VOLUME TITLE:

Inherent Optical Property Measurements and Protocols: Absorption Coefficient

Table of Contents

TABLE OF CONTENTS ....................................................................................................................... 1
PREFACE ............................................................................................................................................. 4

CHAPTER 1: THE ABSORPTION COEFFICIENT, AN OVERVIEW ................................................. 5
  1.1 Absorption by Pure Water ........................................................................................................ 5
  1.1.1 Visible, Near-Infrared, and Infrared domains ..................................................................... 6
  1.1.2 Ultraviolet domain .............................................................................................................. 6
  1.1.3 Temperature and salinity dependence ................................................................................... 8
  1.2 Absorption by Colored Dissolved Matter (CDM) ................................................................. 8
  1.3 Absorption by Particles in Suspension .................................................................................... 10
  1.4 General Comment on Measuring Absorption Components ................................................ 12
  TABLE 1.1 ....................................................................................................................................... 13
REFERENCES ................................................................................................................................. 20

CHAPTER 2: REFLECTIVE TUBE ABSORPTION METERS ......................................................... 23
  2.1 The Reflective Tube Approach .................................................................................................. 23
  2.1.1 Background: measuring volume absorption coefficients for medium with particles 
       in suspension .............................................................................................................................. 23
  2.1.2 Reflective tube absorption meter concept ........................................................................... 24
  2.2 Description of a Reflective Tube Spectral Absorption Meter ................................................ 27
  2.3 Calibration of a Reflective Tube Spectral Absorption Meter ................................................ 28
  2.3.1 Pure water calibration ......................................................................................................... 28
  2.3.2 Preparation of purified water suitable for calibration ......................................................... 29
  2.3.3 Air calibrations .................................................................................................................. 30
  2.4 Measuring Spectral Absorption Coefficients with Reflective Tube Meters ......................... 31
  2.4.1 Filtering the water intake port of an ac-9 for measurements of absorption by 
       CDOM ...................................................................................................................................... 31
  2.5 Data Analysis Methods ............................................................................................................ 32
  2.5.1 Temperature and salinity corrections .................................................................................. 32
  2.5.2 Scattering correction methods ............................................................................................. 33
  2.6 Quality Control Procedures ..................................................................................................... 34
  2.7 Deployment Strategies of AC-Meters ....................................................................................... 35
       Platform types: .......................................................................................................................... 35
       1. Winched package .................................................................................................................... 35
       2. Slow Decent Rate Optical Package (SlowDROP, Barnard et al. 1999) ................................. 35
       3. Diver’s package (Zaneveld et al. 2001) ............................................................................... 36
       4. Bottom Tripods .................................................................................................................... 36
       5. Moorings and profiling moorings ........................................................................................... 36
       6. In-line .................................................................................................................................... 36
       7. Towed systems ...................................................................................................................... 36
       8. Autonomous Underwater Vehicle (AUV) .............................................................................. 37
REFERENCES ................................................................................................................................. 37
REFERENCES............................................................................................................................................. 69
ACRONYM/ABBREVIATION DEFINITIONS LIST.................................................................................. 71
SYMBOL LIST (BY CHAPTER).................................................................................................................. 73
Preface

This document provides an overview of the absorption coefficient (Chapter 1) and describes protocols for measuring particles in suspension (Chapters 2-4) and on a filter pad (Chapter 5). Two earlier versions of this protocol exist: *Ocean Optics Protocols for Satellite Ocean Color Sensor Validation, Revision 2* (Mitchell et al., 2000) and *Revision 4, Volume IV* (Mitchell et al. 2002). The Mitchell et al. 2000 protocol document details a workshop was held at the Scripps Institute for Oceanography where 24 international scientists compared a number of different methods and instruments for measuring particles on a filter pad. From this intercomparison, they were able to quantify the uncertainty of raw absorbance among the various methods available at that time. The 2002 protocol document was strictly a protocol document; its purpose was to describe the state of the art and most common methodologies at that time. This volume, the newest iteration of the aforementioned protocol documents, does not seek to replicate the earlier documents or to promote one particular method. Rather the goal here is to provide a comprehensive overview of the most common methods for measuring particles in the water or on a filter pad and an updated and cohesive protocol for state-of-the-art technologies that have been developed since the 2000 and 2002 NASA Technical Memoranda.
Chapter 1: The Absorption Coefficient, An Overview

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Inherent Optical Properties (IOPs) of each discrete constituent of the water medium are additive, so that the total (or combined) absorption and scattering properties of a sample of natural water consist of the sums of the IOPs of pure water itself (with or without dissolved salts), each discrete particle and aggregate, and each dissolved substance. 'Discrete' here specifically refers to particles not being too close in proximity; typically, they must be separated by at least three times their radii or there will be interference in their scattering properties (van de Hulst 1981). This condition is considered fulfilled in natural waters except for only extremely turbid environments. Note that even for a single 'discrete' particle, the scattering intensity and its angular pattern will be dependent on the specific orientation of that particle relative to a frame of reference, unless it is a homogeneous sphere. Discontinuities in the refractive index of water due to fine scale variability in temperature and salinity that may be influenced by physical processes, such as turbulence, also constitute a scattering IOP with effects at near-forward angles (Bogucki et al. 2004, 2007, Mikkelsen et al. 2008). IOPs of individual constituents are usually grouped (e.g., dissolved and particulate, with respect to particle type, etc.) based on methodological capabilities and constraints, or conceptual convenience. IOPs can be described with respect to spectral variability (typically in the UV-visible-NIR range for underwater optics and remote sensing applications), and scattering has an angular dependency characterized by the volume scattering function (VSF or β), also known as the differential scattering cross-section. Whereas the VSF specifically describes angular scattering of unpolarized radiation, scattering of the polarized elements of the Stokes vector can similarly be described, and may contain unique information about particle characteristics.

Different combinations of individual biogeochemical constituents of natural water collectively determine the IOPs (including magnitude, spectral shape, and angular dependence), which in turn strongly influence remote sensing reflectance (Gordon et al. 1988; Morel 1988; Morel et al. 2002; Werdell et al. 2013). The physical basis for determining constituent concentrations of natural waters from ocean color measurements lies in methods and algorithms that effectively invert these relationships.

1.1 Absorption by Pure Water

It is challenging to experimentally determine the absorption of pure water, \( a_w \) (m\(^{-1}\)), in the laboratory, due principally to the difficulty of making and maintaining pure water, a powerful solvent, during the course of an experiment. The UV range is particularly sensitive to dissolved organic and inorganic absorbing contaminants, and absorption by water is generally low relative to measurement signal-to-noise at wavelengths shorter than about 500 nm. Methods used to determine pure water absorption include conventional transmission, an integrating cavity absorption meter (ICAM; see Chapter 3 of this volume), and photothermal techniques such as laser calorimetry, photoacoustics, photothermal deflection, and the thermal lens (Grundinkina 1956; Ghormley and Hochanadel 1971; Tam and Patel 1979; Quickenden and Irvin 1980; Boivin et al. 1986; Sogandres and Fry 1997; Pope and Fry 1997; Cruz et al. 2011; Kröckel and Schmidt 2014). Note that some studies employing transmission-based methods report their values as absorption even though attenuation is actually measured, so that the contribution from molecular scattering must be removed (Section 2.5.2). This is particularly important in the UV portion of the spectrum where molecular scattering from water is similar in magnitude to its absorption. Other studies using the ICAM and photothermal techniques do not have contributions from molecular scattering in their measurements. Because of the difficulty in making water with sufficient purity, others have also taken the approach of trying to infer pure water absorption from passive radiometric measurements in the world’s clearest waters (Smith and Baker 1981; Morel et al. 2007; Lee et al. 2014). There is value in this approach, as water in some locations, such as the central South Pacific gyre, is maintained naturally at very high levels of clarity, which at least can be used to stipulate upper bounds for pure water absorption. However, background absorbing constituents in these waters are nonetheless still present and require assumptions in accounting for their effects.
For detailed discussions on the physical basis of absorption by water, see Jonasz and Fournier (2007) and Wozniak and Dera (2007).

### 1.1.1 Visible, Near-Infrared, and Infrared domains

It is accepted that the work of Pope and Fry (1997) represents the state-of-the-art for pure water absorption from about 420 to 725 nm due to the fidelity of the ICAM technique, including its long effective path length (~10 m) and insensitivity to scattering, and the level of water purity achieved in the study. Portions of their data in the visible have been verified by other studies using completely different techniques (e.g., Sogandres and Fry 1997; Cruz et al. 2011). The resolution of these data is fine enough to show expected inflections from overtone modes of water absorption, allowing precise modeling with combination Gaussian fitting informed by physical theory (Jonasz and Fournier 2007). For the NIR and IR domains (from 730 to 1230 nm), the values of Kou et al. (1993) are accepted as state-of-the-art. Note that the reported values in Pope and Fry and Kou et al. overlap in the range ~667 to 727.5 nm, and are offset ~0.04 m\(^{-1}\) higher for Kou et al. at 670 nm and ~0.07 m\(^{-1}\) higher for Kou et al. at 725 nm. This offset is not taken into account in the Table 1 data (other than to choose the carefully collected Pope and Fry data for the spectral range of overlap), as we have no basis for doing so at this time. On an absolute basis, this discrepancy is significant.

#### 1.1.2 Ultraviolet domain

Water purity is absolutely essential for pure water absorption measurements in the UV, as a wide range of both organic and inorganic dissolved substances absorb, often quite strongly, in this region, whereas absorption by water is comparatively low. As a result, state-of-the-art studies for water absorption in the UV have used sophisticated and exhaustive measures to purify water, including oxidative steps, extreme deionization quantified with conductivity readings, UV oxidation, and removal of dissolved oxygen gas. The highest quality data in the UV are thus accepted to be Quickenden and Irvin (1980; range between 196 and 320 nm), Ghormley and Hachanadel (1971; range between 180 and 215 nm), and Kröckel and Schmidt (2014; range between 181 and 340 nm), hereafter referred to as GH-QI-KS. All of these data agree within experimental error in the regions of overlap, providing continuous, high quality measurements from 180 to 340 nm. Note that the “absorptivity” values of Quickenden and Irvin (1980) are base 10 logarithms of the inverse of transmission divided by path length, so the values must be multiplied by 2.303 to convert to the absorption coefficient. Molecular scattering of water was subtracted from all of these data to derive pure water absorption. Other notable high-quality absorption data in (or near) the UV were collected by Boivin (1986) at 254, 313, 366, and 406 nm, and by Grundinkina (1956; as cited by Jonasz and Fournier 2007) from 200 to 350 nm. Neither of these studies accounted for possible absorption from dissolved oxygen and the purification steps overall were not as rigorous as the previously mentioned studies. The values of Sogandres and Fry (1997) and Pope and Fry (1997) in the UV are significantly higher than these other careful works, indicating possible contamination in their purified water for this spectral range.

Jonasz and Fournier (2007) provide physical equations based on theory for pure water absorption in the UV that produce an excellent fit to the GH-QI-KS measurements:

\[
a_w = 7.067 	imes 10^{-40} \exp\left(\frac{8r}{\lambda - \Delta\lambda}\right) + 5 \times 10^6 \nu^{-5/4} \exp\left(-0.076 Z_e\right) \exp\left(\frac{\nu}{\nu + 0.03}\right),
\]

where

\[
Z_e = \left(\frac{\nu^{11/2} - 2/3}{\nu^{11/2}}\right)^2, \quad \nu = 10^7 \left(\frac{1}{\nu} - \frac{1}{\lambda}\right).
\]

\(\Delta\lambda = 0.0465(T - 298)\Delta\lambda = 0.0465(T - 25)\), \(\lambda_e\) is a reference wavelength arbitrarily chosen as 150 nm, and \(T\) is temperature in degrees Kelvin. These equations allow for the explicit treatment of the effects of temperature on pure water absorption in the UV. Values between 180 and 340 nm in Table 1.1 were derived from this analytical model solved at 22°C. Conveniently, at 340 nm the analytical model agrees with the extrapolated values recommended by Morel et al. (2007; see \(a_w\) values in their Table 2, based on an extrapolation between the data of Quickenden and Irvin (1980) and Pope and Fry (1997)). The values of Morel et al. (2007) are used between 340 and 420 nm in Table 1.1. While providing satisfying continuity in the values for pure water absorption, it should be emphasized that the values between 340 and 420 nm (a relatively wide and ecologically important spectral range) are merely extrapolated; there is a clear need for high quality water absorption measurements in this spectral range. Addendum: a recent study by Mason et al. (2016) includes measurements of absorption in this spectral range.
Recent work by Cruz et al. (2009, 2011) using a thermal lens technique presents three values for pure water absorption in (and near) the UV at 351, 364, and 406 nm that are significantly lower than the extrapolation of data from GH-QI-KS in the region between 340 and 420 nm. The Cruz et al. values at longer wavelengths are consistent with Pope and Fry (1997) within measurement errors. The smallest absorption value, measured at 364 nm, is more than a factor of 3 less than the extrapolation in this region, effectively creating a much more significant transmission window in that part of the UV than currently thought. The Cruz et al. data would shift the minimum in pure water absorption from the 400-420 nm range to somewhere likely between 360 and 380 nm. Such a “hole” in pure water absorption in this region is not consistent with expectations of a monotonic exponential function through this region from physical theory (Jonasz and Fournier 2007). Their absorption data between 351 and 406 nm have an entirely new shape relative to other high-quality measurements from the literature in this region (particularly Grundinkina 1956 and Boivin 1986). In this spectral range, possible errors in other studies due to organic contaminants in their purified water and/or scattering-reflection effects would be spectrally broad and monotonic, inconsistent with a \(~20\) nm FWHM error spectrum peaking in the 360-380 nm range. The Cruz et al. measurements also, paradoxically, were made with water purified with a typical Millipore MilliQ® Plus ultrafiltration system of 18 MΩ cm purity, without any additional purification or any removal of dissolved gases, contrasting markedly with exhaustive purification measures taken in the most comprehensive works (e.g., GH-QI-KS). These data therefore cannot be considered at this time without further verification.

Recent work by Lee et al. (2015) found values offset about 0.002 m\(^{-1}\) lower from 350 to 500 nm than the values recommended here based on semi-analytic inversion of in situ radiometric data and models that accounted for the absorbing components besides pure seawater in the water column. These data were collected alongside the radiometric measurements of Morel et al. (2007) that guided the conclusions on recommended pure water values in that work (see above; these are essentially the values recommended in Table 1.1 for this spectral region). Considering associated uncertainties and assumptions in the radiometric inversion method, the Lee et al. (2015) values are not deemed inconsistent with the recommended values.

Jonasz and Fournier (2007) suggest that the effect of dissolved oxygen alone may explain the differences between the oxygen free water data of GH-QI-KS and the data collected with water saturated in oxygen from Boivin (1986) and Grundinkina (1956). Jonasz and Fournier (2007) additionally provide physical relationships based on data from Heidt and Johnson (1956) to represent both the effects of oxygen being present on pure water absorption and the direct absorption by oxygen dissolved in water in the spectral range 200 - 215 nm. This approach was supported by good agreement with the direct measurements of Grundinkina (1956) in that spectral range. Since the physical data collected by Heidt and Johnson (1956) did not extend longer than 215 nm, Jonasz and Fournier (2007) fit the data of Grundinkina (1956) and Boivin (1986) using the same physical relationship used to fit the oxygen free pure water absorption data of GH-QI-KS. Assuming this fit is only accounting for the presence of oxygen in water, significant absorption effects from dissolved oxygen are apparent out to at least \(~370\) nm, where the GH-QI and Boivin (1986) values converge (also see Morel et al. 2007, their Fig. 10). Detectable absorption from dissolved oxygen at wavelengths longer than about 280 nm appears inconsistent with the findings of previous studies (e.g., Copin-Montegut 1971 as cited in Shifrin 1988), although we are not aware of any careful measurements to resolve potentially very low (but still perhaps significant) absorption from oxygen in the long UV range. Regarding the differences between GH-QI-KS and the data of Grundinkina (1956) and Boivin (1986), Fig. 2 from Quickenden and Irvin (1980), which shows the decrease in absorption following sequential purification steps, may be instructive, as water of “purity 2” (only deionized and distilled) is a close approximation to the higher values and spectral shape of absorption presented by these other authors. The final “purity 4” water from Quickenden and Irvin (1980) had several additional distillation and oxidation steps. All levels of purity had oxygen removed through bubbling with nitrogen gas, so that the “purity 2” water (and perhaps the water of Grundinkina 1956 and Boivin 1986) presumably contained organic contaminants.

Importantly, dissolved inorganic molecules besides oxygen, such as \(\text{NO}_3\), Br\(^-\), and other salt ions comprising sea salts all have significant absorption in the UV (Armstrong and Boalch 1961; Ogura and Hanya 1966; Johnson and Coletti 2002; as cited in Shifrin 1988: Lenoble 1956, Copin-Montegut 1971). Note these effects have received scarce attention in recent literature. At 230 nm, these constituents all have more than an order of magnitude higher absorption than the values of GH-QI-KS, with steeply increasing absorption at shorter UV wavelengths. An unresolved question is how much these constituents may absorb at wavelengths longer than 300 nm, as the tail absorption effects have typically not been studied with the
required accuracy. Again, even relatively small contributions could be significant since pure water absorption is very low, particularly in the 320 to 420 nm range (\(<= 0.01 \text{ m}^{-1}\)). Armstrong and Boalch (1961) found significant effects of sea salt absorption out to 400 nm, but rigorous purification steps were not taken, so it is unclear if their additions of artificial sea salts introduced organic contaminants.

In summary, it is worth emphasizing that UV absorption for seawater devoid of particles and dissolved organic substances will be substantially influenced by the typical assortment of dissolved inorganic constituents, so that the absorption values in the UV presented in Table 1.1 will require supplementation based on high quality molar absorptivity data for these constituents (which are currently not available to our knowledge) and ancillary measurements of their respective concentrations. This is a critical area of needed research in the future study of radiative transfer in the UV.

### 1.1.3 Temperature and salinity dependence

The absorption by pure water exhibits linear dependencies on temperature and salinity, which have been quantified empirically by Pegau et al. (1997), Twardowski et al. (1999), and Sullivan et al. (2006) for reflective tube absorption devices with individual spectral bandwidths of approximately 10-18 nm full-width-half-max (FWHM). Sullivan et al. (2006) further provided estimated values for the linear slopes of temperature and salinity dependencies with the effect of spectral smearing from bandwidth limitations removed, which should be closer to what may be considered physical constants describing the effect. Recently, Röttgers et al. (2014) determined these coefficients with an integrating cavity absorption meter and a spectrophotometer with a spectral range spanning 400 to \(-\)2700 nm. The Röttgers et al. data agree within the experimental error of the Sullivan et al. coefficients, but exhibit finer detail due to improved signal-to-noise and narrower bandwidths (3 nm for 400 - 700 nm, 2 nm for 700-850 nm, and 2-4 nm for > 850 nm). We recommend the Röttgers et al. coefficients for describing the physical phenomenon, which are reproduced in Table 1.1.

For applying pure water absorption values to measurements, the spectral bandwidth characteristics of the sensor and the temperature and salinity of the water should be accounted for, which, when optimal accuracy is desirable, becomes rapidly quite complex. For the linear dependency with respect to temperature, the Röttgers et al. values may be convolved with the spectral bandwidth of the measurement device to derive a coefficient specific for that device at that centroid wavelength. With a concurrent measurement of ambient temperature, the effect of the temperature dependence can then be removed by choosing a reference temperature for all data (Section 2.5.1). Alternatively, empirically derived coefficients specific for that sensor may be used, if available. For salinity, the effect is more challenging since the physical effect of pure water dependence on salt content (e.g., as reported by Röttgers et al., 2014) is always convolved with some instrument specific transmission effect resulting from the interaction of optical interfaces with solutions of varying refractive index (Sullivan et al. 2006). In this case, using empirically derived coefficients for a specific sensing device would be advisable. For this reason, the Sullivan et al. (2006) coefficients for temperature and salinity dependencies of pure seawater absorption specific for the WET Labs ac-\(s\) are also provided in Table 1.1. Note also that the pure seawater absorption values discussed above have been measured at specific ambient temperature and spectral bandwidth, e.g., the Pope and Fry (1997) values were measured at 22\(^\circ\) C with a nominal bandwidth of 1.9 nm, which, for optimal accuracy, should be accounted for in some applications. Moreover, when working in the NIR spectral range, caution should be exercised due to strong spectral gradients and significant absolute peak values in temperature and salinity dependencies in pure water absorption.

### 1.2 Absorption by Colored Dissolved Matter (CDM)

Material in the dissolved fraction of natural water that absorbs light is known as Colored Dissolved Matter (CDM). Since CDM absorption in the visible range is dominated by refractory organic humic substances, material in the dissolved fraction is commonly referred to as Colored Dissolved Organic Matter (CDOM), or gelbstoff (i.e., ‘yellow substances,’ after Kalle 1966). The associated absorption coefficient is \(a_\lambda (\lambda)\) with units of \(\text{m}^{-1}\). A primary source of CDOM in natural waters is terrestrial runoff, with riverine inputs in the coastal ocean being a substantial driver of observed distributions. A key sink for CDOM is photodegradation in surface waters. Normally, absorption by a dissolved substance will vary linearly with its concentration, as described by the Lambert-Beer Law. However, since CDOM is a broad pool of many dissolved compounds collectively known as humic substances, and since the composition of this pool varies, absorption (or fluorescence) by CDOM cannot generally be used to quantifiably derive CDOM...
concentrations (Blough and Blough 1994). Spectra of $a_g$ monotonically decrease with increasing wavelength (Fig. 1.1), and are typically modeled reasonably well with an exponential or power law model (Bricaud et al. 1981; Twardowski et al. 2004). Either model fit, however, is only an approximation of the spectral shape of absorption from a complex mixture of compounds, so the spectral range over which a slope is derived is an essential piece of information that should be additionally reported (Twardowski et al. 2004; Loiselle et al. 2009). Note that much of the literature quantifies CDOM concentration by the associated magnitude of the absorption coefficient at a specific wavelength.

Figure 1.1. Typical spectral shapes of absorption by different components in seawater. a) qualitative comparison of the shapes of absorption spectra of pure water ($a_w$), phytoplankton ($a_{ph}$), non-algal particulate (also detrital) matter ($a_{nap}$), and CDOM ($a_g$); b) absolute spectral absorption coefficients of total absorption ($a_t$), total particulate absorption ($a_p = a_{ph} + a_{nap}$), and $a_g$. Absorption spectra were analyzed on a sample collected from the German Bight (R. Röttgers, unpubl. data).
Preparing a sample for measurement involves removing particles via filtration, but the filter type and pore size are important considerations. For processing samples in the lab, glass fiber disk filters (GF/F) are sometimes used, but care should be taken to pre-rinse these filters, as glass fibers may leach into the filtrate. The nominal pore size of GF/Fs are 0.7 \mu m, but may be <0.5 \mu m, according to Chavez et al. (1995). A better option is polycarbonate disk filters that do not contaminate the filtrate and have a more restrictive pore size of 0.2 \mu m, although sample flow rates through these filters are slower than for GF/Fs. Another option is hydrophilic nylon, pleated capsule filters that can accommodate substantial flow rates with a relatively small pore size of 0.2 \mu m. These are preferred for \textit{in situ}, continuous flow methods for determining absorption. The outer capsule of these filters may be carefully removed to additionally enhance flow rates. Note that time is important, as the material passing through filters can recombine into particles following filtration (Verdugo 2012).

Possible effects of contamination of absorption measurements from any colloidal particles remaining in the filtrate depend on the pore size of the filter that was used, turbidity characteristics of the original sample, and the method for determining absorption. Such particles may have non-negligible absorption, and may cause a scattering error for certain measurement devices (e.g., reflective tube absorption meters and conventional bench top spectrophotometers). Possible scattering errors for reflective tube absorption meters have been found to be negligible for a wide range of natural waters passing through a 0.2 \mu m pleated capsule filter by confirming agreement with concurrent measurements of attenuation (i.e., absorption plus scattering) (Twardowski et al. 1999, 2004). It may be assumed that if there is negligible scattering in these filtered samples, that any particulate absorption cross-section should also be negligible. However, scattering errors have been found previously for samples with high sediment loads dominated by clays, analyzed with a bench top spectrophotometer. Röttgers and Doerffer (2007) also noted a scattering error for bench top spectrophotometric measurements of North Sea samples passed through 0.22 \mu m filters. The effect may have resulted from microbubbles induced by vacuum filtration, making the impact sporadic.

Once a sample is 0.2 \mu m filtered, it may be stored at 4° C for at least several weeks before analysis without biasing laboratory absorption measurements (Green and Blough 1994). It is advisable to refilter samples after storage, as any particles forming from coagulation during storage should be removed. Care should be taken to ensure water blanks and samples are at the same ambient temperature (Section 1.1). Caution should also be exercised in handling samples to avoid contamination.

1.3 Absorption by Particles in Suspension
Spectral absorption determined in a whole sample, i.e., containing both particulate and dissolved fractions, is typically represented as $a_p(\lambda)$. Since many techniques use pure water blanks, this is a commonly measured IOP. Total spectral absorption $a(\lambda)$, important for remote sensing algorithm work, would then be derived by adding water absorption $a_w(\lambda)$ to $a_p(\lambda)$ (accounting for specific temperature and salinity characteristics of the water). If $a_p(\lambda)$ is obtained from measurements then the determination of the particulate absorption coefficient, $a_p(\lambda)$, requires subtraction of $a_w(\lambda)$ from $a_p(\lambda)$, which indicates that $a_w(\lambda)$ must also be measured or known. There also exist techniques for measuring the particulate absorption coefficient more directly, for example the so-called filter-pad technique, further described in Section 5 of this volume (e.g., Mitchell 1990; Tassan and Ferrari 1995; Stramski et al. 2016).

It is usually convenient to partition the spectral absorption coefficient associated with particles, $a_p(\lambda)$ with units m$^{-1}$, into the spectral absorption coefficient of pigment-containing phytoplankton, $a_{ph}(\lambda)$, and the spectral absorption coefficient of non-algal particles, $a_{NAP}(\lambda)$ (note that historically a term detrital absorption coefficient denoted as $a_d$ has been used to refer essentially to non-algal absorption). This two-component description of particulate absorption is useful because the pigments in phytoplankton produce unique spectral structure whereas most NAP absorption spectra monotonically decrease with increasing wavelength (with notable exceptions for mineral particles containing iron; see Babin and Stramski 2004, Estapa et al. 2012). The convenience of this grouping extends to bench top absorption measurement techniques that allow individual quantification of phytoplankton and NAP through the use of pigment extracting solvents such as methanol (Kishino et al. 1985). Note that, as a result of this experimental method, $a_{ph}(\lambda)$ specifically represents the absorption by extractable pigments only, primarily associated with phytoplankton. The absorbing fraction of NAP, $a_{NAP}(\lambda)$ obtained from this method is generally assumed to be composed of organic detrital material and minerogenic particles, although other absorbing compounds such as non-extractable components of phytoplankton cells (for example, phycobilins) and...
heterotrophic microorganisms may also contribute to NAP absorption. Nevertheless, the difference between the measured total particulate absorption, \(a_p(\lambda)\), and \(a_{NAP}(\lambda)\) is commonly assumed to represent phytoplankton absorption coefficient, \(a_{ph}(\lambda)\). This extraction-based method as applied to a filter-pad technique has long been in routine use in the analysis of particulate absorption and its components in natural seawater samples, (e.g., Bricaud and Stramski 1990). Example spectra of \(a_{ph}\), \(a_{NAP}\), and \(a_g\) are shown in Fig 1.1.

Other approaches to experimentally separate the absorption contributions of phytoplankton pigments and non-algal particles or organic and inorganic particles have been also proposed in the past such as exposure of sample to UV radiation (Konовалov and Bekasova 1969), bleaching of sample with a strong oxidizing agent sodium hypochlorite (Ferrari and Tassan 1999), and combustion of sample at high temperature (Bowers et al. 1996). To our knowledge the UV treatment was used only in early work of Russian investigators. Bleaching with sodium hypochlorite is generally considered to oxidize phytoplankton pigments faster than other particulate organic matter, so this method has been commonly assumed to separate the absorption signals associated with these two components. The use of strong bleaching agent can, however, introduce unwanted effects and artifacts, especially in the short-wavelength portion of the visible spectrum and in the UV, which is a significant limitation of its applicability. The method based on high-temperature combustion involves the removal of organic material from particulate sample at 500°C. The absorption measurement of the combusted particles is assumed to represent the inorganic (mineral) particles. Thus the difference between the measured total particulate absorption coefficient, \(a_p(\lambda)\), and the mineral absorption coefficient, \(a_{in}(\lambda)\), provides an estimate of the absorption coefficient of organic particles. Note that in this method the organic particles comprise phytoplankton pigments and other combustible organic material including detrital matter. The combustion method may affect the optical properties of the inorganic particles remaining in the sample after the high-temperature treatment, which is a significant limitation. The bleaching and combustion methods have not been in routine use and the methanol extraction has remained as most widely used method for experimental partitioning of \(a_p(\lambda)\) into \(a_{NAP}(\lambda)\) and \(a_{ph}(\lambda)\) components.

The particulate absorption coefficient or its components can be represented as a product of mass-specific absorption coefficient of a specific constituent and the mass concentration of that constituent in water. For example, the phytoplankton absorption coefficient, \(a_{ph}(\lambda)\), can be expressed as a product of chlorophyll \(a\)-specific absorption coefficient of phytoplankton, \(a^*_{ph}(\lambda)\) with units \(\text{m}^2 \text{mg}^{-1}\), and concentration of chlorophyll-\(a\), Chl, with units \(\text{mg} \text{m}^{-3}\) (e.g., Prieur and Sathyendranath 1981) Therefore, \(a_{ph}(\lambda)\) can be derived if \(a^*_{ph}(\lambda)\) and Chl are known or assumed. There is a large body of literature on Chl-specific phytoplankton absorption based on both field measurements of natural phytoplankton populations and lab measurements of phytoplankton cultures; for example, empirical relationships between \(a^*_{ph}(\lambda)\) and Chl have been established on the basis of large field data sets which enable estimations of \(a^*_{ph}\) and also \(a_{ph}(\lambda)\), from measurements of Chl (Bricaud et al. 1995). Similar relationships were established for chlorophyll-specific absorption coefficient of total particulate matter, \(a^{**}_p(\lambda)\) (Bricaud et al. 1998). The determinations of mass-specific absorption coefficients for non-algal particles, notably for mineral fraction of particulate matter or mixed particulate assemblages dominated by mineral fraction have been also addressed in numerous studies in the past (e.g., Bowers et al. 1996; Binding et al. 2003; Babin and Stramski 2004; Stramski et al. 2004; Bowers and Binding 2006; Stramski et al. 2007; Estapa et al. 2012). In these studies, the mass-specific absorption coefficients were expressed on the basis of determinations of mass concentrations of mineral particles, total suspended particulate matter, or iron content of particulate matter.
1.4 General Comment on Measuring Absorption Components

Some IOPs can be resolved directly, whereas others must be derived or even inferred from other measurements. Some sensors and methods are designed for \textit{in situ} data collection, whereas others are intended for laboratory use. Laboratory-based methods have the advantages of a stable environment and power, and the ability to process samples before measurement if desired. Disadvantages include the requirement of sample collection and transfer, which may alter constituents of the water media in some ways and logistically restricts the number of possible samples and associated spatial resolving capability. Laboratory methods capable of accommodating continuously flowing samples from a ship can allow greater lateral spatial resolution in IOPs. The next several chapters detail the current state-of-the-art for in-water and lab based methods of determining the absorption coefficient and its components.
Table 1.1. Current state-of-the-art in pure water absorption coefficients and uncertainties between 180 and 1230 nm (see text for sources and detail) and coefficients for the dependency of pure water absorption on temperature and salinity for available spectral ranges. Rottgers et al. (2014) temperature and salinity dependencies represent best estimates of the physical constants whereas the Sullivan et al. (2006) values are specific to WET Labs ac-s devices. Addendum: Table has not been updated with recent values in the 250-550 nm range from Mason et al. (2016).
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REFERENCES


Chapter 2: Reflective Tube Absorption Meters

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The present chapter focuses on absorption measurements from commercial devices known as the ac-9 and ac-s (WET Labs, Inc., Philomath, OR, USA), which concurrently measure spectral absorption and attenuation (Zaneveld et al. 1992). These sensors and associated methods have defined the conventional in-water approach for measuring absorption in natural waters over the last 25 years. These sensors have been deployed in support of ocean color algorithm development and validation activities from ships in vertical profiling and underway flow-through systems, moored platforms, towed platforms, autonomous underwater vehicles, autonomous profilers, and helicopters (e.g., Twardowski et al. 2005).

2.1 The Reflective Tube Approach

2.1.1 Background: measuring volume absorption coefficients for medium with particles in suspension

To determine the spectral volume absorption coefficient \( a(\lambda) \) with a source and detector pair arranged on a common axis of length \( \Delta r \), the flux reaching the detector window \( \phi_k \) from the incident source flux \( \phi_i \) must include the sum of directly transmitted and scattered fluxes, i.e. \( \phi_k = \phi_i + \phi_s \). If the source and collector are equal in area and the water path between them enclosed in a perfectly reflecting tube, then all forward scattered photons would be redirected into the beam and reach the detector. For the present, we will postpone consideration of the flux loss due to backscattered photons and treat it as being negligible.

Under this construct and assumption, the Eq. 2.1 may be written as:

\[
\lim_{\Delta r \to 0} \frac{\phi_i(\lambda) + \phi_s(\lambda) - \phi_k(\lambda)}{\phi_i(\lambda) \Delta r} = \lim_{\Delta r \to 0} \frac{A(\lambda)}{\Delta r} = a(\lambda)
\]

where \( A \) is absorptance and represents the ratio of absorbed flux to incident flux.

Equation 2.1 may be expressed in differential form (Eq. 2.2):

\[
\frac{d\phi_k(\lambda, r)}{\phi(\lambda, r)} = -a(\lambda) dr.
\]

Eq. 2.2 can be integrated over discrete path 0 to \( r_T \) to obtain Eq. 2.3:

\[
a(\lambda) = \frac{\ln \phi_o(\lambda, 0, 0, \bullet) - \ln \phi_k(\lambda, r_T, 0, \bullet)}{r_T} = \frac{-\ln T_k(\lambda, r_T)}{r_T} \text{m}^{-1}.
\]

Therefore, knowing path length \( r_T \), \( a \) can be derived from measurements of incident and transmitted fluxes. In practice, relative intensities for these fluxes are measured and absolute absorption coefficients are derived using a reference material as a blank (Section 2.3). The typical reference material for ocean optics applications has been purified water, discussed later in this chapter.

Absorption measurement accuracy \( da/a \) is approximately equivalent to \( dS(e^{ar}/ar) \), where \( S \) is the electronic noise in the measured signals (Hajerslev 1994). Accuracy is thus optimized when \( ar = 1 \). Theoretically, this relationship can be used to choose an optimal path length \( r \) for a water type of interest with specific \( a \). The optimal path length achieves a balance between progressive loss of transmitted signal with longer path lengths (i.e., signal-to-noise limitation for the transmission detector) and progressive loss of ability to resolve smaller changes in transmitted versus incident power with smaller path lengths (coupled A/D bit noise limitation). Increasing the path length therefore provides a large change in transmitted power relative to incident power, which is a desirable characteristic for resolving the amount of absorbed flux, but signal-to-noise continually decreases for the transmission detector. The opposite is
true for decreasing path lengths. In practice, very long path lengths (i.e., several meters would be ideal for
the open ocean) are not possible with the practical embodiment of a sensor, so increases in accuracy have
been primarily achieved through minimizing $dS$ by optimizing electronics.

Technology intended for in situ measurements has a myriad of design challenges associated with
working in a medium that is chemically active and conductive, often exposed to high ambient light, under
significant pressure, laden with living and nonliving particles that may foul optical windows and
mechanical components, highly variable in temperature, and relatively viscous with associated drag and
boundary layer effects. The most significant advantages are measurement in the ambient medium with as
little sample disruption as possible (particularly when the measurement can be made in a remote volume)
and high spatial resolution. Sampling rate for in situ sensors directly influences spatial resolving capability.
Various forms of autonomous deployment have the potential to dramatically increase the temporal and/or
spatial resolving capabilities for absorption relative to conventional static ship profiling, although possible
errors from calibration drift and biofouling must be effectively managed. Considering these challenges,
impressive levels of accuracy have nonetheless been achieved using in-water reflective tube sensing
capabilities when the proper protocols are followed.

2.1.2 Reflective tube absorption meter concept

The reflecting tube method has been used to measure spectral absorption in the laboratory for many
decades (James and Birge 1938). The basic method involves retention of most of the forward scattered
light in the detected signal when passing a collimated light beam through a particle suspension, enabled by
using a highly reflective cuvette that redirects scattered light toward a diffuser in front of a detector. A
highly reflecting cuvette may be simply achieved from a quartz tube surrounded by air (Zaneveld et al.
1992, 1994; Kirk 1992, 1995). It is thus readily apparent that a typical cylindrical cuvette used with bench
top spectrophotometers is a suitable reflecting tube; such an apparatus may be made an effective reflective
tube absorption meter by placing a diffuser such as opal glass or a dampened filter pad at the end of the
cuvette (Shibata 1957; Yentsch 1962). The method is therefore relatively straightforward to carry out with
typical commercially available bench top equipment.

As mentioned, a reflective tube absorption meter has also been the primary method for carrying out in situ
absorption measurements in the field for the last 25 years (Zaneveld et al. 1992). The primary
disadvantage in the general method is that a significant amount of scattered light in the cuvette is not
directed toward the diffuser, resulting in a scattering error that requires some sort of correction scheme
(Zaneveld et al. 1994). Additionally, as natural particle composition varies, the fraction of scattered light
that is not considered in the measurement also varies.

In Section 2.1 it was observed that to determine the absorption coefficient associated with transmission
over an optical path length $r_t$, it would be necessary to measure the sum of transmitted and scattered flux
at the detector, $\Phi_K(r_t) = \Phi_T(r_t) + \Phi_B(r_t)$. Neglecting backscattering (typically no more than 2-3% of
total scattering), it was suggested that perhaps one might redirect all forward scattered flux to the detector
using an ideal reflective tube, and determine the absorption coefficient as

$$a = \frac{-1}{r_t} \ln \left( \frac{\Phi_T(r_t) + \Phi_B(r_t)}{\Phi(0)} \right).$$

(2.4)

Of course, a perfectly reflecting tube cannot be realized in a practical embodiment of an instrument.
Nevertheless, because the scattering phase function of suspended particles in natural waters is strongly
peaked in the forward direction (e.g., Jonasz and Fournier 2007), it is generally possible to retain about 75
- 85% of scattered photons in the beam reaching the diffuse detector apparatus of such an instrument for
natural waters. Note that the exact fraction is a function of the phase function of a particular natural
hydrosol and the properties of the specific reflecting tube. James and Birge (1938) built a laboratory version
of such an instrument to measure absorption spectra of lake waters, and Zaneveld et al. (1992) introduced
an instrument of this type for in situ absorption measurements. In some sense, such an instrument is simply
a poor transmissometer, failing to exclude all of the singly scattered photons from its beam transmittance
measurement, and therefore, in its ideal realization would measure only losses due by absorption as per
Eqs. 2.1 and 2.2.
The transmittance, absorption, scattering and reflection interaction processes that occur in a real reflective tube absorption meter are illustrated schematically in Fig. 2.1. A source emits collimated flux with a cross-sectional area slightly less than that of the reflective tube, and flux reaching the other end of the tube is measured by a detector behind a diffuser that covers its entire cross-sectional area. The diffuser is necessary to ensure the detected signal does not have any bias toward the directionality of the rays received at the end of the cuvette. Ray paths extending directly from the source to the diffuse detector indicate direct transmittance of flux. Ray paths that terminate within the water volume enclosed by the tube indicate absorbed flux. In natural waters a large fraction of scattered photons are only slightly deflected in the near forward direction (Fig. 2.1) and proceed directly to the large-area detector without encountering the tube walls. Ray paths with larger scattering angles may encounter the water-quartz interface, where refraction and reflection take place; the refracted portion is transmitted to the outer quartz-air interface, where another refraction and reflection interaction occurs. For simplicity in this conceptual discussion, we do not consider multiple reflection and refractive transmittance interactions within the thin quartz layer. Ray paths containing a scattering angle less than the critical angle $\psi_c$ associated with total internal reflection (TIR) at the outer quartz-air interface, are totally reflected on each encounter with the tube wall and are transmitted to the detector over a slightly elongated path; for a quartz reflective tube, $\psi_c \approx 42^\circ$, and thus the total internal reflectance represents a large fraction of all flux scattered by particles.

Flux transmitted along ray paths with a scattering angle in the range $\psi_c < \psi < \frac{\pi}{2}$ undergoes partial transmittance losses $[1 - \rho_\theta (\psi)]$ at each encounter with the reflectance tube, with the reflected portion continuing over a zig-zag path until either reaching the detector or disappearing due to attenuation by absorption and transmission losses in multiple encounters with the tube wall. Flux along ray paths containing a scattering angle $\psi \geq \frac{\pi}{2}$, i.e. backscattered flux, is generally lost from the forward transmittance altogether.

![Figure 2.1. Schematic illustration of light interactions and transmission in a reflective tube absorption meter.](image)

**Figure 2.1.** Schematic illustration of light interactions and transmission in a reflective tube absorption meter. Ray paths ending in the water represent absorption, and those extending directly from the source to diffuse detector represent beam transmittance. Other ray paths indicate scattering interactions: 1) backward scattered paths do not reach the detector, 2) paths with forward scattering at an angle less than the critical angle, i.e. $\psi \leq \psi_c$, experience total internal reflection by the tube and reach the detector over an elongated optical path, and 3) forward scattered ray paths at angles in the range $\psi_c < \psi < \frac{\pi}{2}$ experience partial losses from the tube at the quartz-air interface, and may or may not reach the detector depending on whether the internally reflected path survives the absorption process. Light paths reflecting off windows at the end of the tube are not shown for clarity.

Given the above, in the single scattering approximation, the flux measured by the detector of a reflective tube absorption meter may thus be written as:

$$\text{Flux} = C \int |\mathbf{E}(\mathbf{r}, \omega)|^2 \, d\mathbf{r}.$$
\[ \Phi_m(r_f) = \Phi_i(r_f) + 2\pi \Phi_o(0) \int_0^{r_f} \int_0^\infty \beta(\psi) e^{-\frac{2\pi}{r_o^2} \sin \psi d\psi} dr + 2\pi \Phi_o(0) \int_0^{r_f} \int_0^\infty \beta(\psi) e^{-\frac{2\pi}{r_o^2} \sin \psi d\psi} \left[ \rho(\psi) \right]^{N(r_i-r)} \sin \psi d\psi dr, \quad (2.5) \]

where \( \rho(\psi) \) is net reflectance of the quartz tube beyond the critical angle, and the exponent \( N(r_i-r;\psi) \) is the average number of wall reflections required for a ray path to reach the detector following a scattering event at distance \( r \) and angle \( \psi \). The first integral on the right-hand-side of Eq. 2.5 represents flux scattered at angles less than the critical angle over the optical path, and the second integral represents flux reaching the detector following scattering by angles greater than the critical angle. In either case, the path length to the detector from a scattering interaction at distance \( r \) is \( \frac{r_f - r}{\cos \psi} \), and both types of scattered-reflected paths are attenuated by absorption over this elongated path. The second term also is reduced by incomplete reflectance in \( N(r_i-r;\psi) \geq 1 \) interactions with the reflective tube. This is not a complete description, as some light scattered close to the diffuser at angles larger than \( \Psi_r \) will still impinge on the diffuse-detector assembly and some light will be reflected off both source and detector windows back into the tube.

The measured absorption coefficient is therefore greater than the true absorption coefficient since

\[ a_m = -\frac{1}{r_f} \ln \left( \frac{\Phi_m(r_f)}{\Phi_o(0)} \right) > a = -\frac{1}{r_f} \ln \left( \frac{\Phi_i(r_f) + \Phi_o(r_f)}{\Phi_o(0)} \right), \]

and the two may be related as

\[ a_m = a + 2\pi \int_0^\infty W(\psi) \beta(\psi) \sin \psi d\psi, \quad (2.6) \]

where the weighting coefficient \( W(\psi) \) accounts for the absorption and wall reflection losses in the two integral terms of Eq. 2.5 and for the exclusion of backscattering in the measured flux. In other words, the weighting coefficient \( W(\psi) \) may be interpreted as the fraction of light that is scattered at angle \( \psi \) that does not reach the absorption detector; it may take values from 0, indicating all light scattered at that angle reaches the detector, to 1, indicating that none of the light reaches the detector. Note this error term, often denoted as \( \varepsilon \), is a function of the angular shape of the VSF (\( \beta \)) and thus will vary with associated natural variability in particle composition.

McKee et al. (2013; and also mentioned in Leymarie et al. 2010) numerically modeled the weighting function for the scattering error of WET Labs ac devices with Monte Carlo simulations. They computed a presumably more accurate weighting function for a theoretical 100% TIR cuvette, accounting for all possible reflections (Fig. 2.2). They additionally tested the effect of varying the reflectivity efficiency (from 95 to 100%) of the flow tube wall, since it may be reasonably assumed that, either through imperfections in the manufacturing of the tube and/or wear through use, ideal or even consistent reflectivity may not be achieved in practice. All modeled weighting functions (including the ideal 100% reflectivity case) exhibited non-negligible weightings at angles smaller than the angle of TIR, i.e., the error included significant scattering at angles smaller than the angle of TIR (Fig. 2.2). Because the VSF is steeply forward peaked, these weighting functions are expected to appreciably increase the relative error, from about 5-15% of total scattering (Zaneveld et al. 1994), to an estimated 15-25% (McKee et al. 2013; Rötgers et al. 2014). The amount of scattering in the angular range \( \Psi < \text{TIR} \) that is included increases dramatically with small decreases in the reflectivity of the flow tube surface from the ideal value of 100%.

Beyond typical random electronic noise, uncertainty of absorption coefficients determined from measurements with a reflective tube instrument is largely determined by the uncertainty of the methods used to correct for the integrated scattering error (Zaneveld et al. 1994), which will be discussed in Section 2.5. The remaining sections of this chapter summarize protocols related to characterization, measurement...
and data analysis for the commercially available WET Labs reflective tube absorption meters, known as the ac-9 and ac-s.

![Diagram](image)

Figure 2.2. Modeled angular weighting functions for the scattering error of the reflective flow tube used in WET Labs ac devices, assuming different initial reflectivities of the inner surface of the tube (from McKee et al. 2013). Angle of total internal reflection (TIR) for a quartz tube surrounded by an air gap is ~42°.

### 2.2 Description of a Reflective Tube Spectral Absorption Meter

The following sections pertain to the commercially available ac-9 and ac-s devices manufactured by WET Labs, Inc. As of 2014 the ac-9 is not commercially sold but is still serviceable by WET Labs. These sensors concurrently measure absorption and attenuation through two separate optical systems sharing a rotating wheel with embedded interference filters, integrated into a single device (Fig. 2.3). For each optical path, the quasi-collimated beam from a dedicated tungsten lamp source is sampled by a reference detector using a beam splitter, with the remaining beam passing through the interference filter and subsequently entering the sample volume through an optical glass window. The absorption measurement uses a reflecting quartz tube surrounded by an air gap as a flow cell, with a diffuse collector at the end of the tube, in front of a large area detector. For spectral discrimination, the ac-s uses a linear variable filter (LVF) spliced into 2 segments, individually mounted on the rotating wheel, with each segment imaged in typically 42 discrete spectral locations to provide 84 wavelengths in typically the 398–730 nm spectral range. The spectral split typically occurs around 574 to 578 nm. Individual spectral increments are therefore about 4 nm, and have full-width-half-maximum (FWHM) bandwidths ranging between about 10 nm for centroid wavelengths near the center of each filter, to about 18 nm for centroid wavelengths near the edges of each filter. With the ~4 nm spectral resolution of the ac-s, there are methods of analytically approximating removal of the smoothing or damping effect of the bandwidths on spectra (Sullivan et al. 2006; Chase et al. 2013, with code provided to implement). The ac-9 uses 9 individual interference filters, each with a typical bandwidth of 10 nm. Because of the bandwidths used for both ac-9 and ac-s, absorption measurements near the peak for in vivo chlorophyll absorption (~675 nm) include some fraction of chlorophyll fluorescence (centered at ~683 nm), although the fluoresced light is only a few percent at most relative to the absorbed light and fluorescence overlaps the tail of the 10 nm FWHM bandwidth of the absorption measurement centered at 675 nm. Because of the inherent similarities between the ac-s and the ac-9, all procedures described in this document generally pertain to both instruments, except where noted.

WET Labs ac devices employ either a 10 cm or 25 cm path length for the sample volume. As the optimal path length in measuring absorption for a given environment is normally equivalent to the inverse of the absorption coefficient of the natural water medium (hydrosol) of interest (Section 2.1), the two path length choices for ac devices are theoretically optimal for water with 10 m⁻¹ and 4 m⁻¹ absorption, respectively. The vast majority of coastal and open ocean waters exhibit absorption coefficients far lower than these values; in fact, open ocean absorption values in the green part of the visible are typically 1-2
orders of magnitude lower than the 4 m\(^{-1}\) value. However, 20 m path lengths are impractical for routine in situ measurements. Adequate signal-to-noise is nonetheless achievable using a 25-cm path length due to advances in A/D conversion and stable, quiet electronics over the past several decades. Acceptable accuracies are even achievable for the clearest waters on Earth with a 25-cm path (Twardowski et al. 2007; Claustre et al. 2007). Accuracy can be further increased by averaging over a large number of measurements, e.g., when deploying ac-meters on moorings or in-line systems or on profiling systems with slow rates of descent/ascent (Slade et al. 2010).

The ac-9 and ac-s were introduced in 1993 and 2002, respectively. WET Labs provides detailed protocols for calibrating and using this instrument, and for analyzing its data, both in the ac-9 and ac-s User Manuals, and in a detailed Protocols manual (Van Zee et al. 2002), all of which are available online at www.wetlabs.com. Additional detailed background information related to characterization, calibration, and data analysis methods for this instrument may be found in Zaneveld et al. (1992) and Twardowski et al. (1999). Here, we will briefly highlight critical aspects of the protocols that must be carefully followed to obtain accurate \(a(\lambda)\) measurements using this, or a similar, instrument in the field.

![Figure 2.3. Schematic illustration of the ac-9 beam attenuation and absorption meter (courtesy of WET Labs).](image)

### 2.3 Calibration of a Reflective Tube Spectral Absorption Meter

#### 2.3.1 Pure water calibration

Reflective tube absorption measurements require calibration to some reference medium because gains for the \(F_m\) and \(F_i\) detectors are relative and not absolute measures of power. Even if these detectors were calibrated to absolute power using the best techniques available, one would also have to account for the transmission and reflection characteristics of every interface in the optical path to avoid using a reference. Detector responses and the component interface characteristics also change over time with use, so that a complete reassessment would continually be required. It is far simpler to calibrate by passing a reference solution with rigorously characterized optical properties through the sample volume in the exact configuration the sensor will be used for actual measurements. This can be repeated over time to track
calibration drift. An acceptable substance for such calibrations at this time is purified water produced by commercially available water polishing systems with resin cartridges for the removal of organic impurities and a UV oxidizing lamp to remove CDOM. If the interest is only in particulate measurements, periodic measurements of dissolved materials (e.g. water passing through a 0.2 µm filter) can serve as the appropriate reference, with any purified water calibration effectively canceling (e.g., Boss and Zaneveld, 2003).

The calibration equation for measured absorption $a_m$ blanked to purified water, is:

$$a_m = \frac{1}{r} \ln \left( \frac{V_{samp}(V_{rfac})}{V_{scal}(V_{rsamp})} \right)$$  \hspace{1cm} (2.7)

$$a_{wcal} = \frac{1}{r} \ln \left( \frac{V_{wcal}(V_{rfac})}{V_{scal}(V_{real})} \right)$$  \hspace{1cm} (2.8)

$$a_{corr} = a_m - a_{wcal} = \frac{1}{r} \ln \left( \frac{V_{samp}(V_{rfac})}{V_{wcal}(V_{rsamp})} \right)$$  \hspace{1cm} (2.9)

where $a_{corr}$ is calibration corrected absorption, $a_m$ is absorption measured in water sample, $a_{wcal}$ is water calibration absorption, $r$ is path length, $V_{samp}$ is detector reading (voltage or digital counts) for water sample, $V_{scal}$ is reference reading during water calibration, $V_{wcal}$ is detector reading during water calibration, and $V_{rsamp}$ is reference reading for water sample. Values $V_{scal}$ (detector reading) and $V_{rfac}$ (reference reading) are from a factory water calibration supplied in a sensor-specific device file that should be used for all measurements, i.e., the factory calibration is effectively a baseline blank. Results from $a_{wcal}$ measurements can be used to track instrument drift over time. When $a_{wcal}$ is subtracted from $a_m$, the factory calibration cancels.

All resultant measurements for natural waters thus represent the absorption from all constituents in the water sample minus the absorption from purified water itself. Note the temperature of the calibration water must be recorded to correct for the temperature dependency of pure water absorption (see Chapter 1 and Section 2.5), which is typically carried out by choosing a reference temperature for all data (calibration water and field data).

2.3.2 Preparation of purified water suitable for calibration

The concept behind the water calibrations is simple. The idea is to provide the instruments with a source of bubble-free water purified of optically significant contaminants that can be used as a reference blank. As was mentioned in Chapter 1, making “pure water” is extraordinarily difficult and certainly not possible for routine sensor calibrations. The challenge then is obtaining water of sufficient optical purity on a routine basis that may approximate the pure water ideal for reflective tube absorption measurement calibrations. High end water polishing stations from commercial manufacturers such as Barnstead and Millipore that include resin cartridges for removal of organic impurities and filtration for particle removal produce water of sufficient purity for this purpose.

Water calibrations are performed by the manufacturer, but also should be performed periodically by the user to track short term drift. Instrument drift is particularly of concern when working in clear waters, where water calibrations should be carried out daily to ensure high quality data. Significant drift can also occur during instrument shipping.

WET Labs, manufacturer of ac devices, prepares purified water for instrument calibrations using a commercial deionization system and filtration system. After primary deionization, the water is processed using an Elga Medica Pro-30 polishing system and stored in a large holding tank. To maintain purity, water in the holding tank is recirculated through a UV chamber and additional particle filters. Water for calibrations is drawn through a 0.01 µm filter at the point of delivery. The circulating holding tank allows the highly reactive deionized water to equilibrate with ambient conditions and the UV chamber primarily prevents any biological growth from contaminating the reservoir.

During the manufacturer’s calibration for an ac device, the internal temperature response of the instrument electronics is also determined along with a correction matrix that is implemented during data processing. Since this correction matrix may also drift, it is recommended that an ac device undergoes a full manufacturer’s calibration if consistent departures in absorption are observed over specific internal
temperature ranges. The correction matrix produced by WET Labs is typically for instrument temperature varying from about 10 to 35°C and the correction becomes more significant (increasing potential bias errors in resulting absorption) at internal temperatures greater than about 30°C. For field measurements in extremely cold or warm waters, a calibration over an extended internal temperature range can be requested.

For field calibrations by the user, purified water can be produced in the lab and transported to the ship, especially for short cruises. On some research vessels, a water deionization and purification system is permanently installed to support the scientific party. If so, care must be taken to ensure system is adequately maintained to produce high quality purified water. Alternatively, a portable water purification system may be transported and set up temporarily on the ship. Input water should be pre-filtered and preferably passed through a deionization or reverse osmosis system to increase the lifetime of the cartridges in the purification system. Purified water should be produced in advance of calibrations, stored in a clean acid- and base-rinsed polycarbonate carboy, and be allowed to stand for several hours to equilibrate with ambient temperature and to allow removal small bubbles.

To calibrate an ac-9, the carboy may be equipped with a cap having barb fittings to connect tubing to a pressurization unit that pushes water to the instrument (Fig. 2.4). The carboy is pressurized to a few psi using an oil free air pump, a tank of dry nitrogen gas, or a hand pump. The air supply tube inside the carboy should be kept above the water level to prevent the creation of bubbles when pressurizing the carboy, and the outlet tube should extend to the bottom of the carboy. Tubing connecting the carboy to the ac-9 must be opaque to avoid ambient light leaks; the absorption channel is very sensitive in this regard. Standard Tygon tubing can be wrapped in black tape or certain types of tubing are available with an opaque black sheath. Various types of plastic tubing have chemicals that can leach into the water, possibly affecting the optical properties, although typically the water must sit in the tube for a prolonged period of time to observe this. Thus, most tubing types are fine for calibrations as long as the tubing is kept very clean. Tubing with water flowing from the carboy is connected to the bottom nozzle of the ac-9 flow tube. Tubing connected to the top nozzle (outflow) of the flow tube should have an attached valve, both to control rate of water flow through the system, and to provide backpressure, which helps to keep gases in solution and prevent the formation of small bubbles. After flow appears bubble-free, this valve can be restricting to flow rates as slow as a drip. After practice, a calibration can be achieved with as little as 500 ml purified water. It is recommended that personnel carrying out calibration are initially trained by people who routinely collect high-quality ac meter data.

Whatever the mode of deployment, it is always optimal to calibrate the WET Labs ac device while mounted in the deployment platform or cage, in the same orientation as it will be deployed.

![Figure 2.4. Schematic illustration of a pure-water supply system for field calibrations of an ac-9.](image)

2.3.3 Air calibrations

Instructions for air calibrations are provided by the manufacturer but these cannot be used as an accurate proxy for water calibration drift and thus have limited applicability (Twardowski et al. 1999).
2.4 Measuring Spectral Absorption Coefficients with Reflective Tube Meters

The ac device should be mounted for deployment following directions provided by the manufacturer (Van Zee et al. 2002). Twardowski et al. (1999) also provides additional detail for vertical profiling deployments. Opaque tubing must be attached to the inflow and outflow nozzles of the flow tubes for the absorption and attenuation measurements to avoid ambient light contamination. Sample water must be pumped through the tubes, typically with a submersible pump. A SeaBird Electronics SBE 5 is typically used. The pump is plumbed after the outflow, so the sample is effectively sucked through the sample tubes. A “Y” fitting is typically used to join the flows from the absorption and attenuation paths before reaching the pump. A degassing “Y” fitting (an inverted “Y” with an inserted Teflon plug containing a pin hole in the center) should be used after the “Y” flow fitting and before the pump to allow the entire plumbed volume to degas when the sensor is submerged (to avoid air-locking the pump). The intake tubing should be positioned at the desired sampling location on the platform. A separate intake tube should be used for each flow cell, i.e., a single intake split with a “Y” to each measurement tube should be avoided to prevent any possible particle sorting (Twardowski et al. 1999). If the ac device is vertical, the intake will be attached to the lower nozzle on the flow tubes. The device should be plumbed to enable all air to escape when the sensor is submerged. This is typically much easier to achieve when the ac device is positioned vertically. Flow tubes and optical windows should be kept clean using soft tissues such as lens paper or another low-lint wiper (e.g., Kimwipes®) and a 50% ethanol solution.

Coincident measurements of water temperature and salinity data are required for corrections described below in Section 2.5.1. This is typically achieved with an ancillary CTD. Depth positioning of the CTD relative to the ac device, as well as differences in flow rates during profiling and differences in time lag for data collection, should be accounted for in processing (Twardowski et al. 1999; Sullivan et al. 2006).

Power for the ac device and pump can be provided with onboard batteries or via a sea cable. The ac meter and pump should not be powered on until the sensor is fully submerged and degassed or the pump will not function. Degassing can be promoted by lowering the package several meters. After the ac device and pump are powered on, the package can be raised to surface and allowed to equilibrate before profiling. It is highly recommended to use a sea cable with ac meters so that data can be visualized in real time to make sure bubbles are appropriately flushed and, if CDOM absorption is being measured, particle contamination is not present (see below).

When the instrument package is stored on deck for a prolonged period between casts, cover it with a tarpaulin to protect the absorption meter from direct exposure to the sun. Excessive solar heating of the instrument may exceed the practical limits (5°C to 30°C) of internal temperature corrections for an ac-9, and thus invalidate its measurements until it has cooled sufficiently to restore normal operations.

2.4.1 Filtering the water intake port of an ac-9 for measurements of absorption by CDOM

The absorption coefficient of dissolved material may be measured by attaching a 0.2 µm pore-size filter to the intake(s) of an ac device. Measurements in the filtered intake configuration are also very useful for testing the operational performance of ac-9; quality control procedures using dissolved measurements are discussed in Section 2.6. Note that after particle removal, both the absorption and attenuation measurement should be nominally equivalent. This is a case where the flow may be split to each flow cell with a “Y” connected to a single intake with attached prefilter.

Examples of suitable filters are the Pall Gelman Suporcap 100 and Pall Gelman Maxi-cap (0.2 µm) filters. Generally, these are pleated, hydrophilic filters with large surface areas. These filters have high flow rates at low differential pressure and do not adsorb or leach materials. The outer housings of these commercial filter cartridges may be cut off to expose the pleated filter and increase the flow-rate. Before use, a filter should soak for several hours in clean water to remove air pockets in the filter membrane.

Replace the filter when it becomes visibly discolored. With prolonged measurement in productive coastal waters, this can be daily. Soaking the filter in clean water between measurements can prolong life of the filter. Flow rates through a filter decrease with use, requiring techniques to independently estimate lag time for each cast (Twardowski et al. 1999). Slow flow rates smear fine structure in absorption
measurements. An indirect technique for estimating flow-rate related lag times is to match depths of changes in the \( \alpha \) (715) channel with depths of strong changes in water temperature; these changes are linked because absorption by water is temperature dependent in the near infrared (Section 2.5.1), and the time lag between matched changes can be derived from the depth separation and the profiler rate of descent. Another technique is to profile consecutively at different descent rates. Once the correct flow lag time is chosen, then inflections in vertical structure of absorption become aligned.

A combination of unfiltered and filtered ac measurements can be used to derive particle absorption. There are several combinations that can be used:

- From measurements using a single ac with the c side filtered and the a side unfiltered, particulate absorption can be obtained as \( a_p(\lambda) = a(\lambda) - a_w(\lambda) - [c_g(\lambda) - c_{gw}(\lambda)] \), where the measurements have been corrected using the methods described in Section 2.5 below. The subscript “g” is associated with CDOM, based on historical use of the term “Gelbstoff", or yellow-matter, as a pseudonym of CDOM.

- From measurements with two ac devices, one filtered and one unfiltered, \( a_p(\lambda) \) is derived directly from the filtered measurements, after the corrections of Section 2.5, and \( a_p(\lambda) = a(\lambda) - a_w(\lambda) \), where \( a(\lambda) \) is derived from the unfiltered instrument.

- Another alternative approach is to make successive casts (if profiling) with one instrument, filtering the a intake on one cast, and the c intake on the other. The filtered and unfiltered measurements from the two casts can be combined as above.

The approach yielding the lowest instrumental uncertainty of the particulate absorption is to derive it from filtered and unfiltered measurements with the same instrument on consecutive casts. Calibration offsets, whether known or not, are identical in the filtered and unfiltered measurements on each side, and therefore, the offsets cancel when particle absorption is determined as the difference between the two measurements. On the other hand, potentially larger uncertainty may result from possible changes in the IOP profiles between casts, due to horizontal advection and/or vertical displacement of IOP features by internal waves. For consecutive casts, it is optimal to align optical properties with respect to density.

### 2.5 Data Analysis Methods

A purified-water blank, corrected to a chosen reference temperature (see below), is first subtracted from the raw collected data. Two additional analysis steps are necessary to obtain accurate absorption coefficients from an ac device or similar instrument: 1) corrections for \textit{in situ} water temperature and salinity, and 2) corrections for scattering errors.

#### 2.5.1 Temperature and salinity corrections

The absorption by pure water exhibits linear dependencies on temperature and salinity described in Chapter 1 and Table 1.1. Pegau et al. (1997) and Twardowski et al. (1999) have empirically determined values for the linear slopes for these dependencies for the ac-9 and Sullivan et al. (2006) has values for the ac-s (Table 1.1). It should be noted that the Sullivan et al. (2006) values were for a specific ac-s (one of the first produced). Changes have since been made by WET Labs in wavelength registrations, so these coefficients make not ideally suit other ac-s devices.

Temperature and salinity corrections are applied to measured absorption according to:

\[
a_{\text{in}S}^S(\lambda) = a_{\text{in}}(\lambda) - \frac{\partial a_w(\lambda)}{\partial T}(T - T_c) - \frac{\partial a(\lambda)}{\partial S}S.
\]  

(2.10)

The salinity term is left out when applying to water calibrations. Temperature and salinity must be measured concurrently to apply these corrections. Note any temperature can be chosen for \( T \), since the purified water blank that is corrected to the same \( T_c \) must be subtracted in a previous processing step, i.e., the temperature effect is ultimately being completely removed.

Corrections for temperature and salinity dependences only become significant at red and near-infrared wavelengths (see Table 1.1). However, it should be noted that some scattering correction methods for all
wavelengths discussed in the next section depend on accurate values of \( a_m^{TS}(\lambda_{NIR}) \) and \( c_m^{TS}(\lambda_{NIR}) \) at a near-IR reference wavelength, normally \( \lambda_{NIR} \approx 715 \) nm for an ac device. Since naturally occurring absorption is typically low in the near-IR, especially for oceanic waters, accurately correcting for temperature and salinity becomes critically important in optimizing accuracy in final absorption spectra with these methods.

### 2.5.2 Scattering correction methods

Systematic scattering offsets between true absorption and absorption measured with a reflective tube instrument, as described in Eq. 2.6 and related text in Section 2.2, were evaluated by Zaneveld et al. (1994). They recommended three possible methods for correcting the scattering offsets to the measured absorption \( a_m^{TS}(\lambda) \) after water blank, temperature, and salinity corrections.

**I. Baseline correction.** Subtract the measured absorption at a near infrared reference wavelength, e.g., \( \lambda_{NIR} = 715 \) nm, from the entire absorption spectrum. This method assumes negligible absorption at \( \lambda_{NIR} \) so that the entire measured signal at the reference wavelength is due to wavelength independent scattering errors. The value of \( a_m^{TS}(\lambda_{NIR}) \) should be reported with the corrected absorption values when this method is used. Importantly, if measurements of absorption in the dissolved fraction (CDOM) are also available, any absorption from CDOM observed at the reference wavelength should be removed before applying this method.

**II. Constant percentage error.** Assuming a wavelength-independent scattering phase function appropriate for the type of particles in a given water mass, and a weighting function \( W(\psi) \) based on instrument characteristics, estimate \( F = \varepsilon/b, \) i.e., the scattering error relative to total scattering, multiply this \( F \) by estimated scattering at each wavelength, and subtract from the measured absorption at each wavelength:

\[
a(\lambda) = a_m^{TS}(\lambda) - F [c_m^{TS}(\lambda) - a_m^{TS}(\lambda)].
\]

Note that the \( b \) derived from \([c_m^{TS}(\lambda) - a_m^{TS}(\lambda)]\) is not precisely equivalent to the \( b \) in the \( F \) estimate since the \( a_m^{TS}(\lambda) \) includes the scattering error. Measured \( c_m^{TS}(\lambda) \) also has an acceptance angle error (Voss and Austin 1993; Boss et al. 2009). Since using \( a \text{ priori} \) assumptions of particle composition and subsequent phase functions may be speculative for most measurements in natural waters, this method is not typically applied. The method may be useful, however, if a) measurements in the near-IR were not made, b) the assumption of negligible absorption in the near-IR is thought to be unreasonable (e.g. Tassan and Ferrari 2003; Rottgers et al. 2013), and c) some ancillary information about the particle field may be available that could be used to independently approximate a reasonable proportionality value. Another advantage is uncertainties about temperature and salinity corrections in the near-IR do not affect the rest of the spectrum. Several recent publications (Twardowski et al. 2001; Berthon et al. 2007; Whitmire et al. 2010; Sullivan et al. 2013) have shown using theory and experimentation that backscattering ratios \((b_0/b)\) in a broad range of natural waters are approximately spectrally independent, at least within our measurement capabilities at this time. Thus, it may be reasonably assumed that \( b_0/b \) also will approximately exhibit spectral independence as well. The fraction \( F \) may reasonably vary from about 0.1 to 0.3 for natural particle fields.

**III. Proportional correction.** This method is a combination of the first two, accounting for the spectral variation in \( \varepsilon \) as a constant proportion of total scattering \( b \). The assumption of negligible absorption by dissolved and/or particulate material in the near-IR in natural waters is made, so that the measured absorption, \( a_m \) (near-IR), is then equivalent to \( \varepsilon \). The method also relies on concurrent measurements of attenuation \( c_m(\lambda) \) so that \( b(\lambda) \) may be estimated. The method derives corrected absorption values \( a_m^{corr}(\lambda) \) as follows:

\[
a_m^{corr}(\lambda) = a_m^{TS}(\lambda) - \frac{a_m^{TS}(\lambda_r) - a_m^{TS}(\lambda)}{c_m^{TS}(\lambda_r) - c_m^{TS}(\lambda)} [c_m^{TS}(\lambda) - a_m^{TS}(\lambda)]
\]

where \( \varepsilon(\lambda) \) is the complete term to the right of subtraction, \( a_m^{TS}(\lambda_r) \) is assumed to be \( \varepsilon(\lambda_r) \) at a suitable wavelength in the near-IR (typically 715 nm; note that when evaluated at \( \lambda_r \), the term to the right reduces to \( a_m^{TS}(\lambda_r) = \varepsilon(\lambda_r) \), and the spectrally independent proportion of \( b \) that comprises \( \varepsilon \) is represented by the fraction highlighted in gray in the term on the right. Note this method does take into account that \( a_m^{TS}(\lambda) \)
in the term to the right of subtraction includes $\varepsilon (\lambda)$. Additionally, acceptance angle errors in the $c$ measurement may be expected to approximately cancel.

Considering the primary assumptions for the Zaneveld proportional correction of 1) negligible absorption from dissolved and particulate material in natural waters in the near-IR, and 2) a constant proportionality between the correction $\varepsilon$ and total scattering spectrally, the first of these is generally the most concerning (e.g. Tassan and Ferrari 2003; Röttgers et al. 2013; see discussion above on assume spectral independence in $\varepsilon/b$). In data from the North Sea, Röttgers et al. (2013) found an average of 21% of the measured absorption at 715 nm with an ac-9 resulted from real natural absorption from the dissolved and particulate fractions. Whenever any non-negligible absorption is present in the near-IR, the proportional correction will tend to overcorrect. If this fraction $F_a$ of “true” absorption at 715 nm is known or may be reasonably assumed, then a $(1 - F_a)$ term can be added to the numerator of the right hand $\varepsilon$ term in Eq. 2.12 to improve the accuracy of the correction.

There are some considerations in optimizing accuracy in applying the proportional correction to ac device data, especially in coastal waters. First, if CDOM absorption measurements have been made, non-negligible absorption by dissolved materials in the near-IR can be subtracted out before applying the correction. Note there is typically no scattering error in absorption collected in the dissolved fraction (Section 1.2). Care must also be taken in the choice of a reference wavelength, with the standard 715 nm currently serving as the convention. Since dissolved and particulate material show decreases in magnitude entering the near-IR from the visible, it would seem reasonable to choose a longer wavelength than 715 nm for the reference in the ac devices. However, uncertainties in pure water absorption due to temperature and salinity dependencies in the near-IR increase dramatically for longer wavelengths, making 715 nm a reasonable compromise.

Since the Zaneveld et al. publication in 1994, the proportional correction has generally been regarded as the most accurate method, although the necessity of assuming negligible absorption in the NIR is a significant drawback. Another drawback (also suffered by method 2) is the requirement of ancillary data. Even though attenuation data are recorded by the same instrument in an ac device, the measurement is made in a different sample volume. With sampling intakes for the $a$ and $c$ measurements positioned in close proximity, averaging of data is still usually recommended before applying this correction method to smooth out spiking from large particles that may be present in one channel or the other at any given time. Moreover, recent comparisons between the baseline correction (method 1) and the proportional correction (method 3) have shown similar results, so that the simple baseline correction may be applied in most cases without compromising accuracy relative to method 3, and without injecting additional uncertainty from ancillary measurements.

Another method currently under investigation is measuring the volume scattering function independently and deriving $\varepsilon$ using Eq. 2.6, completely independently from the ac device measurements. The key in applying this method is finding the angular weighting function for the scattering error (see Fig. 2.2) that is most suitable for an ac device reflective tube. A suitable volume scattering function measurement device is also required; currently such sensors only exist as custom builds by a few labs globally. This is an area requiring further research.

### 2.6 Quality Control Procedures

There are several quality assurance tests that can be made to check how well an ac device is operating. For instance, at the most basic level, attenuation physically must be greater than absorption. One of the most important ways to help ensure accurate measurements is replicating water calibrations with better than 0.005 m⁻¹ agreement for all wavelengths, with about 0.002 m⁻¹ agreement achievable for most sensors. If this is not achieved, then there is a problem, such as bubbles in the purified water or inside the flow tubes. Older ac-s devices may not be able to achieve this precision in the blue, however.

Filtering both $a$ and $c$ measurements for an ac device, which can be done by splitting flow from a single filter with a “Y” to both flow tubes, is a useful check, as these two spectra should be equivalent within operational errors, i.e., all convolved random and bias errors, in the absence of particles. The uncertainty from random fluctuations (i.e., standard deviation) should also be $< 0.001$ m⁻¹ for most wavelengths after particles have been removed with a prefilter, although measurements in the blue region with the ac-s can be higher. If multiple ac devices are used, periodic intercomparisons by attaching prefilters to all devices and deploying in the same water is recommended.
Operational uncertainties for an ac-9 that has been calibrated and corrected with optimal accuracy can be as low as 0.004 m$^{-1}$. This may be the expected level of agreement between fully corrected data from two ac-9s deployed in close proximity. Different ac-9s can exhibit different performance. Operational uncertainties for optimally corrected ac-s devices are slightly worse than the ac-9, typically about 0.005 m$^{-1}$. Note that there is nothing wrong with data exhibiting negative values within the uncertainty associated with random fluctuations. Averaging will remove these negative data and improve the effective signal to noise ratio. Averaging also enables a larger effective sample volume, so that relatively rare spiking from large particles may be better statistically represented in the absorption values. This is particularly appropriate for remote sensing applications where IOP data collected in relatively small sample volumes is applied to remote sensing image pixels as large as 1 km$^2$. For an ac-s, spectra should be relatively flat in the near-IR after correcting for temperature and salinity dependencies.

If concurrent profiles of downwelling irradiance $E_d$ were measured, diffuse attenuation coefficient ($K_d$) values may be derived from the exponential decrease with depth. Since $K_d$ is typically a reasonable approximation of attenuation of vector irradiance $R$, one may use Gershun’s equation as an additional check on the accuracy of the absorption measurement, $a = \mu_a K_d$, where $\mu_a$ is the average cosine of the downwelling light field, which can be approximated near the surface from sun elevation and typical sky radance characteristics (Morel and Prieur 1975).

### 2.7 Deployment Strategies of Ac-meters

Ac-meters have been deployed on a variety of platforms. General consideration: if possible, calibrate instrument on package, and the same orientation, as it will be deployed. Sample waters that have not interacted with the package (that is, on a profiling package, have intake on the bottom as you profile downward). It is best if operator can see the data in real time to be able to assess if bubbles are an issue. Ability to obtain data with and without a prefilter on the intake of the same sensor, along the same path, provides very high-quality particulate IOPs (Boss and Zaneveld 2003).

Platform types:

1. **Winched package**

   This category includes CTD rosettes (e.g. Bricaud et al. 1995; Sosik et al. 2001), and other winched packages that use a rectangular or round frame. The package is winched down with the package being significantly negatively buoyant (to avoid towing the package). Package included a CTD for temperature and salinity corrections. Only down-cast data are considered good for particulate measurements. Operator releases wire fast enough for it to be going down even when boat is rocking back and forth (0.5-1 m/s).

   **Advantage:** Can profile to several hundreds of meters rapidly.

   **Disadvantages:** Package accelerates in rough seas, which may cause noise in data due to changes in flow and instrument angle. IOPs exhibit relatively low vertical resolution. Measurements can be affected by ship shadow (if radiometers are included). To obtain dissolved and particulate spectra often two ac-meters are used in parallel (Gardner et al., 2001), or the same one with and without a filter on the intake (Boss et al. 2007).

2. **Slow Decent Rate Optical Package (SlowDROP, Barnard et al. 1999)**

   The package includes a CTD for temperature and salinity corrections and uses a rectangular or round frame with buoyancy balls attached at the top. The package descends due to the influence of gravity. Operator releases cable as package goes down being careful not to have tension on wire. Only down-cast data are considered good for particulate measurements. Calibration of the instrument on the package is important.

   **Advantages:** The package does not accelerate rapidly because it is not tied to the vessel with a tight wire and therefore does not generate spurious peaks nor does it change the angle of sensor as it profiles. This method provides a high vertical resolution IOPs (descent rate ~0.1-0.2 m/s) and can be released such that it is removed from the ship’s shadow (if radiometers are included).
Disadvantage: Requires hard work for profiling to depths below 100 m, often requiring manual power to bring back to surface.

3. Diver’s package (Zaneveld et al. 2001)

Uses sensors mounted on the SCUBA bottle on the divers back. Needs to supply sufficient buoyancy to offset optical package’s weight. Intake is in divers’ hand.

**Advantage:** can obtain data very close to bottom features.

**Disadvantage:** hard to get good positioning. Need to make sure intake’s depth is well represented by CTD.

4. Bottom Tripods

Ac-9s have been deployed for months at a time on bottom tripods (Downing et al. 2009; Slade et al. 2010). System equipped with a switching system (about 10 min/hour) for calibration independent particulate properties and/or cleaned periodically for dissolved measurements. Ability to profile (e.g., with an arm, Sherwood et al. 2012) provide vertical dimension to data. Filter switching occurred on weekly time scales (by divers).

**Advantage:** high temporal data.

**Disadvantage:** rapid fouling requires weekly cleaning and filter changes by divers.

5. Moorings and profiling moorings

Ac meters have been attached on moorings from about 1996 (Change and Dickey 1999, 2001; Roesler and Boss 2008). Measurements are limited to total.

**Advantage:** High temporal resolution measurements spanning from minutes to seasons.

**Disadvantage:** Sensor drift and fouling requires use of bio-fouling measures (Manov et al. 2004) and careful post-processing.

6. In-line

Ac-9 and ac-s instrument have been measuring continuously water flowing to research vessel for quite a long time (Balch et al. 2004; Dall’Olmo et al. 2009; Slade et al. 2010). Systems are equipped with vortex debubblers. In some cases, instruments are kept in a water bath to minimize large instrument temperature changes (NB: if notified, WETLabs provides an extended instrument temperature compensation table for work in high or low latitudes, where instrument temperature can be beyond standard tables). When equipped with an automated switching system, if sufficiently frequent, the particulate measurement can be obtained in a manner that is calibration independent. For dissolved measurements, nearly-daily cleaning calibration with deionized water (DIW) are needed.

**Advantage:** high spatial resolution measurements, calibration independent particulate properties suited for work in very clear water.

**Disadvantage:** only surface waters are sampled. Effects of passage through pumping system and long tubes not fully characterized as of yet.

7. Towed systems

Ac meters have been deployed on towed vehicles (SeaSoar, Triaxus and Acrobat; e.g., Ashjian et al. 2006; Jones et al. 2011). The intake is placed near the front of the vehicle to sample clean water.

**Advantage:** These systems cover a large swath of ocean both horizontally (typically a few kilometers between repeated surface measurements) and vertically (typically a few hundred meters), resolving upper ocean synoptic variability.

**Disadvantage:** It is very important to account for lags between the ac instrument and CTD for temperature and salinity corrections. Two sensors are required to obtain dissolved and total (dissolved plus particulate) measurements.
8. Autonomous Underwater Vehicle (AUV)

Wijesekera et al. (2005) reports on data collected on the Blue Fin AUV with an ac-9 pumped with water coming in from the nose cone with a 1.8 m long tube. Data were used to assess spatial variability of IOPs and radiometric quantities at different depths.

**Advantage:** The AUV can obtain data very close to the surface to assess sub-pixel variability.

**Disadvantage:** Some mixing occurs from the long hose to the front cone.

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Chapter 3: Integrating Cavity Absorption Meters (ICAM)

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The original motivation for the development of the integrating cavity absorption meter (ICAM) was to solve the scattering problems associated with measuring the optical absorption of pure water and ocean water. The ICAM employs a closed cavity with diffuse (Lambertian) reflecting walls to achieve an isotropic, homogeneous illumination of the sample; consequently, the sample illumination is essentially independent of any scattering effects (i.e., scattering cannot change the isotropic and homogeneous character of the sample illumination). The measured optical absorption includes the absorption by scattering particulates in the sample as well as the absorption by the medium in the cavity. Absorption by the suspended particulates is measured in their naturally occurring population densities, without needing to concentrate them by filtration or centrifuge. The light intensity incident on the walls of the cavity provides the critical measurement parameter; it has an inverse dependence on the sample absorption and is not affected by scattering in the sample (elastic scattering does not remove any energy from the cavity). The ICAM takes advantage of the high reflectivity (typically >99%) of the walls of the integrating cavity to achieve a very long effective path length via multiple reflections through the sample; it thereby enhances the sensitivity to a very small absorption by the sample.

In 1970, Elterman introduced the concept of using an integrating cavity to measure absorption (Elterman 1970). His idea provided the basis for development of the ICAM some 25 years later for measurements of the absorption of pure water in the visible spectral region (Pope and Fry 1997). However, the ICAM concept differs from Elterman's approach in that it uses two integrating cavities, one inside the other. The outer cavity provides an approximately isotropic, homogeneous illumination of the sample in the inner cavity. Specifically, light is introduced into the outer cavity, reflects back and forth between the two cavities, and is converted from an inherently anisotropic field into a nearly isotropic one. This isotropic light field then diffuses through the wall of the inner cavity and uniformly illuminates the sample. The signal is obtained from the ratio between the equilibrium radiant energy densities in the inner sample cavity and in the outer cavity (basically, the signal from the outer cavity provides the normalization). Another important extension of the ICAM is the point source integrating cavity absorption meter or PSICAM (Kirk 1997; Röttgers et al. 2005). It employs a single integrating cavity that contains the sample, and a point source inside the cavity to illuminate the sample. For the same reasons, the PSICAM also has the ICAM advantages of a long effective path length and independence of scattering effects.

It is important to contrast the fundamental differences between the ICAM concept and innovative techniques based on integrating cavities that have been implemented by several others (e.g., Bricaud et al. 1983 or Haardt and Maske 1987). Specifically, rather than illumination of the sample from a single direction and using an integrating cavity to try to collect the scattered light, the ICAM provides isotropic illumination of the sample and thereby inherently avoids scattering effects. In addition, rather than a single pass through the sample, the ICAM provides many passes that significantly enhances the sensitivity to a weak absorption.

The ICAM implementation actually uses two integrating cavities, an integrating cavity containing the sample is placed inside a second cavity, see Fig. 3.1. Light is supplied to the outer cavity via a fiber optic through its wall. The wall of the cavity containing the sample has >99 % reflectivity, but since it is inside another integrating cavity the light bounces back and forth and tries many times to get through the wall into the inner cavity. If there are no absorption losses, the optical energy density would be the same in both the outer cavity and the inner (sample) cavity; but, in practice optical energy density is always smaller in the empty sample cavity. The reason for this double cavity arrangement is to obtain an isotropic field distribution in the outer cavity, which then leaks through the inner cavity wall and provides an isotropic illumination of the sample in the inner cavity. In short, the double cavity converts an inherently anisotropic
illumination field into a nearly isotropic one. With no external cavity and only the sample cavity, the input field would have unavoidable directionalities until after at least a couple reflections from the walls.

Figure 3.1. Cross-section of a generic ICAM with an inner integrating cavity containing the sample, and an outer integrating cavity to provide isotropic illumination of the sample in the inner cavity.

3.1 Theoretical Background for the ICAM

The rigorous theoretical basis for our instrument was outlined previously (Fry and Kattawar 1988 and Fry et al. 1992) and is reviewed here. Let the scalar \( L(\mathbf{r}, \hat{\mathbf{\Omega}}) \) denote the radiance in the direction of the unit vector \( \hat{\mathbf{\Omega}} \) at a point \( \mathbf{r} \). Then, at point \( \mathbf{r} \), we can define a vector irradiance

\[
\mathbf{E} = \int_{\Omega} L(\mathbf{r}, \hat{\mathbf{\Omega}}) \hat{\mathbf{\Omega}} \, d\Omega,
\]

and a radiant energy density \( U \),

\[
U = \frac{n}{c} \int_{\Omega} L(\mathbf{r}, \hat{\mathbf{\Omega}}) \, d\Omega,
\]

where the integral is over solid angle \( \Omega \), \( c \) is the velocity of light in vacuum, and a homogeneous medium with refractive index \( n \) is assumed. Now, starting from the equation of radiative transfer, it is straightforward to show that

\[
-\nabla \cdot \mathbf{E} = a \frac{c}{n} U,
\]

where \( a \) is the absorption coefficient (Chandrasekhar 1960). This fundamental relation is valid at every point in a medium, irrespective of the magnitude of any scattering effects. Integrating Eq. 3.3 over a volume \( V \) of the sample and using the divergence theorem on the left-hand side gives

\[
-\int_{S} \mathbf{E} \cdot d\mathbf{S} = a \frac{c}{n} \int_{V} U \, dV.
\]

The left-hand side of Eq. (3.4) is, of course, the net radiant power entering the cavity containing the sample; i.e., it is the power \( P_{\text{abs}} \) that is absorbed (i.e. the power entering the cavity minus the power leaving the cavity). Thus, \( P_{\text{abs}} \) is given by
\[ P_{\text{abs}} = a \frac{c}{n} \int V U dV. \]  

(3.5)

For a homogeneous medium, this result is exact and is, of course, rigorously independent of scattering effects. Assuming the energy density \( U \) is also homogeneous, then Eq. (3.5) becomes

\[ P_{\text{abs}} = a \frac{c}{n} U V, \]

(3.6)

where \( V \) is the volume of the sample. This important result was also obtained by Elterman; however, he used a one-dimensional representation and assumed that the radiant energy (joules) in the cavity was attenuated with distance. A form of more practical use is obtained by relating the energy density \( U \) inside the sample to the normal component of \( \mathbf{E} \) at the inside surface of the sample. This normal component is called the scalar irradiance, \( \mathbf{E}_{\text{out}} \), and is just the outwardly directed irradiance at the surface of the sample. If the radian distribution \( L(\mathbf{r}, \hat{\Omega}) \) in the sample is both homogeneous and isotropic, then \( L \) is a constant and Eqs. (3.1) and (3.2) give, respectively,

\[ E_{\text{out}} = \hat{n} \cdot \int_{\Omega} L(\mathbf{r}, \hat{\Omega}) \hat{\Omega} d\Omega = \pi L, \]

(3.7)

\[ U = \frac{4\pi nL}{c}, \]

(3.8)

where \( \hat{n} \) is an outward unit vector normal to the surface. Combining these equations gives

\[ U = \frac{4n}{c} E_{\text{out}}; \]

(3.9)

and from Eq. (3.6) the final result for the absorbed power is

\[ P_{\text{abs}} = 4aVE_{\text{out}}. \]

(3.10)

To summarize, \( P_{\text{abs}} \) is the power absorbed in the sample, \( a \) is the absorption coefficient of the sample, \( V \) is the sample volume, and \( E_{\text{out}} \) is the outward normal component of the vector irradiance from within the sample at its surface.

By conservation of energy, the power entering the sample volume must equal the power leaving the volume plus the power absorbed,

\[ P_{\text{in}} = P_{\text{out}} + P_{\text{abs}}, \]

(3.11)

which combined with Eq. 3.10 gives

\[ P_{\text{in}} = P_{\text{out}} + 4aVE_{\text{out}}. \]

(3.12)

The power in, \( P_{\text{in}} \), and the power out, \( P_{\text{out}} \), can be written in terms of the normal components of the vector irradiances \( E_{\text{in}} \) and \( E_{\text{out}} \). Specifically, the irradiance on the walls of the outer cavity (i.e. the inside surface of the outer cavity wall and the outside surface of the inner cavity wall) is \( E_{\text{in}} \) and is proportional to the power \( P_{\text{in}} \) being supplied to the inner cavity. See the generic diagram of an ICAM in Figure 3.1. Similarly, the outward irradiance incident on the inside of the wall of the inner sample cavity is \( E_{\text{out}} \) and is proportional to the power exiting the sample through the sample cavity wall, as well as through exit ports, detectors, etc. Designating the proportionality constants as \( K_i \) and \( K_o \), respectively, the energy conservation equation, Eq. (3.12), becomes

\[ K_i E_{\text{in}} = K_o E_{\text{out}} + 4aVE_{\text{out}}. \]

(3.13)

Each irradiance, \( E_{\text{in}} \) and \( E_{\text{out}} \), is sampled by optical fibers and detected by a single photomultiplier tube (using a chopper) to produce the two corresponding signal voltages \( S_i \) and \( S_o \) that are proportional to the irradiances \( E_{\text{in}} \) and \( E_{\text{out}} \).

\[ S_i = g_i E_{\text{in}}; \quad S_o = g_o E_{\text{out}}. \]

(3.14)

Although both signals are obtained from the same detector, the \( g \)'s may be slightly different due to other factors such as coupling to the optical fibers. Eq. (3.13) can now be rewritten as
\[ K_i \frac{S_i}{g_i} = K_o \frac{S_o}{g_o} + 4aV \frac{S_o}{g_o}. \]  

Solving Eq. (3.15) for the absorption coefficient \( a \) gives

\[ a = \frac{K_i}{4V g_i} \frac{S_i}{S_o} - \frac{K_o}{4V g_o} = \frac{1}{4V} \left( \frac{K_i}{g_i} S_i - \frac{K_o}{g_o} \right), \]  

or equivalently,

\[ a = C_i S - C_o, \]  

where \( S \) is the ratio of the measured signal voltages. The simple relation, Eq. (3.17), is the working equation for the ICAM. Its implementation requires determination of two calibration constants: the signal normalization constant \( C_i \) and the offset constant \( C_o \). From Eq. (3.16), these two parameters are constants that are combinations of the other proportionality constants and the volume \( V \),

\[ C_i = \frac{K_i}{4V g_i}; \quad C_o = \frac{K_o}{4V g_o}. \]  

Of course, both of these constants are functions of the wavelength.

Two partial derivatives of these relations will be useful. Eqs. (3.16) and (3.17) give respectively,

\[ \frac{\partial S}{\partial V_i} = \frac{a}{VC_i}; \quad \frac{\partial a}{\partial S_v} = C_i. \]  

Solving Eqs. (3.19) for \( a \), and eliminating \( C_i \) gives,

\[ a = V \frac{\partial S}{\partial V_i} \frac{\partial a'}{\partial S_v}. \]  

Eq. (3.20) gives the absorption \( a \) of an unknown sample. Specifically, the measured signal \( S \) as a function of the volume \( V \) of a sample with an unknown absorption coefficient \( a \) is linear and has the slope

\[ \frac{\partial S}{\partial V_i} ; \]  

and the known absorption coefficient \( a' \) for a variety of samples as a function of the measured signal \( S \) from a fixed sample volume is linear and has the slope

\[ \frac{\partial a'}{\partial S_v}. \]  

Depending on the design of the cavity, it may be necessary to supplement the working equation for the ICAM, Eq. (3.17). For example, in the work by Pope and Fry on the measurement of pure water absorption, the placement of the detector for \( S_0 \) at the midpoint of the cavity required some additional parameters; but, for the most recent measurements of water absorption in the UV, no additional parameters were required (Mason et al. 2016).

### 3.2 Flow-through ICAM

Initially, integrating cavity designs were closed systems that required discrete sampling of, for example, water; they can therefore not be used in situ. Consequently, an important modification of the ICAM was the development of the flow through ICAM; it is basically a long double integrating cavity tube for which the central (sample) cavity tube is open at both ends (Gray et al. 2006; Musser et al. 2009). Water can flow through the central tube with negligible turbulence; intensity measurements are made at the midpoint of this long cavity. There is also a flow through version of the PSICAM. A flow through ICAM is now commercially available from Turner Designs.

The basic design of the instrument is shown in Fig. 3.2. It consists of a central cylindrical quartz tube with open ends to allow water to flow through it. The tube has an inner radius \( r_i \), an outer radius \( r_o \), and a length \( L \). The inner surface of the quartz tube is polished for a smooth water flow, while the outer surface is heavily frosted to help diffuse the light field inside the sample. Surrounding this tube are two cylindrical layers of a high albedo, diffusely reflecting material. The thinner, inner layer completely surrounds and is
in contact with the outer surface of the quartz. The thicker outer layer is set back some distance from the inner one, providing for a gap between the two. The ends of these cylinders are capped, forming a closed cavity.

Figure 3.2. Cross-sections of a generic flow through ICAM with an inner integrating cavity surrounding a quartz tube that is open at both ends and through which the water being measured flows.

The outer cavity could be illuminated using an external light source and optical fibers; or, as in Fig. 3.2, LED’s could be built directly into the outer cavity. A reference fiber inserted into the outer cavity monitors the radiant energy that is illuminating the water in the quartz tube. A signal collecting fiber passes through both the outer and inner layers of the diffuse reflecting material and is placed in contact with the outer surface of the quartz tube. The signal fiber is isolated from the light field in the outer cavity by wrapping it in aluminum foil and surrounding it with a diffuse-reflecting tube in the region between the outer and inner cavity walls.

From an operational view, this design is essentially a variation of the ICAM. It is a cavity within a cavity where light is introduced into the outer cavity and then diffuses into the inner one to be absorbed by the water sample inside. However, with the flow-through design, the inner cavity is not enclosed. So, in addition to allowing water to enter and exit, the open ends of the quartz cylinder allow light to do the same. As a result, the spatial distribution of radiant energy in the water sample will be altered - the light field is neither homogenous nor isotropic. This has several important consequences, and the reader is referred to the discussions in Gray et al. (2006). But, basically the most immediate effect is that the working equations of the original ICAM no longer apply and the instrument must be calibrated with samples of known absorption. In addition, the geometry of the instrument plays a much greater role. Radiant power will be lost out the open ends, and these losses and resulting changes in energy distribution will depend on the length L and the inner and outer radii, r_i and r_o, of the quartz tube. Finally, scattering effects could again become important due to this additional loss mechanism.

It is immediately obvious that the influence of these end effects can be minimized by making the cylinder long in comparison to its diameter, L >> 2r_o. However, if the instrument is too large, it becomes prohibitively expensive and awkward to use in the field. There are also both theoretical and practical limits on how small the instrument can be made. Specifically, as the radius of the quartz cylinder decreases, the surface-area to volume ratio increases; the consequence is that when light reflects off one wall and travels to another, it spends less time in the intervening water sample. Hence, the effective path length of light in the water is decreased, and more radiant power will be absorbed or otherwise lost through the cavity walls. A smaller diameter tube will also be more likely to clog with marine debris and be more difficult to clean.
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Chapter 4: Point-Source Integrating-Cavity Absorption Meter (PSICAM)

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A possibility to overcome problems with scattering and sample handling when determining \(a_p\) is to measure the original sample inside an integrating sphere. The integrating sphere approach avoids scattering to interfere with the optical density determination and provides as well a sufficient sensitivity by a long optical path length (up to several meters). One way to reduce scattering effects to an insignificant level is to arrange an isotropic light field inside the sphere, such that any additional scattering event inside the sphere does not change the light field. A simple way to do this is to use a central isotropic light source, as proposed and theoretically described by Kirk (1995, 1997) as the point-source integrating-cavity absorption meter (PSICAM). The PSICAM concept was further investigated by Leathers et al. (2002) and Lerebourg et al. (2002) and successfully tested by Röttgers et al. (2005). Results with a simple lab instrument are shown by Röttgers et al. (2007) and Röttgers and Doerffer (2007).

Integrating cavities of the PSICAM (Fig. 4.1) can have inner diameters of between 5.0 and 9.0 cm (the smaller diameters are used for highly absorbing water) and are made out of a block of a diffuse, highly reflective, PTFE-based plastic material (OP.DI.MA, Gigahertz Optik, Germany, or Spectralon, Labsphere Inc., USA). The reflectivity of this material is depending on the material thickness and reaches 97 and 99% for a thickness of >10 mm. The surface of these materials is water-repellent and contaminations by natural, soluble or particulate, substances are much reduced. The central light source consists of a small scattering sphere made out of a diffuse quartz glass with an outer diameter of 10.0 mm. A typical, simple lab version of the PSICAM has two openings that can be closed by Teflon stoppers, one for inserting and changing the central light source and one for filling and emptying the cavity. Light is provided by an electronically stabilized 150-watt halogen bulb and is detected by a photodiode array spectroradiometer. The setup allows a spectral range of 370–800 nm; however, strong water absorption at wavelengths > 700 nm typically limits the range to 370–720 nm.

Figure 4.1. Schematic cross-section of a PSICAM showing the central light source, the light detector (top left) with its field of view indicated (dashed lines) and the inner cavity. The light detector is a tip of a fiber optic with the other end connected to a spectroradiometer. The central light source is a sphere made from a diffuse quartz glass sitting on the tip of a fiber optic connected to an external halogen light source.

4.1 Theoretical Considerations of the PSICAM

According to Kirk (1997) and Leathers et al. (2000), the “transmission” difference between two samples \(A\) and \(B\), \(T_{AB}\), in a PSICAM is the ratio of the diffuse reflected irradiance \(F_0\) at the inner wall
when the cavity is filled with either the sample \( A \) or \( B \) (Eq. 4.1). (Note: for simplification, the dependency of wavelength is omitted in the following when not necessary). Each irradiance is proportional to the number of times a photon is reflected by the wall, \( N_c \), before it is absorbed either by the wall or by the sample fluid, hence,

\[
T_{AB} = \frac{F_0^A}{F_0^B} = \frac{N_c^A}{N_c^B}
\]  

(4.1)

\( N_c \) is the fraction of photons reaching the wall directly and indirectly by reflection on the wall for one, or more times (Eq. 4.2). It depends (1) on the probability \( P_0 \) that a photon, coming from the central light source, reaches the wall directly, (2) on the reflectivity of the wall, \( \rho \), and (3) on the probability \( P_s \) that a photon, which is reflected, will return to the wall. In the PSICAM set-up used here the detector does not collect light that comes directly from the light source, thus, for \( N_c \) this gives

\[
N_c = P_0\rho P_s + P_0\rho^2 P_s^2 + \cdots = P_0 \sum_{n=1}^{\infty} (\rho P_s)^n = \frac{P_0 P_s}{1 - \rho P_s}.
\]  

(4.2)

Therefore,

\[
T_{AB} = \frac{P_0^A P_s^A (1 - \rho P_s^B)}{P_0^B P_s^B (1 - \rho P_s^A)}
\]  

(4.3)

\( P_0 \) and \( P_s \) are related to the radii of the PSICAM \( r_0 = r - r_i \) and \( r \), respectively, where \( r \) is the inner radius of the cavity and \( r_i \) the radius of the central light source, and to the absorption coefficient \( a \) in the following way (see Kirk 1997 for details):

\[
P_0(a, r_0) = \exp(-ar_0)
\]  

(4.4)

\[
P_s(a, r) = \frac{1}{2a^2r^2} [1 - \exp(-2ar)(2ar + 1)].
\]  

(4.5)

Finally, the “transmission” in the PSICAM is related to the absorption coefficients \( a_A \) and \( a_B \) of the two solutions as

\[
T_{AB} = \exp[-r_0(a_A - a_B)] \left[ \frac{1 - \rho P_s(a_B, r)}{1 - \rho P_s(a_A, r)} \frac{P_s(a_A, r)}{P_s(a_B, r)} \right]
\]  

(4.6)

When using Eq. (4.5) and (4.6), \( T_{AB} \) is a function of the light absorption of the samples \( a_A \) and \( a_B \), the radii \( r \) and \( r_0 \), and the reflectivity \( \rho \). Solving Eq. (4.6) for the reflectivity gives

\[
\rho = \frac{T_{AB} \exp(-a_B r_0) P_s(a_B, r) - \exp(-a_A r_0) P_s(a_A, r)}{T_{AB} \exp(-a_B r_0) P_s(a_B, r) P_s(a_B, r) - \exp(-a_A r_0) P_s(a_B, r) P_s(a_A, r)}
\]  

(4.7)

### 4.2 Calibration of the PSICAM

The error for absorption determination in a PSICAM is related mainly to the error in determining the inner radius, \( r \), the reflectivity, \( \rho \), and to the “transmission” determination in the PSICAM. The “transmission” measurement is influenced by the stability of the light source and that of the spectroradiometer response. From these errors, the error related to \( \rho \) has the strongest influence: a 1% error in \( \rho \) leads to >10% error in the absorption determination. Hence, \( \rho \) has to be known with a high accuracy. It is determined using Eq. (4.7), by measuring the “transmission” by two solutions with known absorption coefficients. Determining \( \rho \) in this way has the advantage that it will eliminate errors associated with the true \( \rho \) of the wall material, and with \( r_0, a_A, a_B \), and the known water absorption, if the same values are later used for calculating either \( a_A \) or \( a_B \). However, the error of the necessary determination of the absorption coefficient with a photometer, directly influences the error of the absorption determination with the PSICAM.
Practically, $\rho$ is determined following the suggestion and description by Leathers et al. (2000). Therefore, $T_{AB}$ is determined from a sample solution $A$ with an absorption coefficient $a_{A}$ measured against a reference solution $B$ with an absorption coefficient $a_{B}$ in the PSICAM. The reference solution $B$ consists simply of purified water. The assumed absorption coefficient spectrum of this purified water, $a_{w}$, is taken from published pure water absorption coefficients (Pope and Fry 1997), whose can be adjusted and smoothed to have a complete spectrum for the considered wavelengths range (370 – 720 nm). As discussed above any error in this pure water absorption is compensated by the calibration procedure described here, the exact pure water absorption is of less significance.

Solution A is prepared from the colored stain Nigrosine (Certistain, Merck, Germany), following suggestions of Kirk (1997). Compared to other dye solutions Nigrosine has the advantage of having a considerably high absorption coefficient at all required wavelengths. A Nigrosine stock solution is prepared by dissolving a few crystals of Nigrosine in 100 ml purified water. The optical density of this solution is roughly determined photometrically in a 1 cm cuvette at 578 nm, to be able to calculate the necessary volume of this stock solution when later preparing the calibration solutions. A calibration solution with absorption coefficient ($a_{578nm}$) between 0.5 and 2 m$^{-1}$ (on the $\log_{10}$ scale) are prepared by diluting a few milliliters of the 0.2 µm-filtered stock solution in a large enough volume of purified water to conduct several measurements. The exact spectral absorption coefficients of this Nigrosine in solution is determined spectrophotometrically in the range of 350 to 800 nm (using a 10 cm cuvette in a commercial dual-beam spectrophotometer, or in a liquid waveguide system with path lengths of 50 cm to 1 m) and purified water as the reference.

The “transmission” measurements in the PSICAM are conducted in triplicate by determining the light intensity inside the cavity when the cavity is first filled with purified water, $F_{w}$, and second with the calibration solution, $F_{nig}$. In each case the temperature of the fluid ($t_{w}$ and $t_{nig}$) inside the cavity is recorded for a later temperature correction of the pure water absorption. After the calibration solution has been measured, the PSICAM has to be cleaned as the stain adsorbs considerably fast on the cavity wall of the PSICAM. Therefore, the PSICAM is bleached for 15 min with a 0.1 % sodium hypochlorite solution (NaOCl, Riedel de Haen, Germany). Afterward the bleach is removed from the PSICAM by washing the cavity several times with purified water.

The reflectivity is calculated for each pair of pure water/calibration solution using the pure water absorption as $a_{w}$, and the sum of absorptions of pure water and Nigrosine as $a_{A}$. The pure water absorption is calculated beforehand for each fluid using the specific fluid temperature, the instrument-specific temperature correction coefficient (see below) and published values of the water absorption of Pope and Fry (1997). Calibration should be done repetitively and regularly with each measurement set (Fig. 4.2).

**Calibration procedure**

1. Prepare 100 ml Nigrosine stock solution ($A_{580nm1cm}$ ca. 3 OD).
2. Prepare a sufficient volume of Nigrosine calibration solution (1 - 2L; $a_{580nm} = 0.5 - 2$ m$^{-1}$).
3. Determine the Nigrosine absorption, $a_{nig}$, of the calibration solution (10 cm cuvette in spectrophotometer, or using a LWCC system (in triplicate).
4. Determine “transmission” (nigrosine solution vs. purified water) in the PSICAM (in triplicate), cleaning and bleaching of the cavity after each nigrosine solution.
5. Calculate the reflectivity with Eq. (4.7) and (4.5) (including temperature correction of pure water absorption), where
   
   \[
   a_{A} = a_{w}(t_{nig}) + a_{nig},
   \]
   \[
   a_{B} = a_{w}(t_{w}),
   \]
   \[
   T_{AB} = F_{nig}/F_{w},
   \]
   \[
   r_{0} = 0.040 \text{ m}, \text{(example for a 90 mm diameter cavity)},
   \]
   \[
   r = 0.045 \text{ m} \text{(example for a 90 mm diameter cavity)}.
   \]
Figure 4.2. Reflectivity, $\rho$, for a typical PSICAM with indicated confidence limits for repetitive measurements (n=61) done during one ship cruise. Small artifacts at water absorption shoulders, i.e., at 600, 660, and >700 nm are visible due to differences in the optical resolution between PSICAM measurement and that during determination of the pure water absorption; these do have no effects on the determination of the absorption coefficients. The confidence interval represents an error in $\rho$ that would lead to errors in the absorption coefficient of between 1 and 3 % (mean: 1.4 %).

4.3 Measurement and Calculation of the Absorption Coefficient with the PSICAM

Regular measurements are done by measuring the light intensity inside the cavity when it is filled with either purified water or the sample. This can be done in an alternating way until the sample is measured three times. For each measurement, the fluid temperature and the sample salinity need to be recorded for a later temperature and salinity correction of the pure water absorption. In addition, the light intensity might be measured when an additional short-pass filter is placed in front of the external light source to measure the sample's chlorophyll fluorescence, which is used to correct the absorption for the influence of this fluorescence inside the cavity in the range of the fluorescence, i.e. 670 – 700 nm. For each sample measurement, $T_{AB}$ can be calculated two times using the reference measurement taken before and after the sample measurement. The real $T_{AB}$ is the mean of these two values, this corrects for possible constant drifts in the light intensity by either a drift in the lamp output or the detector response.

There is no analytical solution for any absorption coefficient $a(\lambda)$ in Eq. (4.6). When $\rho(\lambda)$ is known, $a(\lambda)$ is determined by solving this equation numerically. This is done by minimizing the least square function $G(a(\lambda))$ for the measured transmission, $T_{\text{meas}}(\lambda)$ using a numerically calculated transmission $T_{\text{num}}(\lambda)$.

$$G(a(\lambda)) = \sqrt{(T_{\text{num}}(\lambda) - T_{\text{meas}}(\lambda))^2}$$  \hspace{1cm} (4.8)

For the absorption coefficient of pure water, the same data have to be used as for the calibration (e.g., Pope and Fry 1997). To obtain the absorption coefficient of the water constituents (besides water), the water absorption coefficient has to be subtracted from the resulting absorption coefficient of the sample.

Measurement procedure

1. Fill the PSICAM with purified water, measure the fluid's temperature ($t_w$) and then the light intensity, $F_w$.
2. Fill the PSICAM with the sample, measure the fluid's temperature ($t_{\text{sample}}$) and then the light intensity, $F_{\text{sample}}$, record the sample's salinity ($S_{\text{sample}}$). Afterwards wash the cavity with purified water.
3. Repeat step 1 and 2 three times for triplicate measurements, at the end measure purified water once more.
4. Calculate the transmissions as $F_{\text{sample}}/F_w$ using the $F_w$ measured before and after each sample
5. Determine the absorption for each transmission using Eq (4.6) and (4.5) by minimizing Eq. (4.8) after the pure water absorption has been corrected for the specific temperature and sample
salinity, where
\[ a_t = a_w(t_{sample}, S_{sample}) + a_{sample}, \]
\[ a_g = a_w(t_g), \]
\[ T_{AB} = F_{sample}/F_w, \]
\[ r_g=0.040 \text{ m}, \text{(example for a 90 mm diameter cavity)}, \]
\[ r=0.045 \text{ m}, \text{(example for a 90 mm diameter cavity)}, \]
and \( a_{sample} \) is the unknown absorption to be fitted.

### 4.4 Corrections for Chlorophyll Fluorescence Inside the PSICAM

As the light inside the PSICAM and the detector spectral responses are not monochromatic, some chlorophyll fluorescence is induced and emitted at about 660 - 710 nm (max 675 - 685 nm). This extra light leads to an underestimation of the absorption coefficient (e.g., by up to 15 % at 675 nm). To correct for this artifact, the fluorescence intensity, \( F_{\text{fluxo}} \), is determined by measuring it when a short-pass filter (SPF; blocking light at > 650 nm) is placed in front of the light source and when the cavity is filled with the sample and the reference. This results in light intensities measurements named \( F_{\text{SPF-sample}} \) and \( F_{\text{SPF-w}} \), respectively. The obtained fluorescence intensity at wavelengths between 660 and 710 nm is corrected for 1) fluorescence re-absorption, due to light absorption in the sample at 660 - 710 nm, and 2) reduction in excitation intensity by placement of the short-pass filter, as
\[
F_{\text{tuor}}(\lambda) = \begin{cases} 
R_F \left[ F_{\text{SPF-sample}}(\lambda) - F_{\text{SPF-w}}(\lambda) \right] & : 660 \text{ nm} \leq \lambda \leq 710 \text{ nm} \\
0 & : \text{else}
\end{cases}
\]
where \( R_F \) is the ratio of absolute absorption of the light inside the cavity by the sample with and without the short-pass filter integrated over all wavelengths, as
\[ R_F = \frac{\sum_\lambda (F_w(\lambda) - F_{\text{sample}}(\lambda))}{\sum_\lambda (F_{\text{SPF-w}}(\lambda) - F_{\text{SPF-sample}}(\lambda))} + 0.1. \tag{4.10}\]

The ratio \( R_F \) compensates for the fact that fluorescence is a function of absorbed light by the pigments not simply irradiated light and that the number of photons absorbed is reduced by the short pass filter at all wavelengths especially at > 650 nm. The additional “0.1” were obtained empirically (comparing spectrally PSICAM and filter pad measurements), and compensate for the fact that only absorption by pigments not by all absorbing material leads to chlorophyll fluorescence such that \( R_F \) is underestimated as only total absorption was taken into account.

Finally, the correct “transmission”, \( T_{AB}^{\text{corr}} \), is calculated as
\[ T_{AB}^{\text{corr}} = \left( F_{\text{sample}} - F_{\text{tuor}} \right)/F_w \tag{4.11}\]

The remaining deviations at 675 nm between PSICAM and filter pad measurements (correctly adjusted for path length amplification) are in the range of a few percent only.

### 4.5 Temperature and Salinity Correction of the Pure Water Absorption in the PSICAM

The absorption of pure water, \( a_w \), is dependent on temperature and salinity. Any difference in temperature and salinity between the sample or the reference to that of the theoretical pure water absorption (i.e. 20°C and 0 PSU) has to be corrected using instrument-specific temperature and salinity correction coefficients, \( \Psi_t^i \) and \( \Psi_s^i \) as
\[ a_w(t, \lambda) = a_w(t_0, \lambda) + (t - t_0)\Psi_t^i(\lambda) \tag{4.12}\]
and
\[ a_w(S, \lambda) = a_w(S_0, \lambda) + (S - S_0)\Psi_s^i(\lambda), \tag{4.13}\]
where \( t \) is the specific temperature, \( S \) the specific salinity, and \( t_0 \) and \( S_0 \) the values at which the pure water absorption had been measured, i.e., 20°C and 0 PSU. Values for \( \Psi_t^i \) and \( \Psi_s^i \) can be determined for each instrument setup. \( \Psi_s^i \) is determined by measuring either a concentrated NaCl solution (100 - 200 gL⁻¹) or an artificial seawater solution (50 - 70 gL⁻¹) and dividing the results by the equivalent PSU value of the
solution. $\Psi_t$ can be determined by measuring the absorption differences of purified water of e.g., 15° and 40° C. As the effects of temperature on the refractive index and scattering by pure water are of minor relevance (in opposite to the situation for salinity), published values of $\Psi_t$ for pure water absorption can be used as well (e.g., Röttgers et al. 2014). Besides correction for temperature, salinity, and chlorophyll fluorescence effects, no further corrections are applied. Due to the spectral distribution of the light source, effects of water Raman and CDOM fluorescence are negligible.

**4.6 Maintenance and Service of the PSICAM**

The PSICAM cavity wall can be cleaned by using pure HPLC-grade ethanol and a lint-free tissue. Touching the wall with unprotected finger should be avoided. Optical influences by organic material attached to the wall can further be removed with bleach using a ca. 0.1% NaOCl solution (500 - 1000 µl NaOCl in 500 ml purified water). The PSICAM should be filled with purified water 24 hours before the measurement/calibration are done, as water will enter the wall material and changes the reflectance.

**4.7 Determination of the Particulate Absorption Coefficient with a PSICAM**

The particulate absorption coefficient, $a_p$, in a water sample is determined by measuring first the absorption coefficient of all water constituents (besides water itself), $a_{pg}$, defined as the sum of $a_g$ and $a_p$, the latter here used for the dissolved part (gelbstoff [CDOM]). The sample is then filtered through 0.2 µm and the filtrate’s absorption coefficient determined as $a_g$. Principally $a_g$ can be determined using other optical methods. Finally, $a_g$ is calculated by subtracting $a_p$ from $a_{pg}$, i.e. $a_g = a_{pg} - a_p$ (Fig. 4.3). The filtration through 0.2 µm allows a proper separation of the absorption by particles larger than 0.2 µm and that by all other material (particulate, colloidal, and dissolved) remaining in the filtrate. When using glass-fiber filter for the determination of $a_p$, it is possible that particulate material is going through the glass fiber filter but retains on the 0.2 µm filter, its absorption is, hence, not part of $a_p$ nor $a_g$.

As pigment bleaching in suspension cannot be handled yet satisfactorily, the absorption coefficient of pigments (phytoplankton), $a_{ph}$, has to be determined by combining PSICAM and filter pad measurements, the latter includes the determination of the non-pigmented part of the particulate absorption coefficient after pigment extraction.
REFERENCES


Chapter 5: Spectrophotometric Measurements of Particulate Absorption Using Filter Pads

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5.1 General Considerations

Prior to the quantitative filter pad approach to assess absorption spectrophotometrically, particulate absorption was measured in cuvettes. These measurements clearly demonstrated the impact of scattering by the suspended particles on the estimation of absorption, because scattered photons are generally not collected by the detector and their contribution is assigned to absorbance. In the extreme, the derived coefficient more resembled beam attenuation rather than absorption. An additional consequence of particle scattering is that it redirects photons through the suspension of absorbing particles, increasing the absolute path length of those photons over that which would have been observed in a non-scattering environment, thereby increasing the probability of absorption. This latter effect is termed path length amplification, the ratio of the mean optical path length to the geometric path length (Butler 1962); it leads to overestimated absorption coefficients and in the extreme to flattened absorption peaks (Duyssens 1956). Modeling suggests that path length amplification is minimized by maintaining dilute suspensions where only single scattering occurs over the geometric path (van de Hulst 1957). In most natural samples, however, the suspended particles are significantly dilute as to require long geometric path cuvettes, which are more susceptible to scattering losses. Filtering particles onto glass fiber filters solved a number of technical issues inherent in the suspension approach but yielded others.

Advantages: Filtering large sample volumes onto glass fiber filters solved the issue of the dilute medium and low signal to noise ratios by concentrating particles. This yielded a higher optical density in the spectrophotometer by increasing the geometric path length. Additionally, the filtration removed the solute from the measurement resulting in separation of the particulate from dissolved fractions of the total absorption. Finally, the extraction of pigments from the filter leaving the non-extractable cellular material and inorganic particles provided a means for estimating the contribution to absorption by the phytoplankton pigments as they were in vivo, i.e. as they were packaged (Kishino et al. 1985; Sosik and Mitchell 1990).

Disadvantages: Glass fiber filters are highly scattering. Depending upon the configuration of the spectrophotometer, this yielded significant losses of the incident light from the detector and if not corrected lead to an estimate of particle absorption that included significant scattering by the filter pad. Additionally, the highly scattering nature of the filter particles increased the optical path length of the photons significantly over the geometric path length, increasing the likelihood of absorption. This effect is called the path length amplification factor and leads to overestimation of the absorption coefficient. Finally, the filter pads have their own optical properties that vary slightly from filter to filter. Because the optical properties of the filter pad are typically much larger than those of the natural particles, variations between filters that are not removed by blank filter subtraction provide non-negligible contributions to the computed sample absorption coefficient.

Prior to the implementation of integrating spheres for filter pads (Section 5.7), particulate absorption was assessed on filter pads configured in the transmission mode on the spectrophotometer (Fig. 5.1a). In this configuration the transmittance through the filter pad with particles is measured relative to the transmittance through a blank filter (Kiefer and SooHoo 1982).

A large portion of the incident light is not detected and although this is mostly corrected for by the reference through a blank filter, the difference is scattered loss for a blank filter is not the same as for a filter with imbedded particles. This error in uncorrected scattering loss is generally lumped into the path length amplification factor, β, the so-called “beta correction factor”, which theoretically should only correct for the increases in the optical path length compared to the geometric path length through the absorbing particles.
Consensus: As spectrophotometric technology has improved, including the implementation of integrating spheres, the disadvantages of the filter pad approach are declining and the uncertainty in filter pad absorption approaches are improving. In the following sections, the three basic configurations for determining particulate absorption from filter pads are described and configuration-specific protocols are outlined (Fig. 5.1). It is now recognized that the internally-mounted integrating sphere approach (IS-mode) is superior to either the transmission mode (T-mode) or the transmission/reflectance mode (TR-mode) in terms of accuracy, precision, labor and sample handling. However, the vast historical data sets were primarily collected using the T-mode and not every lab is able to afford the more expensive integrating sphere accessories. Thus, it is critical to continue providing protocols that maximize the quality of data collected while providing clear methods for identifying the sources of errors and quantifying the uncertainties that do exist.

Figure 5.1. Spectrophotometric configurations for determining filter pad optical density: (a) Transmission mode (T-mode), (b and c) transmission and reflectance mode measured with an integrating sphere with externally mounted samples (TR-mode); (d) internally mounted sample in integrating sphere (IS-mode). Open arrow indicates incident beam, black arrows indicate beams scattered from filter, grey cone indicate detector for the generalized model.

5.2 Sample Collection and Handling

Water samples are collected by clean Niskin bottles (with non-reactive internal tubing). One of the largest sources of error in the measurement is the preferential settling of particles with time as subsamples are collected from the Niskin bottles. Thus, each bottle should be transferred in its entirety to a large volume carboy protected from light during subsampling. Particles are to be kept in suspension while subsampling by careful but vigorous swirling of the carboy. Swirling three times clockwise, followed by three times counter clockwise, followed by three times clockwise effectively resuspends sinking particles. The reversal of swirling direction is critical as it provides a chaotic mixing motion that is critical to avoid a non-uniform distribution of particles due to centrifugal forces that results from uniform swirling. This resuspension method is also necessary in the sample bottle prior to measuring out the filtration volume. Sample bottles should never be shaken.

Place a set of filters into the filtration manifold. Notch each filter to provide a means for identifying the orientation in the spectrophotometer. A sample volume sufficient to obtain an optical density value of 0.1 to 0.4 in the wavelength range of interest is required, for example 400 nm to 700 nm recognizing that there are regions of minimal absorption that may have optical density values $<0.1$ when peak pigment absorption is within the range. This may require two or more filters to be prepared for a single sample in order to maintain the optical density range for both the UV and visible portions of the spectrum. Until experience provides the intuition for filter pad loading, multiple filter volumes should be prepared. Vacuum pressure should not exceed 5 mmHg or 0.1 psi in order to minimize cell breakage. As the final volume of water goes through the filter, the valve should be turned off to prevent air from being drawn through the filter, leading to cell breakage.

Filters should be removed from filter cups for immediate spectrophotometric scanning or immediate freezing and storage (Sosik 1999). Prepare 3 - 5 blank filters along with sample filters, filtering a like volume of pure water (such as MilliQ®) or 0.2 µm-filtered seawater (FSW) through each. Filter fibers compress as more water is filtered through them thus they will have different scattering properties with 50 ml filter volume versus 1000 ml (Roesler 1998). If samples are to be stored from a cruise, collect at least 5 blank filters from each batch used and keep track of which samples and blanks are from each lot to ensure that analyses are processed within a single lot number. If filters are going to be scanned immediately, place them in a petri dish, which has been prepared with a bed of very moist Kim wipes (or like tissues that don’t
shed particles). Put the lid on the petri dish to maintain moisture and wrap in foil to prevent exposure to light. Filters change their optical properties as they dry (Roesler 1998), likely due to enhanced scattering by air pockets (Fig. 5.2). Additional changes occur to samples allowed to dry (Stramski 1990). When making replicate scans on a filter, it is essential to remoisten between the scans.

Figure 5.2. Increase in optical density of a blank filter as a function of time for 250 nm, 300 nm, 400 nm, 500 nm, 600 nm and 700 nm (colorbar). Filter was left in spectrophotometer and scanned every 10 minutes as it dried. Measurements were corrected for initial values.

If filters are going to be stored for later analysis they should be flash frozen with liquid nitrogen either by placing them unfolded in individual labeled Tissue-Teks® (such as the plastic disposable capsules manufactured by Sakura Finetek; Fig. 5.3) and placing them directly into a liquid nitrogen dewar, or by freezing them on a spatula that has been sitting in liquid nitrogen. Once flash frozen the tissues can be quickly placed in a -80°C freezer until analysis. The flash freezing prevents the differential freezing of particulate and dissolved molecules and best preserves the optical properties of the particles.

Figure 5.3. Example of plastic capsules for storing individual sample filters in liquid nitrogen.

Frozen filters, which have lost their original water content but maintained the original salts, are remoistened by placing filter on top of a drop of MilliQ® or other pure water or filtered seawater (FSW) on a glass slide or in a petri dish. The filter should absorb most but not all of the water within a matter of seconds. Scan immediately.

The first scan of the particles provides the measurement of particulate absorption. Non-algal particle absorption is measured on the same sample filters following pigment extraction. This is done by returning each sample filter to the filtration manifold and gently extracting with a small volume (e.g., 10 ml) of methanol. In order to minimally impact the particles on the filter, the methanol is slowly sprayed down the side of the filter cup with a squirt bottle. Gently filter the methanol through the filter pad, taking care not to draw air through. Add another small volume of methanol and let sit for approximately 15 minutes to fully extract remaining pigments. Gently rinse filter with 15 ml of filtered seawater, applied in the same fashion and filter through. This treatment is also performed on a set of blank filters, which are then used in the baseline, zero and blank scans for the extracted sample filters.
5.3 Computing Absorption from Absorbance

5.3.1 The geometric path length

Computing the spectral absorption coefficients, \( a(\lambda) \), from the spectral optical density measurements, \( OD(\lambda) \), follows the relationship:

\[
a(\lambda) = 2.303 \frac{OD(\lambda)}{L}
\]  

(5.1)

where 2.303 converts \( \log_{10} \) to \( \log_e \) and \( L \) is the geometric path length of the sample expressed in units of (m). For filter pad measurements the geometric path length, \( L \), is computed from the volume filtered, \( V \) (ml), and the effective area of the filter, \( A \) (cm\(^2\)), (measured as the area over which particles are collected onto the filter):

\[
L = \frac{(V/A)}{100}
\]

(5.2)

Where the 100 converts the path length units from (cm) to (m).

5.3.2 Optical path length and path length amplification

The assumption in this expression for absorption is that the geometric path length (i.e., \( V/A \)) is equal to the optical path length (the actual average distance that a photon travels through the sample). However, comparisons between particulate samples measured in suspension cuvettes in an integrating sphere and those measured on filter pads indicates that there is an amplification of the mean photon path through the filter compared to geometric path caused by the highly scattering nature of the filter pad. The increased optical path length relative to the geometric path length allows for increased probability for absorption and therefore overestimation. The correction factor for path length amplification is the so-called beta correction, \( \beta \). Recent routine implementation of the center-mounted integrating sphere configuration for both filter pads and suspended cuvette samples have clearly identified that the lack of consensus in published \( \beta \) correction factors is due to errors in measurements used to derive those correction factors (e.g., measurements of the suspended particulates made without an integrating sphere). Stramski et al (2015) proposed \( \beta \) correction factors for all configurations of spectrophotometry and compared their derived factor to published values, a few showed close agreement. The consensus for correcting for path length amplification implements the relationship:

\[
a(\lambda) = 230.3 \frac{OD(\lambda) \beta}{(V/A)}
\]

(5.3)

Note that the factor of 100 (conversion from cm to m) has been incorporated into the 230.3 term; units for \( V \) (ml or cm\(^3\)) and \( A \) (cm\(^2\)). The value of \( \beta \) varies depending upon the spectrophotometric configuration: 1.2804, 1.2287, or 1.0867, for T-Mode, T-R Mode, or IS-Mode, respectively.

5.3.3 Quantifying Uncertainty in the Filter Pad Absorption Coefficients

The set of blank filter scans are used to assess the uncertainty in absorption due to filter to filter variations (Figure 5.4). Compute the average, \( \mu_{\text{blank}}(\lambda) \), and standard deviation, \( \sigma_{\text{blank}}(\lambda) \), optical density spectra for the set. For each sample filter with filter volume \( V \) (ml), the uncertainty in absorption is given by:

\[
\sigma_a(\lambda) = 230.3 \frac{\sigma_{\text{blank}}(\lambda) \beta}{(V/A)}
\]

(5.4)
Figure 5.4. Spectrophotometric scans (optical density spectra) for a set of five blank filter pads that have been baseline corrected (a single or average blank filter pad signature removed) as measured in transmission mode (left) or center-mounted integrating sphere mode (right).

The optical density standard deviation spectrum for the blank filter pads should be somewhat similar from run to run because it represents filter pad to filter pad variations. However, the absorption standard deviation spectrum, $\sigma_{a}(\lambda)$, will be different for every different volume filtered. For example, two similar optical density spectra with magnitudes within the recommended 0.1 to 0.4 range will have very different uncertainties if one results from filtering 100 ml sample and the other from 500 ml sample (Fig. 5.5). This level of uncertainty should be computed for each run of samples.

Figure 5.5. Absorption spectra for two identical particulate optical density spectra for which the sample filter volume was 100 ml (black) and 500 ml (blue). Error bars represent the absorption uncertainty calculated from the standard deviation optical density spectrum for the blank filters. Note that while the uncertainty in blank filter optical density is the same, the absorption uncertainty is not.

A full model for filter pad absorption uncertainty is achieved by arithmetically propagating the uncertainty quantified for each methodological step (JCGM 2008). Deconvolving the absorption equation yields the need for uncertainty estimates for (1) each filter pad, (2) filter to filter variability, (3) sample replication, (4) filter volume, (5) filter pad effective area, (6) $\beta$ correction. An example is provided of the first three is shown in Fig. 5.6. These represent a best-case scenario where the loading of material on the filter was homogeneous over the filter so that when a single filter was measured with 3 different rotations within the beam, the uncertainty between the scans was very low, but increased toward the UV (Fig. 5.6a). Three replicate filters, when the sample was well mixed and great care was taken in measuring the filter volume, provide very low uncertainty (Fig. 5.6b). Propagating the uncertainty associated with replicate scans on replicate samples provides low uncertainty across the spectrum (Fig. 5.6c).

Figure 5.6. Example of best case scenario for sample uncertainty as quantified by a. three replicate scans of a single filter with three rotations within the beam, b. scans of three replicate sample filters, c. arithmetically propagated uncertainty shown by error bars (every 10nm for clarity).

Because the sample optical density is the average of the triplicate filters, the rules for propagation of error are such that the sample uncertainty spectrum is given by:

$$
\sigma_{s}(\lambda) = \frac{1}{3} \sqrt{\sigma_{1}(\lambda)^2 + \sigma_{2}(\lambda)^2 + \sigma_{3}(\lambda)^2}
$$

(Eq. 5.5)
where $\sigma_1(\lambda)$ is the standard deviation spectrum for the first sample filter measured under 3 rotations (Fig. 5.6a), and $\sigma_2$ and $\sigma_3$ are for the second and third replicate filters (Fig. 5.6b). The sample optical density is computed by subtracting the blank filter baseline spectrum which is computed from the standard deviation of multiple blank filters (e.g., Fig. 5.4), so:

$$\sigma_{OD}(\lambda) = \sqrt{\sigma_{\text{blank}}(\lambda)^2 + \sigma_S(\lambda)^2}$$  \hspace{1cm} (5.6)

The uncertainty in the volume filtered, $\sigma_V$, is determined by the graduated cylinder used and each person’s ability to measure volume accurately. The former is determined by the graduated cylinder (resolution to one half the distance between marked intervals), the latter is difficult to quantify but effort should be made to assess the user’s random uncertainty under standard measuring conditions (obviously greater on a ship in rough seas compared to in the laboratory). The uncertainty associated with the effective filter area can be quantified by measuring the effective diameter of a set of filtered samples using digital calipers and heavily loaded filters with a clearly distinguishable edge. As an example, for one filter rig the average effective diameter was approximately 22.3 mm. The uncertainty between filter cups was found to be 0.1 mm, comparable to the uncertainty in measuring a single filter three times. The uncertainty in the beta correction is reported to be approximately 0.004, 0.007, and 0.008 root mean square deviation (Stramski et al. 2015), for IS-Mode, T-R Mode, and T-Mode, respectively. Thus, the uncertainty equation for the absorption as calculated in Eq. 5.5 simplifies to:

$$\sigma_a(\lambda) = a(\lambda) \cdot 230.3 \sqrt{\left(\frac{\beta \cdot \sigma_{OD}(\lambda)}{\sigma_{\text{blank}}(\lambda)}\right)^2 + \left(\frac{\sigma_{V}}{V}\right)^2 + \left(\frac{\sigma_{A}}{A}\right)^2}$$  \hspace{1cm} (5.7)

### 5.3.4 Partitioning Particulate Absorption into Contributions by Phytoplankton and Non-Algal Particulates (NAP)

Once the optical density spectra for particulate and non-algal particulate contributions have been converted to their respective absorption values using Eq. 5.3, the spectral absorption coefficients for phytoplankton, $a_{ph}(\lambda)$, are calculated by difference:

$$a_{ph}(\lambda) = a_p(\lambda) - a_{NAP}(\lambda)$$  \hspace{1cm} (5.8)

The partitioning of the particulate absorption into phytoplankton and non-algal particles is understood to be an operational definition based upon pigment extraction (Fig. 5.7). The phytoplankton component is better described as the “absorption by extractable phytoplankton pigments in vivo”. It necessarily does not include other phytoplankton cellular material such as cell walls, membranes, etc., which instead are included in the “non-algal particle” fraction. Note that this operational definition of non-algal particulate component includes all kinds of non-algal particles such as organic detritus, mineral particles, mixed organic-inorganic particles, and heterotrophic organisms.

![Figure 5.7 Example of particulate absorption spectrum measured on a filter pad (black), the absorption by NAP, measured after methanol extraction (blue), and the phytoplankton absorption determined by difference green.](image-url)
5.4 Measurement of Filter Pad Absorption in Transmission Mode (T-Mode)

While likely the least accurate of the spectrophotometric modes for determining particulate absorption on filter pads, the transmission mode (T-mode) has the longest legacy. That it does not require expensive accessories such as integrating spheres suggests it may continue to be the most utilized configuration mode. For these reasons, it is critical to understand the uncertainties encountered in this approach and strategies for both minimizing uncertainties and correcting for those that remain. Presently the largest uncertainties are those due to scattering losses to the detector that are not accounted for by blank filter correction and scattering impacts on path length amplification. By employing paired analyses with an internally-mounted integrating sphere (IS-mode), both uncertainties can be quantified.

5.4.1 Spectrophotometer configuration in T-Mode

The baseline, blank and sample filter pads will all be placed against the detector side of the sample chamber. The moisture of the filter pad will provide the cohesive properties necessary to hold the filter in place. To protect the spectrophotometer from filter moisture, it is recommended that a thin Plexiglas slide, with a central opening that exceeds the size and shape of opening of the spectrophotometer aperture, be secured to the spectrophotometer for placement of the filters (Fig. 5.8).

The optical density spectrum of a blank filter pad in transmission mode is between 2.2 (0.5% transmission) and 2.5 (0.35% transmission) from 350 nm to 850 nm, and increases exponentially into the UV to a value of approximately 4.1 (0.007% transmission) at 200 nm when corrected for air baseline (Fig. 5.9). Thus, in the visible waveband blank glass fiber filters transmit less than 0.5% of the incident beam to the detector, making for a very low signal to noise ratio. The situation can be vastly improved by balancing the amount of light energy that passes through the sample and reference beams. This is achieved by placing a quartz neutral density (ND) filter against the reference port entering the sample compartment (Fig. 5.8, left diagram). Quartz is preferred over glass because of its superior transmission in the UV portion of the spectrum and the reduced likelihood of being scratched. In this configuration, there is a comparable amount of light energy passing to the detector from both the sample and reference beam, which minimizes the instrumental noise (and in many models, allows the gain to be increased). Fig. 5.9 shows the optical density scan for blank filters relative to air, 0.5 and 2.0 neutral density filters. The 2.0 ND is optimal; the resulting blank filter optical density ranges from 0.3 to 0.4 in the visible, which is equivalent to 50% and 40% transmission, respectively, a vast improvement in signal to noise.
Figure 5.9. Optical density spectra for blank filter pad with air baseline correction applied (blue). Placing a neutral density filter of optical density 0.5 (green) and 2.0 (red) on the entrance port of the reference beam reduces the overall optical density signal of the blank filter pad in dual beam mode by balancing the energy in the sample and reference beams, thereby increasing signal to noise.

5.4.2 Dual beam versus single beam spectrophotometry in T-Mode

Dual beam spectrophotometers are preferred to single beam spectrophotometers because the dual beam automatically corrects for short-term variations in lamp energy that occur both within a single scan and between scans.

Figure 5.10. Example of time series of spectrophotometric air scans collected over approximately 70 minutes every 10 minutes after instrument is turned on. The inset shows the time series of air OD measured at 275 nm (black) and 400 nm (blue) representing the two lamps, deuterium and tungsten, respectively. Instruments should be allowed to warm up for at least 60 minutes as the spectrum of lamp energy changes during warm up. The warm up time can be assessed by running air scans every ten minutes from the time the instrument is turned on until subsequent scans approach differences in optical density < 0.0005 (the target noise value; Fig. 5.10). Establish the warm up time for your instrument; it may change as the lamps age.

5.4.3 Instrument performance, instrument settings and spectrophotometric noise in T-Mode

Instrument performance tests should be performed prior to every measurement session. These include tests for wavelength accuracy, absorbance calibration and instrument noise. Maintaining a record of these tests allows the user to identify misalignment, lamp degradation and detector failures.

The recommended wavelength range for filter pad measurements is 250 nm – 850 nm. The lower (UV) end of the spectrum will be noisy because of the strong absorption by the glass fiber filters and the relatively weak light energy of the instrument; the upper red end of the spectrum will be noisy because of the generally weak light/detector sensitivity and strong scattering by the filter. The crossover wavelength between the deuterium and tungsten lamps is between 300 nm and 350 nm and should be consistently maintained. The wavelength resolution, scan speed and integration times are recommended to be 1 nm;
120 to 300 nm per minute; 0.1 to 0.2 s, respectively. A slit band width (SBW) of 2 nm is recommended. Smaller SBW lead to reduced light energy and lower signal to noise while larger SBWs reduce the resolution of spectral variations associated with distinct pigments.

Spectrophotometric noise varies between manufacturers, between instruments, and over time. This is best assessed by collecting multiple air scans and computing the standard deviation spectrum over the entire wavelength range. The target value is approximately 0.0005 optical density units and is the lowest level of uncertainty.

5.4.4 Baseline, zero and blank scans in T-Mode

Baseline scans are necessary to remove the instrument signal which encompasses the variations due to lamp energy spectrum, spectral sensitivity of the detector and the optical signature of the glass fiber filter. There are two approaches to performing baseline scans: air baselines and filter pad baselines. The end product particulate absorption will be the same but the differences are in what appears on the screen as samples are processed.

The air baseline approach involves collecting a single air scan as a baseline which is automatically removed from subsequent blank and sample scans. The average spectrum of a set of 3 - 5 blank filter pads scans are then subtracted from each sample scan to remove the optical signature of the filter pad. The standard deviation spectrum of the blank scans is used to compute absorption uncertainty using Eq. 5.6. What appears on the screen during measurement is a spectrum that is the sum of the filter pad and the sample optical properties. To maintain the proper sample loading on the filter (optical density between 0.1 and 0.4), the contribution by the blank filter has to be mentally removed. Thus, if the optical density of the blank filter is 0.25 in the UV (as is typical for T-mode) and the sample filter optical density is 0.6, the sample optical density is 0.35, still less than the maximal 0.4 optical density target (Fig. 5.11).

![Figure 5.11. Example of a particulate optical density scan run in T-mode with air as a baseline (black) or with a blank filter as a baseline (blue). Note the sample optical density range is between 0.1 and 0.4 (the target range) for the visible portion of the spectrum but begins to exceed this optimal range in the UV portion of the spectrum.](image)

The filter pad baseline approach involves collecting a single scan of a prepared blank filter pad as the baseline which is automatically removed from subsequent blank and sample filter scans. The average spectrum of the blank filter scans should be spectrally flat about zero (Fig. 5.4). The advantage of this approach is that the scans that appear on the screen show the optical density of the sample material and instantly allow the user to determine if the proper loading has been achieved throughout the spectral range. It also provides an instant assessment of the blank filter spectral variations.

5.4.5 Sample analysis for T-Mode

The sequence of sample scans includes the assessment of a baseline, a series of blank filter pads, and the initial scan of the set of sample filter pads. The initial scan of each sample provides the assessment of particulate optical density, $OD_p(\lambda)$. After pigment extraction (Section 5.2), the sample filters are scanned again to provide assessment of the non-extractable particulate contribution to optical density, also known as non-algal particles, $OD_{NAP}(\lambda)$ (Fig. 5.12).
Figure 5.12. Example of a particulate (blue) and extracted non-algal particle (cyan) optical density scans measured in T-mode with a blank filter as a baseline. Note the magnitude and shape of the optical density spectra in the near IR (~700 nm - 850 nm) is zero and spectrally flat within the uncertainty of T-mode blank filter readings.

The operating protocol of the spectrophotometer with regards to spectral bandwidth, spectral sampling, and scan rates are the same as described earlier in this section. The recommendations regarding maintaining filter hydration between measurements should also be followed. A typical sequence of making measurements is as follows:

1. The baseline scan is initiated with the quartz neutral density filter placed securely to the light source side of the reference port and a moist blank filter placed securely to the detector side of the sample port (diagram). This is the baseline scan. For most instruments, this scan is stored internally and automatically subtracted from subsequent samples scans.

2. Without opening the sample compartment, a second scan is immediately collected. This scan will have the baseline scan automatically removed. Because no changes have been made this scan should be spectrally flat about zero; this the zero scan. If there is some spectral dependence to this scan or noise of a level exceeding 0.001 the blank filter pad should be replaced with a different moist pad and the baseline and zero scan repeated.

3. A series of 3 – 5 blank filters scans are collected relative to the baseline scan; these are the blank scans. These should likewise exhibit no spectral dependence and with signals of order 0.001 throughout the spectrum. The largest variations are likely found in the UV and far-red portions of the spectra (Fig. 5.6). If all the blank filter scans are similar to each other but very different from zero, the baseline filter pad is anomalous and one of the blank pads should be rerun in baseline mode. Repeat the zero and blank scans as above.

4. Sample filters are scanned similarly relative to the baseline scan. A notch at the edge of the filter is used to align the position of the filter on the holder. This provides a mechanism for placing the filter in the same orientation after pigment extraction. Remoistening and rotating the filter 90° for a second scan provides a measure of within sample variability. These measurements provide the optical density signature for computing the spectral particulate absorption coefficients, $a_p(\lambda)$, via Eq. 5.3.

5. After pigment extraction (Section 5.2), each sample filter is rescanned to assess the optical density signature of the non-algal particles for computing absorption properties, $a_{NAP}(\lambda)$.

6. Blank filters are scanned throughout the measurement period to assess any drift in the instrument relative to the initial baseline. If the blank filter spectra vary relative to their initial scans in spectral shape (flat) and magnitude (+/- 0.001 maximally), a new series of baseline, zero and blank scans should be run.

5.4.6 Data processing for T-Mode

General processing of data and calculation of the absorption coefficient is similar to the general guidelines described in Section 5.3. An important variation unique to the T-mode is that the so-called “null
point” correction, in which subtraction of a spectrally-constant value from the NIR spectral region is used to account for large scattering losses. Experience with healthy phytoplankton cultures suggests that there is negligible absorption in the NIR, thus when non-negligible absorption is measured in the NIR using the filter pad technique in T-mode, it is assumed that it is due to scattering losses by the filter pad. The assumption is that these scattering losses are spectrally invariant due to the large size of the scattering fibers of the filter relative to the wavelength of light (and confirmed by their white scattering appearance). Thus, the average absorption value computed in the NIR region is subtracted from the entire spectrum, resulting in a shift down (in the case of positive NIR signal) or shift up (in the case of a negative NIR signal). Problems arise when the sample is composed of particulates other than healthy phytoplankton. In this case the NIR null point correction likely removes some contribution to absorption by these non-algal particles and leads to a larger uncertainty. However, in the absence of other supporting measurements, the null point correction provides the lowest error estimate for T-mode absorption measurements. The data processing procedure is as follows:

1. Instrument drift is quantified from the blank filter pad measurements made at different times throughout the measurement period. If required, all filter baselines and sample spectra are corrected for any observed drift.
2. The average and standard deviation optical density spectra from all blank filter pad scans are computed. If the air baseline approach is used, the average is subtracted from each measured spectrum. If the blank filter baseline approach is used, no additional subtraction is necessary (as the average of the blank filters relative to a blank filter baseline should be zero within 0.001 optical density units).
3. Replicate measurements of baseline-corrected sample filter optical density, \( OD_{f}(\lambda) \), obtained on the same sample filter are averaged.
4. The blank-corrected and averaged \( OD_{f}(\lambda) \) of the sample can be smoothed, for example with a moving average. The choice of smoothing window width and number of iterations is determined based on characteristics of the sample spectra (i.e., presence or absence of sharp peaks, behavior of instrument noise).
5. The particle absorption coefficient, \( a_{f}(\lambda) \), non-algal particle absorption coefficient, \( a_{NAP}(\lambda) \), and standard deviation absorption coefficient, \( \sigma_{f}(\lambda) \), for each sample is calculated from Eq. 5.3.
6. For the particulate and non-algal particle absorption spectra, the null point correction can be applied by subtracting the respective average absorption values in the NIR (e.g. over the range 800 nm – 850 nm).
7. The phytoplankton absorption spectrum is computed from the particulate and non-algal particle absorption spectra by difference using Eq. 5.8.

### 5.5 Measurement of Filter Pad Absorption in T-Mode Using Fiber Optics

#### 5.5.1 General Considerations for Fiber Optic T-Mode

Particulate absorption measurements using the QFT method have been assessed on a fiber-optic based spectrophotometer (Beltz et al. 2006; Miller et al. 2011; Naik and D’Sa 2012). The portable fiber-optic based system consists of a single beam optical path with a light source, a filter holder and a fiber-optic spectrometer all connected serially using optical fibers (Fig. 5.13a). The filter holder consists of a filter fixture for the GF/F filter and a holder (Fig. 5.13b; QFT1-89575, WPI). In its basic configuration, the output of a high intensity light source (Fig. 5.13c; e.g., D2H consisting of a deuterium and halogen lamp; WPI Inc.) is coupled via an optical fiber with a core diameter of 600 \( \mu \text{m} \) to the filter holder. A combination of 600 \( \mu \text{m} \) input fiber and a fused silica lens collimates the input light into an approximately parallel beam of 5 \( \text{mm} \) diameter (Belz et al. 2006). The collimated light beam incident perpendicular to GF/F filter (blank, particulate or extracted) is transmitted or scattered through the filter and is collected by a second collimating lens behind the filter and coupled into an exit 600 \( \mu \text{m} \) fiber that is then connected to a photodiode array spectrometer (Fig. 5.13d; e.g., Tidas, J&M Analytische Messung Regeltechnik GmbH) that is optimized for the spectral range of 195 - 725 nm. The Tidas spectrometer connects via a RS-232 to USB adapter to a Windows based computer with vendor supplied Spectralys software that is used to acquire, display and analyze the spectral data.
the base of 10, were converted to absorption coefficient values (a(sample cell was achieved by using a peristaltic pump [11] at 4 mL/min. Absorbance units, measured with a logarithm to a light source [13] and a photodiode array spectrometer [12] via optical fibers. Consistent sample injection into the effective pathlength of the sample cell.

Prepared, the 100% dilution consists of 2 mL Maalox diluted in 400 ml Milli-Q water. The remaining dilutions had a size Whatman nylon filters. Effects of scattering on absorption measurements were evaluated using a suspension of Colored dissolved organic mater (CDOM) solutions were prepared from suspended particles obtained following seawater sampling onboard the ship. The Lambda relatively inexpensive

Advantages: The fiber optic based spectrophotometer for QFT measurements is small and portable and relatively inexpensive in comparison to the laboratory based spectrophotometers (e.g., Perkin-Elmer Lambda-850). It can be easily setup on a ship during field campaigns and absorption measurements of suspended particles obtained following seawater sampling onboard the ship. The use of a photodiode array-based spectrometer also allows for greater sensitivity in the absorbance measurements by increasing the integration time of the detector.

Disadvantages: Results of a comparison study of particle absorption on a filter indicated small differences (~5%) in OD(λ) between the fiber-optic based QFT system and a high performance spectrophotometer (e.g., Perkin Elmer Lambda 850; Miller et al. 2011; Naik and D’Sa 2012).

5.5.2 Sample analysis for Fiber Optic T-Mode
1. The spectrophotometer (lamps and the spectrometer) should be allowed to warm for one hour before running the samples.
2. The Spectralys software is started.
3. The steps for blank and sample GF/F filter preparation (Section 5.2) should be followed.
4. A blank GF/F filter is placed in the fiber optic filter holder.
5. Integration time is adjusted on the spectrometer to optimize the light transmission through the blank hydrated filter to obtain peak intensity of ~70% and then select absorbance mode.
6. A ‘dark spectrum’ is obtained with the shutter closed.
7. The shutter switch is moved to ‘open’ mode and ‘reference spectrum’ is obtained.
8. The blank filter is replaced with a filter that contains all particles and then non-algal particles following methanol extraction.
9. A ‘sample spectrum’ is obtained and repeated after rotating the filter 90°.
10. The spectra are export and saved as an ascii file.
5.5.3 Data processing for Fiber Optic T-Mode

![Figure 5.14. Comparison of spectral shape of optical density (OD\(_f(\lambda)\)) of particles on GF/F filter measured with the fiber-optic based system and a Perkin-Elmer Lambda 850 spectrophotometer with an integrating sphere (Naik and D’Sa 2012).](image)

1. A null correction should be applied by subtracting the average of spectrally flat region between 712-722 nm.

2. Optical density OD\(_f(\lambda)\) for representative culture samples measured on the fiber optic based system and the Lambda 850 showed overall very good agreement with strong linear relationship observed between OD\(_f(\lambda)\) at chlorophyll absorption peaks (443 and 676 nm) and also over the entire visible domain from 400 to 700 nm (Fig. 5.14). These results suggested that the beta correction factor derived for the Perkin Elmer Lambda 850 with an integrating sphere could be applied to the fiber optic based QFT system. The equation for beta correction for path length amplification effect caused by multiple scattering in the glass-fiber filter applicable to the fiber-optic based absorbance measurements is given as (Naik and D’Sa 2012):

\[
OD_s(\lambda) = 0.405[OD_f(\lambda)] + 0.475[OD_f(\lambda)]^2 \tag{5.9}
\]

where OD\(_s(\lambda)\) is the corrected optical density of particulate matter. The absorption coefficient of the particulate matter (\(a_p(\lambda)\) or \(a_{NAP}(\lambda)\)) was then calculated as:

\[
a_p(\lambda) = 2.303[OD_s(\lambda)] A/V \tag{5.10}
\]

where 2.303 is the factor used to convert log\(_{10}\) to log\(_e\). \(A\) is the filter clearance area (m\(^2\)), and \(V\) is the filtered volume (m\(^3\)). The ratio of \(A\) to \(V\) represents the geometrical path length.

5.6 Measurement of Filter Pad Absorption in Transmittance and Reflectance Mode (T-R Mode)

5.6.1 General Considerations for T-R Mode

Tassan and Ferrari (1995a) described a modification of the light-transmission method that corrects for differences in backscattering between the sample and reference filter, and, thus, compensates for small backscatter differences in between different sample filters. This technique combines light-transmission (T) and light-reflection (R) measurements, carried out using an integrating sphere attached to a dual-beam spectrophotometer. The data analysis is performed by a theoretical model that eliminates the effect of differences in light backscattering by the particles and different filters. Modifications of the T-R experimental routine (Tassan and Ferrari 1998; Ferrari and Tassan 1999) yielded a significant reduction of the experimental error. Absolute errors are typically lower for the T-R method than for the T method (Tassan and Ferrari 2002, Röttgers and Gehrke 2012). Tassan and Ferrari (1995) reported that for Case 1 waters that have negligible inorganic particle load, the amplification factor for GF/F filters determined with the T-R methods is similar to those determined by Mitchell (1990). Similar results were obtained for Case 2 waters (Tassan et al. 2000). The T-R method is particularly suited for applications to samples containing highly scattering mineral particles that are commonly found in Case 2 waters. When sample
measurements of T and R are made with a good spectrophotometer and integrating sphere in between a short time, the compensation of backscatter differences between filters is sufficient to reduce the general scattering error, then a null-point correction is obsolete (Tassan and Ferrari 2003, Röttgers and Gehnke 2012). The method should be considered when a good spectrophotometer equipped with an integrating sphere is at hand, but the sphere does not allow placing a sample inside.

The most recent procedure that includes some modifications of the Tassan and Ferrari (1995a) routine is described by Tassan and Ferrari (2002). Here, the method is described in a simplified way.

5.6.2 Sample analysis for T-R Mode

All common procedure for spectrophotometric measurements as described above shall be followed. The differences are mostly related to the use of the integrating sphere. Properties of the integrating sphere are of lower importance, but usually sphere with a larger diameter provide better performance. A sphere inside a double-beam spectrophotometer has typically four ports, two entrance ports and two exit ports, one set for the sample and the reference beam. The exit ports are normally closed with white reflective plates (typically calibrated reflectance standards), behind these plates often black light traps are placed. Alignment of the two light beams should be checked with respect to the beam position being in the center of these reflective plates. The baseline is recorded with both entrance ports void and both exit ports closed with reflectance standards.

All spectral measurements can be done in the optical density- (OD-) mode and the following procedure is based on OD measurements. A hydrated blank filter is measured for referencing. When using 25 mm GF/F filters, these, when wet, can be placed directly onto the integrating sphere ports. Some extra supports for the filters can be arranged to avoid salt water coming in direct contact with the outside of the integrating sphere. Using glass plates behind the filter as supports is not recommended. Each filter is first measured when placed in front of the sample beam entrance port, when the reference beam entrance port is void and the exit ports are closed with the reflectance standards. This results in the respective OD of the transmittance mode for the sample filter and the reference filter, $OD^T_{f_s}$ and $OD^T_{f_r}$. Secondly, the same filter is measured (after another hydration if necessary) in reflectance mode when placed (sample side facing the light beam) at the sample beam exit port. The reflectance standard at this port is removed, the room behind the filter served as a black light trap (otherwise support the filter with a black material). These measurement results in the respective OD of the reflectance mode for the sample filter and the reference filter, $OD^R_{f_s}$ and $OD^R_{f_r}$.

5.6.3 Data processing for T-R Mode

To be in accordance with the equations provided by Tassan and Ferrari (2002), the ODs are transferred to specific transmittances and reflectances using $OD^T = \log_{10}(1/T)$ and $OD^R = \log_{10}(1/R)$. This results in absolute transmittances and reflectances of the sample and reference filter, $T_{f_s}$, $T_{f_r}$, $R_{f_s}$ and $R_{f_r}$. The ratios of the two T and two R measurements gives T and R spectra of the sample, i.e., $T_f = T_{f_s}/T_{f_r}$ and $R_f = R_{f_s}/R_{f_r}$, respectively. $T_f$ is used to calculate $OD^T_{f_s}$, the optical density of the sample in the transmission mode. This set of measurements is used to calculated the absorbance of the sample as

$$A_f = \frac{1 - T_f + R_f (T_f - R_f)}{1 + R_f T_f} \tau$$

where $\tau$ compensates for the fact that the reflected light inside the filter is diffuse and is no longer parallel, its effect on $A_s$ is low (<3%). The factor was determined empirically and can be calculated for each sample filter by:

$$\tau(\lambda) = 1.15 - 0.17 \ OD^T_{f_s}(\lambda), \quad (5.11)$$

where

$$OD^T_{f_s}(\lambda) = OD^T_{f_s}(\lambda) - 0.5 \ OD^T_{f_s}(750). \quad (5.12)$$

The formulation for $\tau$ is valid for $0.02 < OD^T_{f_s} < 0.7$. 


From $A_s$ the backscatter corrected optical density of the sample can be calculated as $OD_f = \log_{10}(1/(1 - A_s))$.

The calculations of the optical density of the sample in suspension, $OD_{sus}$, is done according to Tassan and Ferrari (1995) as

$$OD_s = 0.423 OD_f + 0.479 OD_f^2.$$  \hspace{1cm} (5.13)

A calculation of the absorption coefficient from $OD_s$ is done as shown above, using the filtered sample volume and the area of the sample patch on the filter.

### 5.7 Measurement of Filter Pad Absorption Inside and Integrating Sphere (IS-Mode)

#### 5.7.1 General considerations for IS-Mode

Historically, the most common implementation of the filter-pad technique involves measuring the transmittance ($T$) of a sample filter relative to a blank reference filter (Mitchell et al. 2003). This method suffers from a poor geometry as a large fraction of light scattered by the filter is not detected by the spectrophotometer, resulting in unknown errors in the spectral determination of filter optical density, $OD(\lambda)$, and ultimately in the particulate absorption coefficient, $a_p(\lambda)$. An alternative approach, referred to as the transmittance-reflectance (T-R) method, employs multiple scans of the sample and reference filters placed at the entrance (transmittance) and exit (reflectance) ports of an integrating sphere (Tassan and Ferrari 1995, 1998). The underlying assumptions of the T-R method are based on the law of energy conversation, but uncertainties arise as these assumptions are not necessarily fully satisfied with the actual measurement configuration. The need for multiple scans at different filter positions also increases uncertainties and makes the method more laborious to implement.

To circumvent these limitations, we recommend an improved refinement of the filter-pad technique in which the sample or reference filter is placed inside an integrating sphere during measurement. This inside sphere (IS-mode) technique ensures the detection of nearly all photons scattered by the sample, resulting in improved accuracy and precision of absorption measurements (Maske and Haardt 1987; Babin and Stramski 2002, 2004; Stramski et al. 2004, 2007; Röttgers and Gehnke 2012; Stramski et al. 2015). Because this method does not require multiple scans of the same filter in different optical configurations, the effort is no more laborious than the traditional T-mode.

#### 5.7.2 Sample preparation for IS-Mode

Sample collection and filtering follow the same guidelines recommended for the general filter-pad technique (Section 5.2). Filter volumes are adjusted to target an optical density of the sample filter between 0.1 and 0.4; for some spectral regions, multiple filtrations of the sample with different volumes may be needed to satisfy these criteria.

#### 5.7.3 Spectrophotometer configuration for IS-Mode

A suitable dual-beam spectrophotometer equipped with an integrating sphere (e.g., 15 cm diameter sphere) is required to implement the IS method. The instrument performance with regards to wavelength accuracy and absorbance calibration should be verified as described in Section 5.4.3.

Some integrating sphere manufacturers provide a fixture for mounting of samples within the beam inside the sphere, which can be adapted to positioning of sample filters. Alternatively, a custom mounting system can be fabricated. The mounting system should center the sample filter perpendicular to the illumination beam, and be secured in a way that ensures reproducible positioning of a filter at the same location. Ideally, the mounting mechanism should be constructed such that only the filter itself interacts with the beam (i.e., no filter supporting structure within the illuminated portion). All materials within the sphere should be made of Spectralon or coated with a similar highly reflective material.

Through the use of various apertures, the size and shape of the sample beam is adjusted to provide a beam illuminating the center of the filtered area. Beam size should be sufficiently large to cover a representative portion of the filter (e.g., 3 x 6 mm).
5.7.4 Sample analysis for IS-Mode

The operating protocol of the spectrophotometer with regards to spectral bandwidth, spectral sampling, and scan rates are the same as described earlier in Section 5.4.3. The recommendations regarding maintaining sample filter hydration between measurements should also be followed. A typical sequence of making measurements is as follows:

1. After a suitable warm-up period, the spectrophotometer is initially autozeroed by scanning air-vs-air with the empty mounting mechanism placed within the sphere; for most instruments, this scan is automatically stored in memory and subtracted from subsequent scans. The scan is then repeated and the data saved to provide an actual measure of instrument baseline. This air-vs-air instrument baseline should be performed and saved at regular intervals to check for instrument drift throughout the course of sample measurements.

2. Hydrated blank filters (minimum of 2 to 3) drawn from the same batch as the sample filters are positioned on the mounting mechanism and placed within the center of the integrating sphere for measurement. These blank filters are scanned (relative to air in the reference beam) and saved for determination of the average filter baseline. These can be run initially before beginning analysis of samples, or spaced intermittently between sample filters.

3. After removal of any excess moisture, the sample filter is positioned on the mounting mechanism and placed within the center of the integrating sphere for measurement. It is useful to notch or mark an edge of each filter before initial measurement to ensure reproducible positioning of the filter for subsequent scans (e.g., for replicate scans and after pigment extraction).

4. The filter is scanned (relative to air in the reference beam) and the measured optical density values (absorbance values) are saved to computer memory. Following the initial measurement, the filter is repositioned in a different orientation (e.g., 90° rotation) and measured a second time to check reproducibility and homogeneity of sample distribution on the filter.

5. Following measurement, sample filters can be extracted in solvent to remove phytoplankton pigments (Section 5.2) and re-measured in the spectrophotometer to estimate the non-algal particulate absorption coefficient, \( a_{NAP}(\lambda) \).

5.7.5 Data processing for IS-Mode

General processing of data and calculation of the absorption coefficient is similar to the guidelines described in Section 5.3 for T-mode. An important exception is that the so-called “null point” correction, in which subtraction of a spectrally constant value from the NIR spectral region is used to account for scattering losses, is not applied. Experience suggests that scattering losses with the IS technique are small enough to be considered negligible, and the application of a null point correction can mask true particulate absorption in the NIR.

The general sequence of data processing is:

1. Instrument drift is checked from the air-vs-air measurements made at different times throughout the measurement period. If needed, all filter baselines and sample spectra are corrected for any observed drift.

2. Measurements from all blank filters are averaged to create the final values of optical density for the filter baseline (relative to air).

3. The spectrum of the final filter baseline is subtracted from each sample filter optical density.

4. Replicate measurements of baseline-corrected sample filter optical density, \( \text{OD}_f(\lambda) \), obtained on the same sample filter are averaged.

5. The blank-corrected and averaged \( \text{OD}_f(\lambda) \) of the sample can be smoothed, for example with a moving average. The choice of smoothing window width and number of iterations is determined based on characteristics of the sample spectra (i.e., presence or absence of sharp peaks, behavior of instrument noise).

6. The particle absorption coefficient, \( a_p(\lambda) \), of each sample is calculated from \( \text{OD}_f(\lambda) \) using the known filtration volume \( (V; \text{m}^3) \), the measured interception area of filtration \( (A; \text{m}^2) \), and an empirically-
determined beta-correction. Omitting the wavelength arguments, the final form of this equation is

\[ a_p = \ln(10) \times 0.323 \times (OD_3)^{1.0867} / (V/A) \] (5.14)

which utilizes a beta-correction modeled as a power function for the relationship between OD, which is subject to path length amplification and the optical density of the same particles in suspension which is not affected by path length amplification (ODs).

\[ OD_s = 0.323 \times (OD_3)^{1.0867} \] (5.15)

This correction was determined empirically using a variety of different particle assemblages (Stramski et al. 2015). Importantly, in these experiments the ODs was also measured within the integrating sphere to provide a very close estimate of the true reference absorption coefficient. The methodology of measurements of particle suspensions placed inside the integrating sphere is described elsewhere (Babin and Stramski 2002, 2004; Stramski et al. 2007).

7. As mentioned previously, no null point scattering correction is applied to the calculated \( a_p(\lambda) \). If a corresponding absorption spectrum of the particles after pigment extraction (\( a_{NAP} \)) is available, this spectrum is adjusted with an offset in the near-infrared so that the average value of \( a_{NAP}(\lambda) \) equals the average value of \( a_p(\lambda) \) in the spectral range 800 - 820 nm. When using the IS technique this adjustment of \( a_{NAP}(\lambda) \) is usually very small which supports the common assumption that phytoplankton pigments do not absorb in this spectral region.

REFERENCES


ACRONYM/ABBREVIATION DEFINITIONS LIST

CDM – Colored dissolved matter
CDOM – Colored dissolved organic matter
cm – centimeter
CTD – Conductivity temperature depth (instrument)
DIW – Deionized water
DROP – Descent rate optical package
FSW – Filtered seawater
FWHM – Full-width-half-max
GF/F – Glass fiber filters
GH-QI-KS – Quickenden and Irvin; Ghormley and Hachanadel; Kröckel and Schmidt
ICAM – Integrating cavity absorption meter
IOP – Inherent optical property
IR – Infrared, 0.7 – 1000 µm
IS – Integrating sphere
LVF – linear variable filters
ND – Neutral density
m – meters
mm – millimeter
mmHg – millimeters of mercury
NAP – Non-algal particles
NIR – Near-infrared, 0.7 - 2 µm
nm – nanometers, $10^{-9}$ meters
PSICAM – Point Source Integrating Cavity Absorption Meter

PSU – Practical salinity unit

psi – pounds per square inch

QFT – Quantitative Filter Technique

SBW – Slit bandwidth

SPF – Short pass filter (blocking light at >650 nm)

T – Transmission

TIR – Total Internal Reflection

TR – Transmittance/reflectance

µm – micrometers, 10⁻⁶ meters

UPW – Ultrapure water

UV – Ultraviolet, 100 – 400 µm

VIS – 400 – 750 nm

VSF – Volume Scattering Function
SYMBOL LIST (BY CHAPTER)

CHAPTER 1

\( a = \) Volume absorption coefficient
\( \lambda_r = \) Reference wavelength (150 nm)
\( Z_c = \left( \frac{\nu_r^{11/12}}{\sqrt{T}} \right)^{2/3} \)
\( T = \) Temperature (degrees Kelvin)
\( a_g = \) Absorption coefficient of dissolved material (CDOM)
\( a_m = \) Absorption coefficient of minerals
\( a_{pg} = \) Absorption coefficient of particulate and dissolved material
\( a_t = \) Total absorption coefficient
\( a_p = \) Absorption coefficient of particles
\( a_g = \) Absorption coefficient of dissolved material
\( a_{NAP} = \) Absorption coefficient of non-algal particles
\( a_{ph} = \) Absorption coefficient of pigment-containing phytoplankton
\( a_{ph}^* = \) Chlorophyll-\( a \)-specific absorption coefficient of phytoplankton
\( a_p^* = \) Chlorophyll-specific absorption coefficient of total particulate matter
\( c_g = \) Attenuation of dissolved material
\( c_w = \) Attenuation of water
\( \nu = 10^7 \left( \frac{1}{\lambda_r} - \frac{1}{\lambda} \right) \)

CHAPTER 2

\( \Phi_K = \) Sum of directly transmitted and scattered fluxes
\( \Phi_i = \) Incident source flux
\( \Phi_B = \) Scattered flux
\( \Phi_T = \) Directly transmitted flux
\( S = \) electronic noise
\( \Phi_o = \) Flux entering the water at the source window
\( r_T = \) Path length
\( A = \) Absorbance
\( \Psi_c = \) Critical angle
\( \Psi = \) Scattering angle
\( \Phi_T = \) Flux measured by the detector
\( \rho_g (\Psi) = \) Net reflectance of the quartz tube beyond the critical angle
\( N (r_T - r; \Psi) = \) Average number of wall reflections required for a ray path to reach the detector following a scattering event
\( W(\Psi) = \) Weighting coefficient
\( a_m = \) Measured absorption coefficient
\( V_{samp} = \) Detector reading for water sample
\( V_{rcal} = \) Reference reading during water calibration
$V_{wcal} = $ Detector reading during water calibration  
$V_{fcal} = $ Detector reading from the factory water calibration, a device file that should be used for all measurements  
$V_{rfac} = $ Reference reading from the factory water calibration, a device file that should be used for all measurements  
$a_{wcal} = $ Absorption of the water calibration  
$a_{m} = $ Temperature and salinity corrected measured absorption  
$c_{m} = $ Temperature and salinity corrected measured attenuation  
$S = $ Salinity (PSU)  
$T = $ Temperature (Celsius)  
$T_r = $ Reference temperature  
$b = $ Total scattering  
$b_b = $ Total backscatter  
$\varepsilon = $ Scattering error  
$W(\Phi) = $ Weighting function  
$F = \varepsilon / b$  
$a_{corr}^{TS} = $ Temperature and salinity corrected total absorption  
$E_d = $ Downwelling irradiance  
$E_u = $ Upwelling irradiance  
$E_o = $ Scalar irradiance  
$E_{ou} = $ Upwelling scalar irradiance  
$E_{od} = $ Downwelling scalar irradiance  
$K_d = $ Downwelling diffuse attenuation coefficient  
$\vec{K} = $ Vertical attenuation coefficient for vector irradiance  
$\hat{n} = $ Outward unit vector normal to the surface  
$K_i = $ Proportionality constant (in)  
$K_o = $ Proportionality constant (out)  
$S_i = $ Signal voltage (in)  
$S_o = $ Signal voltage (out)  
$S = $ Ratio of the measured signal voltages  
$C_i = $ Signal normalization constant  
$C_o = $ Offset constant  
$r_i = $ inner radius of ICAM quartz tube  
$r_o = $ outer radius of ICAM quartz tube  

CHAPTER 3

$E = $ Vector irradiance  
$L = $ Scalar radiance  
$U = $ Radiant energy density  
$n = $ Refractive index  
$V = $ Volume of sample  
$P_{abs} = $ Power that is absorbed (the power entering the cavity minus the power leaving the cavity)

CHAPTER 4

$T_{AB} = $ Transmission difference between two samples
$F_0 =$ Diffuse reflected irradiance
$N_c =$ Number of times a photon is reflected by the wall
$P_0 =$ Probability that a photon, coming from the central light source, reaches the wall directly
$P_r =$ Probability that a photon, which is reflected, will return to the wall
$\rho =$ Reflectivity of the wall
$r =$ Inner radius of the cavity
$r_s =$ Radius of the central light source
$T_{\text{meas}} =$ Measured transmission
$T_{\text{num}} =$ Numerically calculated transmission
$G(a(\lambda)) =$ Least square function to solve for $a(\lambda)$
$t_w =$ Temperature of pure water
$F_w =$ Light intensity of pure water
$t_{\text{sample}} =$ Temperature of sample water
$F_{\text{sample}} =$ Light intensity of sample water
$S_{\text{sample}} =$ Salinity of the sample
$F_{\text{fluor}} =$ Fluorescence intensity
$F_{\text{sample} \, \text{SPF}} =$ Light intensity of sample water using a short pass filter
$F_{\text{w} \, \text{SPF}} =$ Light intensity of pure water using a short pass filter
$\Psi_i^{t} =$ Instrument-specific temperature correction coefficients
$\Psi_s^{i} =$ Instrument-specific salinity correction coefficients

CHAPTER 5

T-mode = Transmission mode
$\beta =$ Beta correction factor
$OD =$ Optical density
$OD_{f} =$Optical density of a filter pad after the baseline and reference filter are subtracted
$OD_{p} =$particulate optical density
$OD_{NAP} =$ Optical density of non-algal particles
$OD_{s} =$ optical density of the same particles in suspension which is not affected by path length amplification
$L =$ Geometric path length
$V =$ Filtration volume
$A =$ Effective area of the filter (cm$^2$)
$\sigma =$ uncertainty in absorption
$\mu_{\text{blank}} =$ Computed mean of blank filter scans
$\sigma_{\text{blank}} =$ Computed standard deviation of blank filter scans
$a_p =$ Absorption coefficient of particles
$a_{NAP} =$ Absorption coefficient of non-algal particles
T-R = Transmittance-Reflectance
$OD_{f\text{r}}^{T} =$ $OD$ of the transmittance mode for the sample filter
$OD_{f\text{r}}^{T} =$ $OD$ of the transmittance mode for the reference filter
$OD_{f\text{r}}^{R} =$ $OD$ of the reflectance mode for the sample filter
$OD_{f\text{r}}^{R} =$ $OD$ of the reflectance mode for the reference filter
$OD^{T} =$ Specific transmittance
$OD^R = \text{Specific reflectance}$
$T_{fs} = \text{Absolute transmittance of sample filter}$
$T_{fr} = \text{Absolute transmittance of reference filter}$
$R_{fs} = \text{Absolute reflectance of sample filter}$
$R_{fr} = \text{Absolute reflectance of reference filter}$
$T_f = \text{Transmittance spectrum of sample filter}$
$R_f = \text{Reflectance spectrum of sample filter}$
$A_f = \text{Absorbance of the sample}$
$\tau = \text{Compensation for reflected light inside the filter that is diffuse}$
$OD_f = \text{Backscatter corrected optical density of the sample}$