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Measurement of the Scattering Properties of Hydrosols*

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The scattering properties of prepared stable hydrosols have been obtained by two independent methods, by integration of volume-scattering function data, and by direct measurement of the total scattering. The correlation coefficient between the two methods has been determined to be 0.99. Data are given for the total attenuation coefficient, the total-scattering coefficient, the forward- and backward-scattering coefficients, and the volume-scattering function for two samples of water and one prepared hydrosol consisting of 40 cc of skim milk in 600 gallons of water. For the prepared hydrosols a correlation coefficient of 0.999 was found between the total scattering coefficient and the volume-scattering function at 45°. A comparison is made between the present data for distilled water and data published by Hulbert in 1945.

INTRODUCTION

DATA for the scattering properties of hydrosols have been found useful in at least three forms: *directional scattering*, which gives the flux scattered from a beam of light, as a function of the angle of observation, by a volume which varies with the angle of observation; *relative volume-scattering function*, which gives the flux scattered from a beam of light, as a function of the angle of observation, by a *constant* volume of hydrosol; and the *volume-scattering function* $\sigma(\theta)$, which gives the flux per unit solid angle scattered in each direction θ, per unit volume, per unit irradiance input. That is

$$\sigma(\theta)=dJ(\theta)/Hdv, \tag{1}$$

where $dJ(\theta)$ represents the watts per unit solid angle scattered in the direction θ, H represents the irradiance in watts/unit area at the volume, and dv represents the experimental volume.

The existence of these three forms of the data is largely a matter of instrument calibration and intended application. *Directional scattering* is useful for intralaboratory correlations, *relative volume-scattering function* exhibits the form of the function and can be integrated to yield the *relative* total scattering coefficient, *volume-scattering function* gives the real value of the optical property, and when integrated yields the real value of the total scattering coefficient, i.e.,

$$s=2\pi\int_0^\pi \sigma(\theta)\,\sin\theta d\theta. \tag{2}$$

This paper is concerned with the correlation between two methods for determining the total-scattering coefficient; first, the classical method, by integration [using Eq. (2)] from experimental values of the volume-scattering function $\sigma(\theta)$, and second, by computation from the direct measurement of the total scattering by an optical-integration technique described by Tyler.[1] A similar comparison of the total scattering of "solutes" was made by Carr and Zimm[2] using small sample volumes contained in special glass cells.

The present work is directed towards the measurement of the volume-scattering function and the total-scattering coefficient of natural hydrosols, such as ocean and lake waters.

EXPERIMENTAL

The experiment made use of prepared stable hydrosols having a wide range of scattering properties. Since the work was directed towards the ultimate goal of *in situ* measurements of the scattering properties of the sea, a scattering agent was chosen which provided irregular particles and which exhibited low absorption in the region of high transmittance for water.

With the instrumentation on hand, it was not possible to make simultaneous measurements, and so it was also important that the prepared hydrosols each be stable for the duration of the measurements. Skim milk seemed to fulfill all of these requirements quite well. Dilute solutions of skim milk are stable scattering agents for an hour or more although they are not stable overnight.

Hydrosol samples were prepared in a large tank, the procedure being to purchase 600 gallons of commercial "distilled" water and make consecutive additions of skim milk, usually in amounts increasing in geometric progression. A mixing technique was worked out which assured a homogeneous sample throughout the tank. The volume-scattering functions were measured with the scattering meter shown in Fig. 1 immersed in the sample. The basic optical design of this instrument has been described by Tyler and Richardson.[3] The source, which is unpolarized, consists of a uniformly irradiated field stop which is imaged on the sample volume so that the stop image is the same size and shape as the exit pupil of the projection lens. The beam is thus cylindrically restricted between the projection lens and the Waldram stop (see Fig. 1). The maximum angular divergence between limiting rays in the beam was

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[1] J. E. Tyler, J. Opt. Soc. Am. 47, 745 (1957).

[2] C. I. Carr, and B. H. Zimm, J. Chem. Phys. 18, 1616–1626 (1950).

[3] J. E. Tyler and W. H. Richardson, J. Opt. Soc. Am. 48, 354 (1958).

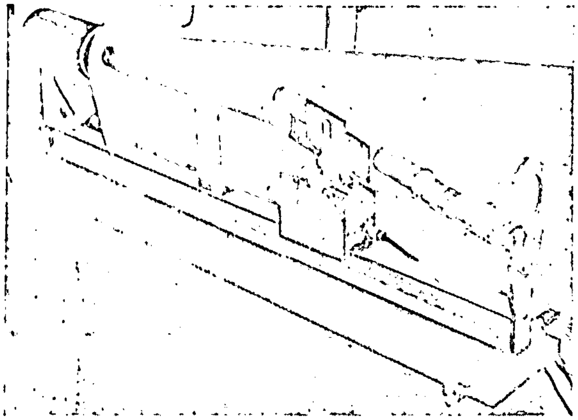

FIG. 1. Scattering meter for measuring the volume-scattering function of hydrosols. The light source is on the left, the detector is on the arm at the right. The Waldram stop in the center, with an oblong aperture, rotates with the detector arm, but on a different axis, and is designed to make the observed volume of hydrosol independent of its angle of observation. (See Fig. 3).

approximately 2°. The detector on the right is an end-on multiplier phototube (a selected Dumont No. 6291—K1242) which was insensitive to changes in the orientation of the plane of polarization of polarized light and which was mounted inside a μ-metal shield to prevent deflection of the electron beam in the dynode stages as a result of changes in orientation with respect to the earth's magnetic field. An optical system similar to that used for the light source was used to restrict the beam of detection. Its maximum angular divergence was approximately 6°.

In order to control stray light (see Fig. 1) an internally baffled tube was provided between the source housing and the Waldram stop, an internally baffled shade was provided for the multiplier phototube, a light trap was provided for the beam of detection and for the light beam (not shown in Fig. 1) and an additional baffle was mounted on the Waldram stop. All baffles had to be provided with vents so that they could be properly drained and flushed with each new sample.

The total attenuation coefficient was also measured by immersion by using the instrument shown in Fig. 2.

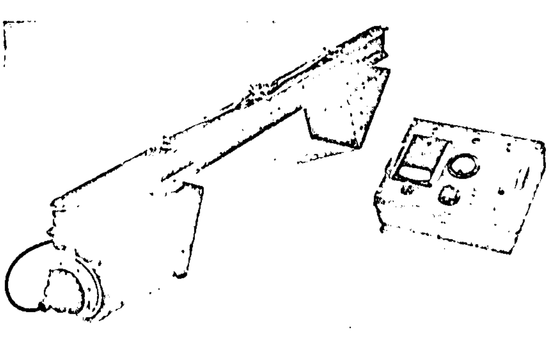

FIG. 2. The α meter for determining the total-attenuation coefficient of hydrosols. The instrument has a monitor cell in the lamp housing at the left to maintain the flux output of the lamp constant.

This instrument also employs a cylindrically restricted beam of light, as described above, and has an angular divergence of less than 1°.

Nearly simultaneously with the immersion measurements, a sample was carefully siphoned into a 5-liter glass sphere described in reference 1 and measured on a Hardy[4] spectrophotometer to obtain data for determining the total scattering coefficient by the optical integration method.

The bandwidth of the immersion measurements was restricted by means of a Wratten filter No. 61 which has a peak transmittance at 522 mμ and half-bandwidth of 56 mμ. By using an independent tungsten source and a Wratten No. 61 filter to illuminate the exit slit of the monochromator of the Hardy instrument, it was demonstrated that the data obtained were the same as data obtained with the monochromator as a source, set at 522-mμ and 10-mμ bandwidth. Spectrophotometric data were taken at this latter wavelength and bandwidth setting.

RESULTS

The results reported here are for unpolarized light. Both the scattering meter and the attenuation meter were insensitive to changes in orientation of the plane of polarization of polarized light. Measurements made on the Hardy spectrophotometer were made insensitive to polarization effects by means of a Buc-Stearns[5] plate.

The volume calibration of the scattering meter has been described in detail in an earlier publication.[3] Recent data for volume calibration which were obtained in air are shown in Fig. 3. The procedure used gives relative volume in air as a function of angle, but can be made absolute for volume in water by computing the real volume at one point ($\theta=90°$) from measurements on the intersecting beams in water.

Computation of the volume-scattering function from the ratio of directional scattering data to volume calibration data, suggested by Pritchard[6] could not be employed in the present measurements. Instead the input irradiance was determined by means of measurements of the direct beam by using the same multiplier phototube assembly that was used to obtain the scattering data. Measurements were made in air and corrected for a water environment. Measurements were also made directly in a water environment. For reasons that could not be determined these two measurements of the input irradiance to the sample volume could not be reconciled to better than 10%, and to this extent, the values reported here should be regarded as those of relative volume scattering function.

For any one series of measurements, the total-scattering coefficient reported by one method, plotted against the total-scattering coefficient obtained by the other

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[4] A. C. Hardy, J. Opt. Soc. Am. **25**, 305 (1935).

[5] G. L. Buc and E. I. Stearns, J. Opt. Soc. Am. **35**, 521 (1945).

[6] B. S. Pritchard and W. G. Elliott, J. Opt. Soc. Am. **50**, 191 (1960).

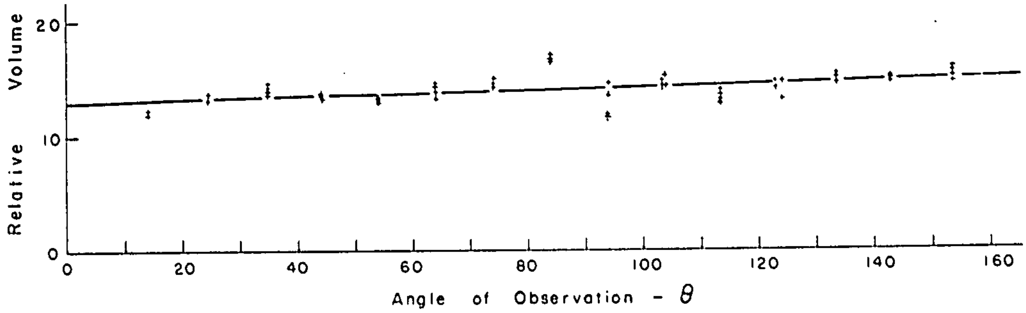

Fig. 3. Volume calibration data for the scattering meter. Data at 84° and 94° are subject to greater error because of the rapid change in reflectance of the calibration screen with θ at and near 90°.

method resulted in a straight line. Because of variation in flux from the lamp of the scattering meter from one series to the next, together with the uncertainty in the determination of the input irradiance, the slopes of the plots for the various series were not all quite the same. If these slopes are not averaged, the correlation coefficient for all runs combined is 0.99. Variability in the input irradiance can be smoothed, of course, by determining the best straight line for each series of runs independently and normalizing all runs to the average slope. When this is done the correlation coefficient is also found to be 0.99. Figure 4 is a graphical representation of the correlation between the two methods. About 100 experimental determinations of the total-scattering coefficient are plotted.

The volume-scattering function is itself of very great interest. Table I gives the volume-scattering functions and other data for two samples of water (in columns A and B) and one prepared hydrosol (in column C). Sample A, called "distilled" water in Table I was of commercial quality. Its optical purity was adequate for the work, but was by no means perfect. Sample A represents the cleanest water measured during the course of this work. Sample B was visibly contaminated in 600-gallon lots.

Skim milk was added to the "distilled" water in small volumes starting with 5 cc per 600 gallons. There is some evidence of solubility, but for additions of 20 cc to 640 cc per 600 gallons, the plot of log T vs concentration is very nearly linear. Column C of Table I gives data for a hydrosol consisting of 40 cc skim milk in 600 gallons of distilled water.

In Table I the total attenuation coefficient α has been obtained experimentally from transmittance measurements made with the α meter illustrated in Fig. 2, using the equation

$$T=e^{-\alpha r}. \tag{3}$$

The definition of α, viz.,

$$\alpha=s+a, \tag{4}$$

where s is the total-scattering coefficient and a is the absorption coefficient, requires that none of the scattered light be included in the transmittance measurement. The question therefore arises as to the effect of the forward scattered light within the beam on the accuracy of α obtained in this way. This problem has been investigated recently by Preisendorfer.[7] From his work the error in the value of α is computed to be less than 0.3%.

In the measurement of the volume-scattering function experimental values could be obtained only between 20° and 160° (due to mechanical interference). Values at 170° and 180° were interpolated and are given in the table. Values were also interpolated for 0° and 10° in order to complete the data for the computation of s. These latter values are, of course, multiplied by the

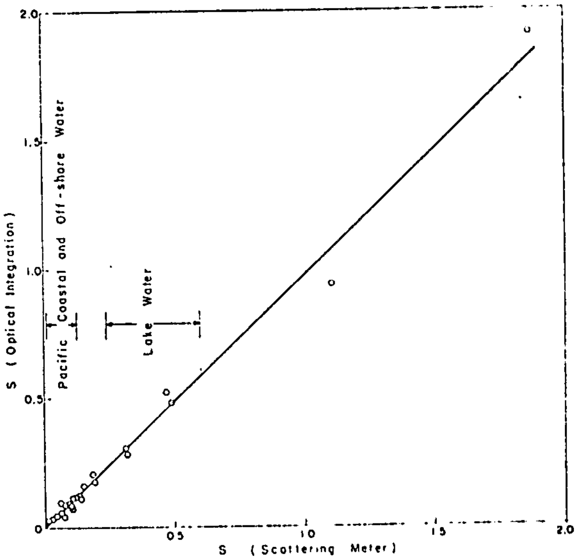

FIG. 4. Plot showing the correlation between the total-scattering coefficient s, obtained by optical integration and from the scattering-meter data. Each point represents between 2 and 6 experimental determinations of s by the two methods. The slopes of the various runs have not been averaged in this plot. The range of values recently obtained for the total-scattering coefficient of lake and ocean waters is indicated. Since the slope of the line is a function of the input irradiance, it is subject to the inaccuracy already noted in the text.

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[7] R. W. Preisendorfer, "A general theory of perturbed light fields, with applications to forward scattering effects in beam transmittance measurements," Visibility Laboratory, SIO, SIO Ref. 58-37, 23 pp., (1958).

TABLE I. Volume-scattering functions and other data for two samples of water and one prepared hydrosol.

Column	"Distilled" water A Per meter	Water sample B Per meter	Hydrosol 40 cc/600 gal C Per meter	1945 Hulburt distilled water D Per meter	1941 Dawson and Hulburt theoretical water E Per meter
Total-attenuation coeff	0.047	0.162	0.264	0.04	
Total-scattering coeff	0.00457	0.0159	0.137	0.00931	0.00194
Absorption coeff (by difference)	0.0424	0.146	0.127	0.0307	
Forward-scattering coeff	0.00396	0.0147	0.112		
Backward-scattering coeff	0.00062	0.00118	0.0255		
% Forward scattering	86.5	92.5	82.0	86.4	50.0
Volume-scattering function					
0°	Interpolated for the computation of total scattering coefficient only.				0.000222
10					0.000219
20	0.00316	0.0125	0.0623		0.000210
30	0.00107	0.00454	0.0330		0.000197
40	0.000520	0.00189	0.0205		0.000180
50	0.000294	0.000883	0.0142		0.000163
60	0.000191	0.000487	0.00982		0.000146
70	0.000128	0.000307	0.00718		0.000133
80	0.000096	0.000228	0.00543		0.000124
90	0.000083	0.000191	0.00448	0.000144	0.000121
100	0.000079	0.000177	0.00408		0.000124
110	0.000082	0.000173	0.00390		0.000133
120	0.000092	0.000179	0.00386		0.000146
130	0.000102	0.000185	0.00403		0.000163
140	0.000112	0.000193	0.00402		0.000180
150	0.000119	0.000204	0.00407		0.000197
160	0.000141	0.000217	0.00421		0.000210
170	0.000161	0.000227	0.00433		0.000219
180	0.000169	0.000230	0.00438		0.000222

sine of 0° and 10°, respectively, in the computation and can vary by a factor of 10 without affecting the total-scattering coefficient significantly. However, the interpolated values of $\sigma(\theta)$ could be very misleading and consequently are not given.

Jerlov,[8] in his paper on "Particle distribution in the ocean," has pointed out that the ratio of the total-scattering coefficient to the scattering at 45° is a constant for the ocean. This is an important observation since it permits the use of simple instrumentation for generating descriptive charts of particle distributions.

TABLE II. Ratio of the forward-scattering coefficient to total-scattering coefficient.

Sample	% Forward scattering
Water sample B	92.5
Distilled water A	86.5
A+5 cc skim milk	83.0
10	82.0
20	82.0
40	82.0
80	81.5
80 (stood 12 hr)	83.0
160	81.5
320	81.0
640	81.0

Figure 5 gives a plot of the volume-scattering function at 45° against the total-scattering coefficient for the same samples reported in Fig. 4. The correlation coefficient here is 0.999.

This does not mean, of course, that the ratio of volume-scattering function at 45° to total-scattering coefficient is independent of particle shape or size. Rather, it means that in hydrosols containing the same type of particles, the value of the volume-scattering function at some fixed angle can be used as a measure of the total-scattering coefficient.

Evidence of the effect of particle shape or size can be found in Table II which gives the ratio of the forward-scattering coefficient to total-scattering coefficient for a series of measurements. For the two samples marked A & B, in which the particle size or shape might be significantly different from those of fresh skim milk, this ratio is significantly higher. Also in the two samples marked 80, although the total scattering remained the same to within 1%, the forward-scattering coefficient increased significantly for the sample in which the particles had 12 hr to aggregate. It is of interest to compare the present data on distilled water, column A of Table I, with data published by Hulbert[9] (column D) and with a theoretical water (column E) calculated from equations given by Dawson and Hulbert.[10] The distilled

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[8] N. G. Jerlov, *Reports of the Swedish Deep-Sea Expedition* (Wettergren and Kerbers Forlag, Göteborg, Sweden, 1953), Vol. III, Physics and Chemistry, No. 3.

[9] E. O. Hulbert, J. Opt Soc. Am. **35**, 698 (1945).

[10] L. H. Dawson and E. O. Hulbert, J. Opt. Soc. Am. **31**, 554 (1941).

waters of columns A and D are very similar as far as the data go, but both are a long way from being the theoretical water of column E.

DISCUSSION

It is well known that the terminology of photometry has been abused. This paper employs terminology which is currently under consideration for adoption by the International Association of Physical Oceanography.

The term volume-scattering function, which has been defined for an arbitrary angle θ in Eq. (1), includes all scattered flux at that angle regardless of the shape or size of the scattering particle or the homogeneity or purity of the scattering medium. It should not be confused with Rayleigh ratio which under special circumstances may be numerically equal to the volume scattering function at 90°. See, for example, Carr and Zimm.[2] The term, total-scattering coefficient, defined in Eq. (2), is derived from the volume-scattering function and should not be confused with turbidity although again under special circumstances the two may be numerically equal.

Values for the volume-scattering function at 0°, 10°, 170°, and 180° were obtained by means of the Gregory-Newton divided-difference interpolation method. This interpolation has no physical significance. It is believed to yield low values of $\sigma(0)$ and $\sigma(10)$.

In the study of the effect of scattering and absorption on image-forming systems underwater it is important to know the gross scattering properties of the existing hydrosol. The methods of measurement do not, therefore, make comparison between the hydrosol and a standard, which may be the practice for other purposes, but simply measure the gross scattering from the mixture of particles that are present.

It is also important in optical studies of ocean water to make the measurements *in situ* since rapid changes take place in a sample removed from its natural environment.

At the present time no instrument exists which is capable of making direct measurements of the total scattering coefficient of the ocean *in situ*. Such an instrument would be very useful and, although the present work has not clarified all of the problems, the results presented in Fig. 4 indicate the potential usefulness of the principle of the Hardy spectrophotometer for this purpose.

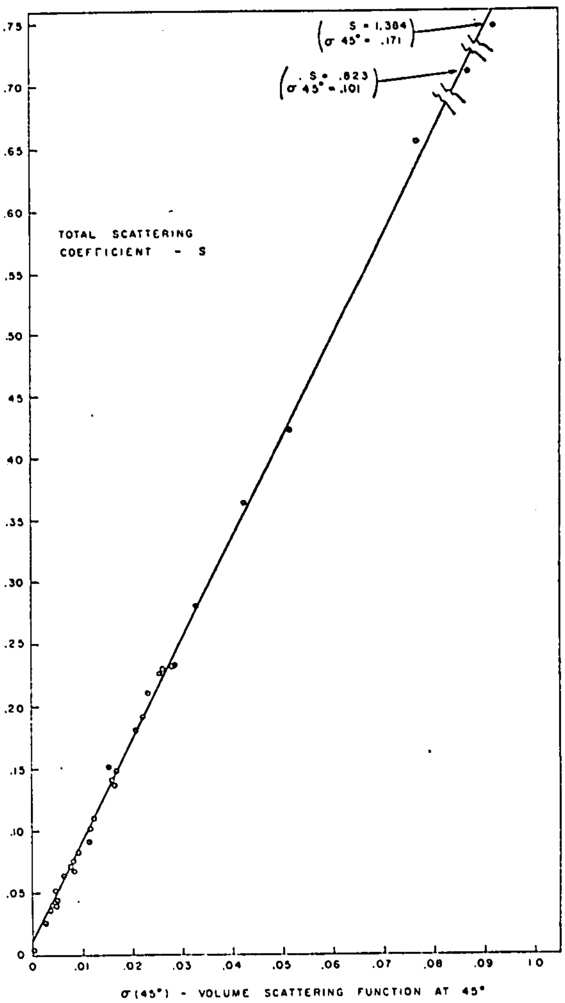

FIG. 5. Graphical representation of the correlation between the total scattering coefficient and the volume-scattering function at 45°. The line represents the "best straight line fit" to the data.