is advocated in this practice, $C_p = 1$.

X4.7 Reflection Factor

X4.7.1 A reflection correction is required to account for light which is reflected at air-glass and (less important) glass-liquid interfaces, where a change in refractive index occurs (**26**). The most serious effect is the reverse asymmetry of the scattered light contributed by reflection from the exit window of the cell. Other reflections arise from scattered light at the back side of the cell at the angle υ, and of light scattered at the angle $180 - \theta$.

X4.7.2 For cylindrical cells, corrected values of the Rayleigh ratio R_θ can be obtained from observed values R_θ' and $R'_{180-\theta}$ as follows:

$$R_\theta = (1/X)\left[R_\theta' - YR'_{180-\theta}\right]$$

where:

$X = [(1-f_l)^2(1-f_a)^2(1-Y^2)]$
$Y = ½[f_l + (1-f_l)f_a]$

$f_a = [(n_g - 1)/(n_g + 1)]^2$
$f_l = [(n_g - n_l)/(n_g + n_l)]^2$

and n_g and n_l are the refractive indices of the glass of the cell and the liquid in the cell, respectively. The forms of the correction for other types of cells are given in the literature (**23**, **26**).

X4.7.3 The reflection correction can be minimized or eliminated by placing a piece of glass which absorbs completely at the wavelength of interest inside the cell at the exit window, coating the exit window and back face of the cell with an absorbing paint, or immersing the cell in a vessel filled with liquid as described in X1.4.2.

X4.8 Refraction Factor

X4.8.1 Because the volume in the scattering medium viewed by the detector optical system depends upon the refractive index of the scattering medium, n_s, and that of the surrounding medium, n_m (which is normally air or the immersion liquid described in X1.4.2), a refraction correction (**27**)C_n is required. For photometers that do not view past the edges of the irradiated volume in the cell (**28**), C_n is given as follows:

$$C_n = (n_s/n_m)^2 \left[1 - \frac{l/2}{l/2 + r} \left(\frac{n-1}{n} \right) \right]$$

where l is the path length of the scattering cell and r is the distance from the center of the cell to the detector. For most photometers, $r >> l$ and

$$C_n = n_s^2 / n_m^2$$

X4.8.2 When the photometer is calibrated with a liquid of refractive index n_w, C_n must be applied to both the calibration step and the measurement step. In this case, n_m cancels out and

$$C_{w \rightarrow s} = n_s^2 / n_w^2$$

This factor multiplies the calibration constant k_w.

X4.9 Volume Factor

X4.9.1 Use of a volume correction factor C_v is required, to account for the change with angle of the volume of scattering solution viewed by the detector system (**27**, **28**). In a detector optical system which does not view past the edges of the irradiated volume, $C_v = \sin\theta$. For a system that views the entire scattering volume, $C_v = 1$.

X4.9.2 A commonly used check of the theoretical volume correction factors of X4.9.1 is made by observing the fluorescence of a solution of 0.05 mg of sodium fluorescein in 100 mL of 1 *M* NaCl. The solution is irradiated with 436-nm light, and a short-wavelength-cutoff filter, absorbing up to a slightly higher wavelength, must be placed in the detector optical system. In this way only the fluoresced light, whose intensity is independent of angle, is observed. Deviations from the factors of X4.9.1 have been shown to result from minor defects in the scattering cell or photometer optics, and the measurements are used to derive an empirical volume correction factor for that cell and photometer.

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SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue () that may impact the use of this standard. (November 1, 2013)

(1) Removed permissive language in 1.2, 1.2.1, 4.3, 6.1, 7.1, 8.2, 8.3, 9.2, 9.3.1, 9.3.2, 9.3.3, 9.5, 9.5.2.1, 9.6, 9.9.1, 10.5.4, 10.6.1, 10.6.2, 12.1, Notes Notes 3-7, Note 10, and in the Appendixes in X1.3.1, X1.4.5, X1.6.2, X1.7.3, X2.2.2, X2.3.2, X2.3.5.1, X2.3.5.2, X3.4, X3.9, X4.2.2, X4.2.3, X4.2.4, X4.4.2, X4.8.1, X4.9.2, and Note X2.1, Note X2.2, Note X4.1.

(2) Made editorial changes for clarification in 9.1, 9.3.3, 10.6.3, Note 8, and in the Appendixes X1.2.3, X1.2.4, X1.4.1, X1.4.2, X1.5.1

(3) Revised the ISO statement in Note 1 to the standard verbiage.