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DEVELOPMENT AND MODELLING OF A POINT SOURCE INTEGRATING CAVITY ABSORPTION METER (PSICAM)

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**DEVELOPMENT AND MODELLING OF A POINT SOURCE
INTEGRATING CAVITY ABSORPTION METER (PSICAM)**

by

CHRISTOPHE Jean-Yves Joël LEREBOURG

A thesis submitted to the University of Plymouth
in partial fulfilment for the degree of

DOCTOR OF PHILOSOPHY

Institute of Marine Studies
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In collaboration with
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Development and modelling of a Point Source Integrating Cavity Absorption Meter (PSICAM)

Christophe Jean-Yves Joël Lerebourg

Abstract

The absorption coefficient is a fundamental parameter in understanding the underwater light field, for solving the Radiative Transfer Equation and understanding/interpreting remotely sensed data from the ocean. Measuring the absorption coefficient is particularly complicated in coastal areas where the optical properties of the water body are the result of a complex mixture of dissolved and particulate components, but mainly because of the interfering effect that scattering has upon the measurements. A great variety of *in situ* instruments and laboratory techniques have been developed to measure total absorption or the absorption by the various fractions that constitute the total absorption. They are, however, all affected by scattering and empirical corrections need to be applied. Among the instruments to measure absorption, a promising one appeared to be one based on an integrating cavity. Kirk (1995, 1997) outlined the principle and theory of an absorption meter based on an integrating sphere: a Point Source Integrating Cavity Absorption Meter (PSICAM). He argued that owing to its design, a PSICAM would be insensitive to scattering.

A novel Monte Carlo code was written to simulate the behaviour of a PSICAM of various cavity radii. The results of the simulations carried out with this code showed that such an absorption meter should indeed be unaffected by scattering even with high levels of scatterers. One important disadvantage deduced from numerical modelling for a PSICAM is its sensitivity to the reflectivity of the integrating cavity.

Several prototype PSICAMs of increasing quality were built and tested with scattering-free standard solutions. A major difficulty in the development of the prototype was found to be the calibration of the integrating sphere reflectivity. A final laboratory instrument made of a Spectralon sphere was built and tested with artificial and natural water samples containing different levels of scattering particles and compared with existing *in situ* and laboratory techniques: the ac-9 transmissometer and the filter paper technique for particulate absorption as well as measurement of Coloured Dissolved Organic Matter. Compared with the ac-9 transmissometer, the PSICAM showed remarkable agreement even for water with very high content of Suspended Particulate Matter. Very good correlations were obtained when compared with traditional CDOM measurement. In some cases, significant discrepancies occurred with filter paper measurements of particulate absorption. From laboratory to *in situ* experiments the PSICAM proved to be a reliable instrument assuming that the instrument was regularly and carefully calibrated. Finally, the PSICAM was deployed during a cruise around the Antarctic Peninsula where total and dissolved absorption measurements were carried out together with chlorophyll absorption measurements after extraction in acetone.

AUTHOR'S DECLARATION

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award.

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A variety of internal seminars were attended. Seminars were given by researchers from the Institute of Marine Studies and from external institutions.

The material in this thesis has been presented by the author at several external conferences.

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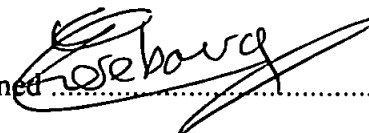
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Chapter 1: Introduction

1.1. Why measure light absorption in the oceans?

Absorption of light is the key factor if we are to understand the behaviour of light under water. It is of major importance for the understanding of the Radiative Transfer Equation and for the understanding and interpretation of remotely sensed data of the ocean. Seawater contains dissolved inorganic salts, dissolved inorganic matter, dissolved gases and a great variety of suspensions including terrigenous particles, phytoplankton, zooplankton, bacteria and detritus. Each of the constituents mixed in very varying proportions produce the complex colour of the oceans. The separation of the components that contribute to absorption has been shown to be important in estimating water column primary production, in predicting the presence of harmful algal blooms and in estimating suspended particulate concentration. A major goal for the understanding of remotely sensed data has been to understand and differentiate the optical signature of these components of the water column and their relationship to the water leaving radiance. The interest in studying the optical properties of natural waters has been very much enhanced since the arrival of space technology into ocean sciences that could provide large amounts of data, on a regular basis and on various size scales, of the optical properties of the ocean. These technologies have made a new method for studying the ocean available to the ocean scientist community and have produced large amounts of data to understand and interpret. In comparison to the amount of data provided by satellite technology, our understanding and tools to investigate *in situ* optical properties was then limited. Various instruments capable of measuring *in situ* optical properties of the ocean have been developed in order to provide ground validation and a better understanding of the satellite data.

The absorption properties of oceanic provinces, where the impact from land drainage and sediment resuspension limited, are well documented. In these area referred to as case 1 water where the optical properties are dominated by phytoplankton, algorithms have been produced to predict phytoplankton concentrations and productivity from satellite imagery. One area which is less well documented, although easier to reach and to study on a regular basis, is the coastal area. These waters are referred to as case 2 waters because their optical signature is the result of a more complex mixture of components: chlorophyll, yellow substances, organic and inorganic components originating from land drainage and sediment resuspension. One difficulty in studying these areas is that they are highly changeable in time and space. Another difficulty in studying the optical properties of these waters and in particular their absorption properties is that they generally contain high concentrations of scattering particles, which corrupt the absorption measurements.

1.2. The problem

There are a great variety of *in situ* instruments or laboratory techniques that can be used to measure absorption. Most of them however are moderately or highly sensitive to scattering by particles. For those techniques, empirical corrections need to be applied for the scattering effect of particles. Other methods separate the dissolved and particulate fraction of a sample and measure them with different techniques. In coastal areas or in oceanic regions of high productivity, it is therefore very difficult to perform an accurate measurement of absorption on a non-disturbed sample.

One of the biggest challenges in optical oceanography today is to understand the phenomena and interactions in the highly dynamic coastal region. A recurrent problem in measuring absorption, particularly in these regions of the ocean as well as in highly productive oceanic regions, appears to be the interfering effect of scattering. It is towards the development

and testing of a new method for absorption measurement that the work presented here is addressed. Kirk (1995, 1997), proposed a design for an absorption meter, which he argued would be insensitive to scattering. He proposed the construction of an absorption meter whose sample to measure would be placed in a spherical integrating cavity and illuminated by a central point source at the centre of the cavity: a Point Source Integrating Cavity Absorption Meter (PSICAM). The sample to be analysed was to be enclosed in an integrating cavity, so that measurement of absorption could be made regardless of the level of scattering. With such a system, the only light losses would be due to absorption. Kirk, (1997) also detailed the optical theory for a PSICAM. The challenge of building and testing such an instrument was the inspiration for this PhD programme of research.

The first part of this work is dedicated to a review of the different optically active components to be found in the marine system, and how and in what proportion they absorb and scatter light. A review of the different existing techniques either *in situ* or in the laboratory to measure absorption as well as scattering is then presented in order to understand their advantages and disadvantages. Prior to building a prototype absorption meter, modelling of the PSICAM was carried out using the theory elaborated by Kirk (1997) for absorbing and non-scattering solutions and then by means of Monte Carlo simulation to investigate the behaviour of the instrument with absorbing and scattering solutions. From the observations made from the modelling experiments, a first basic prototype was built following the advise provided by Kirk (1997) and tested with standard solutions of known absorption. The following strategy was to build and test low cost but increasingly sophisticated prototypes with standard solutions. These prototypes used different materials for the integrating sphere as well as the light source. Once a prototype was tested and proved efficient with standard non-scattering solution, the final step consisted of testing the instrument with artificial and natural water samples containing

scatterers. For the validation of the system with solutions containing scattering particles, the method chosen was to compare the PSICAM measurements with existing and accepted techniques, namely the ac-9 transmissometer and the filter paper technique to measure particulate absorption. The prototype PSICAM was also field tested during an oceanographic cruise around the Antarctic peninsula.

1.3. The propagation of light underwater

Clearly, a crucial aspect of this work is the behaviour of the underwater light field and particularly the changes in that behaviour which occur when the light field interacts with dissolved and particulate material within the water body. There exist two “models” for describing the propagation of light through a medium: the wave model and the photon model.

- The wave model defines light with a specific wavelength λ (nm) and frequency ν (Hz or m^{-1}) related by Equation 1-1

$$\lambda = \frac{c}{\nu} \quad (\text{nm})$$

Equation 1-1

where c is the speed of light in the propagation medium concerned.

- The photon model considers light as indivisible particles referred to as quanta or photons. Thus, a beam of light in air consists of a continuous stream of photons travelling at $c=3.10^8\text{m.s}^{-1}$. This theory, for example, is the one considered when modelling light by the Monte Carlo technique.

Thus light is neither a particle nor a wave but both aspects are necessary for the understanding of light properties. The last part of this chapter will present the basic properties and their definitions used in marine optics.

1.3.1. Defining the light field

The light field may be expressed in terms of polar co-ordinates (Figure 1-1) where

- θ = the zenith angle (the angle between a given light beam and the upward vertical)
- φ = the azimuth angle (the angle between the vertical plane incorporating the light pencil and some other specified vertical plane such as the vertical plane of the sun)

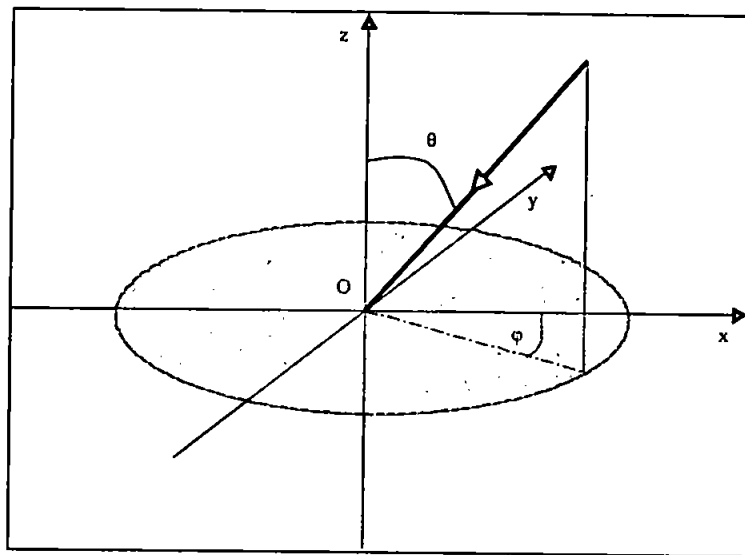


Figure 1-1: Angles defining direction within a light field (from Kirk, 1994)

Common quantities defined for use in underwater optics are:

Radiant flux, Φ is the time rate of flow of radiant energy. It is expressed in $\text{W (J.s}^{-1}\text{)}$ or photon.s^{-1} .

Radiant intensity, I is a measure of the radiant flux per unit solid angle (ω) in a specified direction (Equation 1-2). The radiant intensity of a source in a given direction is the radiant flux emitted by a point source, in an infinitesimal cone containing the given direction, divided by that element of solid angle. I has the unit of W.sr^{-1} or $\text{photon.s}^{-1}.\text{sr}^{-1}$.

$$I(\lambda, \omega) = \frac{d\Phi(\lambda)}{d\omega}$$

Equation 1-2

Radiance, L at a point in space is the radiant flux at that point in a given direction per unit solid angle per unit area at right angles to the direction of propagation (Figure 1-2, Equation 1-3). Radiance has a unit of $\text{W} \cdot \text{m}^{-2} \cdot \text{sr}^{-1}$ or $\text{photon} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{sr}^{-1}$.

$$L(\lambda, \theta, \varphi) = \frac{d^2 \Phi(\lambda)}{dS \cos \theta d\omega}$$

Equation 1-3

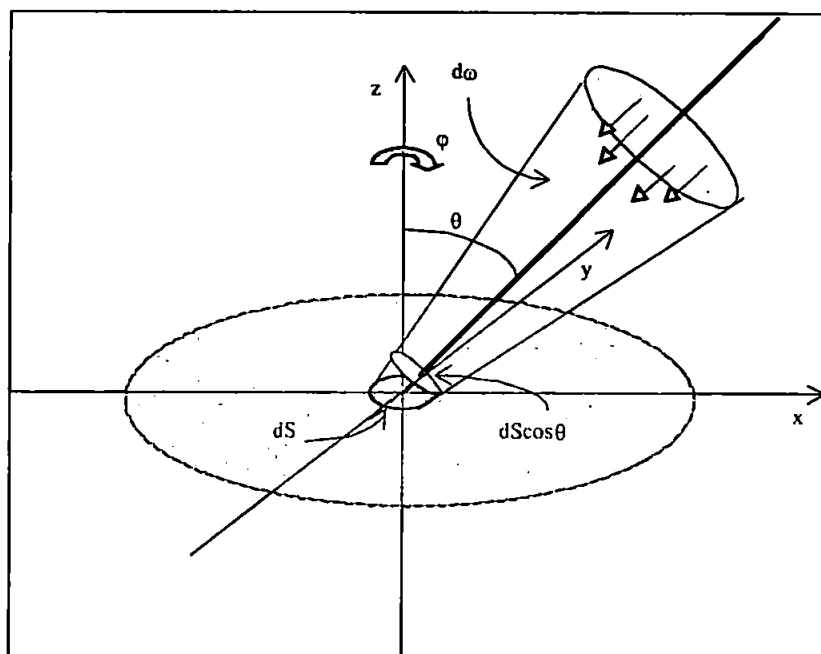


Figure 1-2: Definition of radiance (from Kirk, 1994)

Irradiance, E at a point of a surface is the radiant flux incident on an infinitesimal element of surface, containing the point under consideration, divided by the area of that element (Equation 1-4). E as a unit of $\text{W} \cdot \text{m}^{-2}$ and is defined as:

$$E(\lambda) = \frac{d\Phi(\lambda)}{dS}$$

Equation 1-4

Downward irradiance E_d , and **upward irradiance** E_u , the values of the irradiance on the upper and lower faces, respectively, of a horizontal surface (Equation 1-5). Therefore E_d is the irradiance of the downwelling light and E_u the irradiance due to the upwelling light stream. They both have units of W.m^{-2} or $\text{photon.s}^{-1}.\text{m}^{-2}$ and are defined as:

$$E_d(\lambda) = \int_{2\pi}^0 L(\lambda, \theta, \varphi) \cos \theta d\omega$$

$$E_u(\lambda) = - \int_{2\pi}^0 L(\lambda, \theta, \varphi) \cos \theta d\omega$$

Equation 1-5

The **net downward irradiance**, $\bar{E}$, is the difference between the downward and the upward irradiance (Equation 1-6).

$$\bar{E}(\lambda) = E_d(\lambda) - E_u(\lambda)$$

$$\bar{E}(\lambda) = \int_{\pi}^0 L(\lambda, \theta, \varphi) \cos \theta d\omega$$

Equation 1-6

The net downward irradiance is a measure of the net rate of transfer of energy downwards at that point in the medium.

The **scalar irradiance**, E_0 is the integral of the radiance distribution at a point over all directions about the point (Equation 1-7).

$$E_0(\lambda) = \int_{\pi}^0 L(\lambda, \theta, \varphi) d\omega$$

Equation 1-7

Scalar irradiance is thus a measure of the radiant intensity at a point, which treats radiation from all directions equally (Equation 1-8). It is sometime useful to divide the scalar irradiance into a downward and an upward component: the downward scalar irradiance, E_{0d} and the upward scalar irradiance, E_{0u} :

$$E_{0d}(\lambda) = \int_{2\pi}^0 L(\lambda, \theta, \varphi) d\omega$$

$$E_{0u}(\lambda) = \int_{-2\pi}^0 L(\lambda, \theta, \varphi) d\omega$$

Equation 1-8

Scalar irradiance (total, upward and downward) has the same unit as irradiance (W.m^{-2} or $\text{photon.s}^{-1}.\text{m}^{-2}$).

1.3.2. The Apparent Optical Properties

The AOPs depend both on the medium (i.e. on the inherent optical properties, see section 1.3.3) and on the ambient light field. Therefore, AOPs of a water body can display a great variation in short period of time if a cloud passes in front of the sun or if the wind changes the sea surface state. However, observation shows that certain ratios of the AOPs are relatively insensitive to environmental factors such as sea state. The most commonly used AOPs are described below.

1.3.2.1. Average cosine

The radiance distribution at a particular point in a medium varies markedly over all angles. The complete radiance distribution over all zeniths and azimuth angles represents a large amount of data. These data can be simplified in terms of three average cosines (for downwelling $\bar{\mu}_d$, upwelling $\bar{\mu}_u$, and total light $\bar{\mu}$, Equation 1-9).

$$\bar{\mu}_d(\lambda) = \frac{E_d(\lambda)}{E_{0d}(\lambda)}$$

$$\bar{\mu}_u(\lambda) = \frac{E_u(\lambda)}{E_{0u}(\lambda)}$$

$$\bar{\mu}(\lambda) = \frac{\bar{E}(\lambda)}{E_0(\lambda)} = \frac{E_d(\lambda) + E_u(\lambda)}{E_0(\lambda)}$$

Equation 1-9

1.3.2.2. Reflectance

Another way to simplify the radiance distribution over all zenith and azimuth angles is the irradiance reflectance $R(\lambda, z)$ or Remote Sensing Reflectance $R_{RS}(\theta, \lambda)$ (Equation 1-10). The first one is the ratio of the upward and downward irradiance at a given depth. The latter is defined as the ratio of the water leaving radiance and the downward irradiance measured below the surface.

$$R(\lambda) = \frac{E_u(\lambda)}{E_d(\lambda)}$$

$$R_{RS}(\theta, \lambda) = \frac{L_w(\theta, \lambda)}{E_d(\lambda, 0)}$$

Equation 1-10

1.3.2.2.1. Vertical Attenuation Coefficient

The vertical attenuation coefficients for downward ($K_d(\lambda)$, Equation 1-11), upward ($K_u(\lambda)$, Equation 1-12), net downward ($K_E(\lambda)$, Equation 1-13) and scalar (K_0 , Equation 1-14) irradiance as well as for radiance ($K(\lambda, \theta, \phi)$, Equation 1-15) specify the rate of change of the logarithm of these values with depth. They are defined as:

$$K_d(\lambda) = -\frac{d \ln E_d(\lambda)}{dz} = -\frac{1}{E_d(\lambda)} \frac{d E_d(\lambda)}{dz}$$

Equation 1-11

$$K_u(\lambda) = -\frac{d \ln E_u(\lambda)}{dz} = -\frac{1}{E_u(\lambda)} \frac{d E_u(\lambda)}{dz}$$

Equation 1-12

$$K_E(\lambda) = -\frac{d \ln [E_d(\lambda) - E_u(\lambda)]}{dz} = -\frac{1}{[E_d(\lambda) - E_u(\lambda)]} \frac{d [E_d(\lambda) - E_u(\lambda)]}{dz}$$

Equation 1-13

$$K_0(\lambda) = -\frac{d \ln E_0(\lambda)}{dz} = -\frac{1}{E_0(\lambda)} \frac{d E_0(\lambda)}{dz}$$

Equation 1-14

$$K(\lambda, \theta, \varphi) = -\frac{d \ln L(\lambda, \theta, \varphi)}{dz} = -\frac{1}{L(\lambda, \theta, \varphi)} \frac{d L(\lambda, \theta, \varphi)}{dz}$$

Equation 1-15

1.3.3. The Inherent Optical Properties

The Inherent Optical Properties (IOPs) unlike the AOPs depends only on the characteristics of the water body and not on the structure of the light field (*Preisendorfer, 1961*). They are intrinsic properties of the water body. There are three IOPs: the absorption coefficient $a(\lambda)$, the bulk scattering coefficient $b(\lambda)$ that can also be investigated in terms of its angular distribution (the volume scattering function $\beta(\lambda, \theta)$) and the beam attenuation coefficient $c(\lambda) = a(\lambda) + b(\lambda)$.

In an aquatic medium, photons can be either absorbed or scattered. Therefore, if we are to understand the behaviour of solar radiation in an aquatic medium, we have to measure in which relative proportions water scatters and absorbs light.

Imagining an infinitesimally thin layer illuminated orthogonally by a parallel beam of monochromatic light (Figure 1-3). The absorption coefficient is the fraction of the incident flux that is absorbed, divided by the thickness of the layer. The scattering coefficient is the fraction of the incident flux that is scattered, divided by the thickness of the layer.

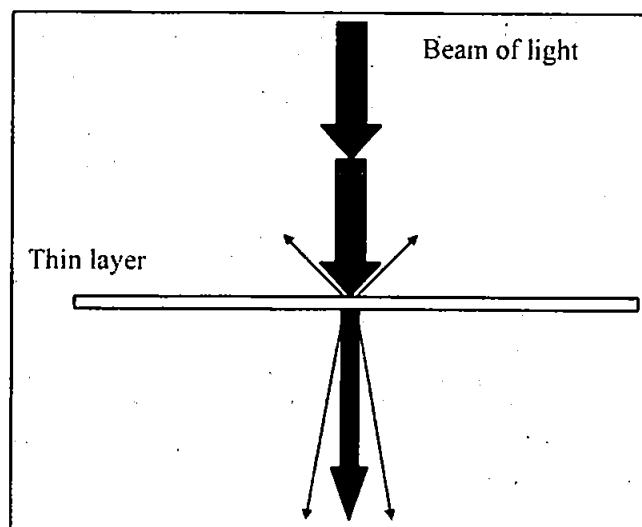


Figure 1-3: Interaction of a beam of light with a thin layer of an aquatic medium (Kirk, 1994)

To calculate the absorption and scattering coefficient, the absorbance (A), the scatterance (B) and the attenuance (C) are first calculated (Equation 1-16). If Φ_0 is the incident radiant flux on the thin layer, Φ_A is the radiant flux absorbed by the layer and Φ_B is the radiant flux scattered by the layer then A and B are calculated as:

$$\begin{aligned}\Delta A(\lambda) &= \frac{\Phi_A(\lambda)}{\Phi_0(\lambda)} \\ \Delta B(\lambda) &= \frac{\Phi_B(\lambda)}{\Phi_0(\lambda)} \\ \Delta C(\lambda) &= \frac{\Phi_C(\lambda)}{\Phi_0(\lambda)} = \frac{\Phi_A(\lambda) + \Phi_B(\lambda)}{\Phi_0(\lambda)}\end{aligned}$$

Equation 1-16

Absorption, scattering and attenuation coefficients have units of m^{-1} and are then calculated as:

$$\begin{aligned}a(\lambda) &= \frac{\Delta A(\lambda)}{\Delta r} \\ b(\lambda) &= \frac{\Delta B(\lambda)}{\Delta r} \\ c(\lambda) &= \frac{\Delta C(\lambda)}{\Delta r}\end{aligned}$$

Equation 1-17

The way in which scattering affects the penetration of light into the medium depends not only on the value of the scattering coefficient but also on the angular distribution of the scattered flux. This angular distribution has a characteristic shape for any given medium and is specified in terms of the Volume Scattering Function (VSF), $\beta(\lambda, \theta)$ (Equation 1-18) that has units of $\text{m}^{-1} \cdot \text{sr}^{-1}$ and is defined as:

$$\beta(\lambda, \theta) = \frac{1}{E(\lambda)} \frac{dI(\lambda, \theta)}{dV}$$

Equation 1-18

An alternate definition of the scattering coefficient is the integral over all direction of the volume scattering coefficient (Equation 1-19):

$$b(\lambda) = 2\pi \int_0^\pi \beta(\lambda, \theta) \sin \theta d\theta = \int_{4\pi} \beta(\lambda, \theta) d\omega$$

Equation 1-19

The forward b_f and backward b_b scattering coefficients (Equation 1-20) in the forward and backward direction are related to the total scattering coefficient as $b = b_f + b_b$ and defined as:

$$b_f(\lambda) = 2\pi \int_0^{\pi/2} \beta(\lambda, \theta) \sin \theta d\theta$$

$$b_b(\lambda) = 2\pi \int_{\pi/2}^{\pi} \beta(\lambda, \theta) \sin \theta d\theta$$

Equation 1-20

Another useful parameter to compare the shape of the angular distribution of scattering in different media separately from the absolute amount of scattering that occurs is the Normalised Volume Scattering Function or scattering phase function $\tilde{\beta}$ (Equation 1-21). $\tilde{\beta}$ has a unit of sr^{-1} and is calculated as:

$$\tilde{\beta}(\lambda, \theta) = \frac{\beta(\lambda, \theta)}{b}$$

Equation 1-21

The integral of $\tilde{\beta}$ over all solid angles is equal to 1.

Additional parameters like the ratio of molecular scattering to total scattering η , the ratio of molecular backscattering to total backscattering scattering η_b and the probability of photon survival $\bar{\omega}$ (also called single scattering albedo) (Equation 1-22) are defined as follows:

$$\eta(\lambda) = \frac{b_w(\lambda)}{b_w(\lambda) + b_p(\lambda)}$$

$$\eta_b(\lambda) = \frac{b_{bw}(\lambda)}{b_{bw}(\lambda) + b_{bp}(\lambda)}$$

$$\bar{\omega}(\lambda) = \frac{b(\lambda)}{a(\lambda) + b(\lambda)}$$

Equation 1-22

1.3.4. Radiative Transfer Theory

Assuming a horizontally stratified water body (with properties everywhere constant at a given depth), with a constant input of monochromatic un-polarised radiation at the surface, and ignoring fluorescence emission within the water, the equation may be written:

$$\frac{d L(z, \lambda, \theta, \varphi)}{dr} = -c(z, \lambda) L(z, \lambda, \theta, \varphi) + L^*(z, \lambda, \theta, \varphi)$$

Equation 1-23

The term on the left is the rate of change of radiance with distance r , along the path specified by zenith and azimuth angles θ and φ at depth z . The rate of change is the result of two opposing processes:

- loss by attenuation along the direction of travel through $c(z)$
- gain by scattering along the path dr of light initially travelling in other directions (θ', φ') into the path (θ, φ) .

The gain term is determined by:

- the volume scattering function of the medium at a depth z , $\beta(z, \theta, \varphi; \theta', \varphi')$ (this notation indicates (λ) that the scattering angle is the angle between the two direction (θ, φ) and (θ', φ')).

- the distribution of the radiance $L(z, \theta', \varphi')$

Each element of irradiance $L(z, \theta', \varphi') d\omega(\theta', \varphi')$ ¹ incident on the volume element along dr gives rise to some scattered radiance in the direction (θ, φ) . The total radiance derived in this way is given by:

$$L^*(z, \lambda, \theta, \varphi) = \int_{2\pi} \beta(z, \lambda, \theta, \varphi; \theta', \varphi') L(z, \lambda, \theta', \varphi') d\omega(\theta', \varphi')$$

Equation 1-24

Having $dr = dz / \cos \theta$, Equation 1-24 become:

$$\cos \theta \frac{dL(z, \lambda, \theta, \varphi)}{dz} = -c(z, \lambda) L(z, \lambda, \theta, \varphi) + L^*(z, \lambda, \theta, \varphi)$$

Equation 1-25

And by integrating each term of this equation over all angles

$$\int_{4\pi} \cos \theta \frac{dL(z, \lambda, \theta, \varphi)}{dz} d\omega = - \int_{4\pi} c(z, \lambda) L(z, \lambda, \theta, \varphi) d\omega + \int_{4\pi} L^*(z, \lambda, \theta, \varphi) d\omega$$

we arrive at the relation originally derived by Gershun (1936):

$$\frac{d\bar{E}(z, \lambda)}{dz} = -c(z, \lambda) E_0(z, \lambda) + b(z, \lambda) E_0(z, \lambda) = -a(z, \lambda) E_0(z, \lambda)$$

Equation 1-26

It follows that

$$a(z, \lambda) = K_E(z, \lambda) \frac{\bar{E}(z, \lambda)}{E_0(z, \lambda)}$$

and we arrive at the relation known as Gershun's equation (Gershun, 1939):

$$a(z, \lambda) = K_E(z, \lambda) \bar{\mu}(z, \lambda)$$

Equation 1-27

¹ $d\omega(\theta', \varphi')$ is an element of solid angle forming an infinitesimal cone containing the direction θ', φ'

1.3.5. *Summary*

The optical properties of natural waters are divided into two types: the AOPs which are highly dependant of the environmental conditions (cloud cover, sea state, sun angle...) and the IOP's, which are intrinsic properties of a water body. Of these properties, the one which will focus our interest is the absorption and its measurement and secondarily scattering, which interfere importantly on the measurement of absorption. Our effort in this thesis will be to model and implement a new version of absorption meter based on an integrating cavity (PSICAM). This new instrument if proved successful could provide the base for a new approach to measure *in situ* absorption even in ocean provinces of high organic or inorganic particulate content as well as a new laboratory technique to measure the different fraction constituting a natural water sample.

Chapter 2: The Absorption and Scattering of underwater light

Since the prime objective of this work is the design of an effective underwater light absorption meter, it must follow a detailed understanding and description of the components responsible for absorption of light underwater. However, it is found that the absorption process interacts with and is, in a large extent, dependent upon the related scattering process. In this chapter, we explore these two processes and their interaction.

2.1. The absorbing components

Light absorption, which takes place in natural waters, is essentially the result of four major components of the aquatic environment:

- i. the water itself
- ii. Dissolved Organic Matter-DOM (also called Coloured Dissolved Organic Matter-CDOM, Gelbstoff or yellow substance)
- iii. the inanimate (organic or inorganic) particulate matter (tripton)
- iv. the photosynthetic biota (phytoplankton and macrophytes)

The photosynthetic biota and inanimate particles constitutes the Suspended Particulate Matter (SPM).

Each of these components has a specific spectral absorption signature that we will describe. Determination of the spectral absorption coefficient $a(\lambda)$ for natural waters is a difficult task for several reasons. Firstly, water itself absorbs only weakly at near-UV and blue wavelengths, so that very sensitive instruments are required. More importantly, scattering, is

never negligible, so that careful consideration must be made of the possible bias of absorption measurement due to scattering. For example at $\lambda=400\text{nm}$, the molecular scattering provides 46% of the beam attenuation coefficient $c(\lambda)$ in pure water. Scattering effect can dominate absorption at all visible wavelengths in water with high suspended loads. In most cases, the absorption by pure water is usually taken as known. The real difficulty is to measure the absorption properties of the various dissolved and particulate components of the natural waters.

2.1.1. Water

Pure water, although it appears colourless is actually a blue liquid. This blue colour is apparent under sunny conditions in clear or tropical oceanic waters or in weakly productive coastal water. The colour of pure water arises because it absorbs very weakly in the blue and green part of the spectrum but scatters significantly. The absorption of pure water starts increasing at wavelength higher than 550 nm and is quite significant in the red region.

Because of the very weak absorption it is very difficult to measure the absorption coefficient of pure water in the blue and green part of the spectrum. The values reported in the literature vary widely. *Smith & Baker (1981)* arrived at a set of upper bound values in the wavelength range $200 \leq \lambda \leq 800\text{nm}$ partly based on their own measurement of vertical attenuation coefficient (K_d) for irradiance in the clearest ocean waters and partly on what they consider to be the best laboratory measurements, i.e. those of *Morel & Prieur (1977)* in the photosynthetic region (380-700 nm). Their work assumed that for the clearest natural waters:

- Absorption by salt and other dissolved substances was negligible
- The only scattering was due to water molecules and salt ions
- There was no fluorescence

They arrived at the inequality:

$$a_w(\lambda) \leq K_d(\lambda) - \frac{1}{2} b_{sw}(\lambda)$$

Equation 2-1

where K_d is the measured vertical attenuation coefficient and b_{sw} is the assumed known scattering coefficient of pure sea water. They then derived $a_w(\lambda)$ from *in situ* measurement of very clear ocean waters.

Sogandares and Fry (1997) measured the absorption spectrum of pure water in the wavelength range $340 \leq \lambda \leq 640 \text{ nm}$ with photothermal deflection spectroscopy (a technique which is relatively insensitive to scattering). They were able using this technique to show for the first time the seventh and eighth harmonics of the O-H stretch.

The most up to date set of data for the absorption coefficient across the visible band of the spectrum (380-700nm) is the one obtained by *Pope and Fry (1997)* using an integrating cavity absorption meter (section 3.1.5). This set of data is in agreement with the data obtained by *Sogandares and Fry (1997)* using photothermal spectroscopy. They found that the absorption in the blue is significantly lower than the previous sets of data obtained from *Smith and Baker (1981)* with a minimum at 418 nm (0.0044 m^{-1}). Figure 2-1 is a log-normal plot that compares the data sets obtained by Smith and Baker (1981) and Pope and Fry (1997). The major improvement for the latest was to be able to measure very low absorption signal in the blue region.

It can be seen (Figure 2-2) that the absorption spectrum of pure water is approximately exponential from the blue to the red. Two thresholds are also visible across this spectrum: a distinct one at ~604 nm and a weak one at ~514 nm. They have been identified as

corresponding respectively to the fifth and the sixth harmonics of the O-H stretch vibration of liquid water (Kirk, 1994).

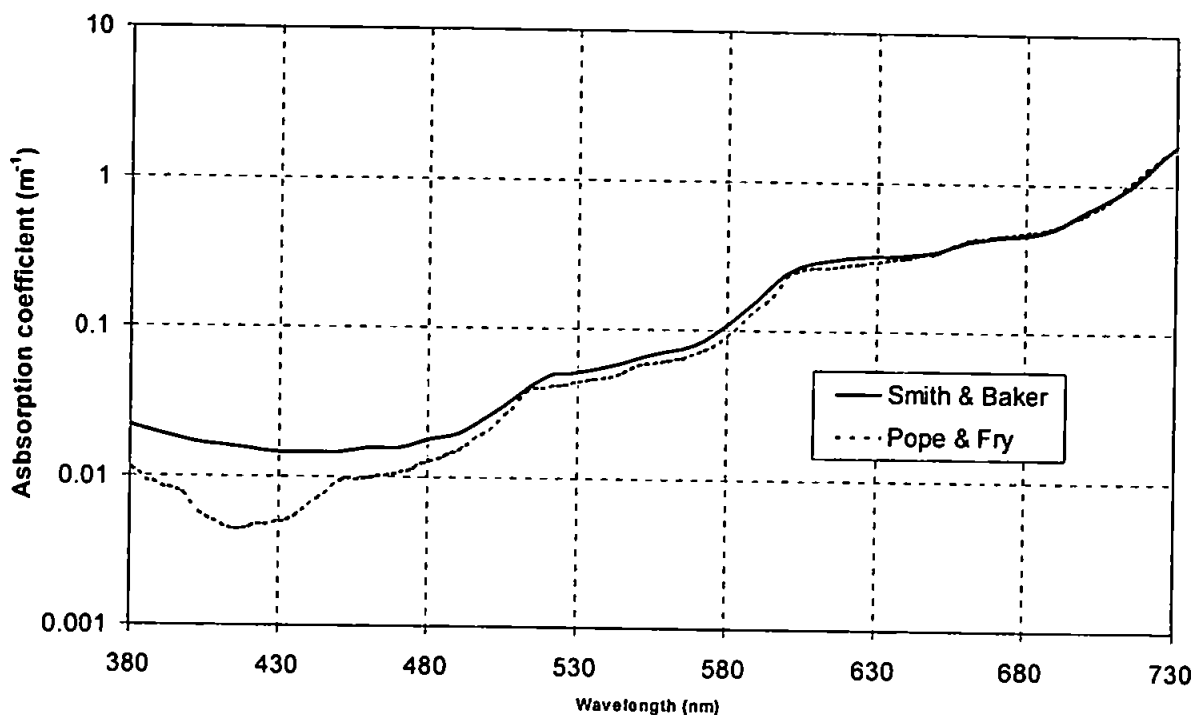


Figure 2-1: log normal plot of $a_w(\lambda)$ obtained from Smith and Baker (1981) and Pope and Fry (1997)

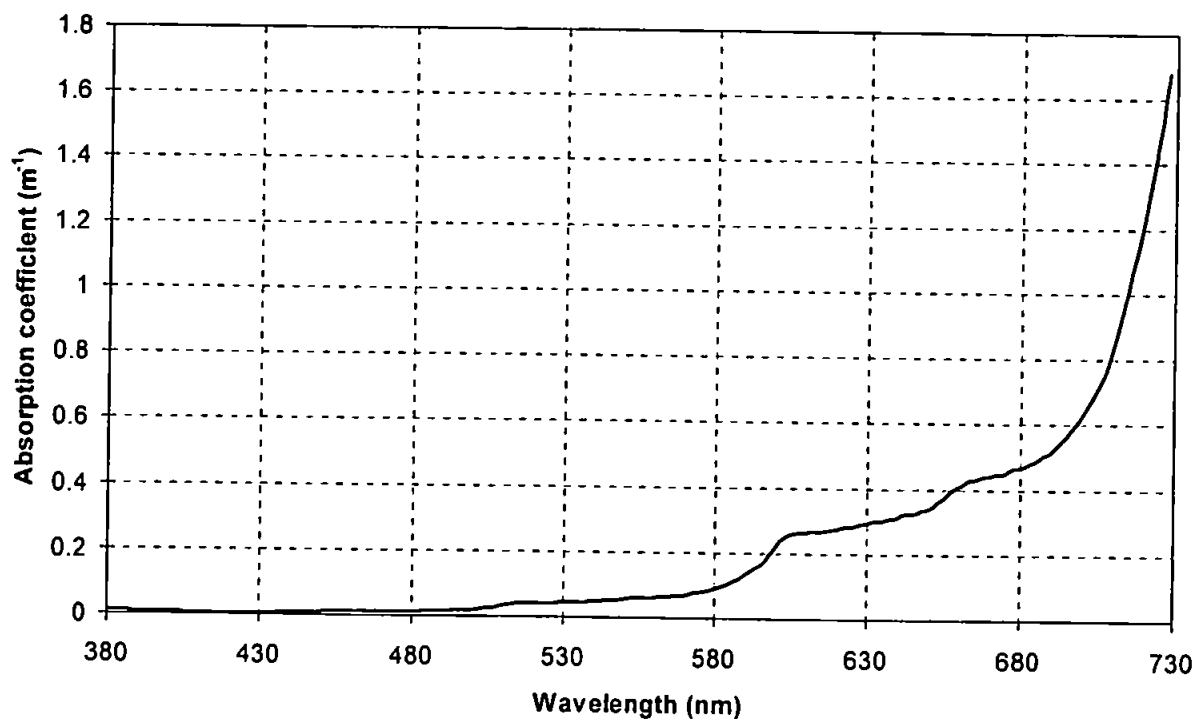


Figure 2-2: Pope and Fry (1997) measurement of pure water absorption

The dependence of light absorption by water upon temperature was studied by various authors (*Pegau and Zaneveld 1993, Buiteveld et. al. 1994, Pegau and Zaneveld 1994, Trabjerg and Hojerslev 1996, Pegau et. al. 1997*). *Pegau and Zaneveld (1994)* measured the temperature dependence of pure water in the visible wavebands with an ac-9 (WetLabs Inc.) in the temperature range 11-34°C. They found the largest dependence ($0.0034 \text{ m}^{-1} \text{ }^{\circ}\text{C}^{-1}$) at the longest wavelength tested (715 nm). The dependence at shorter wavelength was less than a third of that observed at 715 nm. *Trabjerg and Hojerslev (1996)* measured the temperature dependence of pure water and filtered sea water ($S \approx 25\text{‰}$) in a 1 metre pathlength cell. For both samples they found a temperature dependence of $-0.00091 \pm 0.00006 \text{ m}^{-1} \text{ }^{\circ}\text{C}^{-1}$ from 400 to 550 nm for a temperature range of 6-30°C. The dependence for wavelength longer than 600 nm was partially in agreement with previous works with the maximum dependence at 600, 660 and 740nm.

Using an ac-9, *Pegau et al. (1997)*, investigated the absorption dependence on temperature (15-30°C) and salinity (0-38 PSU) of pure and salt water. They confirmed the high dependence of absorption on temperature in the near infra-red for both waters. In the visible the dependence was shown to be less than $0.001 \text{ m}^{-1} \text{ }^{\circ}\text{C}^{-1}$ except around 610 nm. They showed that the effect of salinity was negligible in the visible region but appeared to be important in the near infra-red region. At 715 nm, the dependence was proved to be $-0.00027 \text{ m}^{-1} \text{ PSU}^{-1}$.

Salinity and temperature have little influence on absorption except in the infra-red region, although there can be discrepancies in the values found in the literature. These two parameters can therefore be of importance especially in the case of instrument which measure the transmittance of a natural sample relative to a standard, typically pure water, which is at room temperature and of zero salinity.

2.1.2. Yellow substance (*Gelbstoff*)

When plant tissue decomposes in the soil or in a water body, most of the organic matter is broken down by microbial action within days or weeks to, ultimately, carbon dioxide and inorganic forms of nitrogen, sulphur and phosphorus. In the processes of decomposition, the organic matter passes through a complex form of organic components referred to as humic substances, yellow substance or *Gelbstoff* (Kirk, 1994). These humic substances are very complex molecules that include aromatic rings and long chains of alkyls. Humic substances have both very soluble and insoluble macromolecules and are classified in terms of their solubility behaviour. The soluble ones give the yellow-brown colour of the highly organic concentrated waters. The chemical composition of these humic substances is highly dependent on the characteristics of the vegetation that the rivers are draining and also on the aquatic plant living in both freshwater and seawater.

The absorption spectrum of these yellow substances depends on their concentration. A convenient parameter to describe the concentration of yellow substance is the absorption coefficient at 440 nm ($a_y(440)$). This wavelength is chosen because it corresponds approximately to the mid-point of the blue waveband peak that most classes of algae have in their photosynthetic action spectrum (Kirk, 1994). When the yellow substances absorption is low, the absorption coefficient can be measured in the near ultra-violet (350-400 nm) where absorption is higher, and $a(440)$ determined using the relationship (Bricaud, et. al, 1981):

$$a(\lambda) = a(\lambda_0)e^{-S(\lambda-\lambda_0)}$$

Equation 2-2

where $a(\lambda)$ and $a(\lambda_0)$ are the absorption coefficient at wavelength λ and at the reference wavelength $\lambda_0 = 400\text{nm}$, S is a coefficient describing the exponential slope of the absorption curve. This slope has been estimated for a wide range of seawaters. An average value of 0.014

m^{-1} is accepted as representative of a wide range of coastal and oceanic waters (Bricaud, *et.al.*, 1981; Carder, *et.al.*, 1989 and Roesler, *et.al.*, 1989). The reference absorption coefficient $a_y(440)$ varies roughly from 0 to 2 m^{-1} from clear oceanic waters to estuarine waters, and from 0.5 up to 20 m^{-1} for inland waters (Kirk, 1994).

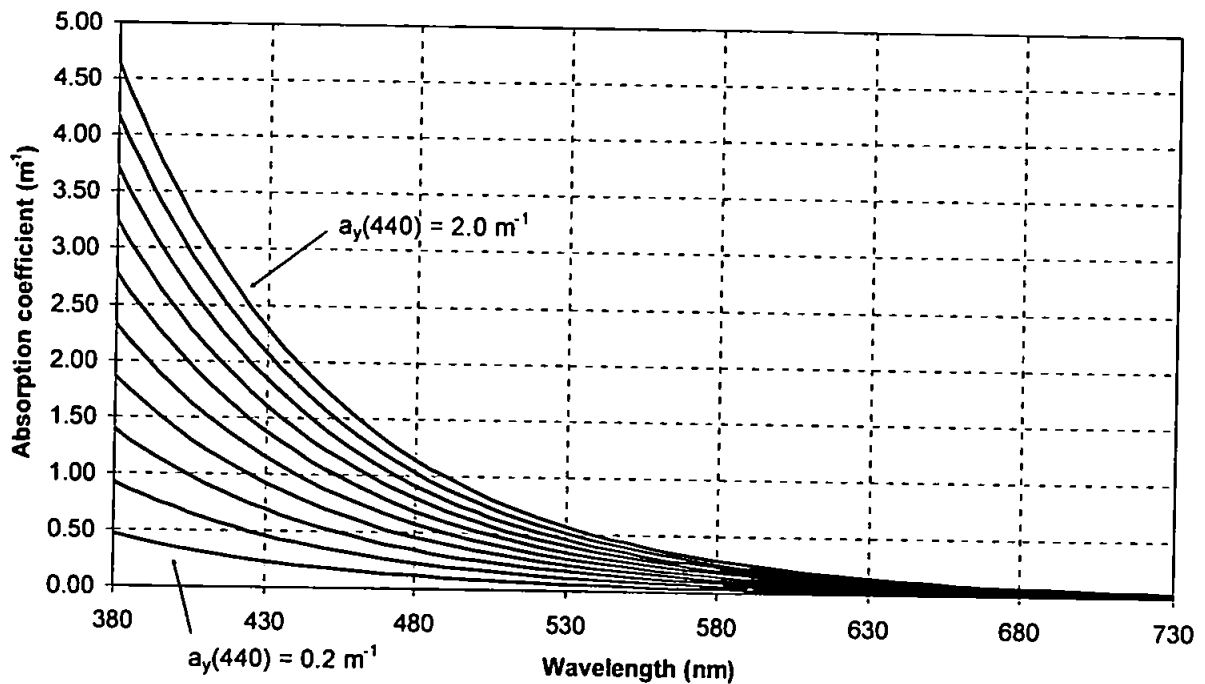


Figure 2-3: absorption coefficient of yellow substances for a range of $a_y(440)$

Figure 2-3 shows that yellow substance preferentially absorbs light in the blue part of the spectrum. The absorption coefficient then decreases exponentially with increasing wavelength.

2.1.3. Organic and inorganic detritus (Tripton)

The tripton is the fraction of the Suspended Particulate Matter whose light absorption properties has been the least investigated because it is so difficult to measure. At typical concentrations, the particulate matter does not absorb strongly but scatters light strongly. Therefore, its measurement would be very inaccurate by normal spectrophotometry. A

convenient way to access its absorption spectrum would be with an Integrating Cavity Absorption Meter.

It is not easy to separate the contribution of phytoplankton and tripton to the total particulate absorption. Several authors have investigated this fraction. *Iturriaga and Siegel (1989)*, made direct examination of individual particles using microspectrophotometry. *Kishino et al. (1985)* measured filter pad absorption before and after chemical extraction of the phytoplankton pigments. *Roesler et al. (1989)* used models based on an assumed ratio of phytoplankton absorption at two wavelengths in the blue and red. *Morrow et al. (1989)* used statistical methods based on typical absorption spectra of phytoplankton and detritus. *Bricaud and Stramski (1990)* used models based on an assumed functional form for detrital absorption.

These various methods showed a similar characteristic absorption spectrum for tripton which like the yellow substance has a decreasing exponential form from short to long wavelength. This similarity is likely due either to humic material adsorbed on suspended particles or to free particulate humic aggregate. In productive waters, or in oceanic waters away from land drainage, some of the light absorbing tripton arises by decomposition of the phytoplankton. The detrital fraction in seawater also has an absorption spectrum of the humic type but sometimes with characteristic features due to the breakpoint products of photosynthetic pigments (Bricaud and Stramski, 1990; Morrow, *et al.*, 1989; Roesler, *et al.*, 1989 and Iturriaga and Siegel, 1989).

Roesler et al., (1989) proposed the following model for tripton absorption:

$$a_m(\lambda) = a_m(400)\exp[-S(\lambda - 400)]$$

Equation 2-3

with S varying from 0.006 to 0.014 with a typical value of 0.011.

The *in situ* absorption coefficient due to particulate matter at 440 nm ($a_{tr}(440)$) is a convenient and useful measure of particulate colour in any water. But it is not as good an indicator as $a_y(440)$ is for the yellow substance.

2.1.4. Phytoplankton

Phytoplankton absorbs light as a source of energy in the photosynthetic process. Spectral characteristics of absorption by phytoplankton result from, and can therefore be used to identify, photosynthetic and auxiliary pigments characteristic of particular phytoplankton taxonomic groups (Sathyendranath, *et al.*, 1987). Investigations and models of primary production must include spectral absorption coefficients of photosynthetic pigments, which determine the ability of phytoplankton to collect light for use in photosynthesis.

The photosynthetic pigments (chlorophyll, carotenoid, biliprotein) contained in the algal cells contribute to the light attenuation in the euphotic zone. Absorption by chlorophyll is characterised by strong absorption bands in the blue and in the red (peaking at 430 and 665 nm for chlorophyll a) with very little absorption in the green. Chlorophyll-*a* occurs in all photosynthetic plants and its concentration in $\text{mg}(\text{chl}_a).\text{m}^{-3}$ is commonly used as a relevant optical measure of phytoplankton abundance. Chlorophyll concentrations typically range from $0.01\text{mg}.\text{m}^{-3}$ in the clearest open ocean waters to $10\text{ mg}.\text{m}^{-3}$ in productive coastal up-welling, to $100\text{ mg}.\text{m}^{-3}$ in eutrophic estuaries.

The absorbing pigments are not evenly distributed within phytoplankton cells but are localized into chloroplasts. This localised distribution of the pigments means that the spectral absorption by a plankton cell or by a collection of cells in water has less pronounced peaks and reduced overall absorption than if the pigments were uniformly distributed throughout the water (Kirk, 1994). This so-called pigment packaging effect is a major source of both inter and intra-

specific variability in spectral absorption by phytoplankton, because the details of the pigment packaging within cells depend not only on species but also on cells size and physiological state. This in turn depends on environmental factors such as ambient lighting and nutrient availability. The inter-specific variation of phytoplankton absorption was studied by *Sathyendranath et. al. (1987)*. Another source of variability in addition to chlorophyll a concentration and packaging is changes in pigment composition (the relative proportion of accessory pigments, namely chlorophyll b and c, pheopigments, biliproteins and carotenoids) since each pigment displays a specific absorption curve (*Kirk 1994*).

The absorption coefficient of phytoplankton species can be calculated as a function of the chlorophyll concentration:

$$a_{phyto}(\lambda) = a_{phyto}^*(\lambda)chl \quad (\text{mg.m}^{-3})$$

Equation 2-4

The specific absorption coefficient of the phytoplankton, a_{phyto}^* depend not only on the total amounts of the photosynthetic pigments present, but also on the size and the shape of the algal cells or colonies within which the pigment are located, which is also a consequence of the nutrients characteristic of the water (*Mitchell and Kiefer, 1988; Bricaud and Stramski, 1990 and Cleveland, 1995*). It is also necessary to introduce a parameterisation taking into account the biological and ecological variability (*Cleveland, 1995*). *Bricaud, et al., (1995)*, proposed a parameterization of a_{phyto}^* as a function of chlorophyll a and pheopigment concentration:

$$a_{phyto}^*(\lambda) = A(\lambda)chl^{-B(\lambda)}$$

Equation 2-5

where A and B are positive parameters depending on the wavelength.

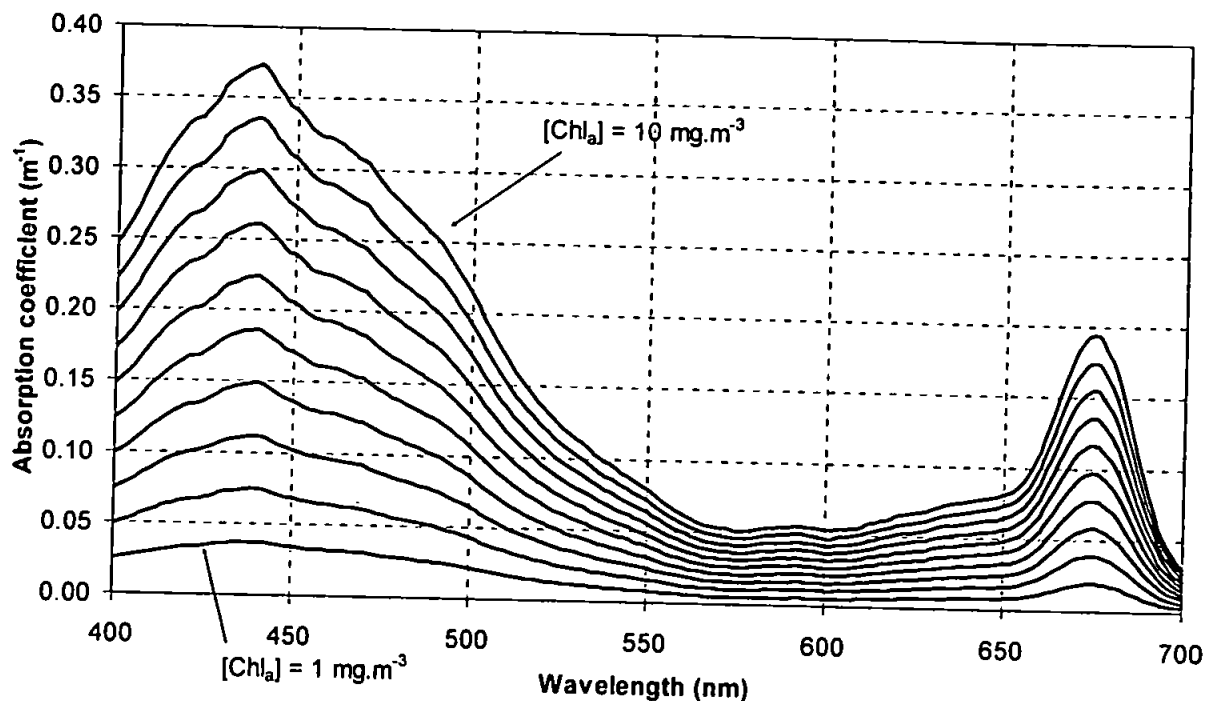


Figure 2-4: Absorption coefficient of phytoplankton for a range of chlorophyll concentration

Figure 2-4 using *Bricaud, et.al., (1995)* parametrisation shows clearly the two absorption maxima of the phytoplankton cells, the blue maximum at ≈ 435 nm and the red maximum at ≈ 670 nm.

The blue peak is higher than the red because of the contribution of accessory pigments. There is relatively little absorption between 550 and 650 nm with a minimum around 600 nm.

2.1.5. Total absorption coefficient bio-optical models

At any wavelength, the aquatic medium has a total absorption coefficient, which is the sum of the absorption coefficients of all the light-absorbing components. The variation of this total absorption coefficient with wavelength is the absorption spectrum of the medium as a whole. For any given water body, the total absorption coefficient at each wavelength is obtained by adding together the known absorption coefficient of pure water, yellow substances, tripton and phytoplankton:

$$a(\lambda) = a_w(\lambda) + a_y(\lambda) + a_{tri}(\lambda) + a_{phy}(\lambda)$$

Equation 2-6

Prieur and Sathyendranath (1981) were the first to develop a model for absorption coefficient in Case 1 waters. Their model was statistically derived and included absorption by phytoplankton pigments, non pigment organic materials and yellow matter derived for phytoplankton degradation. A simplified version of this model was then proposed by *Morel (1991)* (Figure 2-5):

$$a(\lambda) = [a_w(\lambda) + 0.06a_c''(\lambda)C^{0.65}] [1 + 0.2 \exp(-0.014(\lambda - 440))]$$

Equation 2-7

where $a_w(\lambda)$ is the absorption coefficient of pure water $a_c''(\lambda)$ is a non-dimensional statistically derived chlorophyll-specific absorption coefficient and C is the chlorophyll concentration in $\text{mg} \cdot \text{m}^{-3}$. This model obviously has its limitations due to the assumption made to obtain it. Other bio-optical models were produced (*Gordon 1992, Kopelevich 1983*) but are not described here.

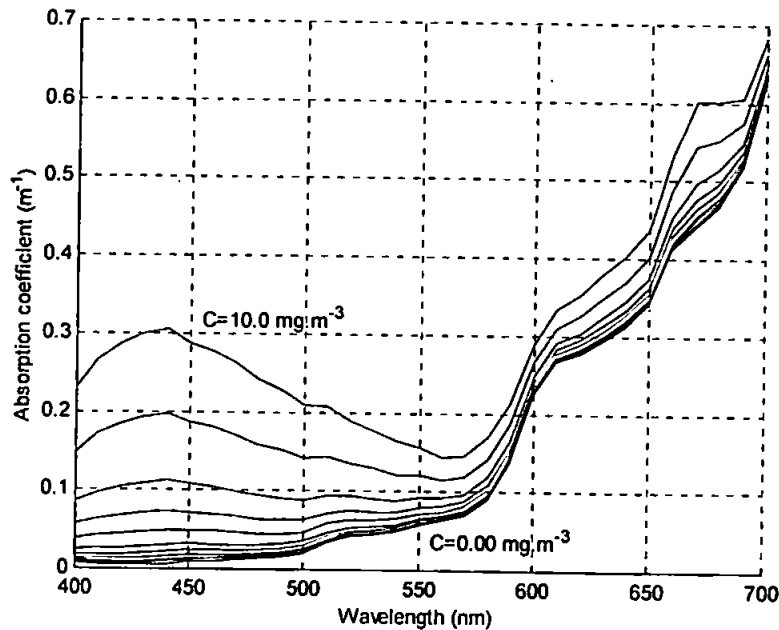


Figure 2-5: Total absorption coefficient model proposed by Morel (1991)

2.2. The scattering of underwater light

2.2.1. The scattering process

Many of the photons entering the marine system undergo scattering more than once before being absorbed. Scattering does not by itself remove light. A scattered photon is still available for photosynthesis for example. The effect of scattering is more to prevent a linear penetration of light. The photons therefore have a zig-zag trajectory as they are scattered from one particle to another. For underwater visibility and imaging, scattered light would not form a coherent image on the retina or on an image, having quite the same effect as scattered light by fog in the atmosphere. Scattering increases the total pathlength which the photons follow in traversing a certain depth and so increases the probability of their being captured by one of the absorbing components of the medium. In addition, some photons are actually scattered back in the upward direction. Thus the effect of scattering is to intensify the vertical attenuation of light.

A photon is scattered when it interacts with some component of the medium in such a way that it is caused to diverge from its original trajectory. Scattering in natural waters can be divided in two categories:

- i. Small scale ($\ll \lambda$) density fluctuations (or Raleigh scattering)
- ii. Large scale ($> \lambda$) organic and inorganic particles (Mie Theory)

These categories, do not correspond to real difference in the physical processes, but correspond to the size domain in which the mathematical theories used to describe scattering are applicable.

2.2.1.1. Rayleigh scattering

Small scale scattering or Rayleigh scattering (in reference to Rayleigh theory of scattering for gases) determines the minimum values for scattering properties encountered in water and salt waters. *Raman (1922) and Shuleikin (1922)* first described the fundamental role played by small scale-scattering in natural waters. According to Rayleigh theory, within any particle, such as an air molecule, in a light field, a dipole is induced by the electrical vector of the field. As the dipole oscillates at the frequency of the exciting radiation, it emits radiation of the same frequency in all directions. It is this radiation which forms the scattered light.

The Rayleigh molecular theory of scattering does not strictly apply to liquids: the strong interaction between the molecules makes it impossible to consider the interaction of the radiation with molecules on an individual basis. In any liquid, however, the continual random motion of the molecules leads to localized microscopic fluctuation of density and therefore of dielectric constant, which can be regarded as a dipole. It is the interaction of these fluctuations with the radiant field that are considered. The Einstein-Smoluchowski theory of scattering relates these fluctuations of density to the associated fluctuations in the index of refraction, which gives rise to scattering.

The Rayleigh theory of scattering apply only when scatterers are small relative to the wavelength of light. This is true in the case of gas molecules and of the small density fluctuations in pure liquids. Even the clearest natural waters are not optically pure and always contain particles. The particles which occur in natural water have a continuous size distribution which is approximately hyperbolic (*Bader, 1970*). The number of particles with diameter greater than D is proportional to $1/D^\gamma$, where γ is a constant for a particular water body, but varies widely from 0.7 to 6 in different water bodies (*Jerlov, 1976*). Although a hyperbolic distribution implies that smaller particles are more numerous than bigger particles, most

scattering in natural water is due to particles of diameter greater than $2\text{ }\mu\text{m}$ (Jerlov, 1976). This is not small relative to the wavelength, and so scattering behaviour different from the density fluctuation type must be expected.

2.2.1.2. Large scale scattering – Mie Scattering

Mie scattering theory (1908) predicts the light scattering behaviour of spherical particles of any size. It enables to calculate the bulk scattering property of a water body considering its individual constituent. Calculations based on Mie theory are playing an increasingly important role in hydrologic optics, primarily because modern computers make it convenient to perform the necessary computations. The physical basis of the theory is similar to that of Raleigh in that it considers the oscillations set up within a polarised body by the incident light field and the light re-radiated (i.e. scattered) from the body as a result of these oscillations. Instead of (as in Rayleigh theory) equating the particle to a single dipole, Mie theory considers, the additive contribution of a series of electrical and magnetic multipoles located within the particle. The solution of Mie's equations is in the form of infinite series of mathematical functions. Details of the solutions are given by *Van de Hulst (1957) and by Bohren and Huffman (1983)*.

The advantage of the Mie theory is that it gives an exact solution to scattering. For very small particles, it also leads to the same predictions as the Rayleigh theory. For particles larger than the wavelength of the light, Mie theory predicts that most of the scattering is in the forward direction within small angles of the beam axis. A series of maxima and minima is predicted at increasing scattering angle, but these are smoothed out when a mixture of particles sizes is present. The disadvantage is that the analytical expressions are fairly complex and do not lend themselves to easy numerical calculations.

The Mie theory may be explained as follows. Suppose that there is a single, homogeneous sphere of diameter D , whose material has a complex index of refraction $m_s = n_s - ik_s$,

and that the sphere is imbedded in an infinite, uniform, non-absorbing medium whose index of refraction is therefore real: $m_m = n_m$. The sphere is illuminated by a collimated beam of monochromatic light of wavelength $\lambda_m = \lambda_{vac}/n_m$, where λ_{vac} is the wavelength in vacuum of light corresponding to the given frequency. The beam is much larger in diameter than the sphere. It is to be found how the incident light is absorbed and scattered by the sphere, determine the angular distribution of the scattered intensity and the state of polarisation of the scattered light.

Mie's solution is often presented in terms of the various absorption and scattering efficiencies. The total scattering efficiency Q_b , gives the fraction of radiant energy incident on the sphere that is scattered into all directions. The incident energy passing through an area equal to the cross-sectional area of the sphere, $A_s = \pi r^2$. Similarly, the absorption efficiency Q_a gives the fraction of incident energy that is absorbed by the sphere. The total attenuation efficiency is therefore calculated as $Q_c = Q_a + Q_b$. The attenuation efficiency of a particle can be greater than unity. This means that a particle can affect the behaviour of more light in the incident beam than will be intercepted by its geometrical cross-section. This applies only to the scattering part of attenuation, i.e. it is possible for a particle to scatter, but not absorb, more light than its geometrical cross section would intercept.

The Mie solution can also be presented in terms of absorption and scattering cross sections. The scattering cross section σ_s , is the cross sectional area of the incident beam that has power equal to the power scattered by the sphere. Similarly, the absorption cross section σ_a , is the cross sectional area of the incident beam that has power equal to the power absorbed by the sphere. The total attenuation cross section σ_c , is the cross sectional area of the incident beam that has power equal to the total power attenuated by the sphere. The scattering cross sections is therefore related to the corresponding efficiencies by the geometrical cross section of the sphere:

$$\sigma_s = Q_s A_s = Q_s \pi r^2 \quad (m^{-2})$$

Equation 2-8

Similarly, $\sigma_a = Q_a A_s$ and $\sigma_c = Q_c A_s$.

The different efficiencies and cross sections depend on the various parameters of the problem:

- wavelength $\lambda_m = \lambda_{vac} / n_m$
- diameter (D) or size parameter (α) describing the size of the sphere relative to the wavelength of the incident light within the medium usually written as: $\alpha = \frac{\pi D}{\lambda_m} = \frac{\pi D n_m}{\lambda_{vac}}$
- index of refraction (m_r) of the sphere and the surrounding medium:

$$m_r = \left(\frac{n_s}{n_m} \right) - i \left(\frac{k_s}{n_m} \right) = n_r - i k_r$$

(n_r can be less than one: a spherical air bubble in water would have $n_r \approx 0.75$.)
- Some of the Mie formulas also involve the phase shift parameter: $\rho = 2\alpha(n_r - 1)$, and the absorption thickness: $\rho' = 4k_r \alpha = a_s D$ where a_s is the absorption coefficient of the material forming the sphere. Phytoplankton cells typically have a_s values of 10^4 - 10^5 m^{-1} at visible wavelengths. a_s must not be confused with the bulk absorption coefficient for natural waters containing phytoplankton.

As an example of the Mie parameter values (Mobley, 1994), consider a phytoplankton cell with $D = 8\mu m$, $n_s = 1.4$, and $a_s = 4 \times 10^5$ m^{-1} . If the cell is floating in water with $n_m = 1.34$, and if the incident light has $\lambda_{vac} = 500$ nm, then $\alpha = 67.4$, $\rho = 6.0$ and $\rho' = 3.2$.

The various single-particle cross sections obtained from Mie theory are the key parameters to construct the equations that give the bulk inherent optical properties. For the most numerous oceanic particles, (virus or colloids at a concentration of 10^{15} m^{-3}), the average distance between particles is greater than ten wavelengths of visible light and for the optically significant phytoplankton, the average separation is thousands of wavelengths Mobley, 1994.

Moreover, these particles usually are randomly distributed and orientated. Therefore, to calculate the total scattering coefficient $b(\lambda)$ from the single particle cross section $\sigma_b(D, m_r, \lambda)$, ocean water can be assumed as a very dilute suspension of random scatterers. Consequently, the intensity of light scattered by an ensemble of particles is given by the sum of the intensities due to the individual particles. Coherent scattering effects are negligible, except at extremely small scattering angles (*Shifrin, 1988; Fry et al., 1992b*).

Because of this optical independence of the individual particles, their individual contributions to scattering can simply be summed up:

$$b(\lambda) = \int_{all\ m_r} \int_{all\ D} \sigma_b(D, m_r, \lambda) n(D) dD dm_r,$$

Equation 2-9

where $n(D)$ is the particle number size distribution. It is a key parameter to connect particle of all different sizes and indices of refraction with the bulk scattering coefficient. $n(D)$ is closely approximated by $n(D) = kD^s$ (*Bader, 1970*) where k is the concentration of particles larger than $1\mu m$ and s is the slope of the distribution ranging typically between -3 and -4 for smaller size range and between -4.5 to less than -5 for larger particles (*Stramski and Kiefer, 1991*).

In practice, Equation 2-9 usually is evaluated separately for particles that have the same index of refraction, but which differ in size. For the i^{th} particle type:

$$\begin{aligned} b_i(\lambda) &= \int_{D'_{min}}^{D'_{max}} \sigma_b^i(D, m_r^i, \lambda) n^i(D) dD \\ &= \int_{D'_{min}}^{D'_{max}} Q_b^i(D, m_r^i, \lambda) \frac{\pi D^2}{4} n^i(D) dD \end{aligned}$$

Equation 2-10

where $D_{\min}^i$ and $D_{\max}^i$ are the minimum and maximum diameters of particles of type i . $\pi D^2/4$ is the projected area of the spherical particle. The value of $b_i(\lambda)$ is the contribution by the i^{th} particle type to the total scattering coefficient $b(\lambda)$. Corresponding equations can be written for other quantities, such as absorption and back-scattering. Mie theory also gives a cross section for scattering through angle θ , $\sigma_d(\theta, \lambda)$ via the same formulation as Equation 2-10.

Early works at predicting bulk properties from assumed particle properties and size distributions are seen in *Kullenberg (1974)* and in *Brown and Gordon (1974)*. Brown and Gordon were unable to reproduce observed back-scattering values using measured particle size distributions. However, their instruments were unable to detect submicrometer particles. They found that Mie theory properly predicted back-scattering if they assumed the presence of numerous sub-micrometer, low index of refraction particles. Bacteria and colloids are most likely to be the particles they assumed. Mie calculations have used three-layers spheres to model the structure of phytoplankton (cell wall chloroplasts and cytoplasm core) and have used polydispersed mixtures of both organic and inorganic particles (*Kitchen and Zanefeld, 1990b*).

The value of Mie theory is that it gives a theoretical structure for the analysis and modeling of the IOP's. Having a limited amount of measured parameters, (beam attenuation, absorption and particle size distributions, irradiance reflectance), Mie theory can be used to determine the unknown parameters: particle refractive index (*Forget, et.al., 1999*), Volume Scattering Functions (*Volten, 1998*). Mie scattering calculations are able to reproduce observed volume scattering functions, except at very small angles, given the proper particle optical properties and size distributions.

The anomalous diffraction theory of *Van de Hulst (1957)* can be used to calculate the scattering efficiency of particles with refractive index up to about twice that of the surrounding medium (*Kirk, 1994*):

$$Q_b = 2 - \left(\frac{4}{\rho} \right) \times \sin \rho + \left(\frac{4}{\rho^2} \right) \times (1 - \cos \rho)$$

Equation 2-11

Where $\rho = \left(\frac{4\pi r}{\lambda} \right) * (m_r - 1)$, m_r being the refractive index of the particle relative to that of the surrounding medium, and r being the radius of the particle. For a non-absorbing particle, $Q_{\text{scat}} = Q_{\text{att}}$.

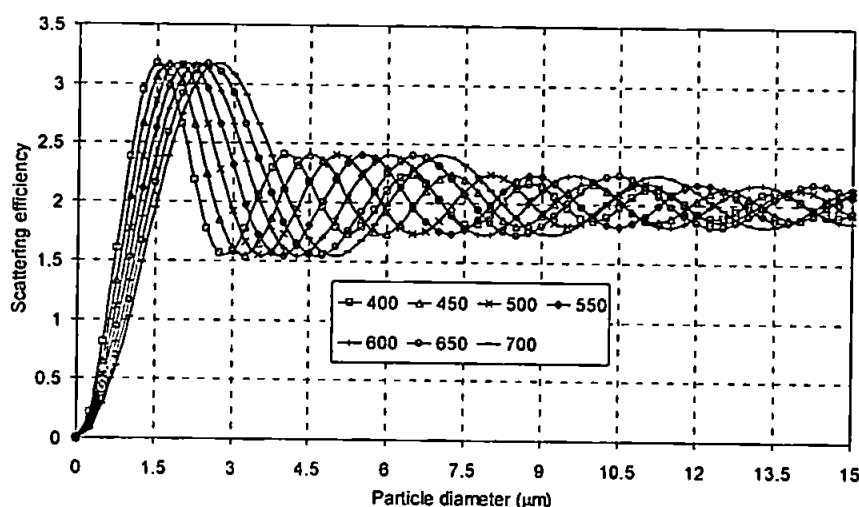


Figure 2-6: Scattering efficiency of non absorbing spherical particles as a function of size calculated using the equation of Van de Hulst (1957). The particles have a refractive index of 1.17 relative to water. Wavelength from 400 to 700 nm.

Figure 2-6 shows the way in which the scattering efficiency for visible light of a spherical non absorbing particle of refractive index relative to water of 1.17 (a typical value for inorganic particles in natural water; (*Kirk, 1994*), varies with particle sizes. It can be seen that the scattering efficiency rises steeply from very low value for very small particles to about 3.2 at a diameter varying from 1.5 to 3 μm depending on the wavelength. With increasing diameter, Q_b oscillates with diminishing amplitude to level off at a value ≈ 2 for very large particle for all visible wavelengths. A similar general pattern of variation of Q_b with size would be exhibited

by any scattering particle of the type found in natural waters at any wavelength in the visible range.

In a natural water sample, the hyperbolic distribution of particle sizes imply that small particles (virus, bacteria and colloids) are more abundant but the smaller particles, although numerous have a lower scattering efficiency

From the scattering efficiency Q_b can be calculated the scattering coefficient using Equation 2-10:

$$b(\lambda) = \int_{D_{min}}^{D_{max}} Q_{bt}(D, m, \lambda) \frac{\pi D^2}{4} n(D) dD$$

Equation 2-12

For our example, we aim to calculate the scattering coefficient of particles of a given sizes. Therefore, the equation becomes:

$$b(\lambda) = Q_{scat}(D, m, \lambda) \frac{\pi D^2}{4} n(D)$$

Equation 2-13

$n(D)$ is the Junge cumulative size function and can be expressed for a concentration of 1 g.m^{-3} by $n(D)=D^{-3}$ (Mobley, 1994; Figure 2-7) or $n(D)=D^{-4}$ (Bader 1970, Nanu and Robertson 1993; Figure 2-8).

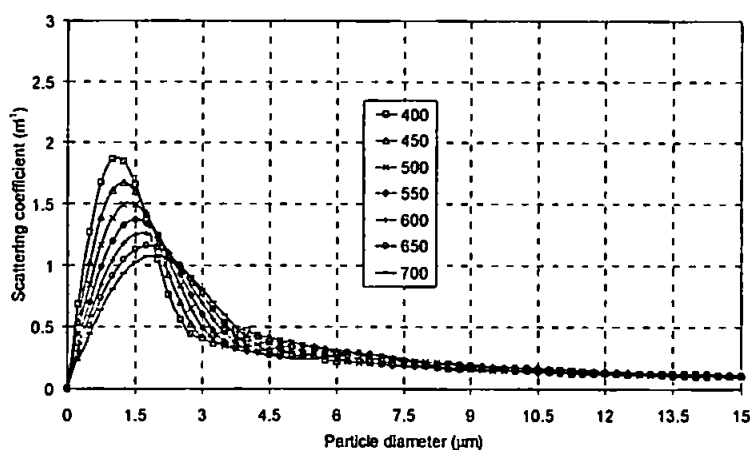


Figure 2-7: $b(\lambda)$ as a function of diameter calculated for a slope of the cumulative size distribution $s=-3$

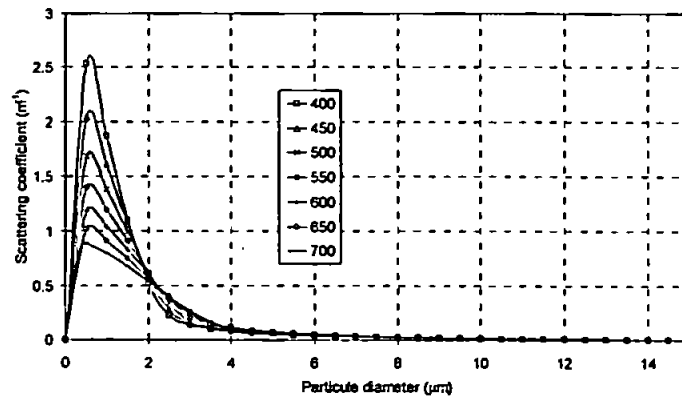


Figure 2-8: $b(\lambda)$ as a function of diameter calculated for a slope of the cumulative size distribution $s=-4$

Figure 2-7 and Figure 2-8 presents the results of such calculation respectively for $s=-3$ and $s=-4$. The scattering coefficient shows a peak situated at different diameters depending on s and λ . The optimum for scattering, from 1.8 to 2.0 μm downward depending on wavelength Figure 2-7 and from 0.6 downward Figure 2-8 the scattering coefficient decreases more steeply for $s=4$ due to the relative abundance of small particles which are less efficient scatterers. As the particle diameter increases beyond the optimum, scattering by the suspension shows a progressive decrease to very low values, with only minor, heavily damped, oscillations corresponding to the oscillations in Q_b for the individual particles. The attenuation of oscillation being more marked for $s=4$. The result of these calculations therefore does not support the statement of *Jerlov (1976)*. They show that most scattering is due to particles between 0.5 μm and 2 μm , which still is not small relative to the wavelength.

2.2.2. The scattering components

The scattering agents in seawater are:

- i. the water itself
- ii. suspended particles
- iii. bubbles

2.2.2.1. Pure water and pure sea water

Morel (1974) has reviewed the theory and observations of scattering by pure water and pure sea water. Scattering by both pure water and pure sea water vary strongly with wavelength. Experimentally, scattering by pure water or pure sea water is found to vary in accordance with $\lambda^{-4.32}$ rather than λ^{-4} (Equation 2-14, Equation 2-15) as predicted by density fluctuation theory for gases. This is a result of the variation of the refractive index of water with wavelength. In sea water the basic theory is the same as for pure water, but random fluctuations in the concentrations of the various ions (Cl^- , Na^+ ...) give rise to higher index of refraction fluctuations, and therefore greater scattering. Pure sea water (35-38‰ salinity) scatters about 30% more intensely than pure water (Figure 2-10). As a result of these differences, the volume scattering function for either pure water or for pure sea water has the form:

$$\beta_w(\theta, \lambda) = \beta_w(90^\circ, \lambda) \left(\frac{\lambda_0}{\lambda} \right)^{4.32} (1 + 0.835 \cos^2 \theta) \quad (\text{m}^{-1} \text{sr}^{-1})$$

Equation 2-14: VSF of pure water or pure sea water

where $\beta_w(90^\circ, \lambda)$ is the value at $\theta = 90^\circ$ of the VSF of pure water or pure sea water. Rather than the form:

$$\beta_{Ray}(\theta, \lambda) = \beta_{Ray}(90^\circ, \lambda) \left(\frac{\lambda_0}{\lambda} \right)^4 (1 + \cos^2 \theta) \quad (\text{m}^{-1} \text{sr}^{-1})$$

Equation 2-15: VSF for gases derived by Raleigh

which is the equation Rayleigh scattering for gases. The 0.835 factor rather than unity is attributable to the anisotropy of the water molecules. The predicted angular distribution of scattering by water is therefore similar to that given by the Rayleigh theory for gases. It is identical in the forward and backward direction and shows a minimum at $\theta = 90^\circ$ (Figure 2-9).

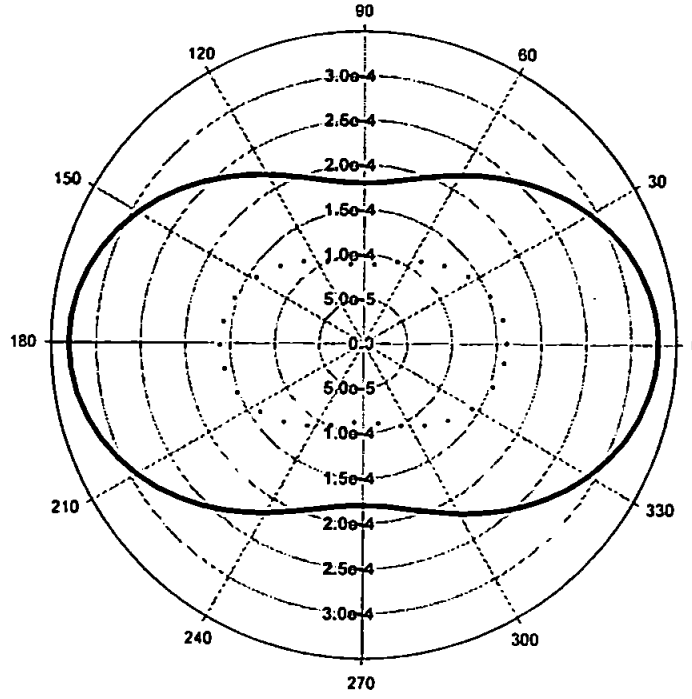


Figure 2-9: VSF of pure sea water for $\lambda = 500$ nm (solid line) and $\lambda = 600$ nm (dotted line), calculated with Equation 2-14, with $\beta(90, 500) = 1.8 \cdot 10^{-4} \text{ m}^{-1}\text{sr}^{-1}$ and $\beta(90, 600) = 0.88 \cdot 10^{-4} \text{ m}^{-1}\text{sr}^{-1}$ (Morel, 1974)

The total scattering coefficient $b_w(\lambda)$ is given by:

$$b_w(\lambda) = 16.06 \left(\frac{\lambda_0}{\lambda} \right)^{4.32} \beta_w(90^\circ, \lambda) \quad (\text{m}^{-1})$$

Equation 2-16 (Morel, 1974)

Haltrin and Kattawar (1991) used the following equation to calculate $b_w(\lambda)$:

$$b_w(\lambda) = 5.826 \cdot 10^{-3} \left(\frac{400}{\lambda} \right)^{4.322} \quad (\text{m}^{-1})$$

Equation 2-17 (Haltrin and Kattawar, 1991)

The following graph present the scattering coefficient of pure water and pure sea water calculated (Morel, 1974; Haltrin and Kattawar, 1991) or measured (Smith and Baker, 1981). For both types of water, it can be seen that there is a strong wavelength dependence with a maximum in the blue part of the spectrum. This explains the blue colour of the ocean. It also appears that the theoretical data match very well the measured ones.

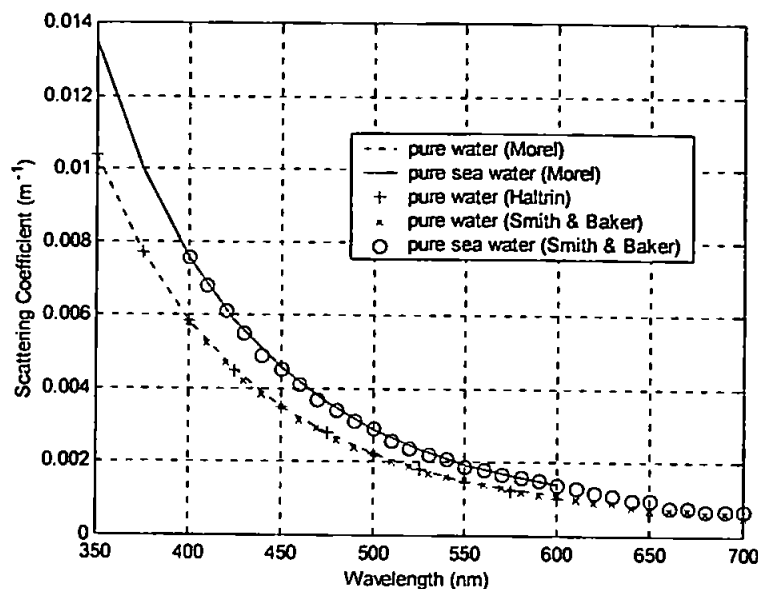


Figure 2-10: Computed or measured values of the scattering coefficient from various authors (Morel, 1974; Haltrin and Kattawar, 1991, Smith and Baker, 1981)

The scattering coefficients of natural waters are always much higher than those of pure water. Unlike absorption, the scattering properties of natural waters are greatly modified by the inorganic particulate content. Even in ocean areas of very low productivity (1000m depth Tyrrhenian sea $b(546)=0.016 \text{ m}^{-1}$ (Morel, 1973), Sargasso Sea $b(633)=0.023$ (Kullemberg, 1968)) $b(440)=0.04 \text{ m}^{-1}$ (Jerlov, 1976) the total scattering coefficient is much greater than the scattering coefficient of pure water for the same wavelength. Scattering coefficient values are on average higher in inland and estuarine waters than in open sea. Indeed, the very high values that can occur in some turbid inland waters are unlikely to be equalled at sea because of flocculation of suspended materials due to the changes in ionic content. Therefore, in studying the optical properties of natural waters, a contribution of the scattering must be expected even in open ocean conditions.

2.2.2.2. Suspended particles

The scattering particle found in natural waters can be divided in two categories:

- Biogenic scatterers mainly zooplankton, phytoplankton, bacteria and virus, dead and fragments of dead cells or macrophytes.
- Terrigenous scatterers derived from land, re-suspension of bottom sediment caused by wave action, tidal currents and storms or airborne dust carried by wind.

Unproductive oceanic waters away from land have the lowest values of scattering since few of these particles are likely to be encountered. Coastal and semi-enclosed marine waters have higher values due to the presence of re-suspended sediments, river-borne terrigenous particulate material and phytoplankton: San Diego Harbor (California) $1.21 \leq b(530) \leq 1.82 \text{ m}^{-1}$ (Petzold, 1972), English Channel $b(546) = 0.65 \text{ m}^{-1}$ (Morel, 1973). High levels of phytoplankton can give rise to high values of the scattering coefficient in oceanic areas such as the Mauritanian up-welling off the west coast of Africa ($0.4 \leq b(550) \leq 1.7 \text{ m}^{-1}$; Morel, 1982). As in the case of absorption, the scattering properties of phytoplankton can vary from one species to another. Algae such as diatoms and coccolithophores which have shells respectively made of silica and carbonate are more intense scatterers than, for example, naked flagellates. (Bricaud, et al., 1983; Bricaud and Morel, 1986; Morel and Bricaud, 1986; Morel, 1987). Blue-green algae with gas vacuoles scatter light much more intensely than those without (Ganf, et.al., 1982). Like the mineral and the detrital particles, algal cells have a scattering phase function which is strongly peaked in the forward direction (Stramski and Morel, 1990). However, the backscattering ratio (b_b/b , the proportion of the total scattering which is in a backwards direction) is much lower (0.0001-0.0004) for the living cells (Bricaud, et al., 1983; Stramski and Morel, 1990) than for the mineral and detrital particles (~ 0.019). This is a

consequence (*Bricaud, et al., 1983*) of the low refractive index relative to water of the living cells (1.015-1.075) (*Carder, et al., 1972; Morel, 1987; Ackleson and Spinrad, 1988*) compared with that of the inorganic particles (1.15-1.20) (*Jerlov, 1976*). The backscattering ratio is greater in the small (picoplankton) cells, such as cyanobacteria, than in the larger eukaryotic cells (*Stramski and Morel, 1990*) i.e. the picoplankton is a more efficient back-scatterer than larger cells.

A contradiction of the assertion that phytoplankton are weak scatters is observed in satellite oceanography. Remote sensing images show that blooms of coccolithophores have a high reflectance and therefore high backward scattering. The investigations carried out on this phenomenon tends to attribute this high backward scattering to the numerous detached coccoliths, rather than from the living cells themselves (*Holligan, et al., 1983; Morel, 1987*).

Another source of scatterers can originate from arid regions of the continents (e.g.: the sahara). Large amounts of dusts can be carried up in the atmosphere by wind, and when subsequently re-deposited in adjoining areas, can significantly increase scattering in the water (*Kopelevich, 1984*).

Figure 2-11 compares the values of the scattering coefficient measured by various authors with the scattering coefficient measured by *Smith and Baker (1981)*. It can be seen that even for the clearest waters, Sargasso Sea and Tyrrhenian sea, the values of $b(\lambda)$ are at least one order of magnitude higher than those for pure water or pure sea water.

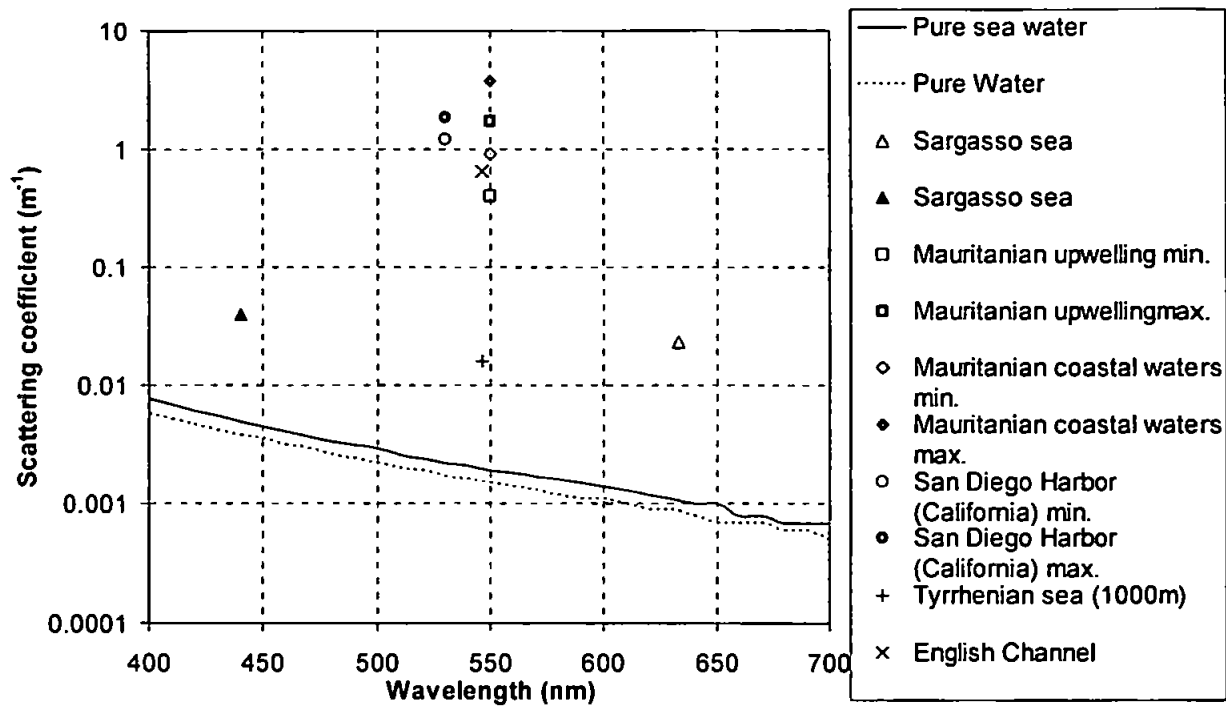


Figure 2-11: scattering coefficient of natural waters measured by various authors (Morel, 1973 ; Kullemberg, 1968 ; Jerlov, 1976 ; Morel, 1982 ; Petzold, 1972 ; Morel, 1973 ; Morel, 1982), compared with pure water and pure sea water.

2.2.2.2.1. Models for the VSF

The volume scattering function for natural waters differs strongly in shape from that of pure water. High purity of water is required to observe the volume scattering function of pure water or pure sea water (Figure 2-9 and Figure 2-10) as described previously. As soon as there is a small amount of particulate matter in the water (which is always the case even for the clearest natural water) the volume scattering function becomes highly peaked in the forward direction, and the scattering coefficient increases by at least a factor of ten. This is typical of scattering by particles of diameter greater than the wavelength of light, and scattering in natural waters is primarily due to such particles.

The contribution of the particulate matter to the total volume scattering function $\beta_t(\theta, \lambda)$ is obtained from:

$$\beta_p(\theta, \lambda) = \beta_t(\theta, \lambda) - \beta_w(\theta, \lambda)$$

Equation 2-18

where the subscript p refers to particles and w refers to pure water (if β is measured in fresh water) or pure sea water (for oceanic measurements).

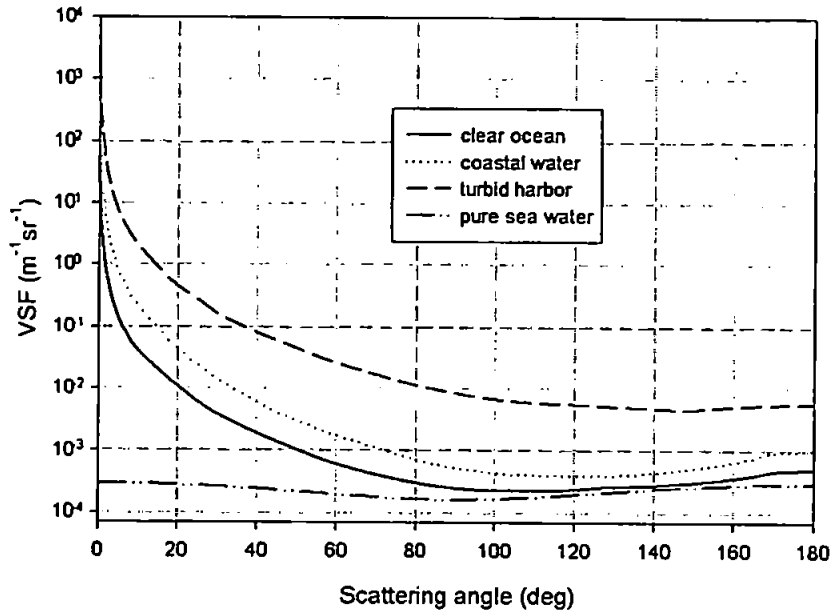


Figure 2-12: Log-log plot of Petzold's measurement of the VSF in three different location and the computed values for the VSF of pure water.

Although having been published thirty years ago, the unique *in situ* scattering measurements from *Petzold (1972)* are still the set of data widely used in modelling the underwater light field. The instrument he used had a spectral response centred at $\lambda = 514$ with a bandwidth of 75nm (Full Width at Half Maximum). These sets of data were used to produce Monte Carlo simulation of the instrument under investigation (see Chapter 4). Figure 2-12 shows Petzold's measurement of $\beta(\theta, 514)$ and the computed $\beta_w(\theta, 514)$ for pure sea water on a log-log plot. The top curve was obtained in the turbid water of San Diego, California (turbid harbour), the centre curve comes from near-shore in San Pedro Channel, California (coastal water) and the bottom curve is from very clear water in the Tongue of the Ocean, Bahama Islands (clear ocean). The same data are displayed on a polar plot in Figure 2-13. Both graphs show the very strong proportion of forward scattering for natural waters including the clear

ocean set of data. The particles cause at least a four order of magnitude increase in scattering between $\theta \approx 90^\circ$ and $\theta \approx 1^\circ$. The contribution of scattering by pure sea water to the total is therefore negligible except at back-scattering angles in the clearest natural waters (*Morel and Gentili 1991*). The backscattering ($\theta > 90^\circ$) constitutes 4.4% of total scattering in the case of clear oceanic water but only 1.9% in the turbid harbour water. The other surprising feature of these volume scattering functions from very different waters is the similarity of their shapes.

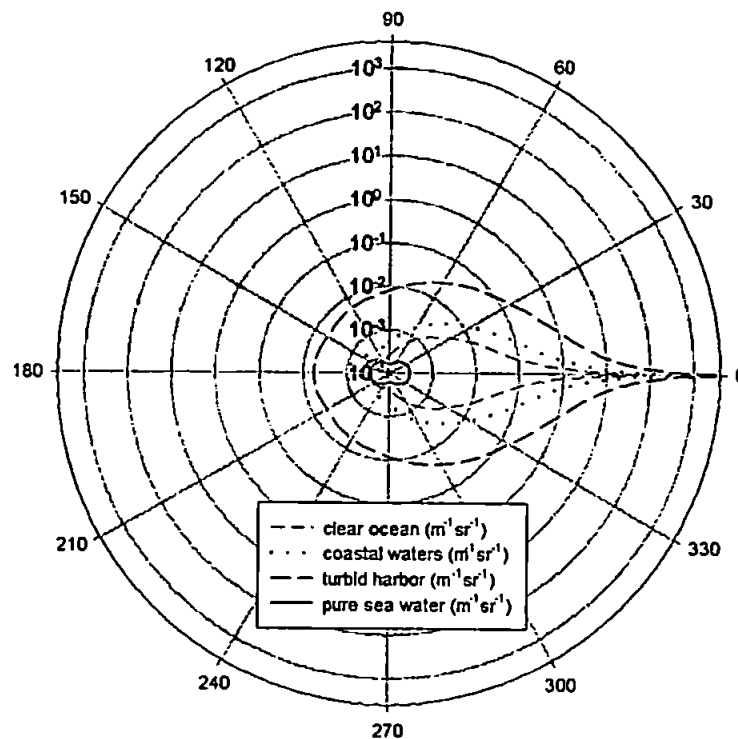


Figure 2-13: Polar plot on semi-log scale of Petzold's measurement of the VSF in three different location and the computed values for the VSF of pure water.

Highly peaked forward scattering like that seen in Figure 2-12 and Figure 2-13 is characteristic of diffraction dominated scattering in a polydisperse system (a system containing particles of many different sizes). Scattering by refraction and reflection from particle surfaces becomes important at large scattering angles ($\theta > 15^\circ$).

Compared with density fluctuation scattering, particle scattering is rather insensitive to the wavelength. The strong $\lambda^{-4.32}$ wavelength dependence described by *Equation 2-16* for pure

water and pure sea water scattering is not observed in natural waters. This is because scattering is dominated by diffraction from polydisperse particles that are usually much larger than the wavelength of visible light (*Mobley, 1994*). Although diffraction depends on the particle size to wavelength ratio, the presence of particles of many sizes diminishes the wavelength effects that are seen in diffraction by a single particle. Moreover, diffraction does not depend on particle composition. However, a wavelength dependence is to be expected, especially at backward scattering angles where refraction, and hence particle composition, is important. Molecular scattering also contributes something to the total scattering at back-scattering angles in clear water (*Morel and Gentili, 1991*). In these clear oceanic waters, density fluctuation scattering is a major contributor for $\theta > 90^\circ$, therefore a more marked inverse dependence on wavelength is to be expected.

Morel (1973) presented the total volume scattering function of two different water types: clear water (Tyrrhenian sea) and turbid water (English Channel) and for three different wavelengths (366, 436 and 546 nm). The clear waters under study showed a definite dependence upon the shape of $\beta(\theta)$ on λ , whereas the particle rich turbid water shows a much weaker wavelength dependence. He then shows that the wavelength dependence is strongest for backscattering angles and weaker for forward scattering.

Few theoretical models describing the VSF have been produced. *Kopelevich (1983)* and *Kopelevich and Mezhericher (1983)* have derived statistically a two parameter model for spectral volume scattering functions. This model distinguishes the contributions by “small” and “large” particles. Small particles are taken to be mineral particles less than 1 μm in diameter and having an index of refraction of $m_r = 1.15$ relative to water. Large particles are biological particles larger than 1 μm in diameter and having an index of refraction $m_r = 1.03$. The model is defined by:

$$\beta(\theta, \lambda) = \beta_w(\theta, \lambda) + \nu_s \beta_s^*(\theta) \left(\frac{550}{\lambda} \right)^{1.7} + \nu_l \beta_l^*(\theta) \left(\frac{550}{\lambda} \right)^{0.3}$$

Equation 2-19

where $\beta_w(\theta, \lambda)$ is the VSF of pure water calculated with Equation 2-14 with $\lambda_0=550\text{nm}$ and an exponent of 4.30, ν_s is the volume concentration of small particles (cm^3 of particles per m^3 of water, i.e. ppm), ν_l the analogous concentration of large particles, $\beta_s^*(\theta)$ is the small particles VSF per unit volume concentration of small particles ($\text{m}^{-1}\text{sr}^{-1}\text{ppm}^{-1}$) and $\beta_l^*(\theta)$ is the analogous large particle concentration specific VSF. Both $\beta_s^*(\theta)$ and $\beta_l^*(\theta)$ are found in Kopelevich's work. The ranges of values for oceanic waters are between 0.01 and 0.20 ppm for ν_s and between 0.01 and 0.40 ppm for ν_l and can be parameterised in terms of the total volume scattering function measured at $\lambda=550\text{nm}$ for $\theta=1^\circ$ and $\theta=45^\circ$:

$$\begin{aligned} \nu_s &= -1.4 \times 10^{-4} \beta(1^\circ, 550) + 10.2 \beta(45^\circ, 550) - 0.002 \\ \nu_l &= 2.2 \times 10^{-2} \beta(1^\circ, 550) - 1.2 \beta(45^\circ, 550) \end{aligned}$$

Equation 2-20

Thus $\beta(\theta, \lambda)$ can be determined from two measurements of the total VSF.

The mathematical form of the Kopelevich's model reveals that large particles give diffractive scattering at very small angles, thus $\beta_l^*(\theta)$ is highly peaked for small θ and the wavelength dependence of the large particle term is weak ($\lambda^{-0.3}$). Small particles contribute more to scattering at large angles and thus have a more symmetric VSF and a stronger wavelength dependence ($\lambda^{-1.7}$).

Mobley (1994) qualitatively compared this model with Petzold's data set and a data set from *Morel (1973)*. He showed that the Kopelevich model for $\beta(\theta, \lambda)$ qualitatively reproduces the wavelength behaviour observed in the clear and turbid waters but the model under-predicts

β at small scattering angles and over-predicts β at large angles compared to the Petzold's measurements.

2.2.2.2.2. Models for Particulate Scattering Coefficient

Because total light scattering in natural water is dominated by the particulate contribution, it is expected to increase in proportion to the concentration of suspended particulate matter. Early work on scattering properties found an approximately linear relationship between turbidimeter measurements and the concentration of suspended matter (*Biscaye and Eittreim, 1973; Sternberg, et al., 1974*). The constant of proportionality can, however vary from one kind of suspended matter to another (*Duchrow and Everhart, 1971*): The refractive index and the size distribution of the particles both influence the relation between $b(\lambda)$ and sediment concentration.

Several simple models are available for the total scattering coefficient $b(\lambda)$. A commonly employed bio-optical model described by *Gordon and Morel (1983)* is:

$$b(\lambda) = \left(\frac{550}{\lambda} \right) (0.30 \pm 0.15) C^{0.62} \quad (m^{-1})$$

Equation 2-21

where λ is in nm and C is the chlorophyll concentration in $mg.m^{-3}$. *Morel (1991b)* adds a pure water term, $b_w(\lambda)$ to the right hand side of the equation so that the models gives the correct value at $C = 0$.

A related bio-optical model for the total back-scattering coefficient $b_b(\lambda)$ is found in *Morel (1988), Stramski and Kiefer (1991)*:

$$b_b(\lambda) = \frac{1}{2} b_w(\lambda) + \left[0.002 + 0.02 \left(\frac{1}{2} - \frac{1}{4} \log C \right) \left(\frac{550}{\lambda} \right) \right] [0.30 C^{0.62} - b_w(550)] \quad (m^{-1})$$

Equation 2-22

This model shows the contributions by pure water and by particles. The first factor in brackets in the second term on the right-hand side of the equation represents the probability of backscattering by a particle. The second factor in brackets is the total scattering by particles. The $(\frac{1}{2} - \frac{1}{4} \log C)$ factor gives the particle contribution a λ^{-1} wavelength dependence in very clear ($C=0.01 \text{ mg.m}^{-3}$) water and no wavelength dependence in very turbid water ($C=100 \text{ mg.m}^{-3}$). The empirically derived models for $b(\lambda)$ and $b_b(\lambda)$ (Equation 2-22 and Equation 2-23) are intended for use only in Case 1 waters. However, even when the model is applied to Case 1 waters, from which it was derived, the predicted $b(\lambda)$ value can easily be in error by a factor of two. If the model is applied to Case 2 waters, the error can be an order of magnitude (*Gordon and Morel 1983*). For a given C value, $b(\lambda)$ is higher in Case 2 waters, because of the presence of additional particles that do not contain chlorophyll.

The integration of Kopelevich's equation (Equation 2-19) over θ yields another model for $b(\lambda)$:

$$b(\lambda) = 0.0017 \left(\frac{550}{\lambda} \right)^{4.3} + 1.34 \nu_s \left(\frac{550}{\lambda} \right)^{1.7} + 0.312 \nu_t \left(\frac{550}{\lambda} \right)^{0.3} \quad (m^{-1})$$

Equation 2-23

where ν_s and ν_t are given by Equation 2-20. Kopelevich claims that the accuracy of this model is 30%. An extension of Kopelevich's model is found in *Haltrin and Kattawar (1991)*:

$$b(\lambda) = b_w(\lambda) + b_{ps}^o(\lambda)P_s + b_{pt}^o(\lambda)P_t$$

Equation 2-24

Here $b_w(\lambda)$ is given by:

$$b_w(\lambda) = 5.826 \times 10^{-3} \left(\frac{400}{\lambda} \right)^{4.322}$$

Equation 2-25

which is essentially the same as Equation 2-21. The terms $b_{ps}^o(\lambda)$ and $b_{pl}^o(\lambda)$ are the specific scattering coefficients for small and large particles, respectively, and are given by:

$$b_{ps}^o(\lambda) = 1.1513 \left(\frac{400}{\lambda} \right)^{1.7} \quad (m^2 g^{-1})$$

$$b_{pl}^o(\lambda) = 0.3411 \left(\frac{400}{\lambda} \right)^{0.3} \quad (m^2 g^{-1})$$

Equation 2-26

P_s and P_l are the concentration of small and large particles, respectively. These quantities are available in the literature and parameterized in terms of chlorophyll concentration

C. This work also presents a model for back-scattering:

$$b_b(\lambda) = \frac{1}{2} b_w(\lambda) + B_s b_{ps}^o(\lambda) P_s + B_l b_{pl}^o(\lambda) P_l$$

Equation 2-27

where $B_s = 0.039$ is the back scattering probability for small particles and $B_l = 0.00064$ is the back-scattering probability for large particles.

The bio-optical models for scattering just discussed are useful but very approximate. The reason for the frequent large discrepancies between model prediction and measurements is because scattering depends not just on particle concentration (as parameterized in terms of chlorophyll concentration), but also on the particle index of refraction and the details of the particle size distribution, which are not well parameterized in terms of chlorophyll concentration alone. Whether or not Kopelevich's model or its derivative Haltrin-Kattawar form, which at least partition the scattering into large and small particle components, is in some sense better than the Gordon-Morel model is not known at present.

The following figure shows the calculation of particle scattering coefficient calculated using Haltrin - Kattawar's and Gordon - Morel's models for a range of chlorophyll concentration from 0 to 3 $mg.m^{-3}$. Both models display the same monotonic curves decreasing

toward the longer wavelength. However, Gordon's model tend to display a more important wavelength dependence.

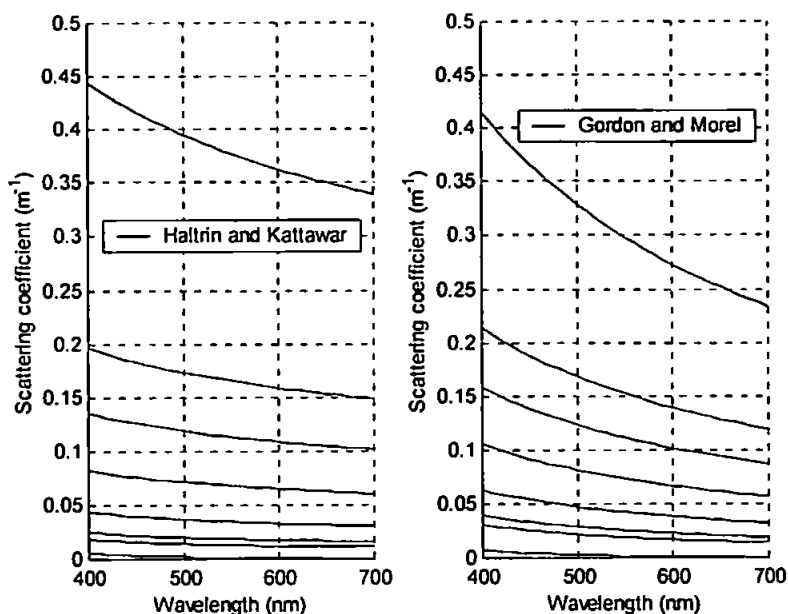


Figure 2-14: Particle scattering coefficient calculated using Haltrin - Kattawar's and Gordon - Morel's models for a range of chlorophyll concentration from 0 to 3 mg.m^{-3} .

Most of the models derived for particulate scattering found in the literature were initially derived for Case 1 water where very little effect of terrigenous material is expected. Applying those models to coastal waters obviously leads to erroneous values of the scattering coefficient. With the recent interest shown on the study of Case 2 waters, it is to be expected that new mathematical models would take into account both biogenic and mineral contributions.

2.2.2.3. Scattering by bubbles

Air bubbles in the ocean are generated mainly by the injection of air by breaking waves. In instruments such as the ac-9 (Wetlabs Inc.) where water is pumped into a measuring cell, additional bubbles are created by cavitation. These bubbles influence light propagation in water where they are present. Pioneering research on the bulk optical properties of bubbles in the ocean was carried out by *Stramski (1994)*. He studied the light scattering capabilities of clean bubble populations with a size distribution following the fourth power, having diameters

between 10 and 150 μm . He found that this class of bubbles can contribute up to approximately 10% of the total scattering coefficient. He used the bubble size distribution measured by *O'Hern et al (1988)* using a holographic method. This bubble size distribution assumes that the bubble number decreases as size increases according to the fourth power law, agreeing generally with acoustical observations. However, many *in situ* measurements (*Kolovayev, 1976; Johnson and Cooke, 1979; De Leeuw and Cohen, 1995*) have observed bubble size distributions with a plateau located between 40 and 80 μm . Although it has been argued that these peaked distributions are an artefact of the optical methods used (*Medwin and Breitz, 1989*), there is still uncertainty in the reasons for the differences between the optical and acoustical results. The light scattering that is due to bubble populations with such a size distribution varies from the situation analysed by *Stamski (1994)*. Furthermore, Stamski considered only clean bubbles. In nature, bubbles quickly acquire organic films after their formation in the sea (*Thorpe, 1982*). These organic films are composed mainly of proteins and lipids (*Glazman, 1983*), whose mean relative refractive indices ($mr=1.20$ for proteins and $mr=1.10$ for lipids) are quite different from those of air bubbles ($mr=0.75$), and thus it is expected that coated bubbles would scatter somewhat differently from clean bubbles.

Zhang et al. (1998) applied Mie theory to estimate the optical efficiency for both clean and organic film coated bubbles in the ocean and to study the effect of thickness and composition of this film coating on the light-scattering capability. Based on published *in situ* observations of bubbles in the ocean water, a generalised bubble size distribution was proposed. The maximum bubble radius used was 300 μm , which corresponds to the maximum radius found in most field experiments. The minimum radius bubble found in the ocean so far is 10 μm measured by holographic techniques (*O'Hern, et.al., 1988*). Even smaller bubbles radius ($\sim 3\mu\text{m}$) was suggested by the results of *Johnson and Cooke (1981)*. Another study by *Yount et.*

al. (1984) found stabilised bubbles of radius of the order of 1 μm or less in distilled water. The gas cavitation nuclei have an estimated radius of $\sim 0.1\mu\text{m}$ (Yount, 1979). In their calculation, they considered a minimum radius of 0.01 μm . the size bubble distribution the proposed is:

$$n(r) = N_0 p(r) \quad (\text{m}^{-3} \mu\text{m}^{-1})$$

Equation 2-28

where N_0 (m^{-3}) is the total bubble number density in a unit volume of water and $p(r)$ (μm^{-1}) is the bubble probability density function at radius r . By use of this generalized bubble size distribution, they calculated scattering and back scattering coefficient of bubble population and compared them with the optical properties of natural particles.

They concluded that in the visible domain, there is no significant difference in total scattering between clean bubbles and bubbles coated with organic film. Bubbles coated with organic film however, exhibit an enhanced back scattering efficiency due to the coating. The enhancement is directly proportional to both the refractive index and the thickness of the film. They showed that for a bubble population with a mean radius greater than 1 μm , the back-scattering efficiency can be enhanced by a factor of 4 because of the organic coating of thickness of 1 μm . They also showed that the effect of absorption by these coated bubbles was negligible.

2.2.3. Conclusion

This chapter described the different absorbing and scattering components encountered in natural waters and the theoretical approaches to investigate them. It appears that they are complicated parameters to measure because of the complexity and the variety of dissolved and particulate components present in natural waters. The experimental identification of the different components signature in a water sample is a difficult task, especially when coastal and

productive waters are considered. The mathematical model to describe the absorption spectra of the various optically active component in sea water appear to be well documented. The mathematical models that have been derived to describe the Volume Scattering Function and the bulk scattering coefficient are, however, still approximate especially in Case 2 waters. The investigation of coastal waters optical properties is a great challenge of optical oceanography. Accurate instrument is therefore needed if this goal is to be achieved.

Chapter 3: The measurement of absorption and scattering

Understanding the propagation of light through the ocean and determining the relationship between the water leaving radiance and the *in situ* oceanographic properties (optical, biological, physical and chemical) remain the largest challenges of optical oceanography. For example, the separation of the optical absorption into its biological and non biological component is of particular interest for the remote sensing of primary production. The determination of the scattering and back-scattering coefficient is crucial for determining the light field. Together with absorption, they determine the amount of energy which is transferred into the ocean and made available for photosynthesis and heat transfers or reflected back into the atmosphere. These optical properties determine the amount of energy captured or released by the world oceans. The goal of much research in optical oceanography has been to differentiate the processes and component (water, yellow substance, organic and inorganic particulate matter) influencing light propagation and to determine their impact on the aquatic ecosystem. This goal has led to the elaboration of a variety of techniques to measure absorption, scattering, back-scattering and the angular scattering function. The techniques developed for this purposes have all their advantages and disadvantages and will be described in this chapter.

3.1. The measurement of absorption

Pegau et al., (1995) reviewed the different existing techniques to measure the absorption coefficient of natural waters. The importance of the absorption coefficient and the difficulty of measuring it accurately in low-signal, scattering suspensions has led to the development of a variety of measurement techniques.

In situ measurement techniques include:

- the reflecting tube absorption meter (*Zaneveld, et. al., 1990; Moore, et. al., 1992*)
- isotropic point source (*Sorenson and Honey, 1968; Maffione, et.al., 1993*)
- methods using Gershun's equation (*Gershun, 1939*) to relate the absorption coefficient to the apparent optical properties (*Tyler, 1960; Hojerslev, 1975; Spitzer and Wermand, 1981; Doss and Wells, 1992; Voss, 1989; Voss and Chapin, 1992*)

Laboratory techniques include:

- the integrating cavity absorption meter (*Fry, et.al., 1992*)
- optoacoustic measurements (*Trees and Voss, 1990*)
- photothermal measurements (*Bennett, et.al., 1986*)
- measurements of the components portion using a spectrophotometer (*Yentsch, 1962; Kiefer and Soohoo, 1982; Roesler, 1989, Tassan and Ferrari, 1995*)

The optoacoustic and photothermal techniques were not investigated here. A number of absorption meters which employ these techniques and are available include:

- The reflective tube absorption meter (RTAM)
- The tethered optical profiling system (TOPS)
- The isotropic point source (IPS)
- The compound radiometer
- The integrating cavity absorption meter (ICAM)
- The spectrophotometer

These meters will now be described in some detail.

3.1.1. Reflecting Tube Absorption Meter (RTAM).

The RTAM uses a collimated beam light source and encloses the sample in a reflective tube. The reflective tube collects the near forward-scattered light so that the radiant flux lost due to absorption may be estimated (*Zaneveld, et.al., 1990*). This instrument actually measures the absorption coefficient plus a small fraction of the scattering coefficient associated with the uncollected scattered light. The uncorrected absorption coefficient a_u is obtained using:

$$a_u = -\frac{1}{L} \ln \left(\frac{V_{sample}}{V_{pw}} \right)$$

Equation 3-1

where L is the path length of the instrument, V_{sample} is the signal voltage for the sample, and V_{pw} is the signal voltage for pure water. Note that this is essentially the same approach as is used in a spectrophotometer. Rather than using a reference cell, the meter is calibrated in the laboratory. Algorithms using simultaneous measurements of the beam attenuation coefficient are then applied to remove the portion of the scattering coefficient included in the signal (Zaneveld, *et al.*, 1992). The various correction methods for an RTAM will be described in *Chapter 6*.

3.1.2. Tethered Optical Profiling System (TOPS).

The Tethered Optical Profiling System used by Pegau *et al.*, (1995) consisted of a multiple radiometer package. The measurement of $E_d(\lambda, z)$, $E_u(\lambda, z)$ and $E_o(\lambda, z)$, respectively the downward irradiance, the upward irradiance and the scalar irradiance allow the calculation of K_E , the net downward irradiance, Equation 3-2

and $\bar{\mu}$, the average cosine, Equation 3-3.

$$K_E = -\frac{1}{E_d - E_u} \times \frac{d}{dz} (E_d - E_u)$$

Equation 3-2

$$\bar{\mu} = \frac{E_d - E_u}{E_o}$$

Equation 3-3

These data are then applied to Gershun's equation (Equation 1-27) to determine $a(\lambda, z)$.

3.1.3. Isotropic Point Source

The isotropic point source technique was first proposed by *Sorenson and Honey (1968)*, who argued that the attenuation of irradiance E from an isotropic source should decay with distance approximately as:

$$E(r) \propto \frac{e^{-ar}}{r^2}$$

Equation 3-4

where a is the absorption coefficient and r is the radial distance from the source. Thus, by measuring the irradiance from the source as a function of r , the absorption coefficient could be determined.

The vector irradiance (more precisely, the radial component of the vector irradiance) from an isotropic point source was derived from the steady state radiative transfer equation without internal source (*Maffione, et. al., 1993*):

$$E(r) = \frac{\Phi_0}{4\pi r^2} \exp\left(-a \int_0^r \frac{dr}{\bar{\mu}}\right)$$

Equation 3-5

where Φ_0 is the radiant flux emitted by the source and $\bar{\mu}$ is the average cosine of the light field from the source. The assumption in Equation 3-5 is that the water column within which $E(r)$ is measured is homogeneous (*Pegau et al., 1995*). The solution to Equation 3-5 for the absorption coefficient is:

$$a(\lambda, z) = \bar{\mu} \left[K_E(\lambda, z) - \frac{2}{r} \right]$$

Equation 3-6

where K_E is the diffuse attenuation coefficient for irradiance. To avoid errors due to the ambient background light, IPS measurements have to be made either at night or in deep water. When $r \rightarrow \infty$, Equation 3-6 reduces to Gershun's equation.

3.1.4. *The Compound Radiometer:*

The compound radiometer estimates the absorption coefficient by measuring the moment of the Legendre polynomial expansion of a radiance distribution. The absorption coefficient is determined by applying the measured moments to a form of Gershun's equation (*Zaneveld and Pak, 1972; Wells, 1983*). This device uses a series of reflectors to measure the integral moments of the radiance distribution at a number of zenith angles (*Doss and Wells, 1992*). The radiance distribution is then deduced from a linear combination of the measured moments. The moments are symmetrical about the vertical axis and optimised to facilitate computation of the inherent optical properties in the form of the D_n series as a function of depth (*Doss and Wells, 1992*). The zeroth-order moment (D_0) is the absorption coefficient, D_∞ is the beam attenuation coefficient, and the intermediate D_n describe moments of the volume scattering function.

3.1.5. *Integrating Cavity Absorption Meter (ICAM)*

The theoretical basis of the Integrating Cavity Absorption Meter was developed by *Elterman (1970)*. In an ICAM, a diffuse light field is set up within a cavity that has a diffusely reflective wall and is filled with the liquid whose absorption properties are to be measured. From the measured effect of the liquid on this light field, the value of its absorption coefficient can be determined. The idea was adopted by *Fry et al. (1992)* who describe the theory and design of an instrument that could be used to measure the absorption coefficient of water. This ICAM has a cylindrical shape and consists of two concentric integrating cavities to ensure that the light inside the inner cavity is isotropic (*Figure 3-1*). *Pope et al., (1997)* used an ICAM to

measure the absorption coefficient of pure water in the wavelength of 380 to 700 nanometres. The ICAM has two specific advantages. First, because of the long path length of the photons as they undergo multiple reflections from the cavity wall before absorption, the instrument can be used to measure low values of absorption coefficient. Second, because the light field is already totally diffuse, it cannot be made more diffuse by scattering because of particles within the cavity. Thus, measurement of absorption is not affected by scattering (*Fry, et al., 1992*).

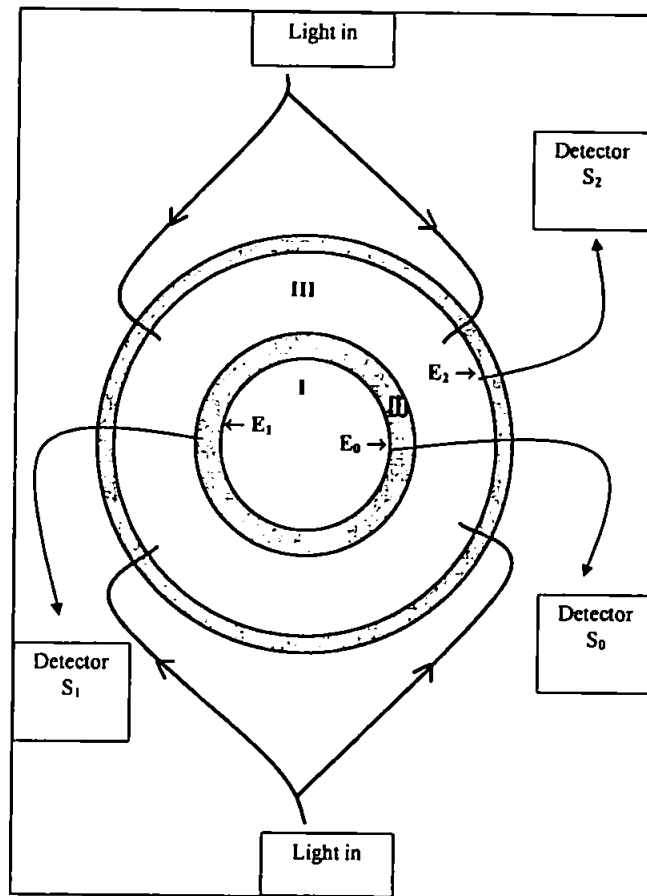


Figure 3-1: cross section of an ICAM

There are two methods of calibration for the ICAM, one described by *Fry et al. (1992b)*, and one developed by the Naval Research Laboratory (*Kennedy, 1992*).

(1) The method describe by *Fry et al.*, expresses the absorption coefficient as a linear function (Equation 3-7) of the voltage signal measured in different parts of the instrument.

$$a(\lambda) = K_1 \frac{S_1(\lambda)}{S_0(\lambda)} - K_2$$

$$a(\lambda) = K_3 \frac{S_2(\lambda)}{S_0(\lambda)} - K_4$$

Equation 3-7

where K_1 , K_2 , K_3 and K_4 are calibrations constant of the instrument and S_0 , S_1 and S_2 are the signal voltage at different places in the cavity (Figure 3-1). The calibration constants K_i can be determined by measuring the known absorption coefficient of a dye solution.

(2) The algorithm developed by NRL calculates an effective path length for the cavity. The effective path length is dependent on the geometry of the cavity, the refractive index of the sample and the field of view of the sensor (*Kennedy, 1992*). The assumptions made with the ICAM are the following:

- The light field within the cavity is isotropic.
- The light field within the sample is isotropic
- The change in energy density is due only to the absorbance of the sample.
- The absorbance of the empty sample is zero.

When an empty cavity reading is used as the zero absorbance value, the absorption coefficient can be determined from Equation 3-8.

$$a(\lambda) = \frac{1}{l} \ln \left(\frac{V_E(\lambda)}{V_S(\lambda)} \right)$$

Equation 3-8

where l is the effective pathlength, $V_E(\lambda)$ and $V_S(\lambda)$ are respectively the signal voltage measured for an empty cavity and a cavity field with a sample.

When used in this way, the integrating cavity absorption meter does not require standardisation, either by measuring known calibration samples with a spectrophotometer or by measuring absorption of clean water to determine the total absorption coefficient of the sample.

3.1.6. Spectrophotometer

Spectrophotometric measurements of absorption are based on two fundamental laws concerning the relationship between the intensities of the radiation incident on and transmitted by a layer of absorbing substances: Lambert's and Beer's laws.

Lambert's law states that the proportion of radiation absorbed by a substance is independent of the intensity of the incident radiation. The law can also be expressed in the form that each successive layer of thickness dl of the medium absorbs the same fraction dl/I of the radiation of intensity I incident upon it. Therefore $dI/I = -\mu dl$, where μ is a constant. This expression becomes on integration:

$$I = I_0 e^{-\mu l}$$

Equation 3-9

where I_0 is the intensity of radiation incident on a layer of thickness l and I is the emergent intensity. Equation 3-9 can also be written as

$$I = I_0 10^{-Kl}$$

$$\text{or } \log_{10} \left(\frac{I_0}{I} \right) = Kl$$

$$\text{where } K = \log_{10}(e^\mu) = 0.4343\mu$$

Equation 3-10

Another important quantity A (absorbance), is defined by:

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \log_{10} \left(\frac{1}{T} \right) = L l$$

Equation 3-11

where T is the fraction of radiation transmitted or transmittance

Beer's law states the relationship between the intensities of the incident and transmitted radiations in a different way: the absorption depends only on the number of absorbing

molecules through which the radiation passes. If the absorbing substance is dissolved in a non-absorbing medium, the absorbance will then be proportional to the concentration of the solution.

Beer's law can therefore be combined with Lambert's law in the form:

$$A = \log_{10} \left(\frac{I_0}{I} \right) = a l \xi$$
$$\text{or } I = I_0 10^{-a l \xi}$$

Equation 3-12

where a is the absorption coefficient, l the pathlength along which the incident radiation is absorbed and ξ the concentration of the absorbing molecules.

A beam of monochromatic light passes through a quartz or plastic cell of known path length. The measured quantity is the intensity (I) of the light that passes through the cell. Two measurements are conducted, one with a cell filled with pure water, (I_0), and a second with the water sample under consideration. The transmittance (T) is then calculated:

$$T(\lambda) = \frac{I(\lambda)}{I_0(\lambda)}$$

Equation 3-13

The absorbance is then calculated using Equation 3-11

and the absorption coefficient is then derived from Beer's law (Equation 3-12).

However, the low concentration and absorption signal of suspended particles in the water column requires that the particles be concentrated before their absorption spectrum can be measured in a spectrophotometer (*Yentsch, 1962*). The most common procedure for a natural water sample is to determine separately the absorption coefficients of the different components. The value of the total absorption coefficient of the medium, at a given wavelength, is then calculated as the sum of the individual absorption coefficients of all the components present.

$$a(\lambda) = a_{DOM}(\lambda) + a_{part}(\lambda) + a_w(\lambda)$$

Equation 3-14

where $a_{DOM}(\lambda)$, $a_{part}(\lambda)$, $a_w(\lambda)$, are respectively the absorption coefficients of Dissolved Organic Matter (Gelbstoff), particulate matter and pure water. This is commonly done by filtering a sample of water to retain the particulate matter on a filter pad. The spectral absorption of the particulate matter, $a_{part}(\lambda)$ is then determined in a spectrophotometer, which measures the transmittance through the filter pad and collected particulate matter. This technique was described by *Bannister (1988)*, *Mitchell (1990)*, *Stramski (1990)*, *Cleveland and Weidemann (1993)*. A variation of this technique consists of measuring the light reflected by the filter pad, as opposed to the transmitted light. These two methods were compared by *Balch and Kilpatrick (1992)*. A method using measurement in both transmittance and reflectance was later developed by *Tassan and Ferrari, 1995*.

Laboratory methods for the measurement of absorption in dilute suspension of particles usually employ spectrophotometers (*Bricaud et. al., 1983*), although photo-acoustic methods have been investigated (*Trees and Voss, 1990*). These methods give good accuracy but are not well suited for ship-borne work.

To arrive at the total absorption, the dissolved absorption $a_y(\lambda)$ must be taken into account. This Gelbstoff substances are rarely negligible even in open ocean. To measure it, a volume of the water sample is filtered. The absorption of the filtrate is then measured, preferably, on a long path cuvette. $a_y(\lambda)$ is often estimated in terms of $a_y(400)$ (*see section 2.1.2*)

3.2. Instrumental Errors – absorption meters

An essential aspect of the assessment and objective comparison of any instrumentation is recognition and, where possible, quantification of any errors inherent in individual

instruments. The errors known to exist and affect the performance of the instruments described in section 3.1 will now be explored.

3.2.1. Reflecting Tube Absorption Meter

The inherent error in the RTAM approach is due to the undetected back-scattered light. Various approaches can be used to estimate this undetected light (*Zaneveld, et.al., 1994*). If simultaneous measurements of the spectral absorption and beam attenuation coefficient are made, *Zaneveld et al., (1994)* showed that an error of less than 1% could be obtained. Otherwise, an error of $\pm 5\%$ is possible with a precision of approximately 0.003 m^{-1} (*Pegau, et al., 1995*). Calibration problems are also encountered. The first one is an instrumental drift that can not be entirely removed using pure water calibration; the second one is cavitation in the flow tube of the instrument (*Pegau, et.al, 1995*). Another source of bias common to all systems that use a pure water reference is the possibility of contaminated “pure” water used in the calibration, and this is impossible to estimate.

3.2.2. Tethered Optical Profiling System (TOPS).

Gershun's equation is used with TOPS irradiance profiles to calculate absorption coefficient with an estimated uncertainty of approximately 10%. This uncertainty includes a contribution from instrument noise of up to 7% (*Pegau et al., 1995*).

3.2.3. Isotropic Point Source

Errors in the IPS method arise from several sources. All of these errors, except for the assumption of water homogeneity, are due to the particular instrumental implementation and optical conditions of the water mass (*Pegau, et al., 1995*). The largest sources of errors are:

1. the assumption of constant radiant output of the isotropic source during each light flash since a reference detector is not used.
2. Variable alignment of the source and detectors due to the variability in water movement.

3. The assumption that $\bar{\mu}=1$ since only vector irradiance and not scalar irradiance was measured.

Errors from 1 and 2 should be random and therefore quantified in the standard error of the regression fit. Errors of 2 can also be systematic if instrument misalignment remains constant during a measurement. The error from the assumption that $\bar{\mu}=1$ (3) is systematic and difficult to quantify (Pegau, et al., 1995).

Another source of error in this method is the approximation that the path length in the exponent is the geometrical radial distance r , when, in fact, scattering increases the mean path by δr so that the expression should be (Pegau, et. al., 1995):

$$E(r) \propto \frac{e^{-a(r+\delta r)}}{r^2}$$

Equation 3-15

If $\delta r \ll r$, the error will be small.

3.2.4. The Compound Radiometer:

The Compound Radiometer has an estimated uncertainty of 0.01m^{-1} in the depth range of 12 to 18 m (Miles and Wells, 1993). This is the range in which the radiometer works best. Performance deteriorates in deep water, due to lack of light and also in very shallow water (Pegau, et al., 1995). The performance of course depends also on the turbidity of the water.

3.2.5. Integrating cavity absorption meter (ICAM)

The algorithm developed by NRL does not require standardisation with a spectrophotometer or the need of pure water to return the total absorption coefficient of the sample. Errors arise from the assumption that absorption in an air-filled cavity is zero. The assumption of an isotropic field within the cavity is also a source of error with this method. The overall error with this method is assumed to be around 1 % (Pegau, et al, 1995). This method of

calibration is more accurate than the first one developed by *Fry et al (1992)* because no calibration with standard dye solution is required.

3.2.6. Spectrophotometer

With a spectrophotometer, using the cuvette technique, a proportion of the light is scattered outside the field of view of the sensors. Therefore, spectrophotometers do not measure the true absorbance but the attenuance (absorbance plus a fraction of scattering). This might be a problem for a solution with a high scattering coefficient relative to the absorption coefficient. The measurement of the blank cell is far less biased by the scattering effect. This problem can be minimised by placing a layer of scattering material between the cell and the incident beam, so that both samples are illuminated by a diffuse beam.

Errors in total absorption coefficients estimated from spectrophotometric measurements arise also from several sources. The first is the unknown error in values of pure water spectral absorption (*Smith and Baker, 1981, Pope and Fry, 1997*).

The filter pad method (*Yentsch, 1962*) is the standard way of measuring particulate absorption at sea. However, this is not an ideal technique. The major problem with this technique is that the intense scattering within the filter pad and the collected particulate matter increases the average distance travelled by the photons passing through the sample, which increases the apparent absorption. Correction must be applied for this increased photon pathlength and this is a potential source of bias. Other sources of errors with this technique include:

- The inability of filters to retain all particles
- Absorption by yellow substances retained on the filter
- Decomposition of pigment during the filtration process
- Errors are associated with separate techniques to measure absorption, due to suspended particles and due to dissolved organic matter.

This technique, later modified by *Tassan and Ferrari, 1995* was used and will be described in the *Chapter 6*.

3.3. Measurement of scattering

Experimentally, $b(\lambda)$ can be estimated by three different ways:

- Measurement and integration of the VSF
- Calculation via the energy conservation equation $c(\lambda) = a(\lambda) + b(\lambda)$
- Calculation via the AOP's
- Calculation via Mie theory (*see section 2.2.1.2*)

3.3.1. Measurement of the Volume Scattering Function

In principle, the theory of an instrument to measure the Volume Scattering Function $\beta(\lambda, \theta)$ is simple. A collimated beam of known spectral irradiance $E(\lambda)$ illuminates a volume of water dV and the scattered intensity $I(\lambda, \theta)$ is measured as a function of angle (Figure 3-2).

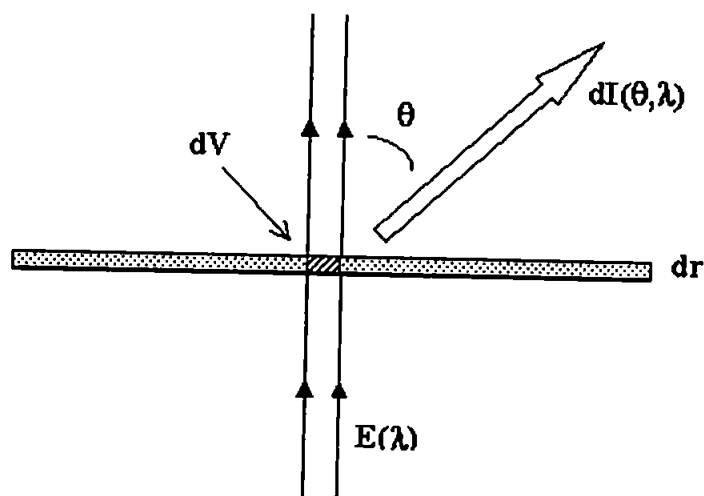


Figure 3-2: Principle of measurement of the VSF

However, the engineering of such an instrument for *in situ* measurement is quite difficult:

- Firstly, the scattered intensity typically increases by five or six orders of magnitude over the angular range from $\theta = 90^\circ$ to $\theta = 0.1^\circ$ for a given natural water sample, and scattering at a given angle θ can vary by two orders of magnitude among water samples. The required dynamic range of an instrument is therefore great.
- Secondly, measurement at near forward ($\theta < 1^\circ$) and near backward ($\theta > 179^\circ$) angles are very difficult to make and the behaviour of $\beta(\theta, \lambda)$ at these angles is crucial for the determination of $b(\lambda)$ by integration (*Equation 1-19*), since typically one-half of all scattering takes place at angles of less than a few degrees.

Owing to the technical difficulties of measuring $\beta(\theta, \lambda)$ at small angles, very few data are available in the literature. *Spinrad et al. (1978)*, *Padmabandu and Fry (1990)*, and *Fry et al. (1992a)* have reported measurements at very small angles on suspensions of polystyrene spheres, but no such measurements have been published for natural water samples. The Padmabandu and Fry technique is interesting because it allows the measurement of β at $\theta = 0^\circ$ exactly, by use of the coupling of two coherent beams in a photorefractive crystal to measure the phase shift that corresponds to 0° scattering. Measurement of $\beta(0, \lambda)$ is of theoretical interest because of its relation to attenuation via the conservation energy equation (*section 3.3.2*).

Enhanced backscatter has been reported in suspensions of latex spheres; a factor of two increase in scattered intensity between $\theta = 179.5^\circ$ and 180° is typical (*Kuga and Ishimaru, 1989*). Measurements in natural waters (*Maffione and Honey, 1992*) show only about 10% increase in $\beta(\theta, \lambda)$ as θ goes from 179.5° to 180° . Recent studies show that small ($< 300\mu\text{m}$) air bubbles in water also can generate important backscatter (*Arnott and Martson, 1988; Zhang, 1998; section 2.2.2.3*).

Because of these design difficulties, only a few instruments have been built for *in situ* measurement of the VSF. *Petzold, (1972)* gives the details of two such instruments, one for small scattering angles and one for larger angles (*see section 3.3.1.1 and 3.3.1.2*). The arrival on

the market of newly developed instrument like HydroScat (2-4-6) (Hobilabs; extrapolate the back-scattering coefficient at 2, 4 or 6 wavelength via the measurement of $\beta(\theta, \lambda)$ at one angle), ECO-VSF (Wetlab) or Hydrobeta (under development HobiLab) might provide the scientific community with a new approach to the measurement of the scattering coefficient. Commercial instruments are available for laboratory measurement of $\beta(\theta, \lambda)$. These instruments are subject to their own problems, such as degradation of samples between the times of collection and measurement. These instruments include

- Fixed angle scattering meter
- Variable angle scattering meter
- Turbidimeter

Among the *in situ* and laboratory techniques mentioned:

- Petzold small and large angle scattering meter
- The ECO-VSF
- The hydrobeta
- The fixed angle and variable angle scattering meter
- The turbidimeter

will be briefly presented in the following sections.

3.3.1.1. Small angle scattering meter

Petzold (1972) developed a small *in-situ* scattering meter using a highly collimated beam of light traversing a 0.5 m pathlength in the water and then being focused by a long-focal-length lens onto a receiver. Light scattered within a very narrow angular range is selected by means of a field stop placed on the focal plane and detected with a PhotoMultiplier Tube. The field stops allowed measurement for three different angles (0.085, 0.17, 0.34°).

3.3.1.2. Large angle scattering meter

This instrument for measuring large angles scattering is designed so that either the light source or the detector is rotated relative to the other. *Petzold (1972)*, designed an *in situ* large

scattering angle meter for $10 \leq \theta \leq 170$ which he used with his small angle scattering meter to produce the data set discussed in *section 2.2.2.2*.

3.3.1.3. ECO-VSF

The ECO-VSF (WetLabs) measures the optical scattering at three different angles: 100, 125 and 150 degrees, and at wavelengths of 450, 530, and 650 nm, thus providing the shape of the Volume Scattering Function (VSF) throughout its angular domain. The VSF from 90 to 180° is then calculated by interpolation and extrapolation. The three-angle measurement allows determination of specific angles of backscattering through interpolation. Conversely, it also can provide the total backscattering coefficient by integration and extrapolation from 90 to 180 degrees. The sensor employs three transmitters coupled to a single receiver to obtain its measurements.

3.3.1.4. Hydrobeta

Hydrobeta (under development, Hydrosat) projects a collimated beam of light through the water, and uses narrow angle radiometers to measure the radiance emerging at various angles. Unlike earlier “free angle” designs, which used a single movable receiver to measure all angles, Hydrobeta uses an array of stationary receivers, viewing a common volume, to measure at discrete angles from 10° to 170° . This approach greatly speeds up the measurement of the VSF. It also allows the receiver to be tailored somewhat to the huge different signal levels found at the different angles (up to four order of magnitude from 1° to 180°; see *section 2.2.2.2*).

3.3.1.5. Variable angle scattering meter

Commercial light scattering photometers for both large and small angles have been developed or adapted by various authors (Aughey and Baum, 1954; Beardsley, 1968; Spilhaus, 1968; Spinrad and Pak, 1978).

3.3.1.6. Fixed angle scattering meter

If a measurement at all angles is not possible, $\beta(\theta)$ can be measured at one convenient angle. A value of $b(\lambda)$ can then be estimated by making an assumption about the shape of the volume scattering function. *Jerlov* (1976) stated that in marine waters, the ratio of the volume scattering function at 45° to the total scattering coefficient is in the range $0.021\text{--}0.035 \text{ sr}^{-1}$. *Kopelevich and Burenkov*, (1971) based on measurements in the Pacific and Indian oceans and in the Black Sea concluded that the error in estimating b from single angle measurements of $\beta(\theta)$ is lower for angles less than 15° . An angle of 4° was considered acceptable. A linear regression of the type:

$$\log(b) = c_1 \log \beta(\theta) + c_2$$

Equation 3-16

where c_1 and c_2 are constants, was found to give more accurate values for b than a simple proportionality relationship.

Oishi (1990) concluded that there is an approximately constant ratio between the back scattering coefficient and the volume scattering function at 120° , so that b_b can be calculated from a scattering measurement at 120° , using the relationship: $b_b \approx 7\beta(120^\circ)$.

3.3.1.7. Turbidimeter

A simplified version of the fixed angle scattering meter is the turbidimeter. A beam of light is directed along the axis of a cylindrical glass cell containing the liquid under investigation. Light scattered from the beam within a broad angle centred on 90° is measured by a photomultiplier located on the side of the cell. The turbidity of the sample is measured relative to that of a standard. Turbidimeters measurements do not provide a direct estimates of scattering properties and are in arbitrary units.

3.3.2. Measurement of $b(\lambda)$ via the Conservation of Energy Equation

In practise, the scattering coefficient is usually determined by the conservation of energy equation: $b(\lambda) = c(\lambda) - a(\lambda)$, after measurements of beam attenuation and absorption coefficient have been made, hence the importance of both these measures. The following paragraphs mention two *in-situ* instruments.

3.3.2.1. Beam transmissometer

Beam transmissometers have been used for a long time in marine optics. In principle, they measure the proportion $c(\lambda)$, of the incident beam which is lost by absorption and scattering along a pathlength r . The beam attenuation coefficient $c(\lambda)$ is given by:

$$c(\lambda) = -\frac{1}{r} \ln(1 - C) \quad (m^{-1})$$

Equation 3-17

In practice, the construction of an instrument which measures $c(\lambda)$ accurately is difficult. The problem is due to the fact that particles scatter mainly in the near forward direction. Therefore, unless the acceptance angle of the detector is $<1^\circ$, the measurement will be corrupted by scattering and the attenuation underestimated. Corrections need to be applied to obtain the value of $c(\lambda)$.

3.3.2.2. The ac-9 transmissometer (WetLabs)

The ac-9 (WetLabs) simultaneously measures the absorption and attenuation coefficient of water at nine different wavelengths (Figure 3-2). The ac-9 is made of two cylindrical cells of 10 or 25 cm length. The first, the a-tube is coated with an absorbing substance and measures the absorption coefficient of the water sample. The absorbing substance covering the cylinder

removes the scattered light from the measurement and therefore gives a fairly good measurement of $a(\lambda)$. The second cell, the c-tube, is coated with a reflective material and measures the attenuation coefficient. The reflective material entraps the light within the cell, thus providing an accurate estimation of the attenuation coefficient although a fraction of the light is lost by back-scattering (*see section 3.1.1*).

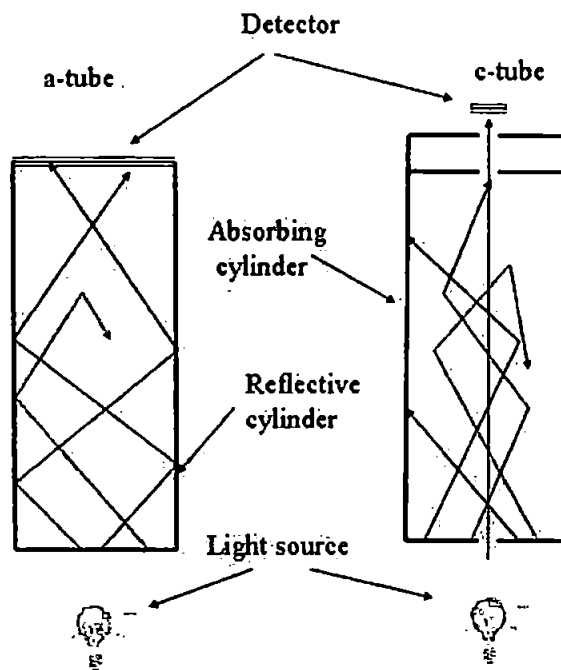


Figure 3-3: principle of the ac-9

3.3.3. Measurement of $b(\lambda)$ via the AOPs

Information on the scattering properties can be derived from the measured irradiance values. For water with a specified VSF and with incident light at a given angle, then at any optical depth ξ , the irradiance reflectance $R(\lambda, z)$, and the average cosine $\bar{\mu}$, of the light are functions of $b(\lambda, z)/a(\lambda, z)$. If the value of $R(\lambda, z)$ at a given optical depth is known, then the value of $\bar{\mu}(\lambda, z)$ and $b(\lambda, z)/a(\lambda, z)$ are fixed, and in principle can be determined.

Kirk (1981a,b) used Monte Carlo simulation to determine the relationship between b/a , $\bar{\mu}$, and R using the volume scattering function determined by *Petzold (1972)* for the turbid

waters of San Diego harbour. He concluded that these relationship ($\bar{\mu}=f(R)$ and $b/a=f(R)$) would be valid for most natural waters of moderate to high turbidity. Using the computer derived curves, it is possible, having a measurement of $R(\lambda,z)$ to obtain the corresponding values of $\bar{\mu}(\lambda,z)$ and $b(\lambda,z)/a(\lambda,z)$. The irradiance values are used to estimate K_E and the value of $a(\lambda,z)$ is calculated via the Gershun equation $a=\bar{\mu} K_E$. Knowing a and b/a , the value of b can be calculated. *Weidemann and Bannister (1986)* and *Oliver (1990)* used the same methods compared with others and found good agreement. Various radiometers can be used to measure the desired AOP's: Profiling Reflectance Radiometer (PRR; Biospherical Instrument), FreeFall (Satlantic Inc.), Scalar Irradiance collector (HobiLabs Inc.), HydroRad (Hobilabs Inc.).

3.4. Conclusion

A good understanding of the inherent optical properties of ocean waters as well as a good understanding of the respective contribution of the different optically active components of these waters is necessary if better interpretation of remotely sensed data and a better understanding of the underwater light field. The need for this knowledge is particularly important in coastal regions where the colour of the ocean is the result of a complex solution of dissolved and particulate components. Through this over view of the various techniques to measure the absorption and scattering coefficients of natural waters, it occurs that there is still scope for improving the measurement techniques. Therefore, despite the amount of *in-situ* or laboratory techniques that can measure absorption, developing an instrument that would measure absorption regardless to the level of scattering is of great interest for optical oceanography.

From the observation of the various techniques to measure absorption, a promising one appeared to be an absorption meter based on an integrating cavity. The advantage of such a

techniques is that using an integrating sphere as a container cell for a water sample, virtually all non absorbed photons would end up at the detector regardless to the level of scattering. The brilliant design used by *Pope, et al.* (1992) achieved this. *Kirk (1995, 1997)* came out with different idea for the design of the integrating sphere which he argued would be easier and cheaper to build as well as more efficient. The theory he developed for this instrument will be presented in *Chapter 4*.

Chapter 4: Principle and modelling of a PSICAM

It has been shown in earlier chapters that absorption is not only difficult to measure because of the very low values that can occur in the blue and green part of the spectrum but also because of the interfering effect that scattering by suspended particles has on a beam of light. Of the various instruments that have been designed to overcome these problems, a promising one appeared to be an absorption meter based on an integrating cavity. In an integrating cavity absorption meter (ICAM), a diffuse light field is set up within the cavity that has a diffusely reflective wall and filled with the liquid whose absorption properties are to be measured. From the effect of the liquid on the light field, the absorption coefficient can be calculated.

An absorption meter based on an integrating cavity was already developed by *Fry et. al. (1992)* and was subsequently used to measure the absorption coefficient of pure water (*Pope and Fry, 1997*) and field tested in the gulf of Mexico (*Pope et. al., 2000*). As describe previously, this instrument was based on two concentric cylindrical integrating cavities so that the measured sample placed in the inner cavity was illuminated by an isotropic light. *Kirk (1995)* came out with a different idea for an absorption meter based on an integrating cavity: using two concentric spherical cavities. He then came out with the idea of using a point source (*Kirk, 1997*) at the centre of the spherical cavity to illuminate it. With this design, the absorption meter would be made of a single spherical cavity which he argued would be cheaper and easier to build and also more effective. In this chapter, we will expose firstly the theory Kirk developed for this instrument with numerical calculation based on his equations and the results of simulation carried out with a Monte-Carlo models.

4.1. PSICAM principle

An Integrating Cavity Absorption Meter has two important advantages. First, because of the high reflectivity of the cavity, the photons follow a very long path length reflecting from one side of the cavity to the other, before being finally absorbed (either by a particle within the medium or by the cavity wall itself). Therefore, an ICAM can be used to measure very low absorption values. Second, the light field being totally diffuse within the cavity, the effect of scattering from the particles of the studied solution will not make it any more diffuse. Thus, a measurement of absorption should not be affected whatever the level of scattering within the sample. *Fry et al.*, (1992) developed such an instrument based on an idea put forward by *Elterman* (1970). It showed as expected insensitivity to scattering and the ability to measure very low absorption values. Their cavity was of cylindrical shape (*Chapter 3*). *Kirk* (1995) showed that using a spherical cavity for an ICAM, explicit equations can be derived for the probability of photon survival in transit across the cavity (P_S), the average number of collision with the wall per photon (C_f) and the average path length per photon (l_f) as a function of absorption coefficient (a) of the medium, cavity radius (r) and reflectivity of the cavity wall (ρ) (Equation 4-1)

$$P_S = \frac{1}{2a^2r^2} [1 - \exp(-2ar)(2ar+1)]$$

$$C_f = \frac{P_S}{1 - \rho P_S}$$

$$l_f = \frac{1}{a} \left(\frac{1 - P_S}{1 - \rho P_S} \right)$$

Equation 4-1: ICAM equations (Kirk, 1995)

The prototype instrument of *Fry et al.*, (1992), is made of two cylindrical cavities whereas the proposed version by Kirk is made of two spherical cavities. An isotropic light field

is achieved as follow (Figure 4-1). In the empty outer cavity (III) is generated a diffuse light field. The inner cavity (I) field with the sample is illuminated by light passing through its wall (II). Light is allowed to do so thanks to the slightly translucent as well as highly reflective cavity wall (II). The properties of the inner cavity wall (including high Lambertian behaviour) create a diffuse light field within cavity I.

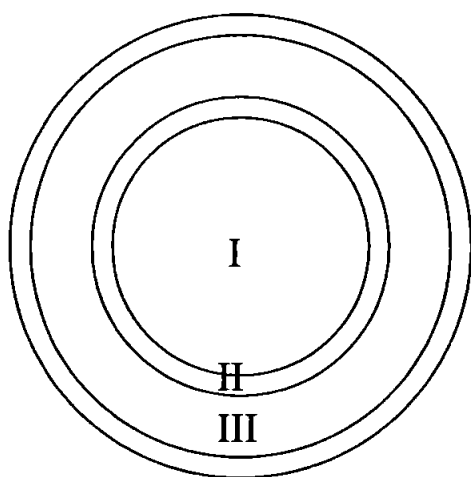


Figure 4-1: Scheme of Kirk's first version of an ICAM (1995): Two spherical cavities.

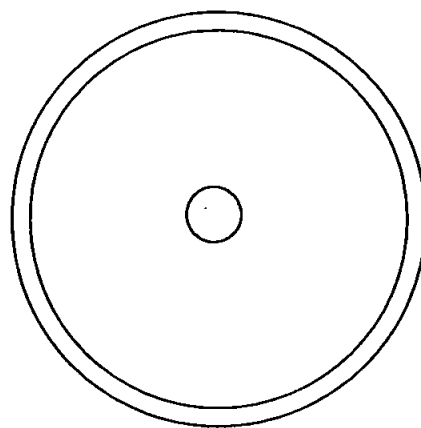


Figure 4-2: Scheme of Kirk's second version of an ICAM: illumination from a Point Source at the centre of the cavity.

In the case of a spherical cavity, *Kirk (1997)* suggested another solution to create a diffuse light field which would be easier and less expensive to build: illuminating a single spherical cavity with a central point source i.e. Point Source Integrating Cavity Absorption Meter (PSICAM, Figure 4-2, Equation 1-2). He argued that assuming that the measured solution is not too strongly absorbing, the photons emitted from the centre of the sphere would undergo one or more Lambertian reflection and consequently create a diffuse light field within the sphere. This assumption actually appears to be a function of the cavity radius to absorption ratio and will be described later.

As for the theory for an ICAM, Kirk derived for a PSICAM explicit equations for the probability of photon survival in transit across the cavity (P_s), the average number of collisions with the wall per photon (C_f) and the average path length per photon (l_f). These quantities are

functions of the same variables: absorption coefficient (a) of the medium, cavity radius (r) and reflectivity of the cavity wall (ρ) (Equation 4-2).

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

$$C_f = \frac{\exp(-ar)}{1 - \rho P_s} = \frac{P_0}{1 - \rho P_s}$$

$$I_f = \frac{1}{a} \left\{ 1 - \exp(-ar) \left[2 - \rho \left(\frac{1 - P_s}{1 - \rho P_s} \right) + \exp(-2ar)(ar + 1) \right] \right\}$$

Equation 4-2: PSICAM equations (1997)

The instrument proposed by Kirk would work like a normal spectrometer measuring the transmittance of a water sample relative to a standard (typically pure water). The irradiance on the cavity wall being proportional to the average number of collisions, he showed that the transmittance could be calculated as:

$$T(\lambda) = \frac{E}{E(0)} = \frac{\exp(-ar)(1 - \rho P_s^w)}{\exp(-a_w r)(1 - \rho P_s)}$$

Equation 4-3

where a_w is the absorption coefficient of pure water and P_s^w the probability of photon survival in transit across a cavity field with pure water. Equation 4-3 can not be solved for absorption but assuming that the radiance distribution is homogeneous and isotropic within the cavity Kirk proposed the solution:

$$a(\lambda) = \left[\frac{\frac{4}{3}a_w(\lambda)r + (1 - \rho(\lambda))}{\frac{4}{3}r} \right] \frac{1}{T(\lambda)} - \frac{3(1 - \rho(\lambda))}{4r}$$

Equation 4-4

We will see later that this equation is a good approximation but a simple least square method can be used to solve Equation 4-3 without any assumptions.

4.2. Investigation of a PSICAM performance

4.2.1. Effect of cavity radius and reflectivity

Kirk (1995) mentioned that the PSICAM would behave as an integrating cavity assuming that the solution under consideration was not too absorbing. Thus there must be an absorption to radius relationship which must fix the cavity radius depending on the water type that is under consideration. Figure 4-3 and Figure 4-4 show the relationship between the probability of photon survival P_o and P_s and the average number of collisions with the wall per photon C_f . The range of absorption and cavity radius selected for the calculations are 0.01 to 10m^{-1} and 0.01 to 0.5m . The calculation for C_f were made for $\rho=0.97, 0.98$ and 0.99 .

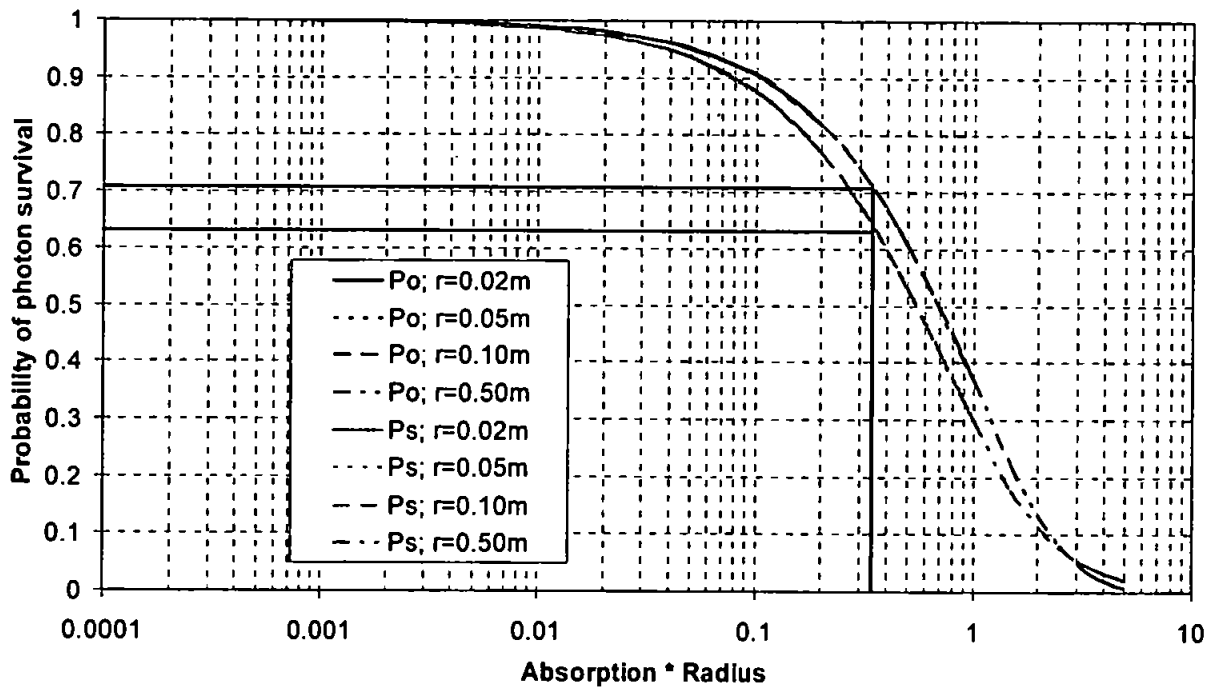


Figure 4-3: Relation between P_s , P_o and the product $a \cdot r$.

It occurs that whatever the cavity radius, the three parameters P_o , P_s and C_f will remain very similar for a given absorption-radius product. In case of both Probabilities of Photon Survival (Figure 4-3), the two parameters remain almost unchanged for a given absorption-radius product. In case of the Average Number of Collision (C_f , Figure 4-4), for a given value

of the wall reflectivity, the absorption-radius product remains almost unchanged. When the value of the reflectivity decreases, C_r logically decreases but major differences only appear for low absorption to radius product, *i.e.* low absorptions. However, this would not be of major influence for the isotropy of the light field within the sphere since a photon would have undergone multiple Lambertian reflections at this stage. Thus, if we fix the average number of

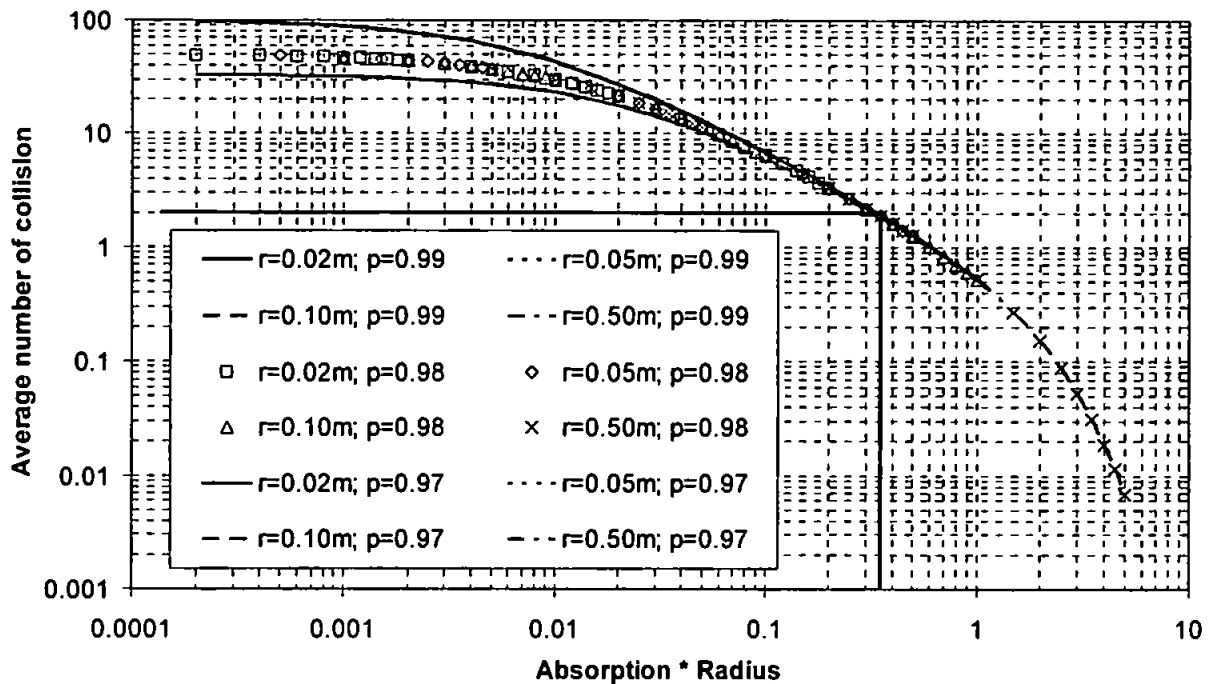


Figure 4-4 Relation between C_r and the product $a*r$

collisions assumed to create an isotropic light field within the sphere, we will be able to determine the adequate cavity radius for a given range of absorption. *Kirk (1997)* mentioned that provided that the medium is not too strongly absorbing, photon in the cavity will have undergone one or more Lambertian reflection from the wall, the light field should be diffused and the cavity should behave like an integrating cavity. One or more Lambertian reflections mean one or more collisions on the cavity wall. If we take two collisions as a limit, this gives us an upper limit for the absorption-radius product of about $a*r=0.35$ corresponding to 0.70, 0.65

and 2 for P_o , P_s and C_f respectively. This limit would be valid for the three values of reflectivity investigated.

Having this upper limit for the product $a \cdot r$, we can calculate the range of cavity radius suitable for a range of absorptions. In Figure 4-5, the solid line represent the upper limit for the cavity radius in relation to a given absorption value. The grey area represents the range of radii suitable for a range of absorptions. The upper and lower limit, respectively 0.50m and 0.02m are arbitrary. They more or less correspond to practical limits for a usable integrating cavity. It is acknowledged that a cavity of 50cm diameter would not be the user friendly compromise in terms of volume of the system, volume of water to handle and power of the light source to illuminate it! The black dashed line on Figure 4-5 represent the cavity radius of our prototype ($r=0.05m$). This gives a maximum measurable absorption of about $7m^{-1}$ for our application.

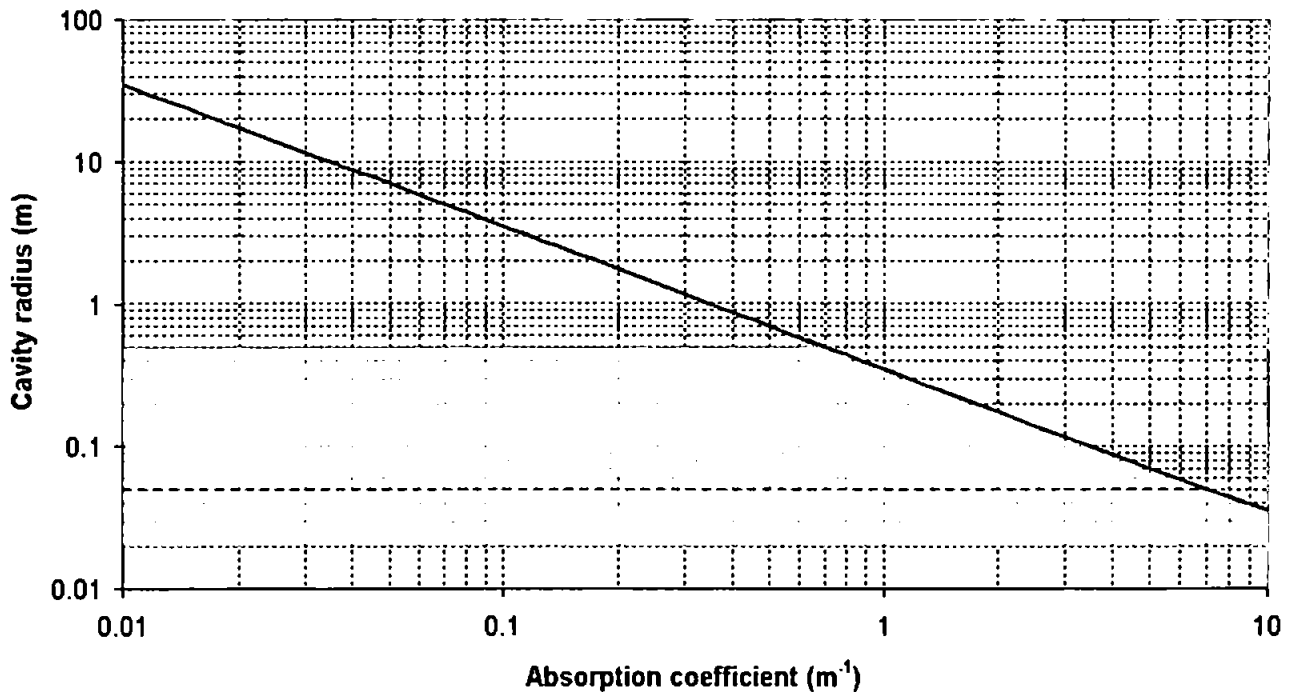


Figure 4-5: Cavity radius versus absorption optimum

From the theoretical equations, we manage to set an empirical maximum value for the cavity radius. We will now consider the minimum size of the integrating cavity. *Kirk (1997)*

stated that a transmittance of no more than 90% would be recommended to achieve an acceptable accuracy. Using Equation 4-3, the evolution of transmittance as a function of reflectivity can be investigated for a set of absorptions (Figure 4-6). The transmittance was calculated for three absorption and reflectivity values respectively $a=0.01$, 0.1 and 1 m^{-1} and $\rho=0.95$, 0.98 and 0.99 . The calculation were made assuming that the reference was an empty cavity of zero absorption and therefore a probability of photon survival $P_s = 1$.

Surprisingly, it appears from Figure 4-6 that for a given cavity radius and a given absorption, the transmittance actually decreases with increasing reflectivity. For the lowest absorption (0.01 m^{-1}), which would correspond to the blue and green part of the pure water absorption spectrum, the transmittance decreases very weakly as a function of the reflectivity. In such a medium, a photon would have an initial path length of several meters. Thus a fairly large cavity would be required to achieve a significant depletion of the transmittance. For the medium value of absorption selected (0.1 m^{-1}), which would correspond to yellow orange and the beginning of red wavelengths for pure water absorption, a cavity radius from 2 up to 10 cm

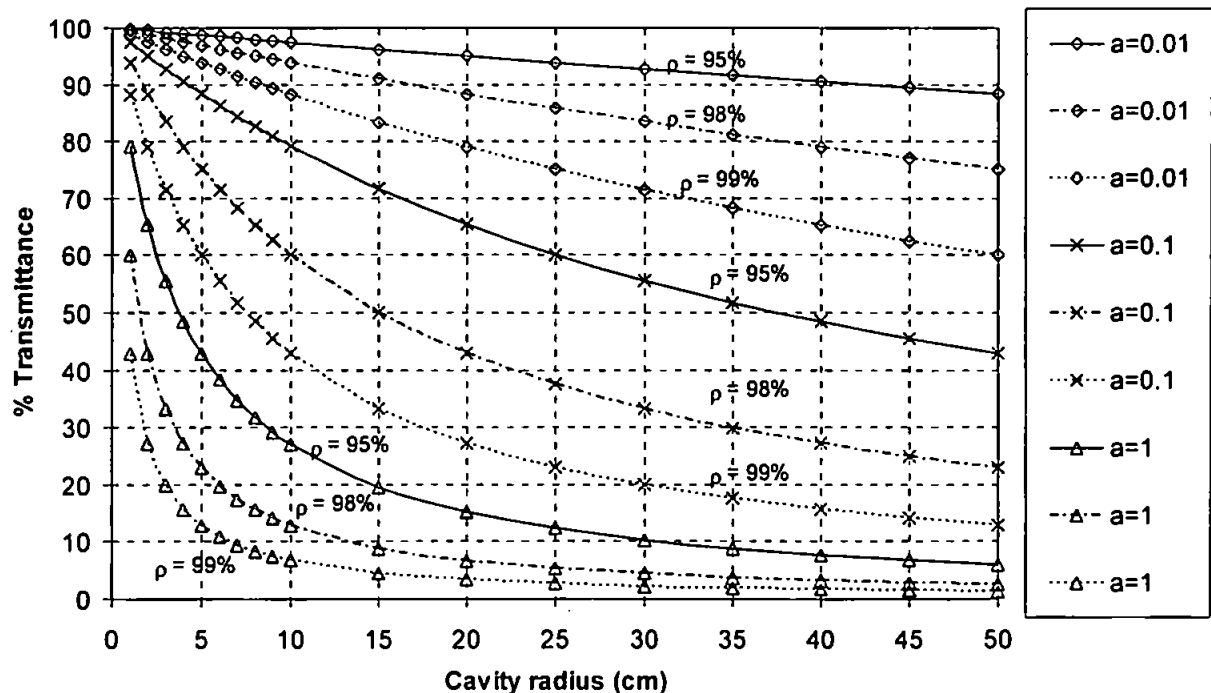


Figure 4-6: Effect of the cavity radius on the theoretical transmittance

would give an reasonable depletion of the transmittance. For the highest values ($a = 1 \text{ m}^{-1}$), which correspond to the absorption range of pure water in the red, the transmittance decreases dramatically with increasing cavity diameter. In such cases lower cavity wall reflectivity would be more suitable. Figure 4-7 displays the theoretical transmittance versus the product of absorption and radius. As before, it appears that for a given reflectivity the transmittance remains similar for a given product $a \cdot r$. Again, it shows that the transmittance actually increases when the reflectivity decreases. Assuming that a transmittance of no more than 90% should be expected for acceptable accuracy (Kirk, 1997), an empirical lower limit can be calculated for the cavity radius. The three vertical dashed lines on Figure 4-7 represent the three limits of the product $a \cdot r$ for the three reflectivities investigated; they are $a \cdot r = 0.0008$, $a \cdot r = 0.0015$ and $a \cdot r = 0.0025$ for $\rho = 0.99$, 0.98 and 0.97 respectively.

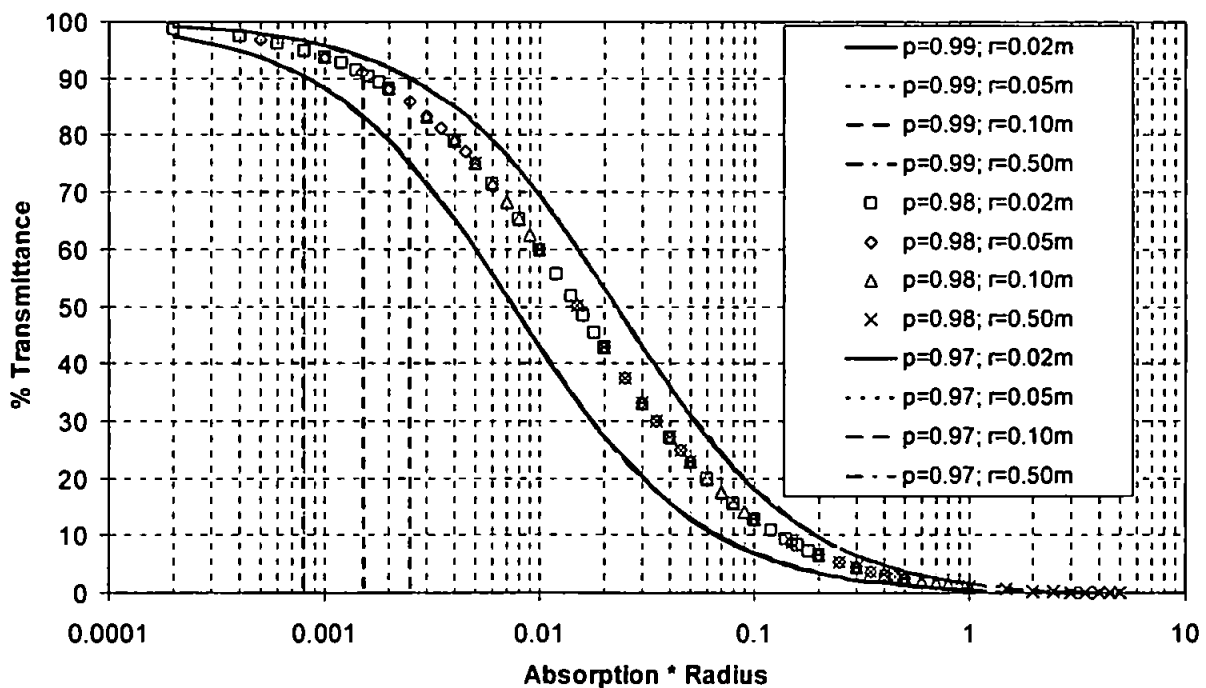


Figure 4-7: Transmittance versus product of absorption and radius.

From these data, we deduced the domain in which the PSICAM would be acceptable in terms of accuracy.

Figure 4-8 shows the optimum range for the cavity radius as a function of the absorption (grey area). The upper limit was shown on Figure 4-5. As before, the two horizontal dotted lines are arbitrary and refer to practical limitations of the cavity radius. In addition, we have now the three lower limits corresponding to the three reflectivity values investigated. It appears that the higher the reflectivity, the lower the absorption a cavity would potentially measure accurately. When investigating a specific wavelength as for LIDAR application for example, one could select the absorption range expected and chose an adequate cavity radius. Since we aim to use a single integrating sphere for the whole visible spectrum we'll have to compromise for the size of the sphere. The horizontal dash-dotted line represents the cavity radius of our three different prototypes. This will provide us with a potential accuracy from $0.02\text{-}0.05\text{m}^{-1}$ depending on the cavity reflectivity up to 7m^{-1} .

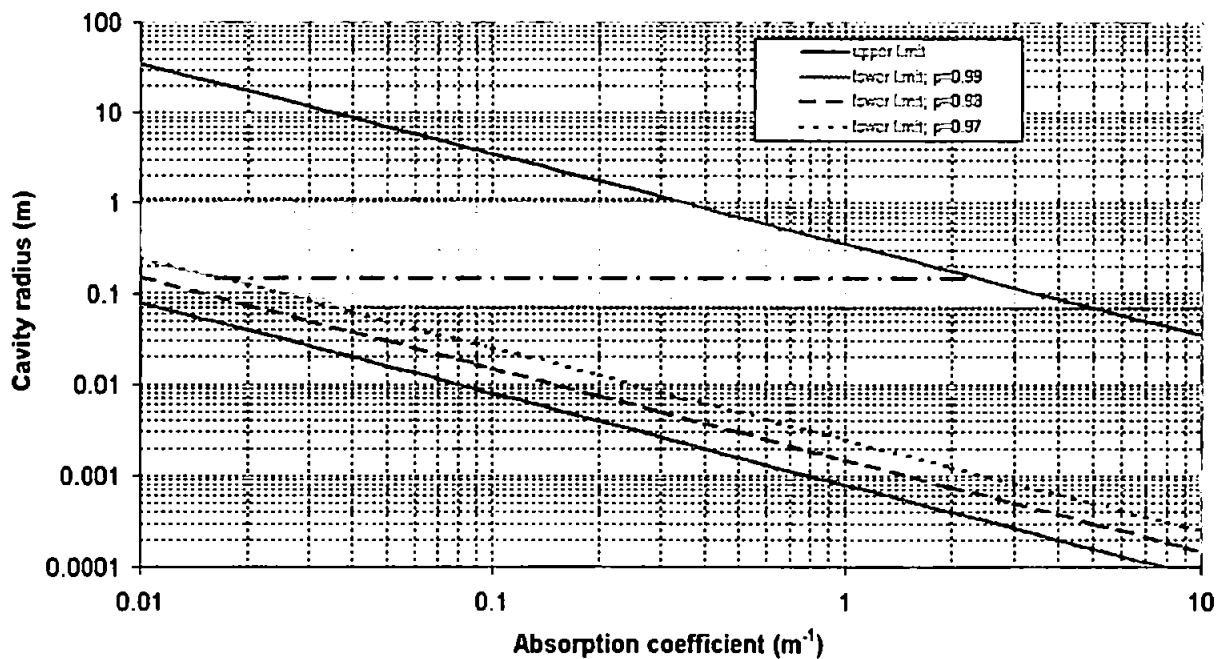


Figure 4-8: Optimum range for the cavity radius versus absorption

The wavelength dependence hasn't been mentioned in this section. It must be remembered that the calculations were performed using zero as reference absorption. In practise, the transmittance will be measured relative to pure water.

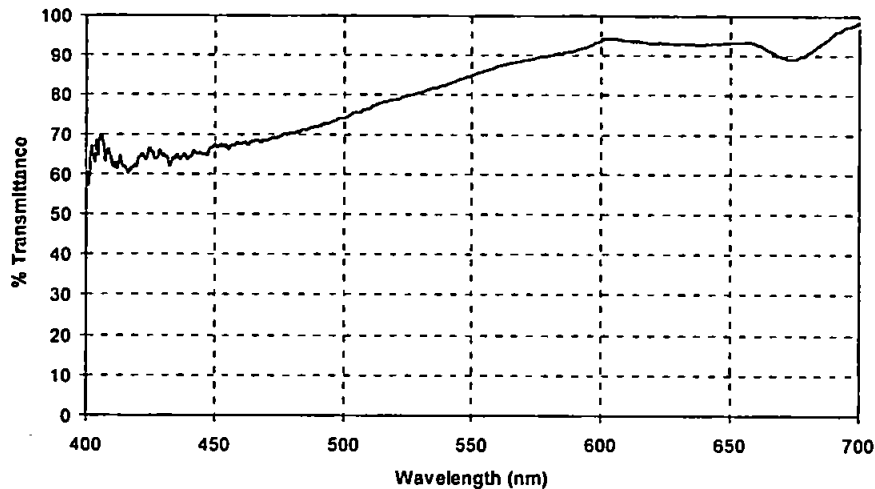


Figure 4-9: Example of a typical transmittance spectrum measured in the English Channel (1st July 2002)

Figure 4-9 is a typical transmittance spectrum measured with a water sample from the English Channel. The transmittance increases from the blue to the red part of the spectrum. This would mean, according to our calculations, that in the red part of the spectrum the calculation will not be as accurate. Indeed, pure water absorbs very weakly in the blue wavebands. The absorption then increases towards the red to peak in the infra-red around 950nm at about 50.0m^{-1} . The other absorbing components expected to be found in seawater absorb mainly in the blue and green part of the spectrum. As a result, the transmittance remains quite high at the end of the visible spectrum.

4.2.2. Calculation of the absorption coefficient

4.2.2.1. Reflectivity

Having a measure of the transmittance, of the three others variables (a_{ref} , r , ρ), a_{ref} and r are supposed to be known but the reflectivity $\rho(\lambda)$ remains to be measured or calculated. In his

paper, *Kirk, (1997)* proposed a simple experiment to measure the reflectivity. From Equation 4-3, the reflectivity can be extracted:

$$\rho(\lambda) = \frac{T_{AB} \exp(-a_B r) - \exp(-a_A r)}{T_{AB} \exp(-a_B r) P_S^A - \exp(-a_A r) P_S^B}$$

Equation 4-5

The solution to calculate $\rho(\lambda)$ proposed by *Kirk (1997)* is to use two standard dye solutions A and B of different concentration which absorb broadly in the visible waveband and measure the transmittance T_{AB} of one relative to the other. From this measurement, the reflectivity can be calculated as in Equation 4-5.

4.2.2.2. Kirk's formula for absorption

There is no linear solution for the absorption in Equation 4-3. Equation 4-4, proposed by *Kirk (1997)* for the calculation of $a(\lambda)$, is an approximation of the equation of transmittance (Equation 4-3). To assess how the calculated absorption will be affected by this approximation, let us calculate a set of transmittances given a set of absorptions, a cavity radius and a reflectivity. Figure 4-10 shows on a semi-log scale the transmittances calculated for a cavity radius of 5cm, a reflectivity of 0.99 and a set of absorption coefficient from 0.01 to 30 m^{-1} . As previously, the reference for the calculation is an empty cavity of zero absorption.

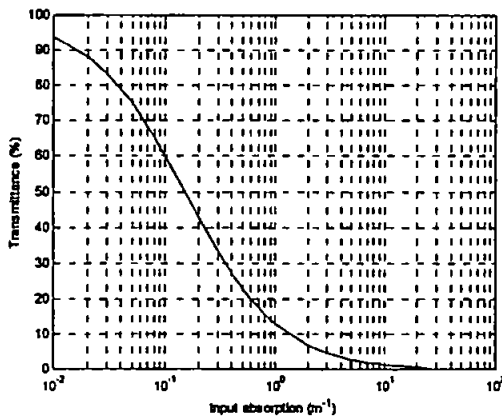


Figure 4-10: Theoretical transmittance calculated with Equation 4-3

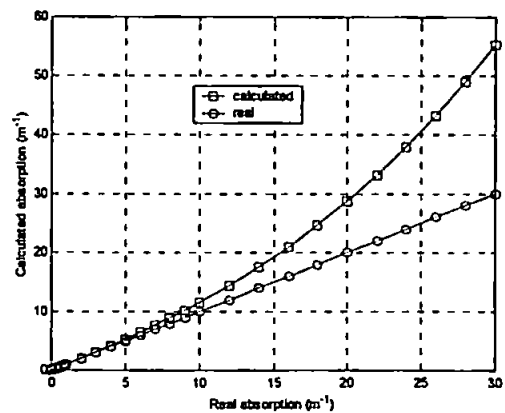


Figure 4-11: Calculated values compared to real values

Figure 4-11 shows the result of the absorption calculated with Equation 4-4 compared with the real values. With increasing absorption, the data calculated deviate from the reality. Figure 4-12 shows the percentage error for four ranges for the set of absorptions. Each of the four graphs displays the percentage error versus real absorption. These graphs show that the error increases with the absorption giving less than 0.25% error for $0.01 \leq a \leq 0.09\text{m}^{-1}$, less than 1% for $0.1 \leq a \leq 0.9\text{m}^{-1}$, less than 5% for $1 \leq a \leq 3\text{m}^{-1}$ and more than 5% for $a \geq 4\text{m}^{-1}$. For the smallest values of absorption ($a \leq 0.2\text{m}^{-1}$) the calculated values are actually slightly underestimated.

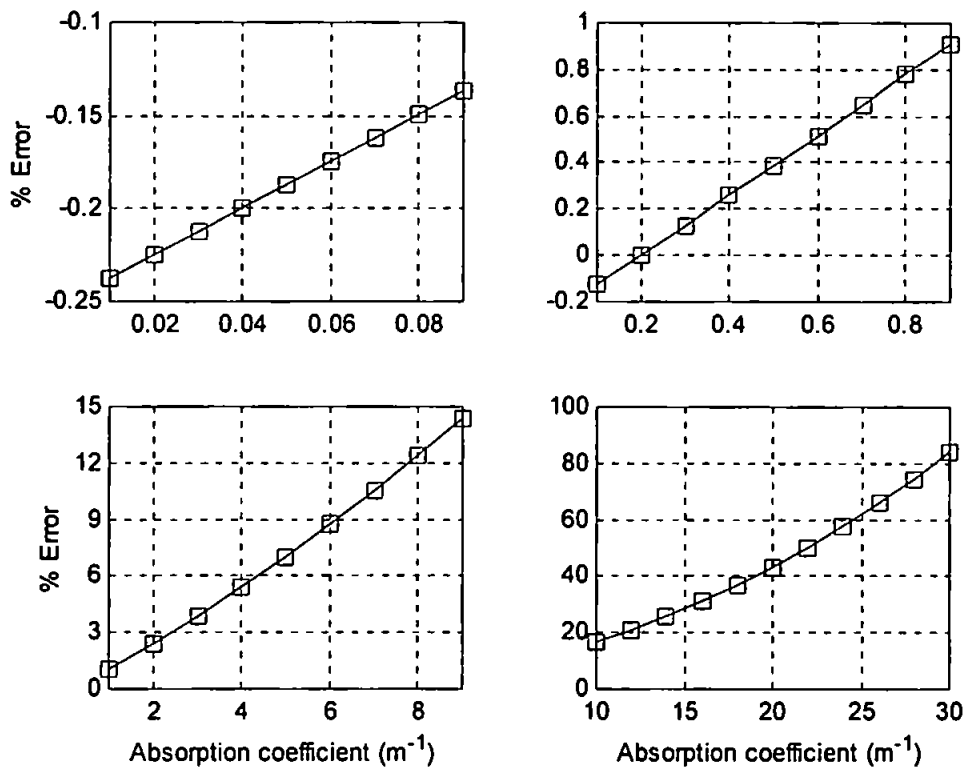


Figure 4-12: Percentage error in the calculated absorption for a cavity radius of 5 cm

Figure 4-13 shows the results of the same calculations for a cavity radius of 2 cm. The error gets smaller for low absorptions: less than 1% in absolute value for absorptions up to 2m^{-1} , and less than 5% for absorptions up to 9m^{-1} . The results are improved very significantly for the higher absorption values.

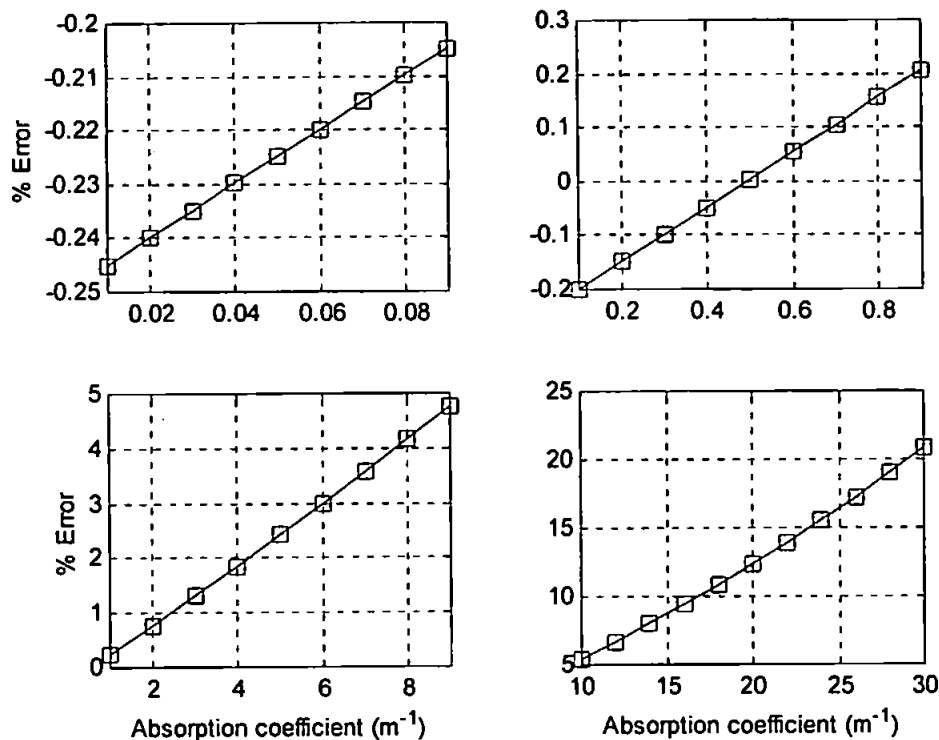


Figure 4-13: Percentage error in the calculated absorption for a cavity radius of 2 cm

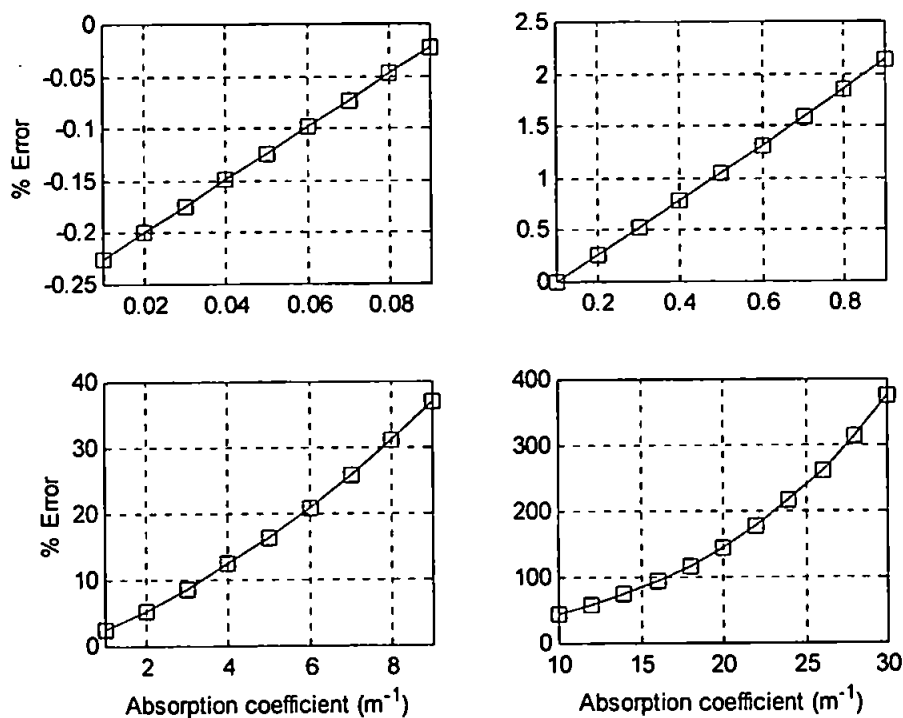


Figure 4-14: Percentage error in the calculated absorption for a cavity radius of 10 cm

Figure 4-14 shows the results of the same calculations for a cavity radius of 10 cm. As would be expected, the error for higher absorption is getting even bigger than for a cavity radius

of 2 and 5cm and remain acceptably small for absorption lowers than 1m^{-1} . Let us remember that Equation 4-4 used for the calculation assumes an isotropic light field within the cavity. In cases of low absorption values, the photons will undergo multiple reflections on the cavity wall before being finally absorbed by the medium or the cavity wall, thus creating a homogeneous light field within the cavity. With increasing absorption, the photons will undergo less and less reflections before being absorbed, thus making the light field less likely to be isotropic. For a given absorption, increasing the cavity radius means minimising the number of reflection a photon will undergo before being absorbed, having at the end the same effect as increasing the absorption.

4.2.2.3. *Least square method*

An alternative manner to calculate the absorption would be to solve numerically the equation of transmittance Equation 4-3 for $a(\lambda)$ using a least square technique. The advantage of this technique is that it does not suppose any assumption about radiance distribution. With this technique, a set of theoretical transmittances is calculated using Equation 4-3 for a given range of absorption coefficients. This gives $T_{th}(\lambda)$. The reflectivity, the absorption coefficient of the reference solution and the radius of the cavity are known parameters. The absorption spectrum of the sample is then the minimum of the function $G(a(\lambda))$ (Equation 4-6), where T_{exp} is the measured transmittance.

$$G(a(\lambda)) = \sqrt{(T_{th}(\lambda) - T_{exp}(\lambda))^2}$$

Equation 4-6

In order to assess this method, the same calculation as for Kirk's formula was carried out. Having the same inputs as previously: cavity radius of 5cm and a cavity reflectivity of

99%, a set of transmittances was calculated for a given set of absorptions. The absorptions were then solved with a least square technique.

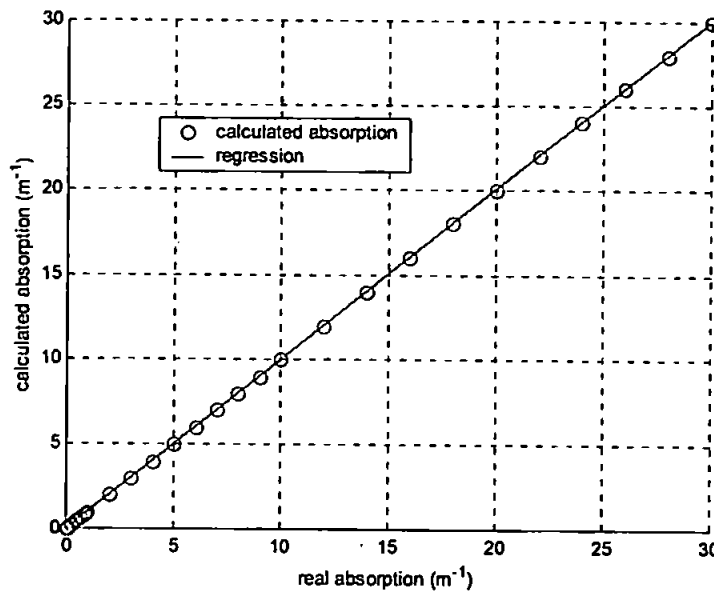


Figure 4-15: Calculated values compared to real values

Figure 4-15 presents the results of these calculations and shows that, provided that the range of absorption chosen for the calculation is adequate, a perfect match between the input absorption and the calculated one ($\text{slope} = 1$ $r^2 = 1$). The error range was found to be smaller than $3 \cdot 10^{-14}$. The only limitation of this method would be the computation time. In our case, the absorption values used for the calculation follow a logarithmic progression from 0.01 to 30 m^{-1} . If accurate calculations are expected, we need to set a small sampling step for the absorption vector making the calculation longer.

4.2.2.4. Conclusion

From these two techniques, the least square method appear to give better results. However, for the range of absorption that we will be interested in for sea water (typically below 5 m^{-1}), Kirk's formula will also be applicable. These two techniques also do not take into account the experimental errors that would be encountered in a real experiment. Therefore,

using the least square technique might be preferable in order to minimise the sources of error. The next section will consider the experimental errors that can be encountered with a PSICAM.

4.2.3. Sensitivity analysis

Leathers et al. (2000) carried out a sensitivity analysis for a PSICAM. They proposed the following equation for the variability of a as a function of the four variables: transmittance (T), reflectivity (ρ), cavity radius (r) and reference absorption spectrum (a_{ref}).

$$\Delta a = \left[\left(\frac{\partial a}{\partial T} \right)^2 (\Delta T)^2 + \left(\frac{\partial a}{\partial \rho} \right)^2 (\Delta \rho)^2 + \left(\frac{\partial a}{\partial r} \right)^2 (\Delta r)^2 + \left(\frac{\partial a}{\partial a_{ref}} \right)^2 (\Delta a_{ref})^2 \right]$$

Equation 4-7

With:

Table 4-1: Constants of the sensitivity equation

Coefficient	Value
$\partial a / \partial T$	-0.72 m^{-1}
$\partial a / \partial \rho$	-16 m^{-1}
$\partial a / \partial r$	-3.2 m^{-2}
$\partial a / \partial a_{ref}$	2.1

They stated that the equation would be valid for visible wavebands in coastal waters for a PSICAM made of Spectralon. The coefficient presented in Table 4-1 correspond to an absorption coefficient of 0.2 m^{-1} , a reference absorption of 0.02 m^{-1} , a cavity radius of 0.05 m and a reflectivity of 0.99 . Using this formula to investigate the influence of the variability of each separate parameter, we arrive at Figure 4-16. The four graphs of this figure are on the same 10 to 5 scale except for the reflectivity graph, which is on a 10 to 1 scale. This analysis reveals, as forecasted by *Kirk (1997)*, the extremely high sensitivity of the instrument to the reflectivity of the cavity wall. An error of 0.2% in the value of the reflectivity leads to more than 10% error in the calculation of the absorption coefficient. Therefore the calculation of the reflectivity

exposed in section 4.2.2.1 via an experimental procedure appears to be critically important for the reliability of the instrument. Moreover, regular reflectivity measurement as well as regular maintenance will be needed to prevent degradation of the sphere reflectivity.

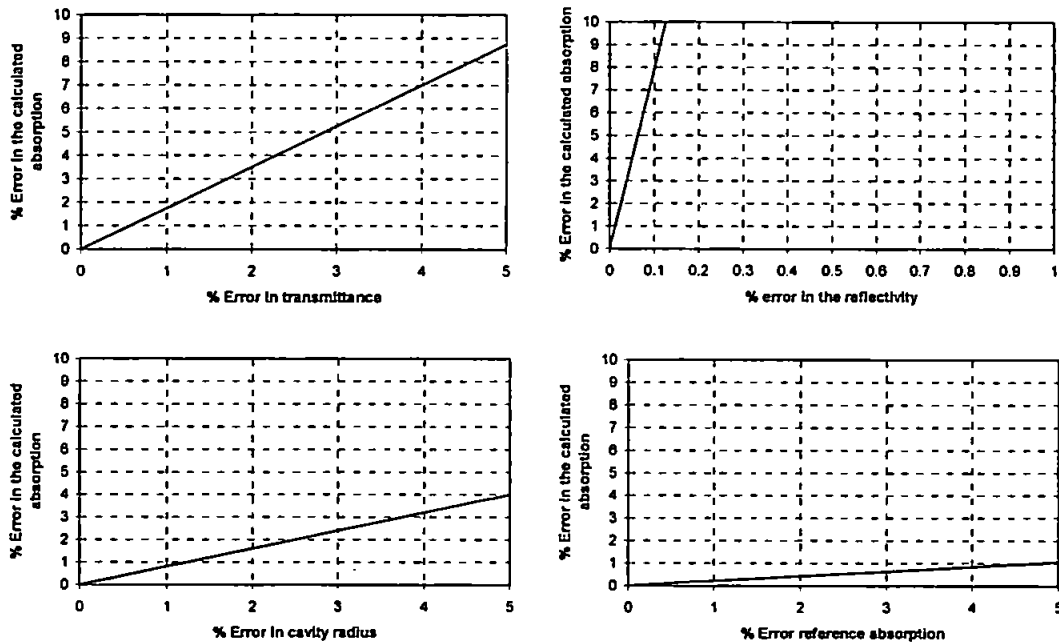


Figure 4-16: Sensitivity analysis for a sphere of 5cm diameter, a reflectivity of 99%, a reference absorption of 0.02m^{-1} and an sample absorption of 0.2m^{-1}

The second important parameter in terms of sensitivity is the measured transmittance for which a 1% error would give about 2% error in the value of the calculated absorption. The most likely source of error for this parameter would be instrumental (stability of the light source and spectrophotometer). Then comes the cavity radius and the value of the reference absorption. We have got almost a one to one relationship for the first one. It should remain constant and therefore easily accounted for. The last source of error would depend upon the quality of the pure water supply. This is, as pointed out previously, the inherent problem of all techniques using pure water as a reference.

The analysis made by *Leather et al.*, (2000) targeted a specific value for the absorption of both the studied solution and the reference solution. A more general sensitivity analysis was

carried out for a range of absorptions between 0.01 and 10 m^{-1} using an empty cavity as a reference for the transmittance, reflectivity and cavity radius calculations and a reference absorption of 0.01 m^{-1} for the calculation of sensitivity with the reference absorption. Three cavity radii were taken into account (0.02 , 0.05 and 0.10 m) and the reflectivity was set to 0.99 . All calculations were carried out using the least square method. Thus, the errors calculated are not the consequence of deviation from the homogeneous energy distribution assumption due to increased absorption. They strictly represent the sensitivity of the system towards its four variables. The principle of the calculations was to derive theoretical transmittances using Equation 4-3 for various absorptions. Then to introduce increasing errors on the four variables one at a time and calculate the absorption using the least square method to assess how the hypothetical measurement would be affected.

This numerical analysis (Figure 4-17 to Figure 4-19) provides the same kind of patterns as Figure 4-16 but gives an idea of how the sensitivity would vary for a range of absorptions.

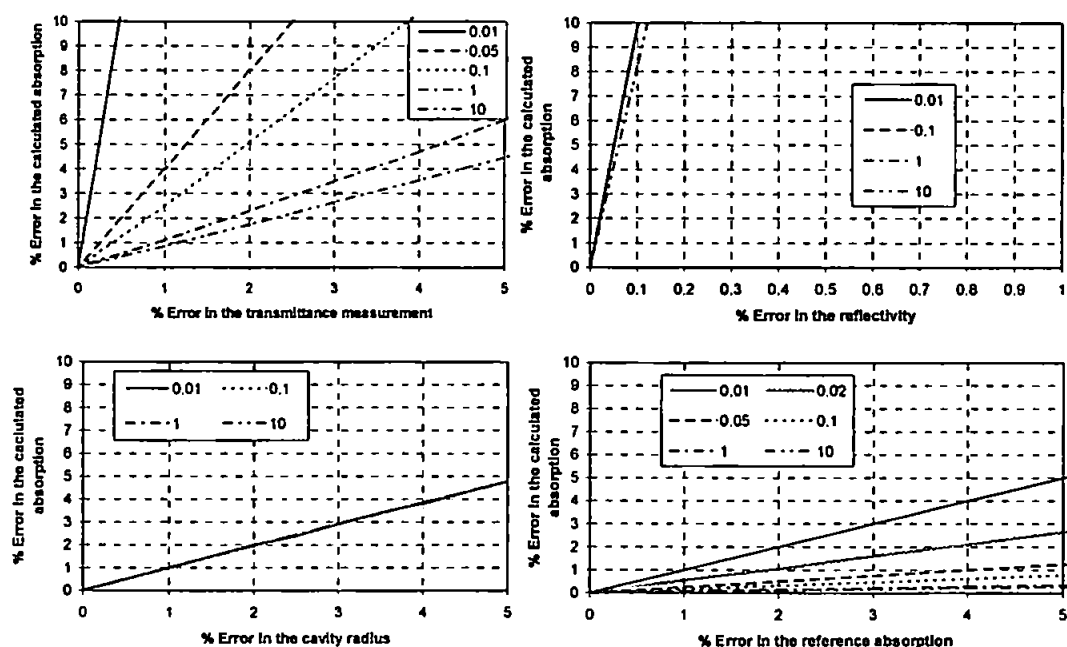


Figure 4-17: Sensitivity analysis for a sphere of 5cm radius

The same patterns are indeed observed but in addition it shows that in the case of the transmittance and the reference absorption, the smaller the absorption, the higher the sensitivity. This agrees with the need for an accurate measurement to achieve a significant depletion of the transmittance. In the case of a transmittance error of 1%, the induced errors in the calculated absorption are 20%, 4%, 2.5%, 1% and 0.8% for absorptions of 0.01, 0.05, 0.1, 1 and 10m^{-1} respectively. In the case of a reference absorption error of 5%, the induced error in the calculated absorptions are 5%, 2.5%, 1.1%, 0.8%, 0.2% and 0.15% for absorptions of 0.01, 0.02, 0.05, 0.1, 1 and 10m^{-1} respectively. On the other hand, the cavity radius does not show any significant dependence toward the absorption value. The four curves for $0.01 \leq a \leq 10\text{m}^{-1}$ being identical. Finally, the reflectivity also shows very little dependence upon the absorption values.

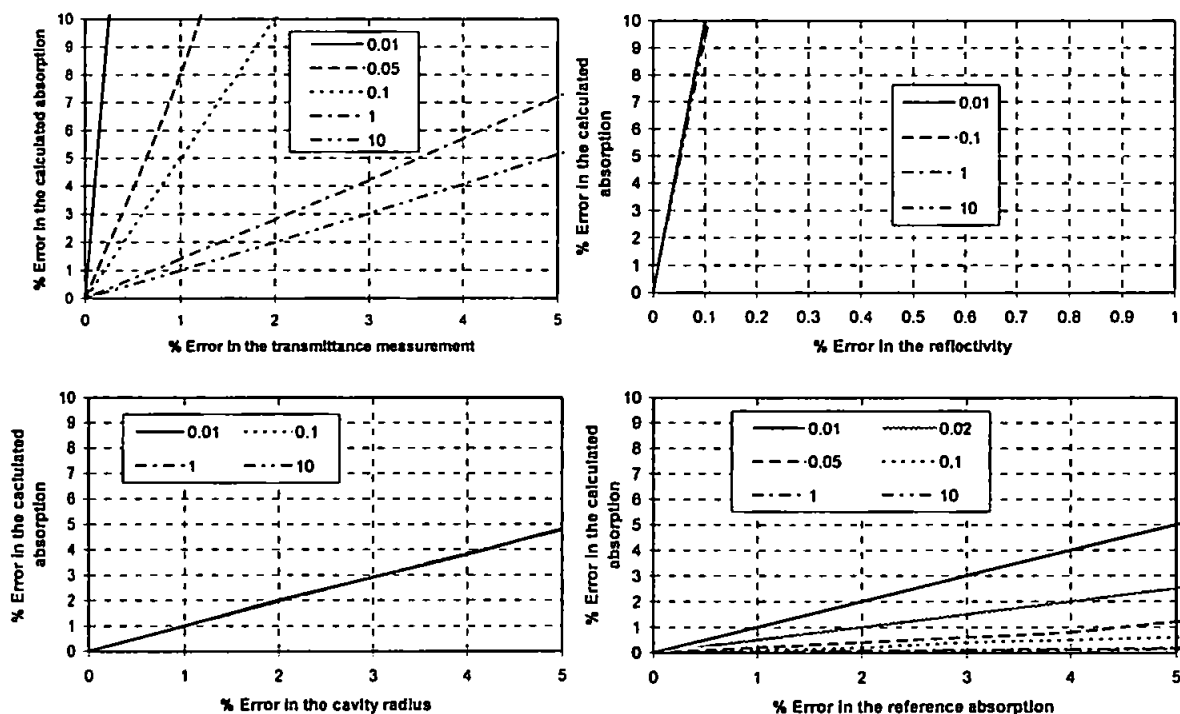


Figure 4-18: Sensitivity analysis for a sphere of 2cm radius

By decreasing the cavity radius to 2cm (Figure 4-18), the sensitivity to the reflectivity remains almost unchanged. As is the sensitivity to the reference absorption and cavity radius. The sensitivity to the transmittance increases but the difference appears more significant for the

lower absorptions. The difference was +0.13%, +0.30%, +2.50%, +4% and +20 % for $a = 10, 1, 0.1, 0.05$ and 0.01 m^{-1} respectively and an initial error of 1% on the transmittance measurement.

Table 4-2: Percentage error in the calculated absorption for an initial error of 1% in the measured transmittance. $\Delta/r_{0.05}$ represents the error variation relative to $r=0.05\text{m}$

Radius (m)	0.02		0.05		0.10	
Absorption (m^{-1})	% Error	$\Delta/r_{0.05}$	% Error		% Error	$\Delta/r_{0.05}$
0.01	40	+20	20		10	-10
0.05	8	+4.0	4.0		2.60	-1.40
0.1	5	+2.50	2.50		1.8	-0.70
1	1.40	+0.30	1.10		1.09	-0.01
10	0.99	+0.13	0.86		0.70	-0.16

On the other hand, by increasing the cavity radius to 10 cm in our example, the sensitivity to the reference absorption and cavity radius still does not show any significant variation. The sensitivity to the reflectivity only shows a variation for high absorptions. The sensitivity to the transmittance is logically minimised. The variation in the sensitivity is also dependent on the absorption (Table 4-2).

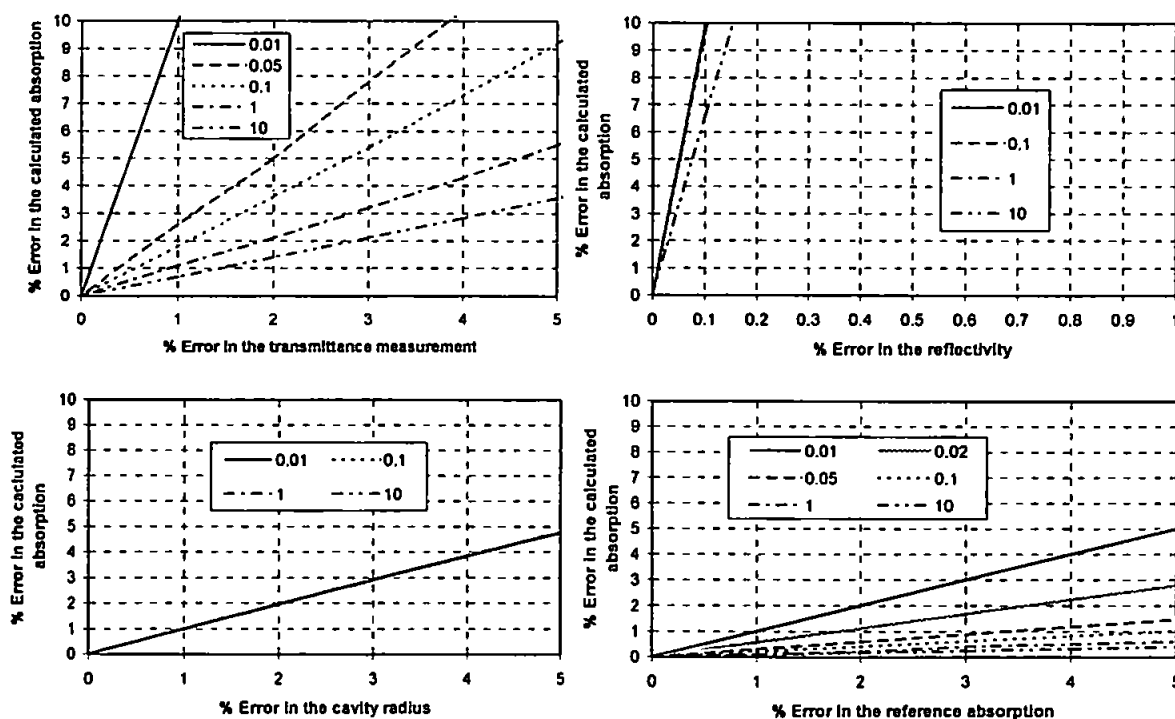


Figure 4-19: Sensitivity analysis for a sphere of 10cm radius

The sensitivity to transmittance varies with the size of the sphere. The sensitivity to cavity radius and the reference absorptions remains quite similar whatever the cavity radius, the last showing a dependence with the absorption of the solution. Of these three parameters, the transmittance and the cavity radius will be fairly well controlled. The error inherent in the transmittance measurement will depend upon the stability of system, principally the light source and the spectrometer. The cavity radius will remain unchanged, assuming the thermal expansion will not be significant, and can be measured accurately enough. The quality of the pure water supply for the reference measurement will always be an uncertainty difficult to estimate. It could be crucial in the blue and green parts of the spectrum where the standard absorbs very weakly. Unfortunately, the reflectivity, the main source of error in the system, changing the cavity radius does not produce any significant improvement in terms of sensitivity. As stated before, it is the key parameter for the efficiency of the system and its spectrum will have to be calibrated regularly.

Although changing the cavity radius does not significantly reduce the sensitivity of the system toward the reflectivity, a cavity with a lower reflectivity proved to be less sensitive. Figure 4-20 shows the error in the calculated absorption versus the error in the value of the reflectivity for the three previously investigated cavity diameters (0.02, 0.05 and 0.10m) and for two values of wall reflectivity ($\rho=0.98$ and 0.97). For a given reflectivity, changing the cavity radius still does not make a significant difference except for the higher absorption values. For $\rho=0.98$, we have about 10% error on the calculated absorption for 0.2% error with the reflectivity. For $\rho=0.97$, a 10% error in the calculated absorption corresponds to 0.3% in the reflectivity value except again for the highest absorption values.

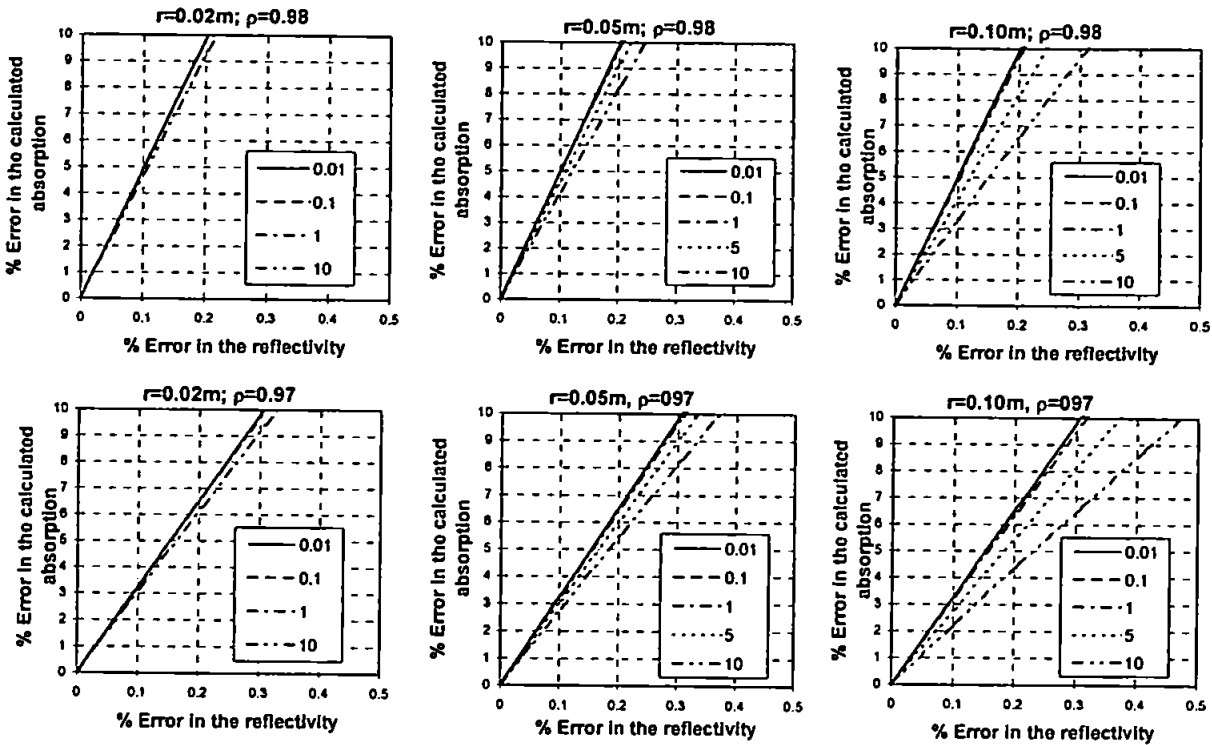


Figure 4-20: Percentage error on the calculated absorption for different radius on and lower reflectivity.

To summarise, Table 4-3 gives the percentage error in the reflectivity responsible for a 10% error in the calculated absorption, for an initial absorption of 0.01 and 10m⁻¹. The sensitivity definitely decreases for lower reflectivity values but remain unfortunately critically important.

Table 4-3: Percentage error in the reflectivity creating a 10% error in the calculated absorption. The left value in each column is the value for a=0.01m⁻¹, the right one a=10m⁻¹.

Reflectivity (%)	99		98		97	
Radius (m)						
0.02	0.10	0.11	0.20	0.21	0.30	0.32
0.05	0.10	0.12	0.20	0.25	0.30	0.38
0.10	0.10	0.15	0.20	0.32	0.30	0.48

Lastly, Figure 4-21 gives an idea of what would be the sensitivity of the system assuming an even lower reflectivity $\rho=0.95$ and a cavity radius of 5cm. As in the previous cases the sensitivity to the cavity radius and the reference absorption remains equal. The sensitivity to reflectivity as expected gets a bit lower. 10% error in the calculated absorption is generated by

about 0.5% error in the reflectivity value. The effect on the transmittance would be an increased sensitivity especially for the smallest absorptions.

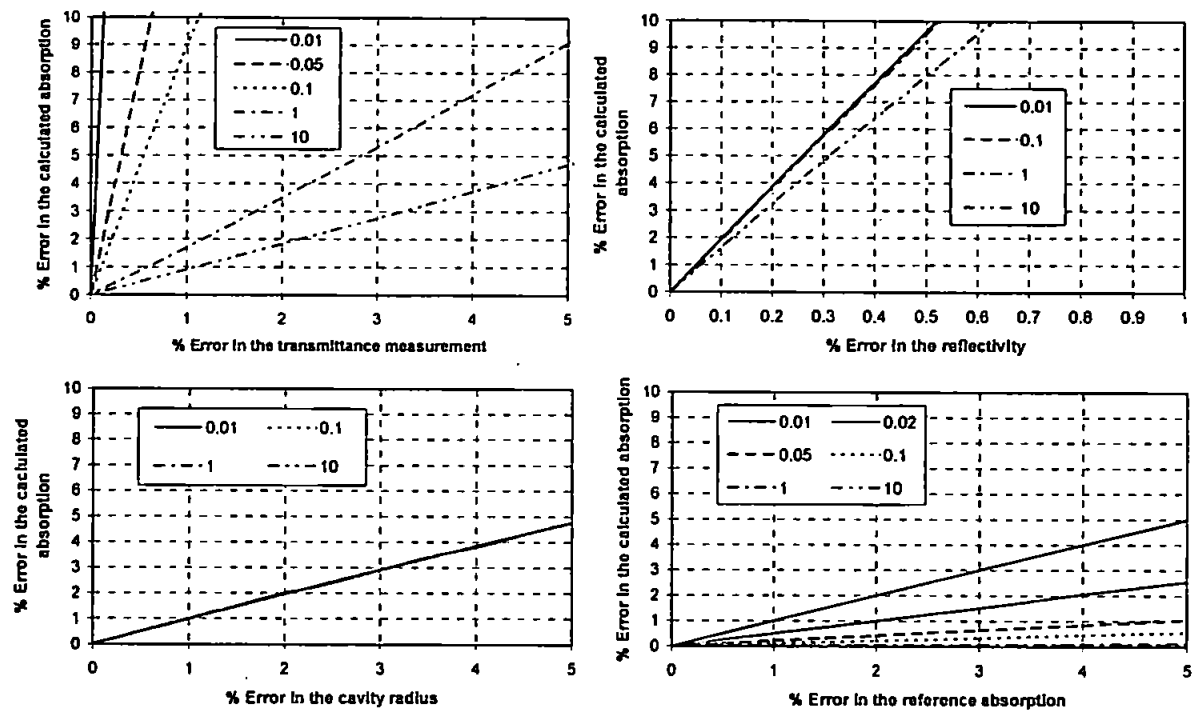


Figure 4-21: Sensitivity of the system for a cavity radius of 5cm and a reflectivity $\rho=0.95$

To conclude, the only way to minimise the sensitivity of the system to reflectivity appears to be by using a less reflective material. Assuming that the system would be stable enough, the resulting increased sensitivity to the transmittance could be overcome. But even so, taking the example with $\rho=0.95$, 0.1% error in the value used for the reflectivity in the calculation would generate about two percent error in the calculate absorption.

4.3. Monte Carlo modelling

4.3.1. Introduction:

The behaviour of light within the water is determined by the inherent optical properties of the aquatic medium. In principle, therefore, it should be possible knowing the absorption, scattering and volume scattering function, to calculate the optical properties of a water body. In

reality, the complex behaviour of a photon population in the water caused by the combined effects of absorption and scattering, themselves dictated by a very complex mixture of components, prevent us from establishing an explicit analytical relationship between the inherent and apparent optical properties of the light field. However, there are computer models which can achieve this by making physically realistic assumptions about the ways in which the behaviour of light at any point in a water body is determined by the scattering and absorption properties of the medium. One of the most common is the Monte Carlo method.

The Monte Carlo modelling technique has been used in a great variety of fields, from gambling applications to nuclear physics and marine optics (*Kirk, 1981a, 1981b, 1992*). Its application to the behaviour of solar photons in the ocean was initiated by *Plass and Kattawar (1972)*, *Gordon and Brown (1973)*, *Gordon et.al. (1975)* and *Gordon (1989a, 1989b, 1991)*. The principles are described in detail in *Kirk (1981a,c)*.

For our purposes, Monte Carlo modelling will determine the behaviour of light within an integrating sphere illuminated from its centre, being given the absorption and scattering coefficient of a hypothetical medium filling the sphere.

4.3.2. Mode of operation of the Monte Carlo code

The behaviour of individual photons within an absorbing and scattering medium is stochastic in nature. The lifetime and the geometrical path followed by any given photon are governed by its random encounters with absorbing molecules and scattering particles (*Kirk, 1994*). The inherent optical properties of a medium (absorption, scattering and volume scattering function) are a measure of the proportion of an incident flux absorbed and scattered per unit distance. They are also related to the probability that any given photon will, within a certain path, be absorbed or scattered at a certain angle.

The Monte Carlo method requires simple but numerous calculations and is therefore only made feasible thanks to computer calculation. It uses the stochastic nature of photon behaviour and follows the fate of a large number of photons, one at a time, passing into an imaginary body of water with specified inherent optical properties. Random numbers are used in conjunction with appropriate cumulative frequency distributions (based on the optical properties of the particular water assumed to be present) to choose path lengths between each interaction with the medium, to decide whether the interaction is one of scattering or absorption, to select the scattering angles and so on.

Our Monte Carlo model (Figure 4-22), follows the fate of a large number of simulated photons, travelling one at a time from the light source situated at the centre of the sphere through the integrating cavity until it is finally absorbed by the water phase or the wall of the integrating cavity. Two different scattering phase functions are used. The first and most simple considers isotropic scattering: when a photon hit a particle, it is equally likely to be scattered in any direction in space. The second and supposedly closer to the reality is the seawater scattering phase function measured by *Petzold (1972)* in the turbid waters of San Diego Harbour (Figure 4-24). This phase function assumes that the majority of the photons will be scattered in the near forward direction of the initial path. From the behaviour of all simulated photons, are calculated the probability P_0 of photon survival from the centre of the sphere to the cavity wall and P_s , the probability of photon survival in transit from wall to wall. From those two measurements are then calculated the average path length and the average number of collision on the cavity wall per photon as describe in Equation 4-2. The step-by-step operation of the model is set out in more details on Figure 4-22. For each run, the diameter of the cavity, the maximum number of simulated photons and the wall reflectivity are specified. The position of any photon at any time in its journey is specified in terms of its Cartesian co-ordinates (x, y, z) or spherical co-ordinates

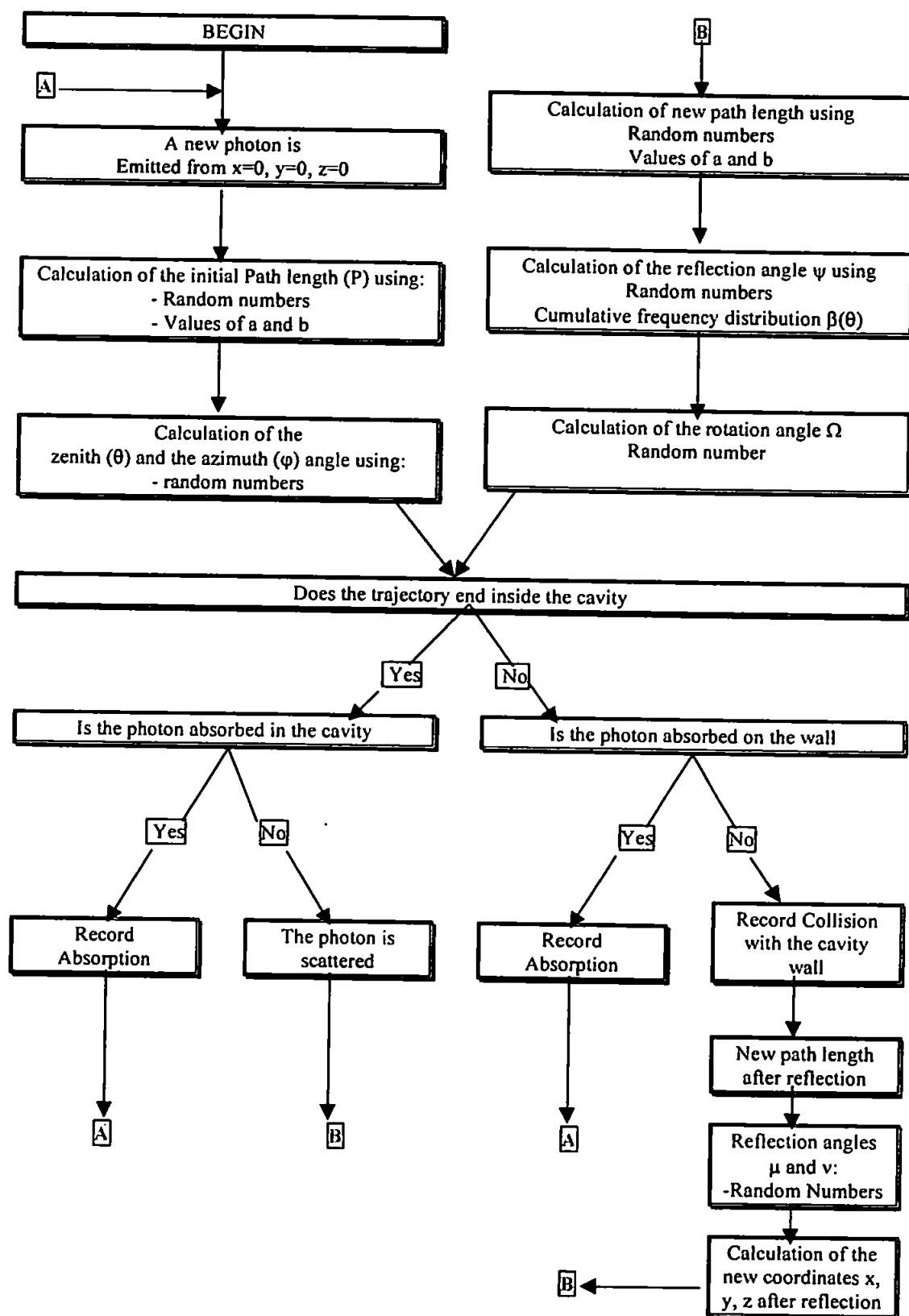


Figure 4-22: Monte-Carlo flow Diagram

(P, θ, φ) (Figure 4-23) whether one or the other is better for the calculations. For the Cartesian co-ordinates, the x-y plan is the equatorial plan of the sphere and the z-axis is perpendicular to this plan. The origin of the three-dimensional axis is the centre of the sphere, the $(O, \vec{i}, \vec{j}, \vec{k})$ base being direct ortho-normal. For the spherical co-ordinates the origin corresponds to $O(0,0,0)$ in Cartesian co-ordinates, $\varphi=0$ corresponds to the unit vector $\vec{i}$ and $\theta=0$ corresponds to unit vector $\vec{k}$. One passes from one co-ordinate system to the other according to Equation 4-9 and Equation 4-10.

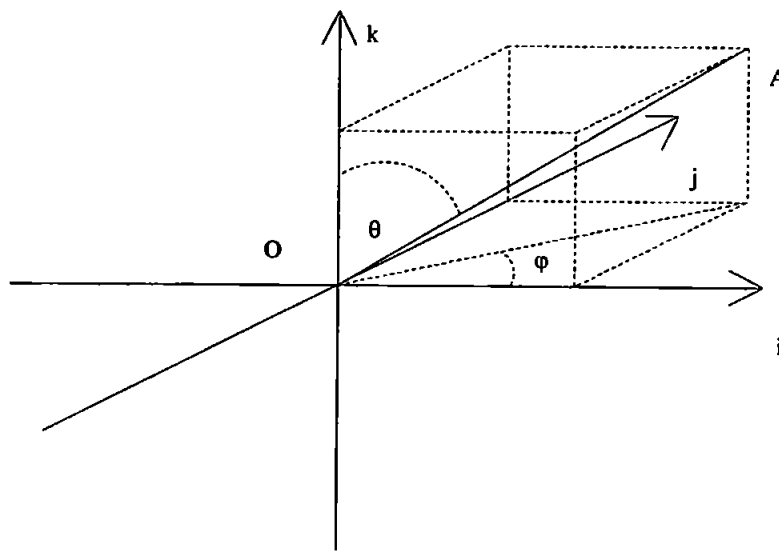


Figure 4-23: From Cartesian to spherical co-ordinates

The light source is assumed to be a diffuse point source situated at the centre of the sphere. Each emitted photon therefore start from the centre of the sphere with co-ordinates $x=0$, $y=0$ and $z=0$. For each emitted photon, three random numbers ($0 \leq r < 1$) are generated. One to determine the initial path length (P) before the first interaction with the medium, one to determine the azimuth angle (φ) and the last one to determine the zenith angle (θ) of the emitted photon (Equation 4-8).

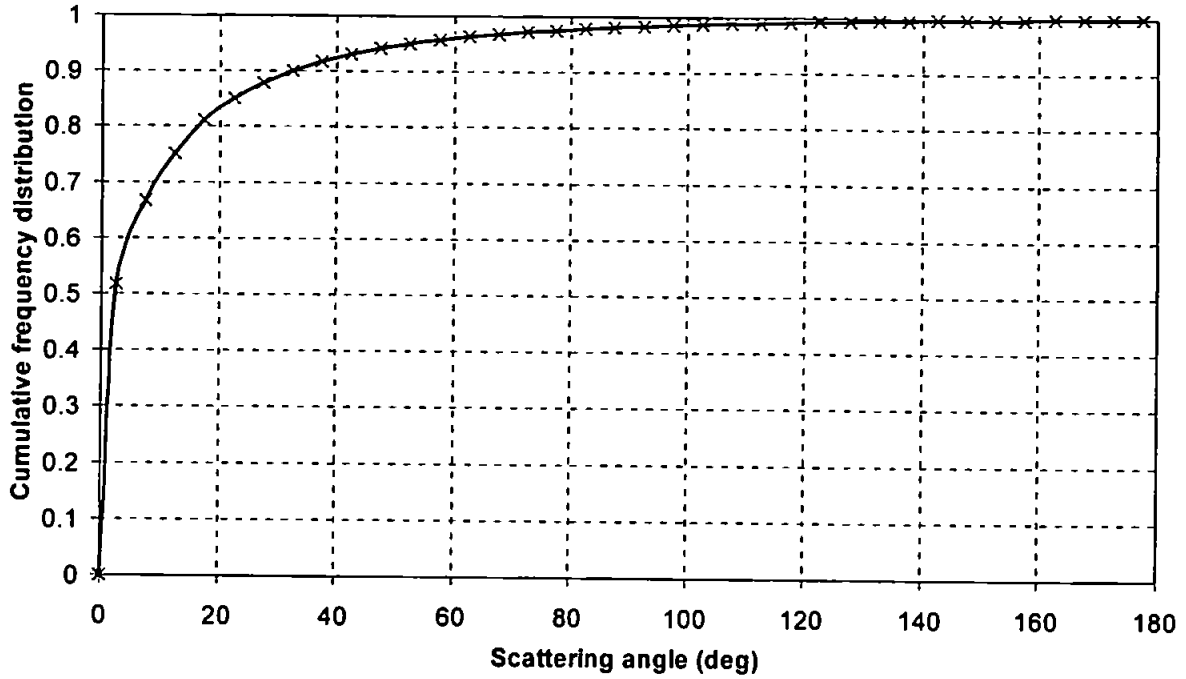


Figure 4-24: cumulative frequency distribution (Petzold, 1972, San Diego Harbour)

$$P = -\frac{1}{a+b} \ln(1-r)$$

$$\varphi = 2\pi r \quad (0 \leq \varphi < 2\pi)$$

$$\theta = \pi r \quad (0 \leq \theta < \pi)$$

Equation 4-8

At this stage, two situations are possible.

First, if the new point is inside the cavity, a new random number is calculated to determine if the next interaction is one of scattering or one of absorption, the rule being:

- if $r \leq a/(a+b)$ the photon is assumed to be absorbed
- otherwise it is assumed to be scattered

If the photon is absorbed, its number of wall to wall transits is recorded and a new photon is emitted. If the photon is scattered, three random numbers are generated to determine the path length (P) before the next interaction, the angle of scattering ($0 \leq \psi < \pi$) according to a cumulative frequency distribution (Figure 4-24) and the angle of rotation ($0 \leq \Omega < 2\pi$) around the initial trajectory.

Second, if the new point is outside the cavity then the co-ordinates of intersection on the cavity are calculated and a random number determine if the photon is absorbed on the cavity wall or reflected, ρ being the reflectivity of the wall. The rule in this case is:

- if $r > (1 - \rho)$ the photon is assumed to be reflected
- otherwise, it is assumed to be absorbed

If the photon is absorbed, the number of wall to wall transits is recorded, and then a new photon is emitted from the centre of the sphere. If not, the photon is assumed to undergo a Lambertian reflection on the cavity wall. Two random numbers are generated to determine the angle of reflection on the zenith and azimuth plan and the new co-ordinates x, y, z after reflection are calculated. The path length after reflection is calculated as the original one minus the distance traversed before the collision.

At this stage, two situations are possible:

The new point is inside the cavity in which case random numbers are generated to determine the nature of the next interaction, the angle of scattering (ψ), the angle of rotation (Ω) and so on, or the new point is outside the cavity in which case the intersection with the sphere is calculated and so on.

4.3.3. Mathematics of the Monte Carlo Code

The position of each photon is expressed at any time in terms of Cartesian (x, y, z) or spherical (P = path, θ = zenith angle, ϕ = azimuth angle) co-ordinates depending which one is better to use for the various calculations. Basically, the model uses spherical co-ordinates for emission and scattering and to decide if the photon is inside the sphere. Cartesian co-ordinates are used to calculate the intersection of any given trajectory with the sphere and the new co-ordinates after being scattered by a particle or reflected on the cavity wall.

$$\left\{ \begin{array}{l} x = P * \sin(\theta) * \cos(\varphi) \\ y = P * \sin(\theta) * \sin(\varphi) \\ z = P * \cos(\theta) \end{array} \right.$$

Equation 4-9: From spherical to Cartesian co-ordinates

$$\left\{ \begin{array}{l} P = \sqrt{x^2 + y^2 + z^2} \\ \theta = a \cos\left(\frac{z}{P}\right) \\ \varphi = \left\{ \begin{array}{ll} a \cos\left(\frac{x}{\sqrt{x^2 + y^2}}\right) & \text{if } y > 0 \\ 2 * \pi + a \sin\left(\frac{y}{\sqrt{x^2 + y^2}}\right) & \text{if } y < 0 \text{ and } x \geq 0 \\ \pi + a \cos\left(\frac{-x}{\sqrt{x^2 + y^2}}\right) & \text{if } y < 0 \text{ and } x < 0 \\ \pi \text{ if } y = 0 \text{ and } x < 0 & 0 \text{ if } y = 0 \text{ and } x > 0 \end{array} \right. \end{array} \right.$$

Equation 4-10: Cartesian to spherical co-ordinates

4.3.3.1. Emission, scattering and absorption

A photon is initially emitted from the centre of the cavity. The initial trajectory of the photon is calculated using Equation 4-8. To explain the emission and scattering principle, we will assume a cavity of infinite radius. The photon will continue its path, being scattered or not until it is finally absorbed. After emission, the photon will be in position described by x_a, y_a, z_a its cartesian co-ordinates and OA, θ_A, φ_A , its spherical co-ordinates. A first rotation matrix is calculated:

$$rot1 = \begin{bmatrix} -\sin \varphi_A & -\cos \theta_A \cos \varphi_A & \sin \theta_A \cos \varphi_A \\ \cos \varphi_A & -\cos \theta_A \sin \varphi_A & \sin \theta_A \sin \varphi_A \\ 0 & \sin \theta_A & \cos \theta_A \end{bmatrix}$$

This matrix expresses the rotation of the new base $(A, \vec{I}, \vec{J}, \vec{K})$ (Figure 4-25) in the original base $(O, \vec{i}, \vec{j}, \vec{k})$. If the photon is not absorbed then it will be scattered. New co-ordinates are calculated for the scattered photon in the base $(A, \vec{I}, \vec{J}, \vec{K})$: AB, ψ_B, Ω_B . A new rotation matrix is calculated:

$$rot2 = \begin{bmatrix} \cos \Omega_B \cos \psi_B & -\sin \Omega_B & \cos \Omega_B \sin \psi_B \\ \sin \Omega_B \cos \psi_B & \cos \Omega_B & \sin \Omega_B \sin \psi_B \\ -\sin \psi_B & 0 & \cos \psi_B \end{bmatrix}$$

This matrix expresses the rotation of the new base $(B, \vec{L}, \vec{M}, \vec{N})$ in the original $(A, \vec{I}, \vec{J}, \vec{K})$ (Figure 4-25). The co-ordinates of B are then calculated in the base $(O, \vec{i}, \vec{j}, \vec{k})$:

$$\vec{OB}_O = \vec{OA}_O + rot1 * \vec{AB}_A$$

where $\vec{OB}_O$ and $\vec{OA}_O$ are the vectors expressed in the base $(O, \vec{i}, \vec{j}, \vec{k})$ and $\vec{AB}_A$ is the vector expressed in base $(A, \vec{I}, \vec{J}, \vec{K})$. If in B, the photon is not absorbed, it is scattered again. The co-ordinates of the new point C are calculated. Its position is calculated in base $(O, \vec{i}, \vec{j}, \vec{k})$ as

$$\vec{OC} = \vec{OA}_O + rot1 * (\vec{AB}_A + rot2 * \vec{BC}_B)$$

and so on until it is finally absorbed.

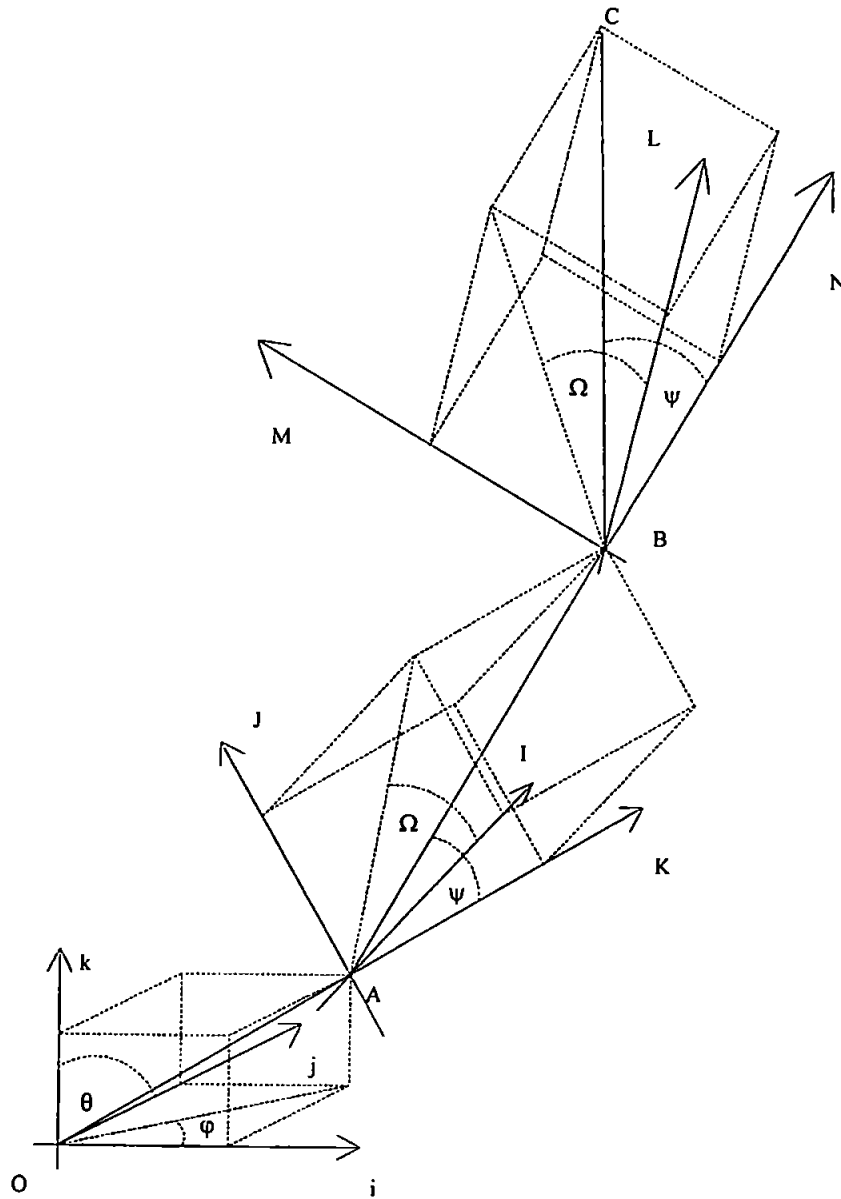


Figure 4-25: Schematic of the bases used for scattering calculations.

4.3.3.2. Collision on the cavity wall

If at any time during its transit, the photon ends up “outside” the cavity, we must calculate the point of collision between its trajectory and the sphere and from this point calculate new co-ordinates after reflection on the cavity wall. First, the intersection between the straight line describing the trajectory of the photon and a sphere of radius r is calculated. We have three unknowns (x_c, y_c, z_c) the co-ordinates of the collision point C. To find these we need a system of three equations. We know the last position of the photon A (x_a, y_a, z_a) and the new position outside the sphere B (x_b, y_b, z_b) . In three dimensions, a straight line is defined as the intersection of two planes $z=ax+by+c$. A first plane P_1 containing A, B and E is calculated. The point E is created so that $\overrightarrow{AB} \cdot \overrightarrow{AE} = 0$ is verified. The second plane P_2 containing A, B and D is calculated with the created point D verifying $\overrightarrow{AB} \wedge \overrightarrow{AE} = \overrightarrow{AD}$. We have now to solve a system of three equations and three unknowns:

$$\begin{cases} z = ax + by + c & (P_1) \\ z = dx + ey + d & (P_2) \\ x^2 + y^2 + z^2 = r^2 & (Sphere) \end{cases}$$

This is a system of second order which has one or two solutions. In general the system will have two solutions except if the trajectory of the photon is tangent to the sphere. One of the two collision point is decided depending on the direction the photon is travelling.

Having the collision point, new co-ordinates after reflection are calculated (AB, μ, ν) assuming a Lambertian reflection. Two rotation matrixes are used to allow calculation of the new point after reflection. Taking the example of Figure 4-26, the photon hit the cavity at A and is reflected at B. The first matrix $rot1$ calculates the rotation of the base $(A, \vec{i}, \vec{j}, \vec{k})$ into the base $(O, \vec{i}, \vec{j}, \vec{k})$:

$$rot1 = \begin{bmatrix} -\sin \varphi_A & -\cos \theta_A \cos \varphi_A & \sin \theta_A \cos \varphi_A \\ \cos \varphi_A & -\cos \theta_A \sin \varphi_A & \sin \theta_A \sin \varphi_A \\ 0 & \sin \theta_A & \cos \theta_A \end{bmatrix}$$

The co-ordinates of B are then calculated in the base $(O, \vec{i}, \vec{j}, \vec{k})$:

$$\overline{OB}_O = \overline{OA}_O + rot1 * \overline{AB}_A$$

where $\overline{OB}_O$ and $\overline{OA}_O$ are the vectors expressed in the base $(O, \vec{i}, \vec{j}, \vec{k})$ and $\overline{AB}_A$ is the vector expressed in base $(A, \vec{I}, \vec{J}, \vec{K})$. If in B, the photon is not absorbed, it is scattered again.

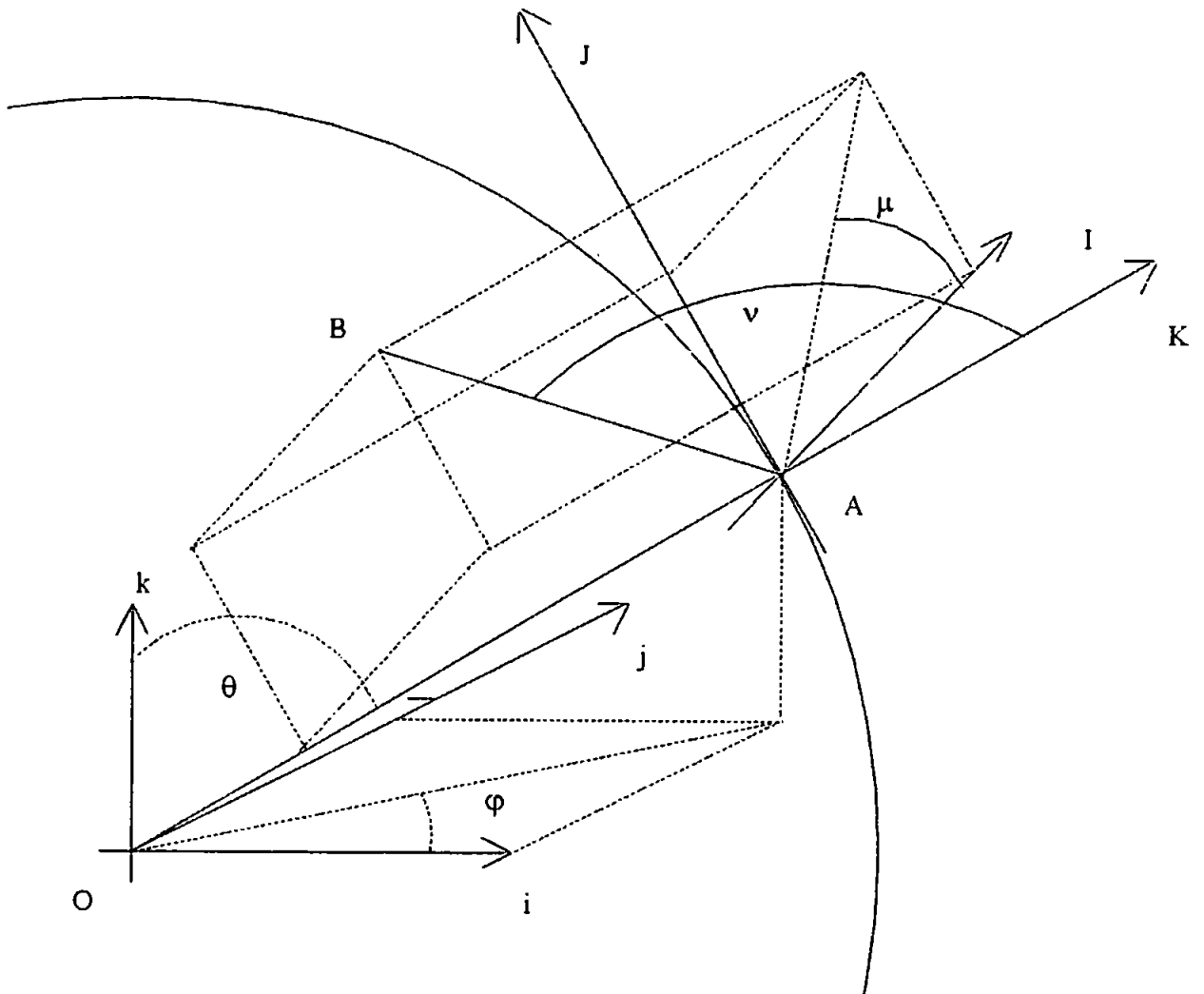


Figure 4-26: Schematic of the bases used for reflection calculations.

The second rotation matrix needed, $rot2$, will calculate the co-ordinates of the new point C emitted from $(B, \vec{L}, \vec{M}, \vec{N})$ into $(O, \vec{i}, \vec{j}, \vec{k})$:

$$rot2 = \begin{bmatrix} \cos \mu \cos \nu & -\sin \mu & \cos \mu \sin \nu \\ \sin \mu \cos \nu & \cos \mu & \sin \mu \sin \nu \\ -\sin \nu & 0 & \cos \nu \end{bmatrix}$$

Again, this goes on until the photon is finally absorbed within the cavity or on the cavity wall.

4.3.4. *Limitations of the code*

Monte Carlo models are a powerful way to simulate the behaviour of photons. However, the code produced has its limitations. The output values from the code are the results of probabilistic calculations. The probability of photon survival is calculated as follows. The number of wall to wall transits and the total number a photons which collided with wall and were reflected are recorded. The probability of photon survival is then calculated as the ratio of the total number wall collisions and reflections to the total number of wall to wall transits. With this method, if the absorption is rather small then the number of wall to wall transits will become extremely large and the probability will therefore get closer and closer to one. Table 4-4 gives an example of what's happening. We calculated for a set of absorption values the theoretical value of P_s and the result of the simulation for $b=0m^{-1}$, $r=0.05m$ and $\rho=0.999$ for various number of simulated photons (MP).

These data show that for small values of absorption coefficient, the simulated probability of photon survival will tend to one. If we try to decrease the number of simulated photons, this actually diminishes the total number of wall to wall transits for the set of data and hopefully removes the artefacts from the calculation. In other words, by changing the total number of simulated photons, we can adjust the model to fit the theory for $b=0m^{-1}$. Doing so

changes the limit in our example for $a=0.5\text{m}^{-1}$ and $a=0.1\text{m}^{-1}$. For $a=0.05\text{m}^{-1}$, the value remains $P_s=1$. On the other hand, for fairly high absorption values ($a=10\text{m}^{-1}$), the simulated value for P_s is also overestimated relative to the theoretical equation. The simulations for $a=5\text{m}^{-1}$ are also slightly overestimated. Overall, our code for a cavity of 0.05 m radius, and a reflectivity $\rho=0.999$ would be applicable for a set of absorptions from 2 to 0.1m^{-1} if the number of simulated photons is adjusted properly.

Table 4-4: Calculated Probability of photon survival for a cavity of $r=0.05$ m and $\rho=0.999$ for a set of absorptions.

a (m^{-1})	10	5	2	1.5	1	0.5	0.1	0.05
<i>Theory</i>	0.528	0.722	0.876	0.905	0.936	0.967	0.993	0.997
<i>MP</i>								
10^5	0.535	0.723	0.877	0.905	0.935	0.967	0.993	1
2.10^5	0.533	0.724	0.876	0.906	0.936	0.967	1	1
3.10^5	0.535	0.724	0.876	0.906	0.936	0.967	1	1
4.10^5	0.535	0.723	0.876	0.906	0.936	0.967	1	1
5.10^5	0.533	0.723	0.876	0.906	0.936	0.967	1	1
6.10^5	0.535	0.723	0.876	0.905	0.936	1	1	1
7.10^5	0.533	0.723	0.876	0.906	0.936	1	1	1
8.10^5	0.533	0.723	0.876	0.906	0.936	1	1	1
9.10^5	0.534	0.723	0.876	0.905	0.936	1	1	1
10^6	0.534	0.723	0.876	0.905	0.936	1	1	1

The same calculation was carried out for a sphere of 0.1m radius and a reflectivity $\rho=0.999$ (Table 4-5).

Table 4-5: Calculated Probability of photon survival for a cavity of $r=0.1$ m and $\rho=0.999$ for a set of absorptions.

a (m^{-1})	10	5	2	1.5	1	0.5	0.1	0.05
<i>Theory</i>	0.297	0.528	0.769	0.821	0.876	0.936	0.987	0.993
<i>MP</i>								
10^5	0.312	0.526	0.768	0.822	0.877	0.936	0.987	1
2.10^5	0.310	0.521	0.768	0.822	0.876	0.936	1	1
3.10^5	0.312	0.522	0.769	0.821	0.877	0.936	1	1
4.10^5	0.311	0.527	0.768	0.821	0.876	0.936	1	1
5.10^5	0.310	0.525	0.768	0.821	0.876	0.936	1	1
6.10^5	0.310	0.525	0.769	0.822	0.877	1	1	1
7.10^5	0.310	0.525	0.768	0.822	0.876	1	1	1
8.10^5	0.310	0.526	0.768	0.821	0.876	1	1	1
9.10^5	0.310	0.528	0.769	0.821	0.876	1	1	1
10^6	0.311	0.528	0.769	0.821	0.876	1	1	1

The same patterns are again observed. For small values of absorption, the simulated probability of photon survival is 1 depending on the number of simulated photons and the probability is overestimated for high values of absorption. In this configuration, the model would be applicable for absorptions from 5 to 0.1m^{-1} if the number of simulated photons were properly selected.

Again, the same simulation was carried out for a cavity of radius $r=0.02\text{m}$ and a reflectivity $\rho=0.999$ (Table 4-6). As predictable, reducing the cavity diameter makes the instrument more efficient for higher absorption values. The domain in which our model would be usable would now be from 0.5 to 5m^{-1} , again assuming that the number of simulated photons is adequate.

Table 4-6: Calculated Probability of photon survival for a cavity of $r=0.02\text{ m}$ and $\rho=0.999$ for a set of absorption

$a\ (\text{m}^{-1})$	10	5	2	1.5	1	0.5	0.1	0.05
<i>Theory</i>	0.769	0.876	0.948	0.961	0.974	0.987	0.997	0.999
<i>MP</i>								
10^5	0.769	0.877	0.948	0.961	0.974	0.987	1	1
2.10^5	0.769	0.877	0.948	0.961	0.974	0.987	1	1
3.10^5	0.771	0.876	0.948	0.961	0.974	1	1	1
4.10^5	0.770	0.876	0.948	0.961	0.974	1	1	1
5.10^5	0.770	0.877	0.948	0.961	1	1	1	1
6.10^5	0.770	0.876	0.948	0.961	1	1	1	1
7.10^5	0.770	0.876	0.948	0.969	1	1	1	1
8.10^5	0.770	0.876	0.948	1	1	1	1	1
9.10^5	0.770	0.876	0.948	1	1	1	1	1
10^6	0.770	0.876	1	1	1	1	1	1

The other parameter, which didn't show much flexibility in our code, was the reflectivity. The reflectivity used for the previous simulation was $\rho=0.999$. If we decrease ρ to 0.99 in the model, the following will happen: decreasing ρ will increase the probability of the photon being absorbed on the cavity wall. If we imagine a single photon emitted from the centre of the sphere, it will at first collide with the wall and then start colliding a given number of

times on the wall before being absorbed either by the medium or the cavity wall. Suppose that the photon is absorbed after the 91st transit across the cavity. If it is absorbed by the medium, it will have survived 90 transits on 91 giving a probability $P_s=0.989$. If it is absorbed by the cavity, it will have survived 91 transits of 91 giving a probability $P_s=1$. For a large set of simulated photons, this would have the effect of overestimating the probability of photon survival. This problem of our code also contributes to the overestimation presented before. For small absorption values, the probability of a photon being absorbed on the wall is increased. Various modifications were made in the code to try to eliminate the problem but proved unsuccessful.

The code we developed is restricted to a certain domain of application. Not being able to test the model with different values of wall reflectivity is regrettable especially knowing the importance of this parameter to the capabilities of the instrument. However restricted this model is, we launched various simulations to assess the response of the instrument with increasing levels of scattering in terms of probability of photon survival, average number of collisions with the wall and average pathlength per photon.

4.3.5. Simulations

The influence of scattering was investigated using the Monte Carlo code for four different cavity radius ($r= 0.02, 0.05$ and 0.10m) for the three parameters P_s , C_f and I_f given in *Kirk's, paper (1997)*. Two types of scattering properties were taken into account for the various simulations: isotropic scattering and the scattering data measured by *Petzold (1975)*.

4.3.5.1. Probability of photon survival

Firstly, the evolution of P_0 and P_s was calculated using Equation 4-2, thus assuming no scattering, for the three cavity radii under investigation as a function of the absorption coefficient (Figure 4-27). P_0 , the probability of a photon to survive the initial transit from the

source to the wall is logically always higher than P_s , the probability of a photon to survive a transit from the wall back to the wall. The travel distance required is doubled in case of P_s . Logically, the probability also decreases with increasing cavity radius and with increasing absorption.

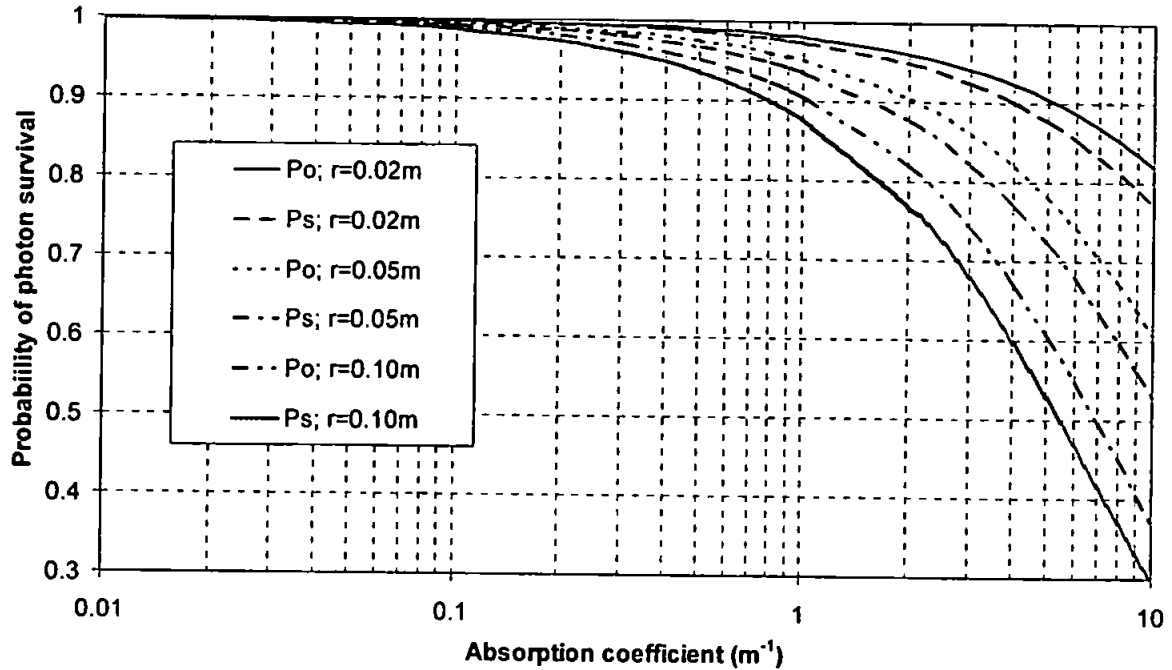


Figure 4-27: Probability of photon survival; $\rho=0.999$

A Monte Carlo simulation was carried out to investigate the evolution of the probability of photon survival from the centre of the sphere (emission) to the wall (P_0) and in transit from wall to wall of the cavity P_s . As pointed out by *Leather et al., (2000)*, the value of P_s itself varies very little with increasing scattering but the error in the ratio $1/(1-\rho P_s)$ which determines the average number of collision with the wall is more significant. Figure 4-28 shows the evolution with increasing scattering of the percentage error in P_0 and $1/(1-\rho P_s)$. This simulation consider a sphere of 0.05m radius, a wall reflectivity $\rho=0.999$ and an absorption $a=1\text{m}^{-1}$.

Figure 4-28 shows the same patterns as the one obtained by *Leather et. al (2000)*. The value of P_0 obtained by Monte Carlo simulation decreases with increasing scattering. The theoretical value of P_0 therefore overestimates it when b increases. This result is actually

easy to forecast. A photon emitted from the centre of the sphere will undergo more and more interactions with the medium before finally reaching the cavity wall if scattering increases. These multiple interactions are quite likely to change its initial trajectory and even scatter the photon backward. Being scattered backward is more likely in the case of isotropic scattering. The overall effect will be to increase its path length before reaching the wall for the first time and consequently increase its probability of being absorbed before reaching the wall. The percentage error for P_0 was found to increase almost linearly with increasing scattering. $\%Error=0.1*b$; $r^2=0.99$ for isotropic scattering, $\%Error=0.006*b$; $r^2=0.98$ for Petzold scattering. This result shows that for calculations made with Petzold's scattering function, the percentage error is much smaller. For example, with isotropic scattering, the percentage error was found to be about 0.1% and 10% for $b= 10$ and 100m^{-1} respectively, whereas it was found to be about 0.06% and 0.55% for $b= 10$ and 100m^{-1} respectively with Petzold's scattering function. This scattering function indeed assumes that the great majority of the photons are scattered in a near forward angle of the initial trajectory. As a result, photons are more likely, although being scattered, to follow a trajectory close to a linear one.

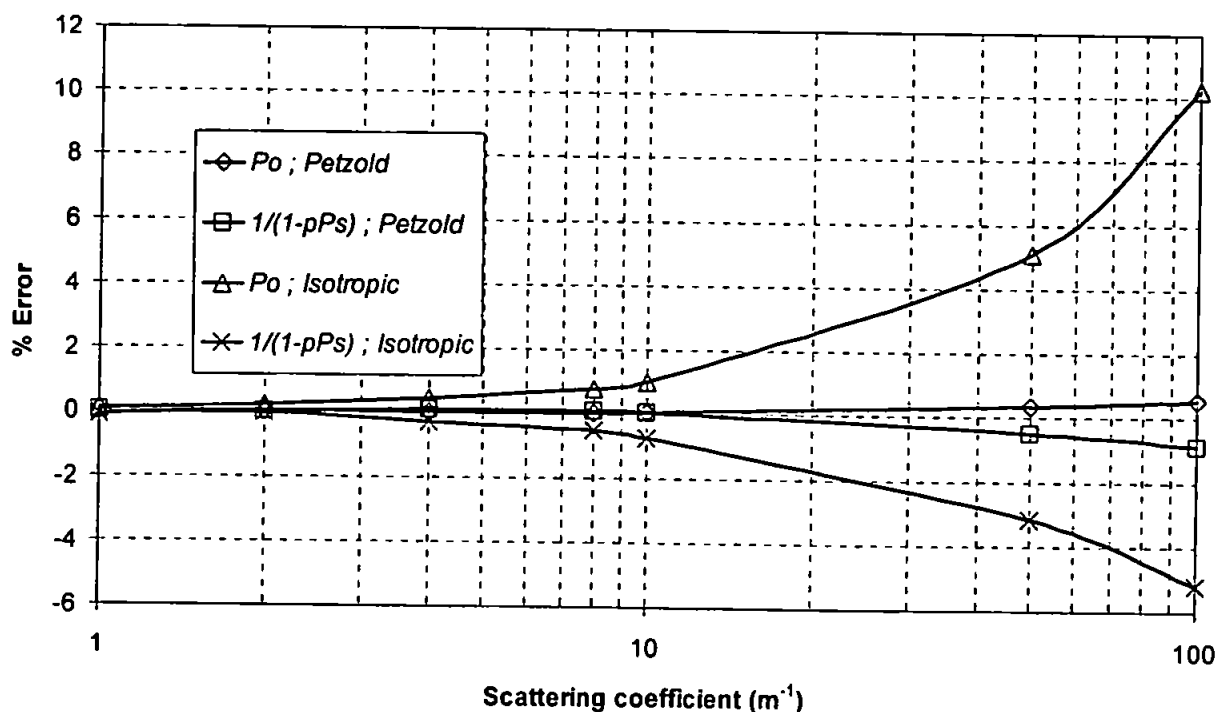


Figure 4-28 : Percentage error in P_0 and $1/(1-pP_s)$ for $a=1$ and $r=0.05$.

When travelling from the wall back to the wall, P_s appears to be overestimated by the model with increasing scattering, probably because when leaving the wall, increasing levels of scattering makes it more likely that the photon will be scattered back to the wall. This phenomenon is once again less significant when Petzold's scattering is considered. With isotropic scattering, the percentage error was found to be about -0.7% and -5% for $b=10$ and 100m^{-1} respectively, whereas it was found to be about -0.036% and -0.8% for $b=10$ and 100m^{-1} respectively with Petzold's scattering function.

Figure 4-29 to Figure 4-31 show the results of a Monte Carlo simulation for the same sphere configuration but for three different absorptions, $a=0.1$, 0.5 and 2m^{-1} . The patterns are very similar but the percentage error increases as a consequence of the increased absorption. If we take for example the data for $a=2\text{m}^{-1}$, we have now for P_0 an error of about 1.9% and 19% for $b=10\text{m}^{-1}$ and 100m^{-1} respectively in case of isotropic scattering and 0.12% and 1.15% for $b=10\text{m}^{-1}$ and 100m^{-1} respectively in case of Petzold's scattering. For the ratio $(1/(1-\rho P_s))$, the figures becomes -1.3% and -9% for $b=10\text{m}^{-1}$ and 100m^{-1} respectively in case of isotropic scattering and -0.2% and -1.3% % for $b=10\text{m}^{-1}$ and 100m^{-1} respectively in case of Petzold's scattering. On the other hand the results for $a=0.1$ and 0.5m^{-1} display much smaller percentage error.

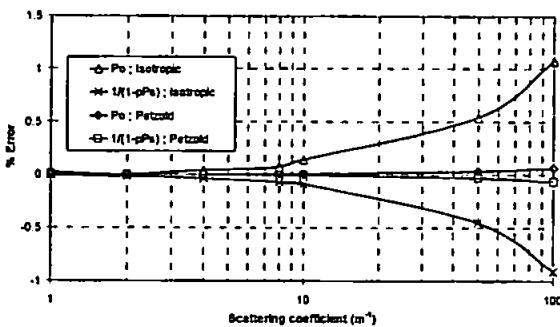


Figure 4-29: Percentage error in P_0 and $1/(1-\rho P_s)$ for $a=0.1$ and $r=0.05\text{m}$

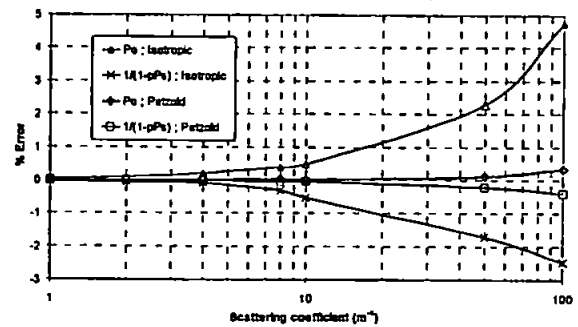


Figure 4-30: Percentage error in P_0 and $1/(1-\rho P_s)$ for $a=0.5$ and $r=0.05\text{m}$

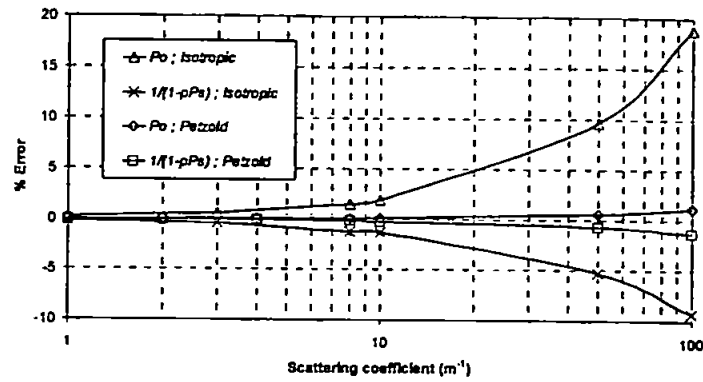


Figure 4-31: Percentage error in P_0 and $1/(1-pP_s)$ for $a=2$ and $r=0.05m$

A similar simulation was carried out for a cavity diameter of 0.10m for four values of absorption (0.1, 1, 2 and $5m^{-1}$) and a wall reflectivity of 0.999. Figure 4-32 to Figure 4-35 show the results of those simulations. As before, the same features are observed either for isotropic or Petzold's scattering.

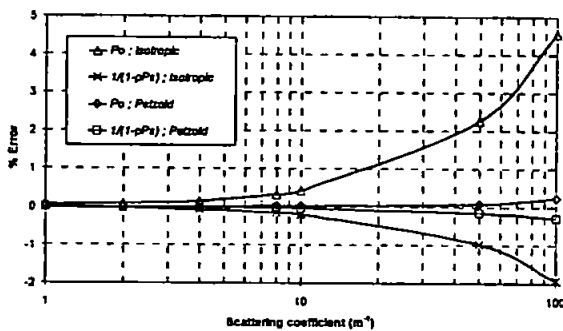


Figure 4-32: Percentage error in P_0 and $1/(1-pP_s)$ for $a=0.1m^{-1}$ and $r=0.10m$.

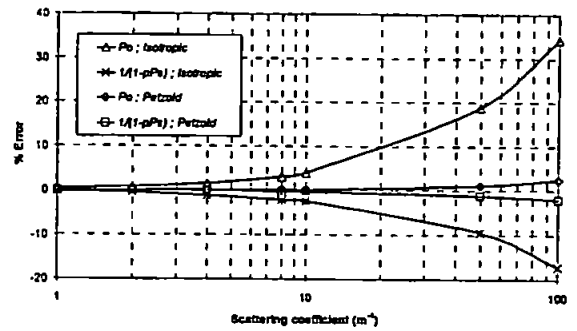


Figure 4-34: Percentage error in P_0 and $1/(1-pP_s)$ for $a=1m^{-1}$ and $r=0.10m$.

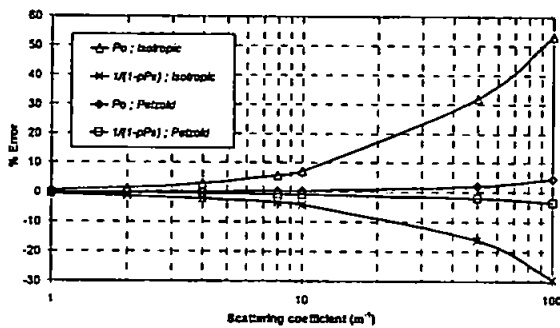


Figure 4-33: Percentage error in P_0 and $1/(1-pP_s)$ for $a=2m^{-1}$ and $r=0.10m$.

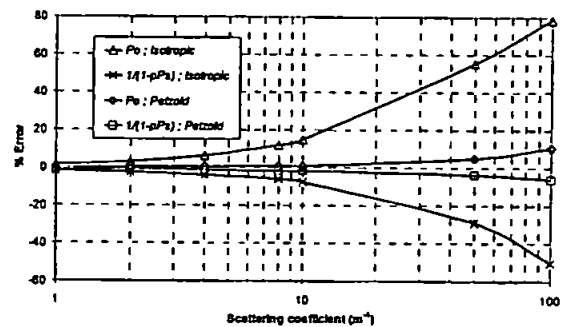


Figure 4-35: Percentage error in P_0 and $1/(1-pP_s)$ for $a=5m^{-1}$ and $r=0.10m$.

Figure 4-32 to Figure 4-34 compared to Figure 4-28, Figure 4-29 and Figure 4-31 shows that for given absorptions $a=0.1$, 1 and 2m^{-1} , increasing the cavity radius would result in an increased percentage error in both P_0 and $1/(1-\rho P_s)$. The figures in the case of $a=1\text{m}^{-1}$ are for P_0 about 4% and 35% for $b=10$ and 100m^{-1} respectively the in case of isotropic scattering and 0.2% and 2.5% for $b=10$ and 100m^{-1} respectively in the case of Petzold's scattering. The four figures also show that increasing absorption results in a more significant percentage error with increasing scattering.

The simulation carried out for a cavity radius of 0.02m and absorption of 1 , 3 and 5m^{-1} (Figure 4-36 to Figure 4-38) led to the same conclusion.

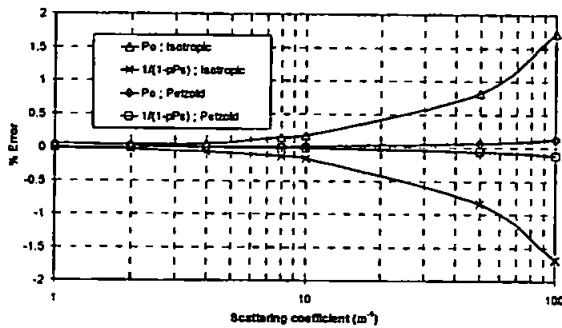


Figure 4-36: Percentage error in P_0 and $1/(1-\rho P_s)$ for $a=1$ and $r=0.02\text{m}$.

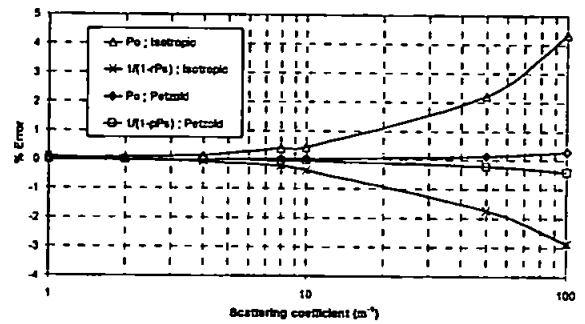


Figure 4-37: Percentage error in P_0 and $1/(1-\rho P_s)$ for $a=3$ and $r=0.02\text{m}$.

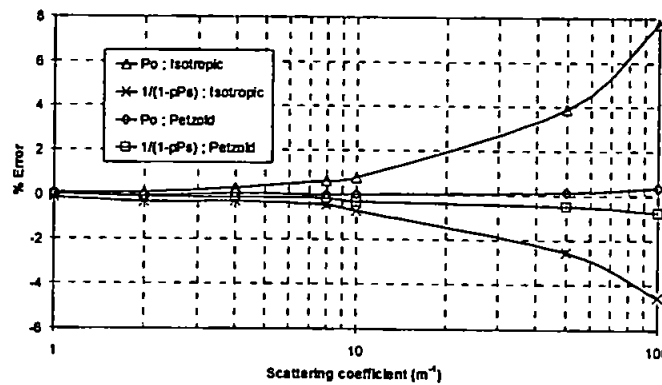


Figure 4-38: Percentage error in P_0 and $1/(1-\rho P_s)$ for $a=5$ and $r=0.02\text{m}$.

4.3.5.2. Average number of collisions

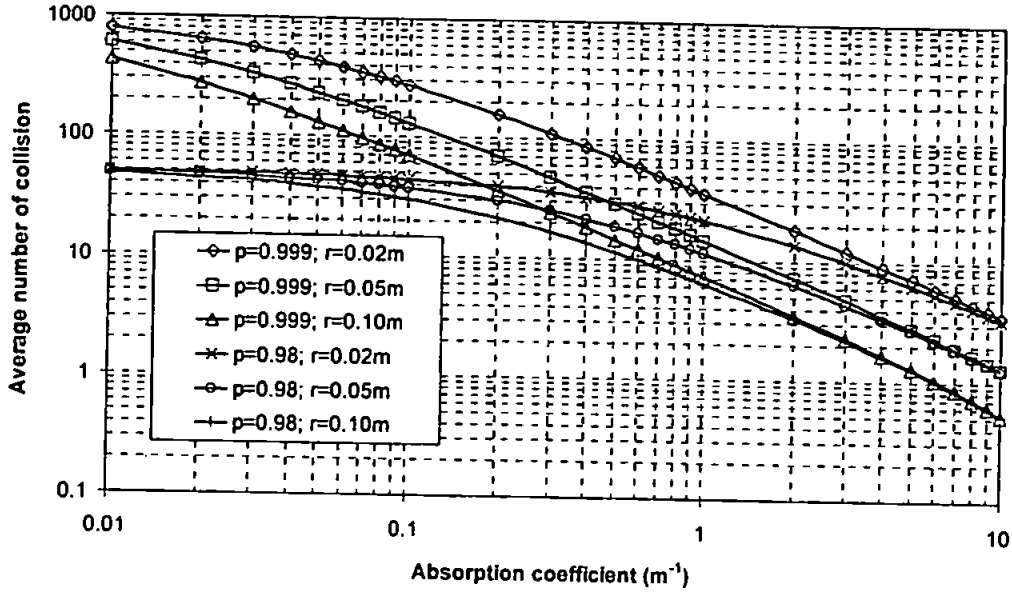


Figure 4-39: Theoretical average number of collision

Firstly, the evolution of C_f was calculated using Equation 4-2, thus assuming no scattering, for the three cavity radii under investigation as a function of absorption coefficient and for two wall reflectivities ($\rho=0.999$ and 0.98 ; Figure 4-39). Two separate areas can be identify in Figure 4-39. The reflectivity dominated part for low absorption and the absorption dominated part for absorption higher than 1m^{-1} . For the latter, given a cavity radius, similar results are obtained whatever the reflectivity. For high absorption values, the absorption on the cavity wall becomes less significant, the major source of photon depletion being absorption within the medium. For very low absorption, absorption on the cavity wall becomes more dominant relative to the absorption on the cavity wall. For $\rho=0.98$, and low absorption values it occurs than the cavity radius does not make significant differences and the same average number of collision is observed. This does not appear on the graph for $\rho=0.999$ but if the calculation were carried out for lower absorption, the same feature would be observed.

With the results of the simulations with the probability of photon survival, we calculated the error in the average number of collision with the wall as the ratio $P_0/(1-\rho P_s)$ (Equation 4-2).

The error in C_f is of major interest since C_f is directly proportional to the irradiance on the cavity wall (Kirk 1995, 1997, Leather et.al. 2000). The number of photons colliding on an area of the cavity wall is indeed proportional to the irradiance this area will receive. With the data used to calculate C_f , the error observed for P_0 and P_s previously (% error on P_0 positive and % error in $1/(1-pP_s)$ negative) should compensate themselves and result in a quite small percentage error in C_f .

The average number of collisions with the wall logically decreases with increasing absorption. When scattering increases, the average number of collisions appeared to decrease. The percentage error observed was much smaller than the one observed for P_0 and P_s , the effect on both probabilities compensating each other.

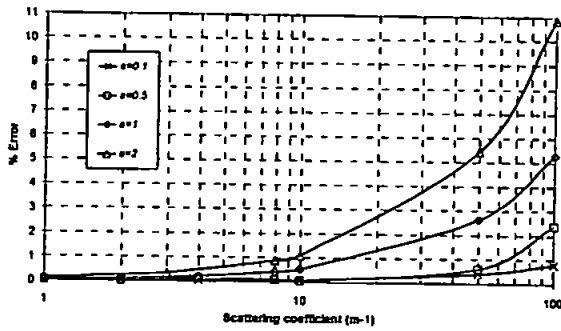


Figure 4-40: Percentage error in the average number of collisions for $r=0.05m$; Isotropic scattering

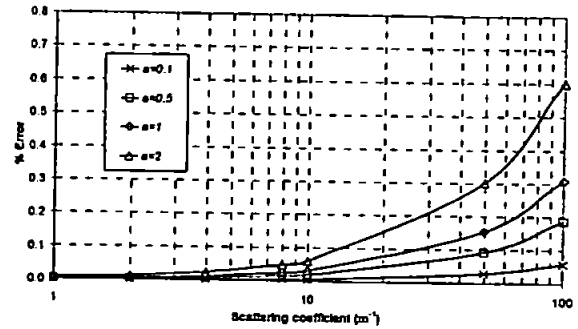


Figure 4-41: Percentage error in the average number of collisions for $r=0.05m$; Petzold scattering

For a cavity radius of 0.05, if we consider isotropic scattering, the error in C_f was found to be 0.25% and 5.6% for $b=10$ and $100m^{-1}$ respectively for $a=1m^{-1}$ and 0.6% and 11% for $b=10$ and $100m^{-1}$ respectively for $a=2m^{-1}$. For Petzold's scattering, the error in C_f was found to be less than 0.1% and 0.3% for $b=10$ and $100m^{-1}$ respectively for both $a=1$ and $2m^{-1}$. For the simulation carried out with a cavity radius $r=0.1m$, higher percentage error were found with again a big difference between isotropic and Petzold's scattering. A maximum errors of 0.5% with $a=5m^{-1}$ for $b=10m^{-1}$ and a maximum error of 5% with $a=5m^{-1}$ for $b=100m^{-1}$ for Petzold's and isotropic scattering respectively.

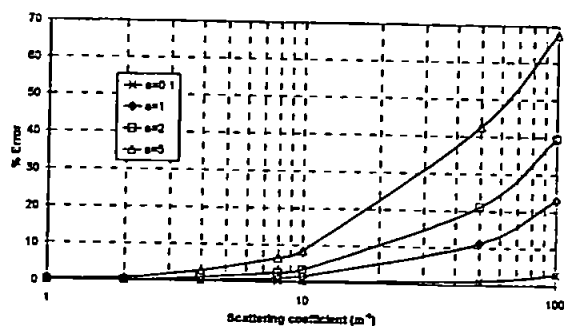


Figure 4-42: Percentage error in the average number of collisions for $r=0.1\text{m}$ Isotropic scattering.

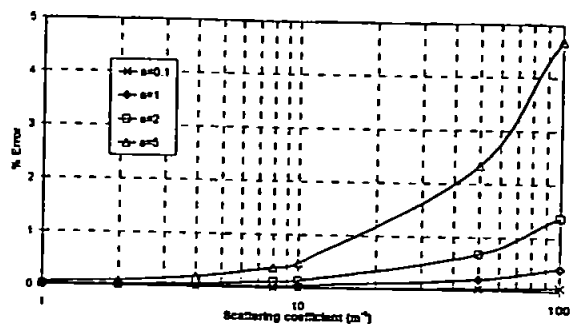


Figure 4-43: Percentage error in the average number of collisions for $r=0.1\text{m}$ Petzold scattering.

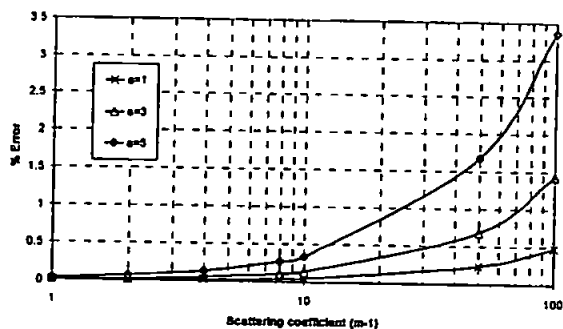


Figure 4-44: Percentage error in the average number of collisions for $r=0.02\text{m}$; Isotropic scattering.

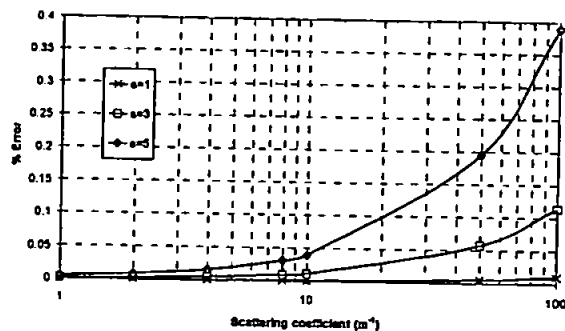


Figure 4-45: Percentage error in the average number of collisions for $r=0.02\text{m}$; Petzold scattering.

4.3.5.3. Average path length

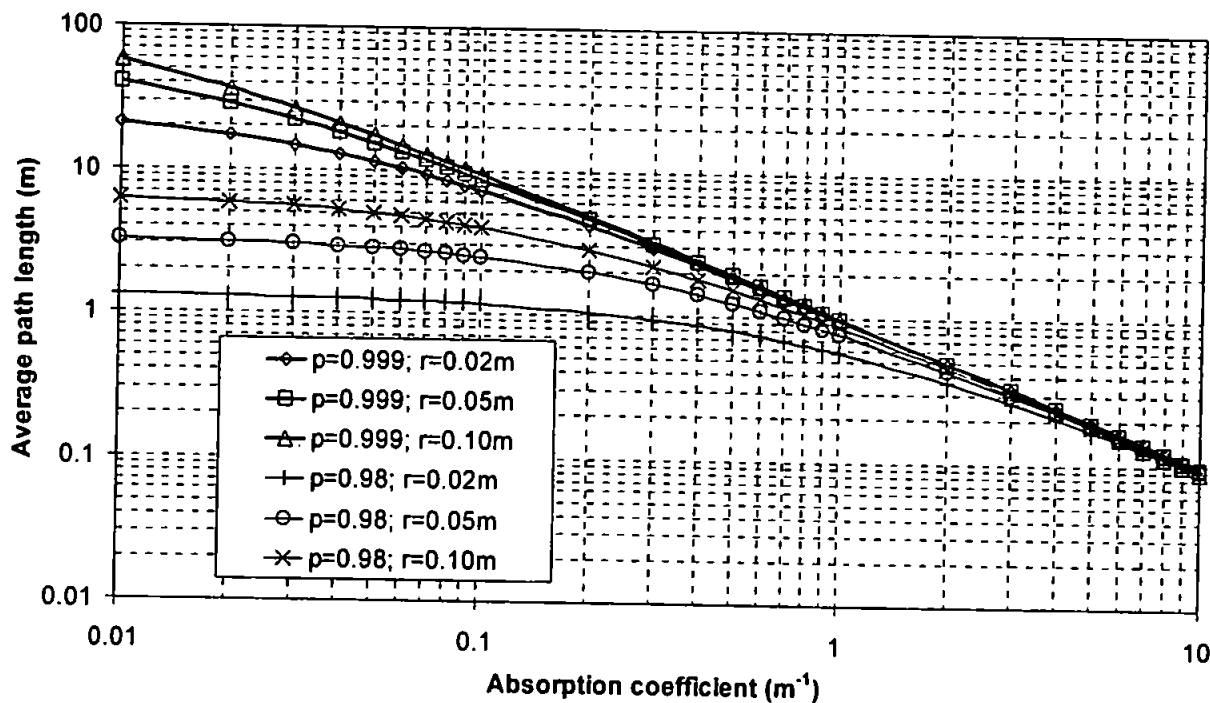


Figure 4-46: Theoretical average path length

The average path length per photon is not as revealing as the average number of collisions, which can be linked to the irradiance received on the surface of the sphere. However, it shows clearly the benefit of the integrating cavity in allowing a photon to perform a very long path length thus allowing the measurement of very low signals. For example, if we suppose an absorption of 1m^{-1} , Equation 4-8 would predict an initial path from 0 to more than 2m, which can only be feasible if the photon can be confined in a reflective volume. Figure 4-46 displays the calculated average path length for three cavity radii (0.02m, 0.05m and 0.10m) and two cavity wall reflectivities ($\rho=0.999$ and 0.98). Similarly, the graph can be divided into two parts, the reflectivity dominated part and the absorption dominated part. The latter concern absorption values higher than 1m^{-1} . In this part of the graph, the path length has an approximately inverse relationship with absorption. In this case, whatever the radius or the reflectivity, the absorption coefficient is the principal parameter that dictates the average path length. In the first part of the graph, having very low absorption, the reflectivity is a dominant source of photon depletion. For a given reflectivity, the bigger the radius, the less the photon depletion.

The next six graphs present the result of Monte Carlo simulations for the average path length for three different cavity radii and various absorption values. As a rule, the average path length is underestimated by Equation 4-2 for l_t , when scattering increases. As explained previously, increasing levels of scattering makes it more likely that once a photon collides with the cavity wall, it is scattered back to the wall or in a close vicinity of the collision point, thus multiplying the number of collisions with the wall and increasing the risk of being absorbed by it. Figure 4-47 to Figure 4-52 show the average path lengths per photon for the different cavity radii for both isotropic and Petzold's scattering. In all cases, the higher the absorption, the less the percentage error. Referring to Figure 4-46 the smaller the absorption, the longer the path length. Since scattering tends to increase the probability of a photon becoming absorbed on the

cavity wall, the probability of a photon not completing its entire path length is also increased. At the end a photon in a low absorbing medium with significant scattering will have its path length more significantly shortened than a photon in a higher absorbing medium.

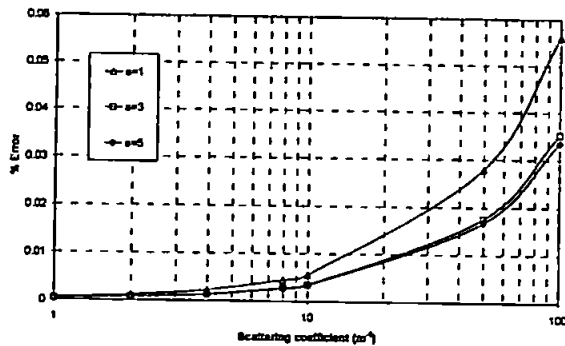


Figure 4-47: Percentage error in the average path length for $r=0.02\text{m}$, isotropic scattering.

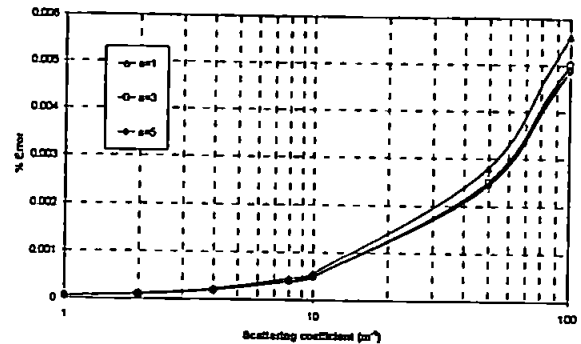


Figure 4-48: Percentage error in the average path length for $r=0.02\text{m}$, Petzold scattering.

As expected, for a given absorption value, increasing the cavity radius increases the percentage error but not as drastically as for the probability of photon survival or the average number of collision. For example, considering an absorption $a=1\text{m}^{-1}$ and $b=100\text{m}^{-1}$, the percentage error goes from 0.056, 0.077, 0.12% for $r=0.02, 0.05$ and 0.10m in case of isotropic scattering and 0.0056, 0.013 and 0.015% for $r=0.02, 0.05$ and 0.10m in case of Petzold's scattering.

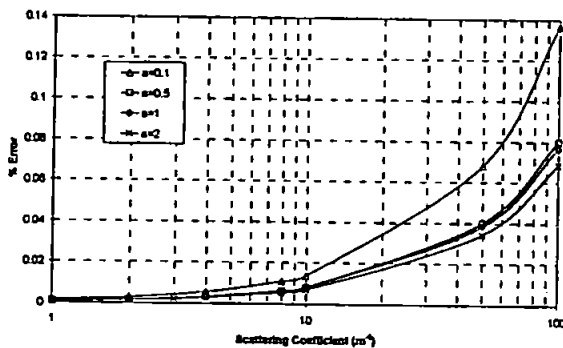


Figure 4-49: Percentage error in the average path length for $r=0.05\text{m}$; Isotropic scattering.

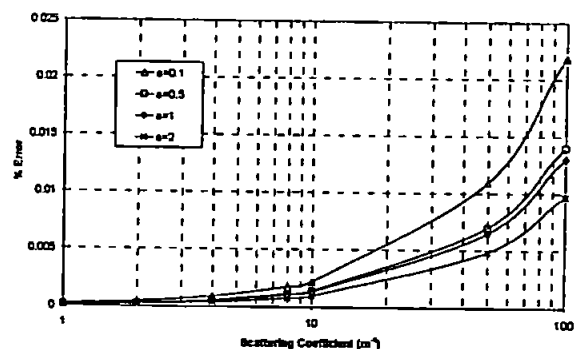


Figure 4-50: Percentage error in the average path length for $r=0.05\text{m}$; Petzold scattering.

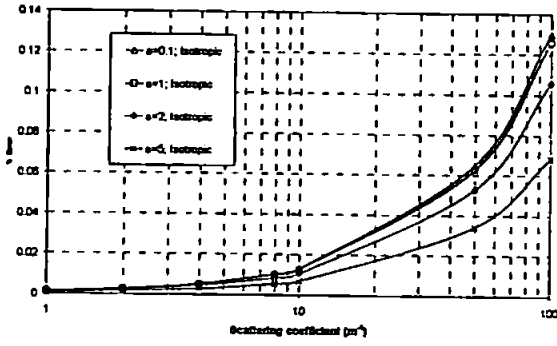


Figure 4-51: Percentage error in the average path length for $r=0.10\text{m}$; Isotropic scattering.

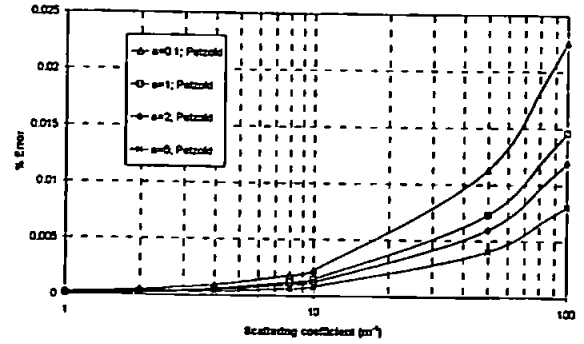


Figure 4-52: Percentage error in the average path length for $r=0.10\text{m}$, Petzold scattering.

4.3.6. Discussion

In this chapter, the analysis of the intrinsic sensitivity of the instrument and its sensitivity toward scattering was investigated. The calculations performed with the code are in agreement with the results of *Leather et al., (2000)*, showing that for the scattering ranges encountered in marine waters, the influence on the absorption measurement would be insignificant assuming a Petzold scattering function. We arrived at the same conclusion that for increasing values of b , the effect of scattering would increase with increasing absorption but also increase with increasing cavity radius. Section 4.2.3 suggested that using a less reflective material could minimise the sensitivity of the system.

According to the calculations made from the theoretical equation produced by *Kirk (1997)*, we established that the cavity radius should be taken into account for the type of water measured, basically case 1 or case 2. For case 1 water values, a bigger cavity radius would be more suitable for an optimum measurement. A longer path would be necessary to allow a significant depletion of the initial light beam. The cavity radius chosen for our prototype was 5cm, which should allow acceptable accuracy in both case 1 and case 2 waters.

Chapter 5: Development of a Prototype PSICAM

This chapter describes the development and the first experiments carried out with a prototype Point Source Integrating Cavity Absorption meter. The instrument itself can be schematically divided in three pieces:

- the light source
- the integrating cavity
- the light detector (i.e. spectrophotometer)

Each of these components will be described separately in the following sections. The strategy adopted for the development of a PSICAM was to build increasingly sophisticated versions for the integrating cavity and the light source. Three different integrating cavities and four light sources were tested. The light detector remained the same throughout the development of the system. Each prototype was calibrated and tested with standard solution of various colours prepared from food colouring solutions. The solutions under study were measured relative to a reference solution which is UV treated Milli-Q water.

5.1. Light Detectors

Two main classes of light detectors have been developed to detect and measure radiant energy: thermal and quantum detectors. In thermal detectors, radiant energy is absorbed and converted into heat energy and the detector responds to the consequent change in temperature of the absorbing medium. Quantum detectors respond directly to the number of incident photons, rather than to the cumulative energy carried by the photons. Quantum detectors include photovoltaic cells, photoconductive and photo-emissive detectors.

5.1.1. Photovoltaic cells

Photovoltaic cells consist of two different substances in contact. Light incident on the photovoltaic detector generates a difference of electric potential between the two different parts of the detector and as a consequence there is a in the current flow in the electrical circuit containing the cell. This current is measured by a current meter included in the circuit. When no light is incident on the detector, no current flow is generated. The greater the number of photons, the greater the current in the circuit.

5.1.2. Photoconductive detector

Photoconductive detectors are based on the specific properties of metal like selenium which are more conductive when light falls upon it. The greater the number of photons falling on the photoconductive cell, the greater the conductivity and therefore the greater the current flow in the circuit. Some dark current flows even if no light is incident on the cell since the photoconductive substance is still conductive even in the absence of light.

5.1.3. Photo-emissive cell – photo-multiplier

A photo-emissive or photoelectric cell consist of an evacuated tube containing a negatively charge electrode (photocathode), usually made of an alkaline metal such as cesium, sodium or potassium, and a positively charge electrode (anode). When light is incident on the photocathode, the photon dislodges an electron from its surface. These photoelectrons are drawn across to the anode, thus generating a current in the circuit containing the cell. In principle, no current would flow if no light were incident on the photocathode, but in practice a small dark current flows because of electrons spontaneously emitted by random thermal motions in the cathode.

A variant of the photoemissive cell is the photomultiplier tube (PMT). Rather than having a single photocathode and anode, a PMT has a series of anodes (called dynodes), each of which is held at a higher positive voltage than the previous one, the electrons liberated from the photocathode by the incident light are attracted by the first dynode. When these original electrons strike the first dynode, they generate additional electrons, which are then attracted to the second dynode. The electrons striking the second dynode liberate still more electrons, which are attracted to the third dynode, and so on. The electron cascade enables the PMT to amplify greatly (typically by a factor of one million) the current, which would result from the photoelectrons alone. However, PMT response is very sensitive to temperature, the response is not stable with time owing to the changes in the dynodes caused by electron bombardment, and stable high voltage power supplies are required for operation. For these reasons, PMT's have been supplanted by solid state detectors in many oceanographic instruments.

5.1.4. Silicon photodiodes

Light incident on a photo-diode frees electrons from the silicon but does not eject the electron from the diode. The resulting positively charged silicon ions are held fixed in position by the crystal lattice whereas the free electrons can move in response to an applied electromotive force. These electrons thus generate a current when the photodiode is included in a series circuit. The diode thus works as a photoconductive cell. The photodiode does not amplify the current as does the PMT and is therefore much less sensitive. The advantage is that photodiodes have good stability, are easy to calibrate, require little power and are cheap.

When operated as light detectors, diode junctions have the external electromotive force applied so as to separate the photoelectrons and their parent ions, thus generating the measured current. If the electrons are allowed to combine with the ions, then photons are emitted from the

diode. These photons have the same energy as the photons required to liberate electrons from the semiconductor atoms. When operated in this way, the diode is called a Light Emitting Diode (LED). LED's have the same general properties (stability, low cost...) as photodiodes, and are often employed as light sources in oceanographic instruments.

5.1.5. Charge-coupled device

The Charge-Coupled Device (CCD) consists of linear or arrays of small ($\approx 10 \mu\text{m}$) patches of silicon. When light is incident on the array, electrons are released from each silicon patch in proportion to the radiant energy falling on the patch. The charge released by each spot is measured. Since the location of the silicon spots is accurately known, the pattern of released charges provides a map of the energy falling on the CCD array.

5.2. Spectrophotometer

The spectrophotometer used for the prototype is manufactured by Ocean Optics Inc. It is a portable fibre optic spectrophotometer (PC2000) fitted with a diffraction grating whose characteristics are shown in Figure 5-1: 600 lines per mm, 650nm spectral range, best efficiency ($>30\%$) between 350 and 850nm with a maximum at 500nm. It is a linear CCD array silicon detector type. The light enters the spectrophotometer by means of a fibre optic through a slit of $25\mu\text{m}$ width and $1000\mu\text{m}$ height. The optical resolution of the instrument is a function of the number of detector elements (2048 for a PC2000) and the entrance slit, which is 1.33nm resolution in our case. Owing to the diffraction grating efficiency and the fact that measurement will be made in an aqueous medium, it was decided to limit absorption measurement to the 400 to 700 nm band. The spectrometer was connected to the integrating sphere with a $1000 \mu\text{m}$ diameter fibre optic.

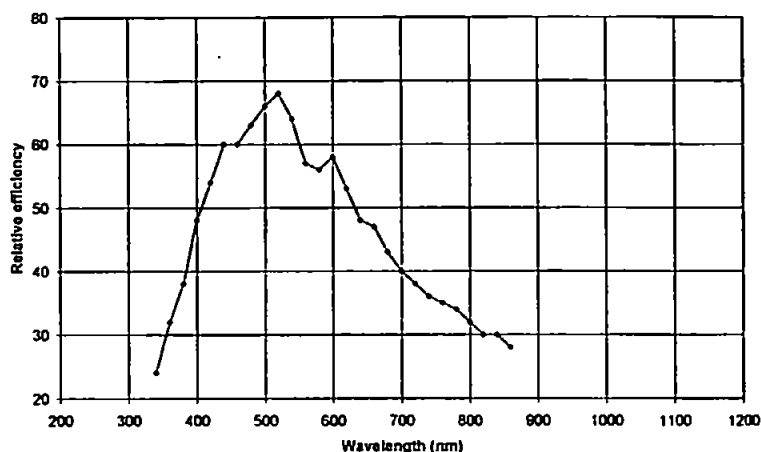


Figure 5-1: Efficiency of the spectrophotometer's diffraction grating (www.oceanoptics.com)

5.3. *The integrating sphere*

The second and most important part of the device is the integrating sphere. An integrating sphere is usually used for calibration purposes. A light source illuminates the sphere and the highly reflecting properties of the sphere make the light bound many times on the wall so that a diffuse light field is generated. Standard integrating spheres are coated on the inner side with barium sulphate, which gives the reflective properties of the sphere. Unfortunately, barium sulphate is highly soluble and a standard integrating sphere can not be filled with an aqueous solution. A solution proposed by *Kirk (1997)* was to use a round-bottomed flask embedded in barium sulphate. A basic prototype following this idea was build and used as a base to test various light sources and make the first attempts at absorption measurement.

5.4. *First prototype*

Two basic prototypes following the suggestion of *Kirk (1997)* were built for a first assessment. The first one was without a baffle, that is the detector was able to receive a proportion of direct light. The second was fitted with a baffle to protect the detector from direct illumination.

5.4.1. Prototype sphere without baffle

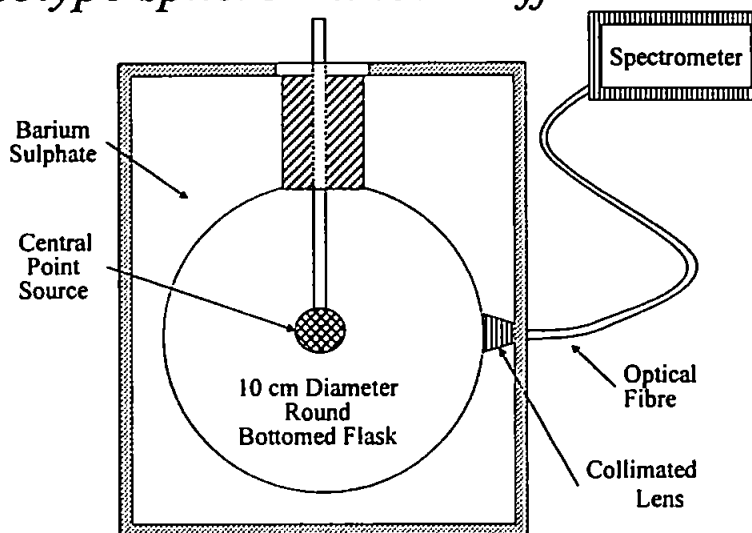


Figure 5-2: First version of the prototype PSICAM. Single neck round bottomed flask.

The first prototype PSICAM (Figure 5-2) was made out of a 500-ml round-bottomed flask with a 24/29 ground glass neck embedded in barium sulphate as suggested by Kirk (1997). The light source was a small tungsten bulb (12V, 3 Watts) within a diffusing Delrin sphere located at the centre of the cavity by means of a white plastic stem passing through the neck of the flask. The light collector was a 10 degrees field of view collimated lens looking toward the light source and fitted to a fibre optic via a SMA connector. The spectrophotometer therefore measures a radiance ratio rather than an irradiance ratio. This simplification from Kirk's theory (1997) is acceptable if the light field within the sphere is isotropic. The spectral distribution of the light field within the sphere was then recorded with the PC2000 spectrophotometer. Although the light source was only 3 Watts, the integration time required for the experiment carried out with this system never exceeded 600ms. This basic and low cost version of a PSICAM was used for a preliminary assessment of the instrument.

5.4.1.1. Reflectivity measurement

For the first experiment with this prototype, we tried to calculate the reflectivity of the cavity. To do this, we used a standard black solution. Its absorption spectrum was measured on

an UNICAM Helios spectrophotometer (Figure 5-3, bottom). The dye solution was chosen to be fairly absorbing relative to pure water in order to minimise the possible errors with pure water standards. The transmittance of this solution was then measured in the PSICAM (Figure 5-3 top). The reflectivity was consecutively calculated as proposed in the literature (Kirk, 1997; Figure 5-4).

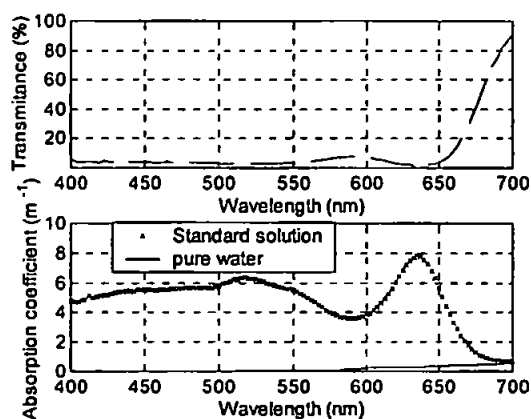


Figure 5-3: Transmittance of the standard solution relative to pure water (top). Absorption spectrum of the dye solution (bottom)

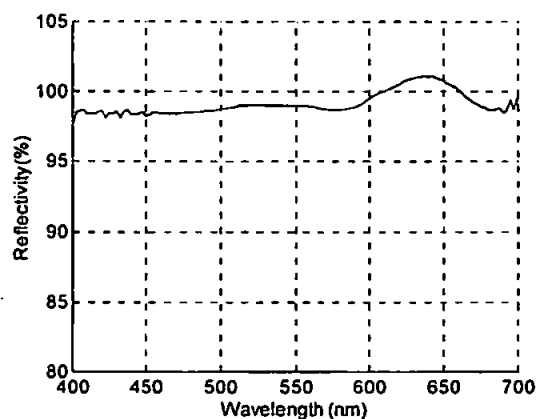


Figure 5-4: Reflectivity spectrum of the cavity

The calculated reflectivity has an average of 99.12% for the studied wavelength, 98.70% if we except the portion of the spectrum where it is higher than 100%. This artefact in the red region of the spectrum was first attributed to the imperfection of the prototype: material of the light source, stability of the light, the cavity not being a perfect sphere. Despite the reflectivity spectrum deduced from the experiment, an attempt was made to calculate the absorption spectrum of a dye solution.

5.4.1.2. Absorption measurement

For this experiment the absorption of a green standard solution ($C=0.05\text{ml/l}$) was used. The absorption spectrum of the standard solution was first measured in a 1cm path length cuvette with a UNICAM Helios spectrometer. The transmittance of the solution was then measured relative to pure water with the PSICAM.

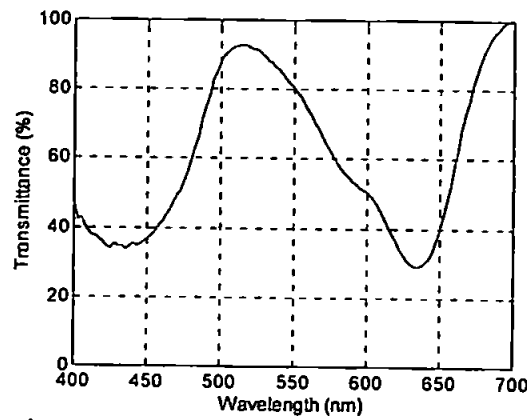


Figure 5-5: Transmittance spectrum of the green standard measured with the PSICAM.

For the calculations, three reflectivity spectra were used: the calculated spectrum of Figure 5-4, the average 99.12% calculated for the total spectrum and the average of 98.70% which was calculated excluding the portion of the spectrum higher than a 100%. The results of these calculations are presented from Figure 5-6 to Figure 5-11. In the first column, are presented the calculated absorption spectrum (dotted line) compared to the standard (solid line) for each value of the reflectivity. In the second column are represented the corresponding calculated versus standard absorptions for each reflectivity considered. On those, the straight line corresponds to the one to one relationship.

For Figure 5-6, where the calculated reflectivity was used, the general shape of the absorption spectrum is correct except for both peaks (from 400 to 450nm and 600 to 650nm) where the values are underestimated. The best recovery appears for the lower absorption values, which corresponds to transmittances higher than 60%. In the blue part of the spectrum, the calculated absorptions appear noisy in comparison to the rest of the spectrum, which is not surprising since both the reflectivity spectrum (Figure 5-4) and the transmittance (Figure 5-5) are noisy in this part of the spectrum. In the red part of the spectrum, for the region of the spectrum where ρ is higher than 100%, the reflectivity is underestimated. Looking at the relationship between calculated and standard absorption (Figure 5-7), it appears that the values of absorption below 0.3m^{-1} approximately follow a one to one relationship, the higher ones

being underestimated overall. One other possibility of errors for the peaks of the absorption is that we may have gone beyond the linear domain of the PSICAM.

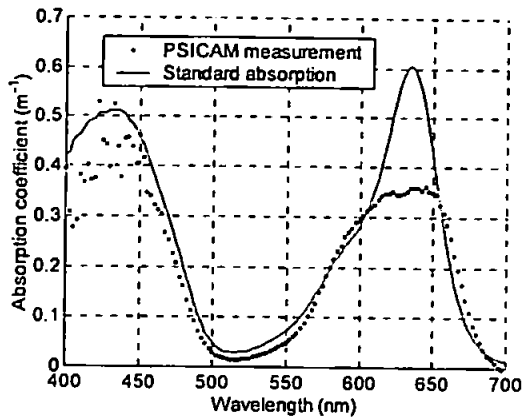


Figure 5-6: absorption spectrum of the dye solution; ρ spectrum

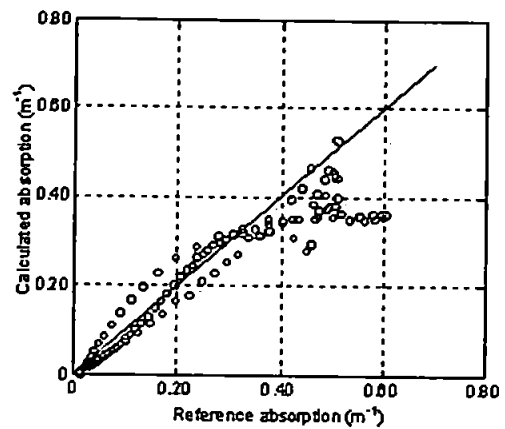


Figure 5-7: Calculated absorption versus real absorption; ρ spectrum

If we assume the same value of reflectivity for the total spectrum, it follows that the value of ρ is overestimated for the blue part of the spectrum and underestimated for the red part of the spectrum. Doing this the results remain relatively unchanged for the green wavebands where the absorption is minimum. The consequences for the blue and red regions are different. The absorption being largely underestimated for the first one and largely overestimated for the last. These two features appear very clearly on Figure 5-9 and Figure 5-11 where the graphs are divided in two distinct parts. From the knowledge of the previous chapter, it is no surprise that the results can be very different depending on the value of the reflectivity spectrum used for the calculations.

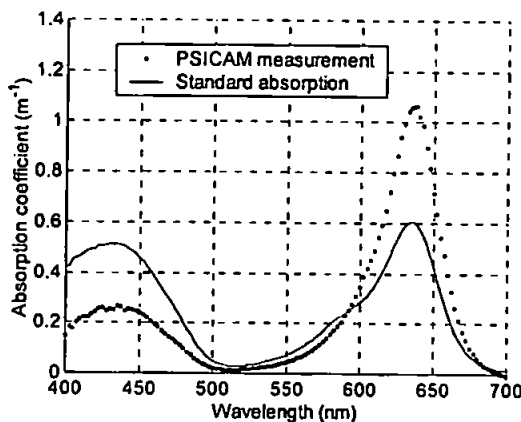


Figure 5-8: Calculated absorption with $\rho=99.12\%$

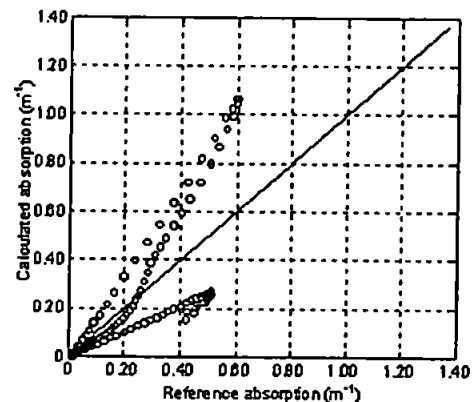
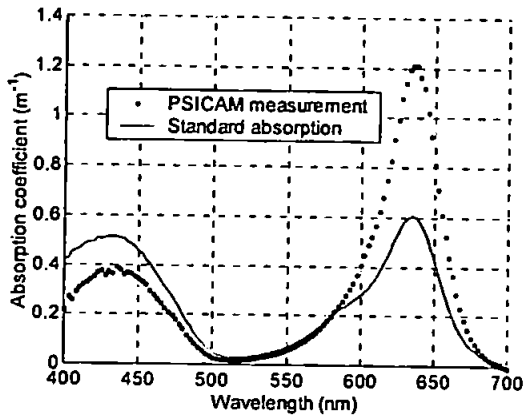
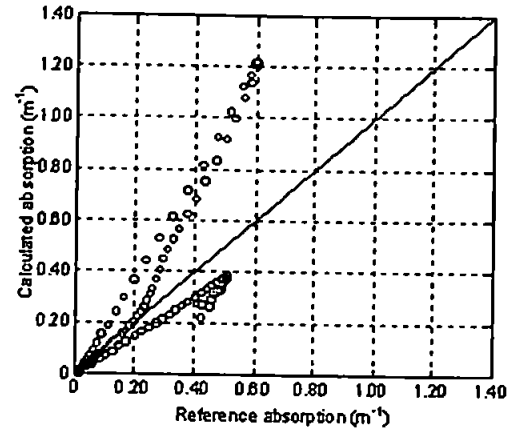


Figure 5-9: Calculated absorption versus real absorption; $\rho=99.12$

Figure 5-10: Calculated absorption with $\rho=98.70$ Figure 5-11: Calculated absorption versus real absorption; $\rho=98.70$

This first test with a prototype PSICAM showed, as in the previous chapter, the importance of the reflectivity in the calculations, and that despite using an approximated reflectivity spectrum and a crude approximation of the prototype, the general shape of the absorption spectrum could be recovered.

One aspect that must be pointed out with this prototype is that the light detector (a 10° field of view collimated lens) is looking toward the light source. By definition, no direct light should be measured by the detector for a proper integrating cavity. This was changed for a second version of the instrument by adding a baffle on the light source to protect the detector from direct illumination (Figure 5-12).

5.4.2. Prototype sphere with baffle

5.4.2.1. Reflectivity measurement

The first consequence of adding a baffle was the need to increase the integration time up to 800ms to obtain acceptable readings. As before, we tried to estimate the reflectivity of the sphere with this added baffle on the light source (Figure 5-12). The same experiment was carried out, measuring the transmittance of a standard solution relative to pure water.

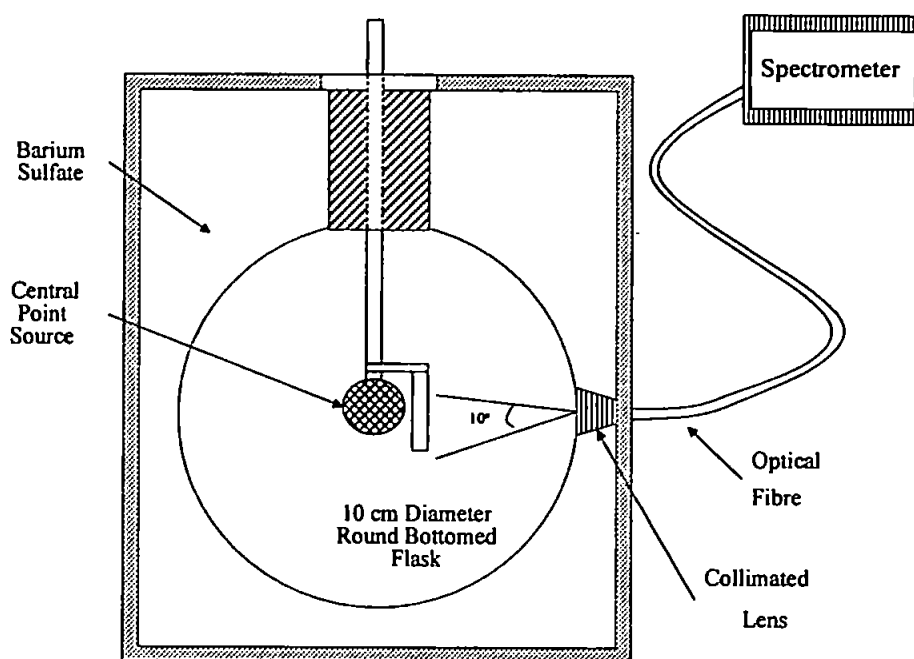


Figure 5-12: First version of the prototype PSICAM. Single neck round bottomed flask. Light source with a baffle.

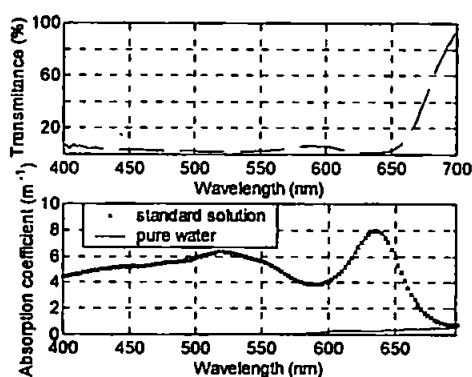


Figure 5-13: Transmittance of the standard solution relative to pure water (top). Absorption spectrum of the dye solution (bottom)

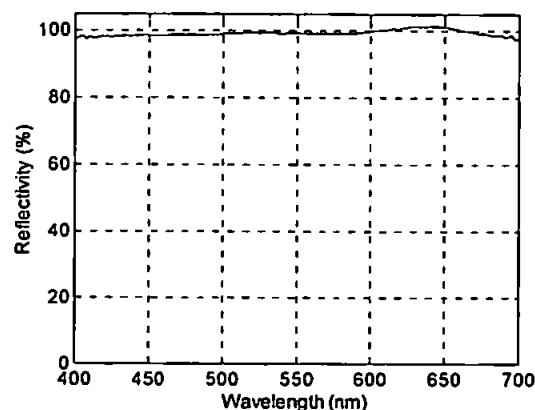


Figure 5-14: Reflectivity spectrum of the cavity

The calculated reflectivity is apparently higher than 100% between 600 and 650nm. The first assumption that the calculation was affected by the absence of a baffle appears erroneous. The quality of the materials used for the prototype, however were still held responsible for this artefact.

5.4.2.2. Absorption measurement

Despite the problem of calculating the reflectivity spectrum, an attempt to calculate the absorption coefficient of a standard solution was carried out. We measured the transmittance of

two green solutions of known absorption ($C=0.1$ and 0.2ml/l) relative to pure water. The absorption spectrum of each solution was measured on a Unicam UV-Visible spectrophotometer. The absorption spectrum was then calculated using the reflectivity spectrum of Figure 5-14 and its average $\rho=0.9968$.

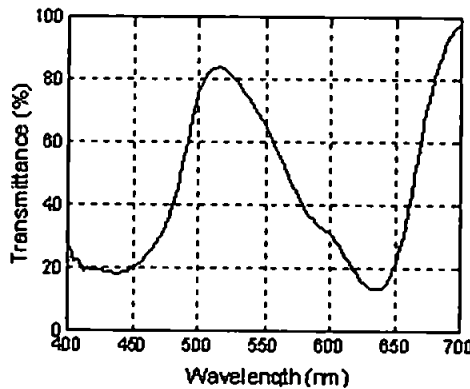


Figure 5-15: transmittance spectrum relative to pure water of $C1=0.1\text{ml/l}$

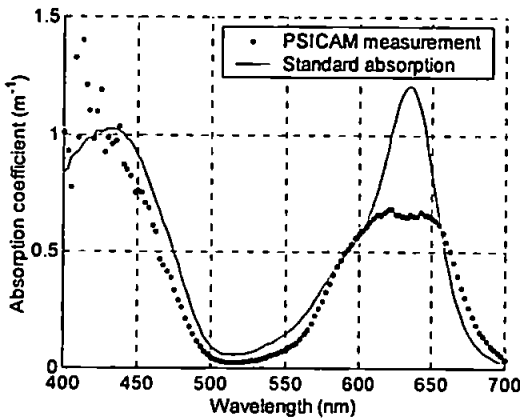


Figure 5-16: Absorption spectra of solution $C=0.1\text{ml/l}$ with the calculated ρ

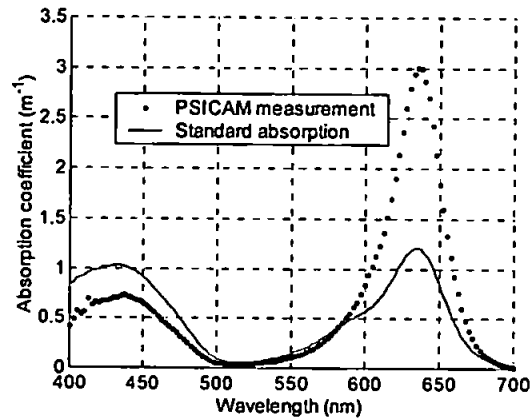


Figure 5-18: Absorption spectra of solution $C=0.1\text{ml/l}$ with average $\rho=98.96$

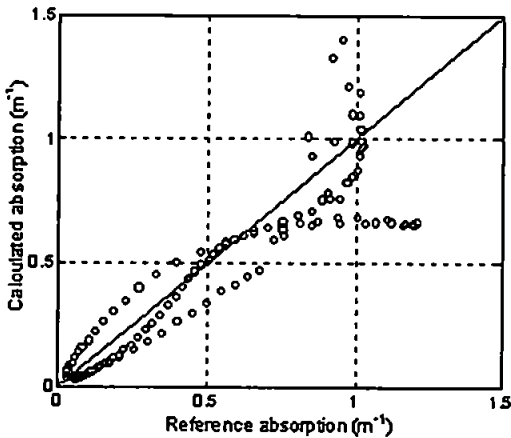


Figure 5-17: PSICAM measurement versus standard absorption

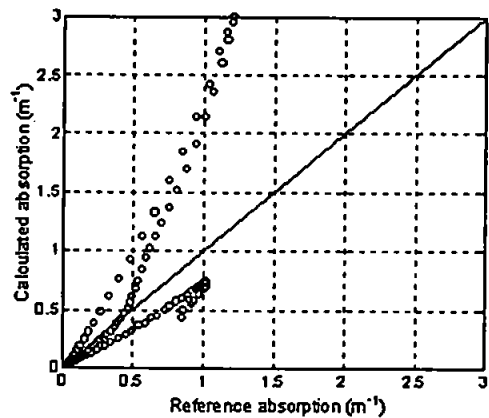


Figure 5-19: PSICAM measurement versus standard absorption

Despite adding a baffle on the system to protect the detector from direct illumination, the result of the experiment remains very similar. When the measured reflectivity spectrum was used for the calculations, the main error occurred between 600 and 650 nm where the calculated reflectivity was higher than 100%. The results are however better than previously in the blue part of the spectrum although still quite noisy. This noisy signal originates in the illumination of the system and not in the reflectivity used for the calculation. When the average reflectivity was used, the same features as before were observed: the best fit in the green part of the spectrum underestimated in the blue wavelengths and overestimated in the red ones. This lead to the suggestion that the PSICAM could be less efficient with low transmittance values, i.e. the linearity domain of the system.

5.4.3. *Discussion*

There are various facts that can explain the important discrepancies between the absorption measured with the PSICAM and with a standard bench spectrophotometer. The obvious reason is the value of the wall reflectivity used for the calculations. It proved more difficult to measure it than expected. We have seen earlier that it is a critical parameter for the calculations of the absorption. The fact that we calculated reflectivity values higher than 100% prove that our procedure failed. The dye solutions were very concentrated with a transmittance of less than 10% for most of the spectrum. Moreover, this first prototype, with or without a baffle was very basic. The materials we used to make the light source were of low quality in terms of reflectivity. Using a single neck bottle, we had to remove the light source each time a new liquid was pored into the sphere, which contributed to the unreliability of the light input. An attempt to estimate this source of error showed that up to 7% variation could occur by

removing and putting back the light source. A last point about this system is that having a light bulb within a diffusing sphere, the light source was heating up fairly quickly. This approach for the light source was abandoned for the next prototype.

This first version of the instrument enabled us to have a first approach to the instrument using basic material for the light source. No further experiments were made with this system but a new improved version was built based upon what had been learned from the first one.

5.5. Second prototype

The improved version (Figure 5-20) was based upon a two-neck round-bottomed flask in order to have two separate ports, one for the stem of the light source, one for the input and output of water. With this arrangement, the light source was not removed throughout the set of experiments. This prevented any distortion relative to the reference measurement. As previously, the glass flask was embedded in barium sulphate. This time, the bedding was done with more care to produce a surface as homogenous as possible. The barium sulphate was sieved through a 500 μm grid to remove the coarse grains. Again, the sensor was a collimated lens so that a radiance ratio and not an irradiance ratio was obtained to calculate the transmittance. The sensor had a ten degrees field of view and was positioned at an angle so that no direct illumination from the light source was picked up. The sensor looks toward the light source in the vertical plane and makes a 30 degrees angle with the horizontal plan looking toward the bottom part of the flask (Figure 5-20). The flasks used to build both integrating cavities were standard chemistry apparatus, so was not perfectly spherical. Moreover, the necks added extra volume to the sphere. For the experiments, we assumed a perfect sphere of 5.25 cm radius.

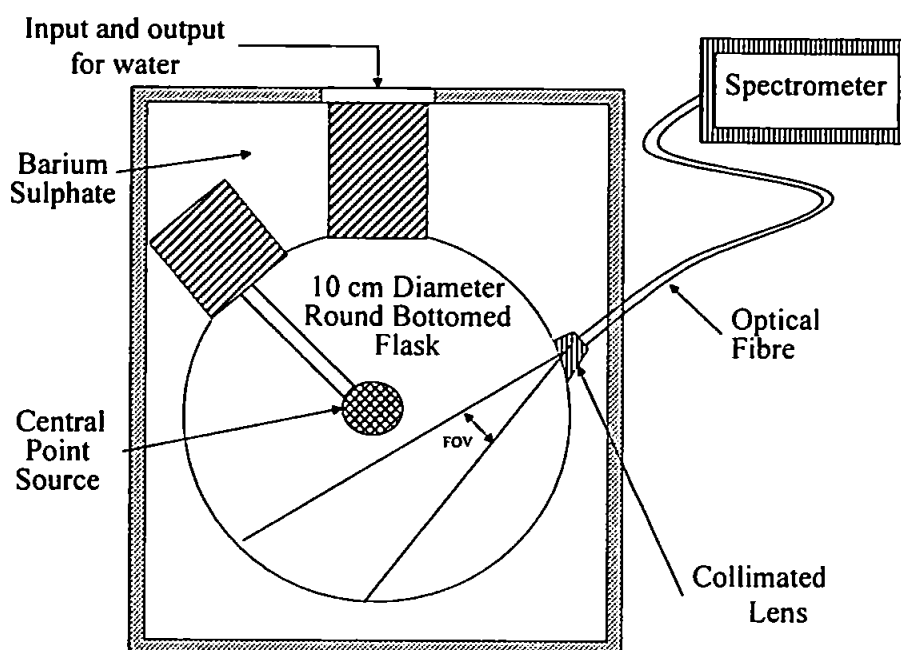


Figure 5-20: Second prototype

5.5.1. Light source

The first prototype used a tungsten light bulb within a Delrin sphere to create the isotropic light source. One of the problems with this light source was that it was heating up very quickly. This could potentially cause errors in the measurements. Making a proper point source for the instrument was the biggest challenge. This light source needed to be small so as not to interfere too much with the cavity, but powerful enough to strongly illuminate the cavity. With this second prototype, a number of illumination systems were tried.

5.5.1.1. Ocean Optics Inc. LS-1 tungsten light source.

Experiments were conducted using the halogen tungsten light source (6.5W) provided with the Ocean Optics spectrometer as a light source for our PSICAM. The LS-1 light source was adapted to fit a three millimetres diameter fibre bundle. The illuminated side of the bundle was a Teflon stem terminated by a Teflon sphere. This light source was actually too weak to properly illuminate the sphere so that excessively long integration times were required to obtain usable signals.

5.5.1.2. *White Light Emitting Diode.*

Experiments were also carried out with white LEDs. Three LEDs were placed in a Teflon cylinder and held in the centre of the cavity by a Teflon stem. For practical reasons the point source was cylindrical in this case. The advantage of using LED's was that they do not produce heat and therefore can be like our first prototype placed within the sphere. Again, the illumination of the cavity was rather too small, and integration times required to get measurable signals were around 40 second (see emission spectrum in Figure 5-21).

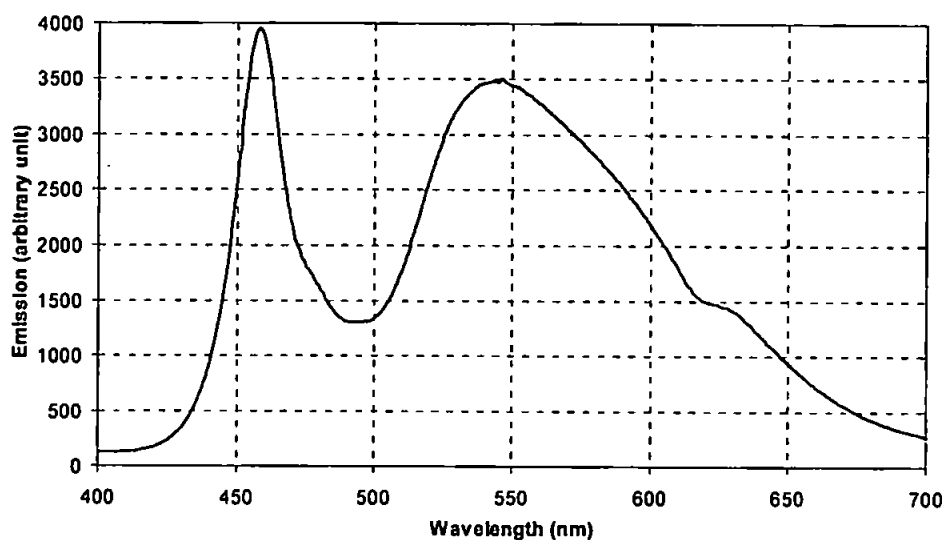


Figure 5-21: Emission spectrum of a white LED

5.5.1.3. *Halogen generator and fibre bundle.*

The last light source tried consisted of a 75W-halogen generator (see emission spectrum, Figure 5-22) especially designed to fit a fibre bundle.

As before, the end of the bundle was held in a Teflon stem and terminated by a Teflon bulb. The fibre bundle used was six millimetres in diameter and could therefore carry a significantly higher amount of light. On the other hand this bundle increased the diameter of the stem in comparison with the three millimetres one. The experiment carried out with this light source showed that it was far the brightest one and allowed a significant reduction in the integration time. It was therefore the light source chosen for this second prototype. An attempt

with this halogen light fitted to a three millimetres fibre bundle was also investigated. The sphere and teflon stem diameter was indeed smaller but the illumination of the integrating sphere too weak.

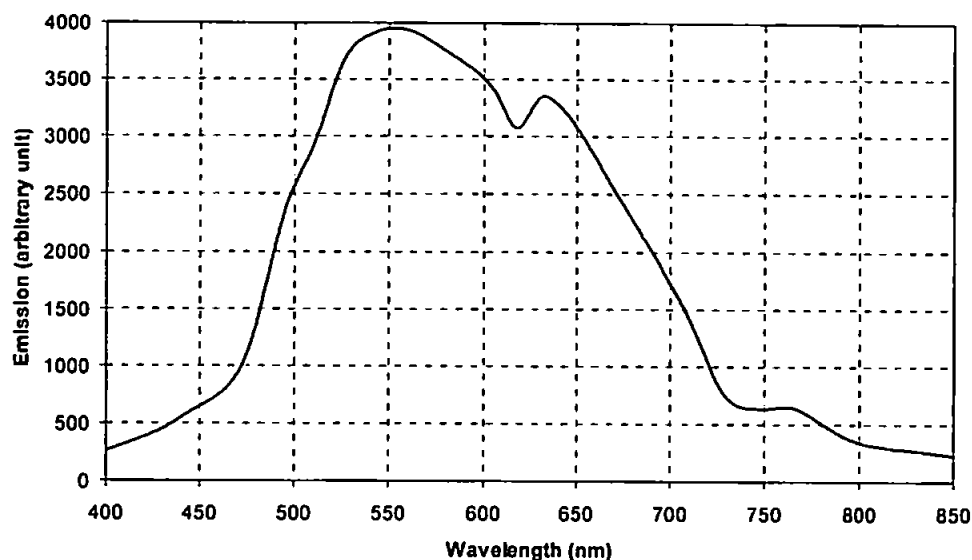


Figure 5-22: Emission spectrum of the halogen generator

5.5.1.4. Stability of the light source

As pointed out previously, one potential source of error from the light source was that we had to remove it each time a new sample needed to be pored into the sphere. This was corrected by building PSICAM with a non removable light source. The other source of error from the light source was its stability of emission over time. The stability of this halogen generator was investigated with the OOI PC2000 spectrophotometer. The experiment consisted of measuring the evolution of its emission spectrum with time. For this experiment, a collimated lens fitted to the spectrometer through a 1000 μ m fibre optic was used. One measurement every minute was taken over three and a half hours. Figure 5-23 shows the evolution of the percentage change relative to the first measurement, taken immediately after the light was switched on.

This graph shows that the highest variations occur for the shorter wavelengths with a significant difference between 400 and 425 nm. The smallest variations occur for wavelengths

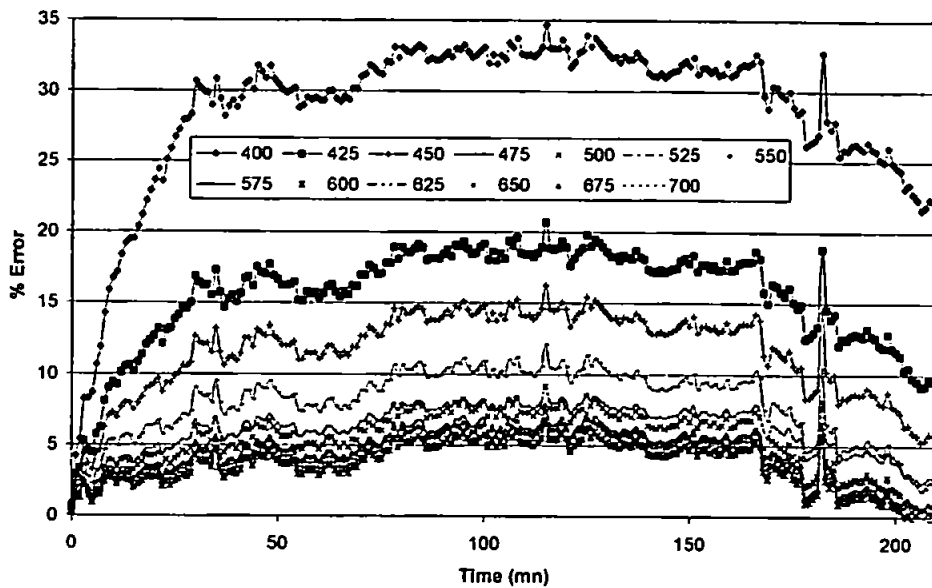


Figure 5-23: Stability of the halogen generator for 13 wavelengths

between 500 and 700nm. Overall this graph shows that a warming up time of forty minutes is necessary to achieve even moderate stability ($\pm 2\%$). In order to minimise this problem, a reference measurement is taken between each sample measurement. The halogen bulb is in this configuration powered by a power supply, which is not highly stabilised. The system was tested, however with a different power supply (Figure 5-24). The same procedure was followed to test the stability of the light source with a Gresham Lion Ltd. power supply.

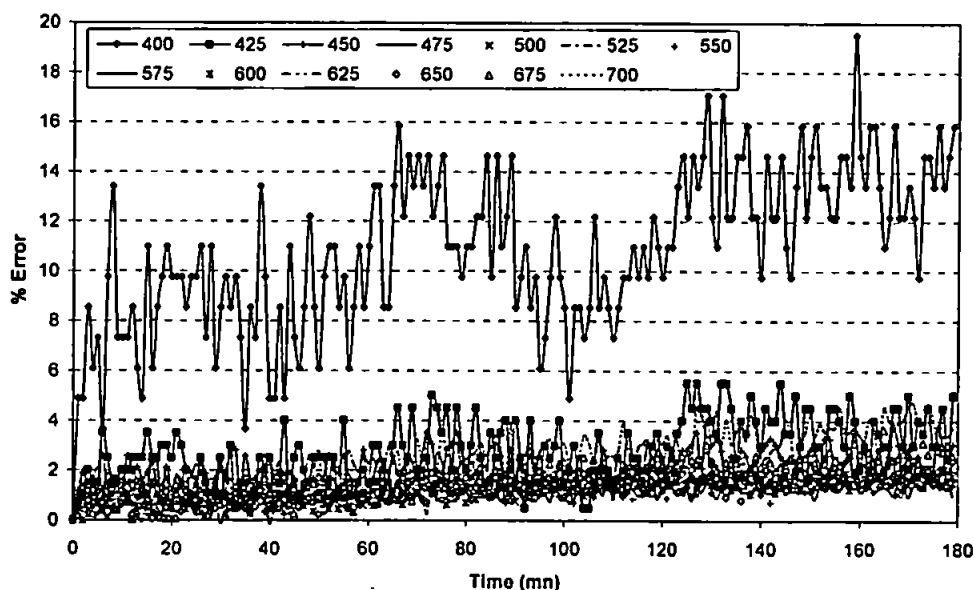


Figure 5-24: Stability of the light source with Gresham Lion Ltd. power supply.

Figure 5-24 shows the result of this experiment carried out over 180 minutes. As before, the 400 and 425 nm wavebands appear to be the most unstable whatever the warming up time. However, the rest of the spectrum comes out much more stable with this power supply. Figure 5-25 shows a detail of Figure 5-24 over the range 110 / 120 mn. It shows that over this period of time, up to 5% variation can be expected at 400 nm and up to 2% variation for 425 nm. For the rest of the spectrum less than 2% variation is encountered.

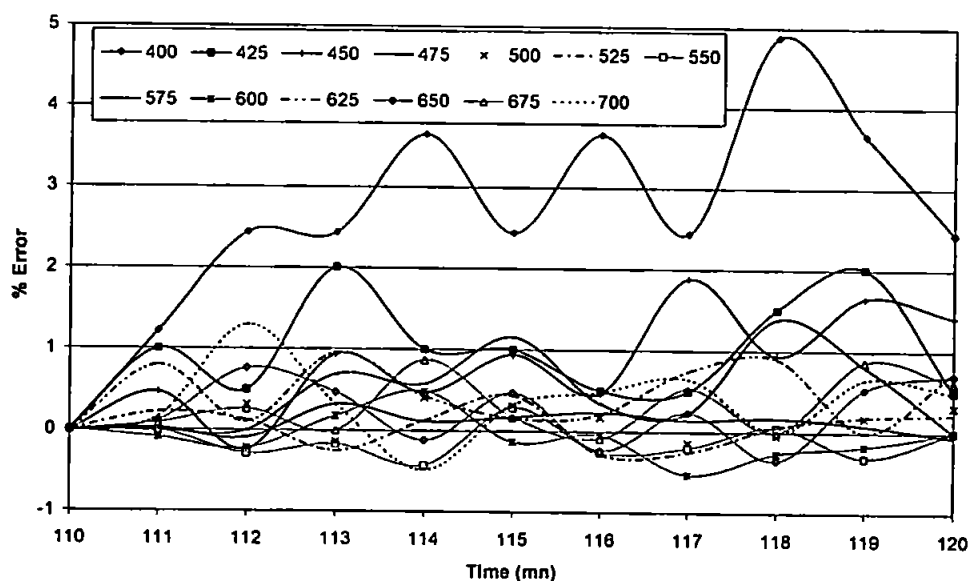


Figure 5-25: Detail of Figure 5-24 for the range 110 / 120 mn

Finally, the stability of the spectrophotometer was tested (Figure 5-25). The procedure consisted of covering the input port of the OOI PC 2000 and measuring the signal with the same integration time as for the experiments with the PSICAM. Surprisingly, this experiment showed that the spectrophotometer itself was responsible for an important part of the variation.

The Gresham Lion Ltd. power supply was chosen for the experiment but a blank was done after each samples to limit the risks of deviation from the reference measurement. Five to ten minute is indeed a reasonable amount of time to make a reference measurement, empty the

sphere with a peristaltic pump, pour the sample, empty again and pour pure water in again for a new reference measurement.

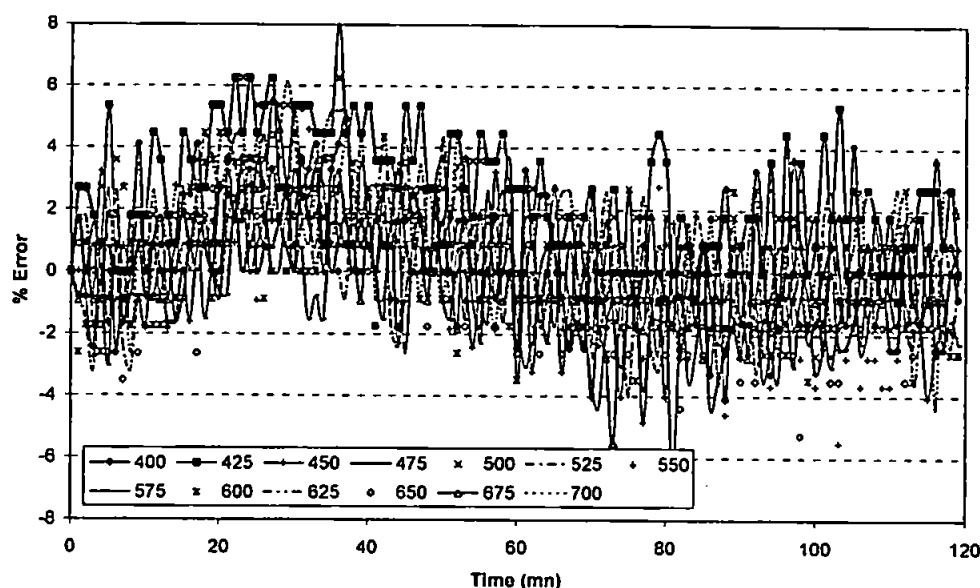


Figure 5-26: Stability of the spectrophotometer

5.5.2. Experiment with standard solutions

As for the first prototype, the first experiments with this new prototype were carried out with standard dye solutions. This time the standard solutions used were of various colours. The first step was therefore to calculate the molecular absorption of those standard dyes. The absorbance spectra of the standard solutions were measured with a UNICAM Helios spectrophotometer using a one centimetre path length cuvette (Figure 5-27 to Figure 5-30). The measurements were carried out using four dye solutions (green, blue, red and black) for different sets of concentrations (Table 5-1). Using a one centimetre cuvette, solutions of different concentration had to be measured in the PSICAM and in the spectrophotometer. For this reason the absorption coefficient of the more diluted standard solution measured with the PSICAM were derived from the measurements of concentrated solution in the UNICAM

spectrophotometer. The principle was to prepare a stock solution of the dyes and then prepare the samples for both the PSICAM and the spectrophotometer from the same stock solution.

Table 5-1: Set of dye concentrations used to calculate the linear range of the spectrometer

Dye Solutions	Concentration (ml l ⁻¹)								
Blue	0.5	1.0	1.5	2.0	2.5	5	10	25	50
Green	1	5	10	15	25	50	#	#	#
Red	0.5	1	1.5	2	5	10	25	#	#
Black	0.1	0.25	0.5	1.0	2.0	2.5	#	#	#

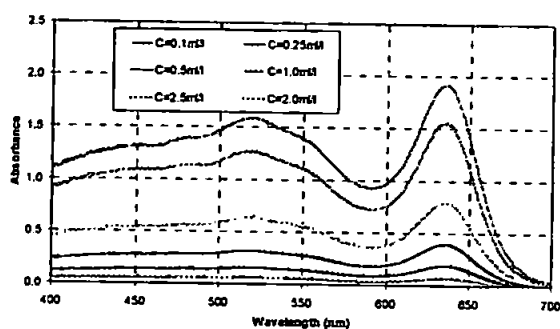


Figure 5-27: Absorbance spectra of the black solutions.

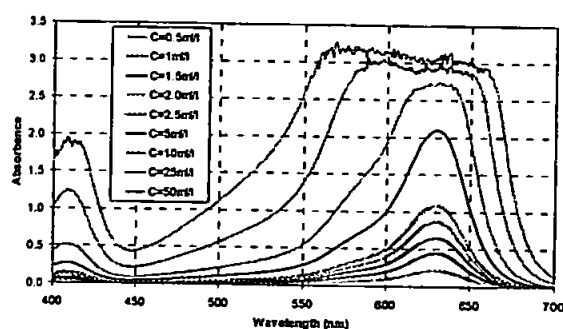


Figure 5-28: Absorbance spectra of the blue solutions.

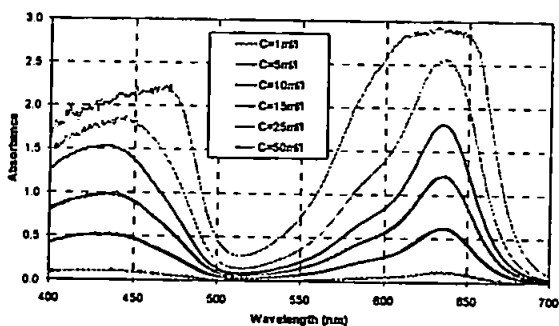


Figure 5-29: Absorbance spectra of the green solutions.

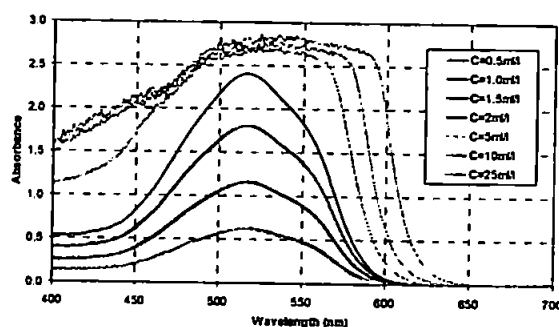


Figure 5-30: Absorbance spectra of the red solutions.

From the absorbance spectra of each solution was calculated the molecular absorption coefficient ($a_{\text{Mol}}(\lambda) = A(\lambda)/(l \cdot C)$ (m⁻¹.ml⁻¹.l); Figure 5-31, Figure 5-33, Figure 5-35 and Figure 5-37). It can be seen that for the concentrations above the linear range of the instrument the resulting molecular absorption is very much underestimated. Finally, using the concentrations within the linear range of the instrument, an average molecular absorption was calculated (Figure 5-32, Figure 5-34, Figure 5-36 and Figure 5-38). The maximum concentrations taken

into account for the average molecular absorption were 5ml/l, 15ml/l and 2ml/l for the blue, green and red solutions respectively. The set of concentrations used for the black dye remained in the linear range of the instrument. These values of molecular absorption were then used as a reference for the experiments carried out with the PSICAM. The absorption coefficient of a given solution being calculated as $a(\lambda) = a_{Mol}(\lambda) \cdot C$ where C is the concentration in $ml.l^{-1}$ of the standard solution.

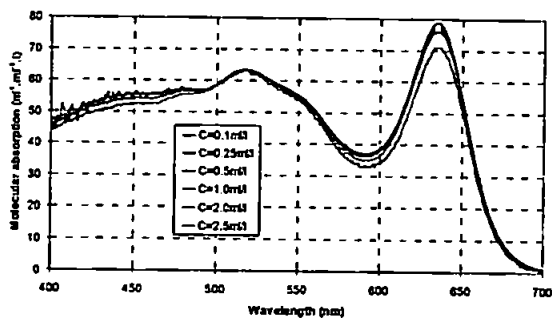


Figure 5-31: Molecular absorption for the black solutions.

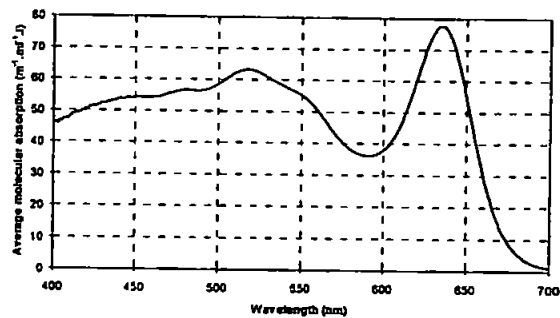


Figure 5-32: Average molecular absorption for the black solution.

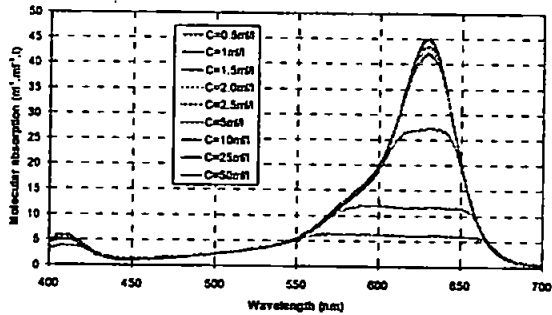


Figure 5-33: Molecular absorption for the blue solutions.

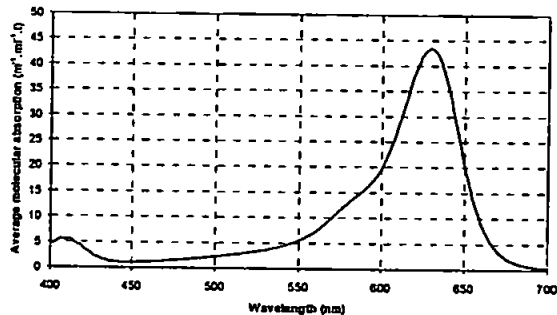


Figure 5-34: Average molecular absorption for the blue solution.

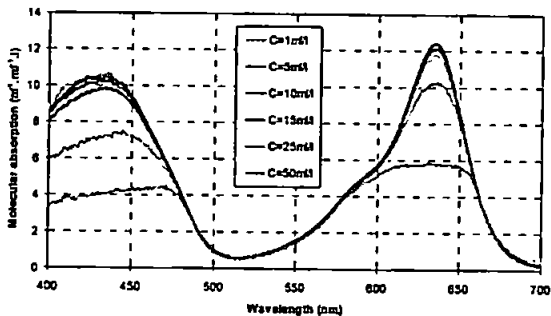


Figure 5-35: Molecular absorption for the green solutions.

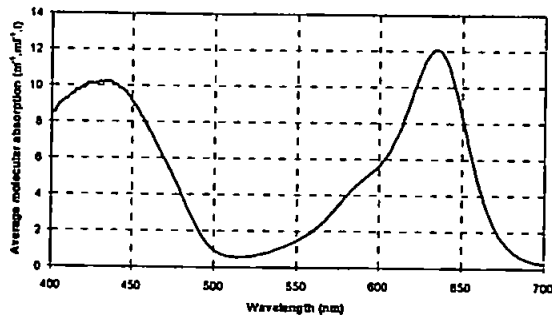


Figure 5-36: Average molecular absorption for the green solution.

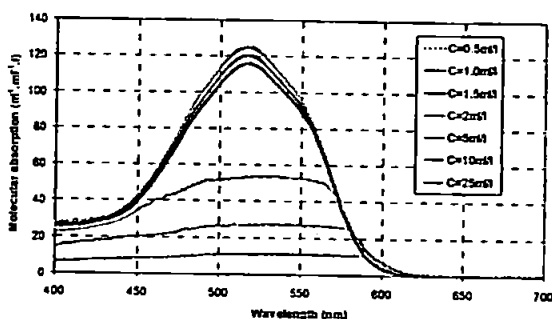


Figure 5-37: Molecular absorption for the red solutions.

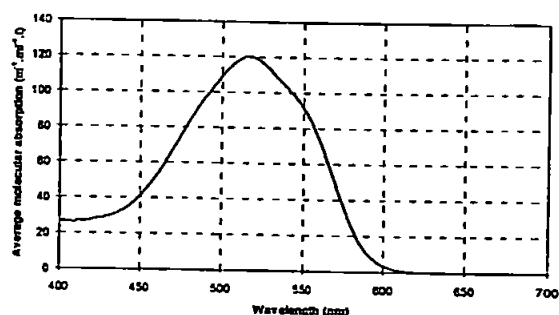


Figure 5-38: Average molecular absorption for the red solution.

5.5.2.1. Calculation of the reflectivity

To estimate the reflectivity of the sphere, two standard black solutions of known absorption coefficient a_A ($C=0.01\text{ml.l}^{-1}$) and a_B ($C=0.03\text{ml.l}^{-1}$) were used. The transmittance of solution B was measured relative to solution A. The reflectivity was then calculated from the equations of transmittance (Equation 4-5).

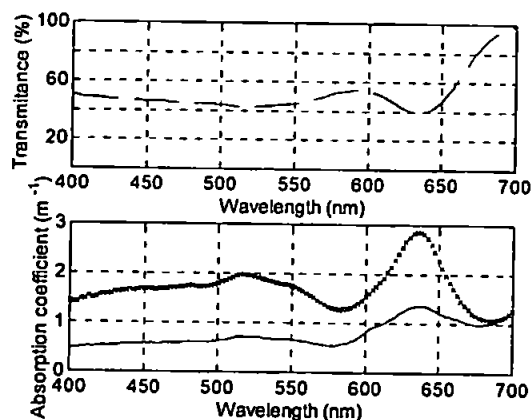


Figure 5-39: Transmittance spectrum of solution B relative to A (top). Absorption spectrum of the two solutions.

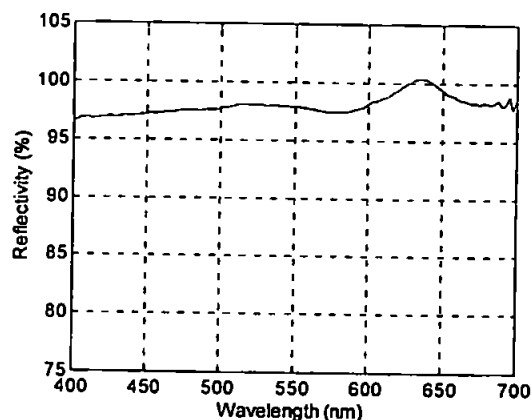


Figure 5-40: Measured reflectivity spectrum

The black solutions used are more diluted than previously, which results in a transmittance spectrum higher than in the previous experiments (Figure 5-39). It is always higher than 40%. The spectrum remains between 40 and 60% from 400 to 650 nm and increases to 100% from 650 to 700 nm. The reflectivity spectrum calculated (Figure 5-40) has an average of 97.97% and is maximum around 640 nm. As in the previous experiments, the spectrum is still slightly higher than 100% in this region. This reflectivity spectrum was subsequently used for

the measurement of four standard solutions: blue, green, red and black of concentration 0.1, 0.1 and 0.02ml/l and 0.01ml/l respectively.

5.5.2.2. Calculation of absorption of standard solutions

For this experiment, four standard solutions were prepared and measured in the PSICAM. One reference measurement was made between each sample. The results of these experiments are presented in Figure 5-41 to Figure 5-48. For each solution is presented the absorption spectrum measured with the PSICAM (solid line) and calculated using the average molecular absorption calculated previously (crosses). The one to one relationship between the two techniques is also presented for each standard solution.

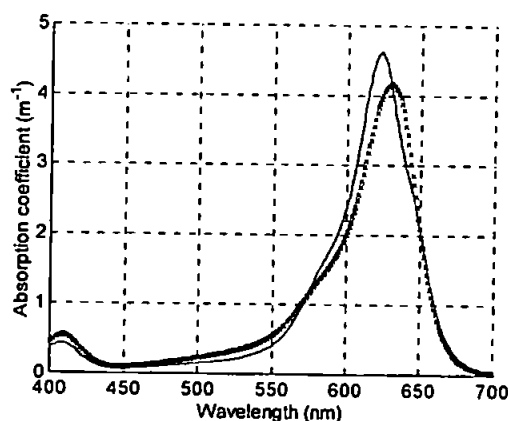


Figure 5-41: Blue solution absorption spectra.

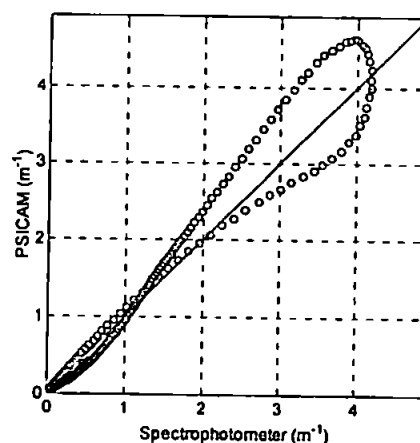


Figure 5-42: Blue solutions regression.

For most of the tested solutions, the PSICAM replicates the general shape of the absorption spectrum, except for the black solution. The best recovery occurs for the red solution in which, maximum absorption occurs around 520nm. The same characteristic occurs for the green and black solutions around 640nm which correspond to the portion of the spectrum where the calculated reflectivity is higher than 100%. In this area of both spectra, the absorption maximum is very much underestimated and the PSICAM spectrum shows two intermediate

maxima around 620 and 650 nm for both standard solutions. Surprisingly, this feature does not appear in the case of the blue solution which shows an absorption maximum at 630nm. This is probably related to the amplitude of the absorption maximum, much higher than for the blue and green solutions. The red solution is not affected by the reflectivity spectrum because it does not absorb for wavelengths greater than 610nm.

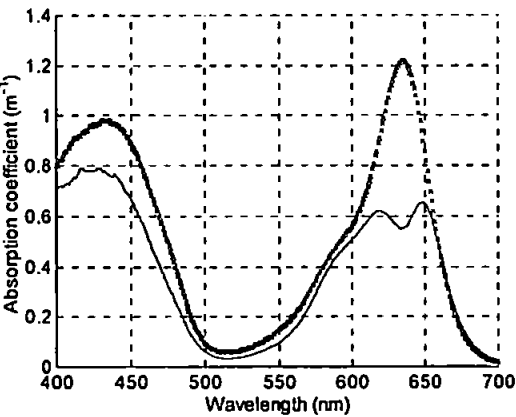


Figure 5-43: Green solution absorption spectra.

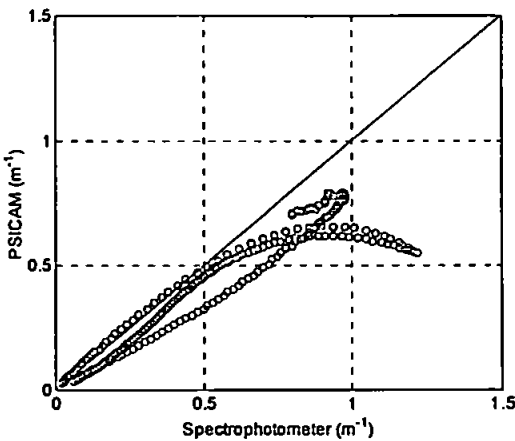


Figure 5-44: Green solution regression.

In general, the two instruments give comparable results for the lower absorption. The PSICAM tends to underestimate the standard absorption for the higher values except for the blue solution, which presents the highest absorption.

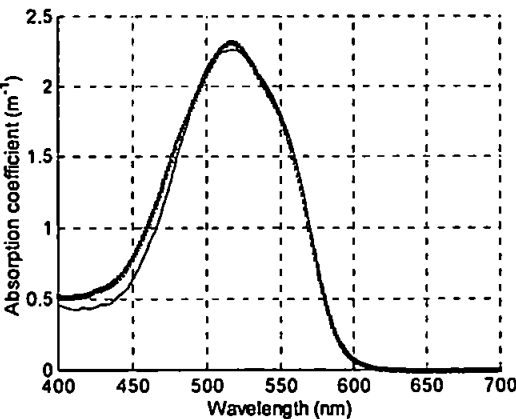


Figure 5-45: Red solution absorption spectra.

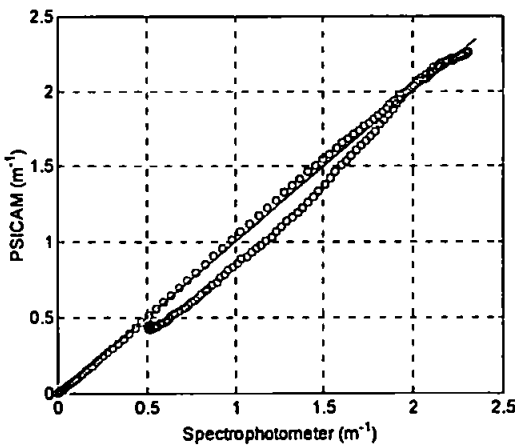


Figure 5-46: Red solution regression.

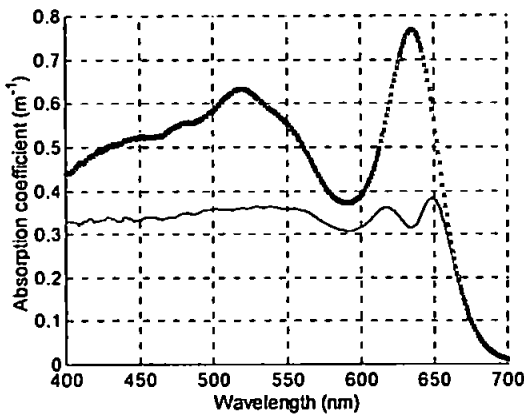


Figure 5-47: Black solution absorption spectra.

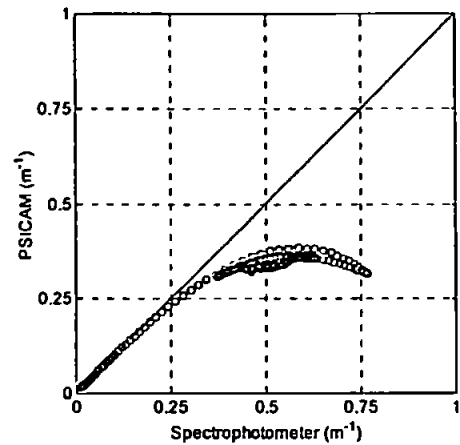


Figure 5-48: Black solution regression.

Figure 5-49 show the one to one relationship for all the measured solutions on a log-log scale to emphasizes the behavior at low absorption values. It is difficult to discriminate a trend on this plot. The majority of the values measured by the PSICAM are underestimated. What is revealed by this set of measures is the general imprecision of the instrument. The two marked artifacts on Figure 5-49 for the green and black solutions are however hardly understandable. For the black solution, the shape of the absorption spectrum is not replicates for the short wavelength. These artifacts occur for absorption ranges, which for other wavelength or other standard solutions have been measured without such marked discrepancies.

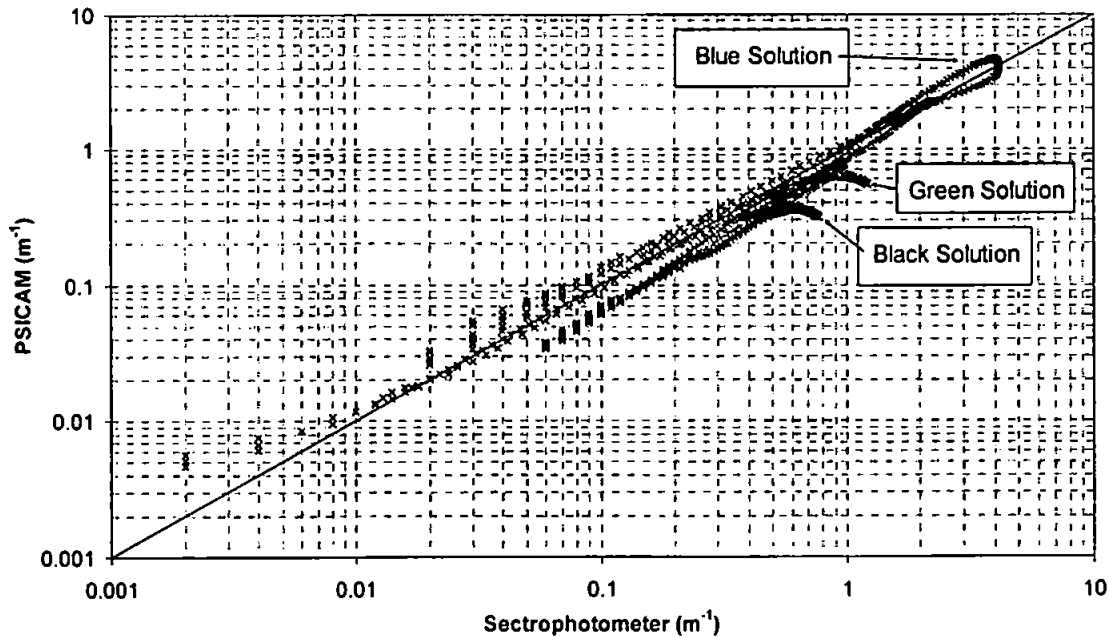


Figure 5-49: One to one relationship for all the measured solutions.

5.5.2.3. *Discussion*

The second prototype proved more accurate than the first ones using a single neck round-bottomed flask as an integrating sphere. Having two separate ports for the light source also seemed an improvement in terms of reliability of the reference measurement. The experiment carried out with standard solutions showed that the PSICAM can replicate the shape of the absorption spectrum although the errors are quite significant for some of the solutions. It is more than likely that these errors originate in the value of the reflectivity spectrum used for the calculations. This is the parameter that once again is the most important for the efficiency of the instrument and that we have not measured accurately enough so far.

This second prototype however is still not ideal. The errors relative to the stability of the light source have been dealt with although there is still scope for improvement. The light collector position has been changed so that no direct light is picked up from the source. The last uncertainty about the general design of the sphere is now the shape of the sphere. As mentioned previously, the sphere is not strictly spherical and the port for the water input adds an extra volume to the sphere. This effect on the efficiency of the PSICAM is difficult to quantify. For these reasons, a last prototype was built with an integrating sphere made of Spectralon, for which the diameter was much more accurately known.

5.6. *Spectralon prototype*

Spectralon is an optical material manufactured by Labsphere Inc. It is chemically similar to Teflon (polytetrafluoroethylene), which gives Spectralon similar chemical properties: it is chemically inert and hydrophobic. The principal difference with Teflon is that micro bubbles are injected during the process of fabrication, which gives Spectralon a highly reflective and Lambertian behaviour. The new integrating sphere was made of a 10.50 cm diameter Spectralon sphere. The light collector is like previously a 10° field of view collimated lens. The port for the

light collector is situated in the equatorial plan of the sphere and making a 30° angle with the vertical. The light source is still a 75Watts halogen generator. The light source is carried by means of a 6mm fibre bundle terminated by a Teflon sphere to produce a diffuse light source held at the centre of the integrating sphere with a Spectralon stem (Figure 5-50).

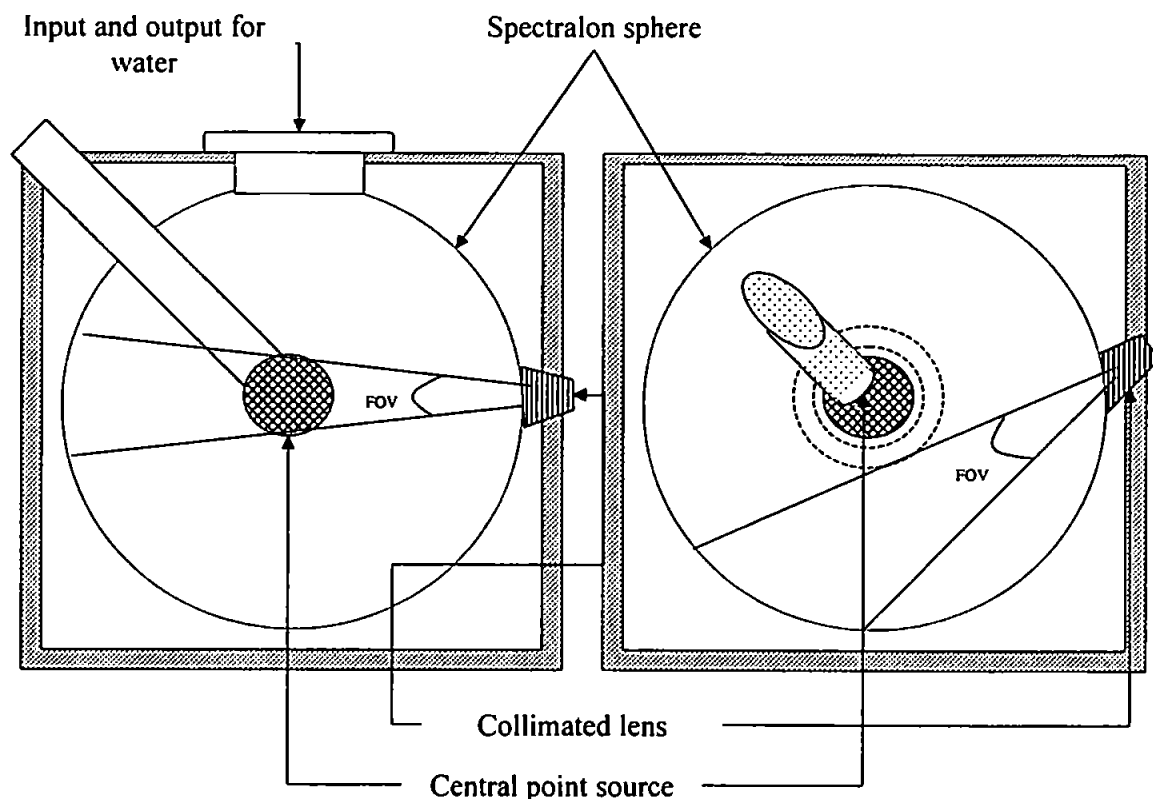


Figure 5-50: Spectralon prototype ; side (left) view, top view (right)

5.6.1. Spectralon prototype 1 cm cuvette

5.6.1.1. Reflectivity

The reflectivity of the cavity wall was calculated in the same way as for the previous prototype. A stock solution of the black dye was prepared. From this stock solution different concentrations were prepared and measured in a 1cm cuvette to calculate the molecular absorption coefficient. Then two diluted solutions $A=0.0025\text{ml.l}^{-1}$ and $B=0.005\text{ml.l}^{-1}$ were prepared from the stock solution; their calculated absorption spectrum is shown in Figure 5-51 (bottom). Their absorption spectrum was calculated knowing their respective concentrations. Finally, the transmittance of solution B relative to A was measured in the PSICAM (Figure

5-51, top) and the reflectivity calculated from the equation found in the literature (Equation 4-5, Figure 5-52). The transmittance spectrum remains between 60 and 80% from 400 to 650nm and then rises up to 100% from 650 to 700nm. The average reflectivity is 0.9947. It increases linearly from 0.9803 at 400 nm to 0.9997 at 674nm then increases rapidly to over 1. The last part of the spectrum is always noisy because the standard solutions do not absorb in this region.

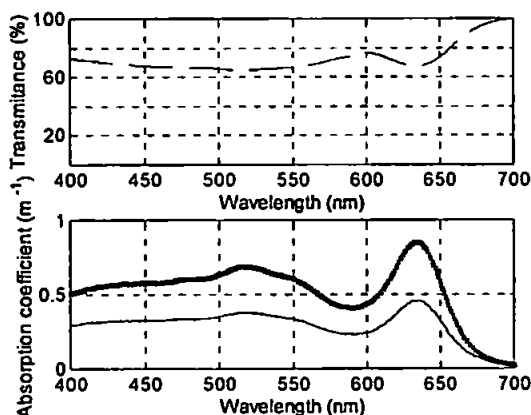


Figure 5-51: Transmittance of Solution B relative to A (top); Absorption spectrum of the standard solutions for the calculation of the cavity reflectivity (bottom).

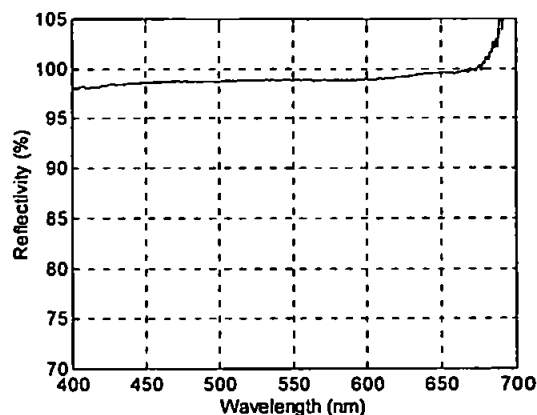


Figure 5-52: Calculated reflectivity spectrum.

5.6.1.2. Experiment with food dye

The reflectivity spectrum calculated above was then used to calculate the absorption spectrum of the standard solution. As previously, four different dyes were used: blue, green red and black. The concentrations used are displayed in Table 5-2.

Table 5-2: Set of concentrations for the standard solutions

	<i>C1</i>	<i>C2</i>	<i>C3</i>	<i>C4</i>
Blue	0.01	0.02	0.1	0.2
Green	0.01	0.02	0.1	0.2
Black	0.001	0.002	0.01	0.02

5.6.1.2.1. Blue standard, using Kirk's equation

Figure 5-53 displays the transmittance spectra of the blue solutions measured with the PSICAM. The blue standard has two transmittance minima: a first one around 420 and a second

more important one around 640nm. The blue dye thus covers a wide range of transmittances across the visible spectrum from 100 to about 5% for the selected concentrations. However, for the two most concentrated solutions ($C=0.1$ and 0.05ml.l^{-1}) the transmittance spectrum appears to be distorted in comparison to the two smaller concentrations, which might indicate that the solutions are above the linear range of the instrument.

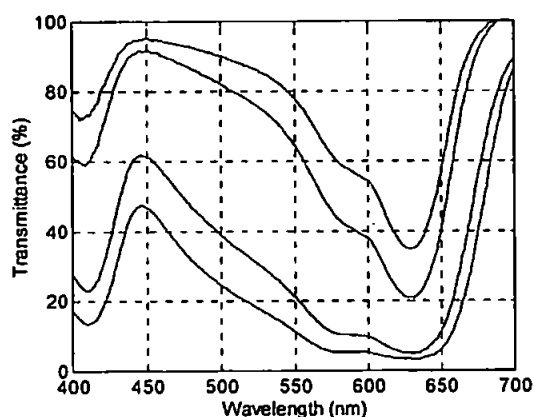


Figure 5-53: Transmittance spectra measured with the PSICAM for the three blue solutions.

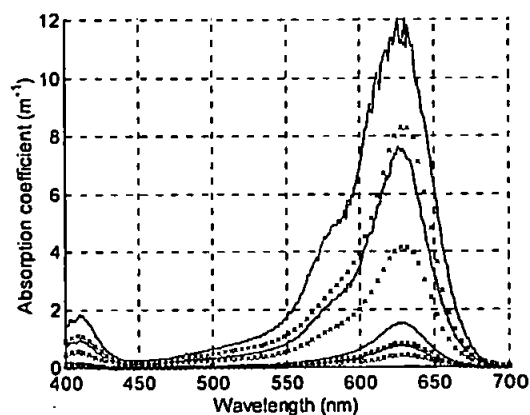


Figure 5-54: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

The calculated absorptions are presented on Figure 5-54. The absorptions calculated by the PSICAM using the reflectivity spectrum of Figure 5-52 are significantly higher than the standards for the four different concentrations. Taking a closer look at each concentration (Figure 5-55 to Figure 5-58), it is apparent that there is an almost constant slope of 1.7 (Table 5-3) between the PSICAM and the spectrophotometer's data. The highest concentration has a smaller slope of 1.5. In this last case (Figure 5-58), the slope of the scatter plot is also 1.7 from 0 to 6m^{-1} (PSICAM measurement). The highest absorption then presents a lower slope of 1.4 relative to the spectrophotometer. This would also indicate that the PSICAM does not respond linearly as was presumed from the transmittance spectrum of the highest concentration.

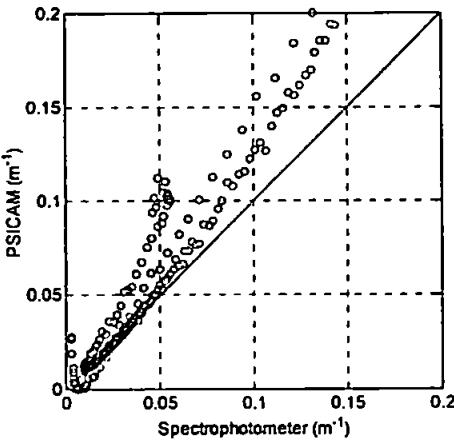


Figure 5-55: PSICAM versus Spectrophotometer for C_1

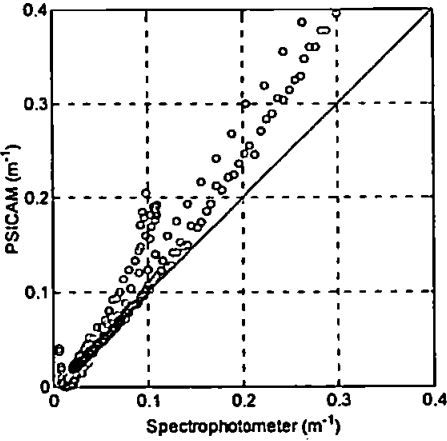


Figure 5-56: PSICAM versus Spectrophotometer for C_2

Table 5-3: Slope, intercept and regression coefficient between the two instruments

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	1.723	-0.018	0.995
C_2	1.737	-0.043	0.994
C_3	1.773	-0.140	0.997
C_4	1.480	0.0905	0.991

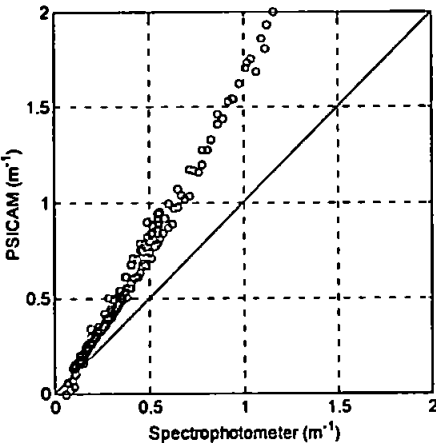


Figure 5-57: PSICAM versus Spectrophotometer for C_3

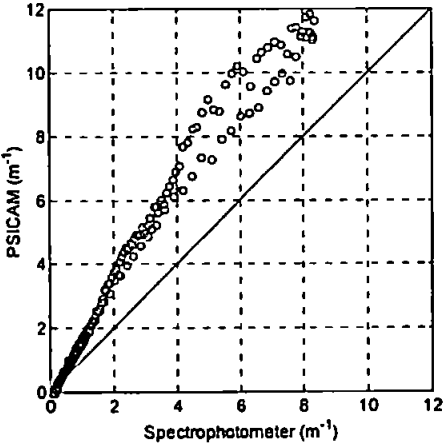


Figure 5-58: PSICAM versus Spectrophotometer for C_4

5.6.1.2.2. Green standard, using Kirk's equation

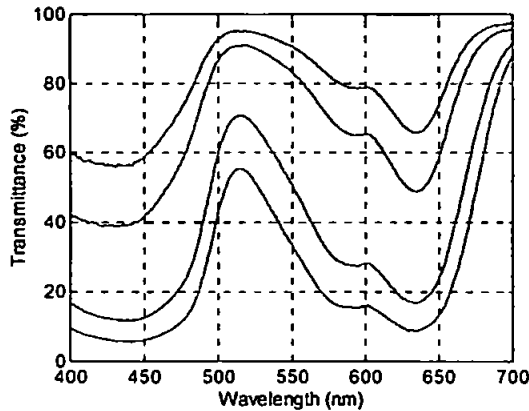


Figure 5-59: Transmittance spectra measured with the PSICAM for the four green solutions.

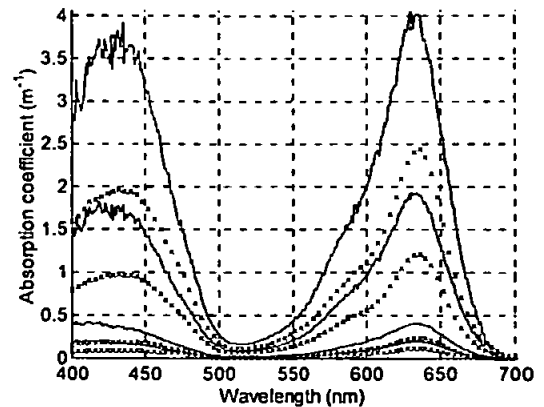


Figure 5-60: Absorption spectra calculated with the PSICAM (solid line) and measured on the spectrophotometer (crosses).

Figure 5-59 presents the transmittance spectra of the four green solutions analysed. The spectra display two minima, a first one around 430nm and a second around 640nm. Again the ranges of concentration selected allow a wide range of transmittance across the visible spectrum. Figure 5-60 presents the calculated absorption spectra using the reflectivity spectrum of Figure 5-52. In this case too the absorption calculated with the PSICAM over estimate the absorption measured with the spectrophotometer. Looking at the one to one relationship between the two instruments (Figure 5-61 to Figure 5-64 and Table 5-4), it is seen that the slopes, as for the previous blue standard, are around 1.7~1.8. The shape of the absorption spectrum is therefore reproduced but with a systematic factor error of 1.7~1.8.

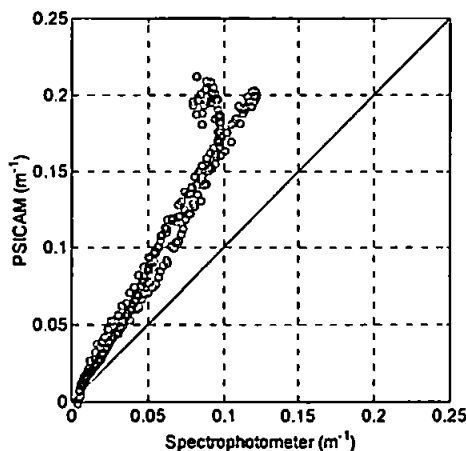


Figure 5-61: PSICAM versus Spectrophotometer for C_1

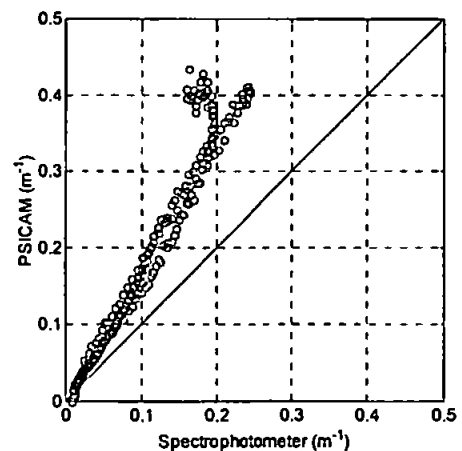


Figure 5-62: PSICAM versus Spectrophotometer for C_2

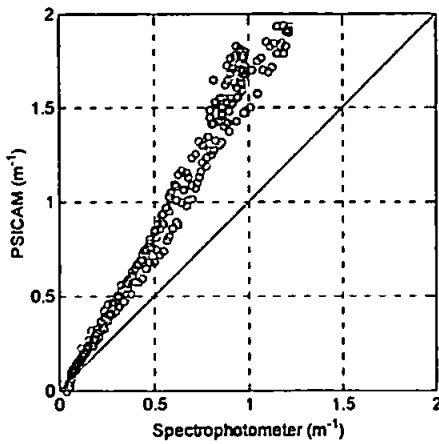


Figure 5-63: PSICAM versus Spectrophotometer for C_3

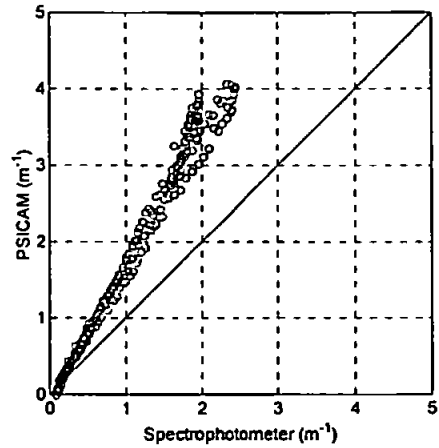


Figure 5-64: PSICAM versus Spectrophotometer for C_4

Table 5-4: Slope, intercept and regression coefficient between the two instruments

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	1.86	-0.007	0.975
C_2	1.88	-0.015	0.975
C_3	1.72	-0.048	0.991
C_4	1.78	-0.099	0.992

5.6.1.2.3. Black standard, using Kirk's equation

The transmittance spectra of the last solution tested are displayed in Figure 5-65. This is the dye that was used for the calibration of the cavity reflectivity. It is broadly transmitting for 400 to 650 nm with a maximum at 600nm. It does not filter longer wavelengths. The calculated absorption spectra are displayed in Figure 5-66. Again, the PSICAM over estimates the spectrophotometer predictions. The slope between the PSICAM and the spectrophotometer remains similar for the two highest concentration (Figure 5-69 and Figure 5-70): 1.55 and 1.68 for C_3 and C_4 respectively. However, the slopes are not comparable for the two lower concentrations: 1.20 and 1.29 for C_1 and C_2 respectively. This is probably biased by the strong discrepancies that appear for the lowest absorption (Figure 5-67 and Figure 5-68) and the error for the short wavelength (circles on Figure 5-67 and Figure 5-68; see detail of the two lower concentrations on Figure 5-71).

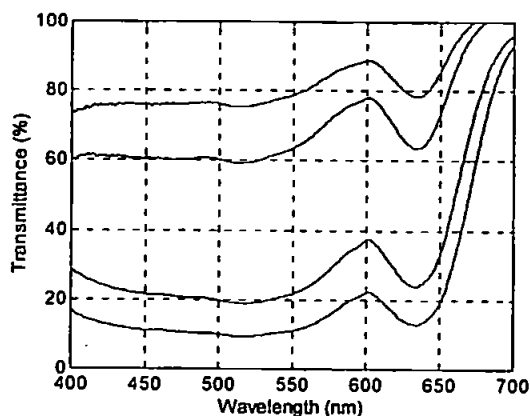


Figure 5-65: Transmittance spectra measured with the PSICAM for the four black solutions.

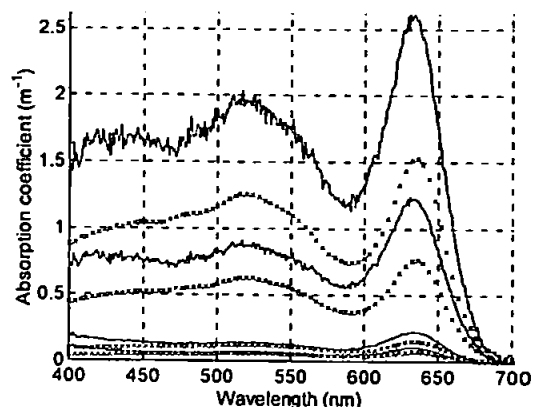


Figure 5-66: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

This artefact is most likely related to the instability of the reference measurement for the lower absorption. This is a part of the spectrum where the diffraction grating is less sensitive and where the light source is the most unstable as explained earlier (*section 5.2*). The origin of the error is also visible on the transmittance spectra of Figure 5-65. For the two highest concentrations, the transmittance spectra increase slightly from 450nm down to 400nm whereas they tend to decrease for the two lowest concentrations.

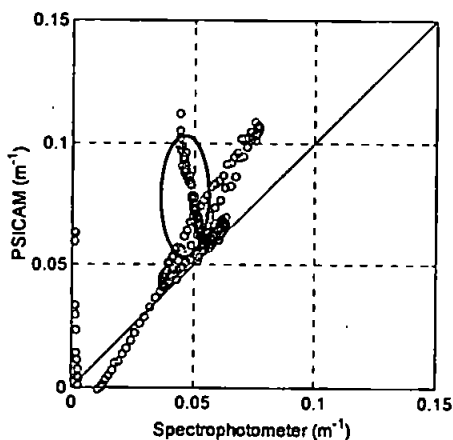


Figure 5-67: PSICAM versus Spectrophotometer for C_1 .

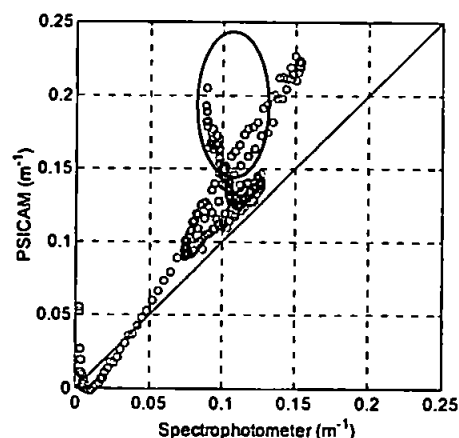


Figure 5-68: PSICAM versus Spectrophotometer for C_2 .

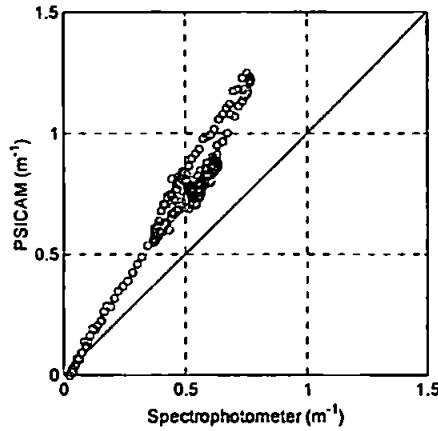


Figure 5-69: PSICAM versus Spectrophotometer for C₃

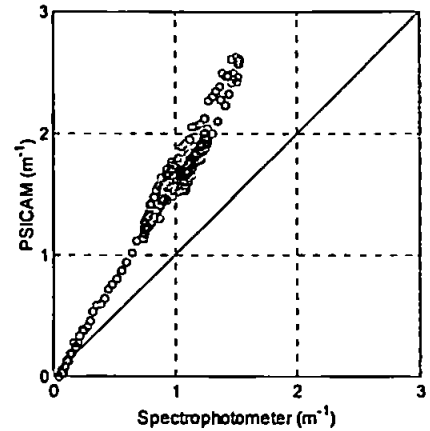


Figure 5-70: PSICAM versus Spectrophotometer for C₄

Table 5-5: Slope, intercept and regression coefficient between the two instruments

	<i>Slope</i>	<i>Intercept</i>	<i>r</i> ²
<i>C</i> ₁	1.209	0.002	0.82
<i>C</i> ₂	1.293	0.0009	0.898
<i>C</i> ₃	1.542	-0.027	0.976
<i>C</i> ₄	1.684	-0.079	0.987

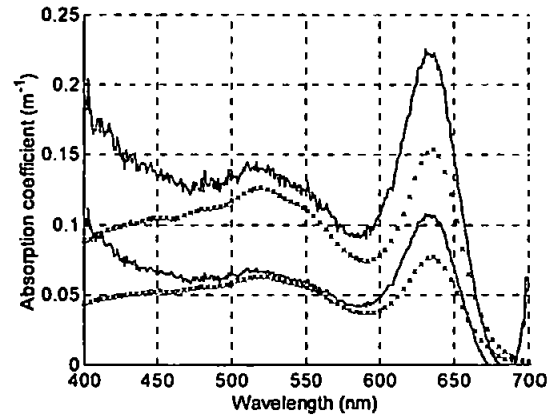


Figure 5-71: Detail of Figure 5-66 for the two lowest concentrations.

5.6.1.3. Conclusion

To some extent, the results obtained with this prototype are of better quality. The absorption spectra shape of the various solutions tested were well reproduced although they systematically over-estimated by a factor going from 1.5 to 1.8. The errors such as those for the lowest concentration of the black solutions for the short wavelength find a logical explanation in the instability of the light source at these wavelengths. Figure 5-72 presents the regression between the PSICAM and spectrophotometer measurement for all the studied solutions. It is apparent from this figure that the PSICAM can be inaccurate for absorptions lower than

0.02m^{-1} . This was actually predicted in the modeling chapter. For the other data, this graph emphasises the systematic error between the two instruments.

With this prototype, the sources of errors mentioned previously are very well minimized. The integrating cavity and light source unit are made of an optical grade material. The cavity diameter is known and the cavity can be assumed to be a perfect sphere although the volume taken by the stem of the light source might still interfere. A reference measurement is taken between each measured sample to minimize the errors originating from baseline shift. This kind of errors is now better understood and mainly appears in the short wavelengths from 400 to 450nm. Potential errors are still the value used for the reflectivity spectrum and the standard used for both the calculation of the reflectivity and the measurement of standard solution. All the results so far were based on the assumption that calculating the absorption coefficient of the standard from measurement in a one centimeter cuvette was accurate enough. From the next experiments, a different approach was taken for the calibration of the instrument.

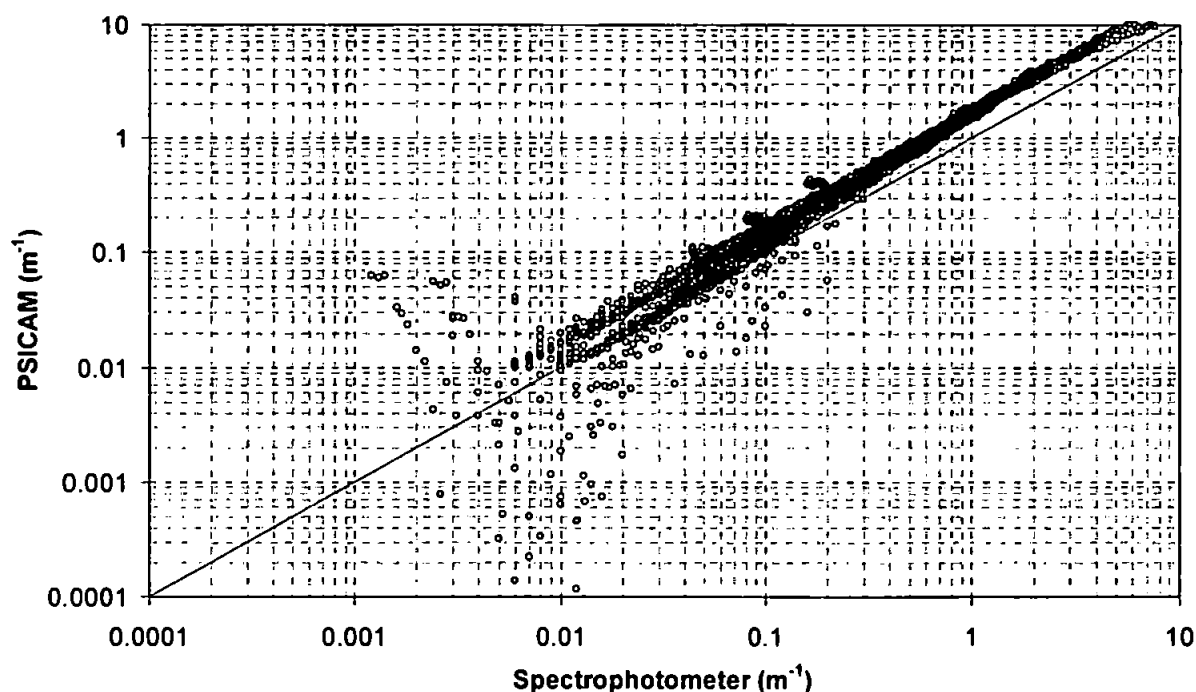


Figure 5-72: PSICAM versus Spectrophotometer for all the measured solutions

5.6.2. Spectralon prototype 10cm cuvette

5.6.2.1. Reflectivity

The first approach to investigate the reflectivity of the Spectralon sphere as well as the other prototype haven't been successful. Initially the source of error was assumed to come for the prototype itself: quality of the material used for the integrating cavity and the light source, stability of the power supply, integrating sphere not strictly spherical. In this experiment, a different approach was used to calculate the reflectivity of the sphere. Four standard solutions of a black dye were prepared and their absorption spectrum measured in a 10 cm cuvette relative to pure water. The concentrations chosen were $C_1=0.001\text{ml.l}^{-1}$, $C_2=0.0025\text{ ml.l}^{-1}$, $C_3=0.005\text{ ml.l}^{-1}$ and $C_4=0.01\text{ml.l}^{-1}$. Their absorption spectra are displayed in Figure 5-51. The transmittance of solutions C_2 , C_3 and C_4 were then measured in the PSICAM relative to solution C_1 . One reference measurement of solution C_1 was made between each sample to avoid deviation of the baseline. The transmittance of each solution is visible in Figure 5-52. The concentrations chosen for the experiment were chosen so that the transmittance depletion covers a wide range over the visible range: between 80 and 70%, 60 and 50% and 40 30% for C_2 , C_3 and C_4 respectively.

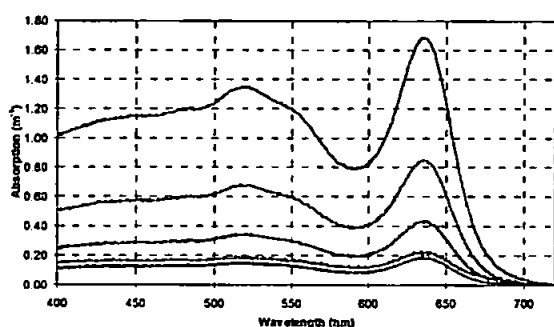


Figure 5-73: Absorption spectrum of the standard solution for the calculation of the cavity reflectivity.

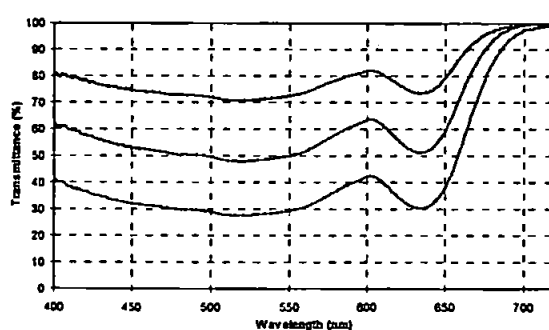


Figure 5-74: Transmittance spectra of the standard solutions relative to C_1 .

The reflectivity spectrum of the integrating cavity was then used using Kirk's formula (Equation 4-5) for the three different solutions tested.

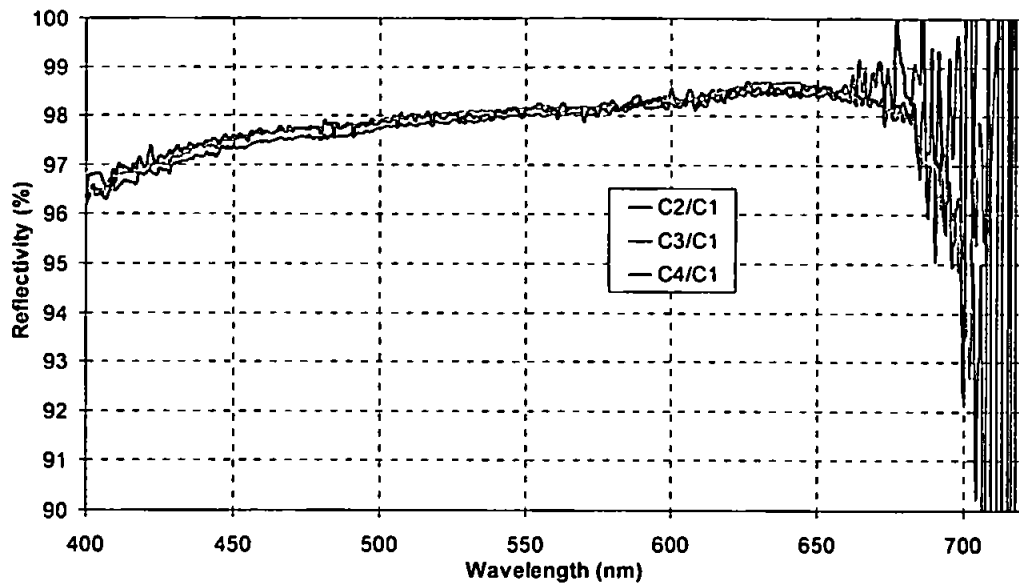


Figure 5-75: Reflectivity spectrum calculated from the transmittance of the standard solutions

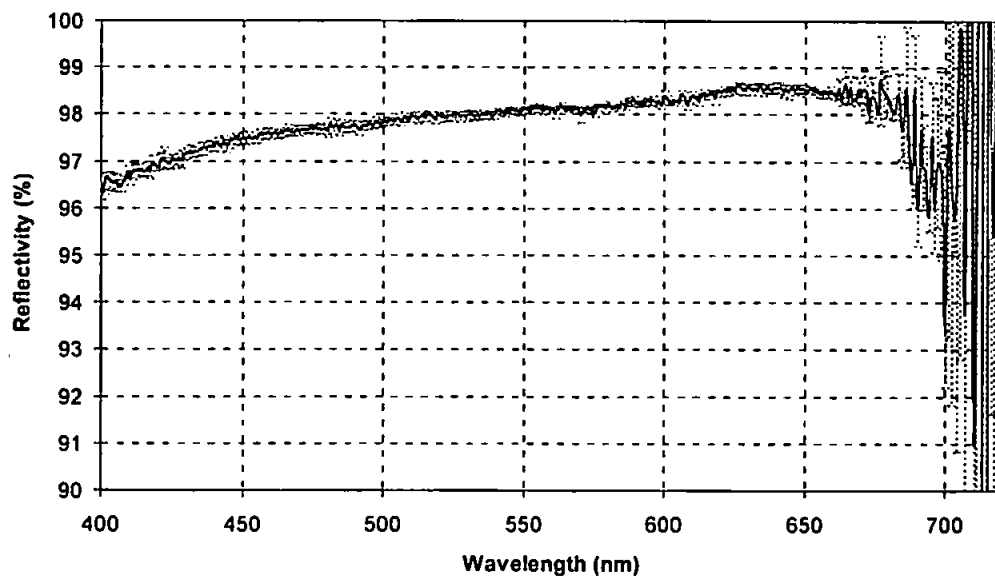


Figure 5-76: Average and Standard deviation of the three calculated reflectivity in Figure 5-76

The three reflectivity spectra calculated presents very similar results (Figure 5-75). The three spectra increase from about 96% at 400nm to peak at 98% around 635nm and then decreases toward the red wavelength. For the longer wavelengths, the calculated reflectivity is

probably erroneous because the dyes used for the standard solutions are very weakly absorbing in this region. Figure 5-76 presents the average and standard deviation of the reflectivity spectrum calculated from the three measurements. The standard deviation remains below 0.01 up to 670nm. From the sensitivity analysis carried out in *Chapter 4*, it is possible to estimate from the standard error the percentage error expectable for the absorption calculation. For the sensitivity analysis, for a cavity radius of 5cm, it is predicted that the percentage error on the calculated absorption is 99 times the error on the reflectivity. It results (Figure 5-77) of a percentage error between 5 and 10% from 450 to 660nm, between 10 and 20% below 450nm and higher than 20% above 660nm. This would be the percentage error expected for the configuration of our PSICAM. This would probably be improved first with a more stable power supply which still gives rise to some uncertainty. For the shorter wavelengths, this corresponds to the minimum efficiency of the diffraction grating of the spectrophotometer. Finally, the error for wavelengths longer than 660nm is more likely to be an effect of the standard solution used.

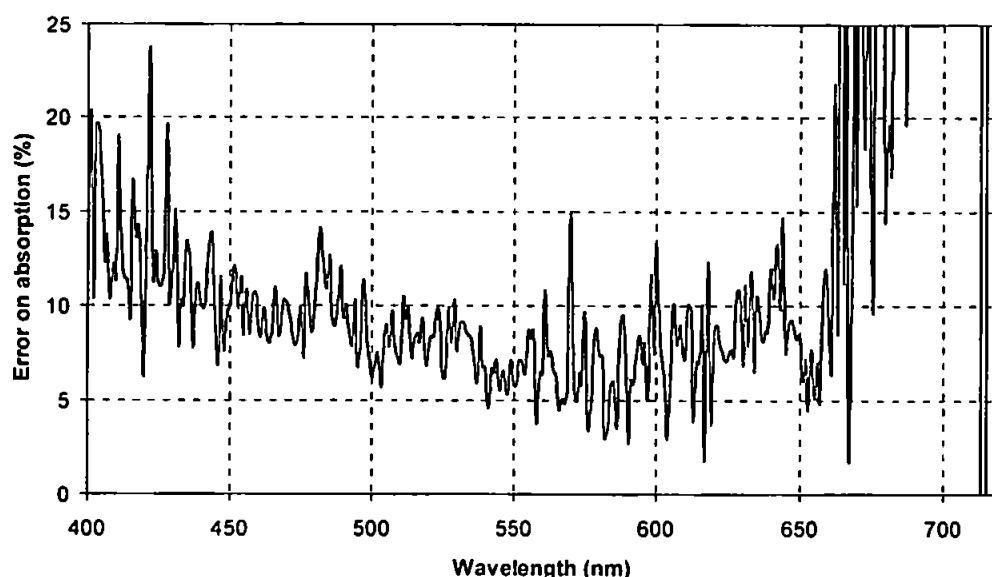


Figure 5-77: Estimated error on the calculated absorption.

5.6.2.2. Experiment with food dye

To test the PSICAM with standard solution, the same procedure was adopted. Various concentrations of dye solutions were prepared and their absorption spectra relative to pure water was measured in a 10 cm cuvette. The transmittance of the standard solution relative to pure water was then measured in the PSICAM so that the same solutions were used both in the spectrophotometer and the PSICAM. The standard solutions prepared were blue, green, red and black and the concentrations were chosen to allow a wide range of transmittance depletion (Figure 5-78 to Figure 5-105). The concentrations prepared are presented in Table 5-6.

Table 5-6: Set of concentrations for the standard solutions

	<i>C1</i>	<i>C2</i>	<i>C3</i>	<i>C4</i>	<i>C5</i>	<i>C6</i>
Blue	<i>5E-3</i>	<i>1E-3</i>	<i>5E-2</i>	#	#	#
Green	<i>5E-3</i>	<i>1E-3</i>	<i>5E-2</i>	<i>1E-1</i>	#	#
Red	<i>2E-4</i>	<i>1E-4</i>	<i>2E-5</i>	#	#	#
Black	<i>5E-4</i>	<i>1E-3E</i>	<i>2.5E-3</i>	<i>5E-3</i>	<i>1E-2</i>	<i>1.5E-2</i>

5.6.2.2.1. Blue standard, using Kirk's equation

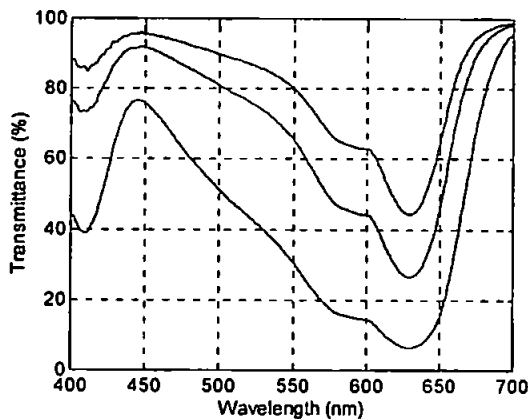


Figure 5-78: Transmittance spectra measured with the PSICAM for the three blue solutions.

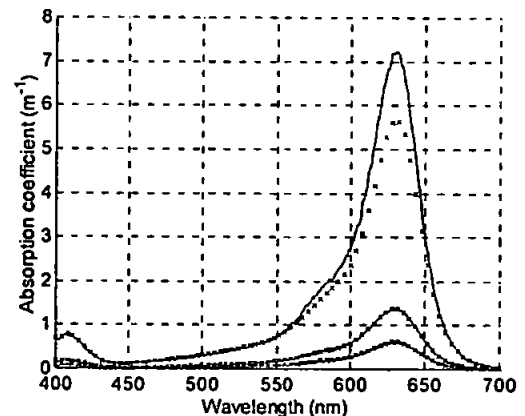


Figure 5-79: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

The standard solutions of different concentrations measured in the PSICAM in case of the blue solution allow a transmittance depletion decreasing to about 10% around 630nm for the highest concentration (Figure 5-78). The transmittance spectra of these solutions are marked by

two peaks: a first one around 410nm and a much more important one around 630nm. The calculated absorption coefficients are presented in Figure 5-79 for the three solutions under investigation. The absorption spectra of the two lowest concentrations are very well correlated between the two instruments. For the highest concentration, a significant discrepancy occurs for the second and most important absorption peak at 630nm. The PSICAM indicated a maximum absorption of 5.65m^{-1} at 631nm whereas the spectrophotometer measures a maximum absorption of 7.25m^{-1} at the same wavelength. A possible explanation of this difference is that the solution probably has absorption above the linear range of both instruments.

Figure 5-80 to Figure 5-82 present the one to one relationship between both instruments for C_1 , C_2 and C_3 respectively. The slopes, intercepts and regression coefficients are displayed in Table 5-7. For the three different concentrations, the regression coefficient is higher than 0.99. The absorption spectrum of the first solution is slightly under-estimated. The second concentration shows the best fit with the spectrophotometer measurement. Both have a slope very close to 1 (respectively 1.02 and 1.05). The highest concentration, as mention previously, shows more important discrepancies with increasing absorption, the absorption peak around 630nm being significantly over-estimated.

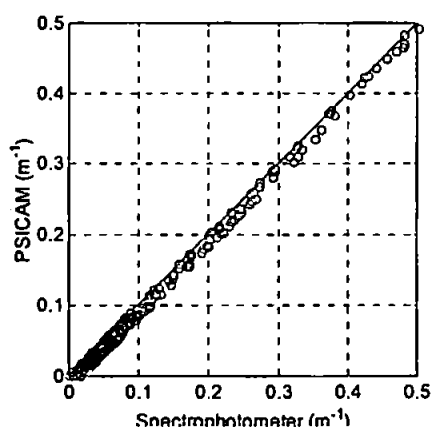


Figure 5-80: PSICAM versus Spectrophotometer for C_1

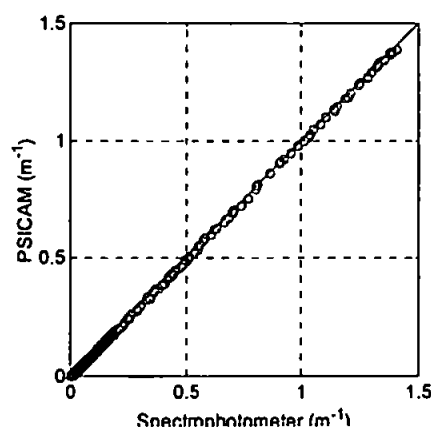


Figure 5-81: PSICAM versus Spectrophotometer for C_2

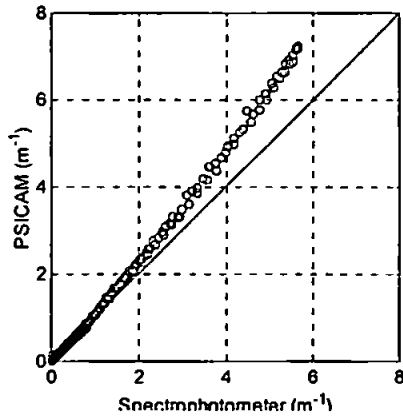


Figure 5-82: PSICAM versus Spectrophotometer for C_3

Table 5-7: Slope, intercept and regression coefficient between the two instruments

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	0.99	-0.01	0.999
C_2	0.99	-0.01	0.999
C_3	1.24	-0.11	0.998

5.6.2.2.2. Least square technique

The least square technique was used to estimate the absorption coefficient of the standard solutions. For the first two concentrations, the differences between the two techniques were insignificant (Table 5-8). However, for the last one, using this technique resulted in a smaller absorption peak of 6.52m^{-1} at 631nm (Figure 5-83). It is indeed possible that owing to the concentration of the solution, the light field within the sphere was not homogeneous and isotropic as expected when using Kirk's equation.

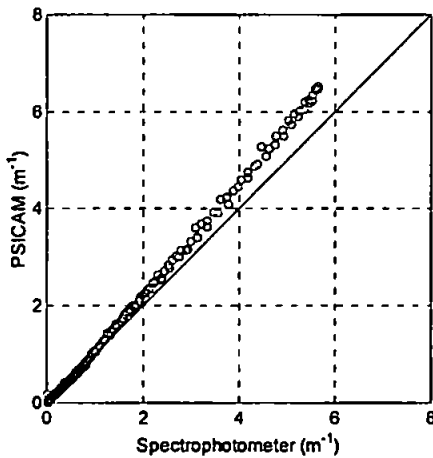


Figure 5-83: PSICAM versus Spectrophotometer for C_3 using least square technique.

Table 5-8: Slope, intercept and regression coefficient between the two instruments with the least square technique.

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	0.99	-0.009	0.999
C_2	0.98	-0.007	0.999
C_3	1.14	-0.060	0.999

5.6.2.2.3. Green standard, using Kirk's equation

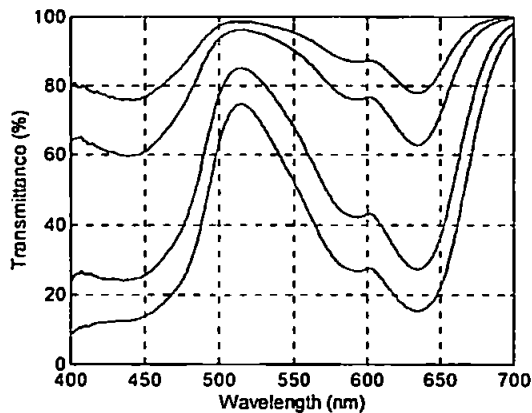


Figure 5-84: Transmittance spectra measured with the PSICAM for the four green solutions.

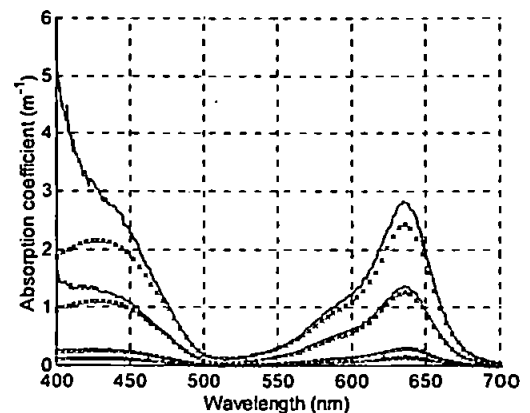


Figure 5-85: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

The standard solutions of different concentrations measured in the PSICAM in case of the green solution allow a transmittance depletion going down to about 10 and 20% around 400 and 640nm respectively for the highest concentration (Figure 5-84). The transmittance spectra of these solutions are marked by two comparable peaks: a first one around 440nm and a second around 640nm, the first peak being smoothed for the highest concentrations. The calculated absorption coefficients are presented on Figure 5-85 for the four solutions under investigation. The absorption spectra of the two lowest concentrations are very well correlated between the two instruments. The third solution is also well correlated except for the shorter wavelength. The PSICAM indeed does not measure a maximum absorption at 440nm and increasing absorption toward the lowest wavelength. For the highest concentration, significant discrepancies occur around 636nm and for wavelength shorter than 460nm. The PSICAM indicated a maximum absorption of 2.84m^{-1} at 636nm whereas the spectrophotometer measures a maximum absorption of 2.43m^{-1} at the same wavelength.

Figure 5-86 to Figure 5-89 present the one to one relationship between both instruments for C_1 , C_2 , C_4 and C_4 respectively. The slopes, intercepts and regression coefficient are

displayed in Table 5-9. For the first two solutions, the regression coefficient is higher than 0.99. It then decreases to 0.98 and 0.92 for C_3 and C_4 respectively. Both have a slope very close to 1 (respectively 1.02 and 1.06) with an intercept of almost zero. The highest concentrations as mentioned previously show more important discrepancies with increasing absorption, the absorption peak around 636nm being significantly over-estimated. This deviation from the reference measurement with the spectrophotometer occurs for absorptions higher than 2m^{-1} . This corresponds to the absorption range where the blue solutions started to deviate from the reference measurement.

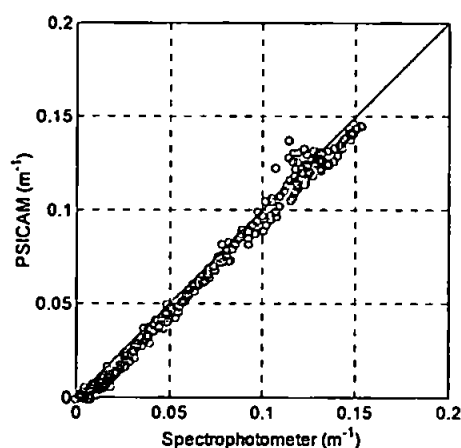


Figure 5-86: PSICAM versus Spectrophotometer for C_1

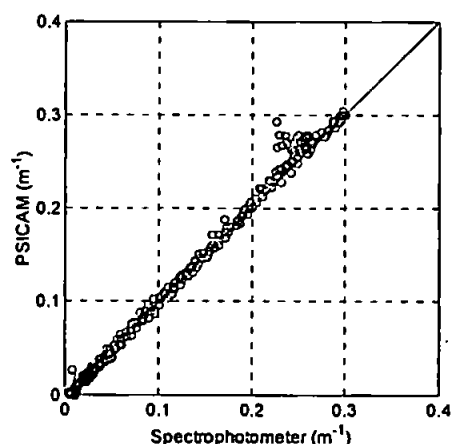


Figure 5-87: PSICAM versus Spectrophotometer for C_2

However, the discrepancies accruing for the shorter wavelength are unlikely to be strictly related to the linear range of the instrument. If absorptions higher than 2m^{-1} are likely to be above the linear range of the instrument, the two absorption peaks of this dye being approximately of the same amplitude, equally important errors would be expected for both peaks. The error for shorter wavelength is much higher than around 636nm. In this case, the transmittance measurement (Figure 5-84) could be responsible for most of the discrepancies since the transmittance peak does not appear markedly on the spectrum. The shorter wavelengths are a portion of the spectrum where the light source is more unstable, the reference measurement being more likely to drift rapidly in this portion of the spectrum.

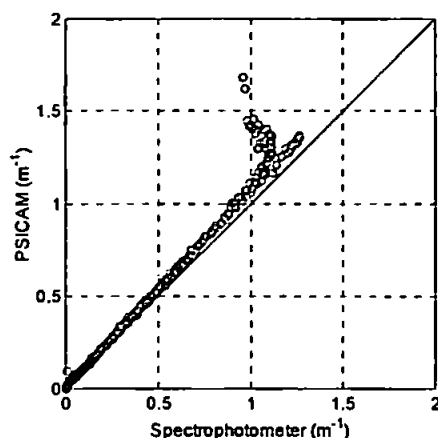


Figure 5-88: PSICAM versus Spectrophotometer for C_3

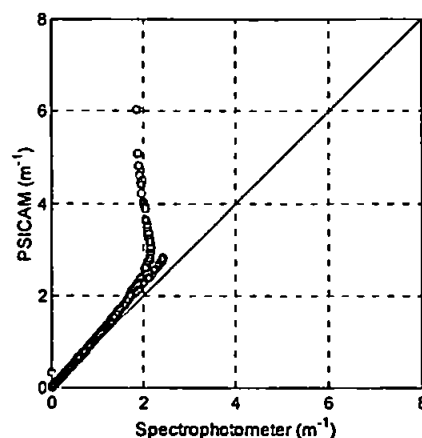


Figure 5-89: PSICAM versus Spectrophotometer for C_4

Table 5-9: Slope, intercept and regression coefficient between the two instruments

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	1.02	-0.006	0.996
C_2	1.06	-0.006	0.997
C_3	1.15	-0.012	0.988
C_4	1.40	-0.116	0.928

5.6.2.2.4. Least square technique

The least square technique was used to estimate the absorption coefficient of the standard solutions. For the first two concentrations, the differences between the two techniques were insignificant (Table 5-10). The last one, using this technique resulted in a smaller absorption peak of 2.72m^{-1} at 636nm (Figure 5-83). No significant changes were observed for the errors at the shorter wavelengths.

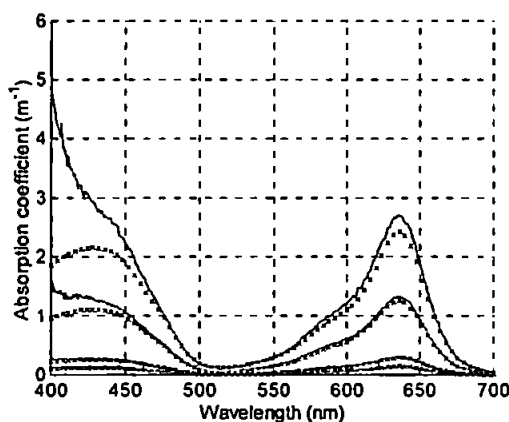


Figure 5-90: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

Table 5-10: Slope, intercept and regression coefficient between the two instruments with the least square technique

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	1.02	-0.006	0.995
C_2	1.06	-0.006	0.996
C_3	1.13	-0.009	0.987
C_4	1.34	-0.09	0.934

5.6.2.2.5. Red standard, using Kirk's equation

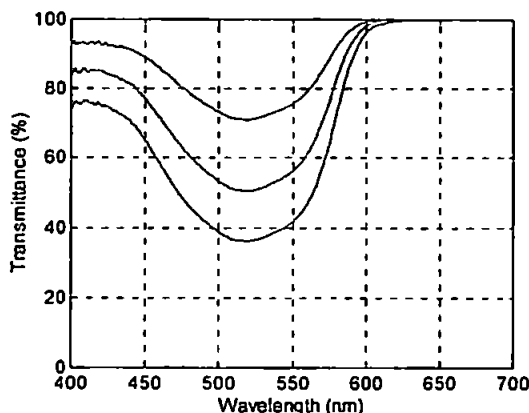


Figure 5-91: Transmittance spectra measured with the PSICAM for the three red solutions.

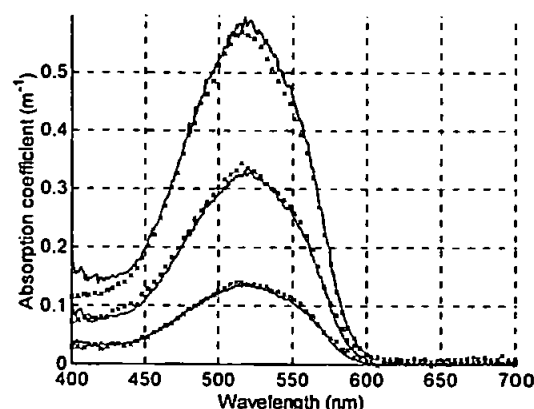


Figure 5-92: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

The standard solutions measured in the PSICAM in case of the red solution allow a transmittance depletion going down to about 40% around 518nm for the highest concentration (Figure 5-91). The transmittance spectra of these solutions are marked by one peak at 518nm. The calculated absorption coefficients are presented in Figure 5-92 for the three solutions under investigation. In this case, a very good correlation is obtained between the two instruments for all the concentrations measured. The PSICAM indicated a maximum absorption of 0.14, 0.33 and 0.59m^{-1} at 518nm for C_1 , C_2 and C_3 respectively. The spectrophotometer measures a maximum absorption of 0.14, 0.34 and 0.56m^{-1} at the same wavelength.

Figure 5-93 to Figure 5-95 present the one to one relationship between both instruments for C_1 , C_2 and C_3 respectively. The slopes, intercepts and regression coefficient are displayed in Table 5-11. For the three different concentrations, the regression coefficient is higher than 0.99. In this case, a very good one to one relationship is obtained between the two instruments. The highest absorption measured in this case being 0.59m^{-1} , the solution used probably stayed within the linear domain of the instrument.

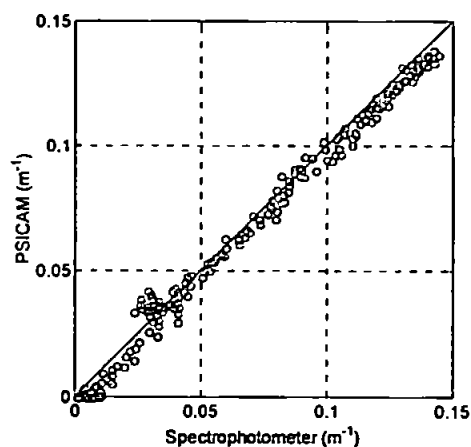


Figure 5-93: PSICAM versus Spectrophotometer for C_1

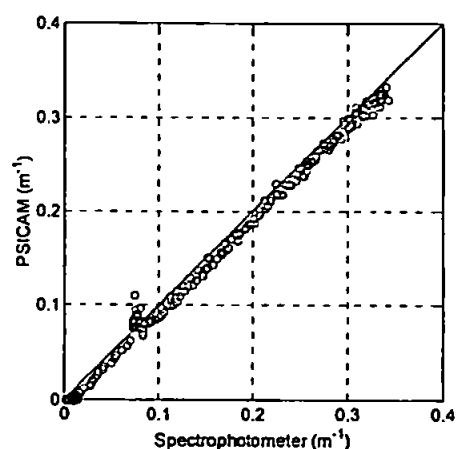


Figure 5-94: PSICAM versus Spectrophotometer for C_2

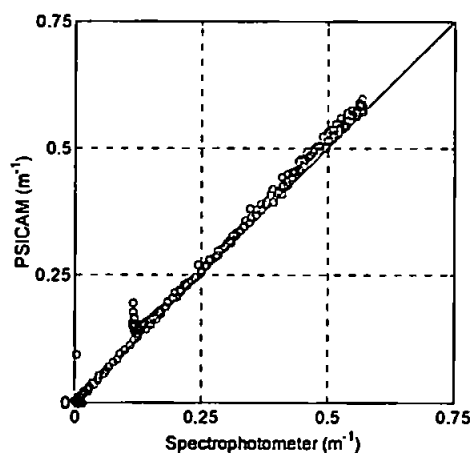


Figure 5-95: PSICAM versus Spectrophotometer for C_3 .

Table 5-11: Slope, intercept and regression coefficient between the two instruments

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	1.002	-0.004	0.995
C_2	0.996	-0.008	0.998
C_3	1.039	7E-4	0.998

5.6.2.2.6. Least square technique

The least square technique was used to estimate the absorption coefficient of the standard solutions. No significant differences appeared between the two techniques. With the knowledge of the two previous experiments, this was expectable because the concentrations used in this case did not result in transmittance spectra lower than thirty percents.

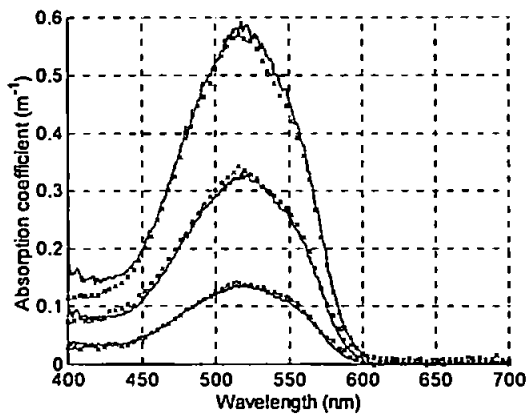


Figure 5-96 Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

Table 5-12: Slope, intercept and regression coefficient between the two instruments with the least square technique.

	<i>Slope</i>	<i>Intercept</i>	<i>r</i> ²
<i>C</i> ₁	1.04	-0.0081	0.928
<i>C</i> ₂	1.01	-0.0126	0.985
<i>C</i> ₃	1.04	-0.0034	0.993

5.6.2.2.7. Black standard, using Kirk's equation

With the three previous dyes, specific absorption bands were investigated. With this last experiment, a black dye was used to cover most of the visible spectrum. As previously, this dye did not absorb in the longer wavelengths.

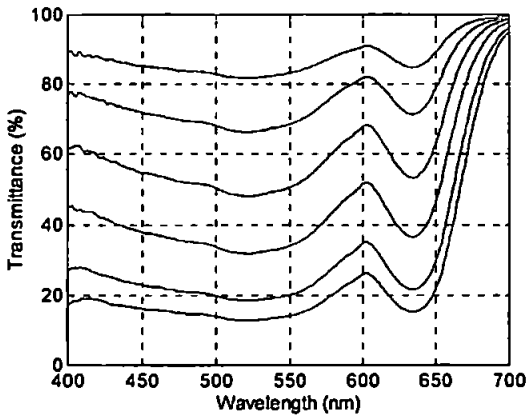


Figure 5-97: Transmittance spectra measured with the PSICAM for the six black solutions.

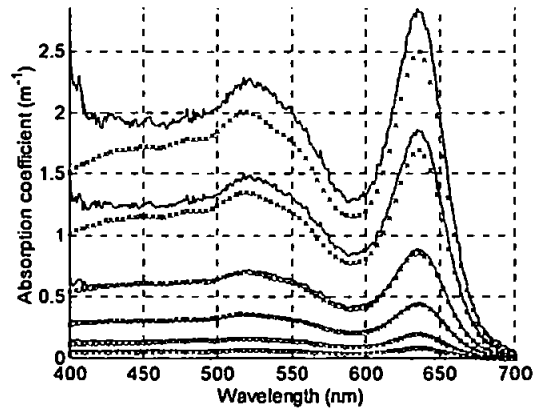


Figure 5-98: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

With the chosen set of concentrations, the range of transmittances covered varied from 90% down to 15%. The dye shows a maximum transmittance around 600nm (Figure 5-97). The calculated absorption coefficients are presented in Figure 5-98 for the six solutions under investigation. Once again, the absorption spectra of the lowest concentrations are very well correlated between the two instruments. It appears that absorptions higher than 1m^{-1} which

corresponds approximately to 40% transmittance is a limit above which the system starts to measure erroneous values. The last two solutions C_5 and C_6 , which have an average transmittance of 30 and 20% respectively, have overestimated absorption with the PSICAM. For solution C_5 , the absorption gets overestimated of up to 0.15m^{-1} and up to 0.35m^{-1} for C_6 , which represent between 5 and 15% error both.

Figure 5-99 to Figure 5-104 present the one to one relationship between both instruments for C_1 , C_2 , C_4 and C_4 respectively. The slopes, intercepts and regression coefficient are displayed in Table 5-13. Having a closer look on the first two solutions C_1 and C_2 (Figure 5-99 and Figure 5-100), they appear to have a constant offset of 0.013 and 0.010m^{-1} respectively.

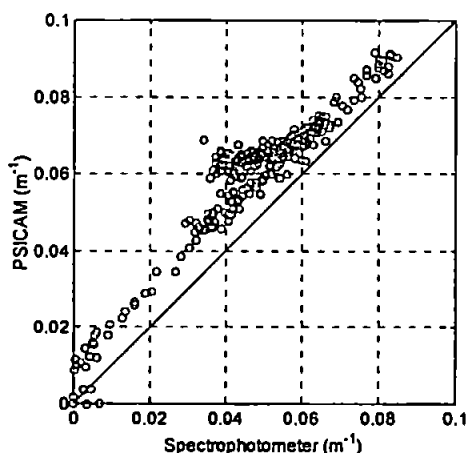


Figure 5-99: PSICAM versus Spectrophotometer for C_1

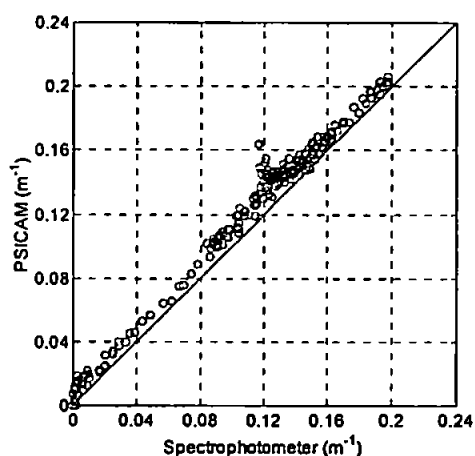


Figure 5-100: PSICAM versus Spectrophotometer for C_2

The best fit is obtained for solutions C_3 and C_4 which have absorption ranges between 0.2 and 1m^{-1} not taking into account the longer wavelength. Both have a slope very close to 1 (respectively 1.004 and 0.980) with an intercept of almost zero.

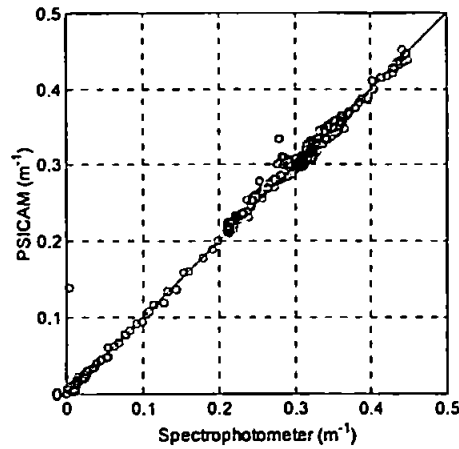


Figure 5-101: PSICAM versus Spectrophotometer for C_3

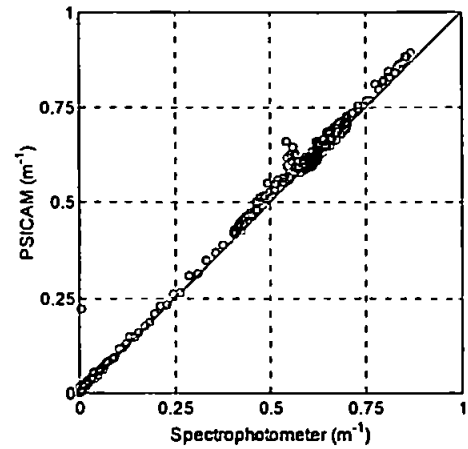


Figure 5-102: PSICAM versus Spectrophotometer for C_4

The highest concentrations C_5 and C_6 (Figure 5-103 and Figure 5-104) as mentioned previously show more important discrepancies. They have average absorptions around 1.2 and 2.0m^{-1} respectively not taking into account the longer wavelengths.

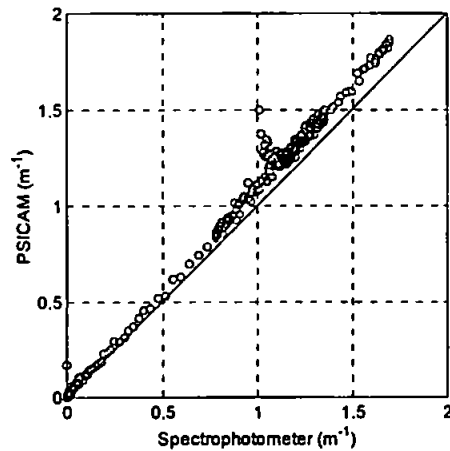


Figure 5-103: PSICAM versus Spectrophotometer for C_5

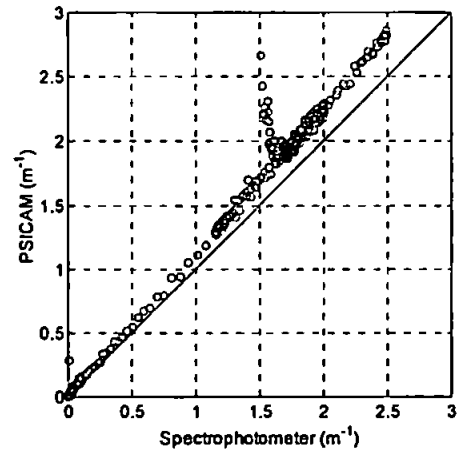


Figure 5-104: PSICAM versus Spectrophotometer for C_6

Table 5-13: Slope, intercept and regression coefficient between the two instruments

	<i>Slope</i>	<i>Intercept</i>	<i>r</i> ²
C_1	0.979	0.013	0.960
C_2	1.004	0.010	0.994
C_3	0.980	0.005	0.996
C_4	1.003	0.013	0.996
C_5	1.082	0.016	0.996
C_6	1.123	0.024	0.990

5.6.2.2.8. Least square technique

The least square technique was used to estimate the absorption coefficient of the standard solutions. For the first four concentrations, the differences between the two techniques were insignificant (Figure 5-105 and Table 5-14). For solution C_5 and C_6 , using this technique resulted in a smaller absorption maximum of 1.81 and 2.70m^{-1} at 636nm for C_5 and C_6 instead of 1.86 and 2.86m^{-1} . No significant changes were observed for the errors at the other wavelengths.

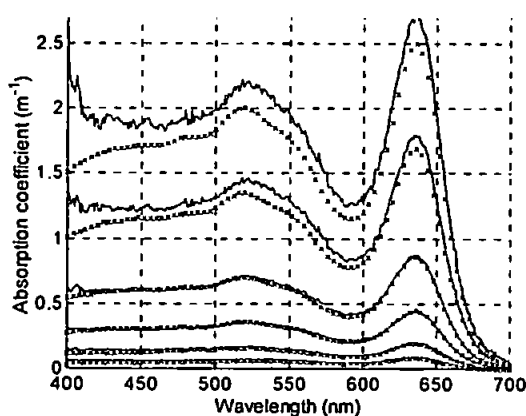


Figure 5-105: Absorption spectra calculated with the PSICAM (solid line) using the least square technique and measured on the Spectrophotometer (crosses).

Table 5-14: Slope, intercept and regression coefficient between the two instruments with the least square technique

	<i>Slope</i>	<i>Intercept</i>	<i>r</i> ²
C_1	0.973	0.013	0.947
C_2	1.004	0.010	0.993
C_3	0.974	0.007	0.994
C_4	0.992	0.015	0.995
C_5	1.059	0.021	0.995
C_6	1.086	0.037	0.989

5.6.2.3. Conclusion

In Figure 5-106 is plotted the PSICAM data versus the spectrophotometer for all of the studied solutions. The graph is on a log-log in order to enhance the lower absorption values, the solid line corresponding to the one to one relationship. A one to one relationship is visible between the two instruments from 0.02 up to 2m^{-1} . For the higher absorptions, there are three separated features which deviate from the one to one relationship. They correspond to the green and black solution errors for the short wavelengths described previously. For absorptions higher than 2m^{-1} , the PSICAM begins to measure significantly higher absorption than the spectrophotometer. For the lower absorptions the limitation appears to be around 0.02m^{-1} . Below this value, the PSICAM lacks accuracy to properly measure the solutions. This accuracy could be improved by a more stabilised light source. However, in the blue part of the spectrum,

the combine characteristics of the tungsten bulb emission spectrum (Figure 5-23), the grating efficiency (Figure 5-1) and the silicon detector of the spectrometer, which are less sensitive in the blue wavelengths are adding to the difficulty of the measurement. As mentioned previously, a pure water reference is made between each measured sample to limit deviation of the base line. However, $\pm 1\%$ deviation of the baseline can occur during the measurement of the sample. Minimizing this kind of deviation would obviously improve the measurement of low absorbing solution. Another solution would be to increase the diameter of the integrating sphere. To achieve accurate measurements for the higher absorbing solutions the cavity radius would need to be smaller as stated in *Chapter 4*.

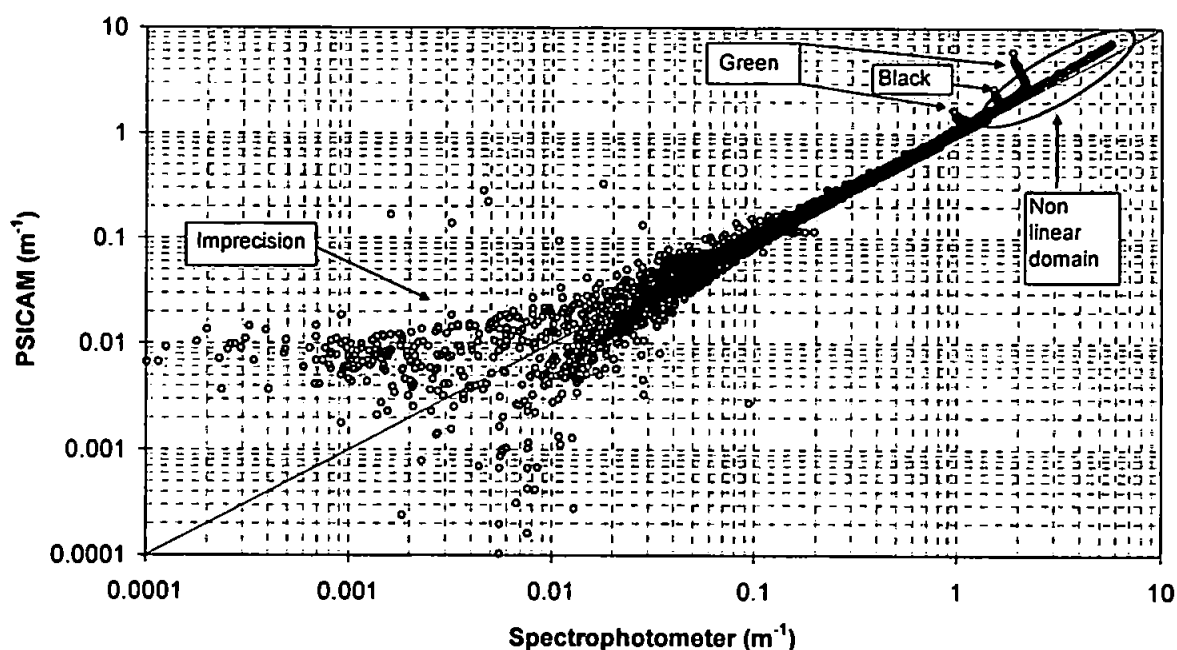


Figure 5-106: PSICAM versus Spectrophotometer for all the measured solutions

With the imprecision knowledge acquired with the various prototypes, it is apparent that the main reason for the initial errors was the imprecision of the absorption spectra of the standard solution used for the calculation of the reflectivity. The high absorptions of the solution measured in the PSICAM which were probably over the linear range of the system. Therefore the initial system with glass sphere was probably good enough to measure the

standard solutions and probably natural samples. The later tests were all carried out with the Spectralon sphere because it presents the closest characteristics to the theory. Further work using a glass sphere embedded in a reflective material would be worth while a glass sphere would have indeed a very important advantage in comparison with a Spectralon sphere: it would be far easier to clean and would be considerably cheaper.

Chapter 6: Validation

6.1. Introduction

It has been shown in the previous chapter that the PSICAM is efficient to measure the absorption coefficient of coloured solutions of various concentrations. The major aspect of the instrument that had to be tested is its response to solutions containing significant amounts of particulate material, which means significant amounts of scattering particles. That was a difficult characteristic of the instrument to test because of the complexity of producing absolute standard solutions containing scattering as well as absorbing particles. To achieve this, a laboratory experiment was set up where the measurement of the PSICAM would be compared with the measurement of an ac-9. The ac-9 as described in a previous chapter is one of the instruments that can achieve accurate measurements even in solutions containing high levels of particulate matter with acceptable accuracy. In addition, the PSICAM was compared with a filter paper technique to measure the particulate absorption. The PSICAM data presented below were calculated using Kirk's equation. The least square technique was also used for the calculation but didn't show major differences (*see Appendix 2*).

The PSICAM was subsequently used to measure natural water absorption and compared with *in situ* measurements of an ac-9, dissolved organic matter measurement and the filter paper technique for the particulate absorption. The PSICAM was also field tested in Antarctic water.

6.2. Laboratory experiment

A laboratory experiment was carried out with the collaboration of Nagur Cherukuru (University of Plymouth) and Gerald Moore (Plymouth Marine Laboratory) where "artificial" water samples were measured with the PSICAM, an ac-9 and the filter pads technique to measure the absorption of suspended particles (*Tassan and Ferrari, 1995*). A water tank of

about one meter cube was filled with milli-Q water in which suspended sediments were added progressively to reach a final concentration of 8.77mg/l. During the course of the experiment samples of the water were taken to measure the concentration of sediments on filter paper. The concentrations measured were 0.03 (pure water background), 0.105, 0.210, 1.310, 2.705 and 8.77mg/l. These sediments were collected from the River Plym, dried and ashed to remove the organic components prior to being added to the tank (Figure 6-1). Water samples were also collected and filtered on 25mm filter paper to measure the particulate absorption. The water in the tank was pumped through a UV light to keep the volume sterile during the course of the experiment. A second pump was kept running to keep the water in the tank homogeneous (Figure 6-1) except during the measurements to avoid formation of micro-bubbles, which could corrupt the ac-9 measurements.

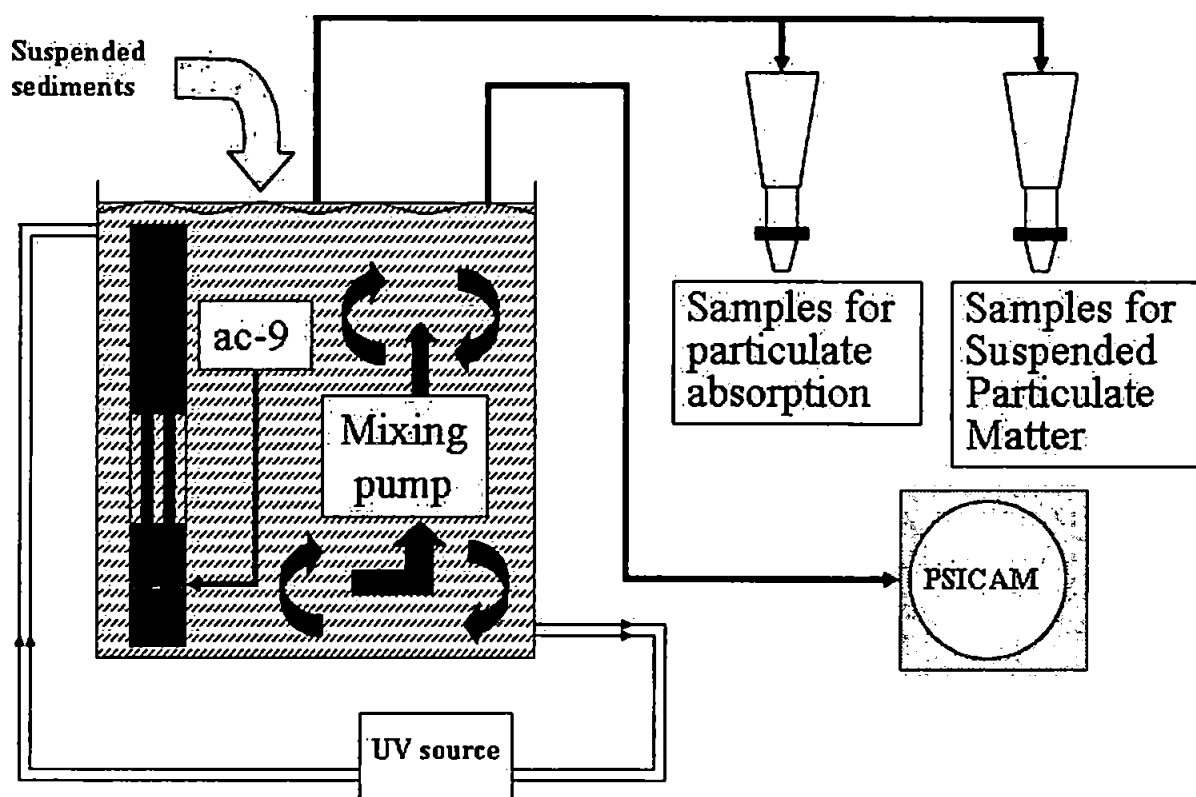


Figure 6-1: Schematic of the laboratory experiment.

6.2.1. Comparison with the ac-9

The ac-9 (WetLabs Inc.), measure both the absorption (a-tube) and attenuation (c-tube) coefficient of a water sample by incorporating a dual path optical configuration in a single instrument. Scattered light that hits the blackened surface of the c-tube is absorbed and therefore does not contribute to the measurement of transmitted intensity. Light radiated through the c-tube is therefore subject to both scattering and absorbing processes. Light passing through the a-tube is absorbed by the water itself and the various dissolved and particulate components of the water. Forward scattering light is reflected back into the water volume by the reflective surface of the tube. The a-tube uses the internal reflection principle in reflecting light back into the water volume. A clear quartz tube is used. The outer surface of the tube is enclosed by a thin volume of air. The difference between the refracting index of air (1) and water (1.33) achieves internal reflection to 41.7 degrees with respect to the optical axis.

The instrument is calibrated to provide a reading of 0.00 for each channel in clean fresh water. The data however needs to be corrected for temperature and salinity offsets. The announced precision by the manufacturer is 0.001m^{-1} .

The data needs to be corrected for back-scattering errors. Attenuation measurements are limited by the acceptance angle of the instrumentation. The finite acceptance angle of the instrumentation means that the instrument collects a portion of the scattered light and thus underestimates the true attenuation coefficient. Correcting attenuation measurements for the errors caused by collection of scattered light is not recommended as it is extremely difficult and of questionable benefit (*Pegau et al., 1994*). The a-tube does not collect all of the light scattered from the beam. The uncollected scattered light causes the instrumentation to overestimate the absorption coefficient. There are three different techniques that can be used for the corrections:

- Subtraction of a reference wavelength where the absorption is assumed to be zero.
- Removal of a fixed proportion of the scattered coefficient.
- Use of a reference wavelength to determine the proportion of the scattering coefficient to be subtracted from the signal.

Each correction technique will be reviewed in the following sections and compared with the results of the PSICAM (in the correction equations, the index *t*, *w*, *m* and *ref* means respectively *total*, *pure water*, *measured* and *reference*).

The general shape of the absorption spectrum obtained from this laboratory experiment is decreasing exponentially with increasing wavelength as expected for inorganic suspended particulate sediment. The measurement of the PSICAM appears to get closer to the ac-9 results for correction 1 and 3, although in each case, the PSICAM underestimates the absorption in comparison with the ac-9. The second correction technique gives the most important difference with the PSICAM measurement. Because the experiment started with pure water, the absorption spectra cover a wider range of absorptions. The scattering coefficient spectrum varied from 0 to about 3.5m^{-1} depending on the correction technique (Figure 6-11).

6.2.1.1. Correction 1

The first method of correcting for scattering errors is to subtract the absorption measurement at a reference wavelength.

$$a_t(\lambda) - a_w(\lambda) = a_m(\lambda) - a(\lambda_{ref})$$

Equation 6-1

This technique assumes that at the reference wavelength, the absorption by particulate and dissolved materials is zero so that the measured absorption coefficient is caused strictly by scattering. It is also assumed that the shape and magnitude of the volume scattering function is independent of wavelength. This technique does allow the scattering correction to vary with

changes in the materials contained within the sample. Commonly, the reference wavelength selected is the near infrared portion (715nm). This correction method being the most basic, the comparison with the ac-9 is presented as a reference. The percentage difference between the two instruments is presented in *appendix 2*.

With this correction technique, the two instruments give similar results (Figure 6-2) although the PSICAM generally underestimates the absorption in comparison with the PSICAM. For the concentration C_0 (pure water back ground) the ac-9 produces negative values (Figure 6-3).

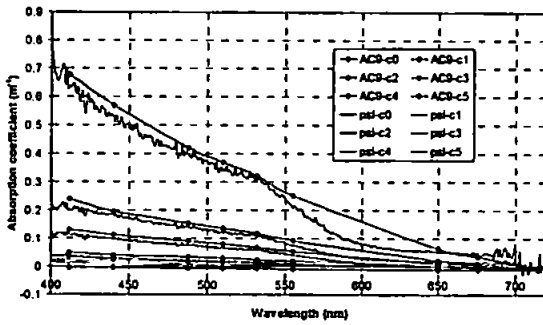


Figure 6-2: Absorption spectra of both instruments obtained with the first correction method.

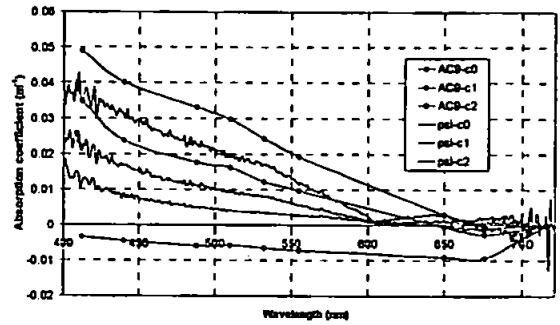


Figure 6-3: Detail of Figure 6-2 for the three lowest concentrations.

6.2.1.2. Correction 2

The second method assumes that the scattering correction is a fixed proportion of the scattering coefficient $b(\lambda)$ such that $b(\lambda)=c(\lambda)-a(\lambda)$. This method takes into account the proportion of the photons which are scattered back in the a-tube and assumed lost as mentioned in a previous chapter:

$$a_i(\lambda) - a_w(\lambda) = a_m(\lambda) - \varepsilon * [c_m(\lambda) - a_m(\lambda)]$$

Equation 6-2

where ϵ is the proportion of the scattering coefficient not detected by the sensor and has a value of ≈ 0.14 for waters where biological particles dominate scattering and increases to ≈ 0.18 when sediments dominate the scattering. The values of ϵ are empirically derived from field data and the third correction technique as well as being modelled by *Kirk (1993)*. This method assumes that the shape of the volume scattering function is independent of wavelength. The magnitude of the scattering correction is, however, allowed to vary with wavelength. Since a reference wavelength is not used there is no requirement that the absorption coefficient is equal to zero at the reference wavelength. A ϵ factor of 0.14 is recommended in the literature (ac-9 user manual) for water dominated by phytoplankton whereas 0.18 is recommended for waters with higher inorganic suspended content because the back-scattering coefficients of suspended inorganic sediments is considerably higher than that of phytoplankton (*Prieur and Sathyendranath, 1981*). For the experiment carried out, an ϵ factor of 0.18 was used, due to the inorganic particulate content of the water samples. Due to the exclusively inorganic particle content of the water samples analyzed, an attempt was made to increase the ϵ factor to try to fit the PSICAM data. It appeared that $\epsilon=0.28$ was needed to fit the PSICAM data for the highest concentrations (Figure 6-6 and Figure 6-7).

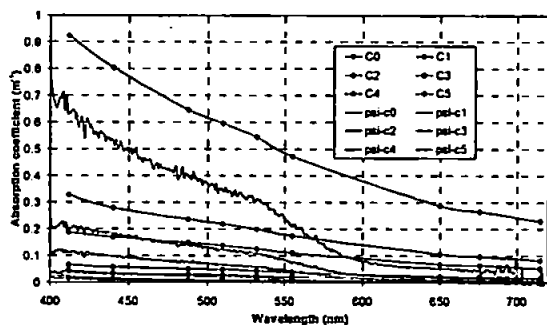


Figure 6-4: Absorption spectra of both instruments obtained with the second correction method ($\epsilon=0.18$).

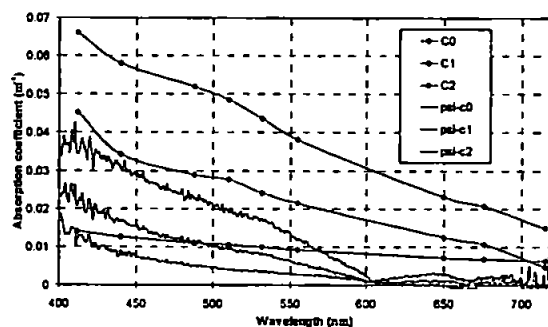


Figure 6-5: Detail of Figure 6-4 for the three lowest concentrations.

Using an ϵ factor of 0.18 for the calculation as recommended for solutions with a high inorganic particulate content, the PSICAM significantly underestimates the values of the ac-9 (Figure 6-4). The detail for the lowest concentrations (Figure 6-5) also shows a major underestimation in comparison to the ac-9. Using this technique, the data from the ac-9 displays an almost linear decreasing curve from 400 to 715nm in which the inflexion point around 650nm does not appear. On the other end, this method unlike the other ones does show some absorbance in the red region of the spectrum. Increasing the ϵ factor was tempted although it might not have a proper physical explanation because the first and third correction method gave comparable results with the PSICAM. Increasing the ϵ factor to such an extent is purely empirical, however it gives more comparable results with the PSICAM for concentrations C_2 to C_5 .

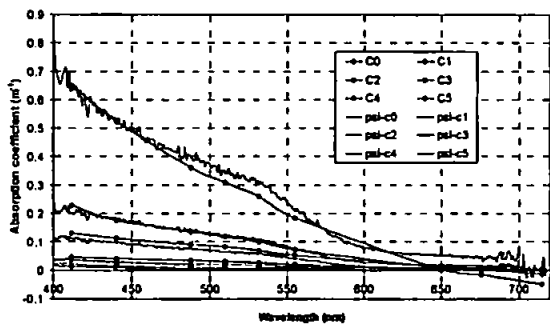


Figure 6-6: Absorption spectra of both instruments obtained with the second correction method ($\epsilon=0.28$).

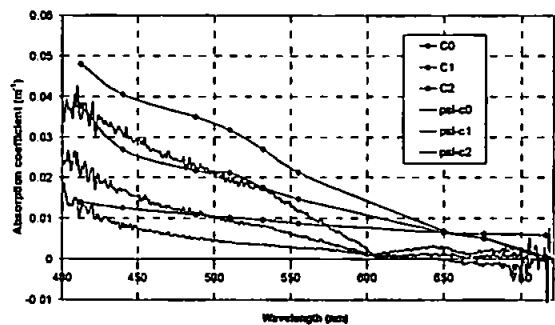


Figure 6-7: Detail of Figure 6-6 for the three lowest concentrations.

The slope, intercept and regression coefficient using $\epsilon=0.28$ are presented in Table 6-1 and the one to one relationship is plotted in Figure 6-8.

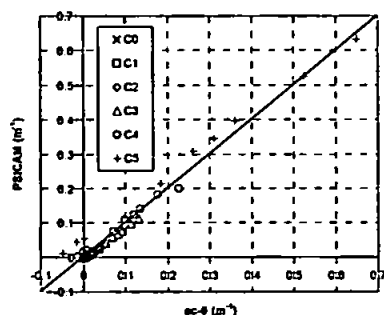


Figure 6-8: Regression between the absorption coefficient measured by PSICAM and the ac-9 with the second correction method.

Table 6-1: Slope, intercept and regression coefficient between the two instruments for $\varepsilon=0.28$.

	Slope	Intercept	r^2
C0	1.3246	-0.0083	0.940
C1	0.7013	-0.0042	0.9843
C2	0.7835	-0.0034	0.9874
C3	0.8443	-0.0005	0.9972
C4	0.8752	0.0155	0.990
C5	0.9016	0.0581	0.998

6.2.1.3. Correction 3

The third correction method is a combination of the first two. It is assumed that there exists a reference wavelength at which the absorption coefficient of particulate and dissolved materials is zero. It is further assumed that the shape of the volume scattering function is independent of wavelength.

$$a_t(\lambda) - a_w(\lambda) = a_m(\lambda) - \frac{a_m(\lambda_{ref})}{[c_m(\lambda_{ref}) - a_m(\lambda_{ref})]} * [c_m(\lambda) - a_m(\lambda)]$$

Equation 6-3

This technique allows for automatic changes in the scattering correction magnitude with wavelength and changes in the types of materials present. It requires the largest number of auxiliary measurements, which makes this technique the most accurate one.

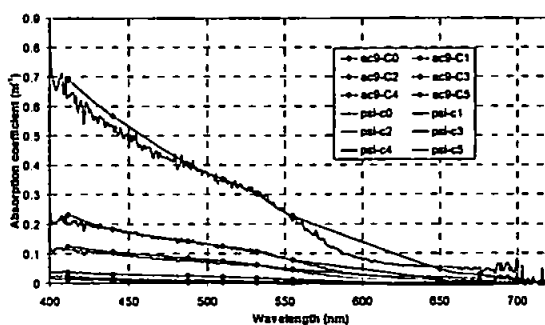


Figure 6-9: Absorption spectra calculated with the third correction method

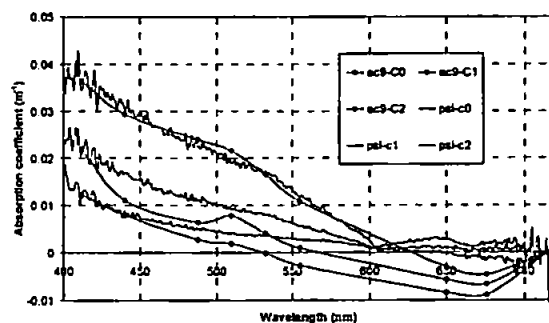


Figure 6-10: Detail of Figure 6-9 the lowest concentrations.

The results of the calculations using this technique show that the PSICAM and the ac-9 give very similar results (Figure 6-9). However, for the lower concentrations, the discrepancies between the two instruments are significant (Figure 6-10). This is to be expected; it was explained in a previous section (*Chapter 4*) that for absorptions lower than 0.02m^{-1} the PSICAM is not sensitive enough. On the other end, as is shown in Figure 6-10, the ac-9 data set shows values below zero. The precision of the ac-9 being 0.001m^{-1} , accurate spectra would be expected. The temperature and scattering corrections have been checked for these data sets. The error might originate in the quality of the initial measurement.

In Figure 6-11 is presented the scattering coefficient deduced from this correction technique. The spectra show very little wavelength dependence. An average of 0.013, 0.095, 0.221, 0.725, 1.268 and 3.573m^{-1} is obtained for different concentrations, which are considerably higher than the absorption values encountered except for the pure water background.

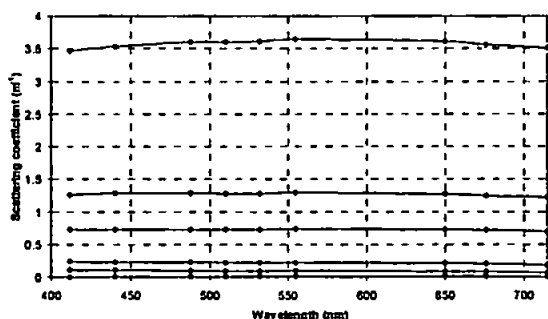


Figure 6-11: Scattering coefficient obtained with the third correction method.

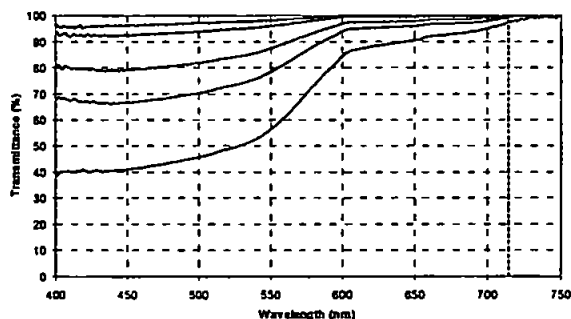


Figure 6-12: Transmittance spectra measured with the PSICAM.

In Figure 6-13 is displayed the absolute value of the percentage error between the two instruments. The 750nm waveband is not shown because using this correction technique, the absorption on this channel is assumed to be zero. The most important ($>50\%$) errors are encountered for the two lowest concentrations ($C_0=0.03\text{mg/l}$, pure water background and

$C_1=0.105\text{mg/l}$). This makes sense with the previous observations regarding the limit of detection of the PSICAM. The absorptions encountered with these two concentrations are below 0.02m^{-1} except for the absorption at 412nm of solution C_1 which is 0.021m^{-1} .

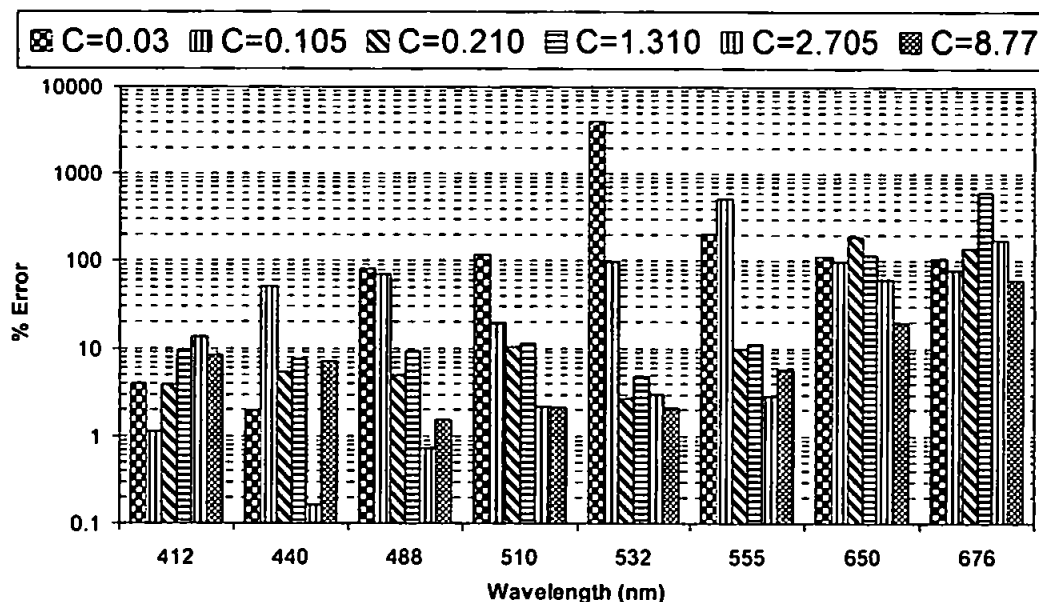


Figure 6-13: Percentage error relative to the ac-9 (absolute value).

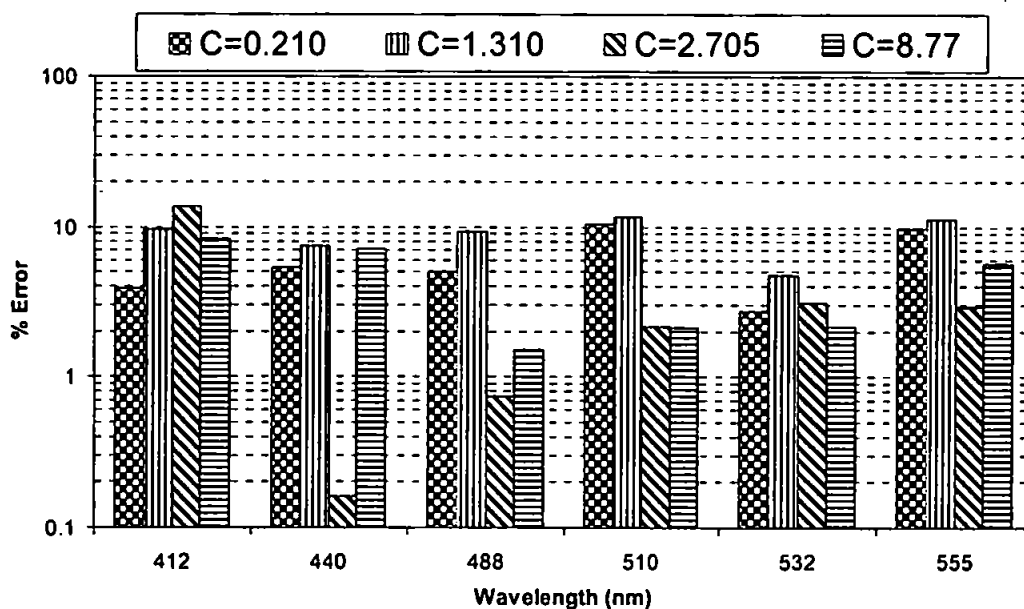


Figure 6-14: Percentage error relative to the ac-9 (absolute value).

Apart from the two lowest concentrations, strong discrepancies ($>50\%$) occur in the red region of the spectrum: 650 and 676nm. The third correction technique assumes that in the red

region and in particular at 715nm, the absorption by suspended particles is zero and that any signal in this region is the result of scattering. Doing this, it also minimizes the absorption at 650 and 676nm. In a solution with high content of inorganic particulate material, as it is in this case, this assumption might not be relevant. If we do not take into account the last two channels of the ac9 (Figure 6-14) and the two lowest concentrations, we arrive at a percentage error between 0.16% and 13%. Nonetheless, it could be argued that the value used for the reflectivity, being quite noisy in the red region, might be responsible for the other estimation of the absorption coefficient. One argument that could be sustained is the fact that there is absorption occurring in the red region that the transmission spectra measured (Figure 6-12). The pure water transmission spectrum is not represented on this figure. It can be seen that no significant depletion in the transmittance occurs for C_1 and C_2 . However, significant depletion occurs for C_3 , C_4 and C_5 . Despite the possibility of errors due to the values of the reflectivity used, it is quite likely that the signal measure in the red region is not entirely due to scattering. The percentage difference calculated between the two instruments is within the range of the percentage error predicted in Figure 5-77, *Chapter 5*.

On Figure 6-15 and Table 6-2, are presented the one to one relationship between the two instruments and the corresponding correlation coefficient, slope and intercept for each concentration. Let us not take into account the first two concentrations where the absorption values are too low for an accurate measurement with the PSICAM. For the four other concentrations, the PSICAM tends to underestimate the absorption coefficient in comparison with the ac-9. The slope encountered goes from 0.869 to 0.906 from C_2 to C_5 for regression coefficients going from 0.95 to 0.99. The intercepts are systematically slightly positive as expected.

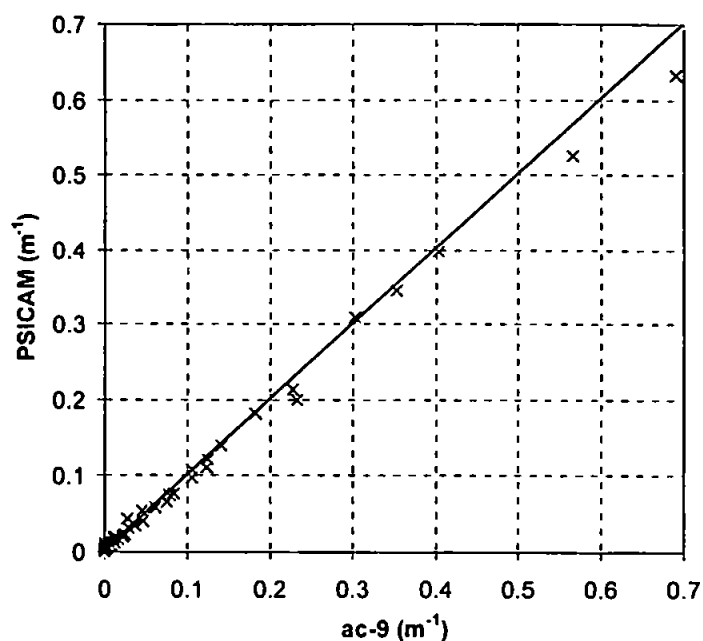


Figure 6-15: Regression between the two instruments.

Table 6-2: Slope, intercept and regression coefficient between the two instruments.

	Slope	Intercept	r^2
C0	0.4969	0.0038	0.7965
C1	0.8878	0.0036	0.8752
C2	0.8737	0.0027	0.9546
C3	0.8698	0.0037	0.995
C4	0.8878	0.0091	0.9884
C5	0.9067	0.018	0.9978

6.2.1.4. Conclusion

With this experiment, we have shown that depending on the correction method used for the ac-9, the PSICAM can produce comparable absorption spectra. The PSICAM produces absorption values within 13% difference of the ac-9 data using the third correction method. Acknowledging that with the calculated reflectivity spectrum used, errors from 5 to 20% were forecasted for 400 to 650 nm and more above 650nm, the differences that occurred with the ac-9 can be considered acceptable.

The results presented above correspond to the third laboratory experiment. Two other laboratory experiments were carried out comparing the PSICAM and an ac-9. The results of these experiments can be found in *Appendix 2*.

6.2.2. Comparison with the filter pad technique

6.2.2.1. Introduction

Light transmission measurements on particles retained in glass fiber filters (Yentsch, 1962) are convenient for determining the light absorption spectrum of particle suspensions consisting mainly of natural phytoplankton and organic and inorganic detritus (Gordon and Morel, 1983). The procedure has a basic advantage: particles can be concentrated so that instrumental accuracy requirements can be met regardless of the high dilutions occurring *in situ* for low productivity regions and regions of little terrigenous inputs. The main problem arises from the large modification of light transmission due to multiple scattering by the filter, which results in an over estimation of particle absorption relative to suspension state (Butler, 1962). Several empirical expressions have been derived for converting the absorption of the retained particles to the equivalent absorption of the particles in suspension. A review of these empirical expressions was made by Cleveland and Weidemann (1993).

Kishino *et al.*, (1984, 1985) proposed a procedure for discriminating absorption by phytoplankton pigments from absorption by detritus based on measurements performed before and after pigment extraction by methanol. Although some doubts remain about the effectiveness of the procedure (Bricaud and Stramski, 1990) and its validity range (little or no effect on some algal species), solvent extraction is the method generally used to identify pigment absorption in natural phytoplankton populations. To minimize the light losses due to forward scattering, which overestimate the sample absorption, a large detector is placed against the sample. The losses due to back-scattering can be minimized by placing the filter in an integrating sphere (Frei *et al.*, 1975).

Tassan and Ferrari (1995), proposed a modification of the standard light-transmission method through the use of a commercially available integrating sphere attachment to a standard

dual beam spectrophotometer. Their technique allow for back-scattering correction. They also provide an alternative procedure for phytoplankton depigmentation, which they argue has a more general validity than the solvent extraction method.

6.2.2.2. Measurement outline

The dual beam spectrophotometer with the integrating sphere attachment (Figure 6-16) permits measurements of filter retained particle samples in both the transmission and reflection mode. The two beams, referred to as sample and reference beam, cross the sphere through ports A1 and B1 respectively. The result of the measurement is the ratio of the radiant fluxes incident on the detector placed inside the sphere that are induced by the sample and reference beam fluxes i.e. $\rho(\lambda) = \Phi_{sb}(\lambda) / \Phi_{rb}(\lambda)$ (where the sub-scripts sb and rb are the radiant flux on the detector due to the sample beam and reference beam respectively).

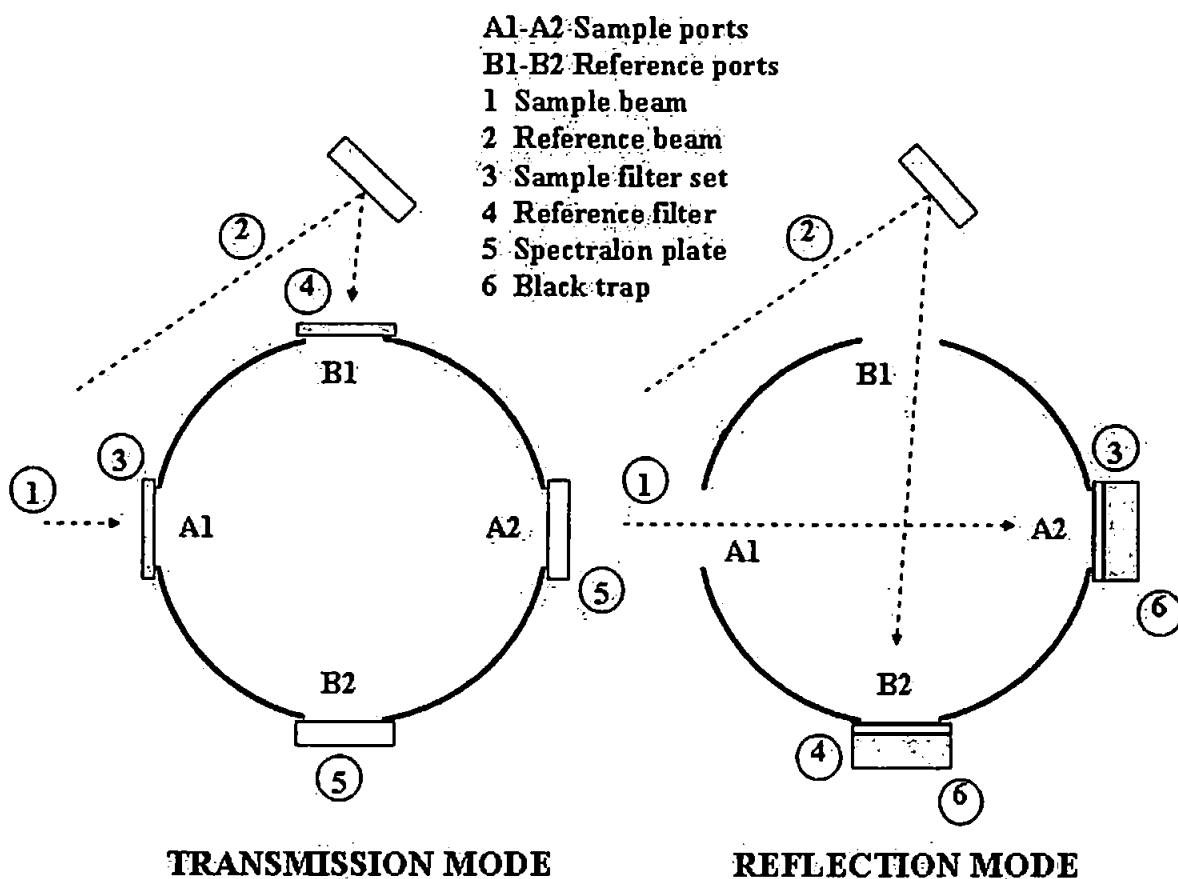


Figure 6-16: Schematic view of the integrating sphere attachment to the dual beam spectrophotometer (from Tassan and Ferrari (1995)).

To measure in the transmittance mode, the sample filter is placed on port A1, with sample side facing the beam, while a reference filter is placed on port B1. Ports A2 and B2 are closed by a Spectralon plate. The result of the measurement in the transmission mode can be expressed as

$$\rho_T = T_S^P M$$

Equation 6-4

where T_S^P is the transmittance of the particle retained on the filter for parallel incident light and M is a factor accounting for any multiple reflection between the particle layer and the supporting filter that would result in increased transmitted light ($M \sim 1$ when back-scattering by the sample is negligible).

For measuring in the reflection mode, ports A1 and B1 are open, the sample filter set is placed on port A2 (sample side facing the beam) and the reference filter is placed on port B2. Absorbing black boxes are placed behind both the sample filter and the reference filter. The result of the measurement in the reflection mode is:

$$\rho_R = \frac{R_{sf}^P}{R_f}$$

Equation 6-5

where R is the reflectance, the subscript sf indicates the filter retained particle sample and f indicates the filter.

6.2.2.2.1. Procedure

The standard procedure for the determination of filter retained particle absorption is based upon interpretation of the single light transmission measurement through Equation 6-4.

The factor M is normally set to 1, the correction for multiple scattering being made through empirical equations. The sample absorbance is calculated as

$$A_s = \log\left(\frac{1}{\rho_T}\right)$$

Equation 6-6

This method leads to an over estimation of the sample absorbance due to the contribution of light scattering by the sample. The correction generally applied for scattering consists of subtracting the absorbance value at 750nm. This relies on the assumption that the phytoplankton absorption is negligible at this wavelength and the scattering is not wavelength dependant. Natural phytoplankton however, always include some detritus whose 750nm absorbance is low but not negligible, so that the observed absorbance at 750nm is the result of both absorption and scattering (*Tassan and Ferrari, 1995*). In practice, this correction method is suitable for oceanic waters (*Gordon and Morel, 1983*). The situation is different for coastal waters due to the presence of inorganic suspended particles coming from various sources. *Tassan and Ferrari (1995)* proposed a different method to measure filter retained absorption and correct for the multiple scattering.

The method they proposed uses both the data provided by double transmission-reflection measurement (Equation 6-4 and Equation 6-5). The procedure to correct for back-scattering is based on the radiation balance equation for the sample filter set:

$$TR + BK + AF + AS = 1$$

Equation 6-7

Where TR is the fraction transmitted into the sphere, BK is the fraction back-scattered, AF is the fraction absorbed by the filter and AS is the fraction absorbed by the sample. From Equation 6-7 can be estimated the absorption of the particles retained on the filter pad (for details of the calculations, see *Tassan and Ferrari, 1995*):

$$a_s = \frac{1 - \rho_T + R_f(\rho_T - \rho_R)}{1 + R_f \rho_T \tau}$$

Equation 6-8

The filter reflectance, R_f is obtained from a measurement in the reflection mode, with a reference filter against port A2 and a Spectralon reflecting plate closing port B2. The factor τ is calculated with an empirical equation $\tau = 1.171 - 0.2615 * \alpha + 0.00013 * \alpha^2$ with $\alpha = \log(1/\rho_T)$ determined by repeating the transmission measurement with the sample-filter set position inverted (sample side facing the sphere cavity). The sample absorption, a_s , is converted to the sample absorbance as:

$$A_s = \log\left(\frac{1}{1 - a_s}\right)$$

Equation 6-9

and then to the equivalent particle suspension absorbance, a_{sus} , by means of the empirical correlation (Equation 6-10).

$$a_{sus} = 2.303 * (0.423 A_s + 0.479 * A_s^2) / E_{path}$$

Equation 6-10

where E_{path} , the equivalent pathlength is calculated as *volume filtered/filter area (m)*

6.2.2.3. Results

During the course of the laboratory experiments, water samples were taken filtered through 25mm glass fibre filters (0.7µm pore size) and analyzed for particulate absorption (Tassan and Ferrari, 1995). One litre was filtered for each water sample. As explained previously, the experiment started with “pure water” and sediments were added to reach a maximum concentration of 8.77gm/l. Since only particulate sediments were added, these sediments having been ashed, it was assumed that no dissolved organic material was present in the water samples. The data presented below compared the total absorption measured with the

PSICAM and the particulate absorption measured on filter paper. Figure 6-17 presents the results of the two techniques for the six solutions measured. Among the six solutions analyzed, only two of them (solution C₂ and C₃) present a good fit between the two techniques (Table 6-3 and Figure 6-19). It can be argued that a portion of the sediment content passed through the glass fiber filter and therefore the two techniques do not measure the same parameters. There is a chance indeed that a source of the differences comes from the previous assumption. However, if this was the only source of error, a similar proportion of difference should be expected between the two measurements. Having the two middle concentrations in acceptable agreement, two hypotheses can be put forward. For the lowest concentrations the amount of particles retained on the filter are not sufficient to allow an accurate measurement. Let us remember however that for these two spectra, the maximum absorption encountered are below the limit of detection of the PSICAM, which is around 0.02m^{-1} .

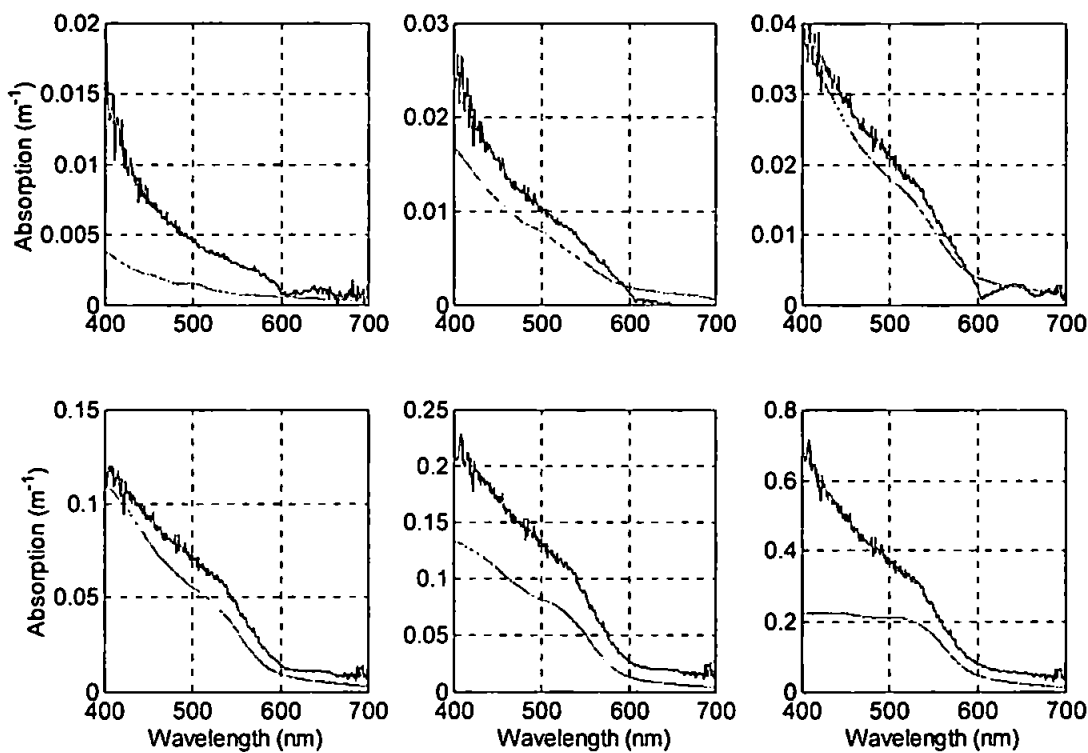


Figure 6-17: Absorption spectra measured with the PSICAM (black line) and with the filter technique (gray line). From top left to bottom right: C₀, C₁, C₂, C₃, C₄ and C₅.

For the two highest concentration of particulate sediment, the linearity range with the filter technique might have been reached leading to underestimation of the absorption coefficient. These two hypotheses can be supported by the observation of the raw absorbance spectra measured with the dual beam spectrophotometer displayed on Figure 6-18. Let us first remember that for this technique, the filters containing the samples are measured in three different ways: two measurements in transmittance (sample on port A1; Figure 6-16) and one measurement in reflectance (sample on port A2; Figure 6-16). For the first transmittance measurement (the direct beam transmittance, PT), the sample side of the filter is facing the beam. For the second transmittance measurement (the diffuse beam transmittance, T), the sample side of the filter is inside the integrating cavity. Finally, for the reflectance measurement (PR), the sample side is inside the integrating cavity.

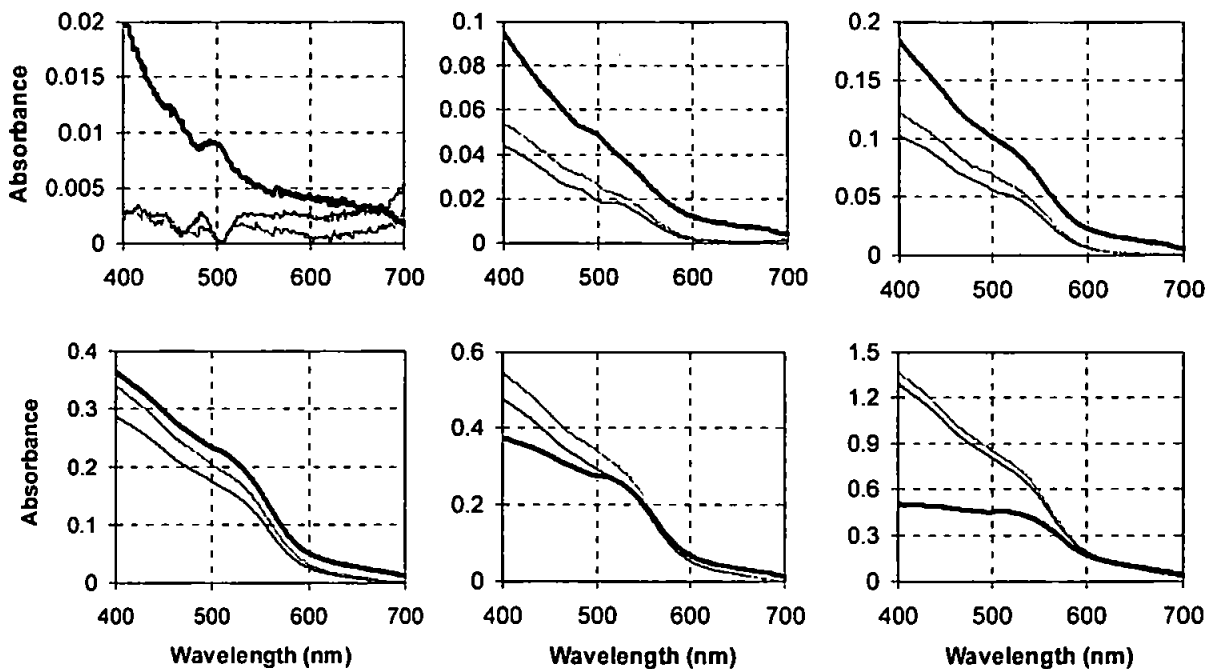


Figure 6-18: Raw absorbance spectra measured with the dual beam spectrophotometer. Direct beam transmittance (thin black), diffuse beam transmittance (thin gray) and reflectance (thick black); from top right to bottom left: C_0 , C_1 , C_2 , C_3 , C_4 and C_5 .

For the two samples where both techniques give comparable absorption spectra ($C_2 = 0.210\text{mg/l}$ and $C_3 = 1.310\text{mg/l}$) the three measurements give similar absorbance spectra, the

reflectance spectra having the highest absorbance. For solution $C_1=0.105\text{mg/l}$, the same pattern is observed: the two spectra measured in transmittance mode are very similar, the difference between the two being the result of different scattering processes. The spectra measured in reflectance gives higher absorbance although in higher proportion than for solution C_2 and C_3 . This is a pattern that was always observed for the natural sample, which will be presented in the next section (*section 6.3*).

For the lowest concentration ($C=0.03\text{mg/l}$; pure water back-ground), a very interesting feature can be observed on the raw data files (Figure 6-18). The two spectra measured in the transmittance mode show similar data. These two spectra show very little absorbance. The absorbance spectra are actually within the range of the baseline (± 0.005). At the other end, the spectrum obtained in reflectance mode does show a typical exponential decrease with increasing wavelength.

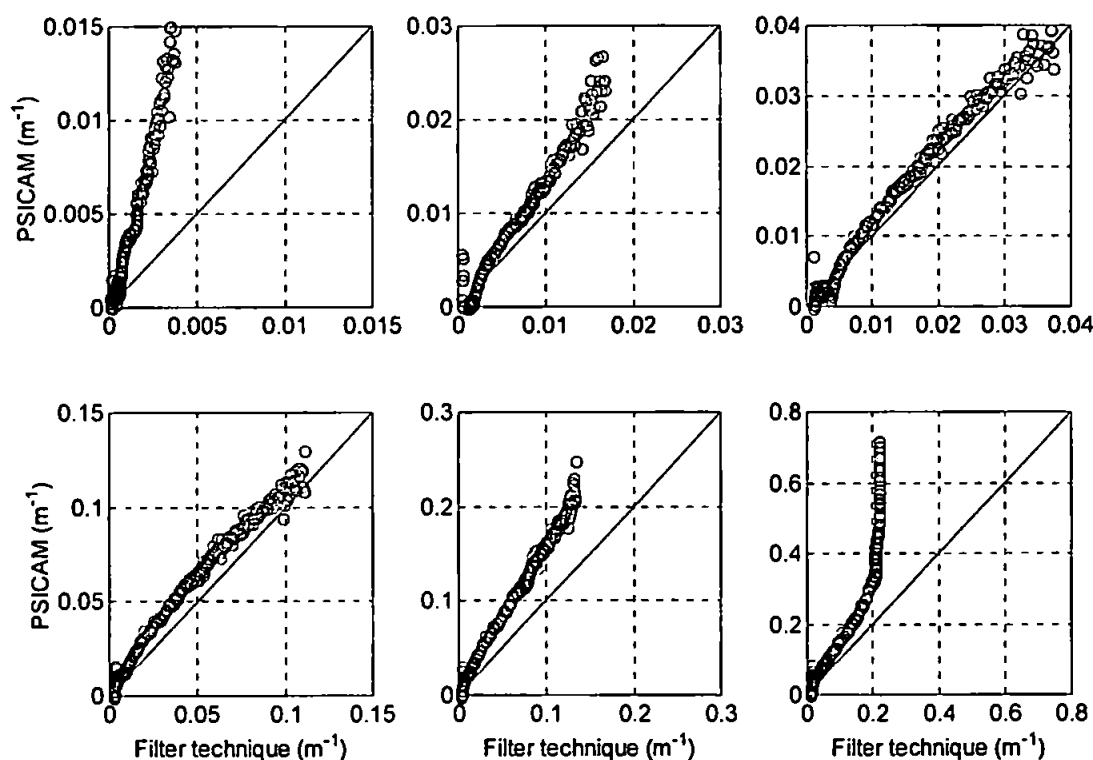


Figure 6-19: Regression between the PSICAM and the filter technique. From top left to bottom left: C_0 , C_1 , C_2 , C_3 , C_4 and C_5 .

Table 6-3: Slope, intercept and r^2 obtained from Figure 6-19

	Slope	Intercept	R^2
C ₀	3.973	-0.0008	0.969
C ₁	1.556	-0.0017	0.968
C ₂	1.109	-0.0002	0.982
C ₃	1.086	0.0058	0.9837
C ₄	1.541	0.0063	0.993
C ₅	2.208	-0.021	0.871

For solutions C₄ and C₅ the patterns of the raw file (Figure 6-18) appear different. The two spectra obtained in the transmittance mode are still very similar but the spectra obtained within the reflectance mode are lower for solution C₄ and appears to reach a plateau for solution C₅. This feature was never observed for natural samples. As for each sample, the same volume was filtered, the increasing amount of sediment deposited on the filter increased proportionally. *Tassan and Ferrari, (1995)*, stated that there is a range of scattering angles close to 90° for which the transmitted light in the transmission mode and the back-scattered light in the reflection mode do not enter the integrating sphere. The range depends on the thickness of the sample filter set and on the size of both the light beam and the sphere entrance port. The corresponding light loss results in an underestimation of PR (spectrum measured in the reflectance mode). The thickness of the sample filter set might in those two cases be responsible for the underestimation if the spectrum in the reflectance mode results in an underestimation of the absorption spectrum.

6.2.3. Conclusion

The filter technique and the PSICAM do show comparable results depending on the concentration range of the samples analyzed (acknowledging that there might be a source of error due to dissolved inorganic material). Within high concentrations of particulate material on the filter, the filter technique underestimates the particulate absorption in comparison to the PSICAM, due to errors in the measurement related to the thickness of the particle layer on the

filter. The problem can be improved by decreasing the amount of water sample filtered, the problem being that in an sampling situation it can be difficult to estimate the Suspended Particulate Matter content of an water sample. Supported by the results obtained with the ac-9, the PSICAM seems to offer better reliability in the experiment. For the lower concentrations, although the filter technique result could be challenge for the first solution analyzed, the PSICAM data can not be entirely trusted, firstly because the absorption range measured is below the experimental limit of 0.02m^{-1} and secondly because similar discrepancies were observed with the ac-9 data.

6.3. In-situ measurements

Station L4 is a sampling site five miles off Plymouth ($50^{\circ} 15' \text{N}$, $04^{\circ} 15' \text{W}$) in about 50m of water. This station is classed neither as case 1 or case 2 water. It has a typical case 1 characteristic during spring and summer with high chlorophyll concentration and low inorganic material content. It turns to case2 characteristic during autumn and winter and has a higher inorganic material signature due to the increase in river input. This station is sampled on a weekly base. Various optical measurements are made for this station including particulate absorption and dissolved absorption. The surface water from this station was measured from September 2001 to March 2003 with the PSICAM for validation purposes. Comparison with in situ measurement of the ac-9 were also made in February and March 2003 together with measurements in more turbid water next to Plymouth Sound break water (BW) and at the mouth of River Tamar estuary (Figure 6-20).

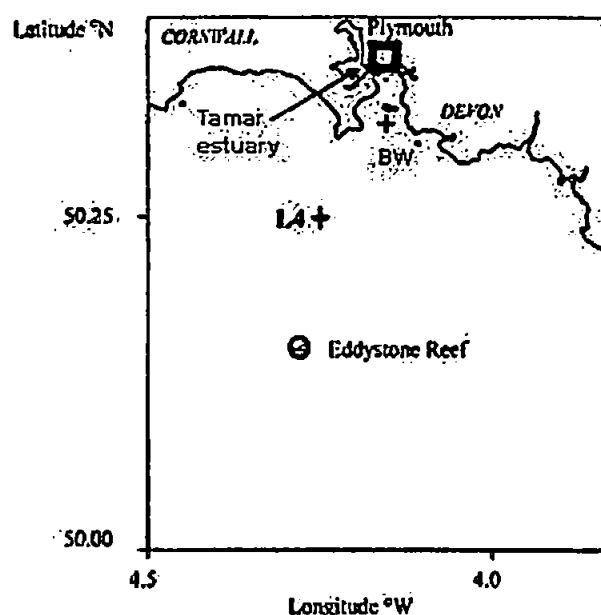


Figure 6-20: Station L4 50° 15'N, 04° 15'W – break water and Tamar estuary.

6.3.1. CDOM / Particulate absorption

The Dissolved Organic Matter (yellow substances) absorption was measured on the visible spectrum after filtration through 0.2µm filters with the sphere and on a 10cm pathlength cuvette with a Perkin Helmer Lambda 2 UV/VIS spectrophotometer.

The particulate absorption was measured as described previously on a dual beam spectrophotometer equipped with an integrating sphere.

For the absorption spectra obtained with the PSICAM, the dissolved absorption spectra were measured after filtration through 0.2µm pore size filter. The particulate absorption was obtained as the difference of the total absorption spectrum minus the dissolved absorption spectrum. The techniques described to measure yellow substance and particulate absorption are the commonly used laboratory techniques to retrieve the total absorption. There is however an obvious bias doing so: there's a proportion of particles whose diameter is between 0.2 and 0.7µm which is not accounted for. Differences between the particulate absorption spectrum measured with the PSICAM and the filter paper technique might be generated from this

difference. The particulate absorption calculated from the PSICAM data takes into account particles of diameter higher than $0.2\mu\text{m}$ whereas the filter paper technique takes into account particles bigger than $0.7\mu\text{m}$.

The comparison with the data obtained with the three techniques will be describe with four type absorption spectra: spring bloom (18 June 2002, Figure 6-21 to Figure 6-23), summer low productivity (22 July 2002, Figure 6-24 to Figure 6-26), autumn bloom (16 September 2002, Figure 6-27 to Figure 6-29) and winter low productivity (25 November 2002, Figure 6-30 to Figure 6-32). The total data set is to be found in *Appendix 3*.

18th June, 2002

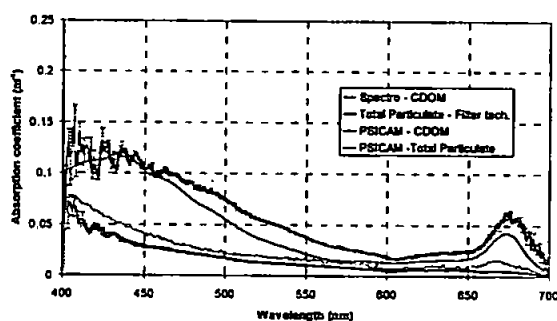


Figure 6-21: Dissolved and Particulate Absorption spectra.

Table 6-4: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	0.9474	0.0136	0.944
DOM	0.795	-0.0018	0.967

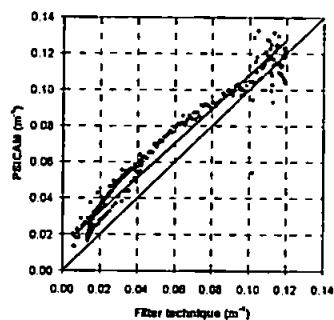


Figure 6-22: Particulate Absorption regression.

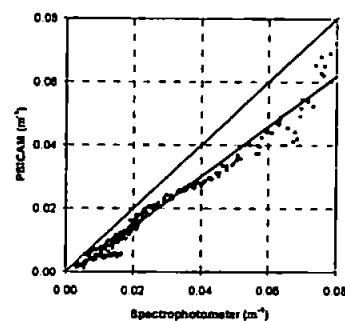


Figure 6-23: DOM regression.

22nd July, 2002

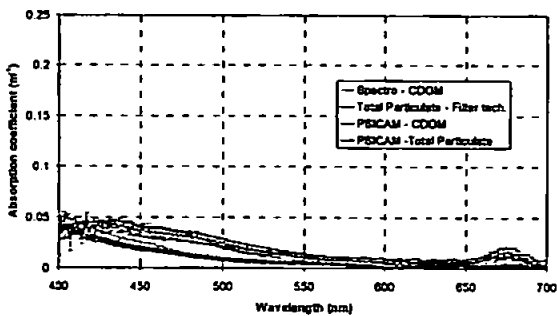


Figure 6-24: Dissolved and Particulate Absorption spectra.

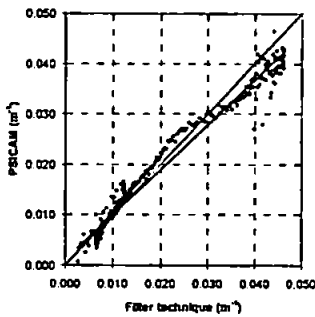


Figure 6-25: Particulate Absorption regression.

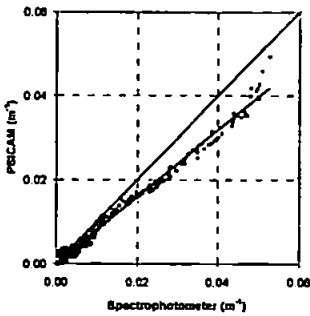


Figure 6-26: DOM regression.

16th September, 2002

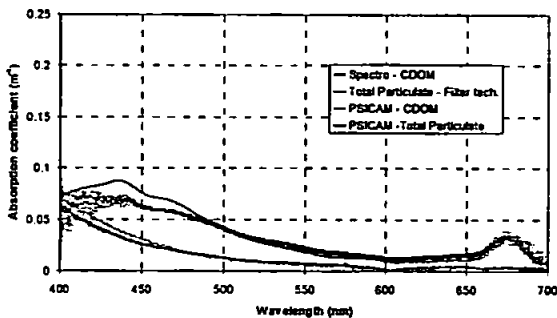


Figure 6-27: Dissolved and Particulate Absorption spectra.

Table 6-6: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	0.751	0.006	0.98
DOM	0.786	0.003	0.991

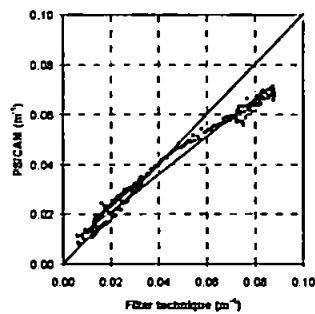


Figure 6-28: Particulate Absorption regression.

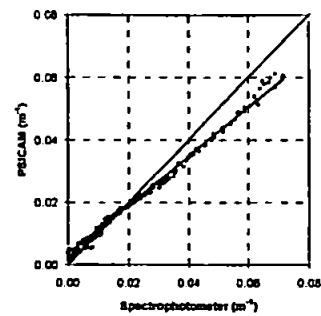


Figure 6-29: DOM regression.

25th November, 2002

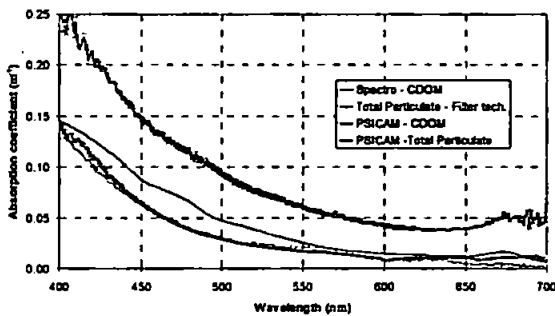


Figure 6-30: Dissolved and Particulate Absorption spectra.

Table 6-7: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	1.465	0.023	0.988
DOM	1.024	0.001	0.987

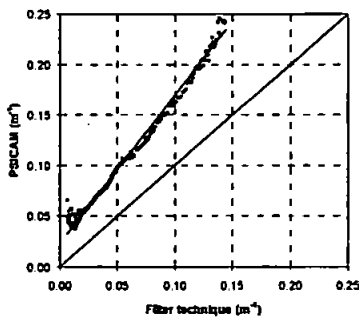


Figure 6-31: Particulate Absorption regression.

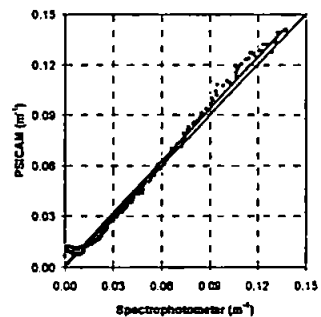


Figure 6-32: DOM regression.

The four selected data sets describe the annual variation of the optical properties at L4 station. The absorption versus wavelength graphs are on the same scale to emphasize the

seasonal variation. On the 18th of June (Figure 6-21), we have a spring bloom situation with a clear chlorophyll absorption peak of 0.05m^{-1} at 670nm and a more important one of 0.12m^{-1} at 440nm. The signal is particularly noisy in the blue wavelength. This comes directly from the transmittance spectrum. At the time of the experiment, the light source was particularly unstable at these wavelengths. The yellow substance spectra have the typical exponential decrease. On the regression graphs (Figure 6-22 and Figure 6-23), it appears that the PSICAM produces a similar particulate absorption spectrum but with an almost constant offset. The DOM spectrum however tends to be underestimated mainly in the blue region of the spectrum.

On the 22nd of July, we have a mid summer situation, with low dissolved and particulate content. A small chlorophyll signature is still visible but of less intensity. For this set of data, the regression is however better than for the previous data (Table 6-5, Figure 6-25Figure 6-26). On the 16th of September, we have a autumn bloom situation. Two absorption maxima characteristic of the chlorophyll absorption can be seen although of less importance than in the spring situation. The expected yellow substance signature is again visible. Both particulate and dissolved absorption spectra tend to be underestimated by the PSICAM although very good correlations are observed (Table 6-6, Figure 6-28 and Figure 6-29). On the last date sampled, we have a winter situation with high levels of dissolved and particulate material due to the influence of river drainage and resuspension. There is no more chlorophyll signature visible on the particulate spectra. The dissolved absorption spectra of both techniques are very similar (Figure 6-32). However, the PSICAM seriously overestimates the particulate absorption spectrum. On this particular date, the amount of particulate material present on the filter pad was very important. To perform the measurement, the filter pad needed to be humidified with filtered water. Doing this, a small amount of material can be lost or displaced on the filter making a less homogeneous surface. This indeed happened for this sample and that is probably

one way to explain the important discrepancies between the two instruments. The results from this date was presented in this section for its characteristic winter absorption spectrum but also to point out that the experimental procedure in some cases can be difficult to apply.

6.3.2. *Ac-9 transmittometer in situ*

A few comparisons between the PSICAM and *in situ* ac-9 measurements were carried out during winter 2003. The measurement were carried out with the ac-9 in three different locations: the station L4, outside Plymouth break water and in the Tamar estuary (Figure 6-20), therefore covering a wide range of optical properties. From the station sampled were taken surface water samples which were later analyzed in the laboratory with the PSICAM. The results of the five days sampled are presented below (Figure 6-33 to Figure 6-40). For each day sampled is displayed the absorption spectrum of both instruments as well as the regression between the two instruments. These measurements having been made during winter, the absorption spectra obtained are characteristic of yellow substance or inorganic particulate matter absorption spectra.

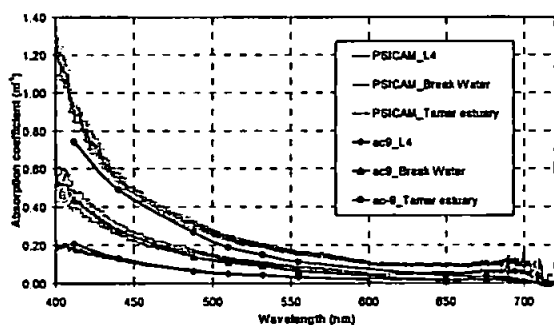


Figure 6-33: Absorption spectra measured with the ac-9 and the PSICAM the 10th February.

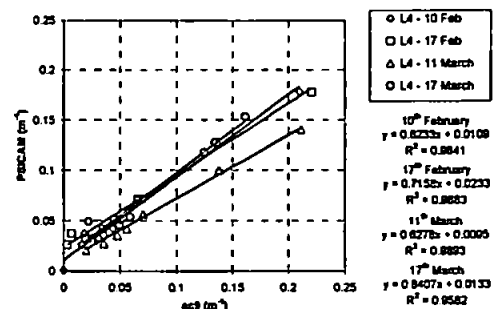


Figure 6-34: Regression of the L4 set of data.

From all the stations sampled, the ac-9 and the PSICAM produced similar absorption spectra. The major differences usually occurred in the red part of the spectrum as that was the case with the laboratory experiments. One of the possible sources of difference between the two instruments is related to the difference in the procedure used with both instruments, one being

an *in situ* measurement, the other being made in a laboratory after sampling. Although the PSICAM measurements were made less than six hours after sampling, modification of the sample might have occurred due to the sampling process. A second possible source of difference is that the sample taken for analysis was a surface water sample. These samples are compared with an ac-9 vertical profile whose first sampling depth is between one and two meters. Although no significant stratification was observed on the temperature and salinity profiles (See Appendix 3), significant variations can occur in the first meter of water. Finally, in highly variable environments such as coastal waters, the time elapse between the ac-9 profile and the water sampling can be enough to show small scale variations.

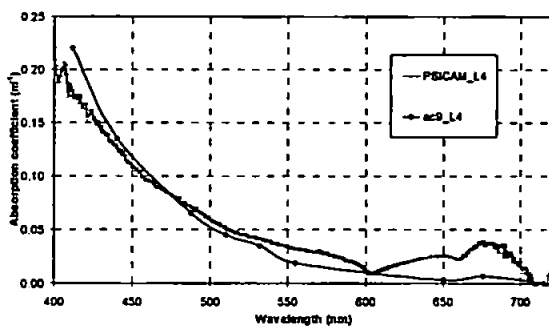


Figure 6-35: Absorption spectra measured with the ac-9 and the PSICAM the 17th February.

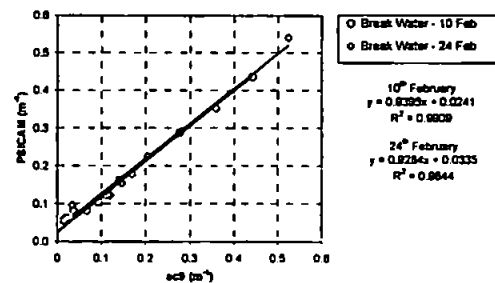


Figure 6-36: Regression of the Break Water set of data.

For water samples of relatively low absorption like such as in Figure 6-35 and Figure 6-40 (L4 station) the temperature effect which occurs at 600, 660 and 715nm is clearly visible, the sample having been measured relative to pure water which was at room temperature.

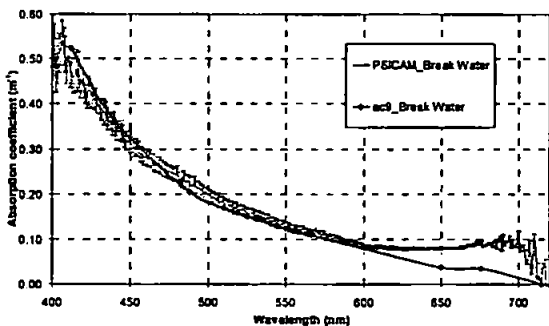


Figure 6-37: Absorption spectra measured with the ac-9 and the PSICAM the 24th February.

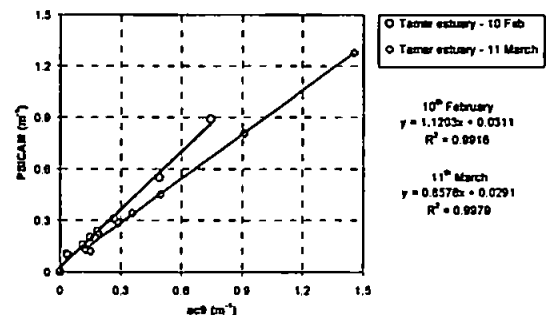


Figure 6-38: Regression of the Tamar estuary set of data.

The regression coefficient between the two techniques, for these eight water samples varies between 0.98 and 1.00 except for the L4 station sample on the 17th of March with $r^2 = 0.95$. There are not enough data to produce reliable statistics for the Break Water station which seems to produce the best correlations between the two instruments (slope > 0.92 and $r^2 > 0.98$). The data points drift from a one to one relationship mainly because of the discrepancies which occur to the red channels.

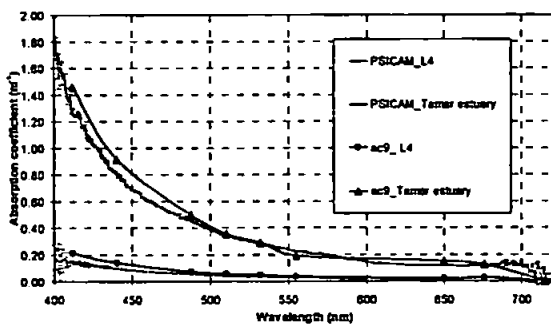


Figure 6-39: Absorption spectra measured with the ac-9 and the PSICAM the 11th March.

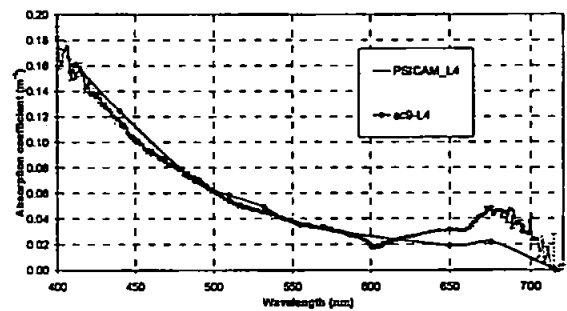


Figure 6-40: Absorption spectra measured with the ac-9 and the PSICAM the 17th March.

With the four samples measured at L4, there is a sample which importantly underestimate the ac-9 measures (17th March). The other three are in accordance with predictions. The tendency is to underestimate the absorption for the shorter wavelength and, as previously overestimate the absorption for the shorter wavelength. Finally, for the samples with highest particulate content (Tamar estuary), the two instruments are well correlated with the major discrepancies appearing in the red part of the spectrum.

To summarize the above data, Figure 6-41 and Figure 6-42 present the percentage differences observed at the different dates and stations sampled.

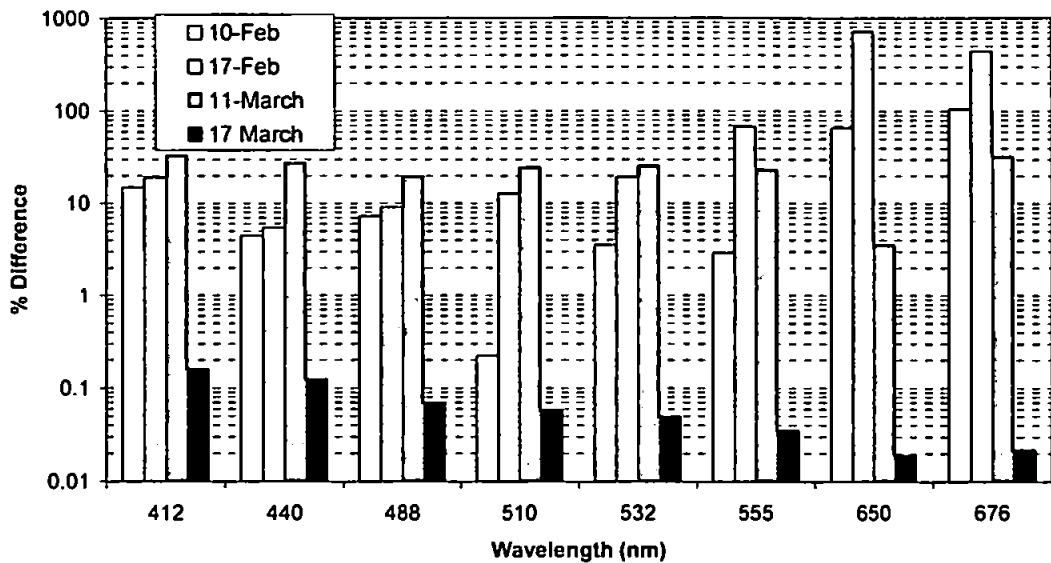


Figure 6-41: Percentage difference observed at station L4

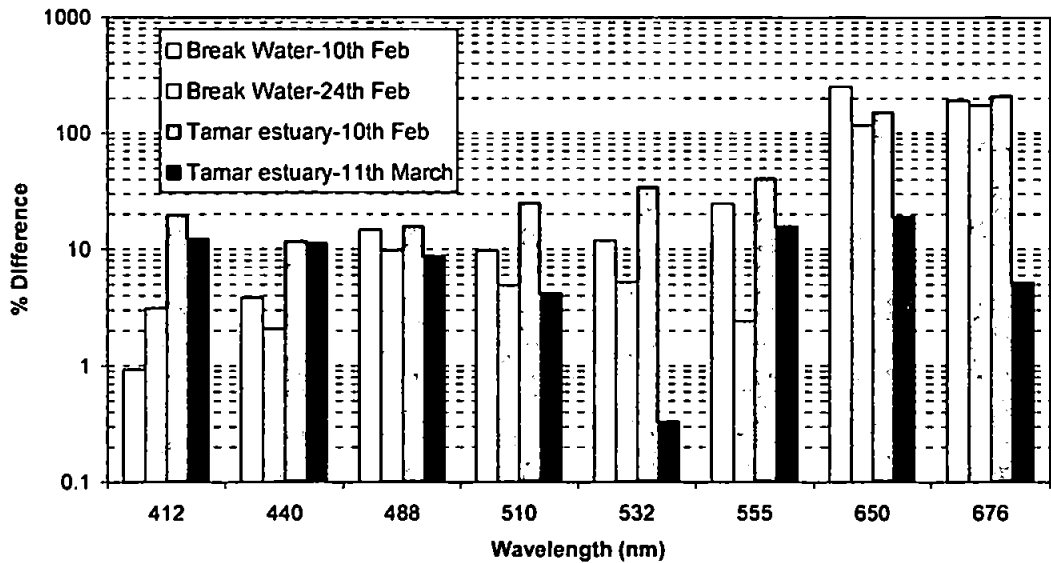


Figure 6-42: Percentage difference observed at the Break Water station and in Tamar estuary.

As it was the case during the laboratory experiment, the most significant differences occur in the red part of the spectrum ($>100\%$). There are two reasons for this: the depletion in the light transmitted is generally small so that the PSICAM may not be able to measure the signal accurately enough. Then the correction method applied assuming that there is a reference wavelength (715nm) at which there is no absorption. This method has for effect to set to zero the absorption at 715nm and also to minimise the absorption in the red region of the spectrum.

In the blue and green wavelengths measured by the ac-9 transmissometer, the percentage differences are usually smaller going from 0.01% to 30% although higher percentages are observed (70% difference at 555nm on the 17th of February). There are unfortunately not enough data to derive any trend but it seems that the data from more turbid waters (Break Water and Tamar estuary) show a smaller difference. This would make sense knowing the characteristic of the integrating sphere but it could also be an artefact of the calculation: the absorption being higher, the uncertainty of the measurement of the PSICAM would appear proportionally less.

6.3.3. *Field test around the Antarctic Peninsula*

The PSICAM has been successfully tested and compared to other instrument such as the ac-9 transmissometer during laboratory experiments with natural samples collected in the Plymouth area or with artificial solutions containing scattering particles. As a field test, the PSICAM was deployed around the Antarctic Peninsula during a cruise on board HMS Endurance from 23rd February to the 13th March 2002. The PSICAM was calibrated before and after the cruise to ensure accurate calculations. Thanks to careful manipulation and maintenance during the on-board experiments, the reflectivity did not show significant variation.

The measurement carried out with the PSICAM consisted of total absorption measurements as well as dissolved absorption measurements after filtration through 0.2µm filters. At each station, two depths were sampled: surface and Secchi depths (see *Appendix 4, figure 1* for the station locations). In addition to the PSICAM data, chlorophyll absorption measurements, after extraction in 90% acetone, were carried out following the method described by *Strickland and Parson (1972)*. The Secchi depth was measured as well as the sea surface temperature for each station. At most of the stations, a temperature profile was obtained.

As an example of the data collected with the PSICAM, a short description of a time series undertaken on the eastern part of James Ross Island will be described (*Appendix 4, figure 1 station G*). The data at this particular location were collected on five different days. For the description, four representative days will be presented (3rd, 5th, 7th and 9th of March; Figure 6-43, Figure 6-44, Figure 6-45, Figure 6-46 respectively). The total data set of the time series as well as the other stations sampled during the cruise can be found in *Appendix 4*.

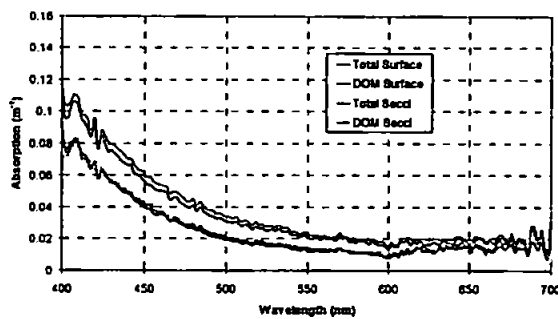


Figure 6-43: Total and dissolved absorption spectra 03/03/02

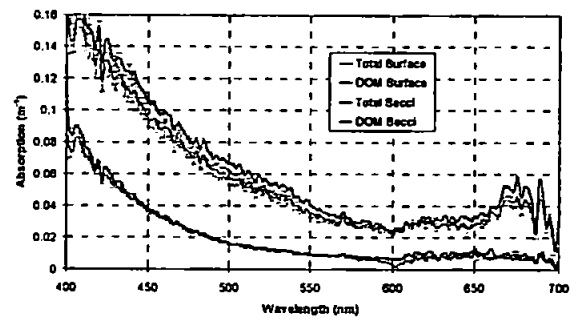


Figure 6-44: Total and dissolved absorption spectra 05/03/02

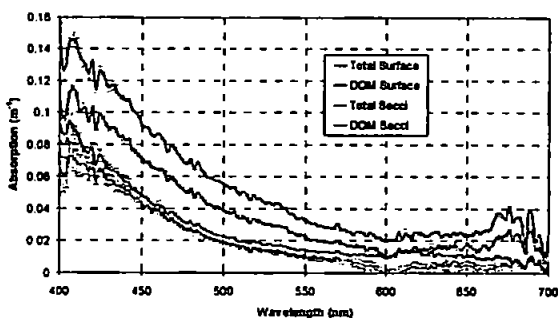


Figure 6-45: Total and dissolved absorption spectra 07/03/02

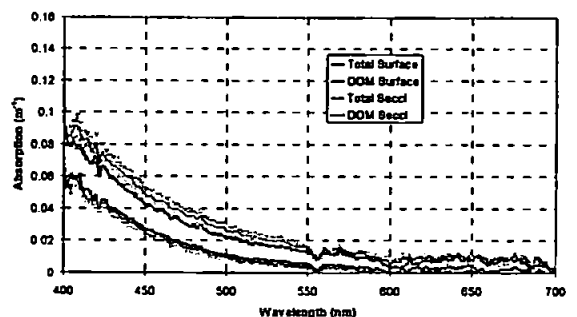


Figure 6-46: Total and dissolved absorption spectra 09/03/02

On each of these graphs are presented the total and dissolved absorption for the surface and Secchi depth. For the dates sampled, there are no significant differences between values at the surface and at the Secchi depth which suggests that there is no important stratification except for the case of total absorption spectrum on the 7th of March. This structure is not,

however, indicated by the temperature profile, which is homogeneous down to 23m for this date (*Appendix 4, figure 28*) and further down for the other dates. The dissolved organic matter profiles do not show very much changes during the sampled dates and display a typical exponential decrease toward the red wavelengths with a maximum absorption around 0.08m^{-1} at 400nm. A very different situation occurs for the total absorption. On the 3rd of March, the total absorption displays an inorganic absorption spectrum. On the 5th of March, the total absorption spectrum displays a strong chlorophyll signature with a maximum in the blue and in the red wavelengths. This chlorophyll signature decreases on the 7th and the situation returns to the initial state on the 9th. The situation observed with the absorption spectra is in agreement with the Secchi depth measurement except for the 9th of March. The other parameters recorded during this time series showed that a calm sea with no wind was observed on the 3rd. A north-north-west wind blew on the 4th creating a rough sea state. No wind and a calm sea were recorded for the following days. Having temperature profiles fairly homogenous during the sampled days, it is unlikely that the sea state observed on the 4th of March would have mixed a subsurface chlorophyll maximum. The more likely situation is that a water body containing higher chlorophyll concentrations was pushed towards James Ross Island and then drifted away from the station. On *Figure 28, Appendix 4*, comparable temperatures were recorded for the 5th, 6th, 7th and 8th (below zero) whereas a warmer water body was encountered on the 9th. This would further support the assumption that a current probably going toward the south southwest changed the water body around the sampled station.

Looking at the temperature profiles, it is rather surprising, when used to temperate weather, that chlorophyll can still be found in zero and subzero temperatures. During the last week of the cruise, the Antarctic winter already started to be felt by an important drop in the air temperature. Snow falls occurred three times during this last week of the cruise.

The PSICAM proved to work reliably during the cruise and the system performed as well as during the laboratory experiments. There are however general aspect of the system that will need to be improved to facilitate its deployment at sea either for open ocean cruises, where the instrument is used on a daily basis for long periods of time, or for coastal cruises where samples of different stations must be analyzed in rapid succession. Firstly, having to make regular blank calibrations to ensure reliability of the measurements proved to be more time consuming than in a laboratory where pure water facilities are at hands. A more stable unit would be a particularly important improvement in sea working conditions. Secondly, a flow-through system would also improve time cost in sea working conditions.

Chapter 7: Discussion and further work

Discussion

The results obtained from numerical modelling showed that, as predicted, the PSICAM should be relatively insensitive to scattering. This instrument owes this potential to its ingenious design: using a reflective sphere instead of a standard linear cell and a central light source, so that no corrections are required for the effect of scattering. This unique characteristic makes of this instrument a potentially very powerful way to measure the absorption coefficient either in productive oceanic regions with high organic particulate content or in coastal regions with high organic and inorganic particulate content. A PSICAM would have the further advantage of being able to measure particulate absorption with very limited handling of the water sample, which also means very limited sources of error due to sample degradation. Furthermore, a PSICAM does not require empirical scattering corrections. Such advantages are particularly interesting for optical remote sensing application where accurate data in coastal area are crucial for the establishment of phytoplankton productivity or chlorophyll concentration algorithms.

This system has however a disadvantage, which was revealed by both the experiments and the theory: accurate measurements of absorption are extremely dependant on the calibration of the cavity reflectivity. The component chosen for the integrating sphere of the final prototype was Spectralon. Although it has high reflective and Lambertian properties, a problem that would be encountered with such a component for routine measurement of natural water samples is the degradation of its surface. Being regularly in contact with sea water will inevitably degrade its surface. The Spectralon sphere used for the experiment described in this thesis was always rinsed very carefully with pure water and its surface checked for traces of fouling and cleaned if necessary. The cavity reflectivity was however regularly calibrated. After a year and

a half of regular use, its properties have not been significantly degraded, although a depletion of the reflectivity was observed (*Figure 7-1*). Nonetheless, the small variations of the reflectivity would have generated important errors in absorption measurements if not taken into account.

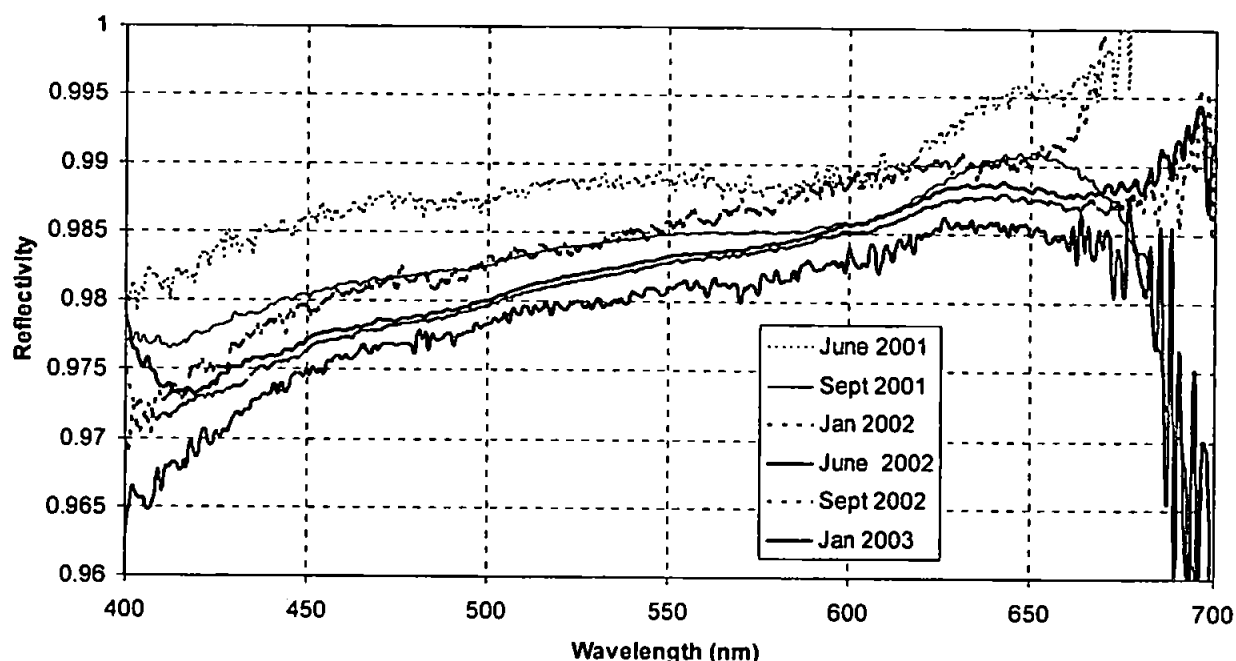


Figure 7-1: Evolution of the reflectivity of the Spectralon integrating sphere

If there is any significant fouling or soiling, the only way to clean the Spectralon is to use a very fine glass paper to erase the degraded surface. For this reason, a more robust material would be preferable for a sea-going instrument. The initial glass integrating sphere embedded in barium sulphate or coated with a reflective material would be easier to clean. Materials like ceramic have not been tested but could also provide a good alternative.

A problem inherent to the prototype that has been developed is the stability of the light source. Having a single beam system necessitates taking regular measurements of the reference solution and this is very time consuming. More importantly, for the critical measurement of the reflectivity of the integrating cavity, light input variations between the reference measurement and the measurement of the standard solution generate small errors in the calculation of the

reflectivity, which in turn create even bigger errors in the calculation of the absorption coefficient of standard solutions or natural samples. It is however acknowledged that particularly in the blue part of the spectrum, the instability of the signal is not only due to the light source but is a combined effect of the light source, the diffraction grating of the spectrophotometer and the sensitivity of the silicon photodiodes.

The various experiments carried out with natural or artificial solutions showed that the PSICAM could equal the performance of existing techniques even with high levels of scattering particles in the solution assuming that the calibration was regularly and carefully made. Testing the efficiency of the PSICAM with absorbing and scattering solutions was a difficult task because of the difficulty in producing absolute standard solutions containing scattering particles. The way to validate the PSICAM was therefore to compare its performance with that of other instruments when measuring natural or artificial solutions containing scattering particles. The first instrument was the ac-9 (WetLabs), an *in situ* technique, and the second was a laboratory technique for measuring particulate absorption using filter paper. Another solution to test the PSICAM efficiency would be to use calibrated beads from which scattering characteristics would be calculated through Mie theory for scattering. This technique has not yet been tried but could also provide valuable results.

The sea trial in the Antarctic waters showed that the laboratory version of the PSICAM could be successfully deployed at sea. This trial revealed, however, certain practical limitations of the system.

Further work

There are a number of ways in which the system could be further improved.

- The first one would be to use a dual beam system for the light source. The initial beam coming from the light would be split by means of a beam splitter. One beam would be measured as the reference input; the second would go through the integrating cavity, to be measured as the output. The transmittance would be calculated as the ratio of the two measured signals. This would provide a much more accurate system since the output of the light source would be monitored; it would also provide a better system of measurement of the reflectivity of the cavity wall.
- The system used was a laboratory version in which the water samples needed to be poured in manually. Another improvement that would reduce the time cost of the analysis would be to use a flow-through system. This would also allow testing the efficiency of the instrument with the effect of bubbles which scatter light.
- As mentioned previously, the integrating cavity should be made of a material easy to clean to facilitate regular use of the instrument.

For the future of the instrument, two possibilities are suggested

Measuring particulate absorption is a very complicated task. The PSICAM as a laboratory instrument could be further developed as a technique to measure particulate absorption. The organic and inorganic fraction could be identified by doing measurements before and after photo-bleaching. It would have a major interest in comparison to the filter pads technique: samples in their natural physical state would be measured. The experiments comparing the PSICAM with the filter pads technique usually showed significant differences.

Having no absolute standard of absorbing and scattering solutions, we can only speculate on the significance of these differences.

The instrument is still a long way from being developed as a submersible unit. The comparison with the ac-9 spectrophotometer looked promising knowing that neither scattering nor temperature and salinity corrections were applied. The temperature effect was, however, visible in most of the experiments and this is an obvious correction that will need to be explored in the future. The second possibility for the instrument before being developed as a submersible unit would be to build a deck unit that could measure water samples pumped from below.

Chapter 8: Conclusions

The review of the different techniques to measure the absorption coefficient in sea water showed that there is still scope for improvement mainly due to the interfering effect that scattering by particles has on the measurements. The complexity of the components present in natural waters makes it necessary to develop techniques that can reliably measure the absorption of the dissolved and particulate fractions. Among the instruments to measure absorption, a promising one appeared to be one based on an integrating cavity. *Kirk (1997)* published the principle and theory of a Point Source Integrating Cavity Absorption Meter (PSICAM). Based on this principle, theoretical and experimental work was carried out with the aim of modelling and developing a PSICAM.

1. Numerical modelling using the equation found in the literature was carried out for absorbing and non-scattering solutions to investigate the effect of the cavity diameter on the system and to carry out a thorough sensitivity analysis.

The results showed that the diameter of the sphere should be taken into account for an optimum efficiency. The size of the integrating cavity should therefore increase from turbid to clear waters to allow a significant depletion of the measured radiance in the sphere. A radius of 10cm would be recommended for oceanic waters whereas 3cm radius would be recommended for estuarine waters. For our prototype, which was destined to be used in coastal waters, a radius of 5cm was adopted and proved quite flexible for various water types.

Kirk (1997) predicted that a PSICAM would be relatively insensitive to scattering. The down side of this concept, however, is that the instrument is extremely sensitive to the reflectivity of the cavity wall, which is measured experimentally. The sensitivity

analysis carried out for different cavity radii and different reflectivity values showed that of the four variables of the system, the PSICAM is most sensitive to the reflectivity. To calculate the absorption spectrum of a given solution, the reflectivity spectrum needs to be known very accurately. If not, the calculated absorption could be dramatically erroneous. The sensitivity analysis, however, showed that using a less reflective cavity wall would slightly reduce the dependence of the instrument upon this parameter.

Finally, theoretical calculations showed that the cavity radius chosen for the prototype (5cm) would allow accurate measurement from 0.02m^{-1} up to 7m^{-1} .

2. A novel Monte Carlo code was written to model the behaviour of a PSICAM with absorbing and scattering solutions and for various cavity diameters.

The results obtained by Monte Carlo modelling showed that the PSICAM has indeed a great potential for measuring absorption regardless of the level of scattering. Monte Carlo simulations showed that for a given integrating cavity radius, the effect of scattering would affect the measurement only for very high levels of scattering. For the scattering ranges encountered in marine waters, the influence on the absorption measurement would be insignificant assuming a Petzold scattering function. Finally, it was shown through Monte Carlo simulation that the scattering effect on the measurement would increase with increasing absorption but also increase with increasing cavity radius.

3. Two integrating cavities made out of round bottomed flasks embedded in barium sulphate were built for a first and cheap assessment, and tested with four light sources

before a final version was adopted. These prototypes were then tested with standard solutions of known absorption.

As predicted by the theory, these experiments showed that great care must be taken in the measurement of the integrating cavity reflectivity. To do this, the absorption spectrum of the standard solution used for the calibration must be measured very accurately.

4. With the experience acquired with the initial prototypes, a final laboratory version of the PSICAM was built using a Spectralon sphere and tested with standard solutions. The tests carried out with non-scattering solutions showed that assuming that the instrument was carefully calibrated, the PSICAM could equal existing techniques in performance. However, the absorption range over which the PSICAM was found to be accurate (from 0.02m^{-1} to 2m^{-1}) differed slightly from the theoretical prediction.

5. The final version of the PSICAM was then compared with existing techniques for the measurement of artificial or natural solutions containing both absorbing and scattering components. The solutions tested were prepared in the laboratory or sampled in Plymouth area. The PSICAM was compared with:

- an ac-9 transmissometer,
- particulate absorption measured on filter paper
- Coloured Dissolved Organic Matter measured in a dual beam spectrophotometer.

The various tests made with natural solutions of dissolved organic components showed that the PSICAM could equal the performance of existing techniques assuming that the calibration was carefully done. The PSICAM produced remarkable correlation with the results of the ac-9 for both artificial and natural water even for solutions of high

particulate content. Significant differences did occur however, particularly in the red region of the spectrum, due to the assumptions of the corrections used with the ac-9 transmissometer. When comparing with the laboratory techniques to measure the particulate absorption, once again, similar absorption spectra were obtained with more or less important differences. The fact that in this case, the analyses were performed on the same samples but in different physical states could explain the differences, keeping in mind that the PSICAM calibrations showed greater standard errors at some wavelengths than at others. Only an improved version of the PSICAM, particularly one with a more stable light source, would give a definitive answer.

6. As a field experiment, the PSICAM was successfully deployed for a research cruise around the Antarctic Peninsula during which total and dissolved absorption measurements were performed together with chlorophyll absorption measurements after pigment extraction in acetone.

Appendix 1: Standard Solution Experiments

A Spectralon prototype – least square method

The results of the experiments carried out with standard solution presented in Chapter 5 used Kirk's formula to retrieve the absorption coefficient. The results of the same experiments using the least square method are presented below.

A.1. Blue solution

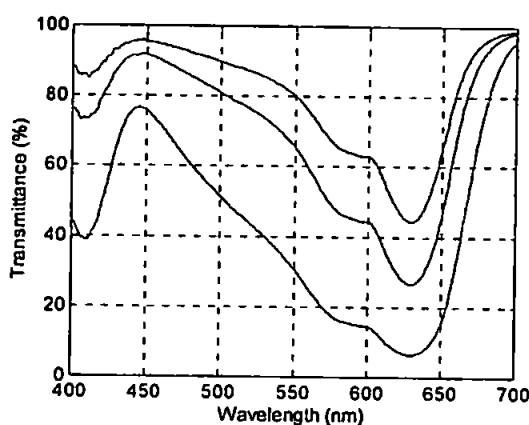


Figure 1: Transmittance spectra measured with the PSICAM for the three blue solutions.

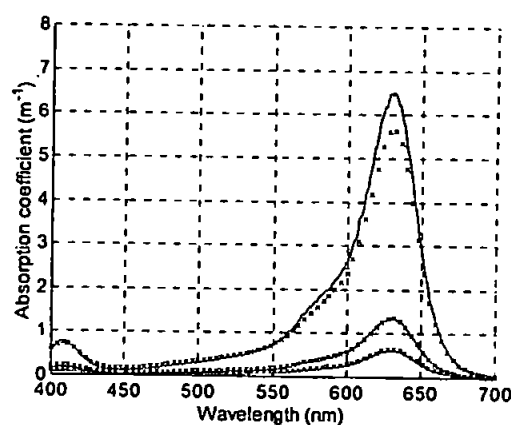


Figure 2: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

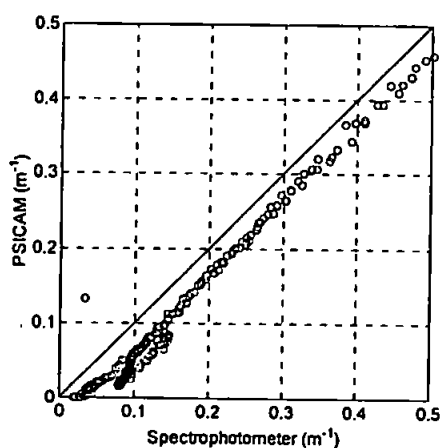


Figure 3: PSICAM versus Spectrophotometer for C_1 calculated with the least square technique.

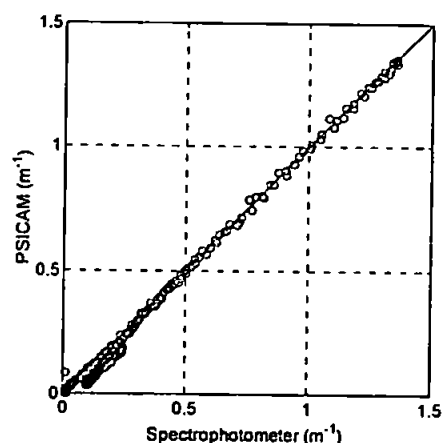


Figure 4: PSICAM versus Spectrophotometer for C_2 calculated with the least square technique.

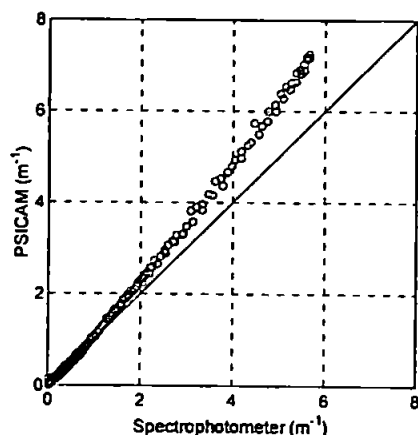


Figure 5: PSICAM versus Spectrophotometer for C_3 calculated with the least square technique.

Table 1: Slope, intercept and regression coefficient between the two instruments with the least square technique.

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	1.01	-0.05	0.996
C_2	1.03	-0.04	0.997
C_3	1.14	-0.08	0.999

A.2. Green solution

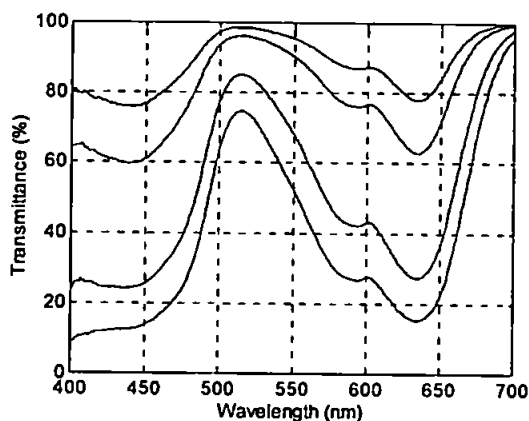


Figure 6: Transmittance spectra measured with the PSICAM for the three blue solutions.

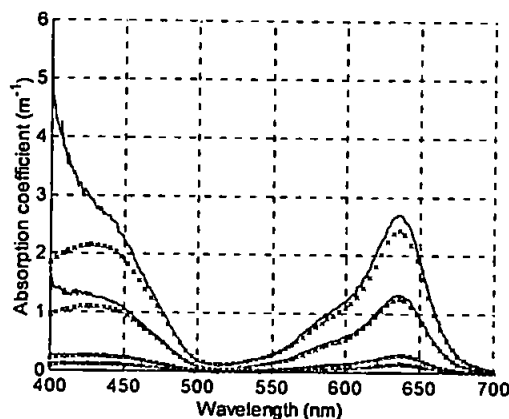


Figure 7: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

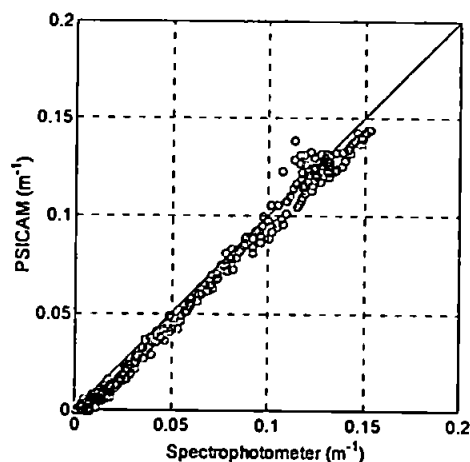


Figure 8: PSICAM versus Spectrophotometer for C_1 calculated with the least square technique.

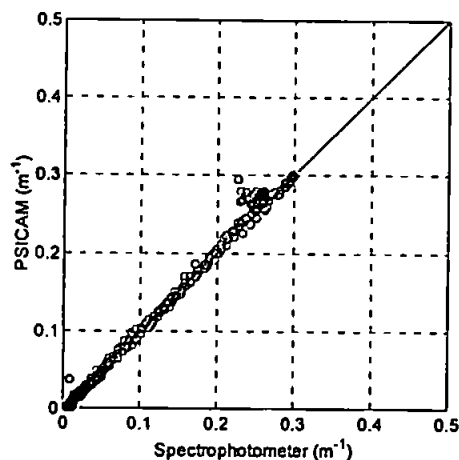


Figure 9: PSICAM versus Spectrophotometer for C_2 calculated with the least square technique.

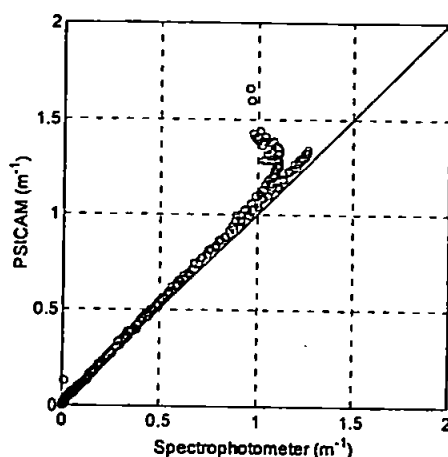


Figure 10: PSICAM versus Spectrophotometer for C_3 calculated with the least square technique.

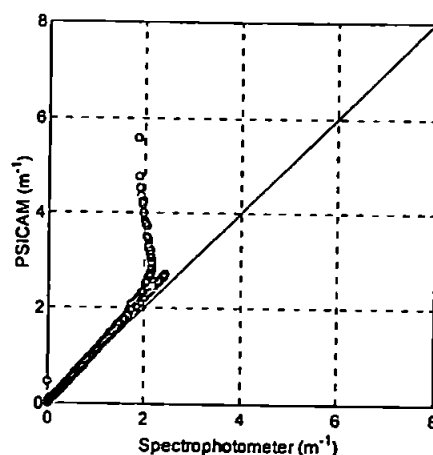


Figure 11: PSICAM versus Spectrophotometer for C_4 calculated with the least square technique.

Table 2: Slope, intercept and regression coefficient between the two instruments with the least square technique.

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	1.02	-0.006	0.995
C_2	1.06	-0.006	0.996
C_3	1.13	-0.009	0.987
C_4	1.34	-0.09	0.934

A.3. Red solution

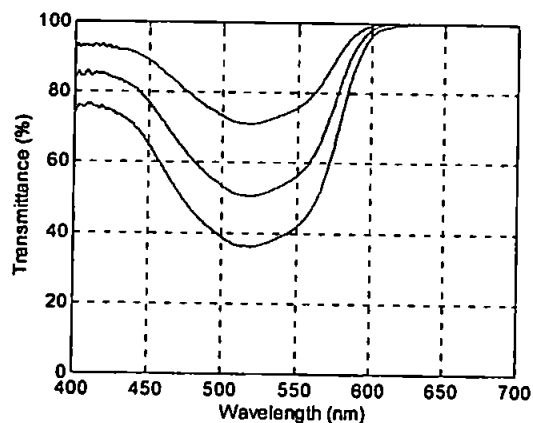


Figure 12: Transmittance spectra measured with the PSICAM for the three three solutions.

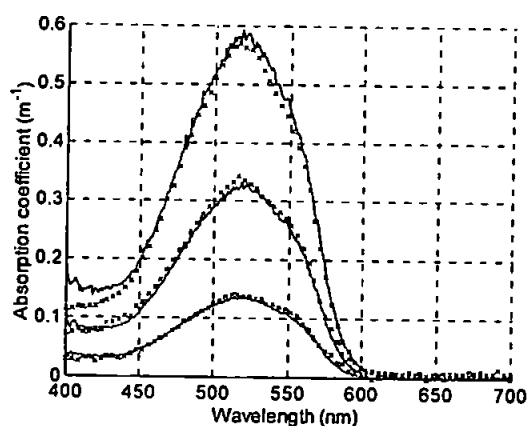


Figure 13: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

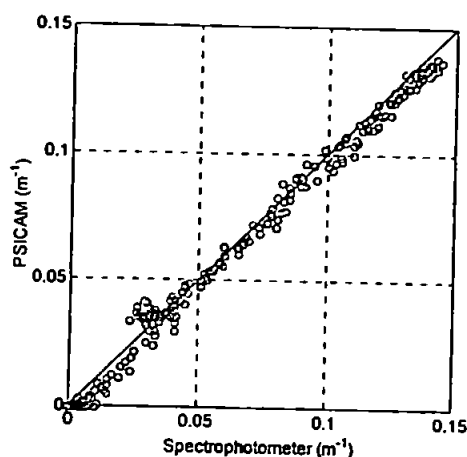


Figure 14: PSICAM versus Spectrophotometer for C_1 calculated with the least square technique.

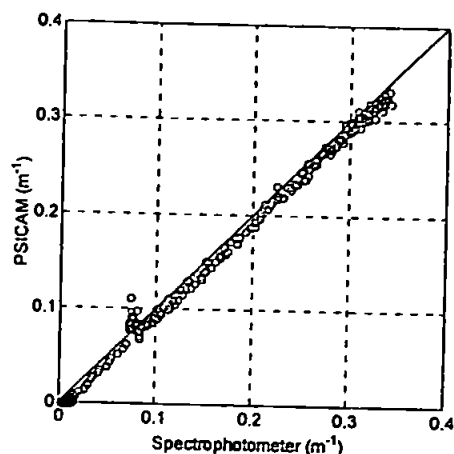


Figure 15: PSICAM versus Spectrophotometer for C_2 calculated with the least square technique.

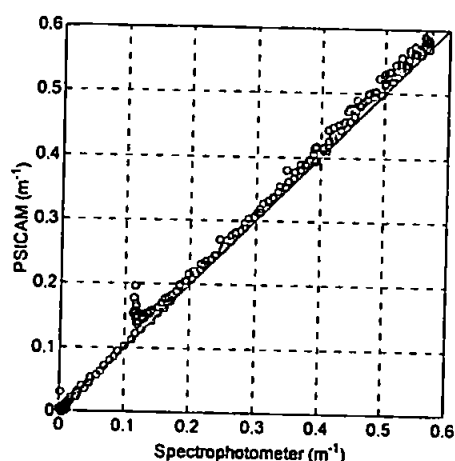


Figure 16: PSICAM versus Spectrophotometer for C_3 calculated with the least square technique.

Table 3: Slope, intercept and regression coefficient between the two instruments with the least square technique.

	<i>Slope</i>	<i>Intercept</i>	r^2
C_1	1.04	-0.0081	0.928
C_2	1.01	-0.0126	0.985
C_3	1.04	-0.0034	0.993

A.4. Black solution

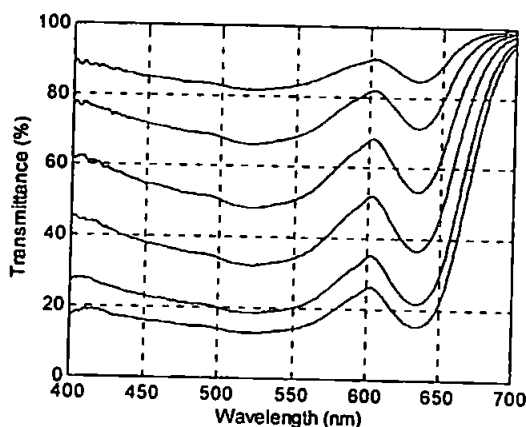


Figure 17: Transmittance spectra measured with the PSICAM for the six black solutions.

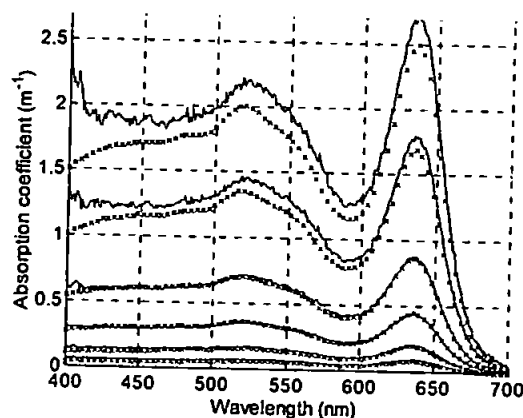


Figure 18: Absorption spectra calculated with the PSICAM (solid line) and measured on the Spectrophotometer (crosses).

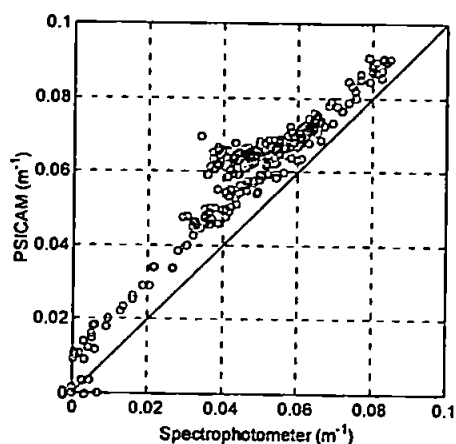


Figure 19: PSICAM versus Spectrophotometer for C_1 calculated with the least square technique.

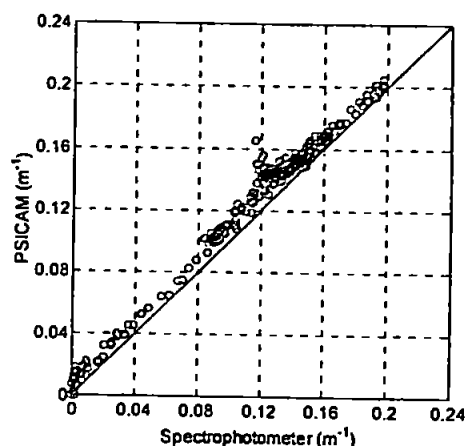


Figure 20: PSICAM versus Spectrophotometer for C_2 calculated with the least square technique.

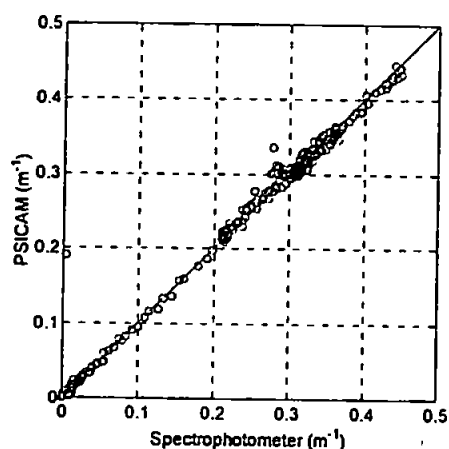


Figure 21: PSICAM versus Spectrophotometer for C_3 calculated with the least square technique.

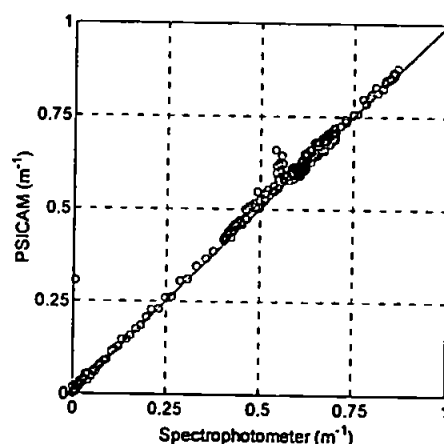


Figure 22: PSICAM versus Spectrophotometer for C_4 calculated with the least square technique.

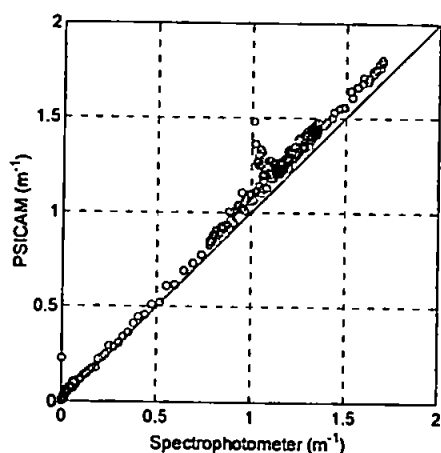


Figure 23: PSICAM versus Spectrophotometer for C_5 calculated with the least square technique.

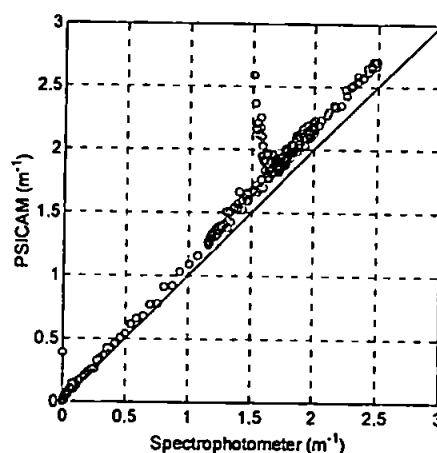


Figure 24: PSICAM versus Spectrophotometer for C_6 calculated with the least square technique.

Table 4: Slope, intercept and regression coefficient between the two instruments with the least square technique.

	<i>Slope</i>	<i>Intercept</i>	<i>r</i> ²
<i>C₁</i>	0.973	0.013	0.947
<i>C₂</i>	1.004	0.010	0.993
<i>C₃</i>	0.974	0.007	0.994
<i>C₄</i>	0.992	0.015	0.995
<i>C₅</i>	1.059	0.021	0.995
<i>C₆</i>	1.086	0.037	0.989

Appendix 2: Laboratory experiments

The laboratory experiment presented in the *Chapter6* was the last of a series of three. The results of the first two experiments are displayed below together with some data of the third experiment that was not presented in the *Chapter6*.

A. Tank experiment 1

The first experiment carried out to test the instrument with scattering solutions consisted of adding suspended sediments to a water tank where the ac-9 was used to measure the water. For this first experiment, the tank was initially filled with tap water, which has a significant yellow substance signature. For each level of concentration, a measurement was carried with the ac-9 and two replicates measurement were carried out with the PSICAM. The sediment used for this experiment was first dried and ashed in order to remove any organic component. A solution was then made with this sediment from which aliquots were added into the tank so that a maximum concentration of 3.5mg.l^{-1} was reached. The suspended sediments concentration measured were 0.855 (tap water back-ground), 1.45 2.00 and 3.5mg/l . First of all, because tap water was used to fill the tank, the initial signal has a yellow substance signature. The shapes of the absorption spectra for the other concentrations also have a typical yellow substance or suspended sediment signature. The scattering coefficient range covered goes from about 1m^{-1} for the tap water background to about 2.5m^{-1} for the highest sediment concentration in the blue wavebands.

A.1. PSICAM data

The absorption coefficients were calculated with both Kirk's empirical equation and using the least square technique (*Figure 1*). No significant differences were observed between the two methods. When compared with the ac-9 data in the following sections, the PSICAM data used came from calculations using Kirk's equation.

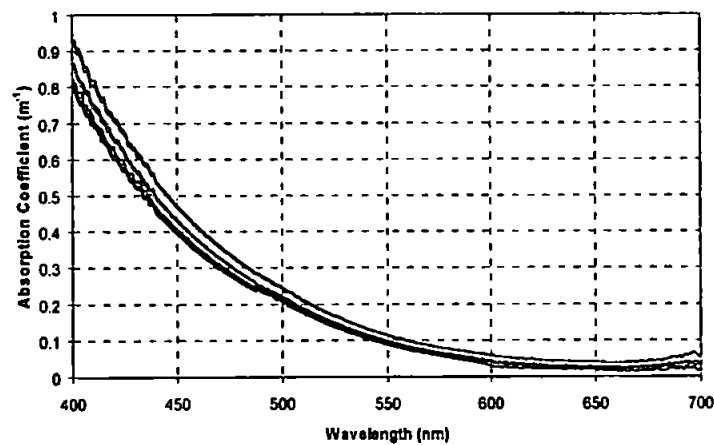


Figure 1: Absorption coefficient with Kirk's formula (black line) and using the least square method (grey line)

A.2. Correction 1

Figure 2 shows the absorption spectra obtained with the PSICAM and the ac-9 when the first correction method was applied.

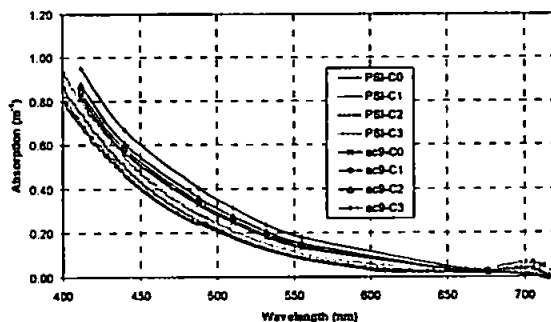


Figure 2: Absorption spectra obtained with both instruments

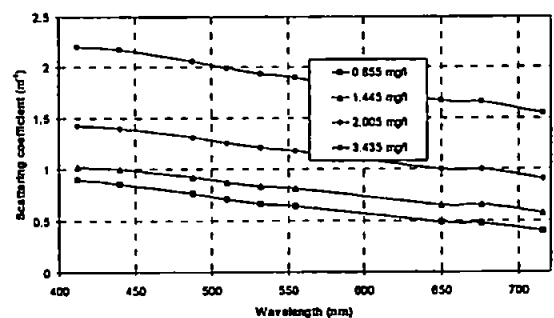


Figure 3: Scattering coefficient spectrum calculated with the ac-9.

Applying the first correction method, it happens that the PSICAM underestimates the ac-9 measurement except in the red region of the spectrum. In *Figure 4* and *Figure 5* are presented the results of both instruments as a function of the Suspended Particulate Matter concentration. They show that there is almost a constant difference with increasing sediment concentration between the two instruments.

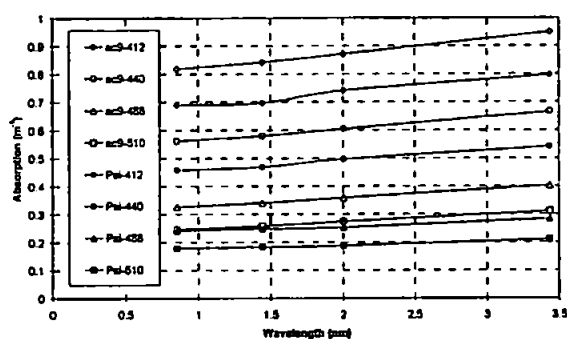


Figure 4: PSICAM and ac-9 results as a function of SPM concentration (412 to 510nm)

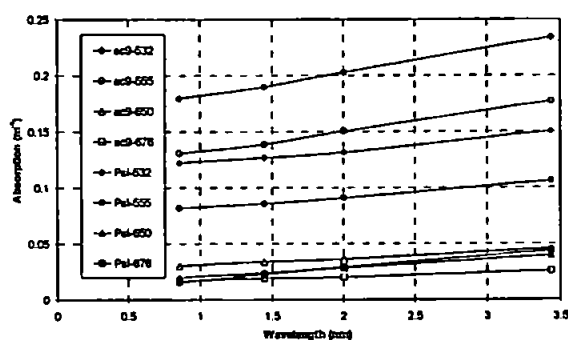


Figure 5: PSICAM and ac-9 results as a function of SPM concentration (632 to 676nm)

On *Figure 6* is presented the PSICAM data versus the ac-9 data. The black straight line represents the one to one relationship. *Table 1* gives details of the slope and r^2 for the four concentrations encountered. This last graph shows that the data from the two instruments are indeed very well correlated ($r^2 = 0.99$ and 0.98 for C_0 and C_3 respectively) but the PSICAM systematically underestimates the absorption calculated with the ac-9.

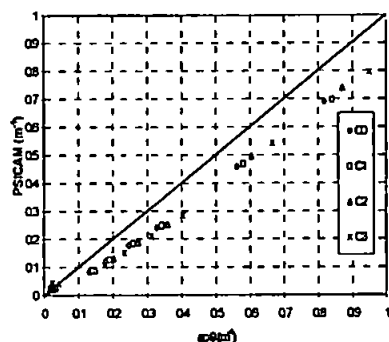


Figure 6: PSICAM measurement vs ac-9

Table 1: Slope and r^2 for the four concentrations

	Slope	r^2
C0	0.8131	0.9926
C1	0.8002	0.9924
C2	0.8109	0.9865
C3	0.7993	0.9849

A.3. Correction 2 $\epsilon = 0.18$

The second correction technique was applied with an ϵ factor equal to 0.18 because of inorganic particulate content. As previously, the results obtained with the PSICAM are lower than the ac-9 results (*Figure 7*). With this technique, the effect at short wavelengths is very similar to the first correction technique. The major difference occurs for the longer wavelength.

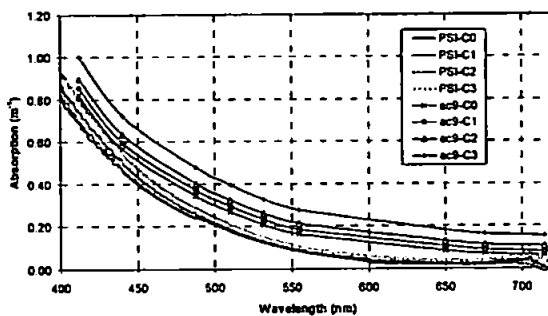


Figure 7: Absorption spectra of both instruments obtained with the second correction method.

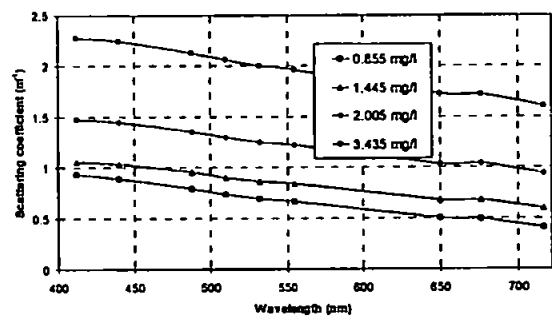


Figure 8: Scattering coefficient obtained with the second correction method.

Figure 9 and *Figure 10* show more clearly that the effect of this correction technique remains very similar to the previous one for wavelengths from 412 to 510nm. However, the difference between the two measurements seems to increase more markedly than previously with the suspended sediment concentration. This is more visible for longer wavelength. For wavelengths higher than 600nm, the PSICAM data show less increase in the absorption than the ac-9 data with increasing sediment concentration.

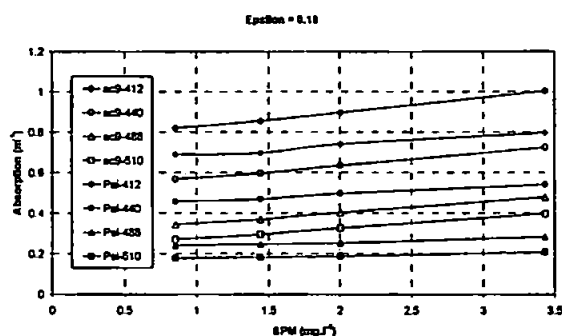


Figure 9: Absorption as a function of the sediment content (412 to 510nm)

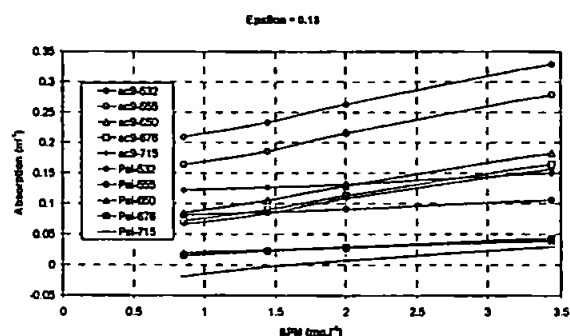


Figure 10: Absorption as a function of the sediment content (532 to 676nm)

On Figure 11 and Table 2 are presented the regression of the PSICAM data versus the ac-9. The regressions are still very good although the PSICAM underestimate the absorption in comparison with the ac-9. In this case however, the regression line does not have a zero intercept.

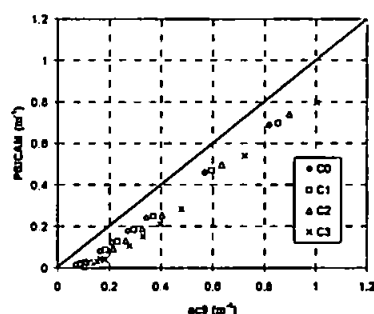


Figure 11: Regression between the PSICAM and the ac-9 with the second correction method.

Table 2: Slope, intercept and r^2 obtained from Figure 11.

	Slope	Intercept	r^2
C0	0.9195	-0.0669	0.9986
C1	0.9009	-0.0758	0.9987
C2	0.9262	-0.0996	0.9965
C3	0.9158	-0.1336	0.9949

A.4. Correction 3

The last correction method provided the best correlation with the PSICAM. In this case, the PSICAM slightly over estimated the absorption in comparison with the ac-9 (Figure 12 to Figure 16).

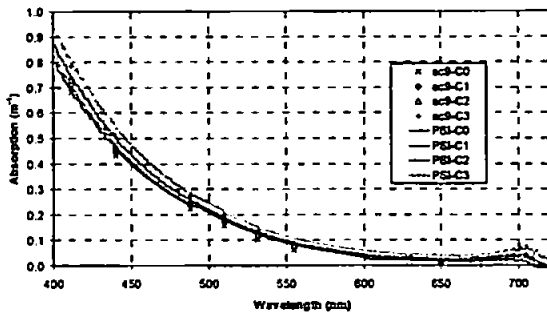


Figure 12: Absorption spectra of both instruments obtained with the third correction method.

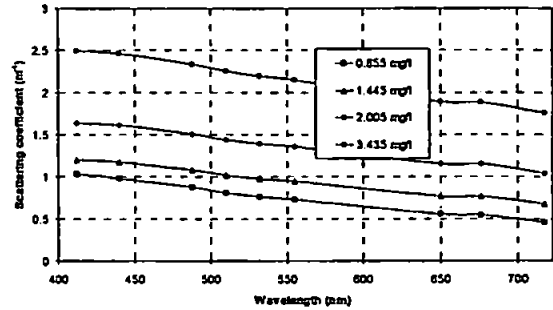


Figure 13: Scattering coefficient obtained with the third correction method.

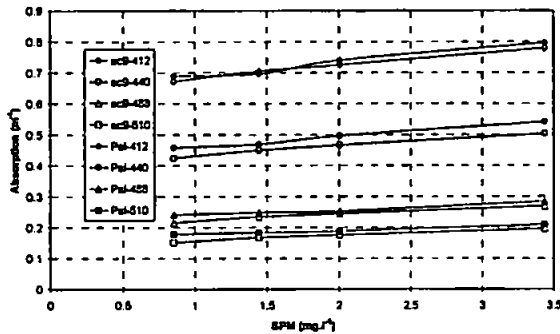


Figure 14: Absorption as a function of the sediment content (412 to 510nm)

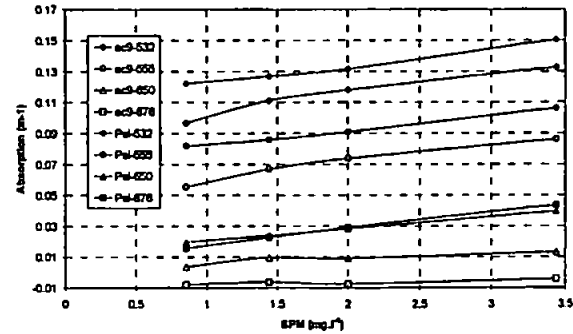


Figure 15: Absorption as a function of the sediment content (532 to 676nm)

Table 4 shows that in this case, the one to one relationship is almost obtained between the two instruments.

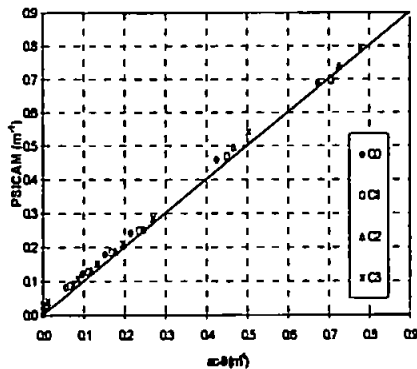


Figure 16: Regression between the PSICAM and the ac-9 with the third correction method.

Table 4: Slope, intercept and r^2 obtained from Figure 16.

	Slope	r^2
C0	1.0551	0.9929
C1	1.0141	0.9947
C2	1.0367	0.9951
C3	1.0434	0.9912

B. Second tank experiment - River Tamar sediments

A second laboratory experiment was carried out. This time, the tank was filled with milli-Q water in which suspended sediment was added. The same procedure as described for the experiment presented in the *Chapter 6* was followed. During the course of the experiment samples of the water were taken to measure the concentration of sediments on filter paper. The concentrations measured were 0.045 (pure water background), 0.635, 2.25 and 6.35 mg/l. Water samples were also taken for particulate absorption analyzes. These sediments were collected on the banks of the Tamar River, dried and ashed to remove the organic components prior adding in the tank.

B.1. PSICAM data

The absorption coefficients were calculated with both Kirk's empirical equation and using the least square technique (*Figure 17*). No significant differences were observed between the two methods. When compared with the ac-9 data in the following sections, the PSICAM data used come for calculations using Kirk's equation.

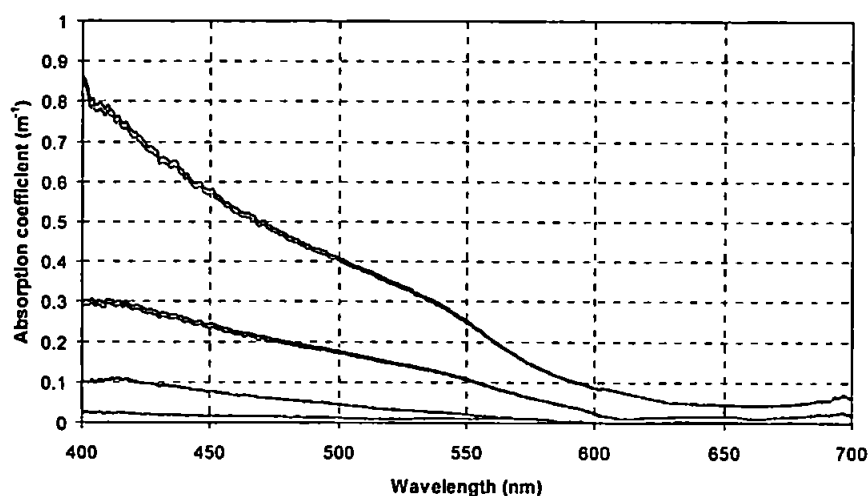


Figure 17: Absorption coefficient with Kirk's formula (black line) and using the least square method (gray line)

The result of each correction technique was compared with the measurement of the PSICAM. The ϵ coefficient for the second correction technique was similarly chosen to 0.18 because of the inorganic particulate content. The general shape of the absorption spectrum is decreasing exponential as expected due to the particulate sediment. The measurement of the PSICAM appears to get closer to the ac-9 results for correction 1 and 3, although in each case, the PSICAM underestimated the absorption in comparison with the ac-9. The second correction technique gives the most important differences with the PSICAM measurement. Because the experiment started with pure water, the absorption spectra cover a wider range of absorption. The scattering coefficient spectrum varied from 0 to about 3m^{-1} depending on the correction technique (Figure 19, Figure 24 and Figure 30).

B.2. Correction 1

With this correction technique, the two instruments gives very similar results (Figure 18) except around 700nm where the PSICAM measures higher absorptions.

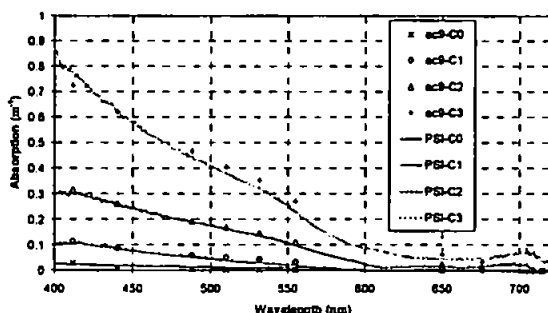


Figure 18: Absorption spectra of both instruments obtained with the first correction method.

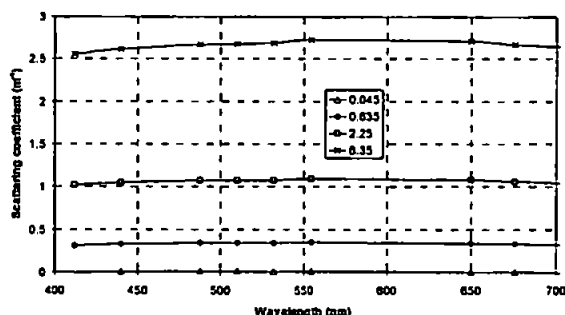


Figure 19: Scattering coefficient obtained with the first correction method.

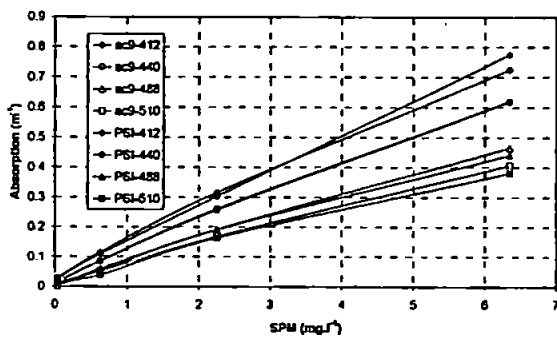


Figure 20: Absorption as a function of the sediment content (412 to 510nm)

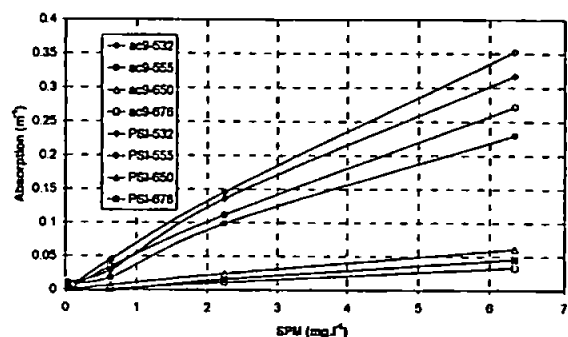


Figure 21: Absorption as a function of the sediment content (532 to 676nm)

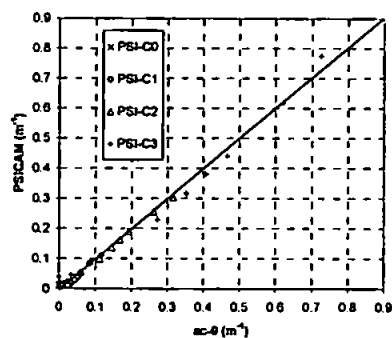


Figure 22: Regression between the PSICAM and the ac-9 with the first correction method.

Table 5: Slope, intercept and r^2 obtained from Figure 22

	Slope	r^2
C0	0.6414	0.5758
C1	0.9002	0.9608
C2	0.9644	0.9951
C3	0.9921	0.9843

B.3. Correction 2 $\epsilon=0.18$

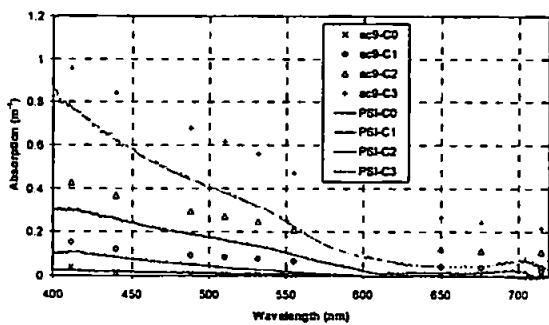


Figure 23: Absorption spectra of both instruments obtained with the second correction method.

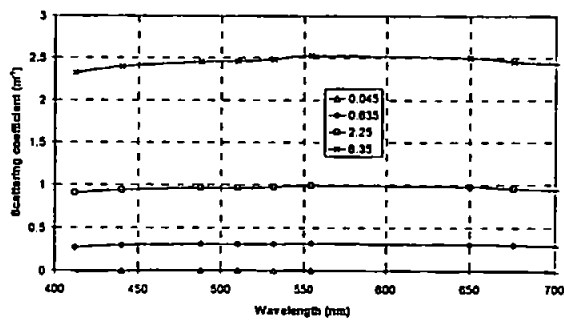


Figure 24: Scattering coefficient obtained with the second correction method.

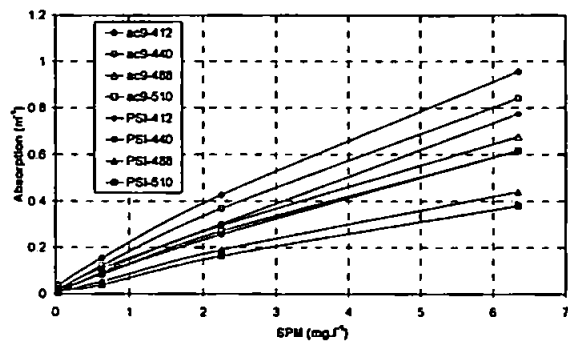


Figure 26: Absorption as a function of the sediment content (412 to 510nm)

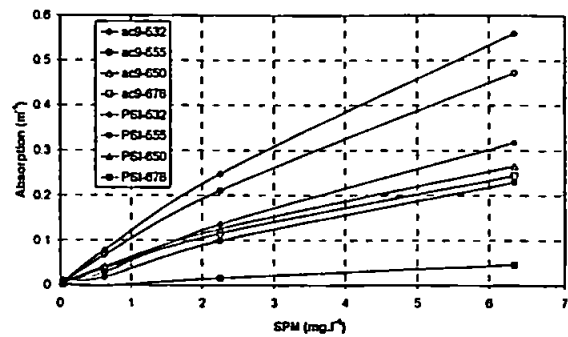


Figure 27: Absorption as a function of the sediment content (532 to 676nm)

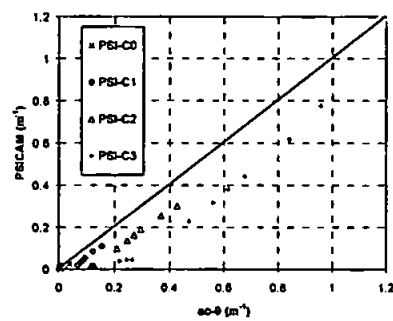


Figure 28: Regression between the PSICAM and the ac-9 with the second correction method.

Table 6: Slope, intercept and r^2 obtained from Figure 28.

	Slope	Intercept	r^2
C0	0.51	0.0038	0.4196
C1	1.0029	-0.0442	0.9875
C2	0.982	-0.1077	0.9947
C3	0.9870	-0.2103	0.9907

B.4. Correction 3

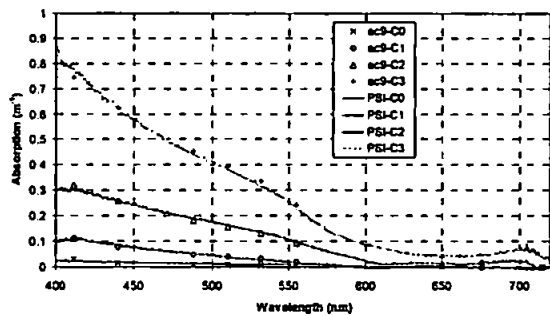


Figure 29: Absorption spectra of both instruments obtained with the third correction method.

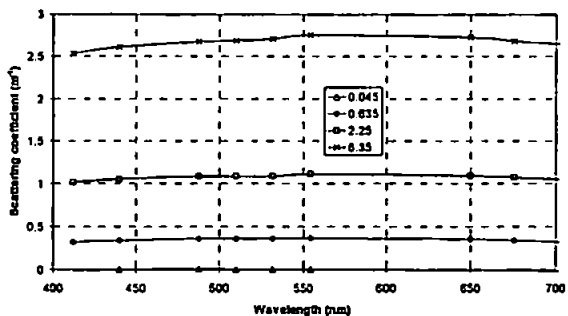


Figure 30: Scattering coefficient obtained with the third correction method.

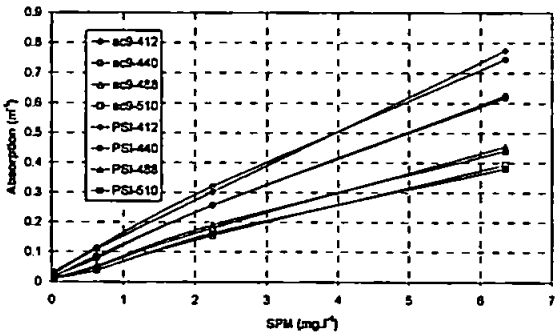


Figure 31: Absorption as a function of the sediment content (412 to 510nm)

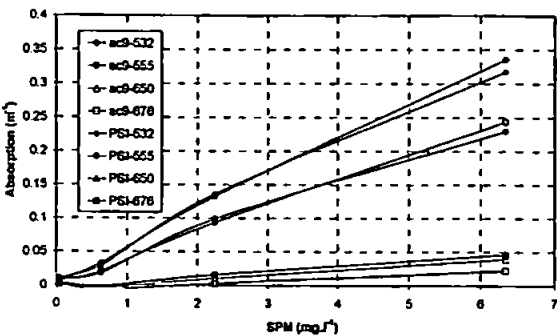


Figure 32: Absorption as a function of the sediment content (532 to 676nm)

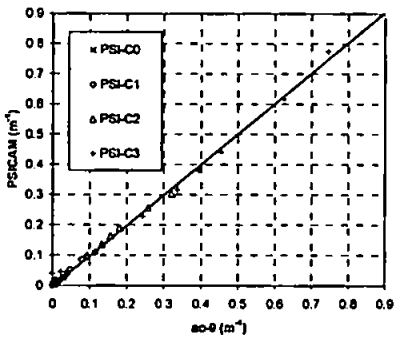


Figure 33: Regression between the PSICAM and the ac-9 with the third correction method.

Table 7: Slope, intercept and r^2 obtained from Figure 33

	Slope	r^2
C0	0.9053	0.7624
C1	0.9962	0.9877
C2	0.9918	0.9906
C3	0.9982	0.9928

B.5. Particulate absorption data

The patterns observed with this data set are similar to the one presented in the *Chapter* 6. The pure water background underestimate significantly the results obtained with both the ac-9 and the PSICAM. For the highest sediment concentration, the spectrum obtained in the reflectance mode is biased so that the absorption coefficient of the solution is minimized.

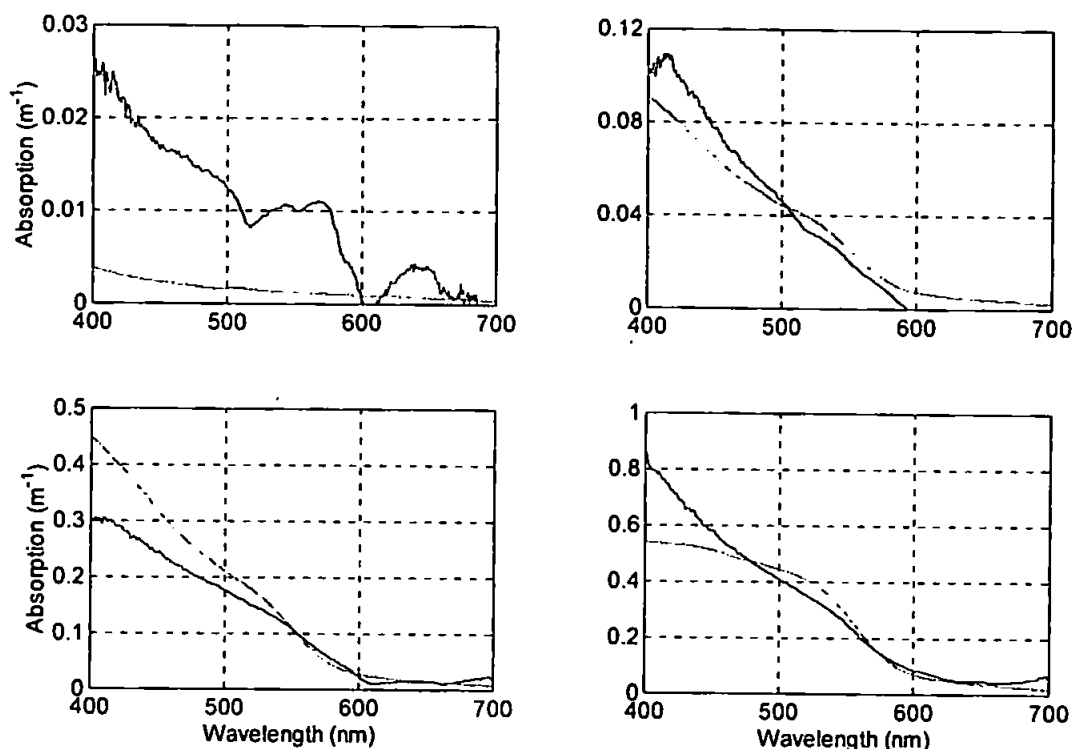


Figure 34: Absorption spectra measured with the PSICAM (black line) and with the filter technique (gray line). From top left to bottom right: C₀, C₁, C₂ and C₃.

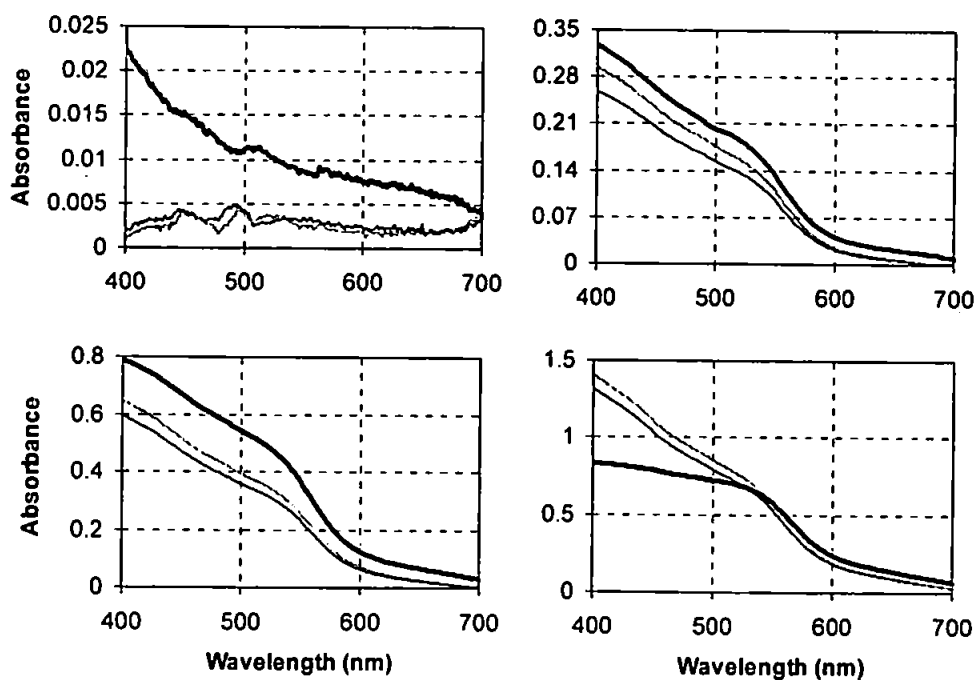


Figure 35: Raw absorbance spectra measured with the dual beam spectrophotometer. Direct beam transmittance (thin black), diffuse beam transmittance (thin gray) and reflectance (thick black); from top right to bottom left: C₀, C₁, C₂ and C₃.

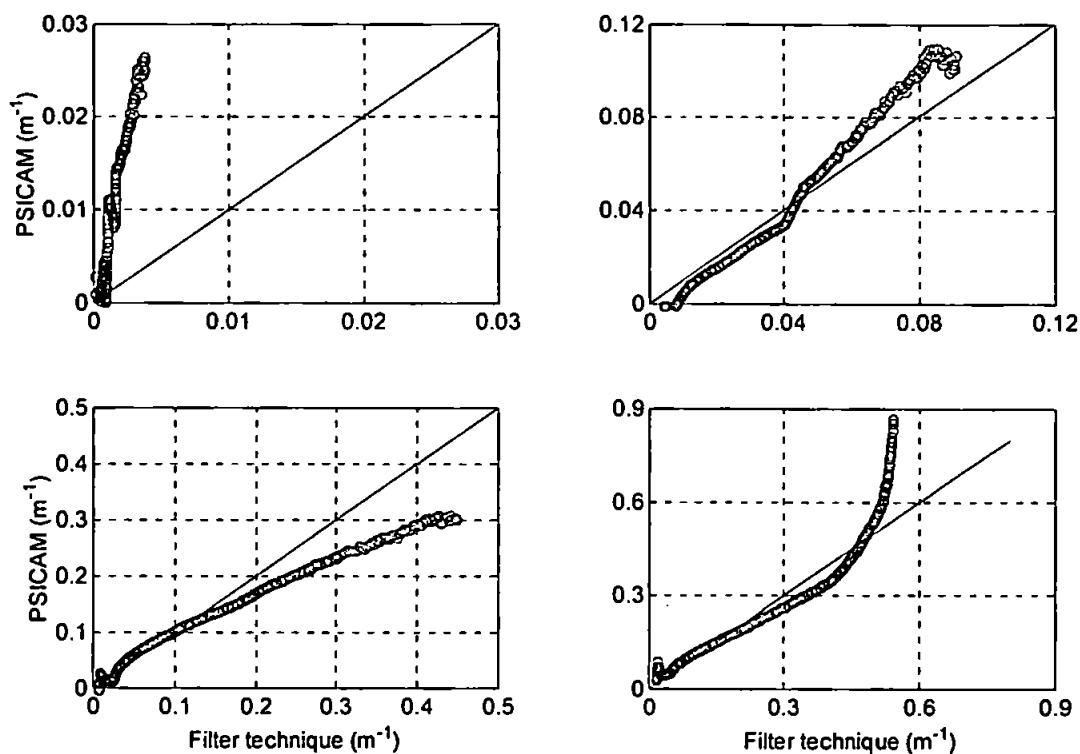


Figure 36: Regression between the PSICAM and the filter technique. From top left to bottom left: C_0 , C_1 , C_2 and C_3 .

Table 8: Slope, intercept and r^2 obtained from Figure .

	Slope	Intercept	R^2
C_0	9.093	-0.0042	0.878
C_1	1.302	-0.009	0.990
C_2	0.723	0.011	0.983
C_3	1.120	-0.003	0.917

C. Third tank experiment

C.1. PSICAM data

Results of the PSICAM calculated with the least square method (black line) and with Kirk's equation (grey line) for the six solutions C_3 , C_4 , C_5 of concentration 1.31, 2.70 and 8.77mg/l respectively (Figure 37) and C_0 , C_1 and C_2 of concentration 0.03, 0.10 and 0.21mg/l respectively (Figure 38) did not show important differences showing that despite the high content of particulate material, the homogenous isotropic assumption was still valid.

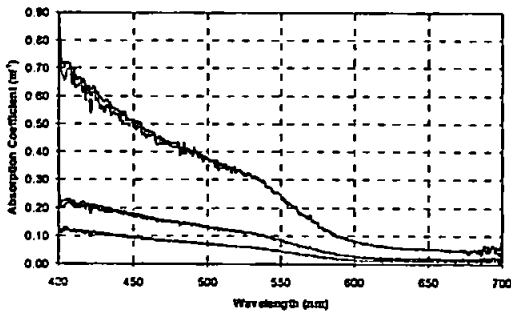


Figure 37: PSICAM results with the least square method and Kirk's equation for C3, C4 and C5.

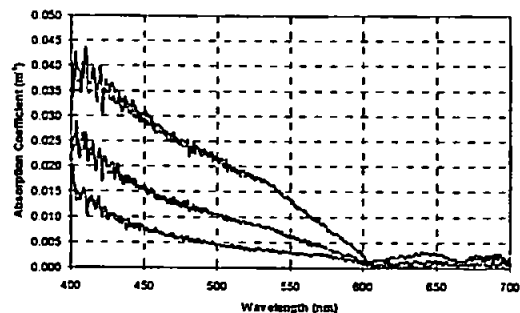


Figure 38: PSICAM results with the least square method and Kirk's equation for C0, C1 and C2.

C.2. Correction 1

Percentage difference between the PSICAM and the ac-9 with the first correction method for the total data set (Figure 39) and without the two lowest concentrations and the three red channels 650, 676 and 715nm(Figure 40)

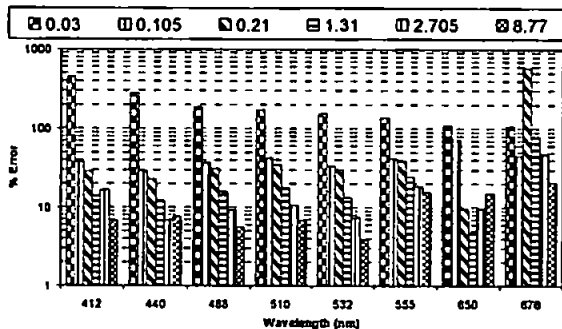


Figure 39: Percentage error in comparison to the ac-9 (all dataset).

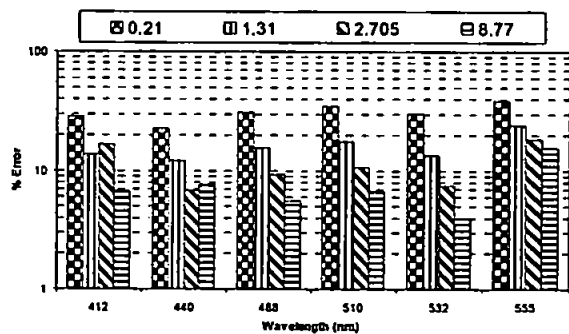


Figure 40: Percentage error in comparison to the ac-9 (reduce data set).

C.3. Correction 2

Percentage difference between the PSICAM and the ac-9 for with the second correction method and an ϵ factor of 0.18 for the all data set (Figure 41) and without the two lowest concentrations and the three red channels 650, 676 and 715nm(Figure 42).

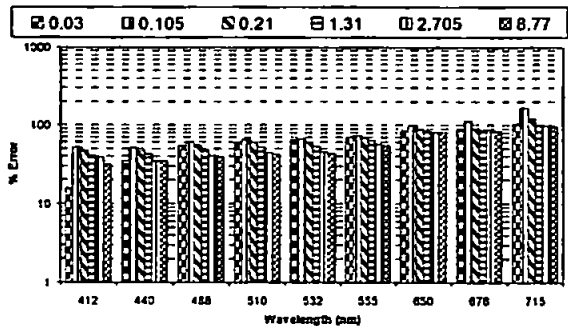


Figure 41: Percentage error in comparison to the ac-9 ($\epsilon=0.18$).

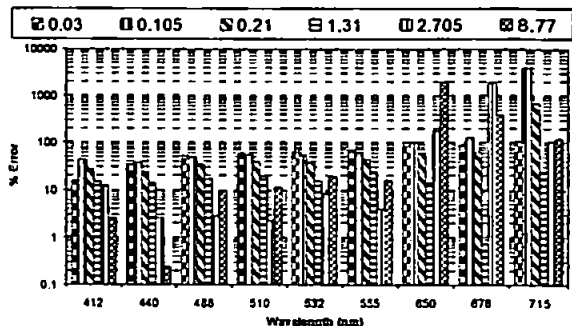


Figure 42: Percentage error in comparison to the ac-9 ($\epsilon=0.28$).

Appendix 3: In situ data

A. Dissolved Organic Matter and Total Particulate Absorption measured at L4

A.1. 27th May, 2002

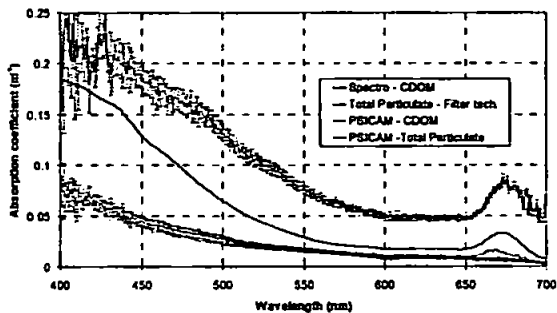


Figure 1: Dissolved and Particulate Absorption spectra.

Table 1: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	1.0593	0.0426	0.948
DOM	1.004	0.0006	0.966

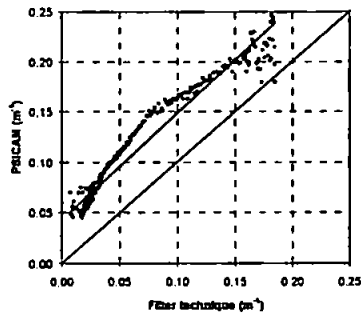


Figure 2: Particulate Absorption regression.

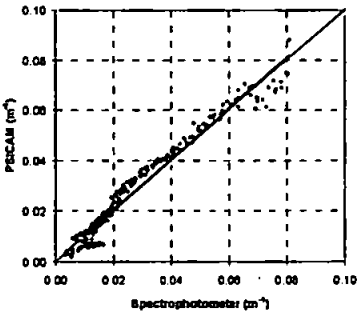


Figure 3: DOM regression.

A.2. 18th June, 2002

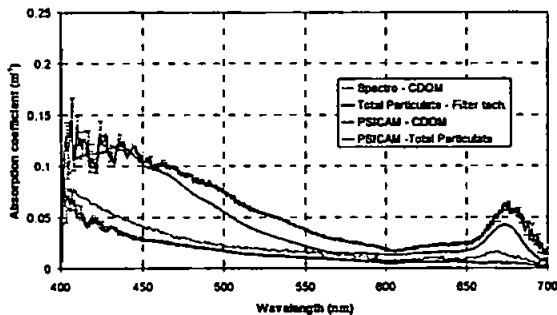


Figure 4: Dissolved and Particulate Absorption spectra.

Table 2: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	0.9474	0.0136	0.944
DOM	0.795	-0.0018	0.967

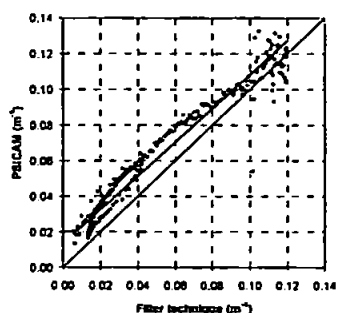


Figure 5: Particulate Absorption regression.

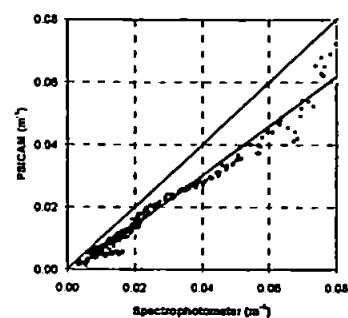


Figure 6: DOM regression.

A.3. 24th June, 2002

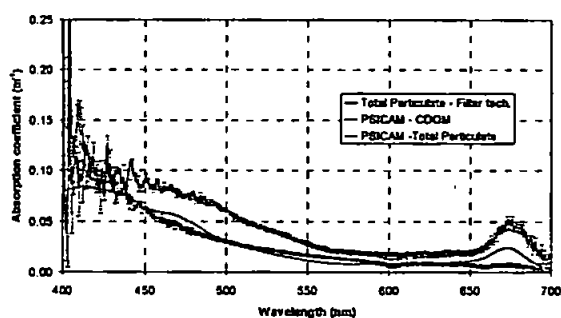


Figure 7: Dissolved and Particulate Absorption spectra.

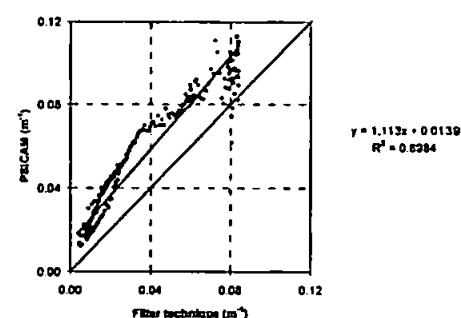


Figure 8: Particulate Absorption regression.

A.4. 1st July, 2002

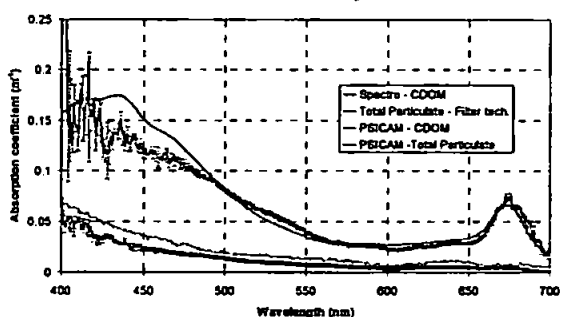


Figure 9: Dissolved and Particulate Absorption spectra.

Table 3: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	0.759	-0.002	0.974
DOM	0.869	0.0057	0.788

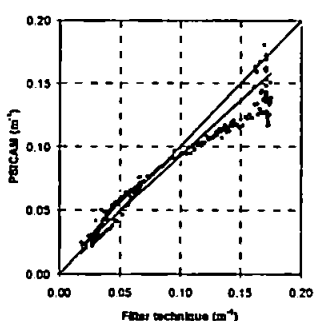


Figure 10: Particulate Absorption regression.

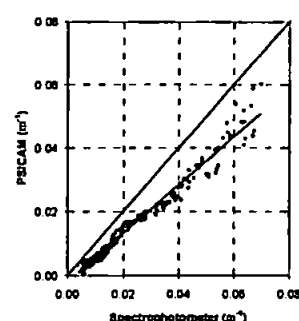


Figure 11: DOM regression.

A.5. 9th July, 2002

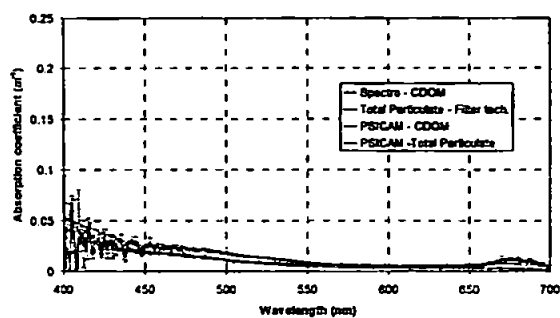


Figure 12: Dissolved and Particulate Absorption spectra.

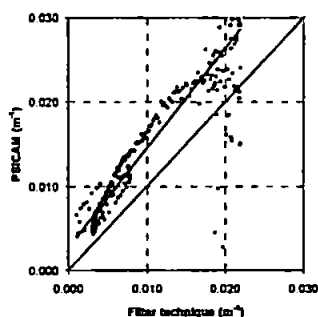


Figure 13: Particulate Absorption regression.

Table 4: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	1.182	0.003	0.730
DOM	0.721	0.003	0.977

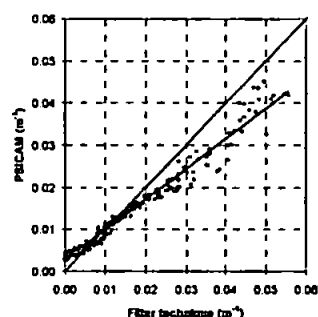


Figure 14: DOM regression.

A.6. 15th July, 2002

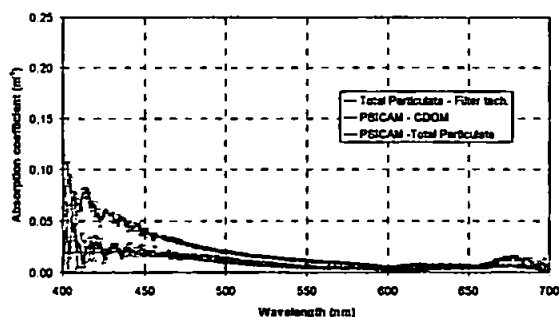


Figure 15: Dissolved and Particulate Absorption spectra.

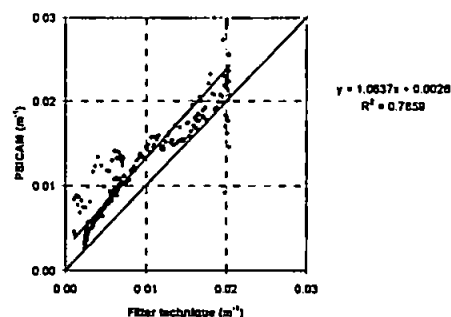


Figure 16: Particulate Absorption regression.

A.7. 22nd July, 2002

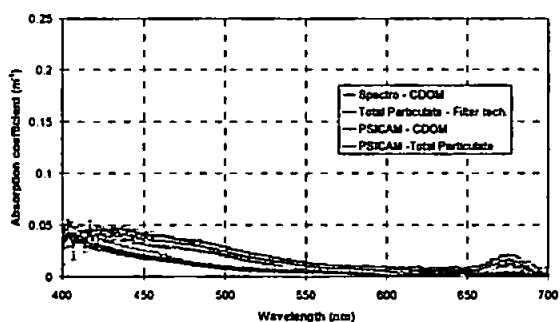


Figure 17: Dissolved and Particulate Absorption spectra.

Table 5: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	0.895	0.001	0.971
DOM	0.791	0.0001	0.9857

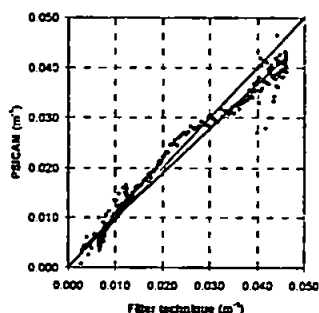


Figure 18: Particulate Absorption regression.

A.8. 29th July, 2002

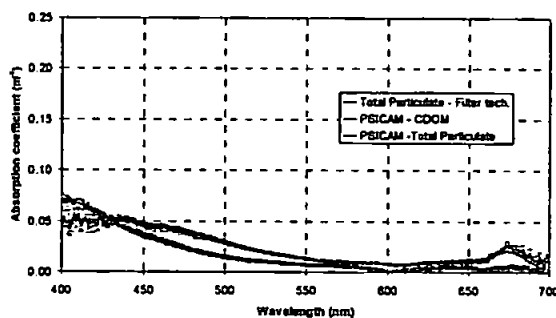


Figure 20: Dissolved and Particulate Absorption spectra.

A.9. 5th Aout, 2002

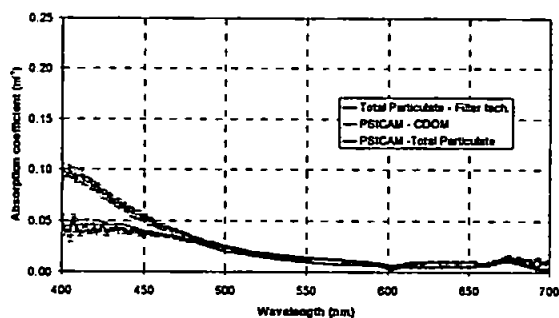


Figure 22: Dissolved and Particulate Absorption spectra.

A.10. 12th Aout, 2002

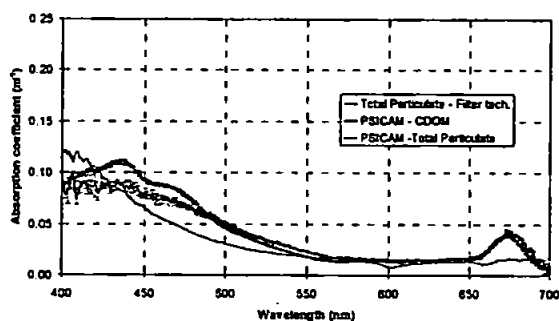


Figure 24: Dissolved and Particulate Absorption spectra.

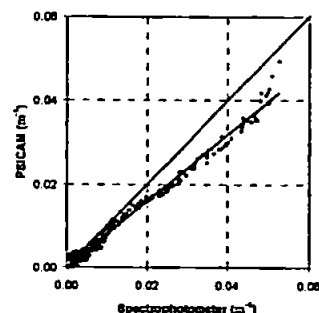


Figure 19: DOM regression.

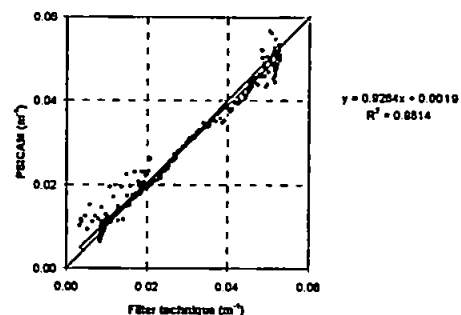


Figure 21: Particulate Absorption regression.

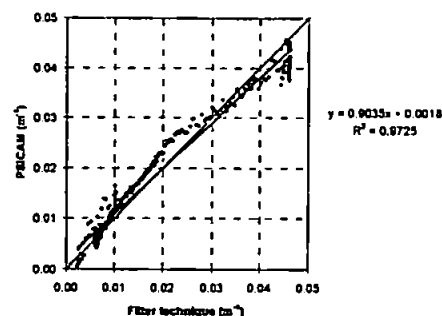


Figure 23: Particulate Absorption regression.

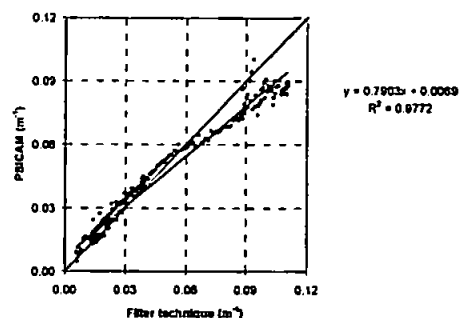


Figure 25: Particulate Absorption regression.

A.11. 20th Aout, 2002

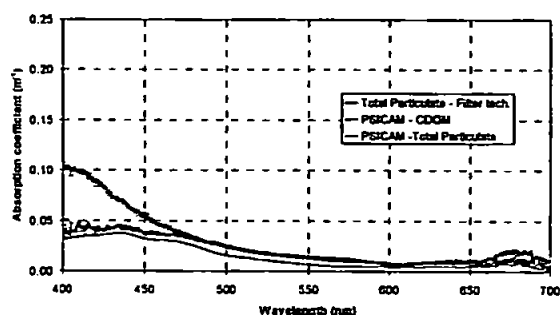


Figure 26: Dissolved and Particulate Absorption spectra.

A.12. 28th Aout, 2002

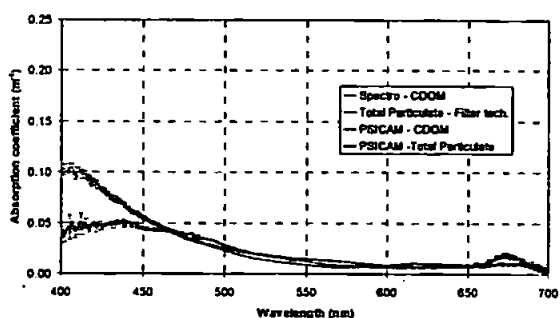


Figure 28: Dissolved and Particulate Absorption spectra.

A.13. 2nd September, 2002

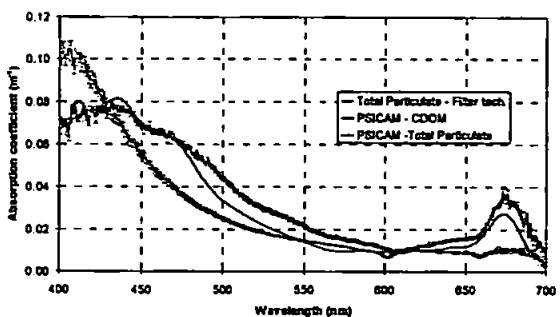


Figure 30: Dissolved and Particulate Absorption spectra.

A.14. 9th September, 2002

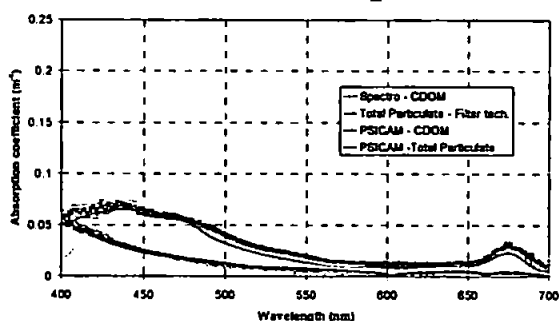


Figure 32: Dissolved and Particulate Absorption spectra.

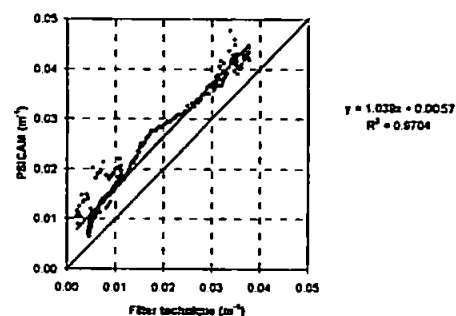


Figure 27: Particulate Absorption regression.

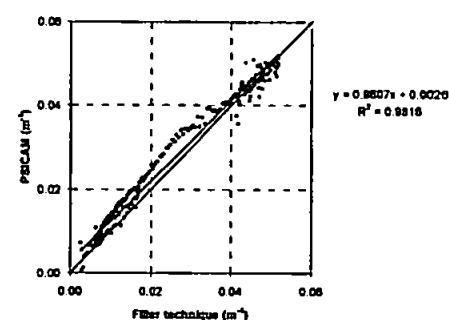


Figure 29: Particulate Absorption regression.

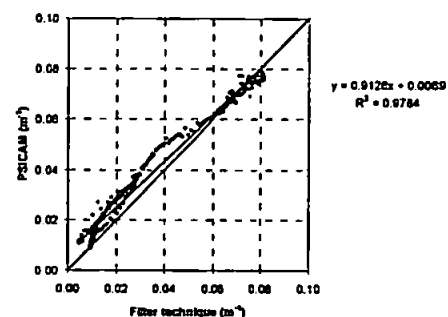


Figure 31: Particulate Absorption regression.

Table 6: Slope, intercept and regression coefficient.

	Slope	Intercept	r ²
Pabs	0.980	0.0052	0.987
DOM	0.825	0.004	0.988

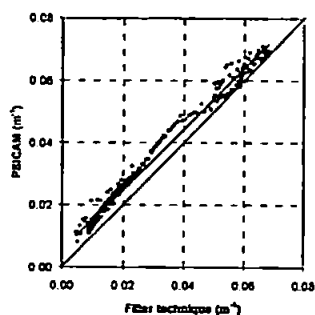


Figure 33: Particulate Absorption regression.

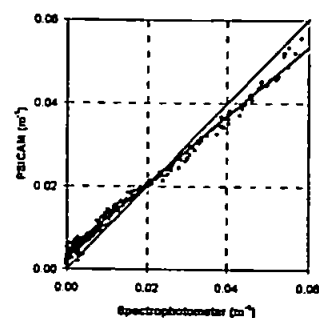


Figure 34: DOM regression.

A.15. 16th September, 2002

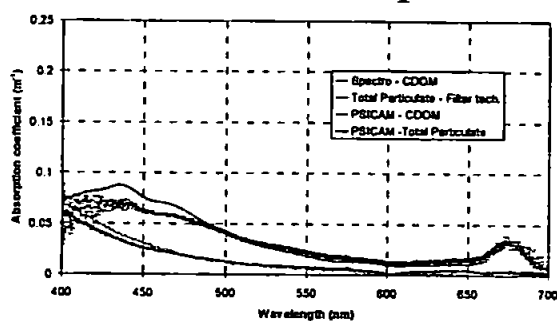


Figure 35: Dissolved and Particulate Absorption spectra.

Table 7: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	0.751	0.006	0.98
DOM	0.786	0.003	0.991

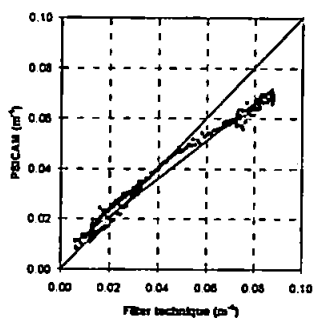


Figure 36: Particulate Absorption regression.

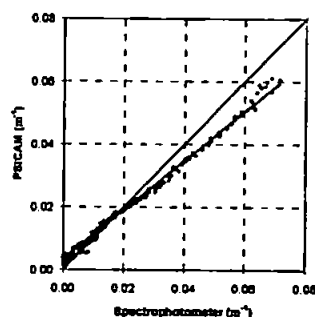


Figure 37: DOM regression.

A.16. 23th September, 2002

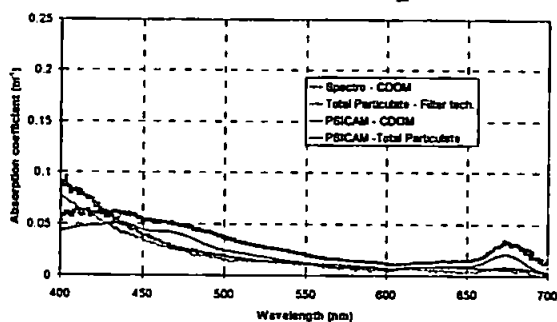


Figure 38: Dissolved and Particulate Absorption spectra.

Table 8: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	1.118	0.006	0.979
DOM	1.178	0.0007	0.989

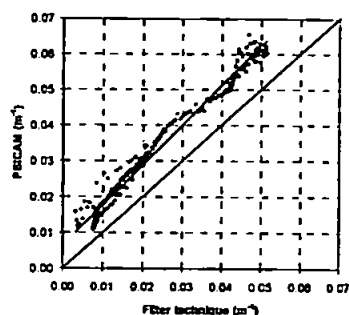


Figure 39: Particulate Absorption regression.

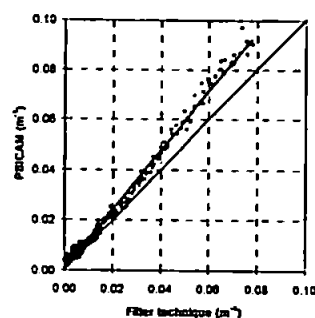


Figure 40: DOM regression.

A.17. 30th September, 2002

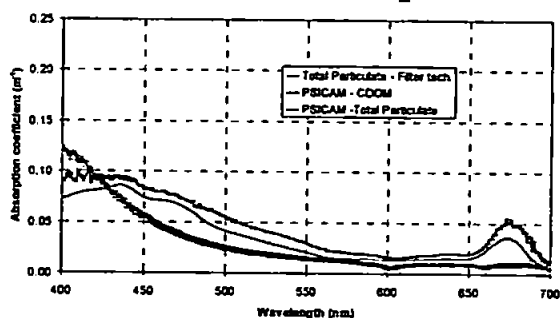


Figure 41: Dissolved and Particulate Absorption spectra.

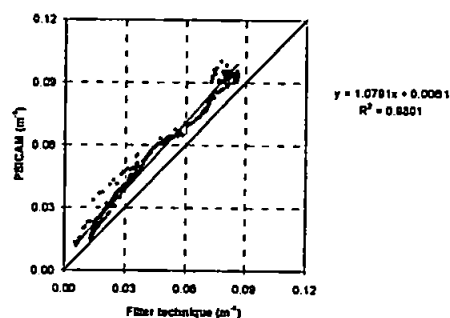


Figure 42: Particulate Absorption regression.

A.18. 7th October, 2002

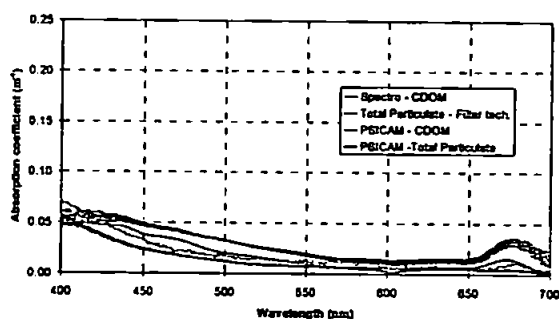


Figure 43: Dissolved and Particulate Absorption spectra.

Table 9: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	0.959	0.0102	0.954
DOM	0.774	-0.0012	0.986

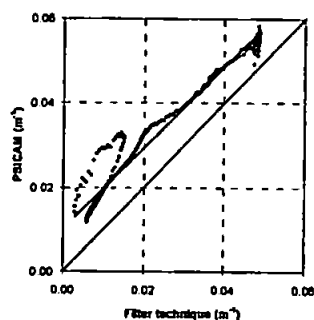


Figure 44: Particulate Absorption regression.

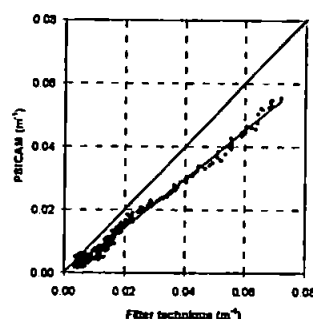


Figure 45: DOM regression.

A.19. 28th October, 2002

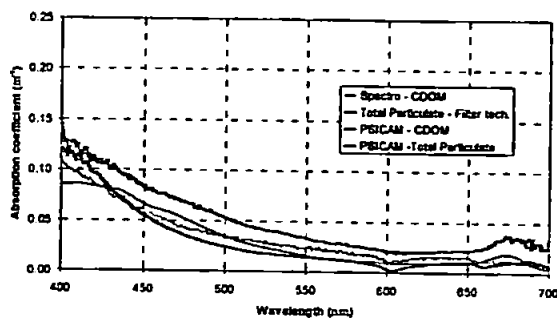


Figure 46: Dissolved and Particulate Absorption spectra.

Table 10: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	1.156	0.013	0.975
DOM	1.168	-0.0098	0.969

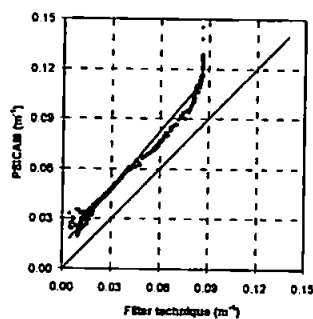


Figure 47: Particulate Absorption regression.

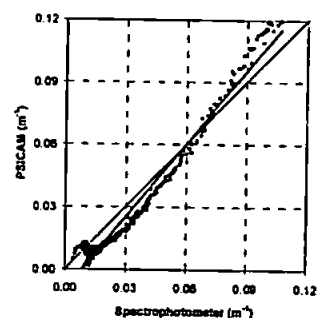


Figure 48: DOM regression.

A.20. 25th November, 2002

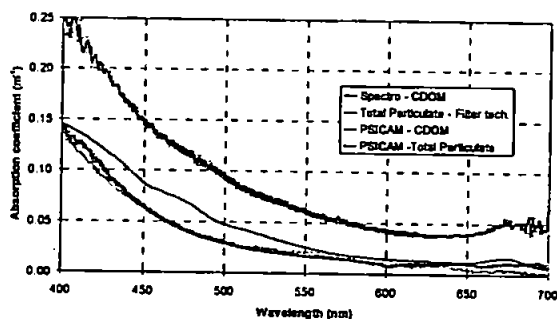


Figure 49: Dissolved and Particulate Absorption spectra.

Table 11: Slope, intercept and regression coefficient.

	Slope	Intercept	r^2
Pabs	1.465	0.023	0.988
DOM	1.024	0.001	0.987

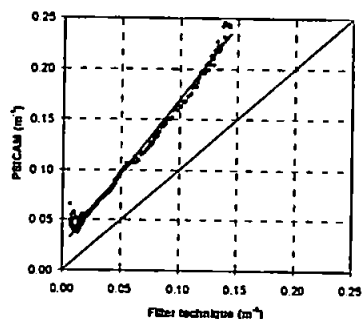


Figure 50: Particulate Absorption regression.

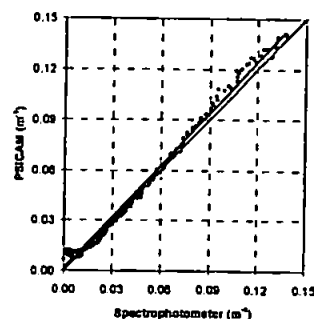
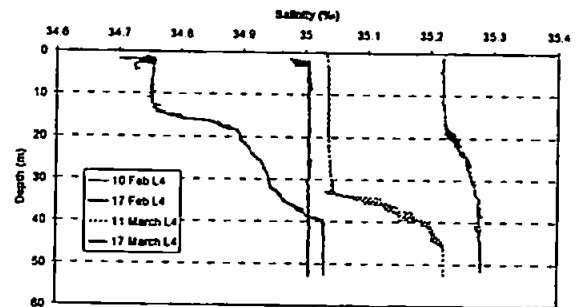
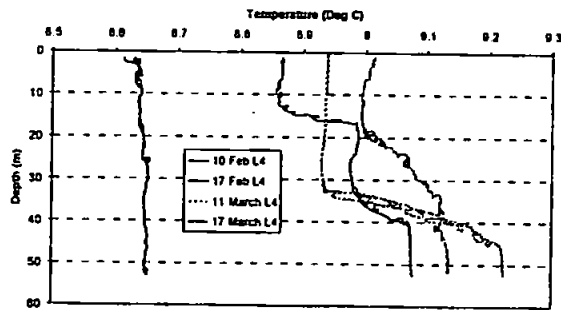


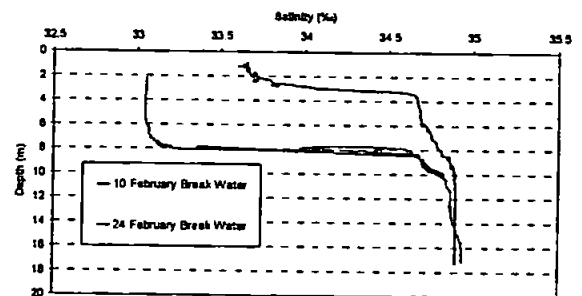
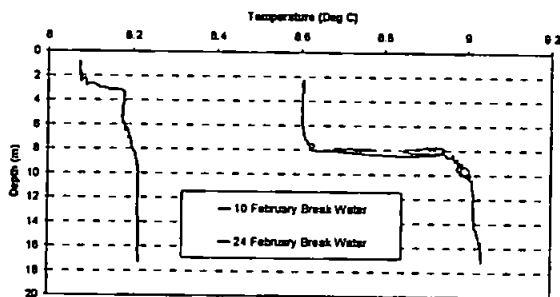
Figure 51: DOM regression.

B. Ac-9 in situ profile – Temperature and Salinity

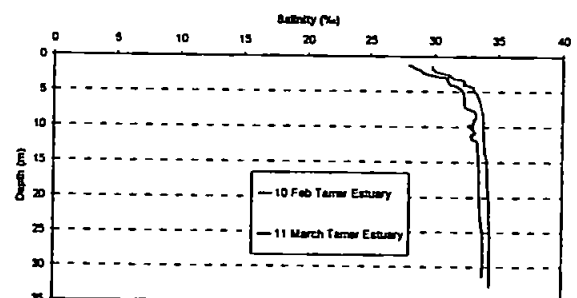
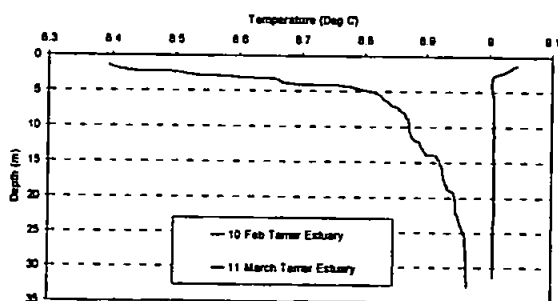
B.1. L4



B.2. Break Water



B.3. Tamar Estuary



Appendix 4: Field test around the Antarctic Peninsula

For each station, two depths were sampled: surface and Secchi depth. For each depth, total and dissolved absorption were measured with the PSICAM after filtration through 0.2µm filters. Chlorophyll-a analyses were performed using the spectrophotometric method after 24h extraction in 90% acetone. The chlorophyll-a concentrations were calculated using SCOR-UNESCO equations (*Strickland and Parson, 1972*):

$$Chl_a = 11.64 * A_{663} - 2.16 A_{645} + 0.10 A_{630} \quad (\mu g / ml)$$

The chlorophyll-a absorption spectra were then calculated using the parametrisation of *Bricaud et al., (1995)*.

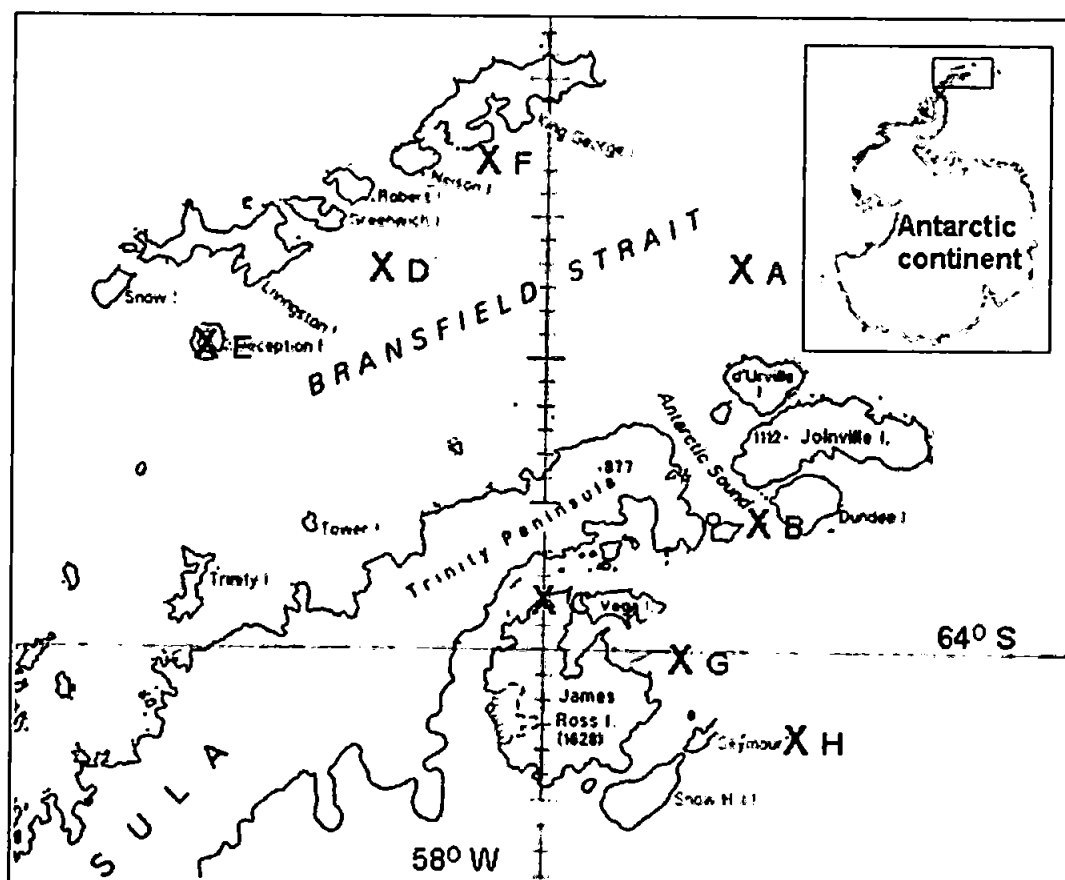


Figure 1: Sampled Stations

A. Time Series in Ross Channel

A.1. Total and DOM absorption spectra

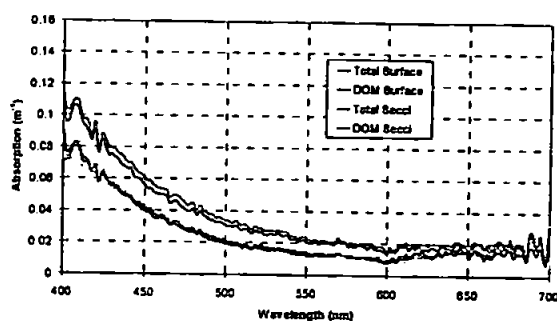


Figure 2: Total and dissolved absorption spectra
03/03/02

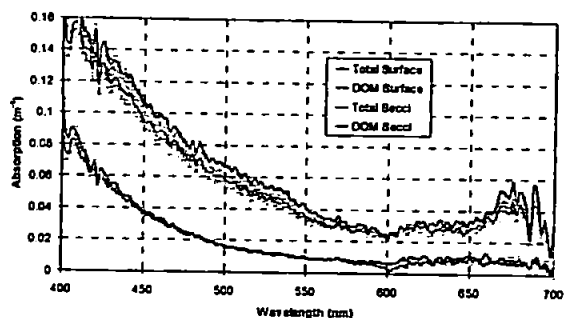


Figure 3: Total and dissolved absorption spectra
05/03/02

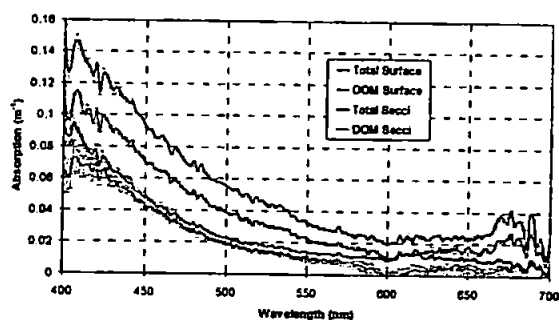


Figure 4: Total and dissolved absorption spectra
07/03/03

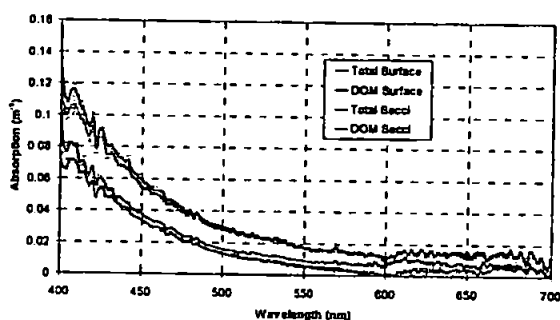


Figure 5: Total and dissolved absorption spectra
08/03/02

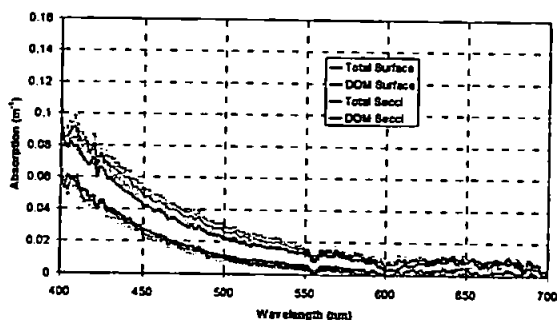


Figure 6: Total and dissolved absorption spectra
09/03/02

A.2. Particulate Absorption Spectra

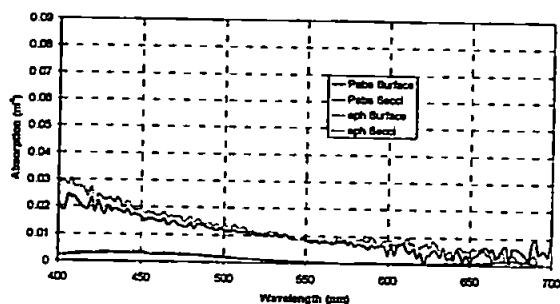


Figure 7: Total particulate and Chlorophyll a absorption - 03/03/02

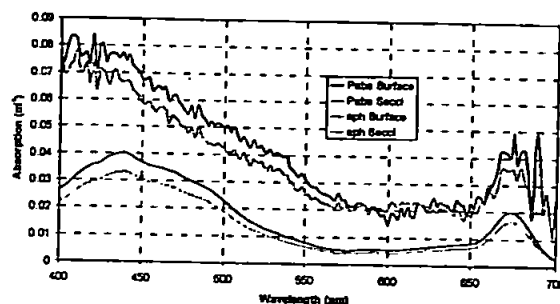


Figure 8: Total particulate and Chlorophyll a absorption - 05/03/02

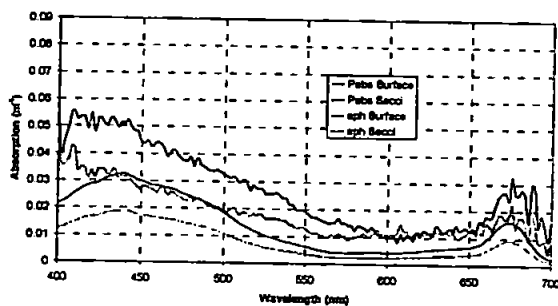


Figure 9: Total particulate and Chlorophyll a absorption - 07/03/02

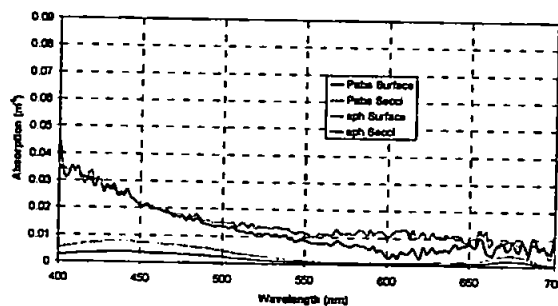


Figure 10: Total particulate and Chlorophyll a absorption - 08/03/02

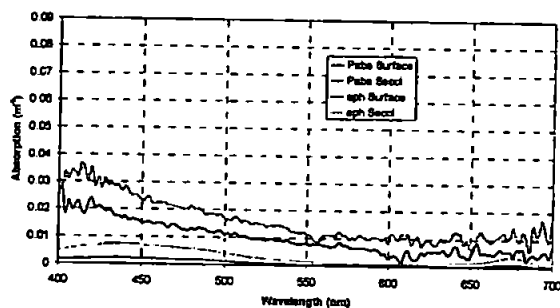


Figure 11: Total particulate and Chlorophyll a absorption - 09/03/02

B. Antarctic Peninsula

B.1. 26 February 2002

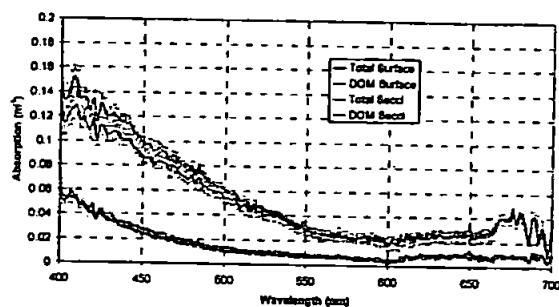


Figure 12: Total and dissolved absorption spectra - morning

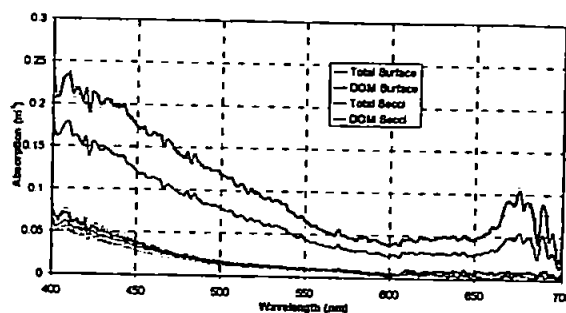


Figure 13: Total and dissolved absorption spectra - afternoon

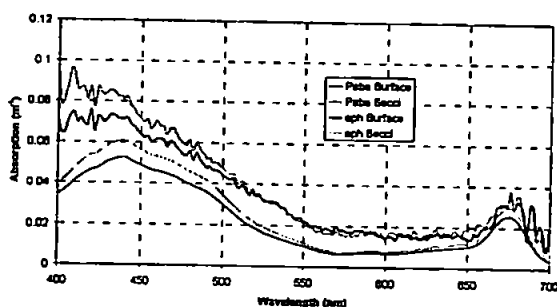


Figure 14: Total particulate and Chlorophyll a absorption - morning

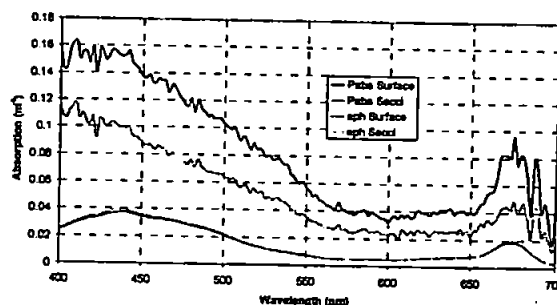


Figure 15: Total particulate and Chlorophyll a absorption - afternoon

B.2. 27th February

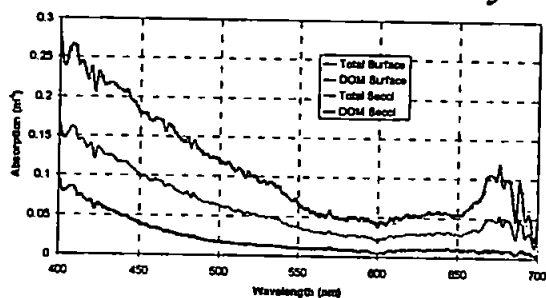


Figure 16: Total and dissolved absorption spectra

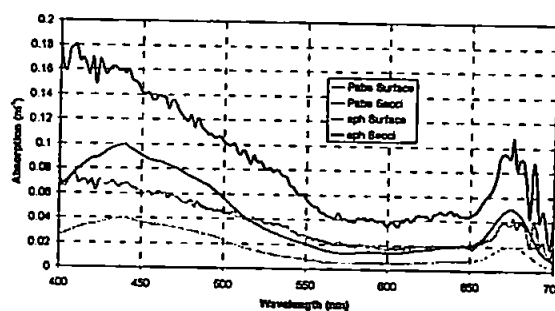


Figure 17: Total particulate and Chlorophyll a absorption

B.3. 28th February

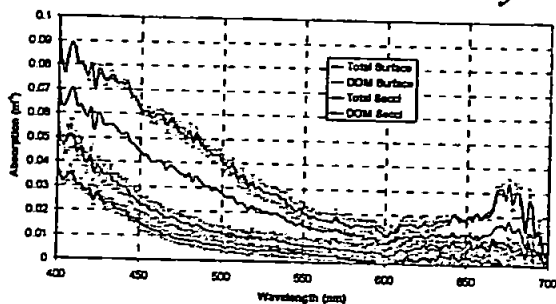


Figure 18: Total and dissolved absorption spectra - morning

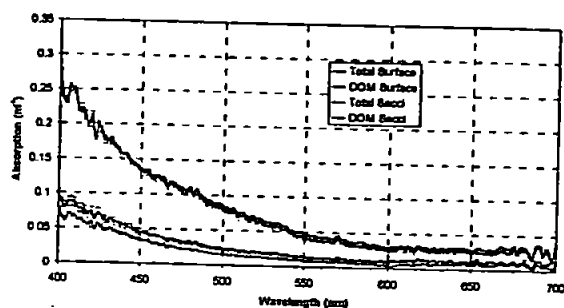


Figure 19: Total and dissolved absorption spectra - afternoon

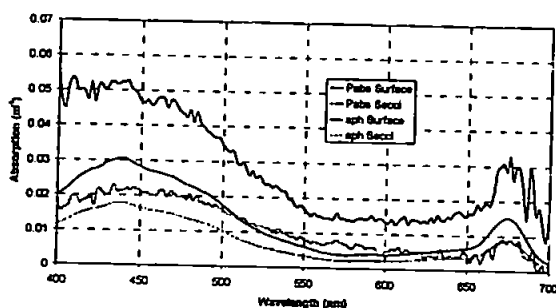


Figure 20: Total particulate and Chlorophyll a absorption - morning

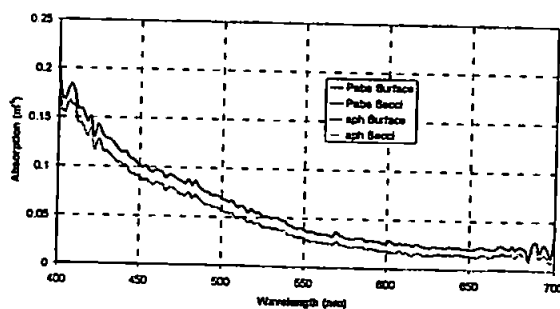


Figure 21: Total particulate and Chlorophyll a absorption - afternoon

afternoon

B.4. 1st March

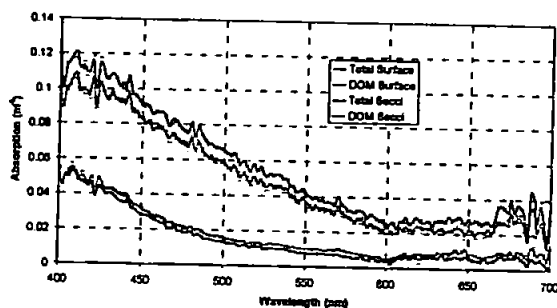


Figure 22: Total and dissolved absorption spectra

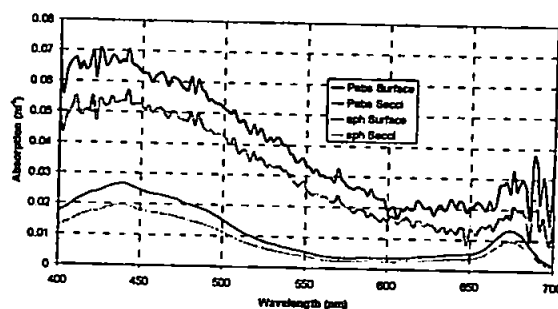


Figure 23: Total particulate and Chlorophyll a absorption

B.5. 2nd March

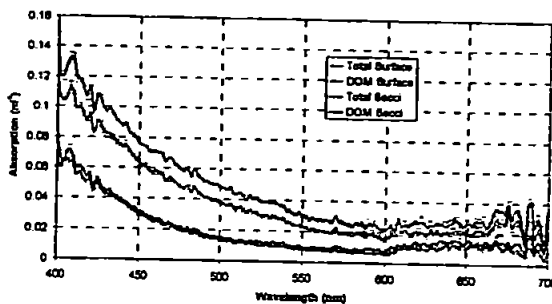


Figure 24: Total and dissolved absorption spectra

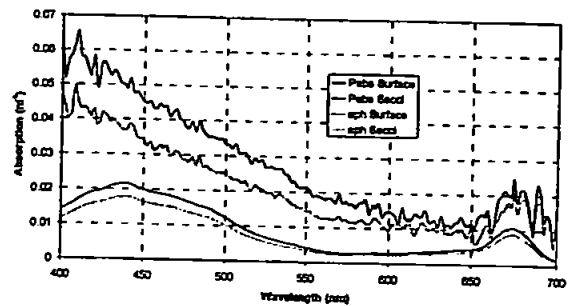


Figure 25: Total particulate and Chlorophyll a absorption

B.6. 11th March

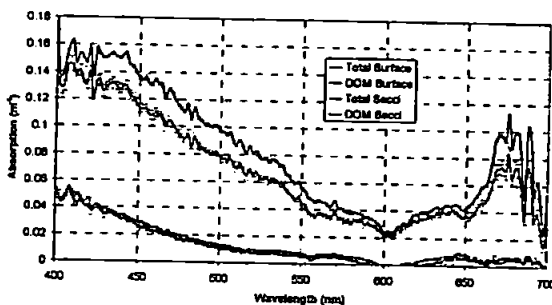


Figure 26: Total and dissolved absorption spectra

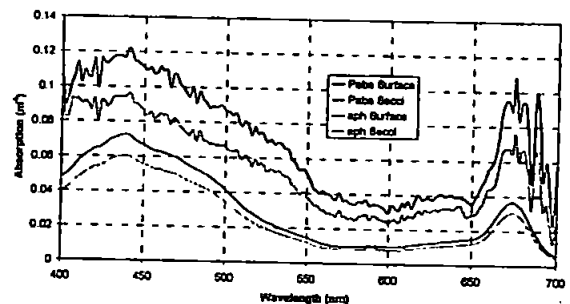


Figure 27: Total particulate and Chlorophyll a absorption

Table 1: Sampled dates, position, Sea Surface Temperature (SST) and Secchi depth

Date	Local Time	Position		SST (DegC)	Secchi (m)	Station
	GMT (-4h00)	South	West			
26/02/02	9h00	62 36.07	56 56.08	1.9	10.5	A
26/02/02	16h15	63 42.51	56 51.90	1.5	15.5	B
27/02/02	8h30	63 47.16	58 00.06	-0.5	15	C
28/02/02	7h15	62 58.43	59 40.94	1.2	12.5	D
28/02/02	18h45	62 58.96	60 33.76	1	7	E
1/03/02	10h15	62 12.27	58 52.00	1.5	5	F
2/03/02	11h15	66 33.89	55 46.83	0.7		H
3/03/02	8h10	64 12.58	56 57.76	-0.5	15	G
5/03/02	8h05	64 07.45	56 54.66	-0.7	10	G
7/03/02	8h35	64 04.45	56 40.01	-0.5	11	G
8/03/02	8h12	64 04.73	56 44.69	-0.6	22	G
9/03/02	10h14	64 05.73	56 55.69	-0.8	8.5	G
11/03/02	11h00	63 49.86	58 02.01	-0.9	10	C

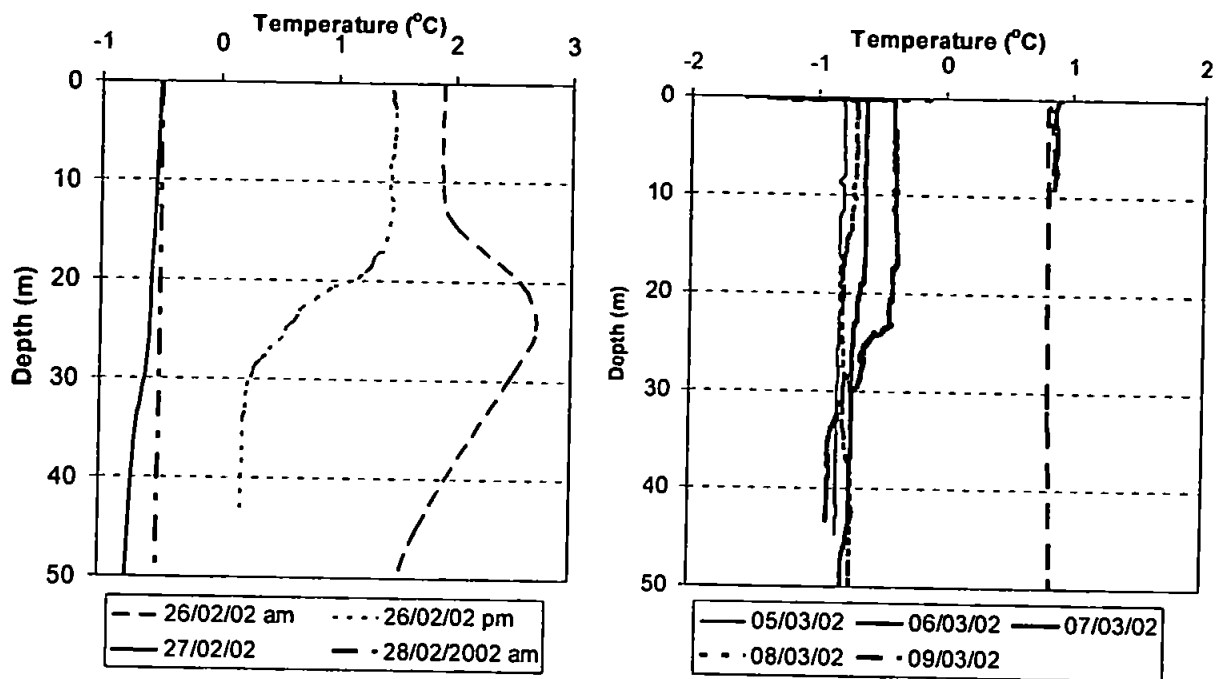


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Development of a point source integrating cavity absorption meter

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Abstract

The different existing techniques for measuring the absorption coefficient are presented with their advantages and disadvantages. The recurrent problem when measuring absorption appears to be the scattering of light by particles. A solution could be a point source integrating cavity absorption meter. In such an instrument, the sample is enclosed in a spherical cavity made with highly reflective walls. As a result the measurement is not affected by scattering. The development and first experiments made with such an absorption meter at the University of Plymouth are presented in this paper.

Keywords: Absorption, scattering, absorption meter, integrating cavity

1. Introduction

Absorption is one of the fundamental processes that determine the shape and magnitude of the light field in a medium. The absorption coefficient is the proportion of flux lost due to absorption from a beam normal to an infinitesimally thin layer of a medium, divided by the thickness of the layer [1]. Knowledge of the absorption coefficient, the volume scattering function and the input radiance distribution are necessary to solve the radiative transfer equation for the radiance distribution as a function of depth. Thus the absorption coefficient has a key role in determining any optical property that is dependent on the radiance distribution, including the remotely sensed reflectance and the diffuse attenuation coefficient. The total absorption coefficient of sea water can be partitioned into the sum of the absorption coefficients due to water, dissolved organic matter, phytoplankton and detrital particles. In addition to its importance in modelling radiative energy transfer in water, the absorption coefficient is important for studies of phytoplankton productivity and taxonomy. The spectral characteristics of absorption by phytoplankton result from, and can therefore be used to identify, photosynthetic and auxiliary pigments characteristic particular of phytoplankton taxonomic groups [2]. Investigations and models of primary production must include spectral absorption coefficients of photosynthetic pigments, which determine the ability of phytoplankton to collect light for use in photosynthesis. The importance of the absorption coefficient and the difficulty of

measuring it accurately in low-signal, scattering suspensions have led to the development of a variety of measurement techniques. Pegau *et al* [3] reviewed six different instruments and compared the results obtained from each. The *in situ* measurement techniques under consideration were the reflective tube absorption meter (RTAM), a tethered optical profiling system (TOPS), the isotropic point source (IPS) and the compound radiometer (CR). The laboratory measurement instruments investigated were the spectrophotometer and the integrating cavity absorption meter (ICAM). Other techniques such as optoacoustic and photothermal measurement and reverse methods using reflectance measurement were not investigated. The first part of this paper reviews the different techniques studied by Pegau *et al*, and their advantages and disadvantages. The second part presents the experiments carried out with a prototype point source integrating cavity absorption meter (PSICAM).

2. The existing techniques

2.1. *In situ* methods

An example of a RTAM is typically the ac-9 designed by Wetlabs. The RTAM uses a collimated light source and encloses the sample in a reflective tube. The reflective tube collects the near forward-scattered light so that the radiant flux lost due to absorption may be estimated [4]. This instrument actually measures the absorption coefficient plus

a small fraction of the scattering coefficient associated with the uncollected scattered light. This error should remain small. Assuming that the photons follow Petzold's scattering phase function [5] they should be scattered mainly in the near forward direction. The uncorrected absorption coefficient a_u is obtained using equation (1):

$$a_u = -\frac{1}{L} \ln\left(\frac{V_{\text{sample}}}{V_{pw}}\right) \quad (1)$$

where L is the path length of the instrument, V_{sample} is the signal voltage for the sample and V_{pw} is the signal voltage for pure water. Note that this is essentially the same approach as is used in a spectrophotometer. Rather than using a reference cell, the meter is calibrated in the laboratory. The inherent error in the RTAM approach is due to the undetected scattered light; if simultaneous measurements of the spectral absorption and beam attenuation coefficient are performed, Zaneveld *et al* [6] showed that an error of less than 1% could be obtained. Otherwise, an error of $\pm 5\%$ is possible with a precision of approximately 0.003 m^{-1} [3]. Calibration problems were also encountered. The first one was an instrumental drift that cannot be entirely removed using pure water calibration; the second one is cavitation in the flow tube of the instrument [3]. Another source of bias common to all systems that use a pure water reference is the possibility of contaminated water, and this is impossible to estimate.

The TOPS comprises a string of radiometers to measure upwelling and downwelling radiance and irradiance. The TOPS used by Pegau *et al* [3] consisted of a multiple radiometer package. The measurement of $E_d(\lambda, z)$, $E_u(\lambda, z)$ and $E_o(\lambda, z)$, respectively, the downward irradiance, the upward irradiance and the scalar irradiance, allow the calculation of K_E , the net downward irradiance equation (2) and $\bar{\mu}$, the average cosine equation (3):

$$K_E = -\frac{1}{E_d - E_u} \frac{d}{dz}(E_d - E_u) \quad (2)$$

$$\bar{\mu} = \frac{E_d - E_u}{E_o} \quad (3)$$

These data are then applied to Gershun's equation (4) to determine $a(\lambda, z)$. The set of instruments deployed by Pegau *et al* [3] was used to calculate the absorption coefficient with an estimated uncertainty of approximately 10%. This uncertainty includes up to 7% instrument noise.

The isotropic point source technique was first proposed by Sorenson (1968), who argued that the attenuation of irradiance E from an isotropic source should decay with distance following equation (5):

$$a(\lambda, z) = K_E(\lambda, z) \bar{\mu}(\lambda, z) \quad (4)$$

$$E(r) \propto \frac{e^{-ar}}{r^2} \quad (5)$$

where a is the absorption coefficient and r is the radial distance from the source. Thus, by measuring the irradiance from the source as a function of r , the absorption coefficient may be determined. The vector irradiance (more precisely, the radial component of the vector irradiance) from an isotropic point

source was derived from the steady state radiative transfer equation without internal source [7]:

$$E(r) = \frac{\Phi_o}{4\pi r^2} \exp\left(-a \int_0^r \frac{dr}{\bar{\mu}}\right) \quad (6)$$

where Φ_o is the radiant flux emitted by the source and $\bar{\mu}$ is the average cosine of the light field from the source, r is the radial distance between the source and the detector and dr is the path variation due to scattering materials. The assumption in equation (6) is that the water column within which $E(r)$ is measured is homogeneous [3]. The solution to equation (6) for the absorption coefficient is

$$a(\lambda, z) = \bar{\mu} \left[K_E(\lambda, z) - \frac{2}{r} \right] \quad (7)$$

where K_E is the diffuse attenuation coefficient for irradiance. To avoid errors due to the ambient background light, IPS measurements have to be made either at night or in deep water. Note that when $r \rightarrow \infty$, we arrive at the Gershun equation (equation (4)). Errors in the IPS method arise from several sources, and all of these errors, except for the assumption of water homogeneity, are due to the particular instrumental implementation and optical conditions of the water mass. The largest sources of errors are: (1) the assumption of constant radiant output of the isotropic source during each light flash since a reference detector is not used, (2) variable alignment of the source and detectors due to the variability in water movement, (3) the assumption that $\bar{\mu} = 1$ since only vector irradiance and not scalar irradiance was measured. Errors from (1) and (2) should be random and therefore quantified in the standard error of the regression fit. Errors of (2) can also be systematic if instrument misalignment remains constant during a measurement. The error from the assumption that $\bar{\mu} = 1$ (3) is systematic and difficult to quantify. Another source of error in this method is the approximation that the path length in the exponent is the geometrical radial distance r , when, in fact, scattering increases the mean path by δr so that the expression should be [3]

$$E(r) \propto \frac{e^{-a(r+\delta r)}}{r^2} \quad (8)$$

If $\delta r \ll r$, the error will be small. The compound radiometer estimates the absorption coefficient by measuring the moment of a Legendre polynomial expansion of a radiance distribution. The absorption coefficient is determined by applying the measured moments to a form of Gershun's equation [8,9]. This device uses a series of reflectors to measure the integral moments of the radiance distribution at a number of zenith angles. The radiance distribution is then deduced from a linear combination of the measured moments. The moments are symmetrical about the vertical axis and optimized to facilitate computation of inherent optical properties in the form of the D_n series [10] equation (9):

$$D_n = c - S_n \quad (9)$$

$$S_n = 2\pi \int \beta(\eta) P_n(\cos \eta) d\eta$$

where c is the attenuation coefficient, $\beta(\eta)$ is the scattering function at an angle η , P_n is the n th Legendre polynomial and

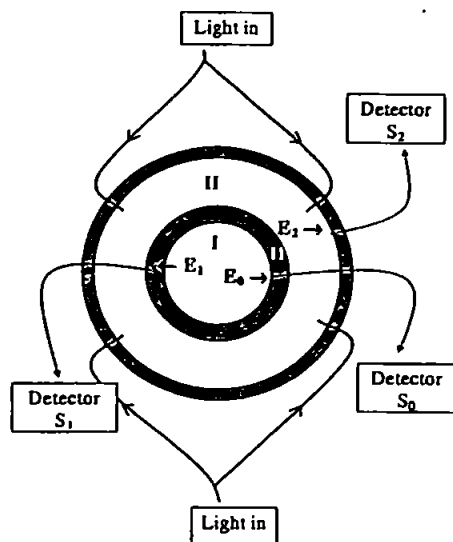


Figure 1. Cross section of the ICAM (from Fry *et al* 1992).

S_n , the n th harmonic or the scattering function. The zeroth-order moment (D_0) is the absorption coefficient, D_∞ is the beam attenuation coefficient, and the intermediate D_n describe moments of the volume scattering function. The compound radiometer has an estimated uncertainty of 0.01 m^{-1} in the depth range of 12 to 18 m [11]. This is the range within which the radiometer works best. Performances deteriorate in deep water, due to lack of light and also in very shallow water [3]. Of course, these performances also depend upon the turbidity of the water.

2.2. Laboratory methods

The theoretical basis of the ICAM was developed by Elterman [12]. In an ICAM, a diffuse light field is set up within a cavity that has a diffusely reflective wall and is filled with the liquid whose absorption properties are to be measured. From the measured effect of the liquid on this light field, the value of its absorption coefficient can be determined. The idea was adopted by Fry *et al* [13] who describe the theory and design of an instrument that could be used to measure the absorption coefficient of water. This ICAM has a cylindrical shape and consists of an integrating cavity within another integrating cavity to ensure that the light inside the inner cavity is isotropic (figure 1). Pope *et al* [14] used an ICAM to measure the absorption coefficient of pure water in the wavelength band of 380 to 700 nm. The ICAM has two specific advantages. First, because of the long path length of the photons as they undergo multiple reflections from the cavity wall before they are finally absorbed, the instrument can be used to measure low values of absorption coefficient. Second, because the light field is already totally diffuse, it cannot be made more diffuse by scattering owing to particles within the cavity. Thus, measurement of absorption is not affected by scattering [13].

There are two methods of calibrating the ICAM, one described by Fry *et al* [13], and one developed by the Naval Research Laboratory [15]. The method described by Fry *et al* expressed the absorption coefficient as a linear function equation (10) of the voltage signal measured in different parts

of the instrument:

$$a(\lambda) = K_1 \frac{S_1(\lambda)}{S_0(\lambda)} - K_2 \quad (10)$$

$$a(\lambda) = K_3 \frac{S_2(\lambda)}{S_0(\lambda)} - K_4$$

where K_1, K_2, K_3 and K_4 are calibration constants of the instrument and S_0, S_1 and S_2 are the signal voltages at different places in the cavity (figure 1). The calibration constant K_1 can be determined by measuring the known absorption coefficient of a dye solution. The algorithm developed by NRL calculates an effective path length for the cavity. The effective path length is dependent on the geometry of the cavity, the refractive index of the sample and the field of view of the sensor [15]. The assumptions made with the ICAM are the following: the light field within the cavity is isotropic, the light field within the sample is isotropic, the change in energy density is due solely to the absorbance of the sample, and the absorbance of the empty cavity is zero. When an empty cavity reading is used as the zero absorbance value, the absorption coefficient can be determined from equation (11):

$$a(\lambda) = \frac{1}{l} \ln \left(\frac{V_E(\lambda)}{V_S(\lambda)} \right) \quad (11)$$

where l is the effective path length (m), and $V_E(\lambda), V_S(\lambda)$ are, respectively, the output signal voltages of an empty cavity and a cavity field with a sample. When used in this way, the ICAM does not require standardization either by measuring known calibration samples with a spectrophotometer or by measuring the absorption of clean water to determine the total absorption coefficient of the sample. Errors arise from the assumption that absorption in an air-filled cavity is zero. The assumption of an isotropic field within the cavity is also a source of error with this method. The overall error with this method is assumed to be around 1% [3]. This method of calibration is more accurate than the first one developed by Fry *et al* [13] in so far as no calibration with standard dye solution is required. With a spectrophotometer, water samples are taken and filtered to measure separately the absorption coefficient of the particles and gelbstoff, the yellow polymers of phenolic and benzenecarboxylic acid produced by bacteria during the decomposition of organic matter. The total absorption coefficient is then determined by summing the component contributions with the absorption coefficient of pure water. The low concentration and absorption signal of suspended particles in the water column requires that the particles be concentrated before their absorption spectrum can be measured in a spectrophotometer [16]. The actual quantity measured by a spectrophotometer is the absorbance (A) or optical density. A beam of monochromatic light passes through a quartz or plastic cell of known path length. The measured quantity is the intensity (I) of the light that passes through the cell. Intensity, I , is equivalent to a radiant flux (Φ) [17], and is calculated as $I = \Phi_0 - \Phi_a$, Φ_0 denoting the incident flux on the cell and Φ_a the absorbed flux. Two measurements are made, one with a cell filled with pure water (I_0), and a second one with the water sample under consideration. The transmittance T is then calculated as

$$T(\lambda) = \frac{I(\lambda)}{I_0(\lambda)} \quad (12)$$

The absorbance is then calculated as

$$A(\lambda) = \log_{10} \left(\frac{1}{T(\lambda)} \right) = \log_{10} \left(\frac{I_0(\lambda)}{I(\lambda)} \right). \quad (13)$$

The absorption coefficient is then derived from the Beer-Lambert equation (14) where $a(\lambda)$ is the absorption coefficient, l is the path length of the cell and C is the concentration of the sample. This law defines a linear relationship between absorbance and the concentration of the sample:

$$A(\lambda) = a(\lambda) * l * C. \quad (14)$$

The most common procedure for a natural water sample is to determine separately the absorption coefficients of the different components. The value of the absorption coefficient of the medium as a whole, at a given wavelength, is equal to the sum of the individual absorption coefficients of all the components present:

$$a(\lambda) = a_{DOM}(\lambda) + a_{phyto}(\lambda) + a_{part}(\lambda) + a_w(\lambda) \quad (15)$$

where $a_{DOM}(\lambda)$, $a_{phyto}(\lambda)$, $a_{part}(\lambda)$ and $a_w(\lambda)$ are, respectively, the absorption coefficients of dissolved organic matter, phytoplankton, particulate matter and pure water. With a spectrophotometer, a proportion of the light is scattered outside the field of view of the sensors. Thus, spectrophotometers do not measure the true absorbance but rather the attenuation (absorbance plus a fraction of scattering). This might be a problem for a solution with a high scattering coefficient relative to the absorption coefficient. The measurement of the blank cell is far less biased by the scattering effect. This problem can be minimized by placing a layer of scattering material between the cell and the incident beam of light, so that both samples are measured with diffused light.

Errors in total absorption coefficients estimated from spectrophotometric measurements also arise from several sources. The first is the unknown error in values of pure water spectral absorption [14, 18]. Additional errors are associated with separate spectrophotometric measurements of absorption, due to suspended particles and due to dissolved organic matter.

3. Point source integrating cavity absorption meter

3.1. PSICAM theory

The different techniques described previously can be classified into two categories. The passive techniques measure the apparent optical properties of a water body and then use Gershun's equation to derive the absorption coefficient. The active techniques which regroup both *in situ* and laboratory techniques use an independent source of light to measure the absorption coefficient. All these techniques present advantages and disadvantages depending upon the goal of the research. If a quick assessment of a large region is needed then most *in situ* techniques will be suitable. If fairly accurate values are required then the RTAM seems to be the recommended approach although it can be biased under certain conditions. However, of the various instruments to measure the absorption coefficient tested by Pegau *et al* [3], a promising one appears to be the instrument based on the ICAM principle. Scattering from bubbles due to cavitation should not affect this

instrument. Kirk [19] described the theory of an ICAM in the case of a spherical cavity. Like the ICAM used by Fry *et al* [13], this instrument consisted of a cavity within another one. The sample to be analysed was placed in the inner one where an isotropic light field was generated. In a later paper [20], Kirk further developed the theory of a PSICAM. In this case, the instrument is made of a single spherical cavity and the light source is a point source at the centre of the cavity. In fact, this PSICAM should be more efficient and easier to build than an ICAM. Kirk [19] showed that if the cavity is spherical, it is possible to derive specific equations for the probability of photon survival (P_s), the average number of collisions with the wall per photon (C_f), the average path length per photon (l_f) as a function of the absorption coefficient, the diameter of the cavity and the reflectivity of the cavity wall (ρ). Such equations were derived (Kirk, 1995, 1997) for both the configuration of a spherical ICAM equation (16) (ICAM) and equation (17) (PSICAM):

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

$$C_f = \frac{P_s}{1 - \rho P_s} \quad (16)$$

$$l_f = \frac{1}{a} \left(\frac{1 - P_s}{1 - \rho P_s} \right)$$

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

$$C_f = \frac{\exp(-ar)}{1 - \rho P_s}$$

$$l_f = \frac{1}{a} \left\{ 1 - \exp(-ar) \left[2 - \rho \left(\frac{1 - P_s}{1 - \rho P_s} \right) + \exp(-2ar)(ar + 1) \right] \right\}. \quad (17)$$

As for a classic bench spectrophotometer, the absorption coefficient will be derived from the measurement of the transmittance relative to pure water calculated as

$$T(\lambda) = \frac{\exp(-ar)(1 - \rho P_s^w)}{\exp(-a_w r)(1 - \rho P_s)} \quad (18)$$

where a_w is the absorption coefficient of pure water and P_s^w is the probability of photon survival in a cavity filled with pure water. Equation (18) cannot be solved but Kirk [20] showed that if we assume that the radiance distribution is homogeneous and isotropic within the cavity (referred to as the homogeneous energy distribution assumption) then we can arrive at the following expression for $a(\lambda)$:

$$a(\lambda) = \left[\frac{\frac{4}{3}a_w(\lambda)r + (1 - \rho(\lambda))}{\frac{4}{3}r} \right] \frac{1}{T(\lambda)} - \frac{3(1 - \rho(\lambda))}{4r} \quad (19)$$

where $a_w(\lambda)$ is known from the literature and $\rho(\lambda)$ is measured with standard dye solutions. The theoretical results showed that a PSICAM has the same essential virtues (long effective path length, insensitivity to scattering) as an ICAM. At high values of $a(\lambda)$ the PSICAM should give rather more accurate results. In principle, therefore, a PSICAM could provide the basis for a simple absorption meter for natural waters regardless of their scattering properties.

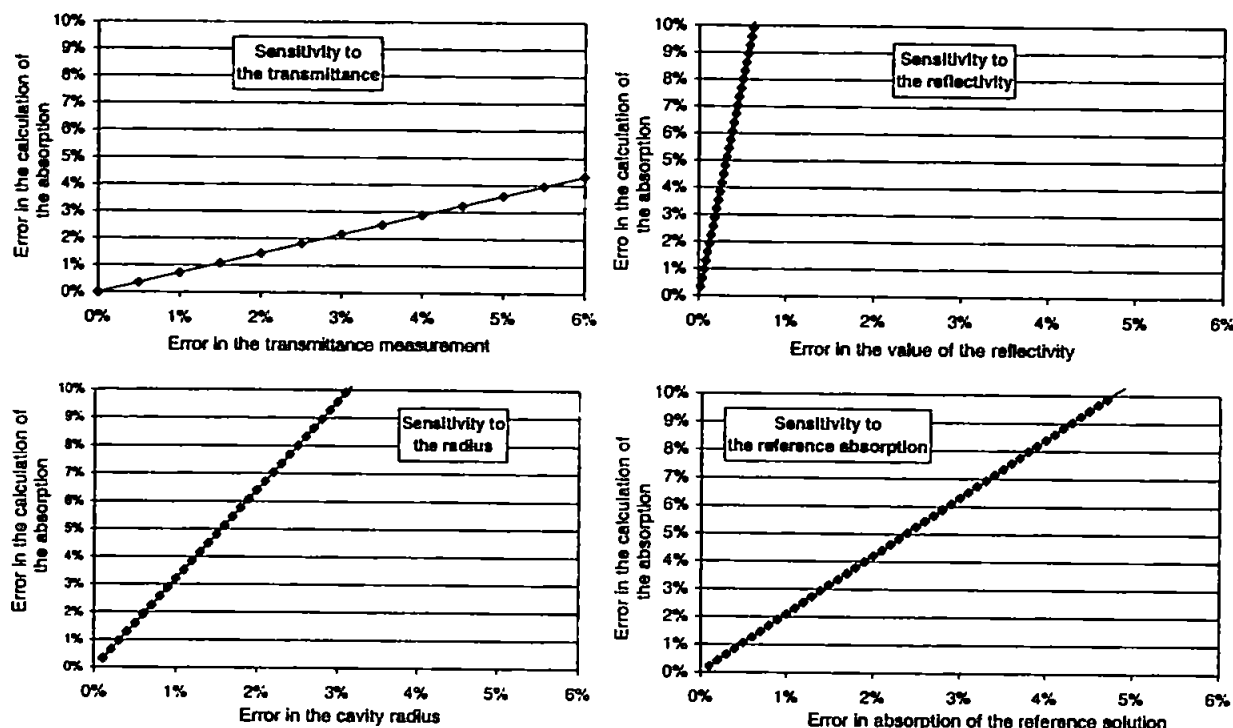


Figure 2. Sensitivity analysis for the four parameters of the integrating sphere.

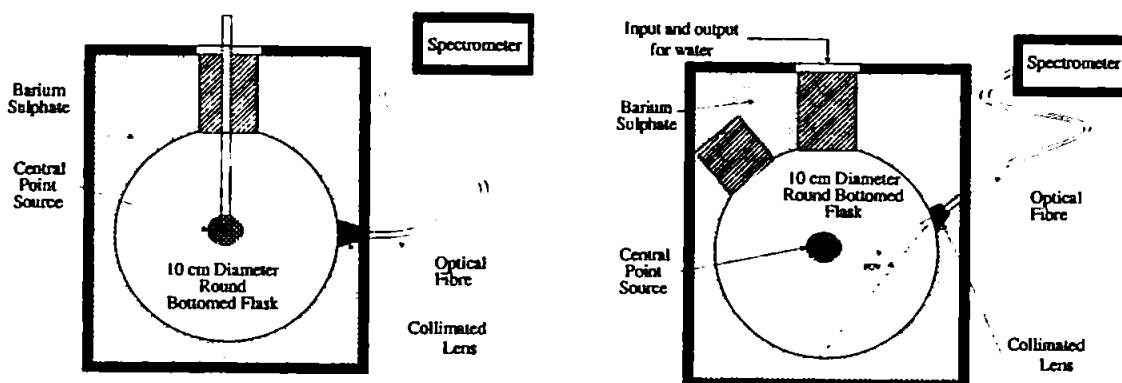


Figure 3. Two different versions of the prototype PSICAM. Single neck round bottomed flask (left). Two necked round bottomed flask (right).

3.2. Sensitivity analysis

A sensitivity analysis (figure 2) was carried out using the formulae found in the literature [5]. This analysis reveals the high sensitivity of the measurements to the reflectivity of the cavity wall. Figure 2 shows that an error of 1% in the value of the reflectivity leads to almost 10% error in the calculation of the absorption coefficient.

The second important parameter in terms of sensitivity is the radius of the cavity in which an error of 3% leads to almost a 10% error in the calculation of the absorption coefficient. This parameter will be discussed later as one of the possible sources of error for our prototype. The reference absorption spectrum and the transmittance can influence the accuracy of the measurement. The first one would depend upon the quality of the pure water supply. This is, as pointed out previously, the inherent problem of all techniques using pure water as a reference. The second would most probably be corrupted by the stability of the light source.

3.3. Laboratory prototype

3.3.1. The integrating sphere. The first prototype PSICAM (figure 3, left) was made out of a 500 ml round-bottomed flask with a 24/29 ground glass neck embedded in barium sulphate as suggested by Kirk [20]. The light source was made of a small tungsten bulb within a diffusing Delrin sphere located at the centre of the cavity by means of a white plastic stem passing through the neck of the flask. The light collector was a 10° field of view collimated lens looking toward the light source and fitted to a fibre optic. The light field within the collector was sampled by means of an optic fibre and its spectral distribution recorded with a spectrophotometer. We used this version for the preliminary PSICAM experiments. Taking into account the observations made with the prototype, an improved version was constructed with modified design, components and light source.

The improved version (figure 3, right) was based upon a two-neck round-bottomed flask in order to have two separate

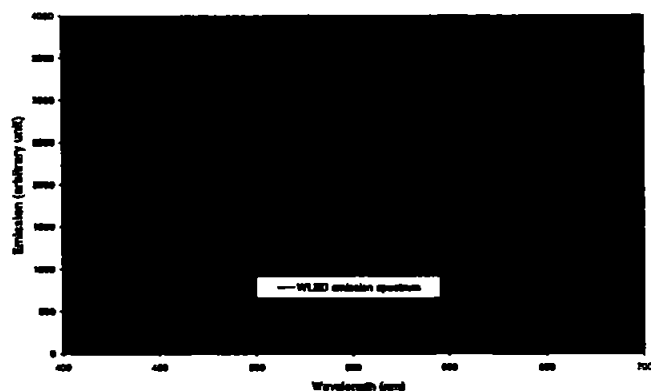


Figure 4. Emission spectrum of a white LED.

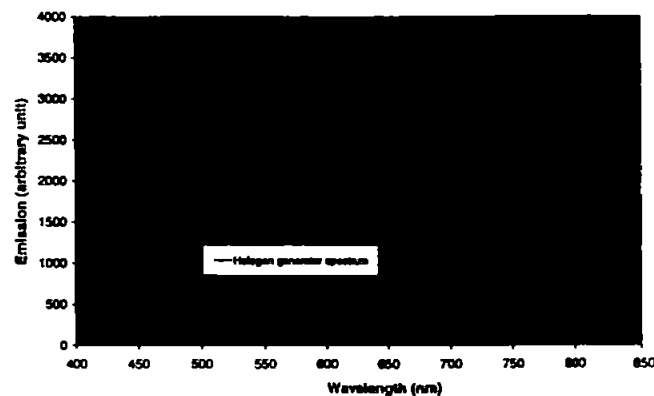


Figure 5. Emission spectrum of the halogen generator.

ports, one for the stem of the light source, one for the input and output of water. The light source was not removed throughout the set of experiments. This prevented any distortion relative to the reference measurement. As previously, the glass flask was embedded in barium sulphate. Again, the sensor was a collimated lens so that a radiance ratio and not an irradiance ratio was obtained to calculate the transmittance. The sensor had a 10° field of view and was positioned at an angle so that no direct illumination from the light source was picked up. The sensor looks toward the light source in the vertical plane and makes a 30° angle with the horizontal looking toward the bottom part of the flask (figure 3, right). The flasks used to build both integrating cavities were standard chemistry apparatus, so were not perfectly spherical. Moreover, the necks added extra volume to the sphere. For the experiments, we assumed a perfect sphere of 5.25 cm radius.

3.3.2. Light source. Making a proper point source for the instrument was the biggest challenge. This light source needed to be small so as not to interfere too much with the cavity, but powerful enough to strongly illuminate the cavity. A number of illumination systems were tried.

Ocean Optics Inc. LS-1 tungsten light source. Experiments were conducted using the halogen tungsten light source (6.5 W) provided with the Ocean Optics spectrometer as a light source for our PSICAM. The LS-1 light source was adapted to fit a 3 mm diameter fibre bundle. The illuminated side of the bundle was a Teflon stem terminated by a Teflon sphere. This light source was actually too weak to properly illuminate the sphere so that excessively long integration times were required to obtain usable signals.

White light emitting diode. Experiments were also carried out with white LEDs. Three LEDs were placed in a Teflon cylinder and held in the centre of the cavity by a Teflon stem. For practical reasons the point source was cylindrical in this case. Again, the illumination of the cavity was rather too small, and integration times required to get measurable signals were around 40 s (see the emission spectrum in figure 4).

Halogen generator and fibre bundle. The last light source tried consisted of a 75 W halogen generator (see the emission spectrum in figure 5) especially designed to fit a fibre bundle.

As before, the end of the bundle was held in a Teflon stem and terminated by a Teflon bulb. The fibre bundle used was 6 mm in diameter and could therefore carry a significantly higher amount of light. On the other hand, this bundle increased the diameter of the stem in comparison with the 3 mm one. The experiment carried out with this light source showed that it was by far the brightest one and allowed a significant reduction in the integration time. The stability of this halogen generator was investigated with the OOI S1000 spectrophotometer. The experiment consisted of measuring the evolution of its emission spectrum with time. For this experiment, a collimated lens fitted to the spectrometer through a $1000\ \mu\text{m}$ fibre optic was used. One measurement per minute was taken over 3.5 h. Figure 6 shows the evolution of the percentage change relative to the first measurement, taken immediately after the light was switched on.

These graphs show that the highest variations occur for the shorter wavelengths with a significant difference between 400 and 425 nm. The smallest variations occur for wavelengths between 500 and 700 nm. Overall, this graph shows that a warming up time of 40 min is necessary to achieve even moderate stability ($\pm 2\%$). In order to minimize this problem, a reference measurement is taken between each sample measurement.

3.3.3. Calculations of the reflectivity and the absorption coefficient. To estimate the reflectivity of the sphere, two standard black solutions of known absorption coefficient a_A and a_B were used. The transmittance of solution B was measured relative to solution A. The reflectivity was then calculated from the transmittance equations (18) and (20):

$$\rho(\lambda) = \frac{T_{AB} \exp(-a_B r) - \exp(-a_A r)}{T_{AB} \exp(-a_B r) P_S^A - \exp(-a_A r) P_S^B}. \quad (20)$$

The instrument measures the transmittance of a water sample relative to pure water. Data used for the pure water absorption coefficients were taken from Pope *et al* [14]. The absorption coefficient can be calculated in two different ways. The first consists of using equation (19) from [20]. There is no analytical solution to the equation of transmittance for $a(\lambda)$. Equation (19) is obtained assuming a homogeneous energy distribution. The second method of calculating the absorption coefficient consists of numerically solving the equation of transmittance for $a(\lambda)$, by minimizing the least square function

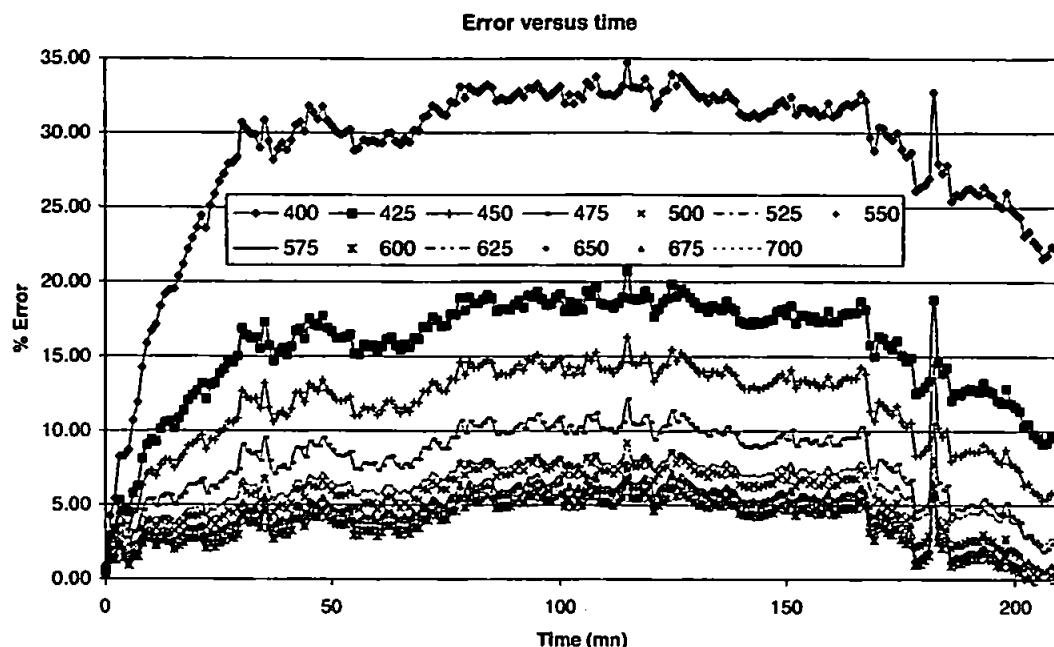


Figure 6. Stability of the halogen generator for 13 wavelengths.

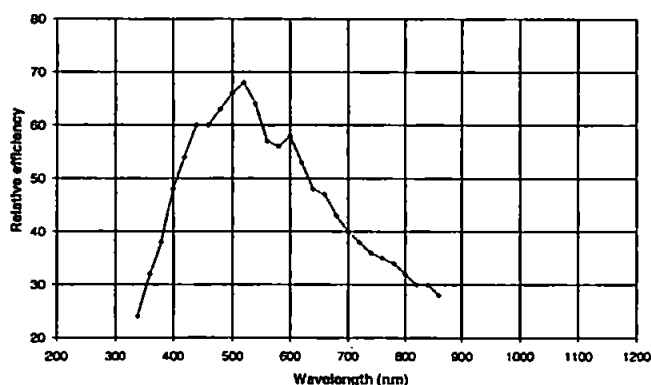


Figure 7. Efficiency of the spectrometer's diffraction grating (www.oceanoptics.com).

$G(a(\lambda))$ equation (21). A set of transmittances is calculated using equation (18) for a given range of absorption coefficients. This gives $T_{\text{num}}(\lambda)$. The reflectivity, the absorption coefficient of the reference solution and the radius of the cavity are known parameters. The absorption spectrum of the sample is then found using the least square method for function $G(a(\lambda))$:

$$G(a(\lambda)) = \sqrt{(T_{\text{num}}(\lambda) - T_{\text{Exp}}(\lambda))^2}. \quad (21)$$

3.3.4. Spectrophotometer. The spectrometer used with an integrating sphere manufactured by Ocean Optics Incorporated was a portable fibre optic spectrometer (S2000) fitted with a diffraction grating whose characteristics are shown in figure 7. Owing to the grating efficiency, it was decided to limit absorption measurement to the 400 to 700 nm band. The spectrometer was connected to the integrating sphere with a 1000 μm fibre optic.

3.3.5. Experiments. The best compromise found so far between the power and size of the light source was using the 75 W halogen generator with a 6 mm fibre bundle enclosed in

Table 1. Set of concentrations used to calculate the linear range of the spectrometer.

Dye Solutions	Concentration (ml l^{-1})				
Blue and Green	1	5	10	25	50
Red	0.5	1	5	10	25
Black	0.1	0.25	0.5	1.0	2.5

a Teflon stem. This system was used to undertake various experiments using dye solutions and Milli-Q water as a reference measurement.

Experiments with standard dye solutions. The first experiments with the prototype were carried out with standard dye solutions to estimate the efficiency of the instrument. The first step was therefore to calculate the molecular absorption of those standard dyes. The absorption coefficients of the standard solutions were measured with the PS 2000 OOI spectrometer using a 1 cm path length cuvette. The measurements were carried out using four dye solutions (green, blue, red and black) for a set of five concentrations (see table 1 and figure 8) in order to estimate the linear range of measurement for the cuvette holder.

The absorbance relative to pure water was measured for the five different concentrations of each dye. Among the five absorption spectra, the concentrations within the linear range of the spectrometer were selected to calculate the molecular absorbance for discrete wavelengths. For the blue, green and red dyes the concentrations were respectively 5, 10 and 1 ml l^{-1} . The set of concentrations used for the black dye remained in the linear range of the instrument. The absorbance was calculated from 400 to 700 nm in steps of 1 nm. Figure 8 illustrates the absorbance spectra from top left to bottom right of the black, green, blue and red standard solutions. The absorption coefficient for each concentration was then calculated using $A(\lambda) = a(\lambda) * l * C$, where $A(\lambda)$

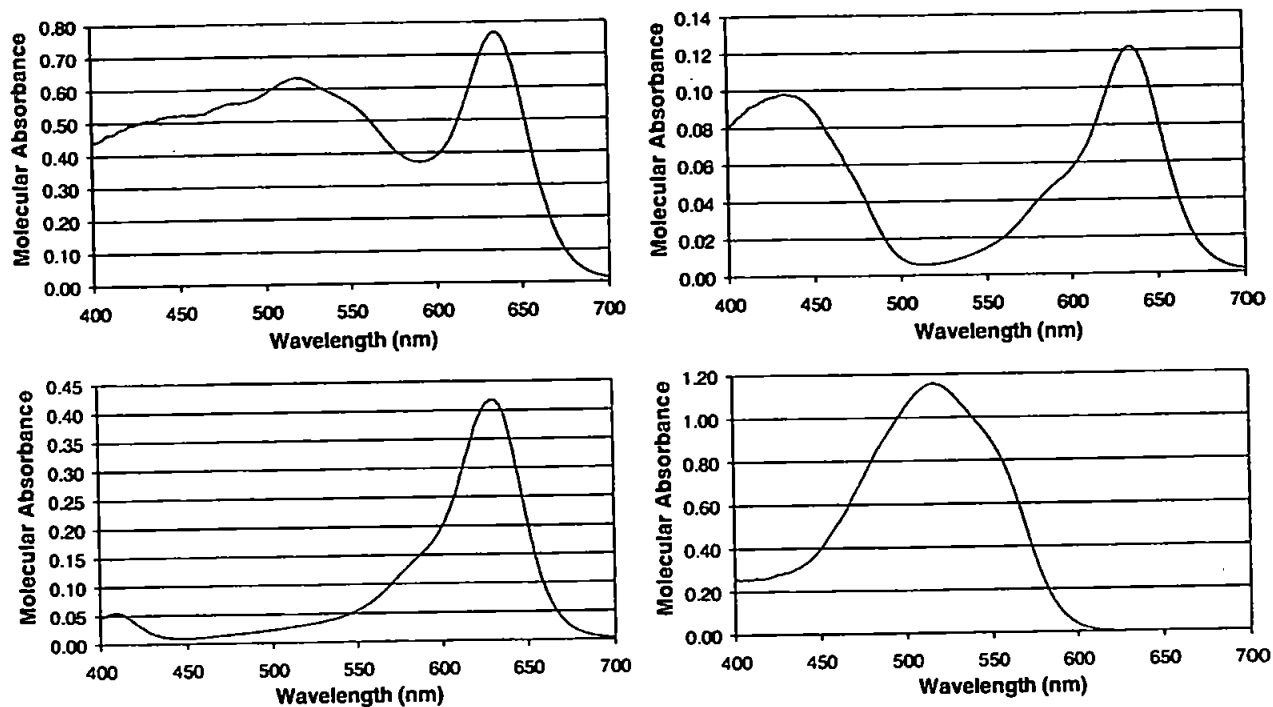


Figure 8. Absorbance spectra of the four standard dye solutions. From top left to bottom right: black, green, blue and red.

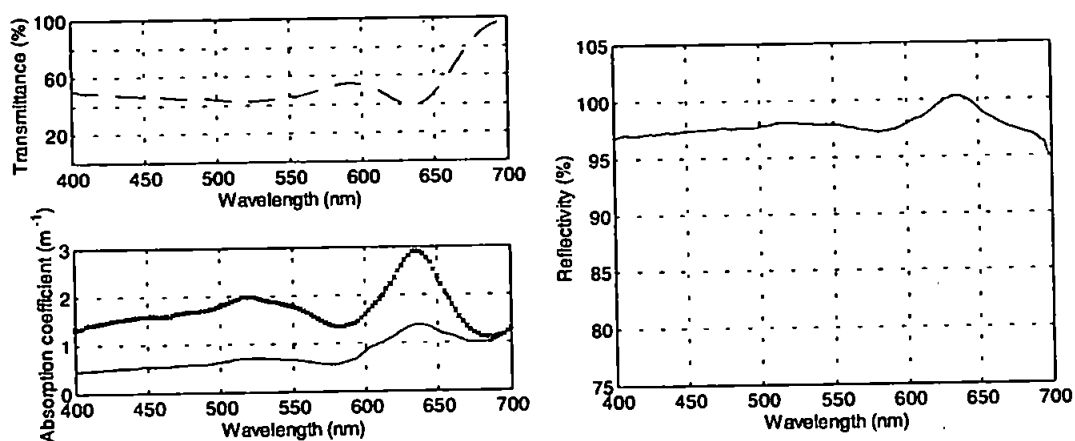


Figure 9. Transmittance spectrum of solution C_b relative to C_a (top left); absorption spectrum of solution C_B and C_A (bottom left); reflectivity spectrum of the cavity wall (right).

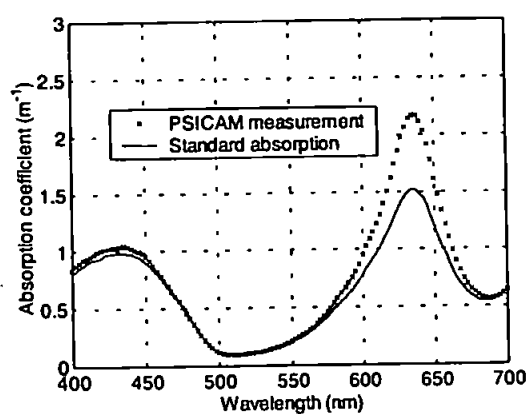


Figure 10. Calculation of the absorption coefficient by the analytical method.

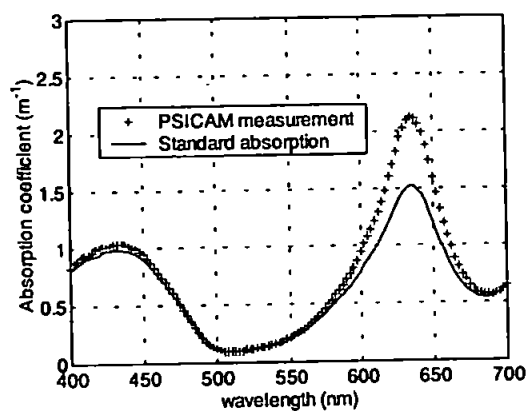


Figure 11. Calculation of the absorption coefficient by the numerical method.

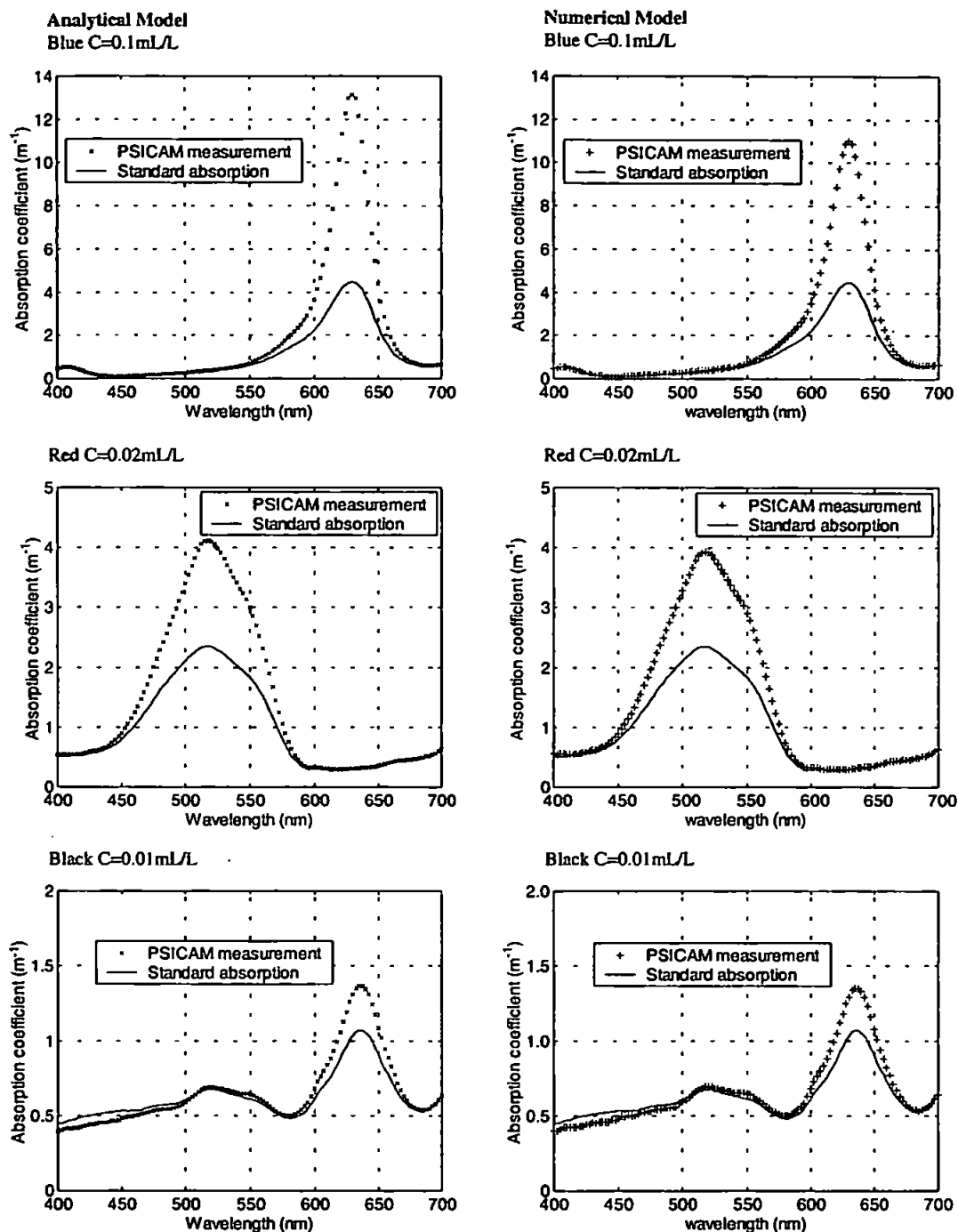


Figure 12. Calculation of the absorption coefficient of three dye solutions by the analytical method (left column) and the numerical method (right column).

is the absorbance, $a(\lambda)$ is the absorption coefficient of the solution, l is the path length of the cuvette (1 cm) and C is the concentration of the solution (ml l^{-1}). Measurements carried out with the PSICAM were then compared with measurements taken in the cuvette holder. The first experiments carried out with the sphere were to estimate the reflectivity of the cavity wall using the method suggested by Kirk [20]. In this case two black standard solutions $C_A = 0.01 \text{ ml l}^{-1}$ and $C_B = 0.03 \text{ ml l}^{-1}$ were used. The results for the calculated reflectivity are shown in figure 9, and these show a reflectivity between 95 and 100% in the visible wavebands except around 640 nm where the calculated reflectivity is higher than 100%. This artefact in the red region is as yet unexplained.

The dyes used in the experiments did not absorb significantly in wavelengths longer than 670 nm, so that we could not obtain an accurate estimation in this region. To calculate the absorption coefficient of standard solutions, we assumed a sphere reflectivity of 96% for all visible wavebands.

Experiments with food dyes. Before trying to measure natural samples various experiments were undertaken with food dyes of known absorption coefficient to assess the efficiency of the system and the methods adopted to calculate the absorption coefficient. Experiments were carried out using green dye for the first attempts with the integrating sphere. Figures 10 and 11 illustrate the calculations of the absorption coefficient

of a green solution ($C = 0.1 \text{ ml l}^{-1}$) by the analytical and numerical methods. Each graph shows the absorption spectrum of the standard solution (solid curve) and the calculated absorption spectrum.

These two graphs show that although the analytical method assumes a homogeneous energy distribution very similar spectra are obtained. The dye solution was a non-scattering solution. The results by both calculations would probably be different in the case of a more scattering sample. The absorption patterns measured by the PSICAM are similar to the reference measurement except in the range 600–670 nm. Ignoring these wavelengths, it appears that the prototype gives fairly acceptable results given the uncertainty of the cavity radius, the reflectivity and the instability of the light source. The graphs presented in figure 12 show the results of measurements by both analytical and numerical methods for the other standard dyes. For this set of solutions, the analytical and numerical methods give similar results. As for the green standard, the blue and black solutions displayed the same artefact in the 600–670 nm waveband. An artefact also occurs with the red solution centred in the green wavelength but is as yet unexplained. All the solutions used for these experiments have fairly high absorption spectrum in comparison to natural samples. It seems that these artefacts are related to the magnitude of the absorption spectrum. This would suggest that it is a problem of nonlinearity of the detector. Further experimentation will be implemented to assess this phenomenon.

4. Conclusions

The different existing techniques used to measure the absorption coefficient have both advantages and disadvantages but a recurrent problem encountered by all methods is the effect of the scattering coefficient which depletes the efficiency of most existing techniques by overestimating the value of the absorption coefficient. In theory, the PSICAM is insensitive to this parameter. The first experiments carried out with the prototype PSICAM have produced very encouraging results despite the simplicity of the design and the unsophisticated nature of the components used to build the system. The next stage in the development of this instrument must involve the use of better materials and components. In particular, we must address the problem of the main limitation of the system: the stability of the light source. The behaviour of the instrument must be investigated with moderately and highly scattering samples. Such an experiment will give the final answer regarding the reliability of this instrument.

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