

# The Scattering Error Correction of Reflecting-Tube Absorption Meters

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## ABSTRACT

In this paper we examine correction methods for the scattering error of reflecting tube absorption meters and spectrophotometers. We model the scattering error of reflecting tube absorption meters for different tube parameters and different inherent optical properties. We show that the only reasonable correction method for an absorption meter without attenuation measurements or a spectrophotometer is the method in which the measured absorption at a wavelength in the near infrared is subtracted. A better correction is obtained if attenuation is measured simultaneously and the absorption at the reference wavelength is multiplied by the ratio of the measured scattering at the measurement wavelength divided by the measured scattering coefficient at the reference wavelength. This is the proportional method. We showed that the important geometrical parameters of the reflecting tube can be obtained by a comparison of measurements and models of polystyrene beads. Finally we examine the improvements that could be obtained if a direct scattering measurement were made simultaneously with the absorption and attenuation measurements.

## 1. INTRODUCTION

The question of optical closure cannot be addressed scientifically until the instrumental problems are understood and accounted for. Even if the instruments that measure the inherent optical properties are perfectly calibrated to some standard, there remain design limitations that will cause variable errors depending on the volume scattering function of the particulate constituents of the water. These errors need to be accounted for and their uncertainty established to get correct readings and error estimates. On the whole, these errors are relatively small and traditionally have been ignored in absorption meters and spectrophotometers.

The reader should not conclude that the *in situ* devices are less accurate than spectrophotometers, simply because we analyze the errors. In fact the reverse is true. Some models of spectrophotometer developed for analytic chemistry are designed for measuring the absorption of solutions only. These models make minimal attempts at collecting the scattered light and are poor choices for measuring the absorption of suspended particulates. Even the best models do not collect all the scattered light and the method of analysis used below would apply to them also.

We will explore the interaction of changes in the volume scattering function ( $\beta(\theta)$ ) with design criteria and calibration methods for an *in situ* absorption meter and a good spectrophotometer setup. First we will consider the reflective-tube absorption (a) meter<sup>1,2</sup> which is designed to collect all of the transmitted light plus most of the scattered light. Errors are introduced since the absorption meter misses scattered light within a certain angular range, losses at the reflective surfaces and increased pathlength of the scattered light. Spectrophotometer errors using a cylindrical glass cuvette are quite similar to reflecting tube errors as nearly the same geometry is used, so that this analysis is also applicable for the measurement that is considered standard. The 1 cm square glass cuvette is limited by critical reflection off the front face at around 50° but increasing reflection losses as this critical angle is reached limits the marginal advantage over the longer tubes. The magnitude of this error depends strongly on the magnitude and angular shape of the volume scattering function. This necessitates obtaining an estimate of the scattering error if the absorption coefficient is to be determined correctly.

## 2. SCATTERING ERROR

Four approaches can be used to estimate the scattering error: 1) the error can be assumed to be a certain percentage of the total scattering coefficient ( $b$ ) and thus can be calculated if the beam attenuation coefficient ( $c$ ) is measured simultaneously with the absorption coefficient (average correction); 2) scattering can be measured over some angular range and a relationship assumed between the measured scattering and the scattering error (scattering meter correction); 3) assuming that at some wavelength there is no particulate absorption and very little absorption by dissolved substances, the absorption measurement at that wavelength will be the absorption of pure water plus the scattering error (constant IR correction); and 4) a combination of any of the above approaches. A combination of 1) and 3) is the proportional method in which the proportion of  $b$  that is the scattering error is constant, but  $b$  itself is known to first order and its wavelength dependence is taken into account.

Attenuation meters also have a scattering error which is caused by the finite reception angle of the receiver and in cylindrically limited instruments by the collimation of the light source. This results in scattered light being accepted by the receiver up to a well defined angle<sup>3</sup> (for well-collimated attenuation meters). However, we have come to question whether the total scattering coefficient is ever really finite in nature<sup>4</sup>. Mie scattering calculations show that, even for relatively steeply sloped size distributions, the large particles continue to add significantly to near forward scattering. In addition, inhomogeneities in the density and temperature of the water itself add to the near forward scattering<sup>5</sup>. For the purpose of this paper, however, we will assume that there is some true  $b$  (either actual or by definition of some standard acceptance angle) and that the scattering error of both the absorption and attenuation meters can be defined as a fraction of this true  $b$ .

A correction algorithm using simultaneous measurements from  $c$  and  $a$  meters ( $c_m$  and  $a_m$ ) results from simultaneously solving the following equations for nonwater absorption and scattering  $a_n$  and  $b_n$ :

$$c_m = c_w + a_n + (1 - e_c)b_n, \quad a_m = a_w + a_n + e_a b_n, \quad (1)$$

where  $c_w$  and  $a_w$  are known<sup>6</sup> and  $e_c$  and  $e_a$  are the estimated scattering errors of the  $c$  and  $a$  meters. This results in the following solutions which are starred to denote that an estimated scattering error is used:

$$a_n^* = (a_m - a_w) + \left( \frac{e_a}{1 - e_c - e_a} \right) (a_m - a_w) - \left( \frac{e_a}{1 - e_c - e_a} \right) (c_m - c_w) \quad (2)$$

$$b_n^* = \frac{(c_m - c_w) - (a_m - a_w)}{1 - e_c - e_w} \quad (3)$$

$$c_n^* = (c_m - c_w) + \left( \frac{e_c}{1 - e_c - e_a} \right) (c_m - c_w) - \left( \frac{e_c}{1 - e_c - e_a} \right) (a_m - a_w) \quad (4)$$

The problem to be resolved, is how to arrive at these estimates of  $e_c(\lambda)$  and  $e_a(\lambda)$  or  $e_a(\lambda) b(\lambda)$ , and what are the magnitude of errors involved in the various methods of making these estimates. The problem is that the percentage errors of both instruments can (depending on instrument design) vary widely from location to location as the nature of the particles changes. They also vary spectrally.

## 3. MODELING THE REFLECTIVE TUBE ABSORPTION METER

Assuming single scattering, we can estimate the efficiency,  $D(\theta)$ , with which scattering at each angle is collected by numerically integrating along the path of the tube (Figure 1).

$$D(\theta, a) = \frac{\sum_n R^{m_n} e^{-a \left( x_n + \frac{L - x_n}{\cos(\theta)} \right)}}{e^{-La}} \quad (5)$$

where  $a$  is the absorption coefficient,  $L$  is the optical pathlength of the tube,  $R$  is the reflectivity of the tube,  $x_n$  is the distance from the entrance window of the tube to the  $n$ th point, and  $m_n$  is the number of times light scattered at that point and angle would reflect off the wall of the tube. We must then multiply this factor by any chosen volume scattering function  $\beta(\theta)$ , normalize by

the total scattering coefficient and integrate over  $\theta$  to obtain the scattering error,  $e_s(\theta_a)$ , relative to the total scattering coefficient as a function of acceptance angle,  $\theta_a$ , of the detector.

$$e_s(\theta_a, a) = 1 - \frac{2\pi}{b} \int_0^{\theta_a} \beta(\theta) D(\theta, a) \sin(\theta) d\theta \quad (6)$$

This equation was numerically integrated. It applies to the reflective tube absorption meter and to spectrophotometers using the 10 cm cylindrical sample cell and a large area diffuser in front of the detector.

The best spectrophotometers for measuring particulate absorption use an integrating cavity which collects all light passing out of the exit face of the sample cell. If the 10 cm cell is used this is still the same as the previous example. If a 1 cm cell is used then the light collected is limited only by the Fresnel reflection of light off the exit face of the sample cell. Thus scattered light is collected up to about  $51^\circ$ . However, 1 cm is generally too short a pathlength to get a significant signal from natural samples. So this method is usually used only with laboratory cultures or by artificially concentrating the sample. To examine the errors of this method, the Fresnel reflection equations were applied to the water/glass and glass/air interfaces to yield the transmittance of the exit window as a function of scattering angle. This function was then convolved with the volume scattering function and integrated as in the previous analysis.

Many spectrophotometers designed only for absorption of dissolved substances use a cylindrically limited light beam and then focus the transmitted light on the detector or diode array with no effort directed specifically at collecting scattered light. The angular efficiency of these systems depend on the geometry of the light stops, lenses and detectors, but can be no better than the reflecting tube design. In general, they are much worse, perhaps collecting scattered light out to only  $10^\circ$ . Thus they have a large scattering error and, with no method of measuring the scattering itself, are useless for measuring particulate absorption.

A prototype of the modern reflective-tube absorption meter had an acceptance angle of  $30^\circ$  and a tube reflectivity of  $95\%^2$ . Recent improvements<sup>7</sup> have increased the acceptance angle to  $41^\circ$ . Theoretically, 100% reflectivity can be accomplished by using a reflecting tube consisting of glass with an air pocket behind it as in the new absorption meters<sup>7</sup> or with the 10 cm sample cell in a spectrophotometer with a large diffusive collector. Fresnel reflection then gives 100% reflection to about  $41^\circ$ . All designs considered here are for 25 cm pathlength instruments. A 10 cm instrument would yield slightly lower scattering errors, but with a loss of sensitivity. A combination of these geometry considerations and a volume scattering function model allow us to calculate errors via equation (2).

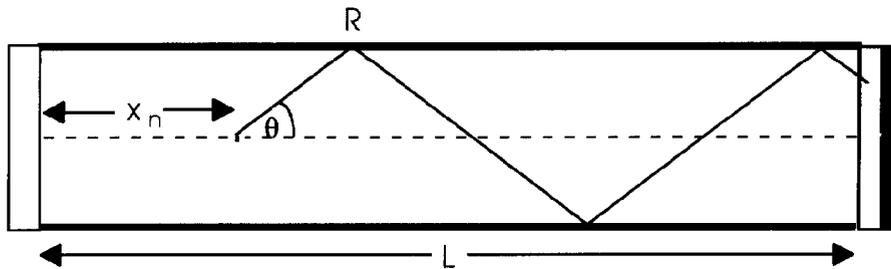


Figure 1. Principle of the reflective-tube absorption meter

#### 4. VARIATIONS IN VOLUME SCATTERING FUNCTIONS

Six models of inherent optical properties based on power law size distributions ( $dN = N_0 D^{-s} dD$ ) have been examined. The parameter  $s$  is the exponent (or slope) of the size distribution. The first three models come from size distributions observed during the ODEX cruise<sup>8</sup> in the Pacific Central Gyre. The "Chl Max" was observed<sup>9</sup> at the chlorophyll maximum near 100 m depth and the exponents of its size distribution were 3.63 from 2 to 6.6  $\mu\text{m}$  diameter and 4.96 from 6.6 to 16  $\mu\text{m}$  diameter. Slopes for the "Mixed Layer" (0-50 m) were similarly 2.97 and 5.41 and for the "Deep" water (125 m) were 3.92 and 4.96. The Mie scattering was computed for three layered spheres<sup>10</sup> with an outer layer with thickness 10% of the radius and an index of refraction equal to 1.09 with no absorption. The core radius was 80% of the radius of the inside of the shell. The core had an

index of refraction of 1.02. The layer between the core and the shell had an index of refraction of approximately 1.09 (adjusted to reflect the anomalous dispersion effect) and had an imaginary component as well to model an absorbing chloroplast layer. The real part of the index of refraction for the chloroplast layer used here is different from that used by Kitchen and Zaneveld<sup>10</sup> because the higher index appears to be more reasonable<sup>11,12</sup>. The Mie scattering was computed on the above size distributions extrapolated from 0.5 to 30  $\mu\text{m}$  diameter.

The particles in the bottom nepheloid layer (BNL) are assumed to be detrital particles. Therefore, we modeled the BNL using a homogeneous sphere with an index of refraction of  $1.09 - 0.005i$  and a particle size distribution exponent (as defined above) of 5. In order to bracket the possible volume scattering function shapes we calculated the errors for two extreme cases. We also used uniform slopes of 3.0 and 5.0 with our 3-layered sphere Mie model. The former might represent a diatom bloom in coastal upwelling areas, while the other might represent a population dominated by bacteria and small phytoplankton.

## 5. RESULTS

### 5.1 Calculation of $e_a$ and $e_c$ for various reflecting tube characteristics and scattering functions.

The scattering errors for a collimated beam c meter as a percentage of the total scattering coefficient are computed (Table I) by integrating the volume scattering function for particles out to the acceptance angle (modeled at  $0.4^\circ$  or  $0.9^\circ$ ) of the detector divided by the total scattering. Table II displays the results of our calculations as described in the first paragraph for various absorption meter designs with varying reflectivities of the reflecting tube and assuming no detection of scattered light beyond the angle given. Again the percentages given are percentages of the total scattering coefficient that are erroneously included in the absorption measurement for the design with the reflection coefficient and maximum acceptance angle as given. Calculations for a total absorption coefficient of  $0.400 \text{ m}^{-1}$  were carried out for all designs. The absolute value of the absorption coefficient only contributes to the error via the correction for increased pathlength of the scattered photons which appears to be minimal for  $a = 0.400 \text{ m}^{-1}$  and is seen (Figure 2) to be only a weak influence on the error, since the error only increases slowly with increasing absorption coefficient.

Table I Scattering errors for attenuation meters for the six models of particle size distribution

	c Meter Errors ( $e_c$ )	
	$\theta_c = 0.4^\circ$	$\theta_c = 0.9^\circ$
"BNL"	0.24%	1.12%
"Chl Max"	1.18%	5.28%
"Mixed Layer"	1.36%	6.24%
"Deep"	1.02%	4.90%
SL=3	4.80%	16.90%
SL=5	0.42%	1.97%
Median	1.10%	5.09%

### 5.2 Dependence of $e_a$ and $e_c$ on $b/a$ using an average correction.

Values of  $a_m$  were computed for the various designs and water types assuming  $c_w = a_w = 0.364$  and  $a_n = 0.036$ .  $b_n$  was assigned values of 1,2,4,8 and 16 times  $a_n$ . Then  $a_n^*$  was computed using equation (2) assuming the median scattering corrections for each design as displayed in tables I and II yielding the following algorithms:

$$a_n^* = 1.1379(a_m - 0.364) - 0.1379(c_m - 0.364) \quad \text{for } R = 95\%, \theta_{\max} = 30^\circ, \theta_c = 0.9^\circ \quad (7)$$

$$a_n^* = 1.1063(a_m - 0.364) - 0.1063(c_m - 0.364) \quad \text{for } R = 95\%, \theta_{\max} = 41^\circ, \theta_c = 0.4^\circ \quad (8)$$

$$a_n^* = 1.0416(a_m - 0.364) - 0.0416(c_m - 0.364) \quad \text{for } R = 100\%, \theta_{\max} = 41^\circ, \theta_c = 0.4^\circ \quad (9)$$

Table II. Scattering errors for absorption meters for the six models of particle size distribution.

	a Meter Errors ( $e_a$ )				
	$a_n + a_n = 0.400$				
	R=95%, $\theta_{max} = 30^\circ$	R=95%, $\theta_{max} = 41^\circ$	R=100%, $\theta_{max} = 30^\circ$	R=100%, $\theta_{max} = 41^\circ$	Best Spectro-
"BNL"	18.0%	14.0%	9.9%	4.1%	3.2%
"Chl Max"	10.8%	8.9%	6.6%	3.8%	3.0%
"Mixed Layer"	8.9%	7.3%	5.3%	3.0%	2.3%
"Deep"	12.2%	10.1%	7.6%	4.4%	3.4%
SL=3	8.9%	7.3%	5.9%	3.6%	2.9%
SL=5	18.6%	15.2%	12.0%	7.0%	5.6%
Median	11.50%	9.50%	7.10%	3.95%	3.10%
<b>from Petzold</b>					
Gyre deep	16.6%	13.5%	13.5%	8.4%	6.1%
Coastal mixed	12.2%	10.0%	9.3%	5.7%	4.2%
Harbor	17.0%	14.2%	13.8%	9.2%	6.9%
Average	15.3%	12.6%	12.2%	7.8%	5.7%

The resulting relative percent errors in absorption coefficients (Figure 3) as a function of  $b_p/a_p$  show the relative importance of angular acceptance and tube reflectivity on the accuracy of the absorption computed in this manner. The error for uncorrected absorption measurements from the spectrophotometer with integrating cavity and the 1 cm cell (Figure 3d) is similar to that for the poorer designs of reflecting tube. We show the uncorrected error for the spectrophotometer since attenuation measurements are not usually available for spectrophotometric measurements. Also shown are similar calculations using volume scattering functions from Petzold<sup>13</sup>. Values from the first degree were not included in b since there are known diffraction errors in Petzold's instrument. The errors using these measured volume scattering functions are higher than our modeled values indicating that we may not have included small enough particles in our model or that we don't have the distribution of particle structures close enough. However, the relative behavior of the errors with water type and the size of the variation are quite similar between our models and Petzold's data.

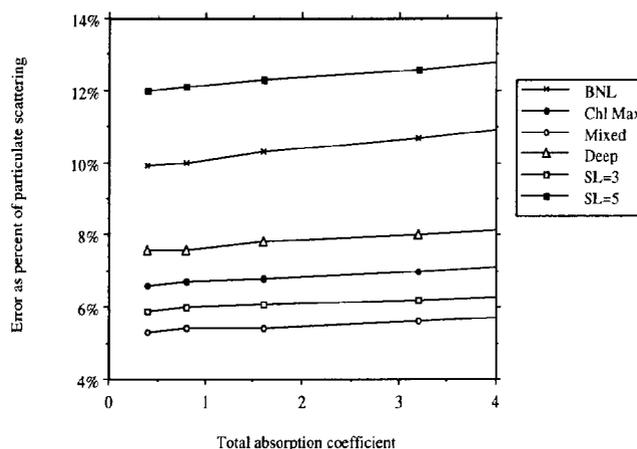


Figure 2. Effect of the total absorption coefficient on the scattering error.

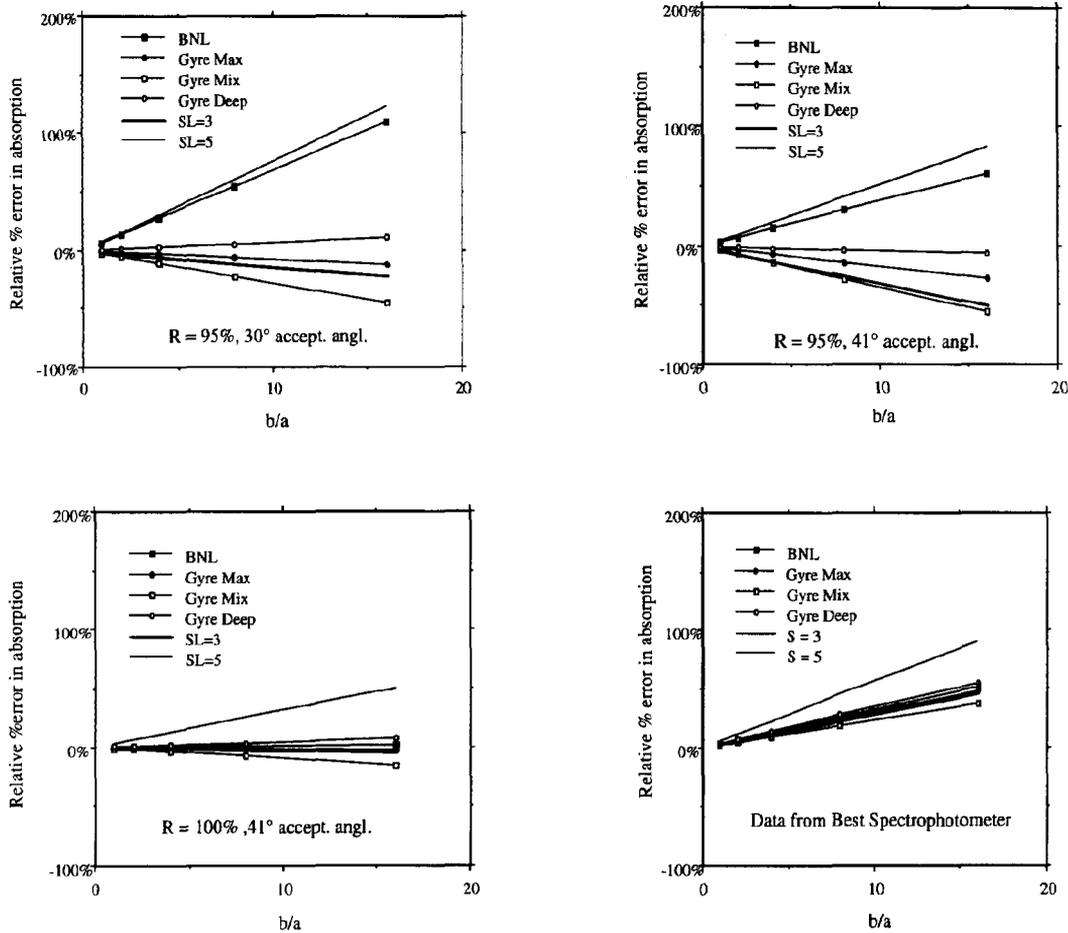


Figure 3. Errors in the corrected absorption after correcting for the scattering error using the median correction (see Tables I and II) except for (d) which is not corrected since attenuation data is not normally available for spectrophotometers.

### 5.3 A correction scheme using measured absorption in the near-infrared.

For what follows we assume that pure water absorption and attenuation have been subtracted. For a given wavelength,  $\lambda$ , the absorption tube overestimates the absorption coefficient as it does not measure all of the scattered light. Designate the proportion of the total scattering coefficient that the device does not receive by  $e_a(\lambda)$ . If the shape of the scattering function does not change much, we may assume that  $e_a(\lambda)$  is not a function of  $\lambda$ .

We assume that the fraction of the scattered light not received by the absorption meter is independent of wavelength. We designate the *true* absorption coefficient at a wavelength by  $a_t(\lambda)$ , and the *measured* absorption coefficient by  $a_m(\lambda)$ . Similarly  $c_t(\lambda)$  and  $c_m(\lambda)$  are the true and measured attenuation coefficients, respectively. We define the scattering coefficients similarly:

$$b_t(\lambda) = c_t(\lambda) - a_t(\lambda) \tag{10}$$

$$b_m(\lambda) = c_m(\lambda) - a_m(\lambda) \tag{11}$$

Assuming that  $e_a$  and  $e_c$  are not functions of  $\lambda$ , we then set:

$$a_t(\lambda) = a_m(\lambda) - e_a b_t(\lambda), \text{ and} \tag{12}$$

$$c_t(\lambda) = a_t(\lambda) + b_t(\lambda) = c_m(\lambda) + e_c b_t(\lambda). \tag{13}$$

We now subtract equation (12) from (13):

$$b_t(\lambda) = b_m(\lambda) + b_t(\lambda)[e_c + e_a], \quad (14)$$

so that:

$$b_t(\lambda) = b_m(\lambda)/(1 - e_c - e_a) \quad (15)$$

We see that the measured scattering coefficient spectrum,  $b_m(\lambda)$ , is proportional by a constant  $[1/(1 - e_c - e_a)]$  to the true scattering spectrum. We may then conclude that:

$$b_t(\lambda_1)/b_t(\lambda_2) = b_m(\lambda_1)/b_m(\lambda_2) \quad (16)$$

We thus see that the acceptance angle of the attenuation meter is immaterial, given the assumptions above.

We now assume that there is some reference wavelength,  $\lambda_r$ , at which the absorption coefficient (excluding the already subtracted water component) is zero. For the present we set  $\lambda_r = 712$  nm, although there may be better choices further in the infrared.

Thus, 
$$a_t(\lambda_r) = 0 \quad (17)$$

Substitution of equation (17) into (12) gives: 
$$a_m(\lambda_r) = e_a b_t(\lambda_r). \quad (18)$$

Hence, 
$$e_a = a_m(\lambda_r)/b_t(\lambda_r). \quad (19)$$

Substitution of equation (19) into (12) gives:

$$a_t(\lambda) = a_m(\lambda) - a_m(\lambda_r) \frac{b_t(\lambda)}{b_t(\lambda_r)} \quad (20)$$

Substitution of equation (16) into the above gives:

$$a_t(\lambda) = a_m(\lambda) - a_m(\lambda_r) \frac{b_m(\lambda)}{b_m(\lambda_r)} \quad (21)$$

Note that we can thus determine the true absorption coefficient at any wavelength, assuming that the ratios of the absorption and attenuation scattering errors to total scattering are not a function of wavelength. We do not need to know the fraction of scattered light not received by the attenuation meter, i.e. we need not know  $e_c$ . This correction scheme will be designated as the "proportional" correction scheme in the remainder of the paper.

For spectrophotometric work one normally cannot take into account the spectral variations in  $b(\lambda)$ . One simply subtracts the absorption at the reference wavelength. This then would imply that  $b_m(\lambda_r) = b_m(\lambda)$  from equation (12), an unnecessary assumption in our case. This standard spectrophotometric correction scheme will be designated as the "constant" correction scheme in the remainder of the paper.

A source of spectral change in the shape of the volume scattering function is the presence of absorption bands<sup>12</sup>. Anomalous dispersion near absorption bands cause changes in the real part of the index of refraction and thus the volume scattering function. To model this, we used the particle size distribution and chloropigment content of particles from the chlorophyll maximum in Central Gyre of the Pacific Ocean<sup>9</sup>. This should be a good estimate of the maximum influence of anomalous dispersion on the correction of absorption meters. The optical model used was a three-layered sphere<sup>10</sup> with a high-index of refraction outer shell, a middle layer containing the absorbing pigments and an inner layer with low-index of refraction cytoplasm. For the volume scattering functions produced by this model, the proportional correction method still produces smaller errors on average than the constant correction method. This is especially true for the fine detail of the spectral structure (Figure 4).

Figure 4 indicates that the blue part of the spectrum may be better matched by the constant correction method. Thinking that this may be due to the larger relative optical size at shorter wavelengths reducing the effective scattering error, we carried out a test for homogeneous non-absorbing spheres with two different size distributions. The results (Table III) still show the proportional correction scheme outperforming the constant subtraction scheme. We conclude that the low error in the constant subtraction method at 412 nm for the phytoplankton model was due to the reduced index of refraction caused by being on the short wavelength side of the 443 nm absorption peak.

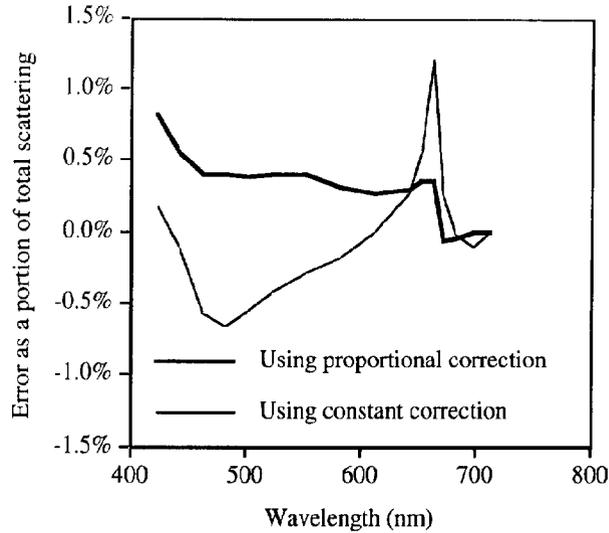


Figure 4. Errors produced by the proportional and constant correction schemes for a volume scattering function derived from an anomalous dispersion model of the phytoplankton maximum in the central gyre.

Table III. Residual scattering errors after correcting by a constant  $a(715)$  and by the proportion  $a(715)/c(715) \times b(\lambda)$  for homogeneous spheres with indices of refraction of 1.1875 and 1.05 relative to water.

wavelength	412 nm		560 nm	
method	constant	proportional	constant	proportional
index of refraction				
	Slope = 3			
1.1875	0.60%	-0.07%	0.32%	0.04%
1.05	0.23%	0.10%	0.12%	0.06%
	Slope = 5			
1.1875	16.23%	-4.04%	10.43%	-1.32%
1.05	9.47%	-3.19%	6.25%	-1.07%
	Kneed, Slopes = 3,5			
1.1875	1.04%	-0.26%	0.53%	-0.11%
1.05	0.26%	0.02%	0.12%	-0.01%

#### 5.4 The effect of temperature on the scattering error correction of a reflecting tube absorption meter.

In the derivations of section 5.3, it was assumed that the measurements were carried out at the same temperature at which the calibration was carried out. Pegau and Zaneveld<sup>14</sup> showed that the absorption of light by pure water in the near infrared is strongly temperature dependent. Maximum temperature dependence was found at 745 nm. A commonly used reference wavelength for reflective tube absorption meters is 715 nm. The absorption coefficient of water at that wavelength is also temperature dependent. The temperature dependence was found to be linear in the temperature range encountered in the ocean<sup>15</sup>. This temperature dependence at 715 nm was measured to be  $0.0035 \text{ m}^{-1}/^{\circ}\text{C} = S(715)$ . We need to derive the effect of this temperature dependence on the correction factor.

Let  $a_i(\lambda_r)$  be the instrumental output at the reference wavelength  $\lambda_r = 715$  nm for the calibration temperature  $T_{cal}$ . The value measured at a different temperature will be designated by  $a_i(\lambda_r, T)$ . We then find that for the absorption of pure water we may set:

$$a_w(\lambda_r, T) = a_w(\lambda_r, T_{cal}) + S(715)(T - T_{cal}) \quad (22)$$

The value determined by the instrument at a temperature  $T$  is due to the true absorption coefficient  $a_t(\lambda, T)$  from which the absorption due to water at the calibration wavelength was subtracted and to which the scattering error must be added, so that

$$a_i(\lambda, T) = a_t(\lambda, T) - a_w(\lambda, T_{cal}) + e_a b_t(\lambda, T) \quad (23)$$

Eq. 23 is also true at the calibration temperature, so that

$$a_i(\lambda, T_{cal}) = a_t(\lambda, T_{cal}) - a_w(\lambda, T_{cal}) + e_a b_t(\lambda, T_{cal}) \quad (24)$$

We will assume that light scattering is not a function of temperature, so that  $b_t(\lambda, T) = b_t(\lambda, T_{cal})$ . Subtracting equations 23 and 24 then gives:

$$a_i(\lambda, T) - a_i(\lambda, T_{cal}) = a_t(\lambda, T) - a_t(\lambda, T_{cal}) \quad (25)$$

Equation 1 showed that the true absorption coefficient is equal to the water absorption plus the non-water absorption. We will assume that the non-water absorption is not a function of temperature, although nothing is known about the temperature dependent absorption of yellow matter or pigments. Subtracting equation 10 for  $T_{cal}$  from equation 10 for  $T$  then gives:

$$a_t(\lambda, T) - a_t(\lambda, T_{cal}) = a_w(\lambda, T) - a_w(\lambda, T_{cal}), \quad (26)$$

so that

$$a_t(\lambda, T) - a_t(\lambda, T_{cal}) = S(\lambda)(T - T_{cal}), \quad (27)$$

from equation 22. Using equation 25 then gives:

$$a_i(\lambda, T_{cal}) = a_i(\lambda, T) - S(\lambda)(T - T_{cal}). \quad (28)$$

We are now ready to return to our earlier final result, equation 21, which is valid at the calibration temperature.

$$a_n(\lambda, T_{cal}) = a_i(\lambda, T_{cal}) - a_i(\lambda_r, T_{cal}) [b_i(\lambda, T_{cal}) / b_i(\lambda_r, T_{cal})] \quad (29)$$

We note once again that light scattering is assumed to be not a function of temperature, so that the temperature designation can be deleted for the scattering coefficients as the values are the same for any temperature. Similarly we assumed that the non-water absorption is not a function of temperature. Using these assumptions and equation 28, equation 29 can be transformed into:

$$a_n(\lambda) = a_i(\lambda, T) - S(\lambda)(T - T_{cal}) - [a_i(\lambda_r, T) - S(\lambda_r)(T - T_{cal})] [b_i(\lambda) / b_i(\lambda_r)] \quad (30)$$

Under most circumstances  $S(\lambda)$  will be considered to be zero except at the reference wavelength, although this is strictly speaking not correct. Pegau and Zaneveld<sup>15</sup> found that at 600nm, for instance  $S(\lambda) = 0.0015 \text{ m}^{-1} \text{ }^\circ\text{C}^{-1}$ .

As an example we see that if  $\lambda_r = 715$  nm and hence  $S(\lambda_r) = 0.0035 \text{ m}^{-1}/^\circ\text{C}$  and if the instrument was calibrated with water at  $15^\circ\text{C}$  and the measurement was made at  $25^\circ\text{C}$ , equation 30 becomes:

$$a_n(\lambda) = a_i(\lambda, T) - [a_i(\lambda_r, T) - 0.035] [b_i(\lambda) / b_i(\lambda_r)] \quad (31)$$

The non-water absorption so determined thus is larger by  $0.035 [b_i(\lambda) / b_i(\lambda_r)]$  (or approximately  $0.035 \text{ m}^{-1}$ ) than if the original equation 12b had been applied without concern for the temperature effect on the absorption of pure water. The temperature effect can be very large in spectrophotometers if the reference water is at room temperature and the sample water is much colder. Pegau and Zaneveld<sup>14</sup> showed that for  $\lambda_r = 750$  nm, this can lead to large apparently negative absorption coefficients.

## 5.5 Use of a scattering sensor to correct a reflecting-tube absorption meter

It may be possible to incorporate a simple scattering sensor into a reflective-tube absorption meter. Any scattering sensor would measure a weighted integral of the volume scattering function between a lower limit and an upper limit. Here we will consider the weighting function to be unity and will study the effect of varying upper and lower limits only. The signal from such a sensor would correlate to a greater or lesser degree with the scattering error depending on how well it matched the angular distribution of the error. To study this, we revert to our six models of the volume scattering function and introduce five different angular ranges that a scattering meter could conceptually measure. For each combination of angular range and volume scattering function we compute the portion of  $b$  that is included in that range. Then, for each reflective tube design and angular range of the scattering sensor, we can correlate the scattering error with the scattering signal for the six volume scattering functions. The

resulting regressions are shown in Table IV. The output of the scattering sensor is given by “B” and the absolute magnitude of the scattering error is given by  $b_e$ .

TABLE IV Regression equations, squared correlation coefficients and maximum residual errors for prediction of  $b_e/b$  for various instrument designs.

a-Meter Design	Scat. Sensor Range	Regression Equation for 6 models of $\beta(\theta)$	$r^2$	max err b
$\theta_a = 30^\circ, R=95\%$	10-30°	$\frac{b_e}{b} = 0.0407 + 0.250 B/b$	0.868	0.023
	20-60°	= 0.0300 + 0.736 B/b	0.949	0.016
	41-90°	= 0.0199 + 3.135 B/b	0.627	0.054
	90-180°	= 0.0752 + 7.258 B/b	0.250	0.065
	120-160°	= 0.0869 + 18.24 B/b	0.173	0.064
$\theta_a = 41^\circ, R=95\%$	10-30°	= 0.0446 + 0.331 B/b	0.912	0.021
	20-60°	= 0.0293 + 0.559 B/b	0.912	0.016
	41-90°	= 0.0155 + 2.555 B/b	0.695	0.038
	90-180°	= 0.0585 + 6.199 B/b	0.304	0.048
	120-160°	= 0.0679 + 15.84 B/b	0.218	0.047
$\theta_a = 30^\circ, R=100\%$	10-30°	= 0.0339 + 0.176 B/b	0.746	0.022
	20-60°	= 0.0249 + 0.401 B/b	0.813	0.018
	<b>41-90°</b>	<b>= 0.0055 + 2.103 B/b</b>	<b>0.816</b>	<b>0.022</b>
	90-180°	= 0.0356 + 5.812 B/b	0.463	0.032
	120-160°	= 0.0427 + 15.62 B/b	0.367	0.032
$\theta_a = 41^\circ, R=100\%$	10-30°	= 0.0282 + 0.059 B/b	0.285	0.020
	20-60°	= 0.0238 + 0.145 B/b	0.358	0.019
	<b>41-90°</b>	<b>= -0.0007 + 1.263 B/b</b>	<b>0.993</b>	<b>0.003</b>
	90-180°	= 0.0116 + 4.267 B/b	0.842	0.010
	120-160°	= 0.0153 + 12.11 B/b	0.744	0.013

The most significant finding in Table IV is that almost all of the regression intercepts are significant. This indicates that a change in scattering sensor signal due to a change in shape of the VSF will mean a different a-meter error than the same change in scattering sensor signal due to a change in total scattering coefficient. We see this from:

$$e_a = \frac{b_e}{b} = A_1 + A_2 \frac{B}{b} \quad \text{yields} \quad b_e = A_1 b + A_2 B \quad (32)$$

which means that we need to know  $b$  in order to apply the above regressions. We remind the reader that  $e_a$  is the proportion of scattered light not detected by the absorption meter. Thus by using a poorly matched scattering sensor we are no better off than by using a simultaneous measurement of  $c$  and the proportional correction scheme. If we are using all three instruments, we now have three equations in three unknowns and can arrive at a better estimate of  $a$ . However, a well matched scattering sensor such as the 41-90° sensor for the 100% reflective tube a-meters does give a negligible intercept (so that  $A_1 = 0$ ) and a small residual error, indicating that it would provide a very good estimation of the correction,  $b_e$ , without a  $c$  measurement. For combinations with a significant intercept, the residual column probably represents the uncertainty using both the scattering sensor and a  $c$ -meter to correct  $a$ .

To apply the above, it would be necessary to document the actual performance of the absorption meter and then design a scattering sensor to match the scattered light not detected. Neither of these tasks are necessarily easy. Finally, the actual regression between the signal from the scattering sensor and scattering error would have to be determined experimentally. In the end though, it would correct much of the variation due to changes in the shape of the volume scattering function that the simultaneous measurement of  $a$  and  $c$  and application of the proportional correction scheme does not address.

## 6. LABORATORY CONFIRMATION

In order to verify the above error analysis we compared the attenuation and apparent absorption of polystyrene spheres with the results of Mie theory calculations of their volume scattering functions in our model of instrument performance. Assuming a 100% reflectance resulted in agreement only at rather low acceptance angles for the absorption meter (Figure 5). However, decreasing the reflectance of the tube to 95% results in agreement at angles very close to the design criterion of 41°. For the 0.5  $\mu\text{m}$  particles the 95% reflectance also results in a much closer agreement in the spectral shape of the measured and predicted results. The improvement in spectral shape at the other two sizes is not appreciable. The 0.5  $\mu\text{m}$  particles provide the best test of the angular inclusion of the absorption meter since the small particles have the highest proportion of large angle scattering. The reduced reflection could be due to imperfections on the outside of the glass tube or by some of the scattered light being intercepted by the O-rings between the end of the glass tube and the receiver window.

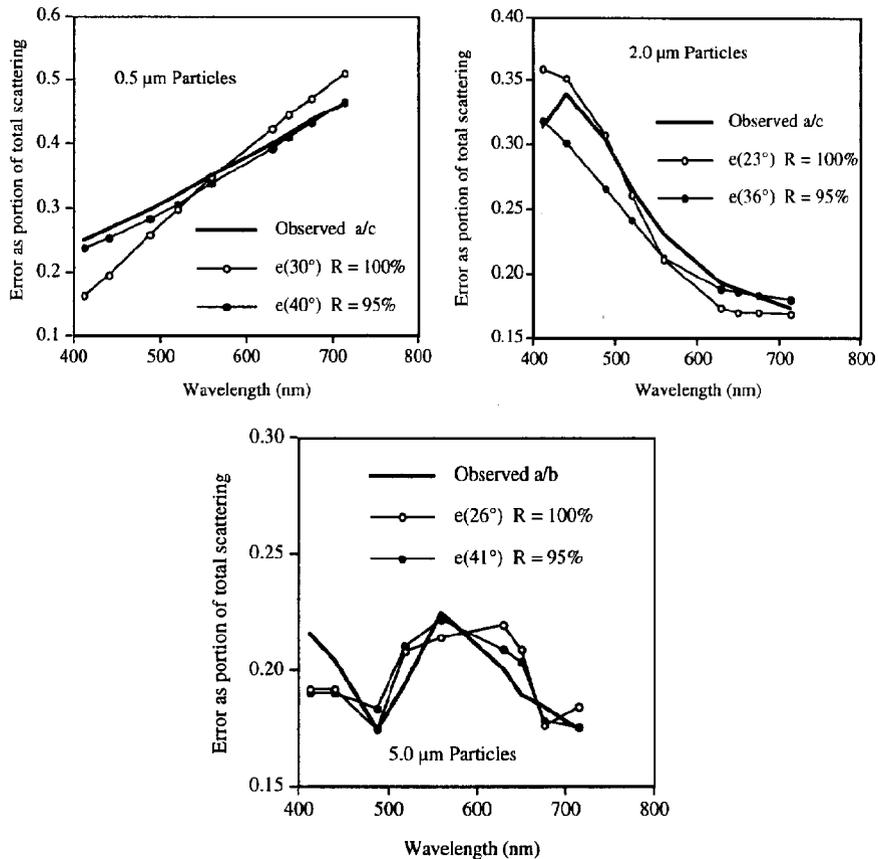


Figure 5. Measured a/c and computed portion of scattering in various angular ranges for three different calibration particles.

## 7. SUMMARY.

In situ reflecting tube absorption meters have allowed us for the first time to obtain continuous vertical profiles of the absorption coefficient in natural waters. The reflecting tube absorption meter has almost the same geometry as a spectrophotometer with a cuvette. The main difference is that the absorption meter uses a collimated beam whereas most spectrophotometers do not. In addition, reflecting tube absorption meters are usually combined with beam attenuation meters.

The geometry of the reflecting tube results in some of the scattered light not being collected by the detector. This undetected light is the scattering error. The scattering error can be estimated in a number of ways, which we examine. We show that the only available correction method for an absorption meter without attenuation measurements or a spectrophotometer is the

constant correction method in which the measured absorption at a wavelength in the near infrared is subtracted. A better correction is obtained if attenuation is measured simultaneously and the absorption at the reference wavelength is multiplied by the ratio of the measured scattering at a given wavelength divided by the measured scattering coefficient at the reference wavelength. This is called the proportional correction method as it takes into account variations in the scattering coefficient as a function of wavelength.

We showed that the important geometrical parameters of the reflecting tube can be obtained by a comparison of measurements and models of polystyrene beads. Finally we examine the improvements that could be obtained if a direct scattering measurement was made simultaneously with the absorption and attenuation measurements. Obviously, if a measurement could be made that nearly exactly matches the light that is not measured by the absorption meter, the absorption coefficient could be measured nearly exactly. The scattering measurement then could also be corrected to be nearly perfect from the collimation angle onward.

## 8. ACKNOWLEDGEMENTS

The support of the Ocean Optics division of the Office of Naval Research (Grant No. N00014-93-1-0649) is gratefully acknowledged.

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