THE PRESENT STATUS OF TURBIDITY MEASUREMENTS

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INTRODUCTION

Every attack on the problems of dispersed systems is disappointing, because of the baffling complexity of the phenomena. One optical method after another has been eagerly snatched, applied, and often abandoned after trial. Diaphanometers, nephelometers, turbidimeters, tyndallmeters, dispersimeters, opacimeters, have been developed and placed on the market, but not one has yet been accepted as a standard instrument for the laboratory. To read the long list of new applications one would expect by now to find such an instrument in every analytical laboratory. Apparently turbidity measurements have not proven satisfactory, and yet the prospects are more hopeful than they seem. Once the limitations of such optical methods are understood, their real possibilities will be appreciated for what they are worth.

Turbidity measurements have the fundamental advantage of revealing properties of the dispersed phase without disturbing its delicate equilibrium. Light vibrations are so gentle that even vital processes are not seriously upset by their passage. It is, therefore, possible to measure the phenomena optically while they are taking place. Gravimetric analysis sacrifices the sample. Moreover, some dispersed phases cannot be separated from the dispersing medium, while others require much time and effort for the separation. Turbidity can be measured without sacrificing the sample, with little time and effort. The optical criterion is extremely sensitive, having been applied with success to measure the light scattered by gas molecules. Needless to say, then, that it surpasses the microbalance in sensitivity. It must not be forgotten, also, that turbidity is a measure of other factors beside concentration. When concentration only is desired this is a disadvantage, but there is good reason to expect that the other variables will soon be of interest also. Such considerations justify a much more serious study of turbidity measurements than they have been given heretofore. In this review are presented briefly the theoretical basis of turbidity measurements and an estimate of the quality of the instruments that have been devised to measure turbidity.

I. SOLUTIONS AND DISPERSIONS

Simple fluids are supposed to consist of but one species of molecule, although some phenomena indicate that even water is much more complex. Solutions, also, are molecularly dispersed, not more than a few molecules at a time associating as aggregates. Even at the surface of solutions, where the molecular structure is different from that in mass, the transition layer is not many molecules thick. When an insoluble substance precipitates from a solution, however, large aggregates of molecules condense about each nucleus forming a dispersed phase. The natural tendency for such aggregates is to combine into still larger ones until the particles attain microscopic dimensions, but in many cases this growth is arrested, leaving a vast number of very small particles presenting a large surface to the solution.

If the dispersed phase is solid the dispersed system is usually called a suspension, if liquid, an emulsion, although "photographic emulsions" consist of solid silver halide grains dispersed in gelatin. Liquid drops dispersed in vapors are called mists, clouds, fog, or smokes. When the particles are submicroscopic, the colloid is called a sol, when coagulated, a gel, etc. Dr. Exton has suggested calling dispersed systems in general *dispersions,* to avoid the unfortunate term *dispersoids,* which is sometimes used. The important characteristic of dispersions is the large rôle played in them by surface phenomena. Cutting a centimeter cube into little cubes one micron on each edge increases the surface ten thousand fold, spread over a million million particles. Over one hundred million silica particles per cubic centimeter, each a tenth micron in diameter, are required to produce even so small a concentration as one milligram per liter, or as it is commonly expressed, one part per million. The red corpuscles present over 400 times as much surface as a cubic centimeter of blood, yet they are several microns in diameter. Think of what an enormous interface is presented by the submicroscopic dispersed phase in a gel!

Dispersions are not in true thermodynamic equilibrium, according to Tolman (1),[1] until the particles are all of the same size and the surface tension between the particles and the medium is zero. But most dispersions are found to contain particles widely distributed in size, so that the tendency toward equilibrium must be resisted by protective membranes or adsorbed layers. Many protein precipitates in the Prudential Laboratory remain dispersed for years. Although the precipitate flocculates easily, and settles to the bottom of the vessel, a slight agitation is sufficient to separate the flocculi again into microscopic particles. Surely in such cases there must be a very positive

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[1] The number in parentheses indicates the paper referred to in the bibliography.

repulsion between the particles which prevents them from coalescing. The smaller particles are in incessant Brownian motion, or thermal agitation, and are therefore continually colliding. While in contact, the particles tend to coalesce and thereby reduce the surface energy, so that to remain separate this tendency must be opposed by repulsive forces between the transition layers. It seems to be the irreversibility of the process of formation of these surface layers which accounts for the comparative stability of many dispersions.

Condensation nuclei

The phenomena of supersaturation show that nuclei are always required to initiate the condensation of a dispersed phase. Very little is known about condensation nuclei except those for water vapor, which have been studied extensively during the last fifty years. The main interest of the earlier investigators, Forbes, Coulier, Mascart, Aitken, Kiessling, and the younger Helmholtz, was in understanding the varied phenomena of the atmosphere, but the later work of Barus, Lenard and Ramsauer, Townsend, J. J. Thomson, and C. T. R. Wilson has led directly to our modern knowledge of the constitution of the atom. One reason for this has been that water vapor is an ideal medium for studying condensation phenomena. It can be supersaturated simply by sudden expansion, and although the drops soon evaporate again, the condensation nuclei can be studied easily in great detail. The classic results with water vapor are fundamental in the study of dispersions.

Lord Kelvin, in 1862, showed that the effect of surface tension alone required a certain degree of supersaturation in the vapor about small particles for thermodynamic equilibrium. The supersaturation increases exponentially as the radius of the particle decreases. If the particle is electrically charged the supersaturation is depressed. The same effect results if the particle has a specific attraction for water, forming a concentrated solutional nucleus with low vapor pressure. Hygroscopic substances can thus induce "incipient condensation" at humidities below 100 per cent, as observed by Aitken in 1880. The thick haze of hot weather is due to this incipient condensation.

The colors of the steam jet have provided a measurement of the size of the millions of condensation nuclei present in every cubic centimeter of ordinary air, but the method of repeated sudden expansion under controlled conditions, as perfected by C. T. R. Wilson (1) in England and Barus (1) in this country, provides a much more powerful instrument of research. If we take ordinary room air and enclose it in a vessel containing some water long enough to become saturated, and then expand it suddenly by raising a piston, a fog will form throughout the air and water will condense on the surfaces of the vessel. If we allow the fog to settle, and the air to become again saturated, another expansion produces another fog. But after repeating this several times, the fog becomes thinner each time, the drops larger as they become fewer, until finally no drops are formed on slight expansion. There are evidently present in the air particles upon which the water vapor condenses, and which settle out in the drops. These are the persistent nuclei, and the water vapor condenses throughout the air only when these are present. Air filtered slowly through cotton wool is free from such nuclei, which range in size from dust particles to the large ions, mere clusters of molecules.

Myriads of persistent nuclei are produced in combustion, evaporate from many chemicals such as phosphorus, result from the bursting of bubbles on solutions, from electrical discharges and from ultraviolet light, x-rays, radium, etc. In addition to these large nuclei are the small ions which are being always continuously produced even in a closed container at a definite rate, and which require above a four-fold supersaturation to induce condensation. Most remarkable of all, at supersaturations above 8, billions of nuclei per cc. are spontaneously produced from the vapor itself, the resulting dense fogs showing large green-centered coronas which are beyond the range of optical theory. Here we are obviously entering the region of molecular kinetics, where the statistical distribution is reproduced by the conditions of thermal equilibrium.

In other vapors the phenomena are similar so that we are led by analogy to believe that precipitation in solutions is governed by the number of nuclei effective at a given supersaturation. Indeed, Von Weimarn (1) has surveyed the laws of precipitation of barium sulfate over a vast range of supersaturations, and finds the same general increase in number of nuclei and fineness of particle with the supersaturation. It must be remembered, however, that increasing the supersaturation in itself produces larger particles when the number of nuclei remains constant, for there is more mass to condense. It is the successive inclusion of new classes of nuclei, smaller in size but vastly greater in number, which distributes the condensing mass into finer aggregates. Once the condensation begins, the number of nuclei is fixed, for the condensation process relieves the supersaturation. Those nuclei which have not become effective at the peak of the supersaturation are still less efficient while it is falling. Of course it often happens that the diffusion process is so slow that wide variations in the supersaturation occur locally. In such cases the precipitation is extremely complicated, and difficult to reproduce.

Precipitation from solutions

First, consider the case where the condensation is regulated by the diffusion process. This requires the simultaneous existence throughout the process of the two reacting phases, with a diffusion layer between presenting all stages of transition in concentration. It is therefore obvious that in this case it makes no difference which phase is added to the other, for the conditions are symmetrical, each phase being present in excess on its side of the transition layer.

At the instant of contact of the two phases, a sharp gradient exists in the concentration, which is gradually wiped out by diffusion, the transition layer increasng in thickness until the supersaturation somewhere in the layer becomes sufficient for precipitation to occur upon the nuclei. The state of affairs at this instant is schematically presented in figure 1, where the ordinates (concentrations) are plotted against the distance across the transition layer. The scales, of course, are all out of proportion. Next to the pure phase of concentration A is a layer of excess of A, the supersaturation of BA increasing as the excess of A decreases, until a layer is reached where there is an excess of B, where the supersaturation of BA decreases as the pure phase of concentration B is approached. It is evident that the nuclei in the different regions of the diffusion layer are in quite different environments. Precipitation begins where the particular local concentration environment is sufficient to induce condensation on the nuclei present. Since the solubility of BA is constant throughout the layer, the solubility of each component is reciprocally as the excess of the other, and this is shown by the dotted line representing the soluble portion of the minor component. The concentration of BA available for precipitation is given by the portion of the ordinate between the dotted line and the total concentration of the lesser component. As soon as condensation begins, however, the whole picture changes with

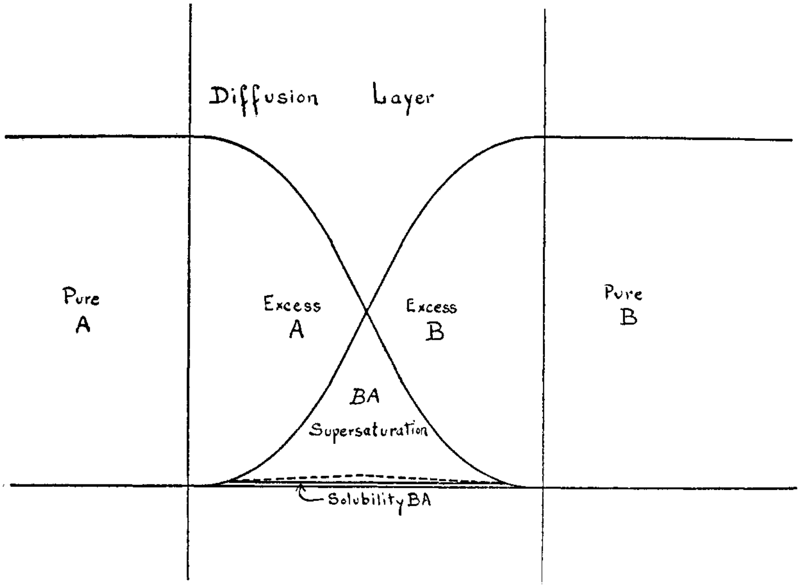

FIG. 1. CONCENTRATION RELATIONS AT START OF PRECIPITATION

explosive rapidity. The supersaturation about the particles practically vanishes, and this prevents any more diffusion of the minor component beyond this zone, while the diffusion to this zone, of the particular components which are condensing into the dispersed phase, is accelerated. In other words, the pure phases must penetrate a sort of "no man's land," where a large proportion of the reactants pass out into the dispersed phase, before they can diffuse into each other.

Some observers have tried to explain the increase in turbidity after precipitation begins as an increase in the number of particles. This seems improbable, for after the most efficient nuclei have induced condensation upon them, only the less efficient nuclei are left, and these could not compete with the larger particles for much of the precipitate. Indeed, the larger particles are more apt to rob the smaller ones, as indicated by Kelvin's formula, so that an actual decrease in the number of particles is more likely to occur. The coalescence of particles on colliding would also diminish the number. One way in which new particles could form would appear to be when the particles already present become poisoned by adsorbed layers at a certain stage of their growth; but in such a case it is hard to understand why the smaller nuclei are not also poisoned by the same adsorbed layers.

The only way in which the precipitation can spread from the thin layer where it starts is by the diffusion of the particles away from the locality. Diffusion is merely the result of thermal agitation (Brownian movement). This may sometimes leave the field open for condensation to start afresh upon other nuclei, but the occurrence of particles of different sizes is more probably due to the varying rate of precipitation as the particles diffuse into regions where the supersaturation is different. A still more potent source of variation is the adsorption of impurities on the surfaces of the particles, which may occur at different stages of their growth, and poison further condensation. It is only when the same supersaturation occurs simultaneously throughout a uniform solution, brought about for example by lowering the temperature, that one would expect to obtain uniform particles.

In many cases of precipitation it makes considerable difference which phase is added to the other. The process is evidently irreversible. If the mixing is complete before precipitation occurs, the excess of the major component never falls below its final value during the addition, if the minor phase is added to the phase in excess. But if the mixing is much more rapid than the condensation, it should be possible to complete the addition before appreciable precipitation, and what occurs thereafter does not depend on which phase is added to the other. Since the dissymmetry cannot occur while both pure phases are present, the minor phase must be exhausted as fast as it is added. Under such conditions there is the minimum possibility of precipitation in an excess of the minor phase, and any particles which might form in such an environment pass into an excess of the major phase after the shortest time. The formation of the colloid particle is lucidly described by Svedberg (2).

Law of particle growth

When the surface of the particles is so large that the condensation is limited by diffusion, we have the rate of increase of the concentration (C) of the dispersed phase

$$\frac{dC}{dt} = k(C_m - C) \tag{1}$$

where C_m and k are constants. For N spherical particles of uniform diameter d, $C = kNd^3$, and assuming N to remain constant, the integral of (1) gives the diffusion law of particle growth

$$kt = \log (1 - \chi^3) \tag{2}$$

where χ is the ratio of the diameter at the instant t, to the final diameter when all the insoluble material (C_m) has precipitated out. The constant of integration, $\log (1 - \chi_o^3)$ can be neglected, and of course the k's are different constants in the different formulas.

When the surface of the particles is also a limiting factor, equation (1) must be modified to

$$\frac{dc}{dt} = kNd^2(C_m - C) \tag{3}$$

which is equivalent to the equation

$$\frac{dx}{dt} = k(1 - \chi^3) \tag{4}$$

with the same assumptions as above. The integral of (4) gives the surface law of particle growth

$$kt = F(\chi) - F(\chi_o) \tag{5}$$

where

$$F(\chi) \equiv \log\left[\frac{1 + \chi + \chi^2}{(1 - \chi)^2}\right] + 2\sqrt{3}\tan^{-1}\left(\frac{2\chi + 1}{\sqrt{3}}\right) \tag{6}$$

and χ_o is the initial value of the diameter ratio.

TABLE 1

	χ										
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.99	1
$F(\chi)-F(\chi_0)$........	0.602	1.205	1.811	2.439	3.103	3.813	4.653	5.707	7.32	12.07	∞

Two factors have been ignored in the above theory, (1) the decrease in the number of particles due to coalescence, (2) the poisoning of their surface for condensation by adsorbed layers. The frequency of collisions which must precede coalescence, is proportional to the number of particles per cubic centimeter and to the rate of diffusion, which is inversely proportional to the particle diameter (assuming the viscous resistance law of Stokes). Hence

$$-\frac{dN}{dt} = k\frac{N}{d} \tag{7}$$

which is equivalent to

$$d\chi = kdt \tag{8}$$

when the concentration of the dispersed phase is fixed. The integral of this equation gives a linear relation for the coalescence law of growth,

$$kt = d - d_o \tag{9}$$

where d_o is the initial diameter (of the nuclei).

The adsorption of impurities probably follows Freundlich's equation, but when coalescence and adsorption are combined with the surface law an integral equation is obtained which we shall not attempt to solve. The crude theory given above will be considered later in the interpretation of the growth of turbidity. A tabulation of the function (6) is given in table 1, for a few values of χ. An interpolation plot on logarithmic paper is most convenient in testing the equation.

II. OPTICS OF DISPERSIONS

Perfect diffusion

The complete theory of the behavior of scattering media in fully diffused light has been worked out by Channon, Renwick, and Storr (1). If I_o be the incident light intensity, I_r the intensity rejected by the diffusing layer, and I_t that transmitted, the rejectance R is defined by the ratio I_r/I_o, and the obstructance Ω by the ratio I_o/I_t. Superposing two layers (m) and (n), the intensity transmitted through them both, taking account of the successive inter-rejections, is

$$\frac{I_o}{\Omega_m\Omega_n}(1 + R_mR_n + R_m^2R_n^2 + R_m^3R_n^3 + - - -) = \frac{I_o}{\Omega_m\Omega_n\,(1 - R_mR_n)}$$

so that the combined obstructance is

$$\Omega_{m+n} = \Omega_m\Omega_n\,(1 - R_mR_n) \tag{10}$$

Since this is symmetrical, the obstructance is independent of the arrangement. The combined rejectance is similarly

$$R_{m+n} = R_m + R_n/\Omega_m^2\,(1 - R_mR_n) \tag{11}$$

The relative obstructance (O) of a layer superposed on a standard of rejectance ρ, is defined as $O \equiv \Omega(1 - R\rho)$, so that the proper expression for the diffuse density is

$$D \equiv \log O = \log \Omega + \log\,(1 - R\rho) \tag{12}$$

where log is the symbol for the logarithm to the base 10. When the rejectance of the sample is very small, as in the black silver deposit of photographic images, the rejectance factor can be neglected. The density is evidently never as great as it would be without the rejectance factor.

The general expression for the obstructance as a function of the thickness (χ) is

$$O_x = P \exp(\alpha\chi) + (1 - P) \exp(- \alpha\chi) \tag{13}$$

where P and α are constants, and exp is the symbol for the exponential function. This is evidently the integral of $d^2O/d\chi^2 = \alpha^2 O$. Schuster (1) has derived a similar equation for the radiation through a foggy atmosphere. The relation for Ω_x is of precisely the same form. It is evident from the form of this expression that the density increases more slowly than the thickness, and indeed Bloch and Renwick (1) have found an approximate form for the density

TABLE 2

OPAL GLASS THICKNESS (χ)	DENSITIES (AIR CONTACT)			DENSITIES (OIL CONTACT)		
	D_χ (approx.)	log O_χ (exact)	Diff.	D_χ (approx.)	log O_χ (exact)	Diff.
mm.						
1	0.282	Used for	0	0.270	Used for	0
2	0.492	constants	0	0.490	constants	0
3	0.680	0.675	−0.005	0.694	0.692	−0.002
4	0.856	0.848	−0.008	0.889	0.887	−0.002
5	1.023	1.015	−0.008	1.076	1.080	−0.004
6	1.185	1.180	−0.005	1.260	1.271	−0.011
7	1.340	1.344	−0.004	1.438	1.462	−0.024

$$D_x = D_1 \chi^n \tag{14}$$

to hold within the limits of experimental error over a five-fold range in thickness. The exponent for the opal glass samples measured was $n = 0.80$ with air contact, and 0.86 with cedar oil contact. When the thickness was expressed in millimeters, the value of P was 1.342 and $\alpha = 0.4392$, for opal glass with oil contact, while for air contact $P = 1.600$ and $\alpha = 0.3838$. The agreement between the approximate and the exact equations is shown in table 2.

The densities calculated from the approximate equation never differed from those observed by more than 0.007, and 0.0023 was the average difference. This agreement is equivalent to a photometric precision of 0.5 per cent, quite up to the best standards of photometry. Richtmyer and Crittenden (1) give for the average deviation of a single observation from the mean of its set, 0.3 per cent, in a study of the photometric precision of 20000 readings by 15 observers.

Their general expression for the rejectance as a function of the thickness is

$$R_x = R_\infty [1 - \exp(-2\alpha\chi)]/[1 - R_\infty^2 \exp(-2\alpha\chi)] \tag{15}$$

where R_∞ is the rejectance of an infinitely thick layer. Their measurements on opal glass gave 91 per cent for the maximum total rejectance of a thick solid block, which checks the values obtained on similar materials by A. H. Taylor (1) with his diffuse reflectometer, by an entirely different method. The laws of perfect diffusion, here briefly outlined, are therefore well established by this work of Channon, Renwick and Storr. Notice that the theory is purely geometrical, and makes no assumptions except that the light is perfectly diffused, and that the diffusing media are large enough to neglect edge effects. It has nothing to do with the mechanism of scattering by the particles constituting the dispersed phase.

The most important consequence of the laws of perfect diffusion for turbidity measurements is that the density increases more slowly than the depth. It disposes once for all of the claim sometimes made that one instrument is better than another because it conforms to the "theoretical" linear relation between density and depth. If the calibration curve of an instrument is linear, which of course is an advantage, it can be due only to some empirical shape factor which compensates for the rejectance factor in equation (12).

We may apply the laws of perfect diffusion to obtain a complete expression for the intensity of a thick Tyndall beam, as used in tyndallmeters and nephelometers. The incident beam is assumed to be of uniform intensity, and so each layer scatters at right angles an increment which is proportional to its thickness. Before reaching the eye, this increment must traverse the depth (χ) of the dispersion, suffering an obstructance Ω_x. Moreover, the rejectances of the layers both above and below contribute their quota to the Tyndall intensity ratio T, and so the total increment (dT) due to the layer ($d\chi$) is given by

$$\frac{dT}{d\chi} = \frac{k}{\Omega\chi} \frac{(1 + R_{a-\chi})}{(1 - R\chi \, R_{a-\chi})} \tag{16}$$

where R_x is the rejectance of the layer above, R_{a-x} is the rejectance of the layer below $d\chi$, and k is a constant. Substituting the functions of χ from (13) and (15) and integrating

$$T = \frac{T_\infty}{1 - R^2_\infty \, u^2} \left[1 - Au - Bu^2 + (E - Fu^2) \, ln \left(\frac{c + u}{c - u} \right) \right] \tag{17}$$

where $u \equiv \exp(-\alpha\chi)$, and A, B, E, F, c, T_∞, and R_∞ are constants, and χ now represents the depth of the Tyndall beam. It is quite obvious from (17) that tyndallmeters and nephelometers give calibration curves even more complicated than do turbidimeters which measure the density of a dispersion. It is only when the concentration of dispersed phase is so small that secondary scattering can be neglected, or when empirical shape factors compensate, with dispersions of a certain range of concentration, that anything like a linear calibration curve is obtained. This limitation must be carefully investigated for every instrument before the results can be interpreted.

The Tyndall phenomenon

The beautiful experiments of Tyndall, which established the real cause of the color and polarization of sky-light, are fundamental in the optics of dispersions. A brief quotation from his papers follows.

> The apparatus with which I work consists, as already stated, of a glass tube about a yard in length, and from $2\frac{1}{2}$ to 3 inches internal diameter. The vapour to be examined is introduced into this tube in the manner described in my last abstract, and upon it the condensed

beam of the electric lamp is permitted to act until the neutrality or the activity of the substance has been declared.

It has hitherto been my aim to render the chemical action of light upon vapours *visible.* For this purpose substances have been chosen, *one,* at least of whose products of decomposition under light shall have a boiling-point so high that as soon as the substance is formed it shall be *precipitated.* By graduating the quantity of the vapour, this precipitation may be rendered of any degree of fineness, forming particles distinguishable by the naked eye, or particles which are probably far beyond the reach of our highest microscopic powers.

I have no reason to doubt that particles may be thus obtained whose diameters constitute but a very small fraction of the length of a wave of violet light.

In all cases when the vapours of the liquids employed are sufficiently attenuated, no matter what the liquid may be, the visible action commences with the formation of a *blue cloud.* I would guard myself at the outset against all misconception as to the use of this term. The blue cloud here referred to is totally invisible in ordinary daylight. To be seen, it requires to be surrounded by darkness, *it only* being illuminated by a powerful beam of light. This blue cloud differs in many important particulars from the finest ordinary clouds, and might justly have assigned to it an intermediate position between these clouds and true cloudless vapour. . . . .

In all cases, and with all substances, the cloud formed at the commencement, when the precipitated particles are sufficiently fine, is *blue,* and it can be made to display a colour rivalling that of the purest Italian sky. In all cases, moreover, this fine blue cloud polarizes *perfectly* the the beam which illuminates it, the direction of polarization enclosing angle of 90° with the axis of the illuminating beam.

It is exceedingly interesting to observe both the perfection and the decay of this polarization. For ten or fifteen minutes after its first appearance the light from a vividly illuminated incipient cloud, looked at horizontally, is absolutely quenched by a Nicol's prism with its longer diagonal vertical. But as the sky-blue is gradually rendered impure by the introduction of particles of too large a size, in other words, as *real* clouds begin to be formed, the polarization begins to deteriorate, a portion of the light passing through the prism in all its positions. It is worthy of note that for some time after the cessation of perfect polarization the *residual* light which passes, when the Nicol is in its position of minimum transmission, is of a gorgeous blue, the whiter light of the light of the cloud being extinguished.* When the cloud texture has become sufficiently coarse to approximate to that of ordinary clouds, the rotation of the Nicol ceases to have any sensible effect on the quality of the light discharged normally.

Rayleigh's law

The theory of the scattering of light by small particles was given by Lord Rayleigh (1) in 1871.

The simplest case is that of a single particle of infinitesimal size compared with the wave length of light. The particle then acts as an electric oscillator, performing forced vibrations in the direction of the impressed force with a certain amplitude, a. The oscillator, therefore, sends out scattered waves in all directions, the vibrations being, of course, in every case perpendicular to the direction of the light, since light waves are transverse. But the component of a normal to a line making an angle Θ with the vibration is $a' = a \sin \Theta$, so that the scattered intensity in this direction, measured by the square of the amplitude is

$$I_s = ka'^2 = ka^2 \sin^2 \Theta \qquad (18)$$

Here the incident light is regarded as plane polarized. By (18) the scattered intensity vanishes when $\Theta = 0$, that is normally to the incident ray, and in the direction of the incident vibration, in agreement with Tyndall's experiment.

If the light is unpolarized it is more convenient to consider, not the direction of vibration, but the direction of light propagation. If unpolarized light is incident along the axis of y, the incident vibration may be regarded as compounded of two vibrations of equal amplitude in the directions of the axes of x and z. If the particle is situated at the origin of coordinates, two vibrations of equal amplitude—a, along x and z—spread out in all directions from the origin as from a source. The components of these vibrations perpendicular to a direction r, defined by the angles α, β, γ, with the axes of x, y, z, are, respectively, $a \sin \alpha$ and a

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* This seems to prove that particles too large to polarize the blue, polarize perfectly light of lower refrangibility.

sin γ. The resultant intensity I_s, of the scattered light along r, is

$$I_s = ka^2 (\sin^2 \alpha + \sin^2 \gamma) \tag{19}$$

but from geometry $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$, and hence

$$I_s = ka^2 (1 + \cos^2 \beta) \tag{20}$$

This gives the variation of the scattered intensity with the angle between the directions of the incident and scattered light. The intensity is a maximum in the direction of the incident light, decreasing to one-half normally, and zero in the opposite direction.

The amplitude of the vibration in the scattered light, on either the elastic solid theory or the electromagnetic theory of light, is proportional to the volume, V, of the small disturbing particle. At a distance r from the particle the amplitude must be inversely proportional to r, so that in order to be dimensionally correct, the ratio of the amplitudes a of the scattered light and a_o, of the incident light of wave length λ must be

$$a/a_o = kV/\lambda^2 r \tag{21}$$

These simple considerations may help to explain Rayleigh's expression for the intensity I_s of the light scattered from N particles each of volume V, the incident intensity being I_o, and the wave length λ. This is

$$\frac{I_s}{I_o} = \frac{n'^2 - n^2}{n^2} \cdot \frac{NV^2}{\lambda^4 r^2} (1 + \cos^2 \beta) \tag{22}$$

Here n is the refractive index of the medium, n' that of the particles. The particles are supposed to be contained in such a small volume that the distance r and the angle β between the scattered and incident beams are the same for all the particles. For particles of different size, all small compared with the wave length, a summation must be made, requiring the size distribution of the particles. When the particles are not small compared with the wave length, terms of higher order must be included, and again the expression becomes complicated.

No account is taken in (22) of secondary scattering. All of the light scattered by the particles in the direction β is supposed to reach the eye without loss. When the medium is densely filled with particles, this factor may become of first importance. The fractional decrease of the intensity I in traversing a thickness, $d\chi$, of the turbid medium is

$$dI/d\chi = -hI/\lambda^4 \tag{23}$$

where h is a constant independent of λ.
Integrating

$$I_\chi = I_o \exp(-h\chi/\lambda^4) \tag{24}$$

where I_0 is the intensity of the light when $\chi = 0$ and I_x is the intensity after traversing a thickness χ.

The most striking characteristic of equations (22) and (24) is the occurrence of the factor $1/\lambda^4$, indicating that the scattered light increases rapidly as the wave length decreases. The scattered light is, therefore, much bluer than the incident light, while the blue is correspondingly absent in the transmitted portion, which contains a relatively large fraction of the red light. This was used by Rayleigh to explain the blue color of the sky, as well as the red colors of the sunset. The blue color may be used as a test of the size of the particles of any turbid medium. Thus the fine blue smoke from the end of a cigar is an indication that the smoke particles are much smaller than the wave length of light. Tyndall's test of complete polarization at right angles to the incident beam is still more sensitive.

The constant h in equation (24) has been evaluated by Schuster (2) from general considerations, independent of any particular theory of the mechanism of scattering. He obtains the same expression as did Lord Rayleigh, using the electromagnetic theory, namely,

$$h = 32\pi^3 (n - 1)^2/3N \tag{25}$$

where n is the refractive index of the dispersion as a whole. If the blue color of the sky is due to air molecules alone, N is Avogadro's constant, and its value is known from other measurements. The experimental researches on the absorption of the atmosphere by Abbot and Fowle give good values for Avogadro's constant, and indicate quite definitely that the extinction coefficient is inversely proportional to the 3.9 power of the wave length, which is quite close to the inverse fourth power of Rayleigh's formula. Crova, Zettwich, and Boutaric have obtained inverse powers approaching, and in some cases even surpassing 4. Boutaric thinks that such excessive powers disagree with Rayleigh's theory, and suggests fluorescence as a possible cause, but Rayleigh has shown that the "residual blue" observed by Tyndall can be explained by taking into account the second order of small quantities, the residual blue varying inversely as the *eighth* power of the wave length. The occurrence of powers higher than 4 is thus accounted for. Powers lower than 4 can be ascribed to larger particles, and Boutaric shows that from 100,000 particles per cubic centimeter of radius 0.05 micron, to 1,000 of radius 0.1 micron, are sufficient to account for the excess of atmospheric absorption over that which can be ascribed to the air molecules. These numbers are not excessive for the persistent nucleation of the atmosphere. The changes in the polarization of sky-light indicate that the particles causing these changes are relatively large (approaching the wave length of light). Rayleigh's theory has received many other experimental verifications.

Rayleigh's theory assumes that the particles are dielectrics, and so does not apply to the metal sols, which show such beautiful and varied colors. A theory of scattering by small particles was worked out by J. J. Thomson, assuming them to be perfect conductors, and Maxwell-Garnett, Mie, and others have extended the theory to larger particles, and imperfect conductors. A large number of researches on gold and silver sols have shown that the absorption band crosses the visible spectrum toward the red, with increasing size of submicroscopic particle, just as the theory demands. The spectral absorption data of Pihlblad are most complete, showing but one absorption band, and confirming quantitatively Mie's theory. As the particles approach molecular dimensions, the absorption spectrum approaches that of the molecular solution. These colors are so characteristic of the particular molecule, however, that no simple theory can apply. Rayleigh's theory owes its simplicity to the fact that the selective effect of scattering is not specific, all non-conducting particles looking alike when small, just as all coarse dispersions of these substances appear white. Our discussion of turbidity measurements will be limited to dispersions of such colorless transparent substances, the specific absorption of which can be neglected, except as represented by the ordinary index of refraction.

Turbidity measurements

The word *turbid* is derived from the Latin verb *turbare,* to disturb. The same meaning is attached to the French *trouble,* and to the German *trübe.* Hence any medium containing small particles in suspension is turbid. While the original meaning of the word had no direct reference to the eye, turbidity has become associated with the appearance of a turbid medium. The small particles scatter light in all directions, making their presence strikingly evident.

Although turbidity seems to be the word most generally used to express the characteristic optical properties of dispersions, it has been defined usually as a concentration, ignoring the other variables under the assumption that they are constant. Qualitatively the word turbidity is used to express the physical properties of a dispersion which afford optical measurement. For a given dispersion each method of measurement gives a characteristic value, but all such values are intimately related optically. The word turbidity will hereafter be used in a quantitative sense as the name for this class of optical quantities. The value of the turbidity, by any method of measurement, must not depend upon the intensity of the light used to observe it, although it may depend upon the color.

The methods fall into three groups, those which measure: (1) the ratio of the Tyndall intensity to that of the incident light, (2) the diffuse density, or logarithm of the reciprocal of the diffuse transmission of a layer of the dispersion, and (3) the depth at which a target disappears beneath the layer of turbid medium. Instruments which measure the Tyndall ratio are called tyndallmeters when the sample is measured directly, and nephelometers when the sample is compared with a standard of known concentration. Instruments which measure the transmitted light, either by the photometric or by the extinction criterion, are called turbidimeters. The three types of turbidity measures will be called, respectively, the Tyndall ratio, the density, and the extinction index. Their characteristics will be considered under instruments and standards, but it may be remarked here that the Tyndall ratio is the only turbidity sensitive to extreme dilutions, while the only one available at high concentrations is the extinction index.

Whatever method is used, the turbidity (T) is proportional to the concentration (C) and to the depth (χ) as a first approximation. Its dependence on color is intimately bound up with size of particle. For particles small compared with the wave length of light, Rayleigh's law (22) states that the Tyndall ratio is proportional to the cube of the particle size (d) and to the inverse fourth power of the wave length (λ). But particles larger than a wave length merely reflect the light from their surfaces, and so the turbidity is proportional to their total surface. We may combine both these relations in a single formula for the turbidity

$$T = \frac{kC\chi d^3}{d^4 + \alpha \lambda^4} \tag{26}$$

where k and α are constants.

Formula (26) holds approximately for both very large and very small particles, but in the transition region, which is probably from a centimicron to a micron, it may depart from the facts more widely. It indicates a very sharp maximum in turbidity when $d/\lambda = (3\alpha)^{1/4}$, for a given concentration and depth. The constant k is specific both to the dispersion and to the method of measurement, but the constant α probably depends upon the method only.

As a function of concentration and depth, equation (26) is of the same form as Beer's law for molecular absorption. For equal turbidities dilutions are proportional to depths, and since the relation is usually tested by diluting a standard dispersion, we shall call it for brevity the *dilution law*. When turbidity is the diffuse density ($T=D$), a comparison with the exact expression (12) shows that the rejectance factor has been neglected, so that (26) holds only for very thin layers, or for very dilute dispersions. For the very concentrated dispersion opal glass, Bloch and Renwick found a power function of the depth to fit their data, the exponent of (χ) having the value of 0.86. The author (4) has used the same approximation formula in his study of the Kober nephelometer, obtaining an exponent 0.904 with a silica suspension containing 120 parts per million, over a four-fold range in depth.

The same formula was also found to fit the variation of the Tyndall ratio with the depth, giving the exponent 0.924. Kober's parabolic approximation formula is equivalent to the power formula for exponents near unity, and his results on ammonia give an exponent 0.9342. Tolman and coworkers (3) have given the calibration curve of their tyndallmeter over a four-hundred fold range in concentration, for silica particles 1 micron in diameter. The ratio of the turbidity to the concentration increases in the range from 3 to 300 mgm. per liter, and then decreases again for higher concentrations. From 6 to 300 mgm. per liter their data fit the power formula, the concentration exponent 1.225 giving an average deviation of 5 per cent. Mecklenburg (4), however, obtained the dilution law with sulfur sols on his tyndallmeter over a thousand fold range in concentration, with an a.d. of less than 0.6 per cent, but this must be fortuitous, for the reproducibility of his instrument is no better than 3 per cent, and some systematic departure from simple proportionality is required by the complicated exact expression (17). Kleinmann claimed that his nephelometer followed the dilution law, but Owe has shown that this is true only for very dilute dispersions. For M/200 barium sulfate, the depth increased as the 0.85 power of the depth of his standard sol, whereas any power function between turbidity, concentration and depth, regardless of exponents, should give direct proportionality.

Wilke and Handovsky have made very careful measurements of the Tyndall ratio for depths varying from 3 to 24 mm., on gelatin and dextrin solutions, with both red and blue color filters. Their results fit the formula

$$T = T_\infty [1 - \exp(-\alpha\chi)] \tag{27}$$

the constant α ranging from 0.12 to 0.21. This expression indicates that the Tyndall ratio approaches a saturation value (T_∞) for very thick layers, which agrees with the exact expression (17). It is quite unlikely, however, that the exact formula reduces to such a simple form as (27) except as a rough approximation. I have shown (4) that it does not even approximately apply to Kober's nephelometer because the illumination is not uniform. The calibration curve of the tyndallmeter designed by the author (3) approximates a power function of the concentration with an average deviation of 6.6 per cent over a two-thousand fold range, with a concentration exponent of 0.838. The systematic deviations, however, show that in reality the law is much more complicated. The best fit with formula (27), using C in place of χ, gives an a.d. of 19 per cent, so that over this wide range the power function is a much better approximation.

When the turbidity is measured by the extinction criterion the product of concentration and depth is only approximately constant. In my study of the turbidity standard of water analysis (3), the exponent of the vanishing depth of the turbidity rod of 1902 was found to vary all the way from 1.1 to 2. It is therefore obvious that the only feature common to all the instruments for measuring turbidity is a rough approximation to the dilution law over limited ranges. The exact theory shows that the reason for this is inherent in the optical properties of dispersions themselves, and is not due to any "imperfections" in the instruments. To be sure, each instrument has its own shape factors and its own edge effects, but even if these could be eliminated, the dilution law (26) would still be merely an approximation. There is little choice between the three measures of turbidity (1) Tyndall ratio (2) diffuse density and (3) extinction index, as to the range over which they approach the dilution law. For practical purposes, each instrument must be calibrated empirically over the concentration range of interest, and so the turbidity might as well be *defined* by the dilution law itself. This, however, leads to the whole question of standards, which will be considered later.

Color and size of particle

The experimental determination of the relation between turbidity and size of particle is quite difficult, especially with submicroscopic particles. It has been attempted by Mecklenburg (4), Tolman, Gerke and coworkers (3), Bechhold and Hebler (2), and by Owe. Mecklenburg found Rayleigh's law to hold for Sven Odén's sulfur sols of graded size, from 5 millimicrons to 0.1 micron, with an average deviation of about 23 per cent, which is very good for such difficult measurements. It must be remembered that the cube of the diameter increases 8000 fold over this range, so that the Tyndall ratio is an extremely sensitive test of Rayleigh's law.

For sulfur particles between 0.1 and 1 micron in diameter, Mecklenburg found the Tyndall ratio to increase less rapidly than Rayleigh's law, indeed approximately as the first power of the diameter, and inversely as the square of the wave length. There is evidence of a discrepancy in his data for this region, however, for the Tyndall intensity at 0.1 micron particle size is almost stationary, and yet increases more rapidly from 0.3 to 0.8 micron. Tolman (2) and his coworkers have obtained a large amount of data on smokes which indicate that the Tyndall ratio actually decreases as the particles grow in size even with submicroscopic particles 0.1 micron in diameter. Of course the laws may be quite different for dispersions in air, but their results with silica suspensions in water steadily increase with increasing fineness down to particles 1 micron in diameter, so that particles which show a maximum Tyndall intensity must be below 1 micron in size. Bechhold and Hebler found the maximum to occur at about 0.8 micron with barium sulfate dispersions in glycerol, and Owe, working later in the same laboratory, found the maximum around 0.2 micron, with the same dispersions. It is well known in the paint industry that the covering power of white pigments increases with the fineness right down to 0.1 micron, as Green has shown. With photographic emulsions, also, the turbidity increases with fineness of grain right down to the limit of resolution of the microscope, which is 0.2 micron. In spite of the great care of Mecklenburg's work, therefore, we must question his data for particles approaching a wavelength in size.

There is one difference between Mecklenburg's data, and that of the others, that may account for the discrepancy. In his commendable effort to eliminate the effects of secondary scattering, he extrapolates his values, with high concentrations quite considerably, in spite of the fact that the data themselves show maxima. With the smaller intensities the extrapolations intersect the axis normally, and so his data for the smaller particles are unambiguous. The results of Bechhold and Hebler on barium sulfate sols with particles ranging in size from 4 to 50 millimicrons are directly proportional to the diameter with an average deviation of 1.6 per cent. It is hard to reconcile such data with those of Mecklenburg, which varied as the cube of the diameter. Certainly such a discrepancy cannot be ascribed to lack of uniformity in particle size, or to inaccurate ultramicroscopic measurements of particle size.

Particles above a micron in size can be measured in the microscope without difficulty, and here there is no disagreement between observers. Tolman and his coworkers find the Tyndall intensity proportional to the surface of silica particles above 2 microns in diameter with an average deviation of 5 per cent, and Bechhold and Hebler agree with an a.d. of 11 per cent for barium sulfate-glycerol sols. Owe has found the Tyndall intensity to decrease very slowly as the sulfate particles increase in size from 0.2 to 0.6 micron, eight different dispersions in glycerol and in glycerol-alcohol giving intensities inversely proportional to the 0.58 power of the diameter with an a.d. of 4 per cent.

Pihlblad has measured the density of sulfur sols in the spectrophotometer over a very wide range of wavelengths and particle size. He confirms Rayleigh's law as regards wavelength with an a.d. of 8 per cent, but the relation of density to particle size is not very clear for particles below 5 centimicrons. For particles between 5 and 15 cμ the ratio of density to diameter is constant to 20 per cent, while above 15 cμ the surface law is definitely followed. The turbidity maximum is therefore between 0.1 and 0.2μ, which agrees with Owe's results with barium sulfate sols, but disagrees with those of Mecklenburg on sulfur sols. Moreover, Pihlblad has found the product of density and diameter constant for every type of sulfur sol he prepared. Thus by Sven Odén's method of fractional coagulation with sodium chloride, the average deviation was 5 per cent for particles between 16 and 55 cμ, with alcoholic sulfur solutions precipitated in water the a.d. was 29 per cent between 15 and 22 cμ, and with sulfur sols obtained by grinding the a.d. was 15 per cent between 12 and 22 cμ. Even with gold sols, which show strong selective absorption, the surface law was followed at wavelength 436 mμ with an a.d. of 8 per cent for particles above 0.1 micron in diameter. These results indicate that the turbidity maximum occurs at particle sizes between 0.1 and 0.2 micron.

On the other hand, Owe has obtained with a wedge colorimeter densities which increased in direct proportion to the diameter right up to 1 micron with the very same barium sulfate dispersions which gave maximum Tyndall ratios at 0.2 micron. Here is another major discrepancy which must be cleared up. It may be connected with the shape of the particle, as Owe suggests. His results indicate that the Tyndall ratio is more sensitive to the dispersing medium than is the diffuse density, and that the shape of the particles also varies in different dispersing media. It must not be forgotten, however, that as the Tyndall ratio increases, its relation to the concentration and the depth becomes extremely complicated, as shown by equation (17). Within its range the turbidimeter is to be preferred over the nephelometer, because the exact theory of the density of concentrated dispersions is so much simpler, and gives a closer approximation to the dilution law. Nevertheless, Owe's density results leave the question of where the turbidity maxmum occurs still in doubt. The interpretation of density measurements will be considered later in the discussion of turbidimeters.

There is quite a different method of obtaining information about size of particle, which is independent of the color, namely, the degree of polarization of the Tyndall beam. Boutaric has obtained some quantitative data on silver chloride dispersions. They indicate that the depolarization $(1-P)$ of the Tyndall beam is proportional to the density (transmitted light), with an average deviation ranging from 5 to 12 per cent for the different growth curves. The ratio of the density in blue light to that in red is constant to 3 per cent, so that the density is inversely proportional to the 3.1 power of the wavelength, which approximates Rayleigh's law. With alcoholic mastic dispersions in water, however, the growth of the particles was practically completed before any measurements could be taken.

It would seem that the turbidity growth curve itself should yield some information regarding the size of particle, if any of the laws of particle growth, above outlined, were followed. For if the diffuse density is a power function of the diameter,

$$D = kdp \tag{28}$$

and it is necessary merely to substitute the *p*'th root of the observed density in place of the diameter (*d*) in the law of growth to see if it represents the facts. When this is done with Boutaric's data on silver chloride dispersions, however, it is found that none of the simple laws of growth, the diffusion, surface, or coalescence laws, yield high enough values of the exponent to be reasonable, as shown by the drift in the constants in table 3. In other words, the actual growth of the particle is much slower, than would occur on a pure surface of the dispersed phase. This indicates that the limiting factor in particle growth is the poisoning of the surface by adsorbed layers. Since the precipitation of silver chloride is comparatively rapid, the dominance of adsorption phenomena over particle growth must be of fairly general occurrence in dispersions, and this is indicated by their frequent persistence in the dispersed condition for such extensive periods of time. Turbidity growth curves, therefore, which are most easily obtained, present an interesting problem for interpretation, and will probably yield considerable knowledge of adsorption phenomena. Incidentally, this dominance of adsorption emphasizes with what meticulous care the technique must be standardized if reproducibility is to be expected in turbidity measurements.

TABLE 3

Particle size from turbidity growth curves

(Boutaric's data on AgCl dispersions 6 mgm./l.)

Application to diffusion law of growth

Relative values of log $(1 - \chi^3)/t$

t (min.)	D/D_m	$p = 6$	$p = 4.5$	$p = 3$	$p = 2$
2	0.278	1627	120	708	344
5	0.405	879	68	451	259
10	0.572	613	51	369	250
30	0.855	374	34	279	226
60	0.990	384	35	167	304
Average					277+13%

Surface law of growth

Relative values of $F(\chi)/t$

$p = 6$	$p = 3$	$p = 1$
292	165	835
132	82	496
77	52	362
36	27	217
(24)	(22)	201

Coalescence law of growth

Relative values of $(\chi - \chi_1)/(t - t_1)$

t (min.)	D	$p = 6$	$p = 3$	$p = 1$
2	0.111			
5	0.162	173	291	170
10	0.229	129	222	148
30	0.342	59	106	82
60	0.396	33	59	49

The laws of particle growth presented above are adapted to testing the relation of turbidity to size of particle because the dispersions have been assumed to be uniform, that is, all the particles have been assumed to be exactly alike. Of course, this is hardly ever the case, particularly during growth. In Smoluchowski's theory of coagulation the particles are taken to be all of the same size at the start, but after coalescence the aggregates are distributed in size because of the varying probabilities of collision. Taking ν_4 original particles, after the lapse of time t, ν_1 single particles are left, the others having coalesced into aggregates, ν_2 of two, ν_3 of three, ν_4 of four particles, etc. Smoluchowski then shows that

$$\nu_1 = \nu_0/(1 + \alpha)^2,\ \nu_2 = \nu_1 \chi,\ \nu_3 = \nu_2 \chi, \text{ etc.} \tag{29}$$

where $\alpha \equiv 4R\pi\epsilon D\nu_o t$, and $\chi\alpha \equiv /(1+\alpha)$. Every time a particle diffuses into the sphere of action of another, the constant probability (ϵ) of coalescence is assumed. R is the radius of this sphere, and D is the diffusion coefficient of the original particles. Westgren and Reitstötter have confirmed the theory on gold sols, finding R to be not much greater than the diameter d_1 of the single particles (see Svedberg (2) p. 218). It is clear that the sphere of action cannot long remain of constant radius, as the aggregates continue to increase in size, but must itself increase. Moreover, the persistence of coarse dispersions for long periods of time shows that the probability ϵ must decrease, probably due to surface poisoning by adsorbed layers, for there is no other factor in Smoluchowski's theory to arrest the growth of the particles.

The distribution of aggregates as a function of the time, indicated by (29), determines the curve of turbidity growth when the relation between turbidity and size of particle is fixed. If the aggregates are all assumed to be spherical, we have $d_2^3 = 2d_1^3$, $d_3^3 = 3d_1^3$, etc., where d_1 is the diameter of the single particle, d_2 that of the double, d_3 that of the triple particles, etc. Assuming Rayleigh's law, the partial turbidities are $T_1 = k\nu_1 d_1^6$, $T_2 = k\nu_2 d_2^6$, etc., and their sum, the total turbidity (T) is therefore, from (29)

$$T = k\ \nu_1\ d_1^6\ [1 + 4\chi + 9\chi^2 + 16\chi^3 + 25\chi^4 + \ldots\ldots..] \tag{30}$$

But the series in χ is simply $(1+\chi)/(1-\chi)^3 = (1+2\alpha)(1+\alpha)^2$, and since $(1+\alpha)^2$ cancels from ν_1, (30) reduces to

$$T = T_o\,(1 + \beta t) \tag{31}$$

where $T_o = k\nu_o d_o^6$ and $\beta = 8\pi\epsilon RD\nu_o$. The turbidity of the dispersion, therefore, increases linearly with the time as long as the particles remain small enough for Rayleigh's law to hold. During the transition to large particles, which diffusely reflect the light in proportion to their total surface, there is a period when the turbidity is proportional to the volume of the particles, and during this period the total turbidity remains constant, for the series $[1 + 2\chi + 3\chi^2 + 4\chi^3 + \ldots.] = (1 + \alpha)^2$. Thereafter, the turbidity falls, although the series is too complicated to evaluate because the surface law gives coefficients to the 2/3 power. The application of Smoluchowski's theory, therefore, seems to explain the general shape of the turbidity growth curves qualitatively, at least, without recourse to any surface poisoning by adsorbed layers. Unfortunately it is not adapted to a quantitative test, but it would probably be found that relatively stable dispersions grow more slowly in size of particle than Smoluchowski's theory would indicate, because of surface poisoning by adsorbed layers. Nevertheless, even when the particles remain uncontaminated the turbidity must increase to a maximum and then gradually decrease as the particles grow in size.

III. INSTRUMENTS AND STANDARDS

The oldest method of measuring turbidity was by means of extinction criterion. For over a hundred years the oceanographer has lowered circular discs of canvas into the sea to measure the depth at which they disappeared. This method is an obvious outgrowth of the simple observation of objects beneath the surface of the sea, which in clear tropical waters are sometimes visible to a depth of over 80 fathoms. The platinum-wire method, now standard in water analysis, originated when Hazen stuck a pin into a piece of wood and lowered it into sewage until it vanished. The earliest form of laboratory apparatus using the extinction criterion was the diaphanometer designed by Horning in 1876.

Kober (4) refers to Mulder (1859) as the first to use turbidity in the determination of atomic weights. Stas estimated the turbidity of his filtrates by pouring them into large flat-bottomed tubes, and observing an illumined scale below holes over which the tubes were placed. Richards did not consider this method delicate enough, and so designed his nephelometer in 1894, the first instrument to exploit the extraordinary sensitiveness of the Tyndall phenomenon. Nevertheless, the disappearance principle continued the favorite in water work, probably because of its simplicity and freedom from difficulties due to color and to comparison standards. Extinction turbidimeters were designed by Parmelee and Ellms, Jackson, Leighton, Weaver, Smith, and others.

One advantage of the disappearance method is its great range. In field work the United States Geological Survey standard platinum wire can be used in streams of crystal purity, or in rivers of solid mud. Indeed, the extinction criterion has found great usefulness in measuring the covering power of paint pigments, and the fineness of grain of photographic emulsions, dispersions so concentrated that even the diffuse density does not vary appreciably with the depth. Sheppard and Elliot have described a dispersimeter in use at the Eastman Kodak Laboratory, and Pfund a cryptometer for grading the covering power of paint. Renwick has used the extinction criterion combined with a turbid wedge at the Ilford Laboratory in England for many years, and Renwick and the author have developed several forms of the wedge turbidimeter for use at the Redpath Laboratory of the Du Pont Company, but no descriptions of these instruments were published. The possibilities of the extinction criterion for concentrated dispersions are demonstrated by the recent microturbidimeter of Conklin, which in his hands rivals the photometric criterion in precision.

The nephelometer of Richards was further improved by Richards and R. C. Wells in 1904, and placed upon the market by the International Instrument Company of Cambridge, Mass.

Richards always insisted on limiting the nephelometer to the comparison of an unknown with controls of exactly the same age and history, and was quite shocked when Wells later used ground glasses of graded densities as constant standards. The warning of Richards (3) sounds prophetic now in view of the neglect of the question of reproducibility on the part of many workers. Nevertheless, Wells took a step in the right direction, for his constant standards enabled him to study reproducibility and the growth of turbidity. The causes of the differences between turbidity and concentration in sulfate determinations were studied by Muer, who pointed out the importance of fixing the acidity and dilution within certain limits before precipitation.

The wide application of the nephelometer in biochemistry was early recognized by Kober (1913). He developed the instrument and made it available through Klett (New York City), his final design representing a considerable improvement over the model of Richards and Wells. Impressed by its extreme sensitiveness, with more industry than caution he and his associates announced methods for quantitating proteins, casein, proteases, nucleases, phosphorus, etc. He seemed to think the trouble with previous work was in the instrument, and so did not stress sufficiently the difficulties of reproducing precipitates, which accounts for the prejudice against the nephelometer among critical workers. Claims of an accuracy better than 1 per cent, made by Kober, Holker, Kleinmann, Weinberg, and others for their instruments are quite extravagant. The limiting factor in turbidity measurements is the reproducibility of the dispersion, not the precision of the instrument. Even crude instruments are sufficiently accurate to show that such claims are quite beside the point.

Meanwhile Bloor (1914) had converted a Duboscq colorimeter into a nephelometer and applied the method to fats in milk, blood, etc. His use of a single standard triolein emulsion was criticised by Csonka (1918). The work of Bloor and Kober aroused considerable interest among American biochemists, as shown in the appearance of rapid methods for acetone by Marriott, for proteins in urine by Folin and Denis, for ammonia by Graves, and for calcium by Lyman. Nephelometric methods were also developed by Woodman, Gookin and Heath for the essential oils, and for mustard gas by Yablick, Perrott and Furman.

After the war the literature began to show the interest in nephelometry among the biochemists in Europe. In Germany the Kleinmann micro-nephelometer, produced by Schmidt and Haensch, represents an optical refinement of the original model of Richards and Wells. Leitz, and H. Krüss of Hamburg also manufacture micromodels of the Duboscq, which can be used for measuring both the density and the Tyndall ratio. Pellin at Paris produce the miniature Duboscq of Baudouin and Bénard. Chénéveau and Audubert have also described a nephelometer. In this country, Bausch and Lomb, and Spencer produce micromodels of the Duboscq, so that there is now available a choice of instruments provided with excellent photometric fields. Many similar instruments have also been described in the literature, usually attempts to use apparatus at hand, or to save expense.

Some biochemists have preferred to use the Duboscq as a turbidimeter matching the densities by transmitted light. During the war in France, Vlès, de Watteville and Lambert developed an "opacimètre" for counting bacteria in flasks which could be sterilized. Color filters and a neutral wedge were used to measure the densities. The nephelometer of Weinberg in Germany we would call a turbidimeter, for the density of a variable depth is matched in a Lummer-Brodhun cube against a standard field controlled by nicol prisms. The extinction criterion has been perfected at the Prudential Laboratory, and the "scopometer" developed by Exton extends its range to high dilutions. In its present form the scopometer is unique in applying both extinction and photometric criteria to both color and turbidity measurements. The extinction criterion was also applied to biochemical work in England by Holker.

The first tyndallmeter was that of Mecklenburg and Valentiner (1), made by Schmidt and Haensch, but it has been considered a research instrument too complicated for general use. The tyndallmeter of Tolman and Vliet was designed especially for smokes, and has been used by Drinker in his studies of air pollution. The author's (3) tyndallmeter was designed frankly for research upon the optics of dispersions.

Densitometers, which are used to measure the density of photographic images, are of course turbidimeters using the photometric criterion, but the rejectances of the black silver deposits are so small that the photographic density follows the dilution law to a high degree of approximation. Bloch and Renwick used a densitometer to obtain the densities of opal glass given in table 2. The decreasing first differences show that the densities soon become insensitive to depth. Indeed, the exact expression (13) shows that the rate of increase of the density with the depth begins at $\alpha\ (2P-1)$ for $\chi=0$ and falls to α for great depths. When P is not much greater than unity, therefore, the density follows the dilution law fairly closely.

Nephelometers and tyndallmeters

One may well pause before such a profusion of instruments and ask what qualities are desirable in a nephelometer or in a tyndallmeter. Most photometrists will agree that a prime requisite in both types is a dividing line which vanishes completely when the fields are matched. A black or a bright dividing line between the fields hurts the precision of the match, and multiplies the effort and fatigue of the eye. The mechanism for controlling the brightness should move quickly and easily, for slowness leads to indecision, but ratchets and pinions must not have "backlash," or "creep" between the match and the reading of the scale. The scale should be convenient and illuminated without glare.

The source of light should be scrutinized more carefully than is usual in colorimetry. It is best to have some sort of standard available to check up the constancy of the illumination frequently. Any lack of rigidity in the lamp supports, or possibility of movement, may become a source of serious error. The worst trouble, however, is the color difference between the comparison fields. In the nephelometer, when standard and unknown are identical except in concentration, a perfect color match should be possible, so that any color difference indicates a color or brightness difference in the incident illumination, just as it does in Duboscq colorimetry. More careful adjustment at the start should eliminate this difficulty. Tyndallmeters should be provided with color filters to overcome the color difference between the constant standard and the sample, and monochromatic filters are advisable on the nephelometer as well, because the Tyndall ratio is a function of the color.

Bechhold and Hebler (1) have reported an interesting phenomenon with two colored hydrosols, using the Kleinmann nephelometer. While they check the dilution law with barium sulfate sols with an average deviation of 0.07 per cent, red kollargol, and blue indigo sols give departures over 100 per cent in some cases, even with color filters over the eyepiece. But when they employ these same solutions, or gelatin filters dyed by them, between the source and the instrument, so that the incident illumination is properly filtered, the departures from the dilution law are again reduced to less than 1 per cent. From this it would appear that these sols are decidedly fluorescent, for otherwise it would make no difference where the color filter is placed.

In choosing color filters to limit the spectral region under observation, high transmission of the dominant hues must be combined with a very sharp edge to the absorption band. The effective wave length is usually near this edge, not at the transmission maximum of the filter, because of the adsorption of the sample, or else due to the drop in visibility at the extremes of the spectrum. For example, the Wratten Stage red no. 27, which is quite stable to light, has a density greater than 2 for wave-lengths below 58 centimicrons, and so the resultant dominant hue is in this region when used with a nephelometer or tyndallmeter on dispersions which give a blue Tyndall beam. The Wratten Stage blue filter no. 47A, with density above 2 for wave-lengths above 51cμ, results in this blue-green color when used over a red solution. The Wratten Mercury green monochromatic filter no. 62, or no. 74 (ε), which is practically the same, are very good filters for limiting the spectrum to the regions of maximum visibility. These gelatin filters are not as permanent as colored glasses, which may be used as control standards, but they are much superior both in transmission and in the sharpness of edge of their absorption bands. With reasonable protection from exposure to light, especially ultraviolet, they are quite stable for years, and they can be accurately reproduced.

There is one danger to guard against religiously in both nephelometers and tyndallmeters, namely stray light. Dispersions are like sponges, integrating the illumination from every source. All instruments should be enclosed unless working in a dark room, and the interior should be matt black. Dust and scratches on the optical parts should be avoided much more carefully than in other optical instruments. But it is better in the course of an investigation not to disturb the adjustments than to run the risk of a discontinuity in the readings due to cleaning and readjustment. Instruments should be sturdy, the adjustments should be reduced to a minimum, lamps and other parts that have to be replaced should be so mounted that there can be no question whatever of their reproducibility. The best tests of stray light are the Zero readings, both with the cells empty and with them full of optically clear distilled water.

With scrupulous cleanliness and care in the technique, the Tyndall criterion is capable of extraordinary sensitivity. Indeed, the method has been used to measure the light scattered by gas molecules themselves, first accomplished by R. J. Strutt, the present Lord Rayleigh, and since developed in extensive researches on both gases and liquids by Raman, Martin and others.

The exact theory of the density of concentrated dispersions is so much simpler than that of the Tyndall ratio, and follows the dilution law so much more closely, that nephelometers and tyndallmeters should be used only for extreme dilutions beyond the range of turbidimeters. To show how far the Tyndall ratio departs from the linear relation of the dilution law, figure 2 has been constructed from Wilke and Handovsky's results. The dotted curves through the observed points are fitted by the approximation formula (27) (solid curve) with an average deviation of 1.9 per cent for the 10 per cent gelatin solution in blue light, an a.d. of 2.5 per cent for the gelatin in red light, and an a.d. of 0.7 per cent for 10 per cent dextrin in blue light. Ruby red and cobalt blue glasses were used as color filters. Results like these make one wonder if the straight lines obtained with such precision on some nephelometers may not be due to some compensating effect. The illumination may increase with the depth, as I have shown occurs on the Kober instrument, or the secondary scattering from layers not directly illuminated may contribute some light not figured in the theory. If this is so, the size of the indirectly illuminated portion must have considerable effect upon the calibration curve. It is obvious, however, that any such empirical compensation must be carefully calibrated before the readings can be interpreted. It is not safe to calibrate with a single stock dispersion, and then assume that thereafter concentrations can be read directly from this curve.

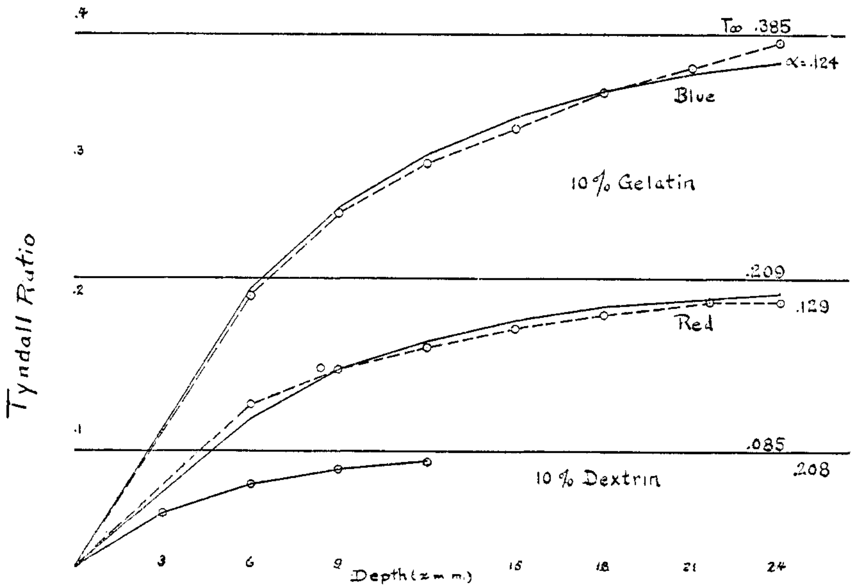

FIG. 2. WILKE AND HANDOVSKY'S DATA

The instrument is really limited to interpolation within a narrow range, just as Richards (3) pointed out in 1906. At extreme dilutions, however, the field for nephelometers and tyndallmeters par excellence, both theory and experiment show that the dilution law is followed.

Turbidimeters

The requirements of a reliable turbidimeter are similar in many respects to those for measuring the absorption of homogeneous media, but there is one very important difference. Since dispersions scatter in every direction light received from every direction, the incident beam must be specified just as definitely for density measurements as for the Tyndall ratio. This is well recognized in photographic densitometry, where the density to parallel light represents more nearly the conditions in practise, while the diffuse density is simpler from the point of view of measurements.

In turbidimetry it is preferable to use the diffuse density, which follows simpler laws and gives more reproducible results. The practical requirement of a small volume of sample, however, introduces edge effects which defy theoretical treatment but which nevertheless, may at least partially compensate for the systematic departure from the simple dilution law which the exact equation (13) requires. Such empirical adjustments, however, always lead to doubt in the interpretation. The dilution law assumes that it makes no difference how closely the particles are packed together, a given number of particles always obstructs the light by the same amount. But in a narrow cell the edge effects upset any such simple relation. If the particles were all crowded into a thin enough layer, the light escaping from the edge could be neglected, while if they were diluted to an extreme, practically all the light would escape edgewise. This shows that the width of the cell is a factor as well as the total number of particles, which contradicts the dilution law. The reason Beer's law holds for molecular absorption is because the molecular scattering is reduced to an utterly negligible quantity by destructive interference, so that all the light is either transmitted regularly, or absorbed as heat.

The extinction criterion possesses the advantage over the photometric criterion of apparent freedom from color difficulties. Anyone can watch an object disappear, whatever its color and regardless of the color of the surrounding field. In practise, therefore, the criterion is easy, except for a feeling of hesitancy which is more pronounced than that with the photometric criterion. In theory the extinction criterion is a measure of the least perceptible increment, or contrast limen (l) of the particular portion of the retina that receives the image of the target, when the adaptation of the eye is fixed by the brightness of the surrounding field (I_x). If I'_x is the target brightness at extinction, and I_o and I'_o are the corresponding brightnesses at the same depth (x) with distilled water in the cell, we have

$$I'_o = I_o\,(1 + k) \text{ and } I'_X = I_X\,(1 + l) \tag{29}$$

where k is the contrast factor with distilled water. The regular transmission (t'_x) and the diffuse transmission (t_x) are respectively, assuming the dilution law,

$$t'_X = \exp(-\,a'CX) \text{ and } t_X = \exp(-\,aCX) \tag{30}$$

where C is the concentration of the dispersion, a' and a are constants. The target brightness includes not only the transmitted rays which combine to produce the image, but also a diffuse portion representing secondary scattering. Assuming this to increase with the depth in proportion to $(1 - t_x)I_o$, we have

$$I'_X = t'_o\,I'_o + b(1 - t_X)\,I_o \tag{31}$$

where b is a constant. Since $I_x = t_x\,I_o$, (29), (30), and (31)

$$CX = \frac{1}{a' - a}\,ln\left[\frac{1 + k}{1 + l + b(1 - 1/t_X)}\right] \tag{32}$$

The right hand member of this equation is constant for a given instrument and dispersion except for the small term in b, which can be neglected, and the contrast limen (l) which is personal to the observer. The extinction criterion therefore follows the dilution law to about the same extent as does the diffuse density, represented by the constant a, provided the visual acuity of the observer remains constant. Any variation in his acuity will change his reading, but not in the same proportion, because l enters in the logarithm. Moreover, different observers will agree in their readings only to the extent that their acuities are the same. Since the visual acuity of each observer is a slightly different function of the color and the brightness level, the extinction criterion is subject to systematic errors which do not vitiate the photometric criterion. Indeed, the photometric criterion is a null method, using the eye as a galvanometer is used in measurements with the potentiometer, while the extinction criterion uses the eye as a direct reading instrument such as a voltmeter. It is a marvel that the eye can be used in such a manner at all, and yet experience shows that normal observers actually do agree to a surprising extent after a little practice together. The personal equation can be largely eliminated by referring the readings to those on a constant standard of about the same value. If the two extinctions appear the same to the observer, the only residual error is the change in his criterion between the readings on the unknown and on the standard.

Equation (32) shows that the extinction index increases slowly when more contrast (k) is used between the target and the field, and decreases slowly when the least perceptible increment (l) grows larger as the result of visual fatigue, etc. In the experience of the author, visual acuity is variable from moment to moment, so that the apparent precision of the extinction criterion is not a safe measure of the real accuracy. Whenever the color difference in the photometric field is eliminated, the photometric criterion is more reliable. For rapid routine work, however, where an average deviation of 5 per cent is permissible, it is much simpler to use the extinction method. With care the average deviation of the method can be kept below 2 per cent, even in routine work, as will be shown later. Incidentally, many authors are quite careless in stating the precision of their measurements. The simplest measure of variability is the average deviation of a single determination, which is used throughout this review.

Turbidity standards

It is not at all certain that it is possible to reproduce a dispersion from specifications with sufficient accuracy for the purposes of a standard. The most that can be expected at present is a fair degree of permanence in a standard, and this rules out dispersions in liquids. Opal glass, however, cannot be obtained of the proper range of turbidities for tyndallmeters, although it is quite satisfactory for turbidimeters. Since it cannot be made accurately to specification, the unit of turbidity should not be defined by opal glass, but it is useful in calibrating instruments. A number of samples of opal glass from different melts would probably be sufficiently permanent to maintain a constant turbidity standard for many years to come, just as incandescent lamps are used to maintain the standard candle.

The specific unit of turbidity might be defined by an arbitrary number, which need not represent the turbidity reading obtained in any actual case. But it is preferable to have the turbidity equal the concentration of the most turbid substance that can be obtained. One could then visualize, from the value of the turbidity, the inherent capacity of the dispersion to scatter and obstruct light. The most that could be expected from a given concentration of material would be a total turbidity equal to 100 per cent of the concentration. Of course, the thickness of the sample to which the specific turbidity refers should be the centimeter. By using the specific turbidity maximum as a unit, the size of particle will be so large that the specificity to color will be small; but to eliminate all ambiguity it should be referred to monochromatic light. The best wave length would be the mercury green line at 546 mμ, which is the most brilliant monochromatic source available, and is very near the maximum of visibility.

The actual evaluation of the standard should be performed by the Bureau of Standards. It must be postponed until more is known about what dispersions give the greatest specific turbidity, but in the meantime the silica standard of water analysis might be assumed to have unit specific turbidity, when measured at a concentration of a gram per liter. The trouble with the silica standard is that the fineness is specified by the vanishing depth (100 mm.) of a platinum wire 1 millimeter in diameter, "in the open air, but not in sunlight, and in a vessel so large that the sides do not shut out the light so as to influence the results. The turbidity of such water is arbitrarily fixed at 100 parts per million." This is very inconvenient for the laboratory. The platinum wire method is not suitable for a standard, because of the uncertain personal equation of the observer, so that even the water analysts themselves have shown a tendency to avoid its use.

Bechhold and Hebler have suggested as a standard a millimolal dispersion of barium sulfate in glycerol, giving particles 2.5 microns in diameter. It is precipitated by mixing 2-millimolal hydroxylamine sulfate with an equal volume of a like concentration of barium chloride, each dissolved in glycerol. They call this the Kraus standard, after their colleague who developed it. Kraus found the standard to follow the dilution law on the Kleinmann nephelometer from 0.02 to 0.8 millimol with an a.d. of 0.07 per cent. The best results were obtained with equivalent amounts of the sulfate and $BaCl_2 \cdot 2H_2O$, for which the turbidity was independent of the method of mixing. Heating to 100° changed the turbidity 5 per cent, but no change occurred in an ice bath. For 24 hours the turbidity remained constant within 4 per cent; in eight days it fell 6 per cent. They also prepared a 5 millimolal standard barium sulfate sol with magnesium sulfate. The dispersing medium was glycerol containing 15 per cent isobutyl alcohol. The particles were less than 90 millimicrons in diameter, and the specific turbidity was 60 per cent of the standard. This sol remained unchanged for 6 months. They check von Weimarn's precipitation laws in general, but the isobutyl alcohol complicates the relations because of its slight solubility in glycerol. The dispersity increased with the excess of the barium ion, but contrary to von Weimarn's laws an excess of sulfate ion did not give stable sols. They do not give any data to show the reproducibility of their standard from specification with glycerol, sulfate and barium from different sources, the situation that would have to be met in practice.

The diffuse density is the most reproducible measure of the turbidity when the proper concentration and depth are chosen. But a dispersion which shows the maximum specific turbidity by density measurements is not at all the one which shows a maximum Tyndall ratio, because absorption of light by particles contributes to the density but subtracts from the Tyndall intensity. The tyndallmeter, therefore, must be used to discover the dispersion of maximum specific turbidity, in spite of its limitation to high dilutions. In some respects this is an advantage, for von Weimarn's laws indicate that large particles precipitate only at low concentrations, and one would expect less alteration in the particles on dilution when they are already widely separated. Once the standard dispersion is specified, however, the advantages of both turbidimeters and tyndallmeters could be utilized, for it seems reasonable to hope that a concentration and suitable depths could be found for precise measurements of all three of the measures Tyndall ratio, density, and extinction index.

The calibration of the instruments can be made by assuming the dilution law for a variety of dispersions. Inconsistencies can probably be ascribed in most cases to changes in the particles on dilution. The dilution must be made with the same solution as the dispersing medium, for otherwise the solubility product requires a change in the total mass of the dispersed phase.

Reproducibility of dispersions

No matter how perfect the instrument is for measuring turbidity, until the dispersions themselves can be reproduced its usefulness is limited. It must not be taken for granted that the same technique will always give the same turbidity with the same concentration of the dispersed phase. It is surprising how little data on reproducibility the literature has to show. Probably more work has been published on silver chloride in water than on any other dispersion, and yet Kleinmann concludes after extensive studies that they are not adapted for nephelometry. He says (1, p. 143): "Doch zeigte es sich, dass bei Innehaltung der sich als relativ günstigst herausstellenden Arbeitsbedingungen eine überwiegende Mehrheit alle Versuche ca. 66⅔% gleiche Teilchengrösse ergab und die Proportionalität der Beziehungen bestätigte. Ein Drittel aller Versuche waren vollständig verschiedene Ausfälle. Es müssen bei der Herstellung kolloider Lösungen Einflüsse ein Rolle spielen, die wir entweder nicht kennen oder noch nicht beherrschen." He prefers his phosphomolybdate strychnin compound, which seems to

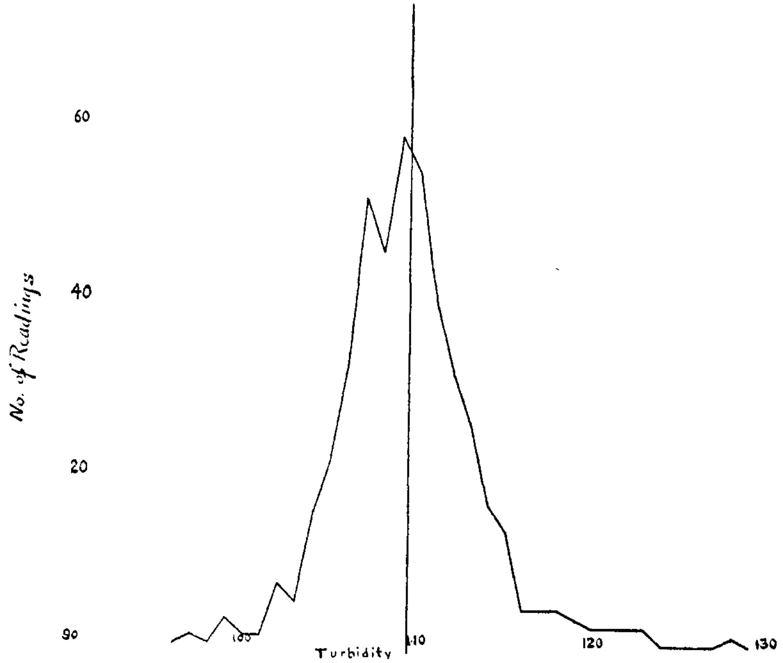

Fig. 3. Reproducibility of Turbidity

follow more regular laws. According to Kober, it was unfortunate for the development of nephelometry that silver chloride dispersions were studied first.

In view of the vagaries of silver chloride suspensions complained of by the nephelometrists, it is interesting to see what reproducibility is obtained in the turbidity of photographic emulsions. Figure 3 shows the frequency curve of 442 turbidities, all the batches of a fixed type measured over a period of twenty months at the Redpath Laboratory of the Du Pont-Pathe Film Manufacturing Company, using the micro-turbidimeter designed by Conklin.[2] The frequency distribution closely approximates the normal probability law, with a standard deviation of 3.9, or a probable error of 2.4 per cent. The average deviation is 2.6 per cent, and the entire range is 27 per cent. One-half the batches, therefore, fall within a range of less than 5 per cent, one in ten would be expected to deviate by more than 5.9 per cent, and one in a hundred by more than 9.3 per cent. When it is considered that these deviations include all the vagaries of plant production as well as the errors of measurement by at least four observers using the extinction criterion, the data seem sufficient to demonstrate the possibility of reproducing silver halide dispersions. It may be remarked that Kleinmann used an excess of silver, while Boutaric used an excess of chloride. Boutaric cautions against pouring the chloride into the silver nitrate, and while his curves are averages of several runs, he makes no mention of any failure to reproduce. Lamb, Carleton and Meldrum revised Wells' technique on silver chloride precipitation, but do not present any data which shows the reproducibility of their final technique.

Chénéveau and Boussu call attention to the necessity of studying carefully and systematically each method, but the following statement of Hibbard best describes the situation.

> Successful turbidimetry depends not only on a satisfactory instrument, but equally as much on a satisfactory method of producing the precipitate to be measured. This must be such that a given weight of the substance to be measured will always produce a precipitate of the same optical quality, so that it will have the same opacity and give the same reading in the turbidimeter. One who has not tried this will hardly realize the difficulty of the problem. By varying the concentration and manner of mixing the reagents, it is possible to produce a precipitate of barium sulfate having 2 or 3 times the opacity of an-

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[2] The author wishes to express here his thanks to Dr. V. B. Sease, Director of Redpath Laboratory, for placing these data at his disposal.

other produced from the same amount of sulfate. Other precipitates are subject to similar variations.

For turbidity measurements the precipitate should be very fine so as not to settle rapidly; yet it must not be of colloidal dimensions. Colloidal precipitates are not uniform in appearance and are not easily compared in the turbidimeter. Moreover, their suspensions are liable to appear colored by transmitted light. Suspensions of large crystals have relatively low opacity and settle very rapidly; therefore, they are not suitable for turbidimetric estimation.

In order to produce a precipitate of uniform physical character, the following conditions must be controlled within somewhat narrow limits: (1) concentration of the 2 ions which combine to produce the precipitate (2) ratio of concentration in solutions mixed (3) manner of mixing (4) time rate of mixing (5) amount of other salts present (6) temperature.

Hibbard found calcium and sulfate techniques that were quite satisfactory, and a fairly acceptable magnesium technique. It is to be hoped that future work will make available a large variety of methods which will reproduce satisfactorily, and thus take full advantage of these convenient optical instruments.

Applications of turbidity measurements

It is evident from the work already cited, that turbidimetry takes its place beside colorimetry as an extremely sensitive method of volumetric chemical analysis. It is already a standard method in water analysis and has established its usefulness on toxic smokes during the war, and on the pollution of air by dust particles. Many raw commercial products are turbid, and must be filtered. Turbidity is a convenient measure of filtration efficiency. In grading the size of particles of pigment, etc., turbidity is a direct statistical measure much more readily determined than the laborious methods of the microscope and ultramicroscope. Tyndallmeters and turbidimeters are particularly adapted to the study of the kinetics of precipitation, coagulation, and peptization reactions, and transformations in sols and gels. Critical opalescence is a sensitive indicator of the critical state.

In the biochemical analysis of blood, urine, spinal fluid, etc., the method has already shown its usefulness, particularly for the proteins for which no comparable color reactions have been found. The extremely sensitive and specific enzyme and precipitin reactions will doubtless yield information by its application. In the standardization of vaccines, and the counting of bacteria and blood corpuscles, some work has already been done. But its field par excellence will undoubtedly be in chemical pathology, for living structures are so delicate that brute methods must destroy the very phenomena they are intended to portray.

In concluding the author desires to express his appreciation of two masters under whom he has worked, Mr. F. F. Renwick and Dr. W. G. Exton, whose intimate knowledge of the subject has exerted a profound influence upon his studies.

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