CHAPTER 8

Turbidimetry; Nephelometry; Colloidimetry*

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* *turba*, cloud (L.); *nephelē* (νεφέλη), cloud, mist (Gk.); *kolla eidos*, glue form (Gk.).

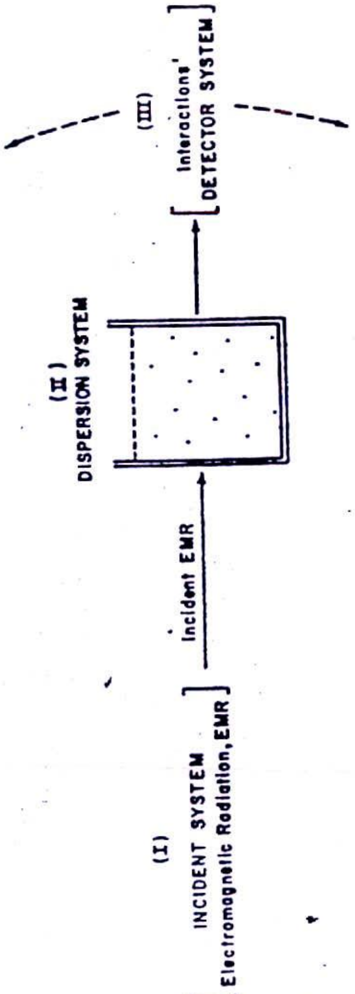

FIGURE 8.1: The systems Involved.

8.1 PREFACE

The established applications of these methods have had rather limited direction to pharmacy. As the scope of this chapter, it is the purpose to report upon the *meaning* of the methods because it is felt that present technologies based in them are important resources for pharmacy.

Also, because there are so many facets to the methods, there appears to be less pedagogical purpose to reciting specific procedures than to directing interests into specific areas by citing selected references according to topics (see Appendix).

8.2 INTRODUCTION

The environment of man provides a number of ordinary examples for his relative visual awareness and reasonings about matter whenever it is distributed in fine particulate state by its dispersion medium.

Such phenomena of ordinary environment as are called milkiness, opalescence, haze, mist, fog, smog, smoke, clouds, searchlight beams, etc., are readily sensed and qualitatively understood. Equally sensed but less understood are the deep-seated cause/effect relationships of such phenomena as the blues of tobacco smoke and of sky, the rich spectral hues of the sunrise, sunset and rainbow, the gray of the dawn and twilight.

It is appropriate to state early and generally here that underlying all such phenomena is the fact of interaction between dispersed fine particles and visible electromagnetic radiation (EMR) passing through the dispersion; and that the factors in interaction have been subjected to rigorous theories and experiments.

A. THE MEANING OF THE PROBLEM

Figure 8.1 and Table 8.1 demonstrate the elements of both the primitive and the advanced problems. From them it can be surmised readily that the accuracy to be expected of any analysis for the characteristics of a dispersion via measurement of interactions is dependent upon as many as possible of the factors and their functional interdependencies, in and among the three systems, being controllable and measurable.

The significant literature on the science of the total problem begins with the reports of recognitions by Richter[1] (using a gold sol) and Tyndall[2] (using an atmosphere of butyl nitrite and HCl) that the colors from or the path of a beam of light directed through the dispersion is revealed by visual observation from the side.

TABLE 8.1: Factors Involved in Interactions between EMR and Dispersions

I	II	III
Intensity I_0 Wavelength λ Bandwidth	Dispersion, as to components*: Number Composition Phase condition Optical properties Scattering particles as to: Size Size distribution Shape Concentration Dielectrics Length of EMR path	Interactions:* Scatterings: Diffractions Refractions Dispersions (spectral) Reflections Polarizations Interferences Absorptions Kinetics Thermodynamics

* It is understood that EMR undergoes no change in wavelength as a result of interaction.

Such phenomena, due to light-scattering, are popularly termed the "Tyndall effect"; the path as the "Tyndall cone." It may be demonstrated more readily by the following simple experiment: Prepare a 6"-square sheet of card-paper with a slit (2" × 1/16") cut at its center. Into a 400 ml. beaker of clear water stir a few drops of milk or a pinch of powdered silica gel. With the room darkened and with a flashlight beam directed through the horizontal slit and the solution, attempt to observe the Tyndall effect and cone from the various angles relative to the direction of the beam path. Observe also the change in direction of the path as the flashlight or the slit is elevated or lowered; the path from its transmitted direction; the effect of turning the slit slowly through a 90° angle; the relative intensities of incident, transmitted and scattered EMR.

Demonstrations with the same purpose but involving more elaborate apparatus are described elsewhere.[3,4]

It is generally understood that observations of the Tyndall effect and cone are made from a horizontal position at a 90° angle. If observation be from the vertical position through the meniscus, the considerable distortion which results can obliterate the otherwise clear path of the cone.

Richards' use[5] of the Tyndall effect, through his design of the first *nephelometer* to enable his determination of the atomic weight of Sr, constituted the classical beginning for practical measurement of dispersions on the basis of their EMR/particle light-scattering interaction. Cruder visual judgments of relative concentration of dispersed particles had been attempted prior to Richards' work.

Since the size factor was recognized early by theorists to be important to interaction characteristics, this discourse concerning the principles involved is greatly assisted by consistent meaning for prevalent terms as to sizes, as follows:

1. *Fine* particles are:
   a. *Small* (or Rayleigh-size), when $L < \lambda/10$

b. *Large* (or Mie-size), when $\lambda/10 < L < 2.5\ \mu$; measurable by electron microscopy or ultramicroscopy

2. *Coarse* particles: when $L > 2.5\ \mu$

where L is the longest dimension, disregarding shape of particle, e.g., diameter of a sphere, or length of a rod.

Because of the small dimensions which in part characterize EMR wavelengths and particle sizes, the following approximate L-values are helpful for the perspective they have when compared with EMR-wavelengths . . . : H_2: 0.1 mμ; O_2: 0.16 mμ; Sucrose: 0.7 mμ; Starch: 8 mμ; Colloidal range: 1–250 mμ; *B. coli*: 1500 mμ; *Anthrax bacillus*: 6 μ; RBC: 8 μ.

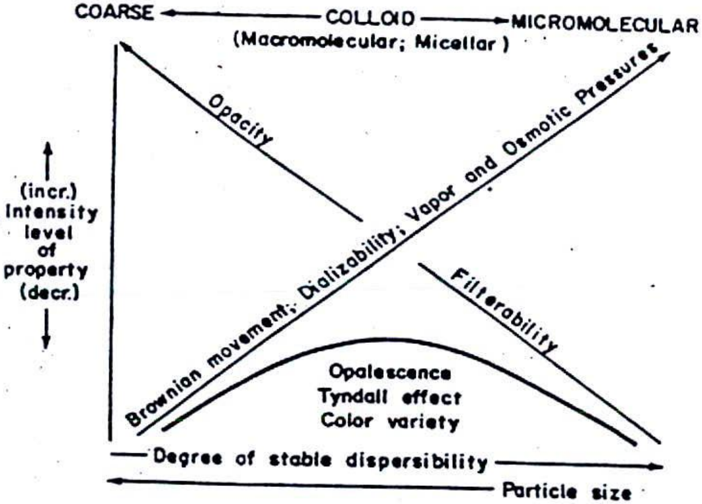

FIGURE 8.2: Effect of particles upon properties of their dispersions. Adaptation, after McBain.[4]

It should be emphasized that light-scattering methods are but one type among many other (such as microscopic, centrifugal, osmotic, X-ray, diffusion, and gas absorption) methods for determining dispersion characteristics.

A correlation may be made among various magnitudes of dispersed particles and their physical properties. Figure 8.2 is a representation of the general effects of three broad categories of particle sizes upon some of the most familiar of these properties. The figure is analogous to being a plot of dispersed particle sizes (X axis) vs. consequent dispersion properties (Y axis). Thereby, the concept is clarified that the gradual change in intensity of any such property and the gradual change in particle size are interdependent, at least for a given species of matter. Specific data would be required to detail the nature of the interdependence.

B. SOME GENERALIZATIONS REGARDING LIGHT-SCATTERING INTERACTIONS BETWEEN VISIBLE EMR AND MATTER

Absorption of EMR by matter is not included as a light-scattering phenomenon. In practical considerations, however, its coincidence with scattering must be evaluated for significance as a factor in the attenuation of incident EMR.

Light scattering principles for dispersions must be considered under the following conditions. It should be emphasized at the beginning that a dispersion system must be such that the particles have the conditioned freedom for mobile random distribution. Thus, the point-sources for scattering interactions are random particles.

1. Matter as a Pure Gas

The dispersed particles may be contained or uncontained. In either case, each interacts individually and without interference by neighboring particles. Thus, the total interaction is the sum of the interactions by the individual particles.

2. Matter as a Pure Liquid

The individual particles are no longer independent of neighboring particles, for the dispersion is much more dense so that in relation to EMR wavelength, the EMR-scattering effects by adjacent particles are out of phase.

If the number of particles in an interacting volume of matter as a liquid is *n* times the number of particles in an interacting equal volume of it as a gas (both at atmospheric pressure), the resultant interaction will show to be less for the liquid form; for, the particles not being independent, their scattering effects will not be independent but rather interferent (cf. Section 8.3A.2).

3. Solutions and Suspensions as Dispersion Systems

Inasmuch as such dispersions mean composition by more than one component, the generalizations are various according to analytic purpose for considering EMR/matter scattering interactions. Each purpose, therefore, determines the necessity for analytic data concerning:

1. The resultant interaction due to the dispersion
2. The resultant interactions due to each:
   a. Dispersing medium
   b. Dispersed phase

These imply a range of possible needs for data which derive *relative* to *absolute* values for interactions with EMR by the dispersion and its components. Thus, in a practical relative analysis, the coincident use of a primary-standard dispersion or of a blank dispersion may provide comparable data of sufficient significance to permit cancellation, without measurement, of interaction due to dispersion medium when the dispersed phase is the primary object of the analysis; and in analyses based on absolute values for interactions, the theoretical and applied significance for such values is exemplified in Section 8.3C.2.e.

The following are the general effective factors in dispersion systems subjected to interaction with EMR. According to what is available in the literature, several of the factors have not yet been evaluated.

1. Number of components in the system:
   a. Dispersed phase (1, 2, 3, . . . components)
   b. Dispersing phase; i.e., the medium (1, 2, 3, . . . components)
2. All components, as to:
   a. Material differences
   b. Optical differences. Ideally, a dispersion which is perfectly transparent will scatter no light. The degree of opalescence (see Fig. 8.2) of a dispersion is due in part to the magnitude of difference between the refractive indices of particles of the dispersed and dispersing phases.

      The property of refraction is not an independent factor since it is intimately related to the material (part 2.a., just listed), to other optical properties (cf. Fig. 8.3), and to particle size and shape.
   c. Gas-, liquid-, and solid-phase states. The necessary qualification that a dispersion must be such that the particles have freedom (though conditioned) for mobile random distribution in order to possess the property of light-scattering restricts them to being either gas-, liquid-, or solid-in-gas or gas-, liquid, or solid-in-liquid.

      Gas-, liquid-, or solid-in-solid systems constitute immobile cases, and are not considered to be in the general realm of dispersions. They do not conform in theory or practice to conventional principles because the point-sources for scattering interaction are fixed in position, resulting in complete interference among scattered wavelets.

Encounter of visible EMR with dispersions may involve its passage along, among, into, and from the particles; depending upon the optical properties. The interactions possible are of several appreciable forms which were cited but not defined in Table 8.1. It is helpful to realize that the relative complexity of a dispersion system contributes, with seeming directness, to the number of such interactions which have a role; and that the interactions involved may somehow combine, interfere with, or be independent of each other.

Figure 8.3 provides a review of the basic meanings of the various types of scattering-interactions phenomena. In each case it is seen that matter in its path is represented to effect some change in EMR. Such changes are directional (q.v. diffraction, refraction, reflection), electromagnetically differentiated (q.v. polarization), and λ_{band} component separated (q.v. spectral dispersion).

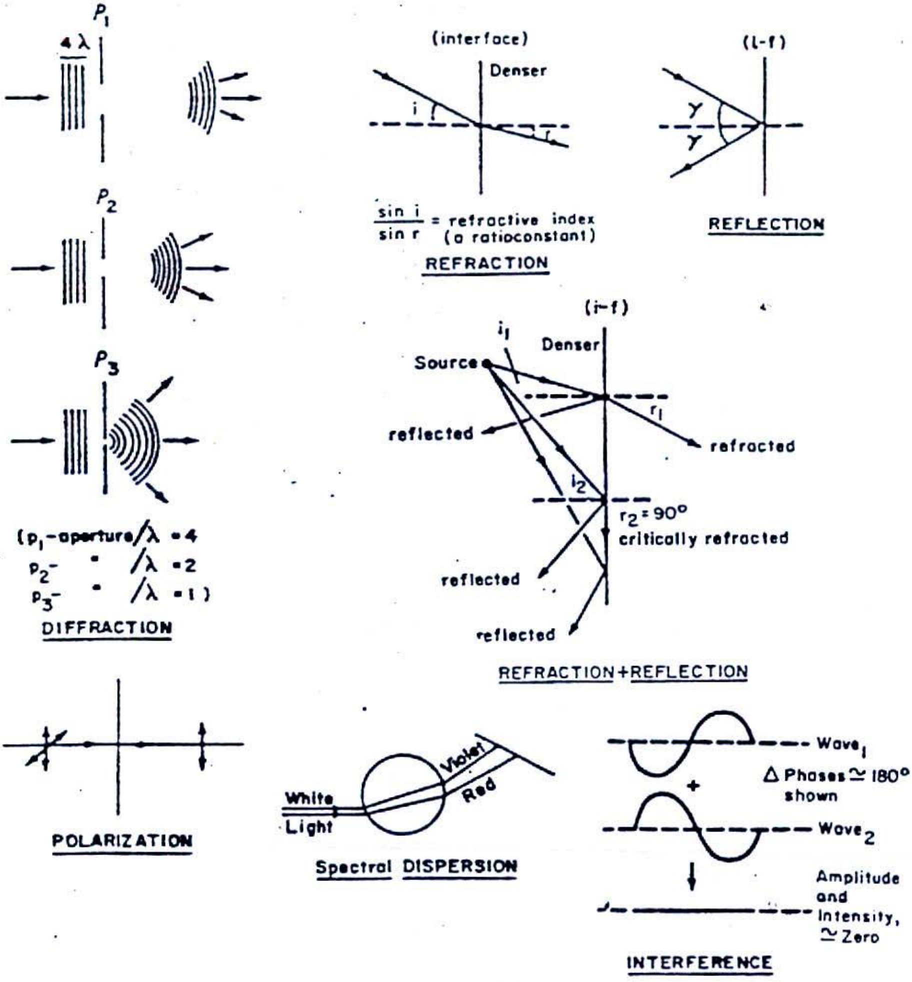

FIGURE 8.3: Basic meaning of EMR/particle interactions.

Projection of Fig. 8.3 evokes Fig. 8.4 to represent the possible angular effects of one particle upon incident EMR. Figure 8.4, in turn, evokes Fig. 8.5 to introduce the significance of interference (q.v. Fig. 8.3). The implications from further projections of meanings of Figs. 8.3–8.5 to dispersion *systems* will be considered in sections which follow. Before continuing however, it is essential to review the meanings of basic terms of spectrometry, such as (true) absorption, transmission, and optical density (see Chapter 1).

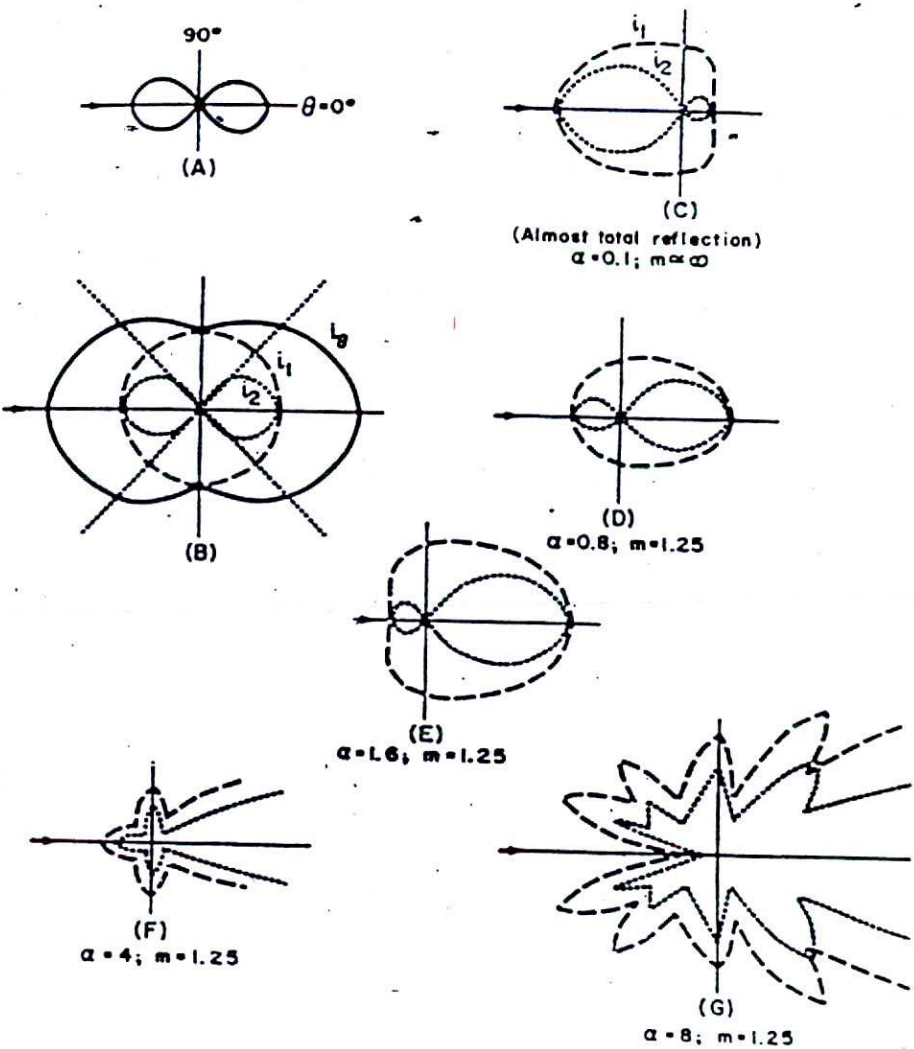

FIGURE 8.4: Theoretical light-scattering envelopes. Particle is at 0/0/0 of the XYZ coordinates. Adaptation, after Blumer.[11]

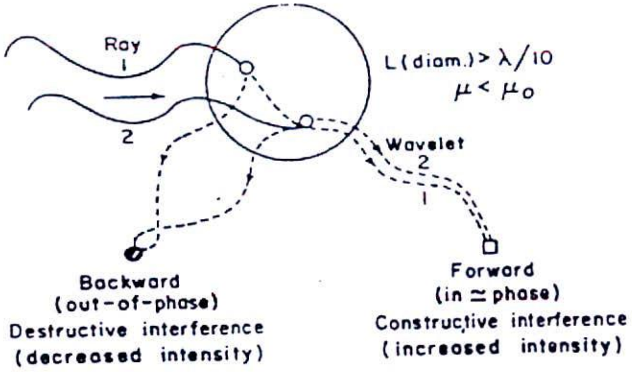

FIGURE 8.5: The forward and backward scatterings from a *large* particle. Adaptation, after Zimm et al.[23]

necessary for the definition of the meanings of such new terms as "apparent absorption" and "multiple scattering."

C. SPECTROMETRY

Concerning all of the interactions between EMR and dispersions, the most extensive science and literature belong to *true* absorption; in fact, much of the knowledge gained from spectral-absorption studies have been basic for studies extended to light-scattering interactions, so that many of the concepts and analytic terms of spectrometry apply equivalently to turbidimetry, nephelometry, and colloidimetry. For adequate background in addition to Chapter 1, familiarity with "Spectrometric Nomenclature"[7] (for conventional terms and definitions) and with references[8–10] [for their historical documentation of the attributed names: Bouguer (1729), Lambert (1760), and Beer (1852) for spectrometric laws] are recommended.*

8.3 PRACTICAL THEORY ON LIGHT-SCATTERING

Throughout the pertinent literature concerning light-scattering interactions in dispersions, there have been a few minor differences among reporters in symbols attributed for scattering factors and terms. The following list collects, for brief definitions, most of the symbols of this section; it includes those which reconcile differences for the purpose of this text.

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[*] The conglomerate meaning of the Bouguer, Lambert, and Beer laws has been expressed variously by names in modern spectrometric literature, most prevalently by Beer's law and the Beer-Lambert law. This text selects "Beer's law" as the term for referring to that meaning.

$$\left.\begin{array}{r}I_0 = \text{incident EMR}\\ I = \text{transmitted EMR}\end{array}\right\}\ \text{intensity (energy flux, ergs per square centimeter per second)}$$

$$\left.\begin{array}{r}\lambda = \text{wavelength (in vacuo)}\\ \lambda' = \text{wavelength (in medium)}\end{array}\right\}\ (\lambda' = \lambda/\mu_0)$$

n = wavelength exponent (of λ^n; $n = 4$ in Rayleigh theory)
θ = scattering angle; reference: transmission angle ($\theta = 0°$)
i_{sc} = scattered-EMR intensity at $\theta°$
i_{sc}/I_0 = Tyndall ratio
r = radius of a spherical particle
L = $2r$ or D (diameter) of a sphere: longest dimension, nonsphere
x = size-parameter for *fine* particles; $x = 2\pi r/\lambda'$
μ = refractive index of particle; of solution in Debye theory
μ_0 = refractive index of medium
m = refractive parameter; $m = \mu/\mu_0$
d = distance of detector from particle (or dispersion volume)
ρ = polarization effect of particle
v' = volume of particle ($4/3\pi r^3$)
n = number of particles per unit volume of dispersion
nv' = volume of particles per unit volume of dispersion
c = concentration of dispersion (grams per centimeter cubed)
l = length of transmission (or scatter) path traversed
M = molecular weight of solute
N = Avogadro's number; $N \simeq 6.03 \times 10^{23}$
K_{sa} = "scattering area" coefficient (of Mie theory)
τ = turbidity

A. FORMULATIONS OF FACTORS AND TERMS FOR FINE-PARTICLE DISPERSIONS

Though the more fundamental theory is based upon consideration of light-scattering by a single particle, applied theory projects single-particle theory to the obvious condition that many particles are present.

The assumption of an *ideal case* consists of the conditions listed in Table 8.2. Complications due to deviations from ideality are discussed in Section 8.3B.

This ideal case enables theoretical considerations to light-scattering phenomena involving *fine* particles to be classified into principal types. Each of these types is based on two parameters of the scattering particles, namely their size (expressed as $x = 2\pi r/\lambda'$) and their refractive index relative to that of the medium (expressed as $m = \mu$ (of particle)/μ_0 (of medium)); it is also based on the scattering-angle parameter θ.

Figure 8.4 summarizes the principal types of light-scattering patterns ("envelopes") from single particles. Of these types A and C have not received extensive study. Incident EMR is unpolarized, except in type A. The solid lines (where shown) represent "finite" limits of vectors (i.e., directed magnitudes) of total scattered intensities. The dashed and dotted lines refer to the scattered polarized components of the incident EMR; thus, the i_1 or $i_\perp$ (dash) and the i_2 and $i_\parallel$ (dot) are the perpendicular and horizontal components, respectively; and thus, the vector sum $i_\theta = i_1 + i_2$ is the resultant intensity at angle θ. Recognition that the vectors are all-directioned evokes the realization that a theoretical single-vector intensity is an "infinitesimal" fraction of the incident-EMR intensity.

TABLE 8.2: An Ideal Case for Theoretical Study of Interactions[a]

1. Incident-EMR intensity I_0 is constant
2. Incident-EMR wavelength λ is monochromatic
3. Isotropicity of } scattering particles
4. Nonabsorption by } scattering particles
5. Monodispersity of } scattering particles
6. Two-component (dispersing + dispersed) system
7. Adequately dilute dispersion for independent EMR/particle interactions

[a] Presumed are: Stability of the dispersion system; variability of the detector position.

Blumer[11] derived the types C, D, E, and F envelopes by calculations from Mie equations. Concurrently, Gans[12] described a correlation between particle size and wavelength (as in $\alpha = \pi D/\lambda'$) by means of scattering envelopes.

1. Rayleigh-Type Scattering[13–17]

Rayleigh-type scattering involves *small* particles, $L < 0.05\ \mu$ (see Fig. 8.4B). The longest particle-dimension (diameter in this instance) does not exceed $\lambda/10$. Under this condition each particle interacts as a single-point dipole oscillator. At $\theta = 90°$ the scattered light is completely polarized. Since the envelope is completely symmetrical, scattering is believed to be due almost entirely to diffraction, practically not at all to refraction and/or reflection.

Rayleigh scattering theory has received expression principally in two equation forms, depending upon the considered type of dispersion and factors involved. Thus, the scattered/incident intensity ratio i_{sc}/I_0:

a. For a gas in a vacuum (e.g., atmosphere; the refractive index relationship between μ_0 and μ need not be considered because the medium is not material) is given by

$$\frac{i_{sc}}{I_0} = \frac{8\pi^4 n\rho^2}{\lambda^4 d^2}(1 + \cos^2\theta) \qquad \text{(Refs. 18,19)} \qquad (8.1)$$

b. For a very dilute solution (the medium is material) is given by

$$\frac{i_{sc}}{I_0} = \frac{nv'^2}{\lambda'^4 d^2}\left(\frac{\mu^2 - \mu_0^2}{\mu^2}\right)(1 + \cos^2\theta) \qquad \text{(Refs. 20,21)} \qquad (8.2)$$

The following points emphasize some of the scattering principles which are conveyed by Eqs. (8.1) and (8.2):

$i_{sc} \propto I_0$ implies that experimental proof of a scattered-intensity envelope, via evaluation of its vectors, would require great precision within and coordination of both the incident and detector systems.

$I \propto I_0 - \Sigma i_{sc}$, in the hypothetical and absolute sense, means that attenuation of incident-EMR intensity is in all directions without loss of EMEnergy because the dispersion is a perfect vacuum having particles which upon encounter undergo only scattering interactions.

$i_{sc} \propto (1 + \cos^2 \theta)$, calculated for all values of θ, describes the geometric shape of the scattered-intensity envelope (i_{sc}) and of the polarized components (i_1 and i_2) of i_{sc}. For a given θ-vector, $i_\theta = i_1 + i_2$; and for a 90° vector, $\cos^2 \theta = 0$ and $i_{sc} = i_1$. The ratio $(1 + \cos^2 \theta)/2$ is termed the "depolarization factor."

$i_{sc} \propto 1/\lambda^4$ is a consistent relationship for *small*-particle dispersions. The relationship is manifest beautifully in nature by atmosphere as the dispersion. Since $\lambda_{\text{blue}} < \lambda_{\text{red}}$ of the visible-EMR range, the former is scattered more and transmitted less than the latter. Thus, the *spectral* dispersions at sunrise and sunset are "riotous" and the blues of the sky, the ocean, and tobacco smoke are less so.

The rainbow as a *spectral* dispersion warrants a different explanation because the raindrop particles are *coarse* in size, prismatic in function, and falling.

$i_{sc} \propto 1/d^2$ expresses that EMR-scattering is in accord with the principle of conservation of energy. Here, EMEnergy (expressed in terms of intensity) is scattered as vectors from a point-source. To a detector in position at a cross-sectional area of vectors, the scattered intensity varies inversely as the square of the distance of the detector from the point-source; in other words, doubling the distance quarters the intensity.

$i_{sc} \propto v'^2$ expresses the role of particle size as a scattering factor. Because of the relationship of v' with r, this role becomes even more impressive when expressed in the equivalent terms of $i_{sc} \propto r^6$; hence the importance of excluding alien particles from dispersions to be subjected to analysis by light-scattering or by spectral-absorption methods.

2. Rayleigh-Gans-Type Scattering[12,16,22,23]

Rayleigh-Gans-type scattering appears to be easiest to understand when it is positioned somewhat "intermediate" in meaning between Rayleigh-type (Section 8.3A.1) and Mie-type (Section 8.3A.3) scatterings. To this end, Fig. 8.5 represents a particle of diameter comparable with λ to have at least two point-sources for scattering. It is to be noted that the forward-scattered wavelets are favorable and the backward-scattered wavelets are unfavorable contributors to scattered-intensity vectors (i_s) for Rayleigh-type scattering. The figure does not attempt to distinguish precisely among the possible scattering mechanisms (see Fig. 8.3).

The two principal and limiting conditions for so-called R-G-type scattering have it that:

a. The refractive-index ratio m is near 1 in value. (If it were 1, there would be no distortion of the path of incident EMR traversing through the particle, and hence no scattering.)
b. The particle size may be greater than that of Rayleigh particles only to the extent that, because of condition a, each volume element of the particle (corresponding to each of its point-sources) interacts as an independent Rayleigh-type scatterer.

Under condition b, the different positions in space of volume elements (and point-sources) result in interference between backward vectors of the independent Rayleigh-type scattering elements.

Figure 8.4D and E exemplify the general intermediate characteristics of R-G-type scattering compared with Rayleigh-type (B) and Mie-type (F, G) scatterings.

3. Mie-Type Scattering[24,25]

Mie-type scattering involves *large* particles, $0.05\mu < L < 2.5\mu$ and refractive-index ratio m not near 1 in value. See Fig. 8.4F and G and Fig. 8.5 in the perspective of R-G-type scattering. Refraction and some diffraction are principal mechanisms for the Mie-scattering phenomena. Particle size (expressed as $\alpha = 2\pi r/\lambda$) and the refractive-index ratio (expressed as $m = \mu/\mu_0$) together constitute the so-called m-α domain, and together with θ are the factors which have received most of the experimental attention to verification of Mie-scattering theory.

The theory of the involvement of the foregoing and other factors was established by Mie[24] and shortly thereafter by Debye,[25] independently. Reviews of and extensions upon their basic theory were conducted subsequently by many others.

Within a clarifying summary of the meaning of the complex Mie theory in relation to light-scattering methods for determining particle characteristics (size, molecular weight, shape), Bender[26] presented the following component equations to explain the involvements of the various factors and terms: when

$$m \ngtr 1.33$$

$$L \ngtr \lambda'/6$$

$$\frac{i_1}{I_0} = \frac{\lambda'^2 n}{8\pi^2 d^2}\left[\frac{a_1}{2} + \frac{a_1 + p_1}{2}\cos\theta\right]^2 \tag{8.3}$$

$$\frac{i_2}{I_0} = \frac{\lambda'^2 n}{8\pi^2 d^2}\left[\frac{a_1}{2}\cos\theta + \frac{a_2}{2}\cos 2\theta + p_1\right]^2 \tag{8.4}$$

whereof (electric dipole moment):

$$a_1 = 2\alpha^3 \frac{(m^2 - 1)}{(m^2 + 2)} \tag{8.5}$$

(electric quadripole moment):

$$a_2 = \frac{-\alpha^5}{6} \frac{(m^2 - 2)}{(m^2 + 3/2)} \tag{8.6}$$

(magnetic dipole moment):

$$p_1 \simeq \frac{-\alpha^5}{15}(m^2 - 1) \tag{8.7}$$

It is because of the *large*-particle size (see Fig. 8.5) that the a_2 and p_1 effects come into play. Moreover, particles having larger m and L magnitudes than those just given contribute more terms to the $[\quad]^2$ factor. *Small* particles have negligible a_2 and p_1 values, so that Eqs. (8.3) and (8.4) become Eq. (8.2) in meaning (Rayleigh-type scattering).

B. COMPLICATIONS DUE TO DEVIATIONS[*] FROM IDEALITY

Figure 8.4B implies that Rayleigh-type scattering has the characteristics for being the most ideal within the ideal case (see Table 8.2), inasmuch as the scattering envelope for it is the most symmetrical in reference to intensity vectors from the scattering particle.

Factors within interacting EMR and dispersion systems which are not in accord with the assumed criteria for factors of the ideal case are realistic because they are *the* case. Several of them have received theoretical and experimental attention.

While considering the deviation from ideality of each factor in turn, it is a helpful simplification to consider all other factors as remaining ideal. In fact, appreciation for the known and unknown complexities of the interaction phenomena of the most primitive problem (Fig. 8.1) dictates this simplification.

1. ΔI_0 (Change in Incident-EMR Intensity)

Since $i_{\theta} \propto I_0$, it is reasonable to expect a change of magnitude, but not of shape, of the scattered-intensity envelope. Furthermore, fluctuating or insufficient I_0 results in problems for the detector system.

2. Polychromaticity, cf. Monochromaticity

When λ_{band} is incident and the particles of the dispersion system are *large* and have the appropriate optical properties, relative possibility exists for interaction by the mechanism of *spectral* dispersion. This is because the

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[*] Bibliography to theoretical and experimental studies of these deviations are cited via the topics index of the Appendix.

exponent n of λ^n has two important dependencies in the *large*-particle realm, namely, $n \propto 1/\lambda'$ and $n \propto 1/$particle size (as α), both of which are implied in Mie theoretical equations.

Spectral dispersion as a prominent scattering mechanism has been demonstrated experimentally, under conditions approaching ideality, by a variety of prepared sols and using λ (visible range). Under the best attained conditions, the interaction results in a "riot" of colors by dispersion of incident λ_{band} into its spectrum. The several θ angles at which the most easily detected components (red and green) appear are termed "orders" (1, 2, 3, . . .) of which those of "red hue" are the more prominent.

The principal application of this phenomenon (high order Tyndall spectrum, HOTS) is to particle-size analysis of colloidal systems.

3. Anisotropy, cf. Isotropy

The basic formulations of the Rayleigh and Mie theories assume that the light-scattering particles are spherical. Anticipation of a possible "-tropic" factor in interaction phenomena begins with the realization that:

a. An *isotropic* particle is uniformly shaped in that it will effect the same type of scattered-intensity envelope regardless of its orientation to I_0.

b. An *anisotropic* particle is not uniformly shaped in that its scattered-intensity envelope is changed by at least certain of its orientations to I_0.

The following are some of the principal implications from anisotropy compared with isotropy:

a. Of a *small* particle.

A small amount of dissymmetry of the scattering envelope occurs, favoring the forward direction. Even though the particle is still interacting as a single-point dipole oscillator, vector norms (most noticeably ca. $\theta = 90°$) are distorted; that is, polarization is less than complete at that angle, resulting in a quantitative circumstance which is termed "depolarization ratio" and expressed as i_2/i_1.

The extent of this dissymmetry is of course relative and small; but even so it may be of sufficient significance to need correction by a factor ("Cabannes factor") in analyses requiring special precision (e.g., molecular-weight determinations). Although polarization measurements at $\theta = 90°$ are difficult because the intensity at that angle is low and small ratios are difficult to detect, approximate measurements have been attempted from a detector position *near* $\theta = 90°$ using a so-called polarization photometer, which is capable of reading for i_1 and i_2 through a bipartite (polarized) disk (one-half of which is for i_1, one-half for i_2).

b. Of a *large* particle.

Figure 8.4D, E, F, and G for spheres show the dissymmetry (reference, $\theta = 90°$ or $270°$) between corresponding forward/backward i_{sc} vectors, due to particle size (although μ also is a factor). Gans[27] theorized to some extent regarding the influence upon scattering by deviation from spherical shape.

It is readily grasped that if the particle is anisotropic (e.g., rod or coil), the number of factors contributing to scattering increases over the number due to particle size alone, so that approximations become necessary. Bender[26] has summarized the meanings of some of the approximations and of the application of the concept of "dissymmetry ratio" (expressed, for example, as i_{45}/i_{135}) which, via appropriate equations, can be related to L of the particle if the shape is known. Thus for each combination of size and anisotropic and refractive properties a *large* particle has in theory its characteristic scattered intensity **envelope**, depolarization ratios, and dissymmetry ratios. From this it is interesting to anticipate the changing effects upon the envelope and ratios by a theoretical change of a spherical *large* particle elongating to a rod to a thread (v' and μ remaining constant); and to anticipate the changing considerations required for evaluating these changing effects from the changing relative particle dimensions within this type of anisotropy.

4. Absorption, cf. Nonabsorption

In experimental light-scattering studies, it is unrealistic to expect to attain the absolute, that is, a dispersion system completely devoid of interactions with EMR other than scattering. Studies reported have been of conditions known or assumed to be practically devoid of *true* absorption, which is an interaction property of relative magnitude and significance, depending upon the chemical composition of dispersion components. Evaluation of the effect of true absorption coincident to any extent with *apparent* absorption has been a neglected aspect of light-scattering analytic methods, for the problems such coincidence presents are formidable and generally have been avoided by design in experimental studies to test validity of scattering-interaction theories. The problems emerge, when true absorption is coincident, because of its dependence as a function of λ'; furthermore, the wavelength exponent of λ'^n is a function of both $1/\lambda'$ and $1/\alpha$ for *large* particles and is 4 for *small* particles, when scattering alone is the interaction.

Spectrometry uses the transmission angle ($\theta = 0^\circ$) to evaluate true absorption by correlating I with I_0 through expression as absorbance (A) or as transmittance (%T), instrumentally. To test whether a dispersion of *small* particles has sufficient true absorption property to affect the practical validity of data concerning its light-scattering properties, the transmission angle is chosen. Since the dispersion itself constitutes a constant (i.e., is invariable for the test), $I_0 - I$ will vary as $1/\lambda'^4$ for measurements over a range of wavelengths when no true absorption is coincident.

When true absorption is unavoidable, the prevalent inclination is to seek a wavelength at which it is minimal and at which light-scattering data are valid in terms of Beer's law or are derived under calibrated conditions.

When the three systems of Fig. 8.1 are properly coordinated and there is no stray EMR, $I = I_0 - [\Sigma i_{sc} + I\ (\text{absorbed})]$.

5. Polydispersity, cf. Monodispersity

It is helpful to begin with the assumption that a polydispersion is an integration of constituent monodispersions (of Section 8.3B.6). The following are principal considerations which polydispersity evokes:

- a. Several values for the expression $\alpha = 2\pi r/\lambda'$ are coincident. Thus, in reference to Fig. 8.4 (assuming m constant):
    1. If the polydispersity is entirely within the limit for *small* particle sizes, the depolarization and dissymmetry ratios for the dispersion system are scarcely deviant from their respective values of zero and 1 in the ideal case.
    2. If the polydispersity (a) spans coincidentally into both *small* and *large* particle realms, or (b) is entirely within the size limits for *large* particles, and because such a dispersion is relatively stable, the determination of size range and size frequencies are formidable theoretical and experimental problems for light-scattering methods. Practical analyses for these size characteristics are directed to obtaining average values which represent concentration of dispersed particles in terms of numbers-average and/or weight-average.
- b. The properties of the components and the conditions in a given dispersion system determine the relative monodispersity . . . polydispersity which prevails. Statement of this implicates a great variety of possible phenomena in dispersions. Particular reference here is to the properties of particles and conditions which can result in changes of their sizes and numbers, or in inherent stability or preservation of their sizes and numbers, for a given weight concentration.

    Thus implied are possibilities for such phenomena as aggregation, coagulation and flocculation, micelle formation, polymerization, growth of microorganisms; and for reverse phenomena of subdivision. Inseparable from considerations to changes in particle size are considerations to coincident changes in particle shape.
- c. Relatively ideal monodispersions are attainable by preparation, but not without thorough knowledge of the properties of components and dispersions and of the required conditions.

6. Multicomponent Systems, cf. Two-component Systems

e.g.: One medium + two particle-species
Two media + one particle-species

It is helpful to begin with the assumption that a three-component system is an integration of constituent one- and two-component systems (cf. Section 8.3B.5). The following are principal considerations which multicomponency evokes:

a. The optical property of refraction differs (μ_0' and μ_0'') as between two media, and differs (μ' and μ'') as between two particle-species. Thus, there are different m ($= \mu/\mu_0$) ratios which have roles.
b. The ideal case would have it that the two particle-species are of the same L; therefore, in regard to their number of point-sources for scattering they are equivalent. However,
   1. If L is *small*, there is little if any distortion of scattering behavior insofar as Rayleigh-type scattering is principally diffractive [Eq. (8.2)].
   2. If L is *large*, refractions become important factors of the integrated scattering behavior, and their evaluation constitutes a complex problem according to Mie theory [Eq. (8.3–8.7)].

      It is not resolved whether or not two miscible media of different μ_0 values are correctly combined into a single μ_0 value for evaluation of scattering properties, although assumption may suggest that this be done for practical purposes. Factors μ and μ_0 do appear as factors and terms (other than as m) of theoretical equations which have to do with extended concepts about scattering phenomena (see Sections 8.3C.2.b, c, and f).

7. Concentrated, cf. Dilute Systems

Rayleigh and Mie equations for scattered intensities by *fine*-particle dispersions are based upon the ideal conditions that the total scattered-intensity from all particles interacting with EMR is the sum of the effective scattered-intensities from each particle. This means that no particle stands in the way of another along any EMR path in their system, and that *infinite dilution* ($c \rightarrow 0$) most satisfies this ideal. Projection of the meanings of Figs. 8.4–8.5 for an individual-particle system to their meaning for a community-of-particles system emphasizes the importance of the dilution condition.

The experimental approach is by *adequately* dilute dispersion and *adequately* short paths. In this way the secondary, tertiary, . . . multiple scatterings due to interactions by neighboring particles are avoided as much as possible. Data which correlate the scattering effects of a dispersion with concentration of scattering particles reveal the validity of adequate dilution when they are extrapolated to zero concentration to enable comparison with corresponding theoretical data.

The "fluctuation theory" referred to in Section 8.3C.2.d involves considerations which lead to an analytic first-approximation due to secondary scattering. This places it in close relation with the condition of "adequately dilute dispersion" of the ideal case (see Table 8.2).

C. THE TURBIDITY OF *FINE*-PARTICLE DISPERSIONS

The empirical meaning of *turbidity* is the visual-sensory one of *cloudiness*. However, in the perspective of the full meanings of light-scattering phenomena and of photoelectric measurement of them, its meaning is profound to the extent that any dispersion of which the scattering particles are in mobile random distribution has a turbidity (cf. Section 8.2B).

The *small* and *large* particles (which, if they are spherical, pertain precisely to Rayleigh, Rayleigh-Gans, and Mie light-scattering principles) together constitute ranges of sizes, shapes, and optical properties which involve interactions principally by diffraction and refraction, and by *spectral* dispersion, under specialized conditions. Within such ranges are particles which are micromolecular to macromolecular, polymeric, aggregate, coagulate, micellar, and microbiological. Of such particles, the determinations of unit and aggregate weights, sizes and size distributions, shapes, and concentrations are at the heart of the purposes of turbidimetry, nephelometry, and colloidimetry.

1. Basic Concept: Turbidity as a Coefficient

Rayleigh and Mie theories indicate that the $\theta = 0°$ detector position (see Fig. 8.4) is a favorable one for measuring an emergent vector of high intensity to characterize a *fine*-particle dispersion by the attenuation it exacts upon the intensity of incident EMR. Thus, in the absence of true absorption $I = I_0 - \Sigma\, i_{90}$.

This places the attenuation due to scattering (*apparent* absorption) into analogous relationship with the *true* absorption Beer's law, which is expressed by:

$$I = I_0 e^{-\epsilon cl} \qquad (8.8)^*$$

so that

$$\log_{10} \frac{I_0}{I} = \epsilon cl/2.303 \qquad (8.9)$$

where $e = 2.7184$ (the base of natural logarithms; whence, $2.7184^{2.303} = 10$) and ϵ is the extinction coefficient, characteristic of λ and the absorbing property of the solute species.

Equations (8.8) and (8.9) mathematically define the amount of attenuation of I_0 as it traverses an adequately dilute solution of the species. The following equations are analogous for the expression of turbidity τ as an extinction phenomenon:

$$I = I_0 e^{-\tau cl} \qquad \text{(Ref. 28a)} \qquad (8.10)\dagger$$

[*] USP and NF use P and P_0 in place of I and I_0; BP uses I and I_0. Equivalence is factorial, since power = intensity × time.

[†] Cf. Rayleigh's expression[13] for extinction: $I = I_0 \exp(-k\lambda^{-4} x)$

so that

$$\log_{10} \frac{I_0}{I} = \tau c l / 2.303 \qquad (8.11)$$

and

$$I = I_0 e^{-\tau l} \qquad \text{(Refs. 18,19,29,30)} \qquad (8.12)$$

so that

$$\log_{10} \frac{I_0}{I} = \tau l / 2.303 \qquad (8.13)$$

where τ (dimension, cm^{-1}) is the extinction coefficient, characteristic of λ and of the scattering property of the dispersed particles. Scattering **property** depends on the number of point-sources and on size of particles; i.e., on effective surface area (n/cm^2).

Thus, turbidity is defined as the fractional decrease, due to scattering, of incident intensity through unit thickness of dispersion traversed. The inclusions of factor c in Eqs. (8.10) and (8.11) clarify the cm^{-1} dimension mathematically, since n/cm^2 of the particles is a function of c. In Eqs. (8.12) and (8.13), the mathematical value of c is *included with* that of τ because of the direct dependence of τ on c.

Equations (8.10)–(8.13) apply the photometric data for the calculation of τ.

The analogy as extinction concepts between spectrometry and turbidimetry may be given further expression as a parallelism, as follows:

Spectrometry (absorption)		Turbidimetry (scattering)
	$T = \frac{I}{I_0}$ (Transmittance) (I_0 is of monochromatic λ)	
(Absorbance, *true*) $A = \log 1/(I/I_0)$ $= \log I_0/I$ $= \epsilon c l$		(Absorbance, *apparent*) $A = \log 1/(I/I_0)$ $= \log I_0/I$ $= \tau c l$*
(A vs. c plot, slope ϵl)	Straight line origin 0/0 for Beer's law	(A vs. c plot, slope τl)
	$A = 2 - \log \%T$	
$\epsilon = 2.303 \log_{10} I_0/I$		$\tau = 2.303 \log_{10} I_0/I$

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* The measurement of A or of $\% T$ as the indication of relative τ is prevalent analytic practice.

Notable are other comparisons, though of lesser equivalence:

a. The I/I_0 (transmittance) ratio is somewhat analogous to the i_{sc}/I_0 (Tyndall) ratio of Eqs. (8.1) and (8.2), and to the component i_1/I_0 and i_2/I_0 (Mie) ratios of Eqs. (8.3) and (8.4).

b. Regarding Beer's law, reasons for deviations by dispersions intended for spectrometry are analogous in principle but not the same in specifics as reasons for deviations by dispersions intended for turbidimetry, the EMR/particle interactions being different. The specifics of the reasons for the former have been documented extensively as involving instability in the number and function of the absorbing species, i.e., involving changes of a chemical nature (dissociation, isomerization, . . .); and the specifics of the reasons for the latter involve instability in the number and function of the scattering species, i.e., involving changes of a physical nature (effective surface area for scattering interactions, mechanism of scattering, . . .). Related to both categories regarding specifics is the factor of concentration of species. Thus the analytic controls for avoiding or minimizing deviations by dispersions regarding Beer's law are a common purpose of both spectrometry and turbidimetry.

2. Extended Concepts

Beyond the basic concept, there are several concepts which require the involvement of other physical considerations and which are variously less familiar.

The following is a selection from the literature of some various other equations containing the turbidity symbol τ.

a.

$$\tau = \frac{kcld^4}{d^4 + \alpha\lambda^4} \qquad (8.14)$$

where k is a constant of dispersion and method, α is a constant of method, and d is diameter of particle. Basing the concept in both Beer's spectrometric law [Eq. (8.8) and Rayleigh theory, Wells[20] and Yoe[21] showed the derivation of the useful approximation which Eq. (8.14) represents. The equation is assumed valid for both *small*- and *coarse*-particle dispersions, but not for the intermediate (*large*-particle) range, and is in reasonable agreement with the dilution principle of Beer's law.

The USP[31] and NF[32] engage this concept for their concept of *turbidance S* as:

$$S = \log_{10} P_0/P = \frac{kbcd^3}{d^4 + \alpha\lambda^4} \qquad (8.15)$$

where b is thickness of dispersion and d is average diameter of particles. The application of these concepts for analyses is in the derivation of S vs. c curves for unknown dispersions, for comparison with such a curve for a standard dispersion.

Furthermore, the compendia use an extension of the concepts for nephelometric analysis by measurement of that portion of incident power which is scattered in a normal ($\theta = 90°$) direction. The expression of this is given the form:

$$P_s = P_0 - P = P_0(1 - 10^{-S}) \tag{8.16}$$

where P_s is that vector of scattered power. When the conditions for the analysis of a given dispersion are fixed, the k, b, d, α, and λ (monochromatic) are a set of constants coverable by the collective constant K. Whence:

$$P_s = P_0(1 - 10^{-Kc}) \tag{8.17}$$

when $S = Kc$.

b.

$$\tau = \frac{8\pi}{3}\left(\frac{2\pi}{\lambda}\right)^4 n\rho^4 \tag{8.18}$$

This is turbidity derived by Debye[30,33] from Rayleigh scattering theory for an *ideal gas* (n molecules per cubic centimeter) of low density, referring to the transmission angle. If the index of refraction μ is introduced as a factor, ρ can be eliminated on the basis that $\mu - 1 = 2\pi n\rho$, deriving (for complete polarization at $\theta = 90°$ where $1 + \cos^2\theta = 1$):

$$\tau = \frac{32\pi^3}{3}\frac{(\mu - 1)^2}{\lambda^4}\frac{1}{n} \tag{8.19}$$

Further derivations by Debye obtained:

$$\tau = \frac{32\pi^3}{3}\frac{1}{\lambda^4}\frac{kT}{\kappa}\left(\mu\frac{\partial\mu}{\partial p}\right)^2 \tag{8.20}$$

where κ is the compressibility, p is hydrostatic pressure, and T is absolute temperature, as the analogous turbidity for a liquid, wherein refraction property is changed from that for a gas in Eq. (8.19) by greater proximity of particles; and obtained:

$$\tau = \frac{32\pi^3}{3}\frac{\mu(\mu - \mu_0)^2}{\lambda^4}\frac{1}{n} \tag{8.21}$$

as the analogous turbidity for a solution.

c.

$$\tau = HcM \tag{8.22}$$

where

$$H = \frac{32\pi^3}{3}\frac{\mu_0^2}{N\lambda^4}\left(\frac{\mu - \mu_0}{c}\right)^4$$

is the "refraction constant" of the dispersion, is Debye's equation[33] for the determination of molecular weight by light-scattering to $\theta = 90°$ in very dilute solutions.

The value of n of Eq. (8.21) is impractical to determine, whereas c is convenient because it can be prepared accurately from pure solute. This is evident from the expression:

$$\frac{\text{No. of solute particles/cc}}{\text{G. of solute/cc}} = \frac{\text{no. of solute particles/mole}}{\text{g. of solute/mole}}$$

which is $n/c = N/M$ and $n = cN/M$ [introduced into Eq. (8.21)].

For derivation of M, μ and μ_0 (by differential refractometry), and τ must be determined by measurement and c must be known by preparation; τ is measured from a pertinent range of concentrations to obtain a linear plot* of c/τ vs. c, which is suitable for extrapolation to zero concentration. M is the reciprocal of the intercepted c/τ value at $c = 0$.

Note that τ/c means "specific turbidity" and c/τ means reciprocal "specific turbidity."

d.

$$H\frac{c}{\tau} = \frac{1}{M} + 2Bc \tag{8.23}$$

where B is an "interaction constant" depending upon the solvent, defines the turbidity due to fluctuations in concentration.

The Debye equation (8.22), and its transposed form ($Hc/\tau = 1/M$) is valid within an upper limit of adequately dilute solution. Inaccuracies from use of it emerge, in solutions which are more concentrated than those which conform to van't Hoff's osmotic pressure law for ideal solutions (wherein osmotic pressure $\propto n$, and N), from incidence of secondary scattering, which causes deviation from the ideal plot-linearity of c/τ vs. c. Also incident are refractive-index and osmotic-pressure changes from density and concentration fluctuations, resulting from thermodynamic interactions; local inhomogeneities occur.

The thermodynamic factors in density and concentration fluctuations have been coordinated within the "fluctuation" theories of Smoluchowski[34] and Einstein[35], and within subsequent elaborations and discussions by others.[6,26,36–42] Application of the correction which the "$2Bc$" term of Eq. (8.23) represents restores the linear relationship of c/τ vs. c, and implies that the equation reduces to Eq. (8.22) in meaning as c reduces toward ideality.

e.

$$\tau = \frac{8\pi}{3}\frac{Ir^2}{I_0} = \frac{8\pi}{3}R_0 \tag{8.24}$$

$$\tau = \frac{16\pi}{3}\frac{i_{90}r^2}{I_0} = \frac{16\pi}{3}R_{90} \tag{8.25}$$

whereof $R_\theta = i_\theta r^2/I_0$ is termed the "Rayleigh ratio," which descriptively means the *reduced-intensity* vector of I_0 scattered by a *small*-particle

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* In such plots there is a λ' of maximum turbidity.

dispersion; and r means the radius of a spherical detector-distance d from the dispersion. In the perspective of Eqs. (8.1) and (8.2), R_θ is seen to contain the "Tyndall ratio" as a factor.

So as to establish a theoretical relationship between turbidity (as an extinction coefficient) and i_{sc} (according to Rayleigh theory), Doty and Steiner[43] derived the concept for Eqs. (8.24) and (8.25) by integrating Eq. (8.2) to give it the meaning of scattering to the surface of the sphere (just discussed) of radius r, as by:

$$\int_0^\pi i_\theta 2\pi r^2 \sin\theta \, d\theta = \frac{8\pi}{3} i_0 r^2$$

Equations (8.24) and (8.25) have notable agreements with the dimensions of Fig. 8.4B, as revealed by:

1. Equating τ in Eq. (8.24) with τ in Eq. (8.25),

$$\frac{8\pi}{3}\frac{Ir^2}{I_0} = \frac{16\pi}{3}\frac{i_{90}r^2}{I_0}$$

   whence, $I = 2i_{90}$.
2. The "depolarization factor," $(1 + \cos^2\theta)/2$, in that it has the value $1/2$ at $\theta = 90°$; that is, $i_\theta = I(1 + \cos^2\theta)/2$.

R_θ calculations have primary usefulness in their application for determining *absolute turbidity* of pure liquids used as dispersion media, and for calibration of instruments. Furthermore, the correction which absolute turbidity implies is applicable to necessary accuracy in determinations of M by light-scattering methods, according to Eqs. (8.22) and (8.23).

f.

$$\tau = K_{sa}\pi r^2 nl \tag{8.26}$$

where K_{sa} is the "scattering area" coefficient. It is a function of $\alpha(= 2\pi r/\lambda')$ and $m(= \mu/\mu_0)$. When τ has the meaning of absorbance (apparent), $K\pi r^2 nl$ is expressed as "extinction coefficient" in a form analogous to transmission-type Eqs. (8.8) and (8.10), as:

$$I = I_0 e^{-K\pi r^2 nl} \tag{8.27}$$

so that

$$\log_{10}\frac{I_0}{I} = K\pi r^2 nl/2.303 \tag{8.28}$$

K_{sa} is coefficient for *large* spherical particles, being related to Eqs. (8.3) and (8.4) via Eqs. (8.5)–(8.7) Its values for incremental values of α and m have been derived by calculations from the Mie equations and have been published as tables of scattering functions. Thus enabled are direct and intrapolated values for application with measured data in the analysis of such dispersions.

Equations (8.26)–(8.28) should be recognized in the literature to have a number of revised and extended forms.

8.4 CORRELATION OF THEORY FOR *FINE-* AND *COARSE*-PARTICLE DISPERSIONS (cf. Fig. 8.2)

What are known of the light-scattering properties of *fine*-particle dispersions form much of the basis for the recognition and solution of equally if not more difficult problems attendant in *coarse*-particle dispersions. As the quantitative considerations to scattering interactions traverse from the *small-* through *large*-particle sizes, there is encountered a relatively "gray" range of sizes where interactions cannot be evaluated by Mie theoretical equations except by approximations. Through and beyond the "gray" range the considerations become somewhat empirical.

The following points describe generally the reasons for empiricisms and limited precisions:

1. The effective scattering-area decreases with increasing size for a given mass-concentration of particles. (Cf. Table 8.3).

TABLE 8.3: Effect of Cubed Subdivision upon Total Surface Area

Edge of cube, cm	No. of cubes	Total volume, cm^3	Total surface area, cm^2
1	1	1	$6 \times 10^0 \times 10^0 = 6$
0.1	10^3	1	$6 \times 10^3 \times 10^{-2} = 60$
0.01	10^6	1	$6 \times 10^6 \times 10^{-4} = 600$
0.001	10^9	1.	$6 \times 10^9 \times 10^{-6} = 6000$
0.0001 (1 μ)	10^{12}	1	$6 \times 10^{12} \times 10^{-8} = 60{,}000$

2. As particle size increases from *small* to *coarse*, the principal mechanism for interaction changes from diffraction through refraction to reflection. (Cf. Fig. 8.3.)

   In the absence of absorptive property, relative reflectivity of matter appears as a relative opacity which is a property which may be due to the thermodynamic factors having roles in the formation, growth, composition, and structure of *coarse* particles.
3. Characteristics inherent in *coarse* particles are that their effective surfaces are not likely to be spherical and smooth (anisotropy), and that the sizes are not likely to be uniform (polydispersity). Furthermore, any *changes* in effective surface from changes in particle size due to growth, aggregation, or fracture result in changes in reflectivity, intensity-vectors, and polarizations, and in anisotropy and polydispersity; and furthermore, the dimensions of *coarse* anisotropy compared to those of visible EMR may contribute to destructive interference. (Cf. Fig. 8.5.)
4. The factors L, λ', μ, and μ_0 have not been determined as to their precise functions in EMR/*coarse*-particle interactions. Lack of evidence of

significant functions is suggestive that reflective interaction is not sensitive to these factors. (Cf. Fig. 8.4C.)

5. As particle size increases from *small* through *large* into *coarse*, there is a coincident increase in proneness to decrease in concentration of their dispersions through gravitational forces. (Cf. Fig. 8.2.)

   While sedimentation is a detrimental factor in some analyses, it is a useful factor in such others as size and size-distribution analyses by light-scattering methods.

Of the foregoing list, the implications of items 3, 4, and 5 indicate that characteristics of *coarse*-particle dispersions are most practically determined by measurements via the transmission angle. To this end, scattering characteristic, expressed as an extinction due to apparent absorption (as absorbance) is the concept preferred for most analyses. Thus, Rose and Lloyd[44] reported upon meaning and application of the formula:

$$\log_{10}\frac{I_0}{I} = KclA_p/2.303 \qquad \text{(cf. Ref. 29)} \qquad (8.29)$$

where K is the total-scattering coefficient, as the ratio: scattering cross-section per geometric cross-section; values are generally near 2, about which it is an oscillating function; c is the concentration of particles (grams per milliliter); l is the length of transmission path; A_p is the projected average particle-area; $A_p = S$ (the so-called Cauchy relation), where S is the *specific surface* of dispersed particles (surface area per unit weight). They applied their formula for the study of a variety of prepared dispersions. These were a series of narrow size distributions. All particles were within the size limits, ca. 2 μ to 60 μ; and were assumed to be spherical. Further reference to the application of their formula is made in Section 8.6C.2.

It is seen that Eq. (8.29) is, in effect, a formula for calculation of *turbidity* and that, within the limits of the dilution principal of Beer's law, it resembles and may be taken to represent an extension of Eq. (8.28), which is based on Mie theory. It is further seen that it retains the analogy with Eqs. (8.10)–(8.13).

8.5 NEPHELOMETRY, cf. TURBIDIMETRY: FOR PRACTICAL ANALYSIS OF DISPERSIONS

Equations (8.10)–(8.13) and (8.26)–(8.29) are considered to be the most useful of the formulas of established theory to coordinate available data for the direct expression of the property of *turbidity* as a function of concentration. With the detector position along the 0° vector, the data sought by measurement basically concerns the transmission ratio (transmittance) I/I_0 when the dispersion is within the limits for accord with the dilution principle of Beer's law.

Nephelometry is a blend of similarities to and differences from turbidimetry. These are expressed within the following items:

1. The principal purpose is the derivation of concentration.
2. The data sought by measurement basically concerns the Tyndall ratio i_{90}/I_0.
3. The detector position is along the 90° vector, against a dark background.
4. The dispersion must be within the limits for accord with the dilution principle of Beer's law.
5. For a given dispersion, the concentration limits for the accord are lower.
6. In general and in the absence of proved data for commenting specifically, its optimal analytic precision derives from dispersions of particles which are intermediate within the broad *small*-to *coarse*-range of sizes.

On the basis of the foregoing comparisons, nephelometry and turbidimetry are not practical alternatives for the analysis of dispersions. The specific reasons are enmeshed with the fact that, for a given dispersion, the data from measurement of the scattered 90° vector is not related to concentration in the same way as is the data from measurement of the 0° vector, which is dependent (by difference) upon *all scattered*-intensity vectors. That is, different segments of the same community of dispersion properties and conditions are the objects of scrutiny by nephelometry and turbidimetry.

The correlation of items 5 and 6 with nephelometry suggests that a short incident wavelength is advantageous when a dispersion of relatively small particles is analyzed. This is because the 90° angle receives a greater proportion of the shorter wavelengths scattered than at lesser angles, and because it is important to derive as much intensity as possible at that angle.

With the support of theory and experiment, Wells[45] gave early (1922) recognition to the advantages of the nephelometric angle over the transmission angle for the analysis of very dilute dispersions, and in fact concluded that the "depth ratios by reflection and by transmission are equal" . . . "in an intermediate range of concentration." Yoe[21] in 1929 stated in introduction: ". . . the nephelometer is limited to the measurement of substances in *low concentration*, usually not stronger than 100 milligrams per liter."

A. HISTORY

Definite pedagogic values emerge from selected reference to the early development of practical light-scattering methods for the analysis of dispersions.

1. General

The review by Wells[20] in 1927 titled "The Present Status of Turbidity," and the book by Yoe[21] in 1929 titled "Nephelometry" are of permanent value for their coverage by text and by bibliography of the classical era of concepts, methods, apparatus, and instruments.

Recognized early during the evolution of these were the many problems inherent in the dispersions themselves, preparatory to their measurement. Prominent among these problems were those which demanded considerations to the particulate properties and dispersion stabilities and reproducibilities; some indication as to the considerations to some of these is given in the reports of Tolman et al.[16–19]

2. The Early Methods

Wells[20] classified the concepts for the photometric measurement of light-scattering dispersions into three main types, which may be described as follows:

a. **Extinction Index.** The extinction index is undoubtedly the oldest concept and is based on empirical theory that there are relationships (though in fact complex* and mathematically unresolved) between the relative turbidity of a dispersion and the thickness of it required to just extinguish visual detection of the source of incident light. The concept is exemplified at one extreme by the more than century-old method in oceanography for determining depths, and at the other extreme by the "Parr Turbidimeter".[50]

b. **Density (Optical).** Like the first concept, that of optical density involves the transmission angle; but unlike the first, it permits concentrations which are sufficiently low so that the dispersion system is in accord with the dilution principle of Beer's law and τ vs. c or A vs. c plot-linearity.

c. **Tyndall Ratio.** The Tyndall ratio involves the nephelometric angle and requires that the dispersion system be in accord with the dilution principle of Beer's law, as previously mentioned. Not previously mentioned are that (1) nephelometry represents an indirect approach, and (2) the requirement of accord is relative, so that near accord may be a first approximation. From these there follow that (1) the indirect approach is enabled by a comparative analysis (correlation of nephelometric data from the dispersion analyzed with that from a prepared standard dispersion of known concentration), and (2) the dilution principle is reexpressed as the inverse proportion principle. This reexpression has the form of an equation which is suitable for comparative analyses:

$$C_u \times I_u = C_s \times I_s \tag{8.30}$$

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[*] It is expected that secondary-, tertiary-, . . . multiple-scatterings contribute much to the complexity.

where C_u and l_u are the concentrations of, and C_s and l_s are the lengths of paths through the unknown and standard dispersions.

Yoe,[21] in his Chapters 2 and 3, described the evolution of the ten visual-photometric models of nephelometers (involving scale readings) spanning the interval from that of the original of Richards[3] in 1894 to that of Kleinmann in 1927. Of the ten, Kober's[51,52] models (1912, 1917, and 1921) initiated the adaptation to nephelometry of the dual-comparator/adjustable-height (l) colorimeter model of Duboscq.

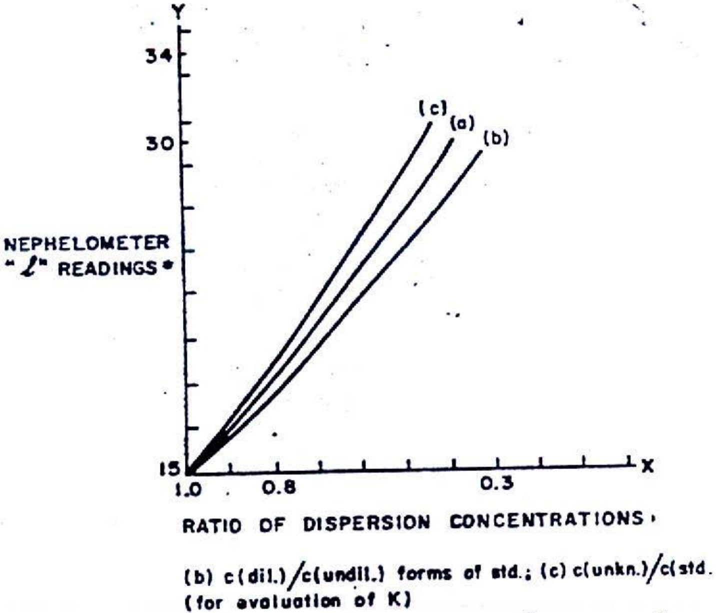

FIGURE 8.6: Nephelometer curves for standardization and analysis. (a) Hypothetical curve: $X = S/Y$; (b) experimental curve from dilutions of std; (c) analytical curve [relative position, left of (a) if K is —ve]: $Y = S/X - (1 - X)SK/X^2$. *"l" for the standard is stationary. Adaptation, after Kober.[51,52]

Strictly, accord with Eq. (8.30) by dual dispersions requires the support of optically sound photometry. Kober's nephelometers admittedly had the imperfection that they performed with *near* accord; that is, smooth and nearly straight l vs. c plots were obtained. To calibrate for this, for improved accuracy, he developed theoretical equations:

$$Y = \frac{S}{X} - \frac{(1 - X)SK}{X^2} \tag{8.31}$$

a standard-dilution formula (standard solutions being, relatively: $X = 1.0$, 0.9, 0.8, 0.7, . . .)

$$X = \frac{S + SK - \sqrt{(S + SK)^2 - 4SKY}}{2Y} \tag{8.32}$$

$$K = \frac{X(S - XY)}{S(1 - X)}, \quad K = kS \tag{8.33}$$

where Y is height (scale reading) of unknown, S is height (scale reading, set position) of standard, X is ratio of dispersions (C_u/C_s), K is the "nephelometric constant" (correlates photometric performance for a given unknown with a given standard and its dilutions, and calculable when Y, S, and X are known); k is a related constant. The expression $X = S/Y$, from Eq. (8.31), is equivalent but not equal to Eq. (8.30), though their factors agree in meaning. Figure 8.6 illustrates this, and that related experimental and analytical plots are also nonlinear. The second term of Eq. (8.31) serves to calibrate when Eq. (8.30) does not apply.

Kober's contribution points to some of the early and perpetual difficulties in nephelometry, viz., the controls over stray light, dispersion characteristics, and photometric design which are essentials to linearity of the I vs. c relationship.

The visual-photometric detector of Kleinmann[21] and subsequently the electrophotometric detectors (e.g., Klett-Summerson, Fisher nephluorophotometer) were dual-comparator instruments designed for built-in accord with Eq. (8.30). The greatest disadvantages of visual photometric methods have been the subjective factors (e.g., capability, fatigue) involved in matching or equal light intensities.

3. The Modern Era

Fifty years after Richards[5] introduced the first nephelometer in 1894, Debye's paper[22] of 1944 on "Light Scattering in Solutions" initiated concepts which were to so stimulate subsequent investigations that practical distinctions became possible from analysis of dispersions of most particle sizes. In step with advanced light-scattering theories have been the advanced designs of instruments to test them. Since the 1930's, the increasing availability of photoelectric detector systems and their application to light-scattering methods have left the subjective factors of the analysis of dispersions only in the *preparation* of the dispersions. Within recent years and for a few specialized analyses, automation for the preparation of the dispersions is receiving experimental attention.

B. QUALIFICATIONS OF PREPARED DISPERSIONS FOR PRACTICAL TURBIDIMETRY OR NEPHELOMETRY

The following summarizes the general conditions which may require controls. Underlying all conditions leading to measurement of dispersions are

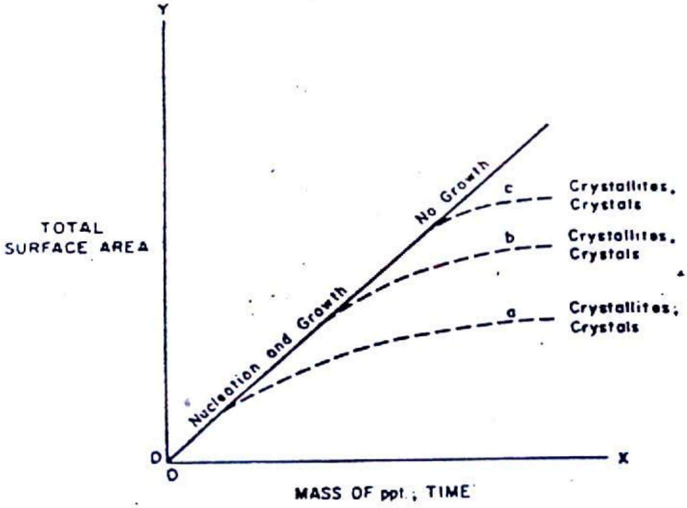

FIGURE 8.7: Nucleation and growths (a,b,c after increasing numbers of nucleates are formed).

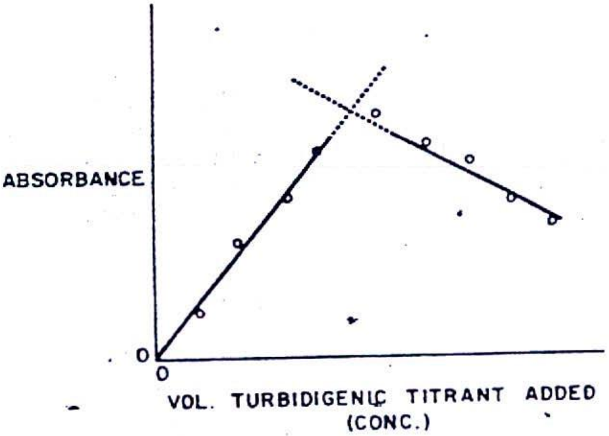

FIGURE 8.8: A turbidimetric titration plot, including extrapolated endpoint.

the environmental factors: time, temperature, interfering coincident substances, ...

1. The dispersed phase:
   a. Is of known identity
   b. When generated by designed chemical reaction: (1) is formed by mixing, in the best order and rate, very dilute solutions of reactants; (2) is formed quantitatively
   c. Is insoluble in the dispersion medium
   d. Is stable as to: (1) identity; (2) particle size and shape
2. The dispersion:
   a. Is stable during the required interval for measurements to be completed; if a stabilizing agent is added, its effect on data must be known
   b. Undergoes no change except in concentration when dilutions are made
   c. Is reproducible
   d. Is free of alien debris and air bubbles

8.6 SPECIAL DISPERSION ANALYSES INVOLVING LIGHT-SCATTERING METHODS

A. TURBIDIMETRIC TITRATIONS

Considerations to the photometry of light-scattering interactions in dispersions of which the suspended particles are by design formed by precipitation are given enhanced meaning by the involved phenomena and mechanisms of nucleation and growth of such particles. Figure 8.7 illustrates a general correlation regarding effective surface area for interaction during the preparation of suspended precipitates in time. The knowledge and, if necessary, control of such phenomena within an analytic procedure can be directed to improved significance of photometric data (cf. Section 8.4).

"Photometric titrations" (originated in concept by Tingle[53] in 1918) is a term with a broad base, including physical-chemical reactions, of stoichiometric importance, of which the end points are obtained from plotted data by measurement of increments in interactions between EMR and a forming dispersion. Susceptible to end-point determinations by this means are such reactions as neutralization, oxidation-reduction, precipitation and complexation. Figure 8.8 illustrates one of the prevalent general types of plots.

Any precipitation reaction whose stoichiometric end point can be designed to appear via a dispersion in which light-scattering interactions are in accord with Beer's law (e.g., $A \propto c$, as a linear plot of apparent absorbance vs. concentration in terms of volumes of standard titrant added) constitutes sound basis for analysis by *turbidimetric* titration. Ringbom[54] initiated this concept in 1941.

The method has significant advantages, principal among which are that:

1. Precise reproducibility of the dispersion is not a critical matter to quantitative validity; this is so:
    - a. As long as the dispersed particles remain sufficiently *fine* for stable suspension and for minimum reflectivity
    - b. As long as the dispersion system, though changing, maintains its accord with Beer's law
    - c. As long as the lines that are plotted to intersect for end point are sufficiently different in slope
2. Though the experimental points in the region of the end point may not define the point, the definition is obtainable by extrapolating the lines to their point of intersection
3. A standard dispersion is not required for reference

Two other matters warrant comment: the plot of different slope, after the end point, represents decrease in apparent absorbance due to dilution of the dispersion by the added volume of unreacting titrant; also, since stirring is an important factor in titrimetry, its effect upon nucleation and growth of particles may indicate it to be a factor requiring control.

B. MICROORGANISMS AS DISPERSED PARTICLES

The measurement of turbidities, which can be related quantitatively to concentration of microorganisms, has evolved, since initiated by McFarland[55] in 1907, to become a substantial field of applied photometry. Turbidity and concentration so related depend upon the absence of immeasurable by-products affecting the dispersion.

Dispersions of microorganisms have many characteristics that are sufficiently different from those of other dispersion systems to warrant description of important features and implications. These are enumerated as follows:

1. The most favorable dispersions for photometric analysis are of those microorganisms whose longest cell (particle) dimensions are within the approximate 1 to 2 μ range, the upper limit of the *large*-particle range. Microorganisms of this range are notable in that they include species which are particulately isotropic (the cocci) and anisotropic (the bacilli); however, cells of a single species may not be of uniform size, even in a pure culture.

Also used are dispersions of a considerable variety of other microorganisms, sizes, and shapes; for, in general, any organism which will give adequately uniform dispersion throughout the steps of a procedure may be used with analytic purpose. Bacteria, protozoa, fungi, and yeasts have been engaged.

2. Because of the *living* property of microorganisms and of all which this embraces, it is to be expected that their dispersions differ profoundly from dispersions of particles without this property. From the standpoint of the

"living" dispersions, their differences appear to be in regard to reasons and mechanisms for changes in particle size, shape, and associations, responses to other materials and their "stoichiometric" relationships, mobility, interaction with EMR, etc.

Furthermore, inasmuch as the environmental factors (such as time, temperature) have special significance to "living" dispersions, their controls within analytic procedures are critical.

3. In the perspective of light-scattering methods, the practical purposes for prepared dispersions of microorganisms are the assay of agents (vitamins and other essential biochemicals; antibiotics) to which specific microorganisms show demonstrable vital response (favorable; unfavorable). The determination of response is by measurement of change in turbidity in time, translated to terms of potency units or chemical equivalents of agent. An essential requirement of the methods is that the analytic procedure is parallel to and its data are comparable with procedure and data based upon a reference standard agent having statutory or other conventional directives for this purpose. The procedures are various and specific.

The foregoing distinctions and implications indicate that light-scattering phenomena in "living" dispersions probably are more complex and more fraught with unknown factors than are the dispersions of lower order.

Their practical turbidimetry assumes their accords with basic concepts (q.v. Section 8.3C.1) by use of the following equations for representing relative turbidity:

$$\mathrm{OD} = 2 - \log G \tag{8.34}$$

(in "optical density" units as indicated by galvanometer readings) and,

$$A = 2 - \log \% T \tag{8.35}$$

(in *apparent* spectrometric units, as by absorbance through per cent transmittance), and

$$D = sC \qquad \text{(Ref. 56, p. 143)} \tag{8.36}$$

(where D is optical density, s is a constant (including dispersion thickness l), and c is number of particles per milliliter). Figure 8.9 gives the general meaning of growth-response curves as determined by photometry via the transmission angle.

The practical nephelometry of such dispersions assumes their accord with the concepts in Eq. (8.30), the inverse proportion principle. The indirectness of nephelometry as a method for dispersion analysis dictates the need for nephelometric standards, a series of temporary, semipermanent or permanent comparable dispersions of graded concentrations. The standards enable *relative* dispersion-concentration to be expressed in terms of nephelometer-scale readings. Permanent nephelometric standards (e.g., Coleman Nephelos system), made possible with durable components, are used extensively.

As implied in Section 8.5, the concentration of microorganisms in a given dispersion determines which of the transmission and nephelometric angles is selected for deriving the photometric data.

Analyses via growth-response curves derived turbidimetrically (Fig. 8.9) or nephelometrically evoke considerations to possible differentiation between chemical and biological stoichiometries. The relationship between growth response and dose is seen to be linear from the origin for growth-promoting agents, but to be nonlinear for growth-inhibiting agents; that is, there is less than complete reciprocal relationship between the two types of responses.

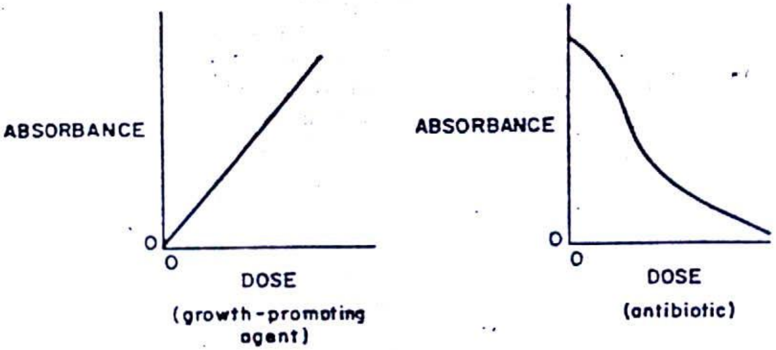

FIGURE 8.9: Growth-response curves.

As the response to a growth-promoting agent, it would appear, each chemical equivalent (and number of molecules) of it results in a fixed increase in the number of cells, whereas the response to a growth-inhibiting agent is less regular because of some growth, some inhibition, and some annihilation. In practice, annihilation is not sought or is not attainable, and may be undesirable because of the unknown factors this condition may introduce.

C. "UNSTABLE" DISPERSIONS

Reference here is to two types of dispersions which individually present special problems for their analysis by light-scattering methods. Their inclusion is for their principles and because they have received considerable study and are certain to receive a great deal of future attention because of the technologies they invite.

1. Aerosols (Literally: Solutions or Suspensions in Air)*

Aerosols are *fine*-particle dispersions of liquid or solid matter in gas media. The apparent examples in nature are within what are accepted to be "atmospheric conditions"—clouds, mist and fog, dust, smog and smoke—all of which

* It is also defined, in modern technology, as a "pressurized package."

are of varying position and concentration because they are relatively free (uncontained). In laboratory studies, the containment necessary ("cloud chamber") for natural samples and for prepared samples is alone sufficient to render the best of such samples poor imitations.

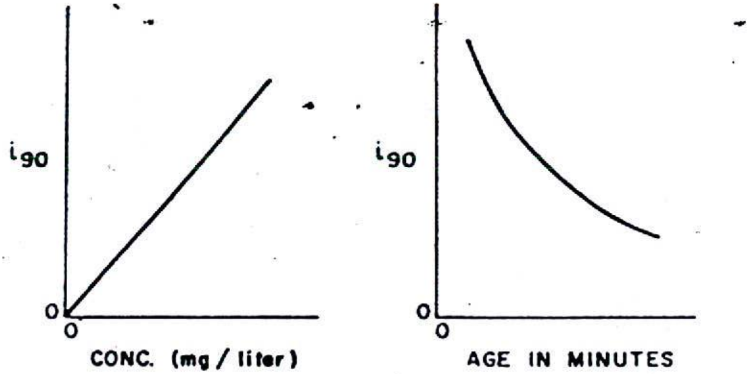

FIGURE 8.10: Relationships with tyndallmeter readings (i_{90}) in smoke aerosols.

Particle size and concentration contribute the most critical factors to the practical "aerosol problem," and data concerning them are at the heart of solutions to the atmospheric pollution problem. In fact, it was for the latter purpose (in the context of chemical warfare science) that the basic work (apparatus, theory, experiments) of Tolman et al.[46–49] in 1919 was motivated.

They submitted as limiting forms for the relation between tyndallmeter reading (T, intensity in footcandles) and size of particles: when concentration $\propto$ number of particles × diameter cubed,

$$T = knd^6 \qquad \text{and} \qquad T = kcd^3 \tag{8.37}$$

(according to Rayleigh law for *small* particles); and

$$T = k'nd'^2 \qquad \text{and} \qquad T = k'c/d' \tag{8.38}$$

(for larger particles, when reflecting area $\propto d'^2$) where k and k' are constants, n is the number of particles per cubic centimeter, and d and d' are particle diameters (determined microscopically). To test the theory they used their designed tyndallmeter, smokes of rosin, tobacco and NH_4Cl (for *small* particles), and liquid suspension of silica (for larger particles). They derived data for the types of correlations illustrated by Fig. 8.10. The linear relationship in the first graph is in accord with the dilution principle (i.e., tyndallmeter intensity $i_{90} \propto c$). The curve in the second illustration is of the effect on i_{90}

of progressive aggregation, settling and adherence to the walls of the container by the particles as a smoke aerosol disappears in time. Furthermore, several distinctions were derived: within certain concentration limits and for the same mass-concentration, the smaller the particle size, the higher the i_{90} because of larger total reflecting surface: for the same mass-concentration, the smaller the particle size the greater the aggregating and aerosol disappearing rates: for different mass-concentrations of the same particle size, the higher the concentration the greater the aerosol disappearing rate.

Subsequently, spectrometric-type equations were introduced for the evaluation of aerosols. For example, Gumprecht and Sliepcevich[57] in 1953 combined corrected forms of such equations with Stokes' law of settling for the study of aerosol polydispersions of kerosene. Thus, the corrected form of Eq. (8.27) is

$$I = I_0 e^{-RK\pi r^2 nl} \tag{8.39}$$

where R is a correction factor for K, for the subtended angle. This, in the integrating form:

$$\log_e \frac{I}{I_0} = -\pi l \int_0^\infty RKr^2 n \, dr \tag{8.40}$$

is for a summation based on the concept that a polydispersion is composed of monodispersions or narrow polydispersions.

Orr and Dallavalle[58] have detailed the involvements in the concept and the use of these equations for size-distribution analysis, with $I \propto$ settling intervals for n and r.

It is noteworthy that photoelectric methods for counting number of particles and oscillatory amplitude methods for measuring particle size in aerosols are dependent upon light-scattering interactions.

2. *Coarse*-Particle Dispersions for the Technology of Powders

In reference to their work with Eq. (8.29), Rose and Lloyd[44] stated: "The mathematical laws of light transmission through a suspension are exact," and to the effect that deviations are due to some transparency of particles and to apparatus imperfections and inadequate experimental design. Thus, if the apparatus can subtend a very small solid angle at the center of I, there is a linear relationship between the attenuation of I, i.e., $\log I/I_0$, and c, even for dispersions of particles of μ sizes.

They listed the following assumptions for ideality in the derivation of their equation:

a. The particles are completely opaque
b. The amount of I_0 reflected from transmissibility is proportional to the total projected area of the particles
c. There are no multiple reflections between particles and between particles and container surfaces

d. l and c are not so great that more than one particle at one time is in a single line of the transmission path

For size-distribution analysis, further derivations gave:

a. That for all sizes (d_x), Eq. (8.29) takes the form

$$\log_n \frac{I_0}{I} = kCl \sum_{0}^{d_x} K_x n \, d_x^2 \qquad \text{(Ref. 44)} \qquad (8.41)$$

b. That for a d_1 to d_2 size distribution, Eq. (8.41) takes the form

$$\log_n \frac{I_0}{I_2} - \log_n \frac{I_0}{I_1} = kCl \sum_{d_1}^{d_2} K_x n \, d_x^2 \qquad \text{(Ref. 59)} \qquad (8.42)$$

where
k = a particle-shape factor
K = the opacity factor, a proportionality constant of transmission data
C = concentration of powder
n = number of particles per gram of powder
d = particle diameter
and where particles are assumed to be spherical.

Equations (8.41) and (8.42) and other published equations of related meanings to particle-size distribution are a basis of the technology of powders for product-quality control in a variety of industries (e.g., pharmaceutic, cosmetic, ceramic). In this perspective, the light-scattering method which is termed "photoextinction" and "photosedimentation"[28,44,59] is prominent, and is of pedagogic value.

D. ANALYSES FOR BIOCHEMICALS

The chemical entities in biological systems are, in general terms, of the following types: micromolecular to macromolecular in range; inorganic or organic; animal, plant, or microorganism as to host.

As is to be expected when any such constituent is the object of analysis by light-scattering methods, its appropriate separation from its biological medium and its transposition into a prepared dispersion medium can be fraught with difficulties which are numerous and technical. To the extent that all difficulties cannot be overcome, which is characteristic of biological systems, resort within procedure is prevalent to use of: replicate sampling, reference standards, control or blank determinations, and null reading. Though analytic results from these resorts are relative, refinements minimize error from any source.

One of the most important problems involved in biochemical analyses is the selection of its most appropriate stoichiometric derivative to represent it in the prepared dispersion, for the derivative must have acceptable formative and particulate as well as insoluble characteristics.

The analysis of enzymes is, as in microbiological growth-promoting or inhibiting methods (Section 8.7B), based upon the measurement of response to progressive action on a suitable substrate. Depending upon the solubility or insolubility of the substrate or products of action, the response is measured as an increased or decreased turbidity with reference to the turbidity at the beginning of action. Time and temperature are important environmental factors.

Biological systems are neither constants nor are they comfortably functional outside of the limits set for them by nature. They are susceptible to abnormalizing conditions which may be recognizable through changes in amounts or identities of biochemicals essential to physiological balance. The cause/effect relationships underlying such conditions and changes are much more obscure than clear.

In the human area of clinical diagnosis of diseased conditions, the scope of biochemical analysis includes considerations to environment, nutrition, microorganisms, drugs, and poisons as well as to the inherent factors of the cause/effect relationships.

E. ANALYSES FOR IMPURITIES IN STANDARD-GRADE CHEMICALS

Near-absolute purity of chemicals may be impractical to achieve or be unnecessary to have. The extent to which impurities may be "overlooked" or be allowed to remain depends upon method of preparation, refinement, and purposes. For the more particular purposes, the labeling of production-control results on containers of analytical and reagent-grade chemicals and the specifications for conformity and limit tests in drug compendia are standard practices.

Analytic procedures, in accord with the principles of turbidimetry and nephelometry (Section 8.5), are available or may be designed for determining *exact* amounts of impurities; all of them require selection of a suitable insoluble derivative in a suitable dispersion of it. When the analytic purpose is merely to determine conformity of a chemical with specified *limit* for amount of impurity, as for Cl^- and $SO_4^{=}$ in the official compendia, instrumental[31,32] or visual[351] methods for comparing dispersions are used.

8.7 COMMERCIAL INSTRUMENTS

Since Kober's[51] first adaptation of a colorimeter (Duboscq) for the analysis of suspensions, the apparatus and instruments for light-scattering measurements have been those of colorimetry and spectrophotometry with adaptations when necessary. Furthermore, fluorometers are being used for nephelometry since the photometric angle is the same.

These fortunate overlaps, the abundance of manufacturers and suppliers, catalogs and bulletins, diagrams of optical systems and descriptions of accessory apparatus, operating, care, and service instructions, and the rate of obsolescence make textual inclusions about these unnecessary; the following outline seems sufficient here.

1. *Models using visual photometry:* Parr turbidimeter,[50] extinction principle; Jackson turbidimeter, optical-density principle; Hellige turbidimeter,[71] combines transmission and Tyndall principles; St. Louis turbidimeter, Tyndall principle with Nessler tubes.
2. *Models using electrophotometry:* Coleman nepho-colorimeter (and certified Nephelos standards), for nephelometry and turbidimetry; Klett-Summerson photoelectric colorimeter, for turbidimetry (micro-macro); Bausch & Lomb Spectronic-20 colorimeter, for turbidimetry; spectrophotometers; fluorometers.
3. *Models of extraordinary precision and applications:* Aminco-Chance dual-wavelength spectrophotometer, for recording small changes in optical transmission through turbid media; Hewlett-Packard light-scattering photometer and Brice-Phoenix light-scattering photometer and Aminco light-scattering photometer, for angular scattering, dissymmetry and depolarization and Rayleigh ratios, absolute turbidity, *M*.

When refractive-index values are required data, the following instrumental models for their determination are used with characteristic precisions: Pulfrich, Abbé, dipping and differential.

Periodical information about optical instruments is published in: *Instruments and Control Systems* (and its *Buyers' Guide* to manufacturers), *Review of Scientific Instruments, Journal of Scientific Instruments, Applied Optics, Journal of the Optical Society of America.*

8.8 EXPERIMENTAL PROCEDURE

DETERMINATION OF CHLORIDE (Cl^-) AND SULFATE (SO_4^{2-}) LIMITS

(Cf. References USP, XVII, p. 870; NF, XII, p. 438; BP, 1963, p. 1052).

Equipment. 1. Individually labeled "dispensing" burettes are convenient if set up for community sources of approximate and exact volumes of specified solutions and reagents.

2. 50-ml volumetric flasks; three per determination.

3. Spectronic-20 colorimeter; specified "test tubes".

Notes. 1. The instrument is conveniently preset if it is to be used in community; thence, the adjustment knobs need not be touched except to check the adjustment periodically. With the instrument set for frequent readings, a null reading made according to:

a. The wavelength (ca. 350 mμ) for maximum absorbance

Cl^- AND SO_4^{2-} IN CALCIUM GLUCONATE

Procedure and Data: (Date:

Locker No: Sample No: Surname (print):

Cl^- Determination
Standard Turbidity

1. Measure 1.00 ml of 0.02 *N* HCl into a clean[a] 50-ml volumetric flask
2. Add 35 ml distilled water
3. Add 1 ml concentrated HNO_3
4. Add 1 ml $AgNO_3$-T.S.[b]
5. Add distilled water, q.s. to 50.00 ml
6. Stopper and invert several times[c]
7. Allow to stand for 5 min, protected from direct sunlight
8. Fill a Spectronic-20 test tube to the mark with the suspension
9. Wipe test tube clean, insert, read

$A^{Cl^-}_{std} =$

Sample Turbidity

1–2. Weigh about 1 g of sample exactly (Wt. =) and transfer via solutions in 35 ml distilled water into a clean[a] 50-ml volumetric flask.

3–9. As for Standard.

$A^{Cl^-}_{sample} =$

Calculations

USP Limit. A 1-g sample of calcium gluconate shows no more Cl^- than corresponds to 1 ml of 0.02 *N* HCl. (ca. 700 ppm).

ionic wt. $Cl^- = 35.453$

$\frac{0.02}{1000} \times 35.453 = 0.00070906$ g Cl^- in 1.0000 g calcium gluconate is 709.06 ppm

$$Wt.^{Cl^-}_{sample} = \frac{A^{Cl^-}_{sample}}{A^{Cl^-}_{std}} \times Wt.^{Cl^-}_{std}$$

$$= \frac{(\qquad)}{(\qquad)} \times (\qquad)$$

$$= (\qquad)\ g$$

$\frac{(\qquad g)}{Wt.\ sample}$ represents [d] ppm

(g)

SO_4^{2-} Determination
Standard Turbidity

1. Measure 1.00 ml of 0.02 *N* H_2SO_4 into a clean[a] 50-ml volumetric flask
2. Add 35 ml distilled water
3. Add 1 ml dilute HCl
4. Add 3 ml $BaCl_2$-T.S.[b]
5. Add distilled water, q.s. to 50.00 ml
6. Stopper and invert several times[c]
7. Allow to stand for 10 min
8. Fill a Spectronic-20 test tube to the mark with the suspension
9. Wipe test tube clean, insert, read

$A^{SO_4^{2-}}_{std} =$

Sample Turbidity

1–2. Weigh about 2 g of sample exactly (Wt. =) and transfer via solution in 35 ml distilled water into a clean[a] 50-ml volumetric flask

3–9. As for Standard.

$A^{SO_4^{2-}}_{sample} =$

Calculations

USP Limit. A 2-g sample of calcium gluconate shows no more SO_4^{2-} than corresponds to 1 ml of 0.02 *N* H_2SO_4 (ca. 500 ppm).

ionic wt. $SO_4^{2-} = 96.0616$

$\frac{0.02}{1000} \times \frac{96.0616}{2} = 0.000960616$ g SO_4^{2-} in 2.0000 g calcium gluconate is 480.308 ppm

$$Wt.^{SO_4^{2-}}_{sample} = \frac{A^{SO_4^{2-}}_{sample}}{A^{SO_4^{2-}}_{std}} \times Wt.^{SO_4^{2-}}_{std}$$

$$= \frac{(\qquad)}{(\qquad)} \times (\qquad)$$

$$= (\qquad)\ g$$

$\frac{(\qquad g)}{Wt.\ sample}$ represents [d] ppm

(g)

---

[a] May be wet.

[b] Omitted in blank.

[c] Do not agitate vigorously.

[d] For undetectable absorbance reading (A_{sample}) report undetectable *trace*. As an added exercise, plot correlation (*A* vs. *t* in minutes) as "standard turbidity" tubes are saved for extended intervals.

Signature:

b. 100% transmittance for the *respective blanks*; i.e., the *blanks* are prepared exactly as for "standard" turbidities, except that they contain distilled water in place of the volumes of precipitant specified in step 4. Thus, these respective *blanks* represent zero absorbance and no turbidity, relatively.

2. The readings for standard and sample turbidities are made from the absorbances scale (as A, for apparent absorbance, turbidity) so as to make applicable the formula corresponding to the colorimetric function of the instrument. It should be emphasized, however, that a reading must be made without undue delay after the specified waiting period (step 7), since suspended particles may eventually aggregate or/and settle to change the status or/and the homogeneity of the turbidity.

3. Significance of results (e.g., accuracy, reproducibility) can be improved by any means that can effect uniformity in size and stability of suspended particles.

4. It is axiomatic that solvent and diluent water used in the procedure must be *turbidimetrically blank* as to suspended particles and as to common and interfering ions.

QUESTIONS

Q8.1. Cite the types of interactions possibly involved upon encounter of EMR with matter. In a general way, diagram the meaning in principle of each type.

Q8.2. What are the principal correlations between particle sizes and types of light-scattering interactions, assuming sphericity for all of the sizes?

Q8.3. Cite the qualifications within the ideal case for the theoretical study of fine-particle dispersions.

Q8.4. List the symbols for the principal factors and terms of the scattering theories for *fine*-particle dispersions. Explain the role of each factor.

Q8.5. Title and describe the complications due to deviations from the ideal case (Q8.3).

Q8.6. What special characteristics do *coarse*-particle dispersions have which set them apart from *fine*-particle dispersions as to analytic approaches to them?

Q8.7. Describe practical turbidimetry and nephelometry, wherein they are similar and wherein they are different.

Q8.8. Cite the qualifications of prepared dispersions for practical turbidimetry and nephelometry.

Q8.9. Speculate as to factors most difficult to control so as to minimize margins of error in the preparation of dispersions for instrumental analysis.

Q8.10. Table 8.3 deals with cubed subdivision. Speculate, and if possible solve, an analogous problem dealing with sphered subdivision (beginning with a diameter of 1 cm).

Q8.11. Reasoning from the substance of the exemplary experiment in Section 8.8, and citing comparable quantities of its appropriate materials for use, design an experiment (and enumerate the steps of its procedure) which will yield data that turbid dispersions are in relative accord/discord with the principles of Beer's law.

APPENDIX: TOPICS INDEX TO REFERENCES AND EXTENDED BIBLIOGRAPHY RELATING TO DISPERSIONS AND LIGHT-SCATTERING PRINCIPLES[a]

General discussions:	6, 18, 20, 21, 26, 29, 81, 125, 195, 236, 247, 278, 298, 299, 300, 352, 353, 394, 418
Colloids, general:	6, 195, 278
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