

Optical properties of turbidity standards

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Abstract

Measurements of light scattering and light attenuation were made for suspensions of formazin and diatomaceous earth. Light scattering was measured for light of wavelength 632.8 nm at angles from 0.1° to 1.0° and for light of wavelengths 400, 500, 550, 600, 650, and 700 nm at 45°. Light attenuation was measured over a 25 cm pathlength for light of 660 nm. These measurements were made for suspensions which varied from 0 to 40 Jackson Turbidity Units of formazin and 0 to 40 mg/l of diatomaceous earth. The results indicate the necessity for multiple optical measurements for determinations of turbidity of water. In addition the tables and curves presented may be used in the calibration of light scattering meters and transmissometers which are used for turbidity studies.

Introduction

Emphasis on the monitoring of environmental parameters had led to the need for a better method of quantifying the turbidity of water. Certain standards have been used in the past as indicators of turbidity. Specifically, formazin and diatomaceous earth are the most common substances used for turbidity calibrations^{1,2} These substances are used because of the availability, ease of preparation and reproducibility of calibration results. In the research described herein transmission measurements were made with light of wavelength 660 nm in various concentrations of formazin in water and diatomaceous earth in water. In addition, volume scattering functions were measured at near-forward angles and at 45° for both substances in various concentrations. The scattering measurements were made with light of wavelength 632.8 nm for the near-forward measurements and 650 nm for the 45° measurements. In addition measurements were made of the volume scattering function at 45° for wavelengths of 400, 450, 500, 600, 650, and 700 nm for both substances. Particle size analyses were made using a Coulter Counter.

The optical properties described above are inherent properties which do not change with changes in the radiance distribution³. Within a water sample light may be attenuated by absorption and/or scattering. The attenuation coefficient, c , therefore represents the ratio of the radiant flux lost from a beam of infinitesimal width to the incident flux and divided by the thickness of the layer of the medium through which the beam is passing. Also,

$$c = a + b$$

where a is the absorption coefficient and b is the scattering coefficient, each defined similarly to c but representing only absorption or scattering, respectively. The units of a , b and c are m^{-1} . The fraction of light transmitted through a pathlength r (in meters) is related to c as follows:

$$T = e^{-cr}$$

The volume scattering function, $\beta(\theta)$, is defined as the radiant intensity (watts/steradians) from a volume element (m^3) in a given direction, (q) per unit of irradiance ($watts/m^2$) and per unit volume:

$$\beta(\theta) = \frac{dI(\theta)}{E dv}$$

where $I(\theta)$ = radiant intensity scattered at angle θ relative to the main beam

$$E = \text{irradiance}$$
$$v = \text{volume}$$

in addition, Austin⁴ has shown that

$$\beta(\theta) = \frac{P_{\theta}}{P_0} \frac{1}{L\Omega}$$

where P_0 is the power of light incident on the sample volume; P_θ is the power leaving the volume at angle θ from the main beam; l is the length of the volume along the direction of propagation of unscattered light; and a is the solid angle into which the light is scattered.

The volume scattering function, $\beta(\theta)$, and the scattering coefficient, b , are related as follows:

$$b = 2\pi \int_0^\pi \beta(\theta) \sin\theta d\theta$$

Measurements of T , c , b for forward angle scattering, and $\beta(45^\circ)$ were made in the research described herein.

The measurements of transmission and scattering were made in order to quantify the optical properties of turbidity standards. The need for such a quantification was emphasized by Austin⁴ and Freeman⁵. By accurately determining the optical properties of turbidity standards intercalibration of optical equipment can be simplified and standardized. The results of this work supply an easily reproducible calibration procedure for light transmission and light scattering measurements. After calibrating a transmissometer or a light scattering meter using a formazin or diatomaceous earth suspension as was done in this research a water sample may be tested for transmission or light scattering. The results can then be compared to a concentration of formazin or diatomaceous earth that gives the same transmission or light scattering value. In this way all water samples could be compared to universal standards of transmission and scattering. No single measurement is sufficient to identify any water mass. Gibbs⁷ and Austin⁴ stress the importance of using many types of optical measurements to identify a water mass. Water masses containing different types of particles may have nearly identical transmission properties⁸. For this reason, various scattering and transmission measurements were made on the turbidity standards used in this work.

Experimental Procedure

The measurements of light transmission were made with a 25 cm pathlength beam transmissometer as described by Bartz, et al.⁶. It operates at a wavelength of 660 nm. Consequently, effects of yellow matter (or dissolved humic acids and by-products of biological activity) in the water will not be seen in the data obtained since the attenuation of 660 nm light by yellow matter is negligible³. The attenuation detected by the beam transmissometer is due only to absorption and scattering of light by particles in the water and the water itself. The use of a 1/4 m pathlength permits measurements of transmission of light in samples having very high attenuation coefficients. Concentrations of formazin were mixed using the method as described in Standard Methods for the Examination of Water and Waste-water¹. The concentrations used for the transmission and 45° scattering measurements were 0, 0.25, 0.5, 0.75, 1.0, 1.5, 2, 3, 6, 12, 24, and 40 Jackson Turbidity Units (JTU).

A concentration of 400 JTU was obtained by mixing 5 ml of a 1% (by weight) hydrazine sulfate solution with 5 ml of a 10% (by weight) solution of hexamethylenetetramine and 90 ml distilled water. Different concentrations (i.e., JTU's) were obtained by diluting the 400 JTU sample with distilled water. The diatomaceous earth was mixed to obtain identical concentrations based on the fact that Jackson Turbidity Units are equivalent to parts per million silica (diatomaceous earth)². Replicate measurements of attenuation and scattering were made for each concentration of each substance. To test the reproducibility of the results two separate batches of both the formazin and diatomaceous earth suspensions were used for the experiment.

Measurements of light scattering were taken at the same time as the transmission determinations. Light scattered at 45° was measured using a Brice-Phoenix light scattering photometer⁹. Measurements were made for light of wavelength 650 nm for each concentration of formazin and diatomaceous earth. In addition, light scattering measurements were made at 400, 450, 500, 550, 600, 650, and 700 nm for an arbitrary concentration of each of the two substances. This was done to determine the qualitative variation of the volume scattering function with wavelength for the formazin and diatomaceous earth.

Using the narrow angle scattering meter and method as described by Spinrad et al.¹⁰ measurements of the volume scattering function at angles between 0.1° and 1.0° were made for a number of concentrations of the formazin and diatomaceous earth suspensions. Specifically, near-forward angle volume scattering functions were determined for formazin concentrations of 0.5, 1, 2, 3, 6 and 12 JTU and for diatomaceous earth concentrations corresponding to 0.5, 1, 2, 3 and 12 JTU. These concentrations were used since they provided the best signal-to-noise ratio in the output of the narrow angle scattering meter. Lower concentrations produce very little scattered light and higher concentrations reduce the main beam reference light to an extremely low value. Measurements of the near-forward volume scattering function are important for correcting errors in transmission determinations which are caused by forward scattered light.

Results and Discussion

The results of the transmission experiment are shown in Table I and Figure 1 for both the formazin and the diatomaceous earth. The transmission, T, as measured, is converted into a beam attenuation coefficient, c, as follows:

$$T = e^{-cr}$$

Where r = optical pathlength (0.25 m in this case)
 c = attenuation coefficient (in units of m^{-1})
 therefore $c = -4 \ln T$.

Table 1.
 $C - C_{\text{water}} (m^{-1})$ $\beta(45^\circ) - \beta(45^\circ)_{\text{water}}$
 $(m^{-1} \text{ ster}^{-1})$

Jackson Turbidity Units	Mean	Corrected for Forward Scatter	Standard Deviation	Mean	Standard Deviation
Diatomaceous Earth					
0	0		0	0	0
.25	.1040		.0194	.00519	.00052
.5	.1967	.3258	.0199	.00724	.00180
.75	.2820		.0068	.01411	.00209
1	.3692	.9263	.0208	.01949	.00030
1.5	.5598		.0363	.03020	.00316
2	.7062	1.564	.0026	.03910	.01112
3	1.063	3.064	.0248	.06480	.00967
6	2.131		.0219	.11097	.01624
12	4.289	8.848	.0976	.24367	.05036
24	8.355		.1527	.42947	.00326
40	13.32		.3889	1.0855	.12780
Formazin					
0	0		0	0	0
.25	.1121		.0048	.00972	.00051
.5	.2203	.2626	.0007	.01811	.00111
.75	.3289		.0053	.02323	.00123
1	.4340	.5070	.0092	.03660	.00077
1.5	.6485		.0099	.05464	.00092
2	.8681	1.019	.0158	.07208	.00204
3	1.2973	1.745	.0230	.10688	.00459
6	2.5950	3.398	.0386	.20920	.01116
12	5.2340	6.154	.0915	.48616	.01389
24	10.2533		.1172	1.07629	.02899
40	16.4300		.1735	2.04907	.07750

The term c_w represents the beam attenuation coefficient of clean water (0 JTU or 0 mg/l of silica). Since we are interested only in the optical properties of the formazin and the diatomaceous earth c_w is subtracted from the value of c as obtained from the transmission data.

The beam transmissometer has an acceptance half-angle of 1.35° in water. This means that any light that is scattered within 1.35° of the main beam will be detected by the instrument and will be deemed to be unattenuated light. To correct for this narrow angle scattering results are used as follows:

The total scattered light within an angle, α , from the main beam is given by

$$b_f = 2\pi \int_0^\alpha \beta(\theta) \sin\theta d\theta$$

where $\beta(\theta)$ is the volume scattering function and is approximately constant in the near-forward region¹⁰.

Therefore,

$$b_f = 2\pi \beta(\theta) \int_0^\alpha \sin\theta \sin\theta \, d\theta$$

$$= 2\pi \beta(\theta) (1 - \cos\alpha).$$

The transmission, as measured will include this scattered light.

So,

$$T_{\text{measured}} = e^{-(c+b_f)}$$

and

$$T_{\text{theoretical}} = e^{-c}$$

Therefore,

$$T_{\text{theoretical}} = T_{\text{measured}} e^{b_f}$$

or

$$\exp(-c_t r) = \exp(-c_m r) \exp(-2\pi \beta(\theta) (1 - \cos\alpha))$$

where c_t and c_m are the theoretical and measured attenuation coefficients, respectively.

For $r = 0.25$ m, this yields,

$$c_t = c_m + 8\pi \beta(\theta) (1 - \cos\alpha)$$

In Table 1 c_m is listed as $(c - c_w)$ and c_t is listed as $(c - c_w)$ corrected for forward scatter. The results as shown in Figure 1 demonstrate the obvious differences in transmission vs. concentration between formazin and diatomaceous earth. Corrected beam attenuation coefficient values are consistently higher for the diatomaceous earth. That is, a concentration (in terms of JTU's) of diatomaceous earth will transmit less light than the same concentration of formazin since the amount of forward scattered light is different for each. The slope of the formazin curve changes less than the slope of the curve for diatomaceous earth when corrections for forward scattering are made. This is due to the fact that the diatomaceous earth suspension has a larger mean particle size than the formazin. Large particles scatter much more light at near-forward angles than do smaller particles. This is shown by the mean values of the near-forward angle volume scattering functions in Table 2. Mean particle diameters are 1.55 μm for the formazin and 8.75 μm for the diatomaceous earth. The scattering at near-forward angles is consistently higher for the diatomaceous earth samples.

Table 2.
JTU or mg/l silica **Mean Near-forward Volume Scattering Function ($\text{m}^{-1} \text{ster}^{-1}$)**

	Diatomaceous Earth	Formazin
0.5	18.51	6.067
1.0	79.86	10.47
2.0	122.9	21.61
3.0	286.9	64.11
6.0	--	115.1
12.0	633.5	231.9

Figure 2 shows the variation of scattering at 45° (650 nm) with concentration of each suspension. The scattering values of pure water (0 JTU or 0 mg/l silica) have been subtracted to yield only the particulate scattering. Scattering values of the formazin are always higher than those of diatomaceous earth at 45°. Whereas the size distribution determined the different curves of near-forward scattering the relative indices of refraction (to water) could be more important in determining the different slopes of the volume scattering functions at 45°. From Figure 2 it would seem that the index of refraction of the formazin is higher than that of the diatomaceous earth. Generally, a size distribution of a single material will scatter more at 45° the higher its index of refraction is^{11, 12}. For near-forward angle scattering particle size

is generally more important than index of refraction in determining the volume scattering function. Using a method as described by Woodward¹³ it is found that multiple light scattering would not be experimentally detectable (at least 10% higher than single scattering values) until the concentration is approximately 40 JTU or 40 mg/l⁴. This is apparent in Figure 2 as the linearity of the curves disappears at some concentration between 24 JTU and 40 JTU.

The qualitative variation of light scattered at 45° with wavelength for formazin and diatomaceous earth is shown in Table 3 and Figures 3 and 4. Arbitrary concentrations (of approximately 1.0 to 3.0 JTU) of each suspension were used to determine the wavelength dependence of scattering for each substance. The results indicate a λ^{-1} dependence of scattering for both the formazin and the diatomaceous earth. This clearly shows that neither of the two samples is colloidal since a colloid would be a Rayleigh scatterer with λ^{-4} scattering dependence. Both formazin and diatomaceous earth are suspensions in which the scattering by particles larger than the wavelength predominates. Morel¹⁵ has shown the λ^{-1} dependence for scattering by particle suspensions.

Table 3.

Spectral Scattering of Formazin	
λ nm	β (45) m⁻¹ ster⁻¹
400	.006370
450	0.04365
500	0.03297
550	0.02858
600	0.02447
650	0.02203
700	0.01637
Spectral Scattering of Diatomaceous Earth	
λ nm	β (45) m⁻¹ ster⁻¹
400	0.20602
450	0.16038
500	0.12755
550	0.11160
600	0.09658
650	0.07542
700	0.05649

Conclusions

The use of JTU's as indicators of turbidity has been questioned^{2, 4, 5, 14}. Callaway, et al.⁸ have demonstrated that water samples having identical particle concentrations may display very different light attenuation coefficients. This has been demonstrated here for two commonly used turbidity references. Obviously, the use of the Jackson Turbidity Unit is inadequate to define the optical properties of a particular water mass. The JTU can, however, be accurately used as an indicator of a particle concentration.

The tables and curves presented in this paper supply information that allows the calibration of beam transmissometers (at 660 nm) and light scattering photometers (at 650 nm) using common, well-tested turbidity standards. The characteristics of the particular instruments (such as acceptance angles) must be known to make use of the information contained herein.

It is important to emphasize that the results obtained here show very clearly that no single optical measurement is sufficient to define a water mass. Measurements of transmission alone or scattering alone do not define turbidity. The single concept of turbidity is best replaced by a matrix of parameters including transmission and scattering (both near-forward and at large angles).

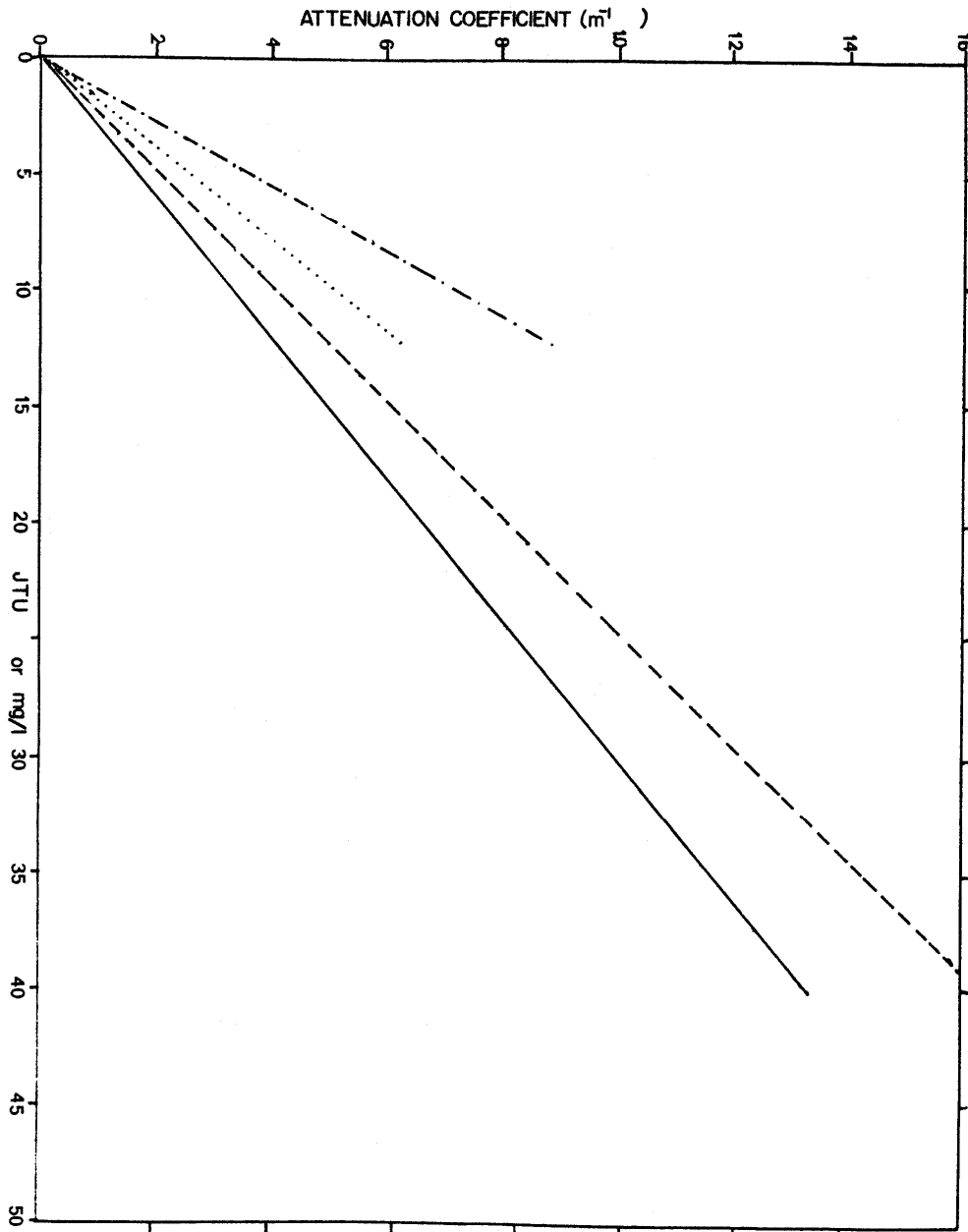
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Figure 1. Beam attenuation coefficient, c , versus particle concentration (in JTU for the formazin and mg/l for the diatomaceous earth). Plots are for formazin corrected for forward scattered light (· · · ·), diatomaceous earth corrected for forward scattered light (- - -), formazin uncorrected (----) and diatomaceous earth uncorrected (—).

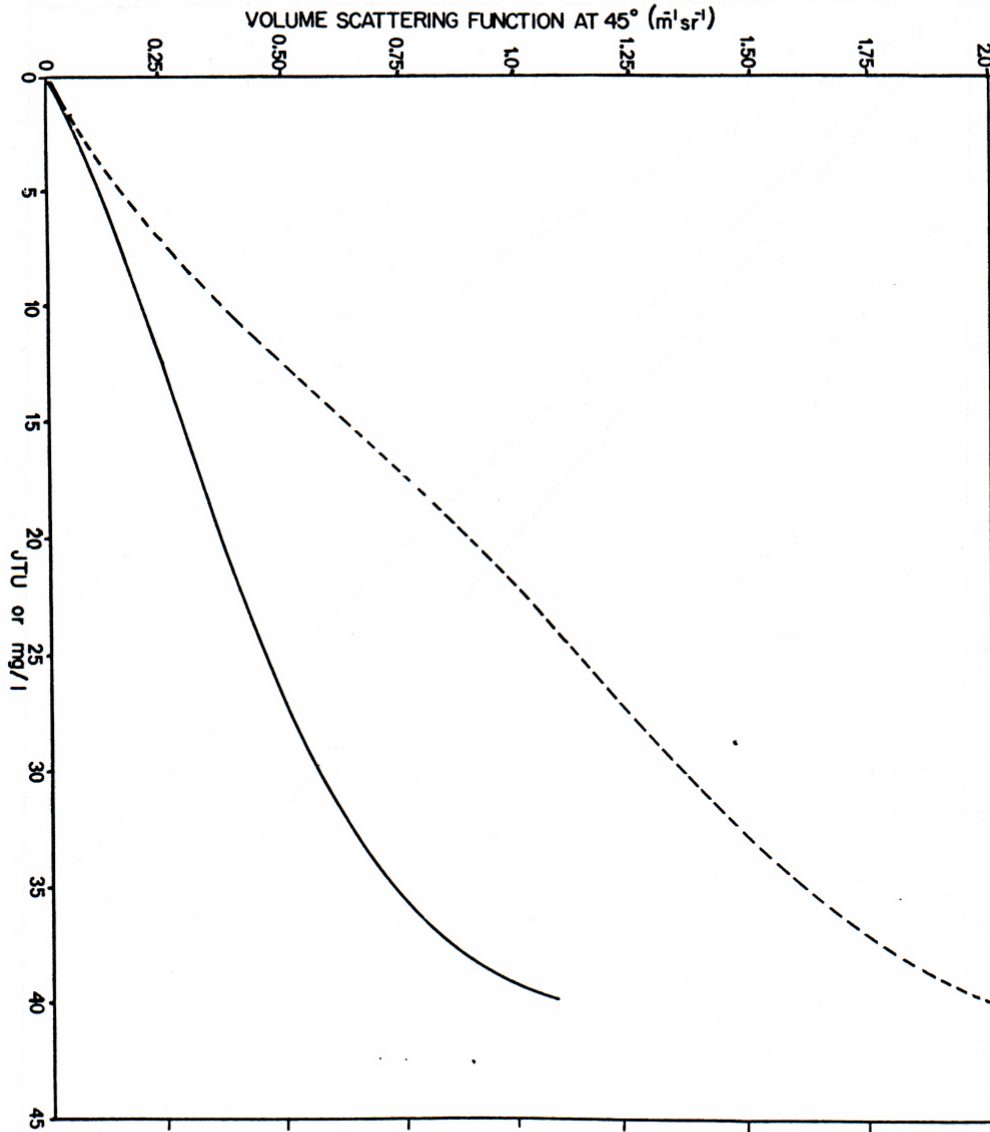
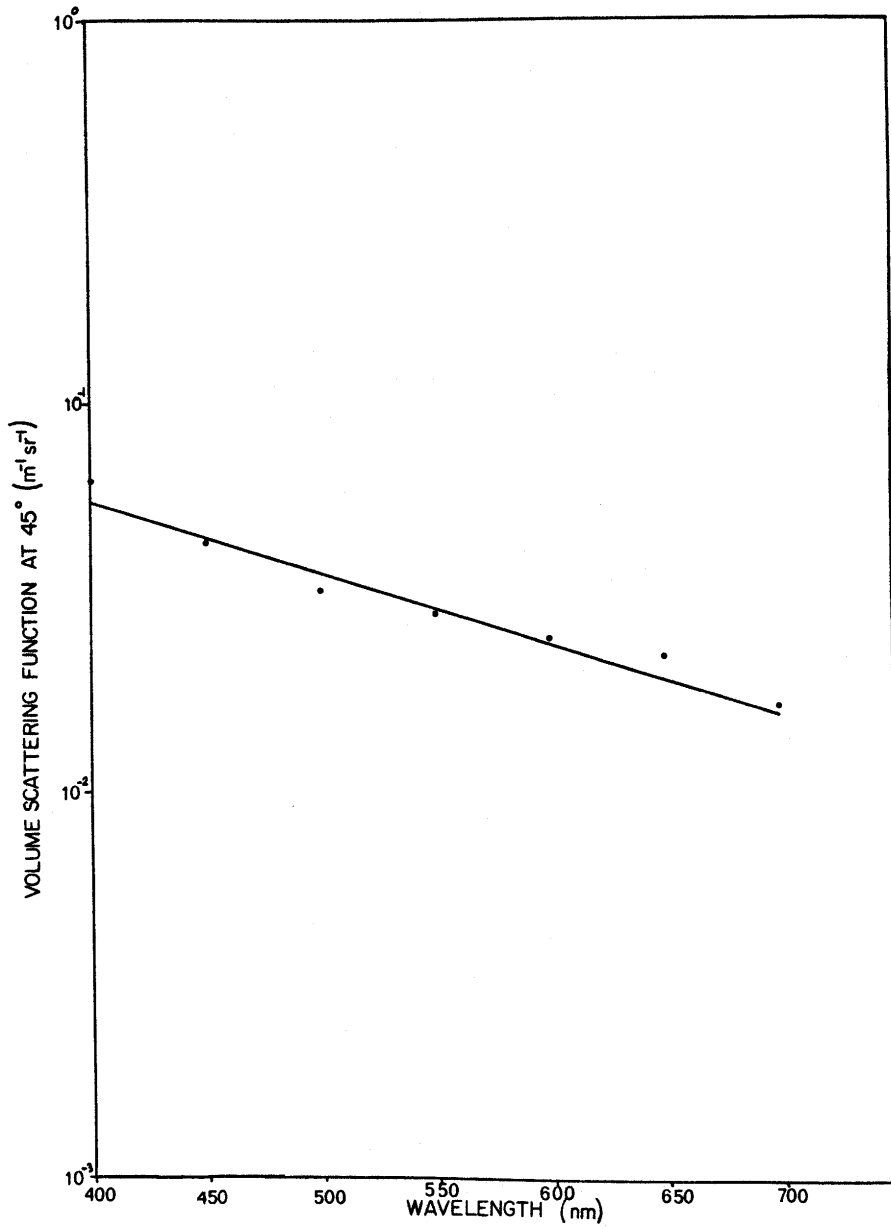
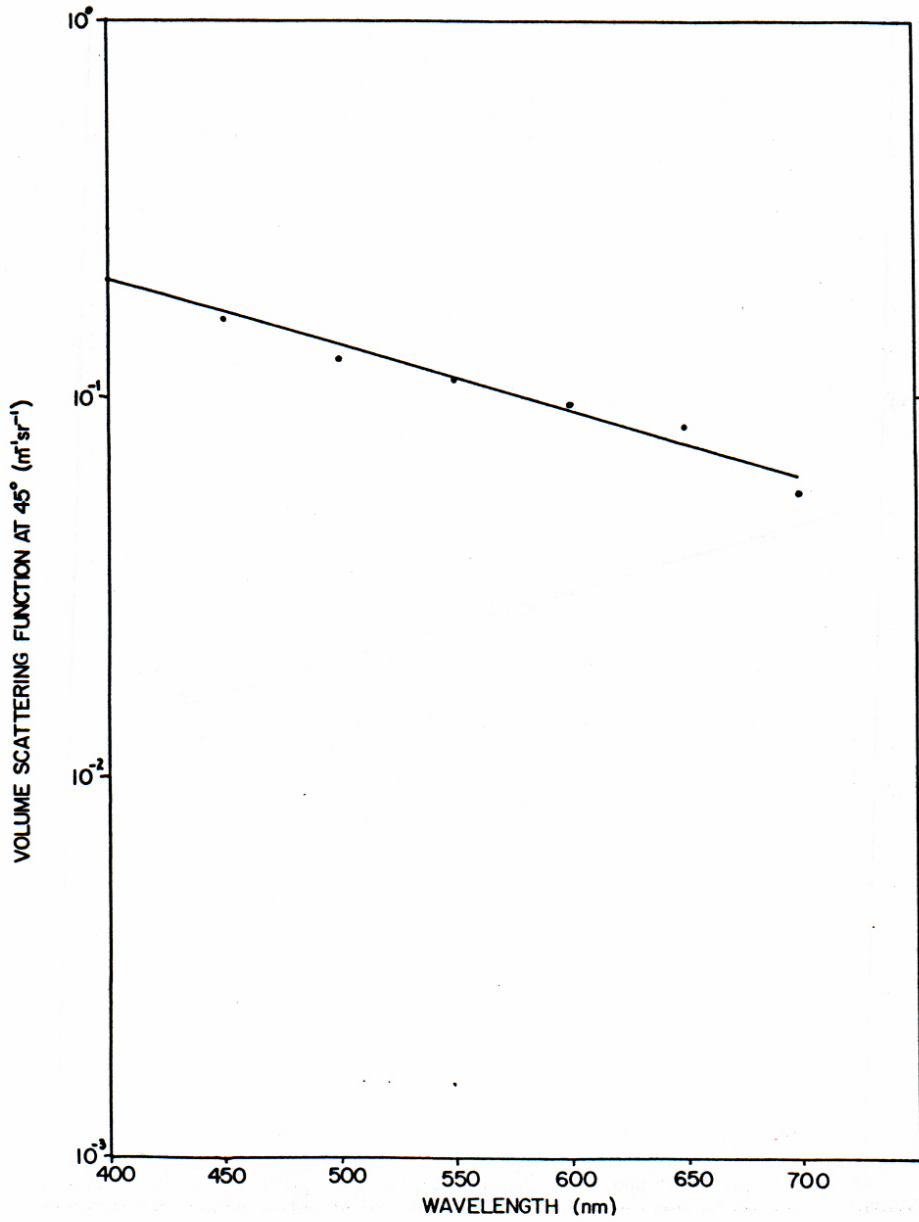


Figure 2. Volume scattering function at 45°, $\beta(45)$, versus particle concentration (in JTU for the formazin and mg/l for the diatomaceous earth) for formazin (----) and diatomaceous earth (—).



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Figure 3. Volume scattering function at 45° $\beta(45)$, versus wavelength, λ , of incident light for formazin sample. Line corresponds to $\beta(45) = 38 \lambda^{-1} - 0.0401$.



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Figure 4. Volume scattering function at 45°, $\beta(45)$, versus wavelength, λ , of incident light for diatomaceous earth sample. Line corresponds to $\beta(45) = 132.86 \lambda^{-1} - 0.1272$.