

**Characterizing a New and Novel Glass
Plate Sampler for Collection of Oceanic
Microlayers**

by

Masaya Shinki
B.Sc., University of Victoria, 2006

A Thesis Submitted in Partial Fulfillment of the
Requirements for the Degree of

Master of Science

in the School of Earth and Ocean Sciences

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Supervisory Committee

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Abstract

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The sea surface microlayer is the upper thin interfacial boundary between ocean water and atmospheric air. The microlayer is known to be influenced by surface-active substances (SAS), largely organic matters adsorbed on the ocean surface. SAS samplers have been developed to investigate the chemical composition and effects of SAS but these samplers lack fast sampling and ease of use. To overcome these deficiencies, a new and novel microlayer sampler equipped with a set of rotating glass disks for fast sampling was built and modified.

In this project, two closely connected scientific issues associated with the sampler were addressed. Firstly, the thickness of the solution layer adsorbed onto the glass disk was investigated in laboratory experiments using a range of optical techniques. Secondly, the sampler itself was evaluated in different oceanic environments and operated with a range of additional scientific sensors.

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1 Introduction

1.1 Background and motivation

The sea surface microlayer is the upper thin interfacial boundary (up to 1,000 μm) between ocean water and atmospheric air (Liss and Duce 1997). This layer has been known to play an important role in air-sea interactions, including heat, mass and momentum transfer (Liss and Duce 1997). Also, this boundary is potentially an important site for photochemical and biological processes (Frew 1997). Over the last four decades, numerous experiments have been made to reveal characteristics of the microlayer (e.g. Liss and Duce 1997; Zhang et al. 2003; Garbe et al. 2004).

Careful studies of the interfacial boundary between the ocean and atmosphere will also provide a better understanding of the flux of atmospheric gases in and out of the ocean (e.g. Liss and Duce 1997; Zhang et al. 2003; Garbe et al. 2004). For example, better quantification of the flux of carbon dioxide (CO_2) across the air-sea interface would give more detailed information about the global carbon cycle. This is of interest because of our increased attention to the Earth's green house effect. The global carbon cycle is a complex system wherein forms of carbon are exchanged between various reservoirs (Figure 1).

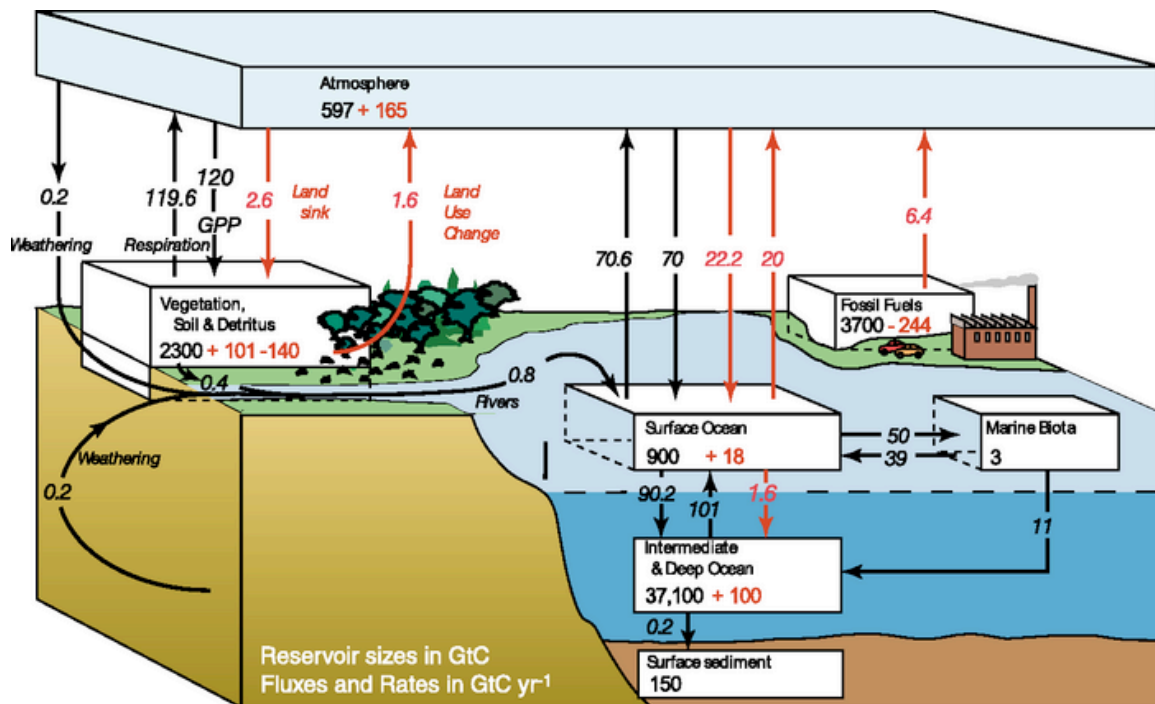


Figure 1. The Global Carbon Cycle (Solomon et al. 2007). It shows the main annual fluxes in GtC yr⁻¹. Pre-industrial ‘natural’ fluxes are seen in black and ‘anthropogenic’ fluxes in red.

According to the Intergovernmental Panel on Climate Change (IPCC) fourth assessment report in 2007 (Solomon et al. 2007), about 7.2 Giga metric tons (abbreviated as GtC) of CO₂ were emitted each year between 2000 and 2005, an increase of about 1 GtC from 1990s. But these numbers are still crude estimates; there are aspects of the carbon cycle that we understand only poorly at present. Understanding the properties of microlayer can provide a better estimates of the carbon cycle and helpful for the global scale issue.

1.2 Literature review and previous understanding

1.2.1 Surface-active substances (SAS) at the sea surface microlayer

Surface-active substances (SAS), also called surfactants or surface films, are composed of chemically diverse substances from a variety of sources (Liss and Duce 1997). The largest source of SAS is believed to come from phytoplankton (Žutic et al. 1981; Wurl et al. 2009). Fragments of dead organisms also contribute to the SAS, but the actual composition of SAS is still not well known. Generally, carbohydrates comprise the major fraction, while proteins and lipids make up minor fractions (Myklesstad 1995; Penna et al. 1999). Phytoplankton blooms and neuston native to the microlayer contribute to the enrichment of SAS. But, even in waters where biological productivity is low, dissolved organic matter including biopolymers and geopolymeric materials can cause the accumulation of SAS when physical conditions are favorable (Liss and Duce 1997). Such substances can be distributed by the atmosphere, or introduced to the marine environment by petroleum seeps and spills (Frew 1997). Numbers of physical processes, including diffusion and turbulent mixing, can accumulate SAS (Liss and Duce 1997).

These films have been shown to influence the air-sea gas exchange and dampen small gravity and capillary waves (Frew 1997). A recent study by Frew et al. (2004a) also shows that SAS reduce air-sea gas exchange by influencing the gas transfer velocity. To understand these physical processes, numerous experiments have been done in wind-wave facilities under controlled and artificial conditions, but it is difficult to simply extrapolate results to oceanic conditions and only a few oceanic results are available (Frew et al. 2004a).

1.2.2 Sampling methods

To collect samples from the ocean microlayer, researchers have developed various types of sampling devices. Currently, the most common microlayer collection implements are metal screens, glass plates and rotating drums (Zhang et al. 2003).

The metal screen technique is one of the earliest methods applied and is very simple (Figure 2). A metal screen, typically 1 m² in area, is brought into contact with the water parallel to its surface, withdrawn, and drained immediately to collect sample water (Garrett and Duce 1980).

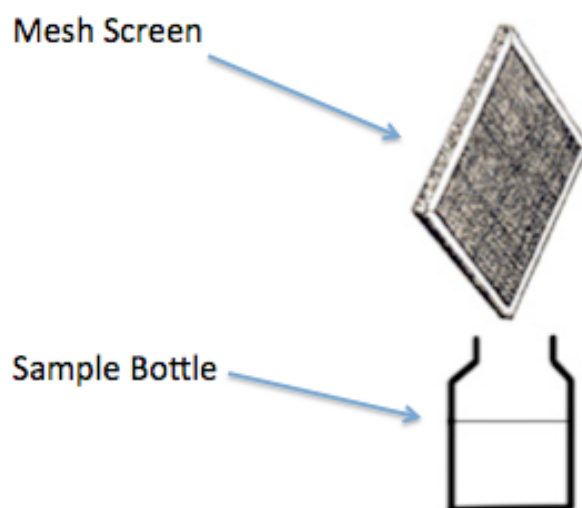


Figure 2. Illustration of a typical mesh screen. This shows a mesh screen in draining position.

The thickness of the collected microlayer is calculated from dividing the volume of water collected by the surface area of the mesh screen (Hunter 1997). The thickness depends on the wire diameter used in the makeup of the screen, which is typically 0.2 - 0.3 mm.

The thicker the wire is, the deeper the sample water is collected from. Typical configurations sample microlayers with thickness in between 150 and 400 μm .

The glass plate technique was originally described by Harvey and Burzell in 1972. It consists of a glass plate, typically 20 x 20 cm, which is lowered vertically and therefore perpendicular into the water (Hunter 1997) (Figure 3).

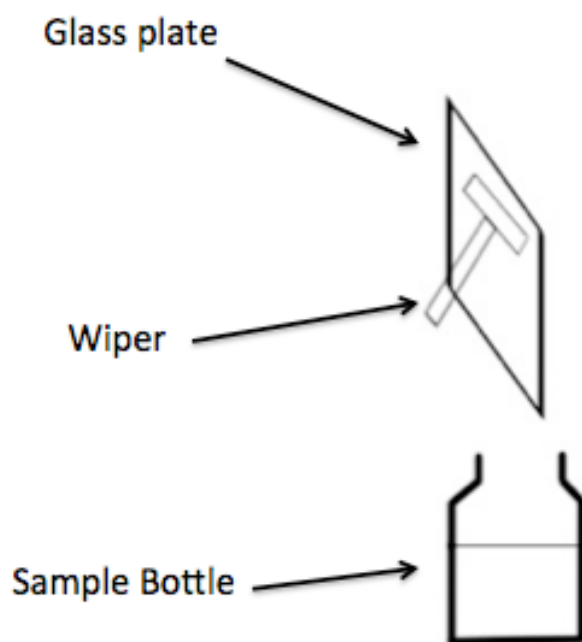


Figure 3. Illustration of the glass plate technique.

Following immersion, the glass plate is withdrawn slowly with constant speed and the water on both sides of the plate is collected with a wiper blade. Because clean glass is a high-energy solid surface and hydrophilic, typically 40-80 μm microlayer of water adheres to the glass plate during each extraction (Hunter 1997). The thickness of the microlayer collected using this particular technique is determined by dividing the volume collected by the surface area of the plate (Zhang et al. 2003) and depends on the speed the

glass plate is withdrawn from the sample water. The slower the withdrawal speed is, the thinner the microlayer thickness becomes.

The rotating drum sampler, originally developed by Harvey (1966), generally consists of a rotating drum with a hydrophilic ceramic surface mounted on floats so that the drum is half-immersed in the water to be sampled (Hunter 1997) (Figure 4).

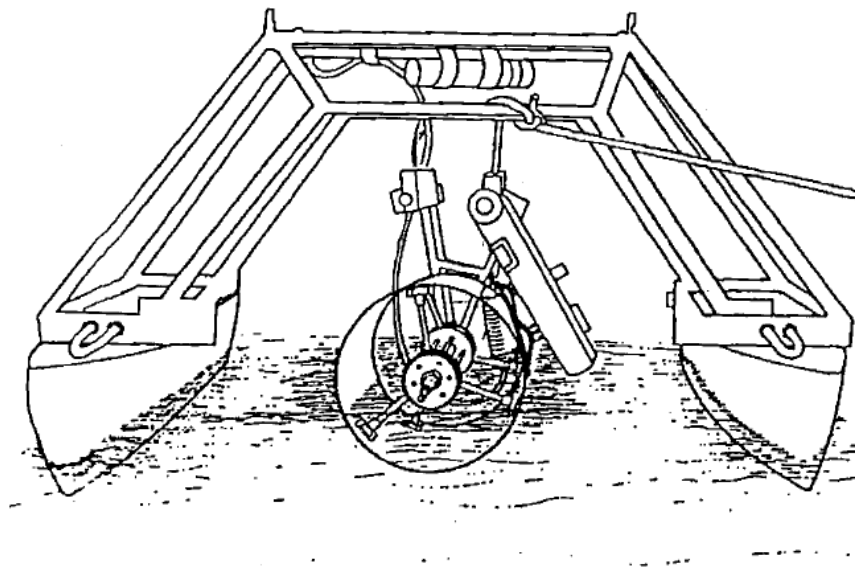


Figure 4. Illustration of rotating drum (center) on a sampling float (From Hunter 1997).

This approach has been adapted by other researchers and has become one of the most popular methods to collect samples (for example, Guitart et al. 2004 and Caccia et al. 2007). Prior to the rotating drum technique, the other methods were all manually operated, making the operation tedious and cumbersome when collecting large sample volumes was the goal. In comparison, the rotating drum sampler's operation is automated and it is easier to collect relatively large volumes of water. As the platform moves across the surface of a water body, the rotating drum delivers water to a wiper blade that scrapes the microlayer into a sampling tank. Its physical principle is similar to

that of the glass plate technique, allowing the microlayer SAS to adsorb onto the drum. A typical value of sample water's thickness is found to be around 60-100 μm (Hunter 1997). The manner in which the thickness is determined is the same as that for the glass plate; the thickness is calculated from dividing a sampled volume by the surface area of the glass drum. The surface area is calculated from a surface area of the drum and number of rotations, which is determined from the rotational speed of the drum over the time of sampling. A major disadvantage of the rotating drum sampler is that it is not suitable for rougher oceanic conditions, as the rotating drum is generally located perpendicular to the direction of travel and requires still waters.

Recently, some efforts have been put into making the drum technique more autonomous. For example, Caccia et al. (2007) have built a sampler consisting of a glass drum, GPS and other modules to navigate it remotely. A capability of more autonomous control allows it to be a useful monitoring tool (Caccia 2004).

1.2.3 Comparisons between different sampling techniques

To examine and evaluate the different available microlayer sampling techniques and to investigate the consistency of results, a number of comparisons have been performed and are reported in the literature.

Carlson (1982) compared the glass plate and the mesh screen techniques with a consistent withdrawal speed of 5-6 cm s^{-1} . The thickness obtained from the glass plate under calm and non-slick ocean surface conditions was $52 \pm 1.8 \mu\text{m}$, while the thickness from a mesh screen varied between $222 \pm 8 \mu\text{m}$ and $465 \pm 4 \mu\text{m}$ depending on wire diameter. It is noted that the term “slick” refers to an oily film accumulated on the ocean surface (Liss and Duce 1997). Carlson concluded that it was not advisable to compare

two techniques directly because they sample waters from different depths that have different properties and recommended the simultaneous use of both methods.

Falkowska (1999) used a Teflon plate (TPM), a glass plate (GPM), and a mesh screen (SM) to study thickness differences between these three methods. The use of TPM with a withdrawal speed of $5\text{--}6\text{ cm s}^{-1}$ collected $10\text{ }\mu\text{m}$, while GPM and SM, with the same withdrawal speed, collected $90\text{ }\mu\text{m}$ and $250\text{ }\mu\text{m}$, respectively. Falkowska argues that, because each method collects different thicknesses, it is almost meaningless to compare samples from different methods.

Zhang et al. (2003) compared four different sampling methods (the mesh screen, the glass plate, the rotating drum, and a funnel technique using a principle which is similar to that of the glass plate) and concluded that the glass plate technique and rotating drum sampler were the most suitable methods to collect samples because they could collect samples from a thinner layer, which they considered important since they found a layer of sudden chemical changes at around $50\text{ }\mu\text{m}$. These changes included concentrations of organic matter, dissolved trace metals, biochemical oxygen demand, surface tensions, and pH (Zhang et al. 2003). Because they considered this change very important, they preferred these two methods to the other methods including the mesh screen. In their study, the glass plate method resulted in a layer thickness of $10\text{--}80\text{ }\mu\text{m}$, while the rotating drum collected $40\text{--}90\text{ }\mu\text{m}$, both of which are an increasing function of withdrawal speed. With a withdrawal rate of 5 cm s^{-1} , the glass plate collected microlayer with thickness of $20\text{--}25\text{ }\mu\text{m}$.

Guitart et al. (2004) compared glass plate, rotating drum, metal screen and a surface slick sampler, which consisted of two 500-mL bottles with two lateral floats. It

would sit on the ocean surface horizontally and as samples fill up the bottle, it would stand vertically. They found no significant differences between samples collected by these methods but recommended the metal screen because of its efficiency to collect samples in relatively short time (about 10 minutes to collect 1 liter of water in their study as compared to 45 minutes to collect using a glass plate; see Table 1).

Operational characteristics of sampling methods

Sampling Method	Theoretical thickness (μm)	Sampling time per 1 L (min)	Sea State ^a
Glass plate	40-60	45	<3
Harvey's roller	70-100	30	<1
Metal screen	200-400	10	<4
Surface slick sampler	1000-2000	2	<6

^a Estimated maximum number of Beaufort scale operability.

Table 1. Theoretical estimates of microlayer thickness and sampling time for several microlayer-sampling techniques. Also included is the maximum sea state possible for the different techniques. (Reproduced from Guitart et al. 2004).

In their study, Guitart et al. themselves did not characterize the layer of thickness where sudden chemical change occurs and adapted other published results, and thus the difference in thickness was not important for them.

In essence, the most desirable sampling method is dependent on available instrumentation and the specific objectives of a given study. However, these results reveal some essential attributes that good sampling methods should have. One is that it is desirable to sample from a layer not thicker than 50 μm to allow for studies of the layer of sudden physical and chemical change. Other attributes are ease of sampling and

sampling efficiency. Ideally, a sampling method should permit quick collection of sample waters and be automated in order to reduce repetitive and tedious tasks, such as collecting multiple samples in quick succession. It is also desirable that a sampling method is capable of autonomous operation, to reduce potential contamination due to support vessels and platforms, and for operation in realistic and often higher sea-states to allow for open ocean measurements.

By examining and comparing existing methods, a group of scientists led by Magnus Eek at Institute of Ocean Science decided that they would build their own remotely operated vehicle and utilize a set of rotating glass disks to achieve the requirements listed above. The sampler was built successfully and has been modified. The second generation of the device is the primary focus of this thesis and details of the device are discussed in the Material section (Section 2.1).

1.2.4 Models to estimate thickness of adsorbed solution layer

Although a glass-disk sampler was used to collecting microlayer samples in several oceanic expeditions, a thorough understanding of the rotating glass disk sampling technique was lacking. In the present study a set of laboratory experiments were undertaken to examine the actual thickness of adsorbed solution layer on a glass surface and the effect of SAS on the glass. Because various fields such as Surface Chemistry concern behaviours of SAS on surface, fundamental theories are available, and those were adapted to the present study. Also, the thickness of adsorbed solution layer has been assumed to be equivalent to the thickness derived from dividing volume of microlayer samples collected by surface area of glass, but few experiments had been carried out to make actual measurements of the adsorbed solution.

Two theories exist that would permit one to estimate thickness of adsorbed solution layer. One of the theories was developed by Schlichting (1987) who examined fluid motion around a horizontal disk that rotates with a uniform angular velocity, ω (Figure 5).

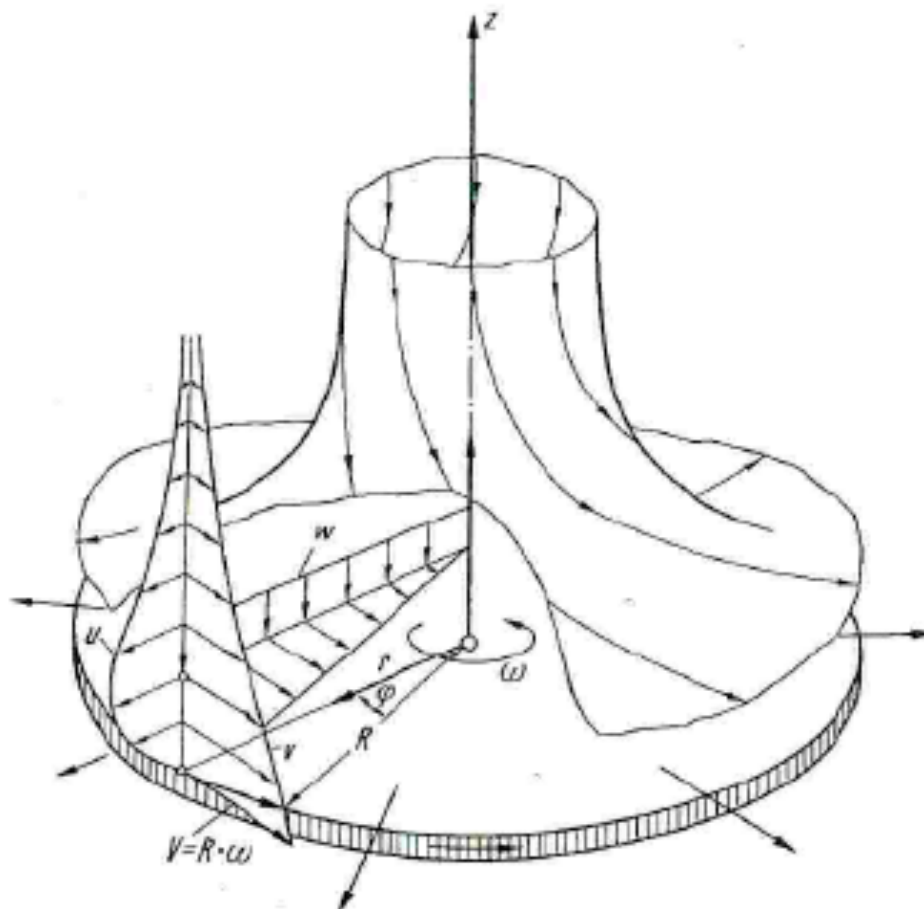


Figure 5. Diagram showing the geometry of a horizontal rotating disk and parameters (Schlichting 1987). The radial direction is r , the circumferential angle ϕ , and the vertical axial distance z . Velocity components are denoted as u , v and w , respectively. ω is the angular velocity.

By analyzing the flow around a disk and using the Navier-Stokes equation, he estimated the thickness, h , as

$$h \sim \sqrt{\frac{\mu}{\rho\omega}} \quad (1)$$

where μ = dynamic viscosity of fluid

ρ = density, and

ω = angular velocity of disk.

A more detailed derivation of this theory can be found in Appendix A.

The other theory was developed by Levich (1962). He looked at the situation where a solid plate is dipped into solution and withdrawn from it. By analyzing the fluid flow of this situation considering viscous force and gravity, he came to conclude that the thickness, h , can be written as,

$$h = 0.93 \frac{(\mu v)^{\frac{2}{3}}}{\sigma^{\frac{1}{6}} (\rho g)^{\frac{1}{2}}} \quad (2)$$

where μ = dynamic viscosity of fluid,

v = withdrawal rate,

σ = surface tension,

ρ = density, and

g = gravity.

Note that this case does not involve rotational movement. Again, the detailed derivation is presented in Appendix B.

Figure 6 shows these estimated thicknesses as a function of rotations per minute (RPM) for a glass disk. It is noted that the relation between the angular velocity and RPM is written as,

$$\omega = \frac{2\pi}{60} RPM. \quad (3)$$

Parameters used here are: $\rho = 1000 \text{ kg m}^{-3}$, $\rho_{\text{ocean}} = 1025 \text{ kg m}^{-3}$, $g = 9.8 \text{ m s}^{-2}$, $\mu = 0.001 \text{ kg m}^{-1} \text{ s}^{-1}$, $\mu_{\text{ocean}} = 0.00108 \text{ kg m}^{-1} \text{ s}^{-1}$, $\sigma = 72 \times 10^{-3} \text{ N m}^{-1}$ and $\sigma_{\text{ocean}} = 74 \times 10^{-3} \text{ N m}^{-1}$. It is noted that the thickness proposed by Schlichting is only an approximation because the calculations do not take into consideration the effect of surface tension, withdrawal speed and the fact that his idea is adapted to a physical setting where the glass disk is in contact with air and water. The estimated thickness is therefore too large to compare with the thickness obtained by Levich's equation. Thus, the result was scaled by a factor of 20 for more appropriate comparison. This factor was an arbitrary number and the reason is described in the discussion section.

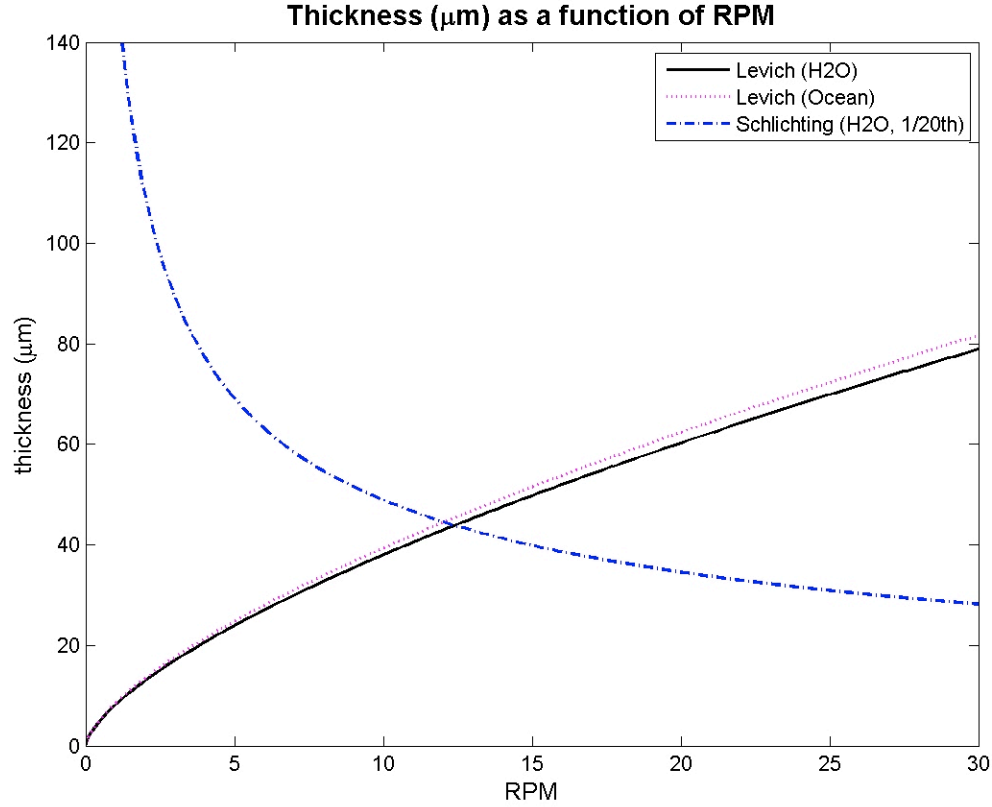


Figure 6. Theoretical thickness change as a function of rotations per minute (RPM). The blue dash-dot line represents the results from Schlichting (1987) divided by an arbitrary value of 20. The black line (pure water) and magenta dotted line (ocean water) are the thickness proposed by Levich (1962). The parameters used were: $\mu = 0.001 \text{ kg m}^{-1} \text{ s}^{-1}$, $\mu_{\text{ocean}} = 0.00108 \text{ kg m}^{-1} \text{ s}^{-1}$, $\rho = 1000 \text{ kg m}^{-3}$, $\rho_{\text{ocean}} = 1025 \text{ kg m}^{-3}$, $\sigma = 72 \times 10^{-3} \text{ N m}^{-1}$, and $\sigma_{\text{ocean}} = 74 \times 10^{-3} \text{ N m}^{-1}$.

As seen in equation (1), the thickness proposed by Schlichting is proportional to the square root of the inverse of the angular velocity of disk. The resulting thickness is therefore a decreasing function of angular velocity. In contrast, the resulting thickness from Levich's equation is an increasing function of rotational speed.

1.3 Scope of this thesis

During the construction and testing of the microlayer sampler, it became apparent that several significant scientific questions needed to be addressed before the sampler

could be used to its full capacity. Two of these are discussed in the subsections below and a thorough study was launched to address these issues. The results of this study are described and discussed in the next section.

1.3.1 Chemical affinity of rotating glass plate

Although there have been many *in situ* studies on the use of glass plates for microlayer sampling, actual data describing how a glass surface attracts a solution are lacking. Therefore, it would be beneficial to investigate the affinity between a glass plate and a microlayer solution. In particular, it would be of significant scientific value to examine thickness of solution layer adsorbed to a glass disk and how it behaves in different environments, such as the presence of salt and SAS.

1.3.2 Evaluation of the microlayer sampler

Because the microlayer sampler we constructed is a novel device, it is vital to evaluate its capabilities in the oceanic environment and analyze the data collected by the device and its sub-components. Part of this evaluation consisted of evaluating whether the components and sensors added to the sampler were operating as planned. Microlayer and bulk-water samples collected by the glass plate module had to be fully investigated to properly understand the module's capability. It was also crucial to check the quality of the other instruments attached to the skimmer and observe the relation between thickness of samples and variables collected by those instruments.

2 Materials and Methods

2.1 The rotating glass-plate microlayer sampler, or skimmer

With the requirements that: 1) a sampler should be able to sample microlayers at thicknesses less than 50 μm , 2) a sampler should allow for relatively quick collection of multiple samples, 3) a sampler should be autonomous to minimize potential contamination of samples, and 4) a sampler should be able to collect samples at higher sea-states, a microlayer sampler based on the glass plate technique was designed and constructed at the Institute of Ocean Sciences in Sidney, British Columbia.

The microlayer sampler, called skimmer, consists of two 1.5 m long by 0.5 m wide, by 0.5 m deep fiberglass hulls connected by an aluminum frame on which propulsion, scientific sensors, control electronics and a computer are mounted in weather proof housings (see Figure 7).



Figure 7. Photograph of the radio controlled vessel with rotating disk microlayer sampler.

The sampler has an onboard computer running a Windows operating system. It is programmable so as to perform autonomous pre-programmed missions or is remotely controllable via a wireless serial connection with a range of up to 3 km. The vehicle is propelled by two 12V DC motors and powered by two 12V rechargeable gel cell batteries located in the fiberglass hulls. In its present configuration, these batteries give the skimmer a range of approximately 4 km at a maximum speed of 1 m s^{-1} . It is equipped with a set of thin glass disks for collecting samples (see Section 2.1.1), a GPS receiver (Garmin GPS18), and a fluorescence spectrometer (Ocean Optics USB2000) for real-time spectral analysis. There is also a small weather station (Davis, Vantage Pro 2) to measure wind speed, wind direction, and air-temperature.

A set of twelve 250 mL bottles for microlayer water samples is located on a rotating disk tray in the center of the sampler (Figure 8). The bottles are filled as pairs

where one bottle is filled with microlayer water collected by the rotating glass disks, while the second bottle is filled by reference bulk water collected at a depth of 1 m. The start-time of each fill and the duration of filling are user controllable or can be programmed in advance for fixed interval sampling.



Figure 8. Photograph of sample bottles in the programmable rotating carousel. This carousel can accommodate up to 12 sample bottles, six of which (interior ones) collect microlayer samples collected from the glass disk array, while the other six (exterior ones) collect sublayer water from 1 meter below the surface. The start time of filling and the filling time are completely programmable for each of the six pairs of bottles in the tray.

2.1.1 Rotating glass disk sampling component

The skimmer is equipped with a set of ten glass disks, 30 cm in diameter and about 0.3 cm in thickness, mounted on an axis parallel to the water surface (Figure 9).

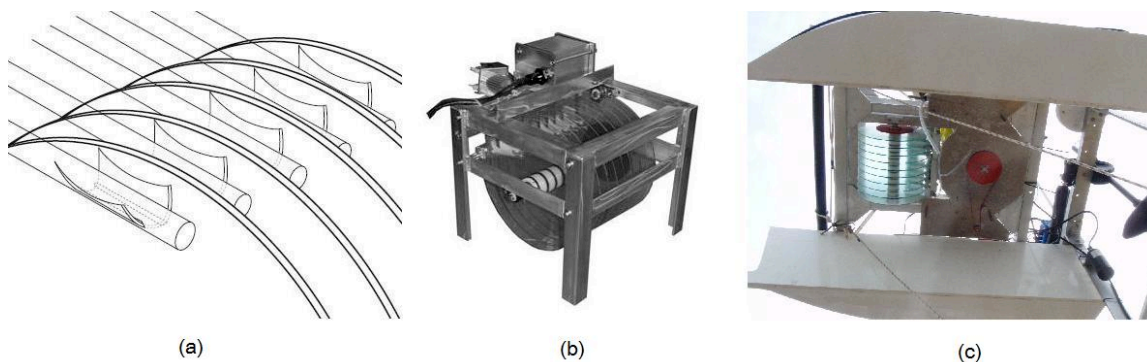


Figure 9. (a) Schematic Diagram showing glass disks with Teflon wipers. (b) Photograph of the glass disk module. (c) Photograph taken from the bottom of skimmer, indicating the location of the glass-disk module.

The axis of the glass disk module is perpendicular to the direction of travel and the module is mounted in front between the pontoons to allow for unobstructed access to clean water. Because the set of glass disks are aligned parallel to the direction of travel, the sampler can travel faster than the conventional drum samplers, where the drum is often aligned perpendicular to the direction of travel and thus pushes sample water while moving and easily disrupt the water. The sampler can work efficiently even in rougher conditions with minimal disruption of the water surface.

A stepper motor (VEXTA by Oriental Motor) placed above rotates the disks at a constant speed controllable by the onboard computer and is set to a specified withdrawal rate, i.e. the rate at which the glass is passing through the air-water interface. Microlayer water that adheres to the disks is removed by a set of Teflon wipers mounted on the descending side of the disks (Figure 9(a)).

A total of nine wipers are used, each mounted between two adjacent glass disks. Each wiper consists of a piece of Teflon sheet threaded through an aluminum tube. The sheet is protruding on both sides of the tube, thus wiping two disks simultaneously. The slit in the aluminum tube is wide enough to allow microlayer water flowing down the

sheet to enter into the tube. Once inside the tube the sample water flows towards an aluminum manifold, which collects the water. From this manifold the microlayer samples are directed to a 12 mm Teflon tube and pumped through the fluorescence spectrometer to the bottle tray shown in Figure 8.

Using this design, it would be very easy to replace one or several of the disks with other disks of different materials, such as Teflon, to evaluate sampling efficiency of different materials, although currently this has not been tried. The withdrawal speed of the glass disks, which is same as the rotational speed of glass disks, can easily be changed so that the sampler can collect a range of microlayer thicknesses. As before, the thickness of the thin films adsorbed to the glass disks can be determined by dividing the volume of sample waters by surface area of the plate (Zhang et al. 2003).

To find out the thickness of adsorbed solution on the glass disk, a preliminary experiment was done by Magnus Eek at the Institute of Ocean Sciences (unpublished results) who originally developed the idea of the rotating glass disk sampler and built the first generation of the skimmer. He used a complete set of 10 glass disks and recorded the volume of water collected within a certain time. By knowing the volume of samples collected within this time and the surface area of the glass disks, he calculated the thickness of adsorbed layer. The result is summarized in Figure 10.

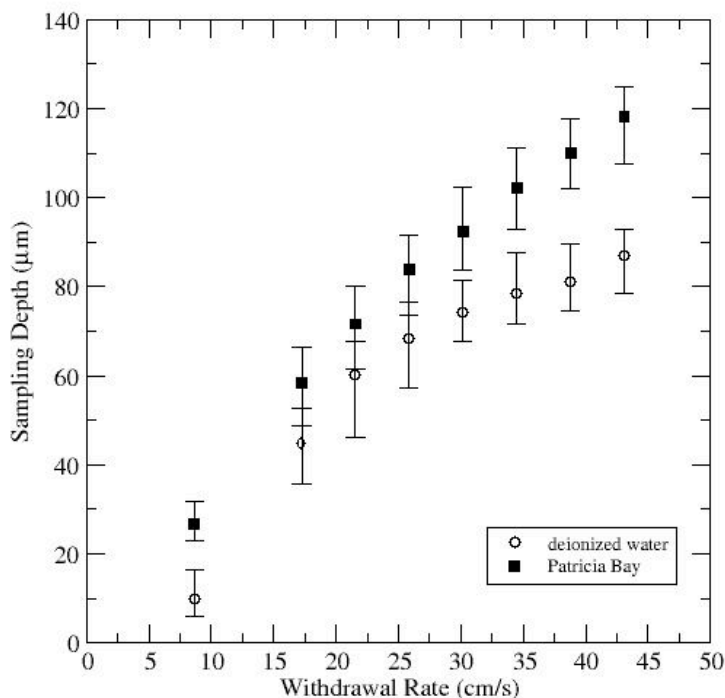


Figure 10. Sampling depth as a function of withdrawal rate, from a laboratory study using two types of water: de-ionized and from Patricia Bay, Saanich Inlet. The error bars are a combination of the experimental variability (2σ) and the varying sampling depth along the disk radius due to velocity differences. The calculation is based on the average sampling depth and withdrawal rate (Magnus Eek, personal communication).

This result suggested a thickness of $27 \mu\text{m}$ with 9 cm s^{-1} withdrawal speed and $118 \mu\text{m}$ with 45 cm s^{-1} .

In general, the glass plate method collects samples within a layer thickness in the range of $40\text{-}60 \mu\text{m}$ (Guitart et al. 2004). This permits studies of the sudden physical and chemical change, which is believed to be located around $50 \mu\text{m}$. The glass plate method is one of the most time-consuming methods according to the study of Guitart et al. (2004), taking about 45 minutes to collect 1 liter of water. However, the simultaneous use of ten

glass disks and automation of the sampling process using wiper blades and bottle carousel significantly reduce the sampling times.

2.1.2 Real time fluorescence spectral analysis

In order to investigate characteristics of the microlayer in the ocean, colored dissolved organic matter (CDOM) is often used as a proxy for SAS in microlayer sample waters (Frew et al. 2004b). CDOM (also known as yellow substances, gelbstoff, or gilvin) is a chemically complex mixture with molecules of varying molecular weight and provenance (Schwarz et al. 2002). It is part of dissolved organic matter (DOM) considered to comprise up to 25% of total DOM (Benner 2002). These organic compounds consist mostly of various humic and fulvic acids, that are brown in color (Mobley 1994). With sufficient concentrations, they make water yellowish brown (Mobley 1994). CDOM strongly absorbs short-wavelength light in the ranging from UV to blue. Investigators commonly use CDOM as a proxy for SAS in microlayer sample waters because CDOM fluorescence correlates strongly with SAS in seawater, although it does not measure non-chromophoric and insoluble SAS (Frew et al. 2004b).

In this study, the fluorescence was measured by an Ocean Optics fluorescence spectrometer (USB2000) operating in the 340-1000 nm band. From each spectrum, it collects 2046 wavelengths with an increment of 0.32 nm on average. The data were integrated over 5 seconds for each recorded spectrum. This implies that, if the skimmer were moving with a velocity of 0.5 m s^{-1} with respect to the water surface, it represents a spatial averaging of approximately 2.5 m. The integration and inter-spectrum times may be varied depending on the scientific objective of each exploration. Longer integration times are required if the CDOM concentrations in the microlayer are low. In coastal

waters, which typically have high SAS and CDOM concentrations, integration times of 2-5 s were found to be appropriate. But, in open ocean sampling, the integration time would have to be increased to more than 10 s. More detailed CDOM analysis of a selected number of samples can be performed in the laboratory.

Figure 11 shows the housing accommodating the spectrometer, light source, and electronics.



Figure 11. (a) Photograph showing the interior of the housing for the fluorescence spectrometer. Electronics and a box for lighting the sample solution are also shown. (b) The interior of the black box where the water is excited by a Mercury lamp can be seen. Sample water is pumped into the yellow housing and flows around the Mercury lamp, the light source, to cool the lamp after being pumped through the black box.

Figure 11 (b) shows the interior of the black box where the sampled water is being excited by a Mercury strobe lamp. In this figure, the transparent tubing going across the black box is visible. Sample water is pumped into the yellow housing and after passing through the cell in the black box, flows in copper tubing wound around the Mercury lamp to cool the lamp before being pumped to the sample bottles in the carousel.

2.1.3 Additional Features

The sampler can also be equipped with a 1.8 m long leg mounted vertically below for deployment of additional sensors being logged either by the onboard computer or internally to each instrument (Figure 12).

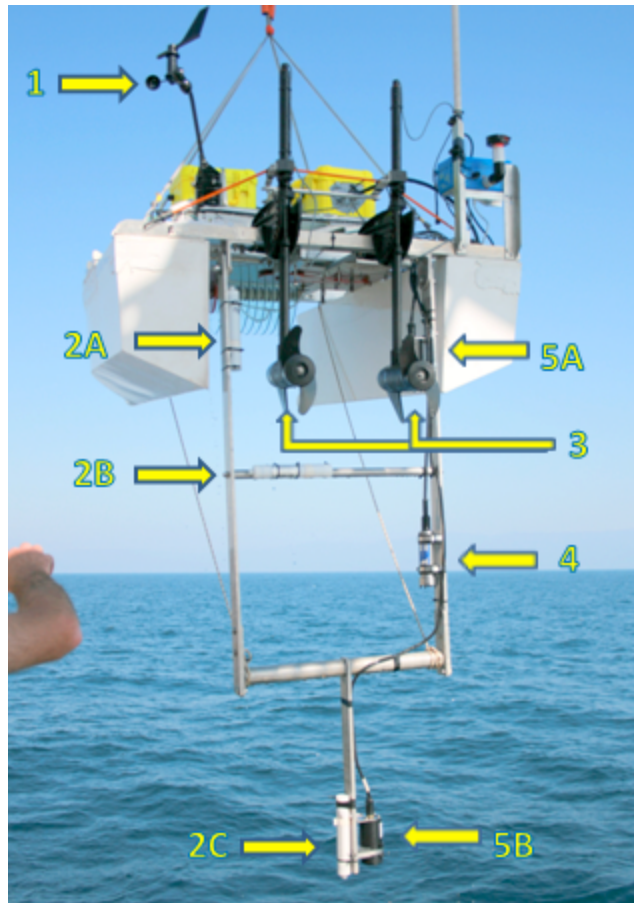


Figure 12. The skimmer showing additional sensors and the instrumented leg deployable from the stern of the vessel. Identifiable sensors and additions include: 1) another photograph of the vessel. It displays a weather station (Davis instrument Vantage Pro 2; marked as 1), 2) three thermistors (RBR TR1050) mounted at different depths (marked as 2A, 2B, and 2C) on a hinged aluminum frame, 3) two 12V separately controllable-DC motors (marked as 3), 4) optical high frequency oxygen sensor (JFE Advantech Co. Ltd. RINKO III; marked as 4), 5) two Wetlabs Scattering meters (marked as 5A and 5B. 5A is ECO BB and 5B is ECO Triplet B).

During different studies, the skimmer was operated with an array of Wetlabs single angle scattering meters (Wetlabs ECO BB and ECO Triplet B), an array of thermistors (RBR TR1050) and a dissolved oxygen sensor (JFE Advantech Co. Ltd. RINKO III).

The optical properties close to the surface in the presence or absence of surfactants were investigated using two backscattering sensors, both made by WET Labs. One is ECO BB, a single-angle backscattering sensor, which measures scattering at 117 degrees. This angle was determined as a minimum convergence point for variations in the volume scattering function induced by suspended materials and water itself (Boss and Pegau 2001). The ECO BB uses one LED source light modulated at 1 kHz. The source light hits the water volume and scattered light is detected at 117° relative to the ray of incident light. Because the ECO BB had a choice of light color from Blue, Green or Red, Red-colored LED (660 nm) was chosen. While the ECO BB has only one sensor, the ECO Triplet B accommodates three sensors in one. The same backscattering meter as in the ECO BB was chosen as well as sensors to monitor CDOM and Chlorophyll-a. The sensor to monitor the level of CDOM uses light with a wavelength of 370-nm to excite CDOM and measures light emission at 460-nm. The sensor for Chlorophyll-a uses light of 470-nm wavelength and measures light emission at 660-nm. Measuring Chlorophyll-a concentration is a good measure of the abundance of phytoplankton, the suspended microscopic algae in upper ocean water. Chlorophyll-a is a pigment in phytoplankton that captures light energy to drive photochemical reactions in the phytoplankton.

Photosynthesis takes up carbon dioxide and releases oxygen. Oxygen (O_2) is used during organism respiration and by decomposition of organic matter. Because the O_2

concentration is an indicator of phytoplankton productivity and the balance between photosynthesis and respiration, it is an important parameter to monitor. The skimmer is equipped with a RINKO III sensor (JFE Advantech Co. Ltd.), which uses phosphorescent material on a sensing foil to measure O_2 concentrations *in situ*. The sensor emits a pulse-excitation light and when the light hits O_2 molecules, red-colored phosphorescence is radiated. This is observed by the sensing foil and the O_2 concentration is determined. Although there are similar sensors available, the fast response time of this sensor (~ 1 s) sets it apart from more standard O_2 sensors (response time ~ 20 -50 s).

It is known that the accumulation and distribution of surfactants are strongly dependent on atmospheric forcing, such as wind speed and air-sea temperature difference. To obtain these measurements a weather station was added to the skimmer. The weather station used is a Vantage Pro 2 made by Davis. It collects humidity, wind speed and direction, temperature and barometric pressure. All these sensors can be seen in Figure 12.

The near-surface temperature field was measured by an array of internally recording temperature loggers (RBR, TR-1050). The skimmer is also designed to carry a downward looking 1.2 MHz Acoustic Doppler Current Profiler (ADCP) (RDI/Teledyne) for upper ocean backscatter measurements and current profiling. The measured microlayer characteristics are related to the optical backscatter, O_2 and temperature measurements with the aid of the flow field observations from the ADCP.

These additional measurements give insight into the role of surfactants on the optical properties of the upper ocean and the air-sea interface, which was a major objective of the externally funded project that paid for the development of the skimmer.

2.2 Materials and Methods to examine thickness of adsorbed solution layer

2.2.1 Materials

2.2.1.1 Design of a laboratory experiment

In order to evaluate the characteristics of a rotating glass disk as a collector of microlayer samples, the thickness of water on such a disk was measured in the laboratory. The theory on which this experiment was based is the Beer-Lambert Law. This law states that transmission of light is related to the distance light travel through a media (called path length, l) and the molar concentration of a light-absorbing solute (Ingle and Crouch 1988),

$$T = \frac{I}{I_0} = 10^{-\epsilon cl} \quad (4)$$

where T = transmittance,

I = Intensity of light after going through absorbing material,

I_0 = Intensity of light without going through absorbing material,

ϵ = Molar absorption coefficient, also called molar extinction coefficient, or molar absorptivity ($M^{-1}cm^{-1}$),

c = concentration of absorbing material ($mol\ L^{-1}$ or M), and

l = path length (cm).

Although the transmittance is an important quantity, because of its exponential nature in relation to other parameters, another quantity is defined for simplicity. Absorbance is defined as

$$A \equiv -\log_{10} \frac{I}{I_0}. \quad (5)$$

The Beer-Lambert Law states that absorbance for liquid can be expressed as

$$A = \epsilon cl. \quad (6)$$

To make use of Beer-Lambert Law on a glass disk, an experiment was designed in which a glass disk was rotated in a known solution. While rotating, light was passed through the glass disk. There was a photodiode on the other side of the light beam measuring the transmitted light intensity, I_0 . A solution was then prepared with a light-absorbing dye, and a laser beam was again passed through the glass disk and its intensity, I , was measured. The ratio of these intensities was used in equation (5) to find absorbance value for unknown thickness, h , of adhered water. That is,

$$A_{2h} = -\log_{10} \frac{I}{I_0}. \quad (7)$$

It is noted that the subscript 2h indicates that the absorbance is for twice the unknown thickness, h . The unknown thickness in this case is the path length. A schematic representation of how to compute the absorbance is illustrated in Figure 13.

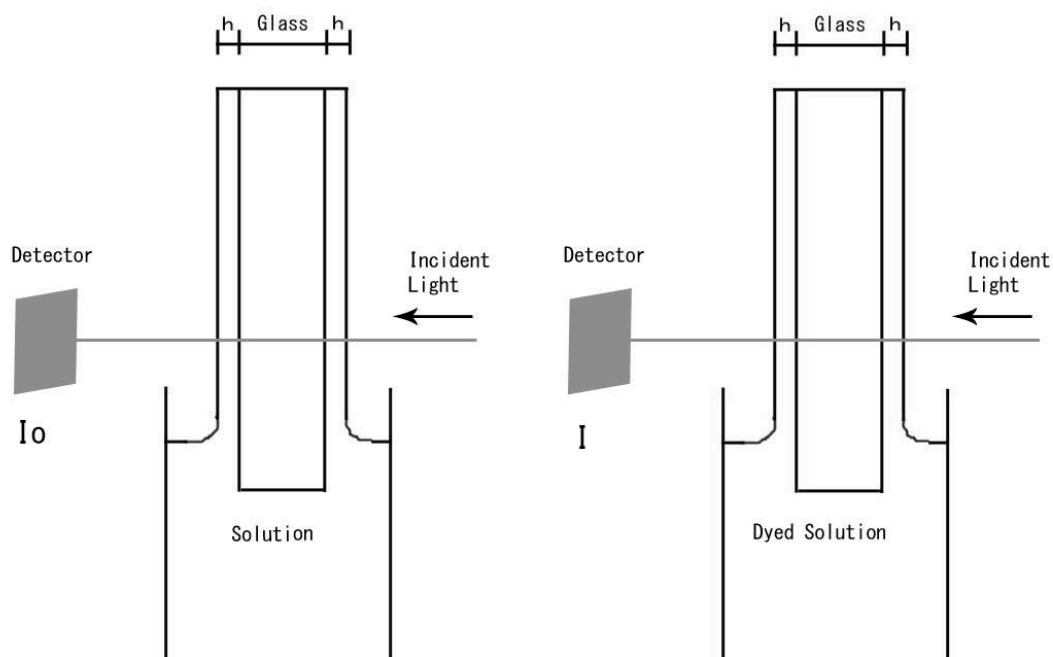


Figure 13. Schematic representation showing the steps involved in obtaining the absorbance of a layer with unknown thickness, h . In this representation, a glass disk is assumed to be rotated in water so that water is adhered to the disk. The thickness of adhered water is designated as h . The left diagram shows the case for solution without any dye. Transmitted intensity of light is designated as I_0 . The right diagram shows the case for dyed solution and where the transmitted light intensity is designated as I .

To determine the unknown thickness, h , another absorbance value was computed.

A fraction of dyed solution was taken and transferred to a cuvette with a known path length of 0.2 cm. The absorbance value was measured by an absorption spectrometer (Varian, Cary 50 Scan UV-Visible Spectrophotometer). This absorbance designated as $A_{0.2}$ can be written as,

$$A_{0.2} = \epsilon cl$$

(8)

where $l = 0.2$ cm is the path length (Figure 14).

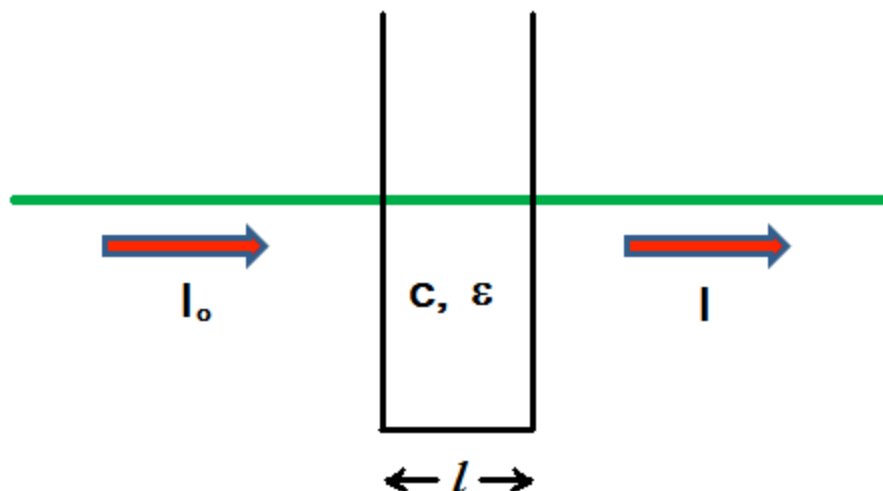


Figure 14. Image of cuvette and the associated parameters discussed in the text. Light with incident intensity, I_0 , is transmitted through a cuvette with a solution that has a certain concentration, c , of light-absorbing material and molar absorption coefficient, ϵ , which is unique to the material. The transmitted light has intensity, I , and an absorption spectroscopy determines absorbance, A , by using the definition of absorbance (i.e., equation (5)).

Now, there are two absorbance values:

$$A_{0.2} = \epsilon c l \quad (9)$$

and

$$A_{2h} = -\log_{10} \frac{I}{I_0} = \epsilon c (2h). \quad (10)$$

Because the molar absorption coefficient, ϵ , and the concentration of the material, c , are both common for each of the two experiments, equations (9) and (10) can be reduced to,

$$\frac{A_{2h}}{A_{0.2}} = \frac{2h}{0.2} \Rightarrow \therefore h = \frac{1}{10} \frac{A_{2h}}{A_{0.2}}. \quad (11)$$

Therefore, the unknown thickness, h , can be computed from these absorbance values using equation (11).

2.2.1.2 Setup in the laboratory

To determine the unknown thickness of adsorbed water, an experiment was designed and executed in the laboratory. The experimental setup consisted of a glass disk (30-cm diameter and 0.3-cm thickness), a gear motor (Merkle-Korff 24V-DC gear motor), water container (40 cm x 15 cm x 10 cm made of Plexiglas), a 532.07-nm green laser (diode-pumped solid-state type; BWN-532-50E by B&W Tek Inc.), two silicon photodiodes (Thorlabs DET100A), a non-polarizing cube beam splitter (Thorlabs BS016), as shown in Figure 15. A detector for the reflected beam was introduced to reduce the influence of laser beam intensity fluctuations. Because the laser intensity was found to fluctuate during the experiment, the transmitted beam intensity was continuously measured to eliminate the influence of these fluctuations.

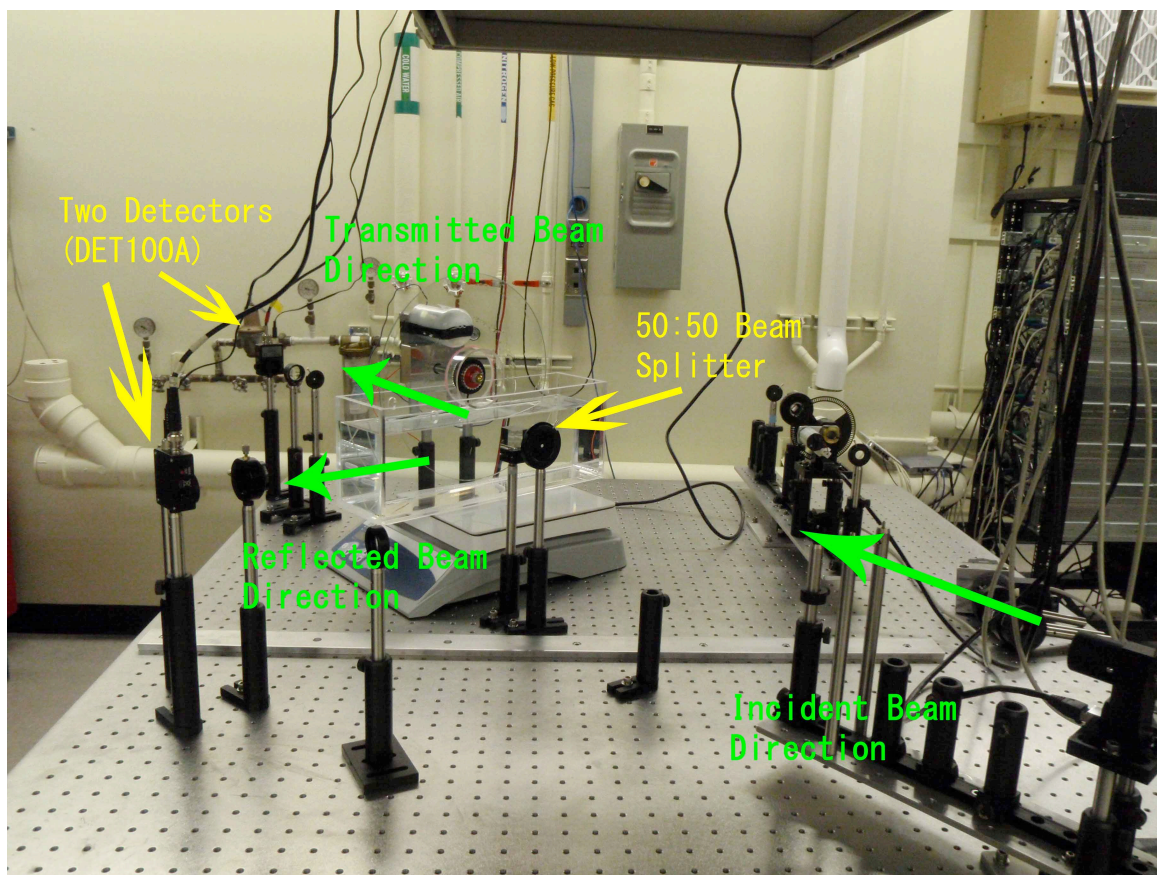


Figure 15. Photograph of the experimental setup in the laboratory. Detectors and direction of laser beam as shown.

The geometry of the glass disk in relation to the water container and the laser is shown in Figure 16 below.

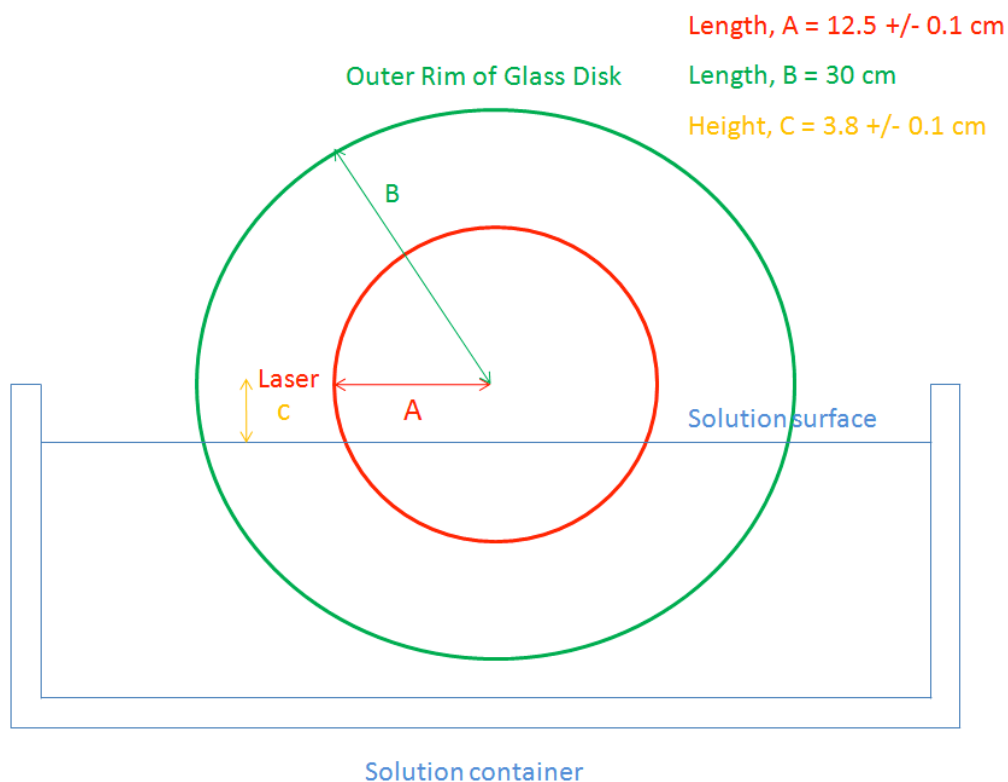


Figure 16. Geometry of Glass disk in relation to the solution container and the point where the laser hit. Glass disk is 30 cm in diameter. The distance between the center of glass disk and the point where the laser hit was 12.5 ± 0.1 cm. Height of the point where the laser hit in relation to solution surface was held constant at 3.8 ± 0.1 cm.

A schematic diagram of the actual experimental setup is shown in Figure 17.

Two lock-in amplifiers (Signal Recovery 7265) were used in the experiment for recording signal strengths detected by the photodiodes.

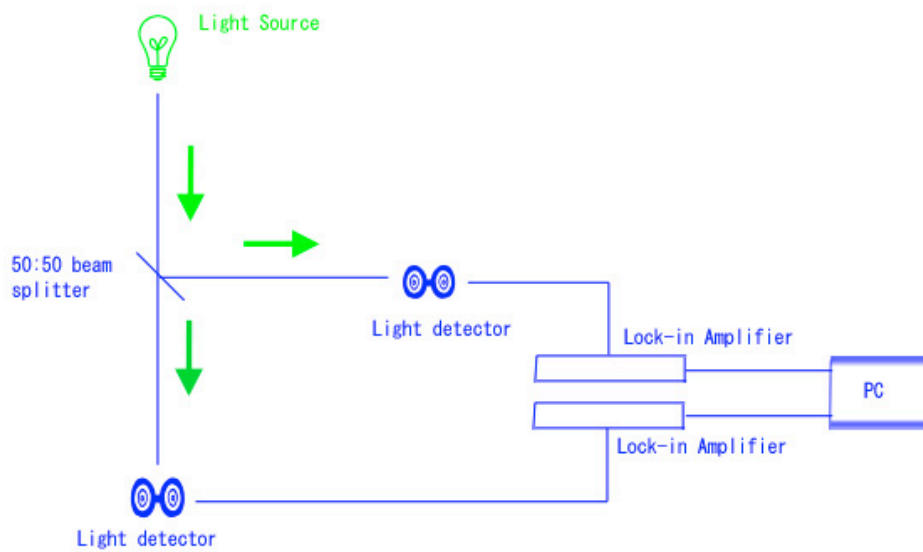


Figure 17. Schematic diagram of the experimental setup. A green laser light is split into a transmitted beam and a reflected beam. Both beams are observed by two light detectors (photodiodes), which are fed into lock-in amplifiers. These beam intensities are recorded on a PC.

In this experiment, Rhodamine B (it is abbreviated as RhoB in this thesis) was used for light-absorbing material. Its IUPAC name is [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride (Figure 18).

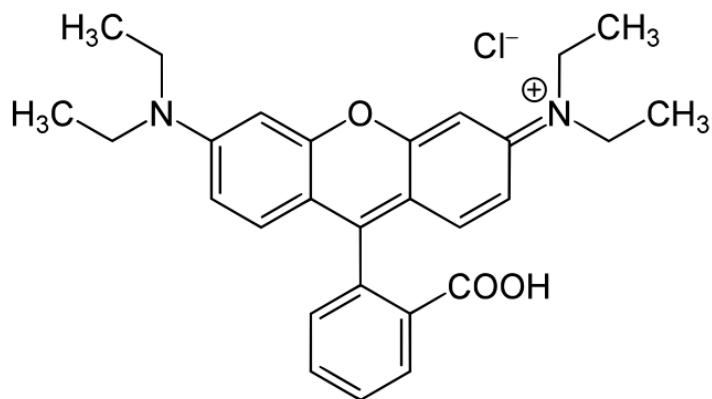


Figure 18. Chemical structure of Rhodamine B. Its IUPAC name is [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride.

RhoB has a very broad absorbing region between 500 and 600 nm, and absorbs light strongly at 532 nm (its molar absorption coefficient is $81954 \text{ cm}^{-1} \text{ M}^{-1}$ according to the data from Oregon Medical Laser Center (2010)). This wavelength corresponds to the wavelength of the green laser used in the experiment. When it came to choosing an appropriate dye, it was important to choose a chemical that showed strong absorbance with a chosen light source because the more absorbing characteristics a dye shows, the less amount of dye is needed. Minimizing a dye concentration helps prevent from changing chemical properties of a subject of study. Because the green laser was available, a dye showing a strong absorbance around 532 nm was explored and eventually it was decided to use RhoB. Figure 19 shows a typical absorption spectrum of RhoB.

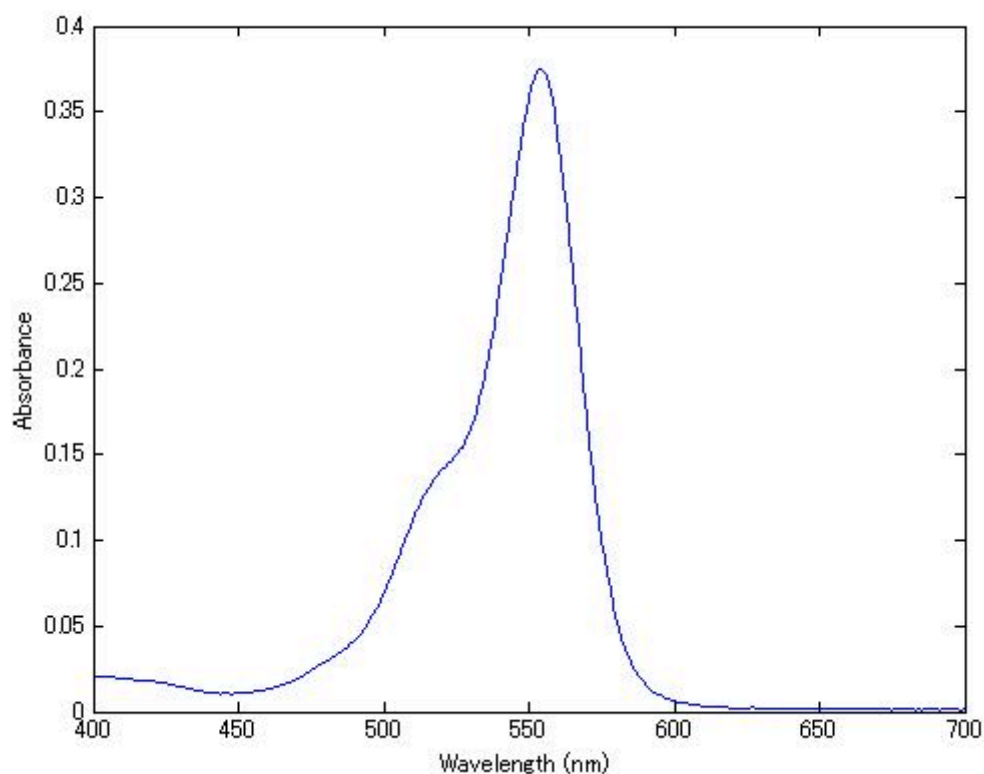


Figure 19. Plot of typical absorption spectrum of Rhodamine B, the light-absorbing dye, used in this experiment. This spectrum was collected from a solution containing 58.5 μM of RhoB in water. Because a green laser (532.07 nm) was used in this experiment, absorbance value at that wavelength was relevant in the experiment (data from Oregon Medical Laser Center 2010).

Figure 20 shows two images and two glass disk diagrams. The left photograph shows water without any dye, while the one on the right shows the same water with dye added. The absorption characteristics of RhoB were utilized to compute the absorbance of the solution we were interested in.

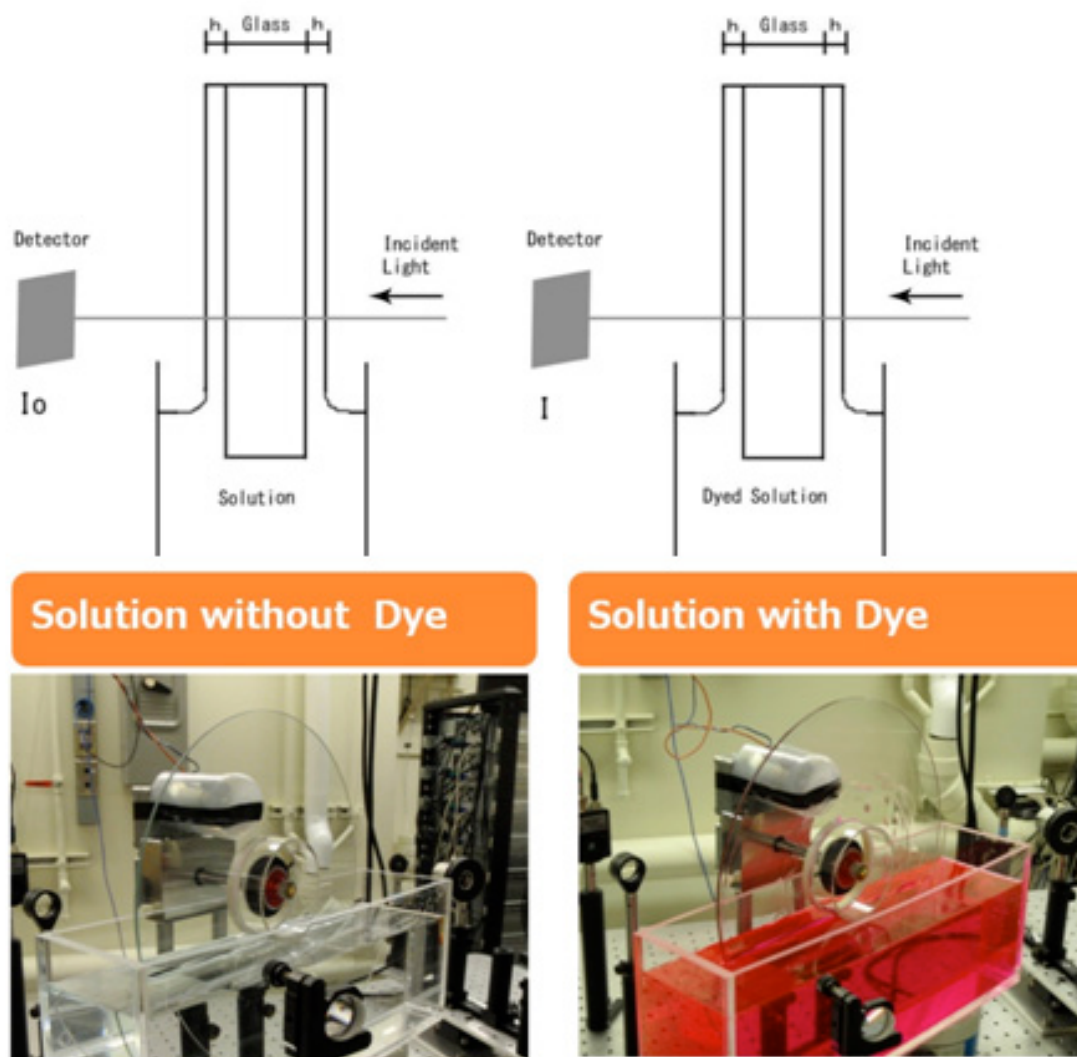


Figure 20. Two photographs of the experimental setup with and without Rhodamine B.

In choosing a motor to rotate the glass disk, two things were considered. One was that the motor needed to have enough power to rotate the weight of a glass disk (about 0.5 kg) smoothly and without vibration. The other consideration was that it had to allow for rotation speeds below 12 RPM. This rotational speed was chosen based on the preliminary experiment done by Magnus Eek (personal communication) and mentioned earlier (Figure 10). According to the study, a rotational speed below $\sim 15 \text{ cm s}^{-1}$ seemed

to create a solution layer thinner than $\sim 50 \mu\text{m}$. Remember that $50 \mu\text{m}$ is the thickness at which there exist physical and chemical gradients (Zhang et al. 2003). It is therefore of great interest to be able to examine these solutions separately. A speed less than 15 cm s^{-1} at the point where the laser hit, is equivalent to less than $\sim 12 \text{ RPM}$ in the present experimental setup. This is why we added the requirement that the motor used should be able to operate at variable speeds up to 12 RPM . It is important to note that, because the glass disk rotates, rotational speed expressed in cm s^{-1} varies along an imaginary line drawn between the center of glass disk and its outer rim. However, by expressing the speed in RPM the observations are independent of location on the disk surface.

Rotational speed and RPM are related through

$$\text{Rotational Speed} \left[\text{in } \frac{\text{cm}}{\text{s}} \right] = 2\pi r \text{RPM} \frac{1 \text{ min}}{60 \text{ sec}} \quad (12)$$

where $r = 12.5 \pm 0.1 \text{ cm}$ is the distance between the center of glass disk and the point where the laser hit.

The temperature of the laboratory where the experiments were conducted was kept constant at 24°C to exclude any temperature effects on the film thickness. For example, Carlson (1982) showed that the thickness decreased with increasing temperature. He showed that a regression line drawn on gathered data has an inverse relationship with increasing temperature, and his results indicated thickness to change from about $40 \mu\text{m}$ at 5°C to about $25 \mu\text{m}$ at 20°C in calm seas. He suggested that the decrease of thickness is likely due to a decrease in the viscosity of seawater.

The rotational speeds of the gear motor used are listed in Table 2.

RPM	2.92	5.28	7.67	10.07	12.5	14.96
s (RPM)	0.03	0.01	0.01	0.03	0.03	0.01

Table 2. The rotational speeds of the gear motor and their uncertainties, s.

These values were obtained by simply recording times it took for the motor to make 10 whole rotations and by converting the values into RPM. In this thesis, RPM values are written as 3, 5.3, 7.7, 10, 12.5 and 15 RPM, respectively, for convenience.

2.2.2 Methods

2.2.2.1 Determination of the minimum required amount of Rhodamine B

When using a dye like Rhodamine B, it is important to recognize that any dye will change the viscosity of the liquid being sampled. For example, Kim and Cho (2003) showed, by using a vegetable dye, that more than 2 vol.% of dye may significantly alter the viscosity of a solution. Although Kim and Cho's study was not specific to sea water and the vegetable dye has a chemical structure different from RhoB, it is important to acknowledge possible changes in viscosity and resulting changes to the thickness of the adsorbed solution layer. The theoretical models introduced in Section 1.2.4 also have viscosity as a controlling parameter. It is therefore essential to minimize the dye concentrations in studies like this.

However, there is also a limit to the sensitivity of the equipment used and the ability to detect low dye concentrations. These conditions placed a lower limit on the dye concentration used. To determine the lower limit of dye required, the stability of the complete setup was studied. In particular, the laser was running for twenty hours to observe any change. During that time, the laser showed fluctuations (Figure 21).

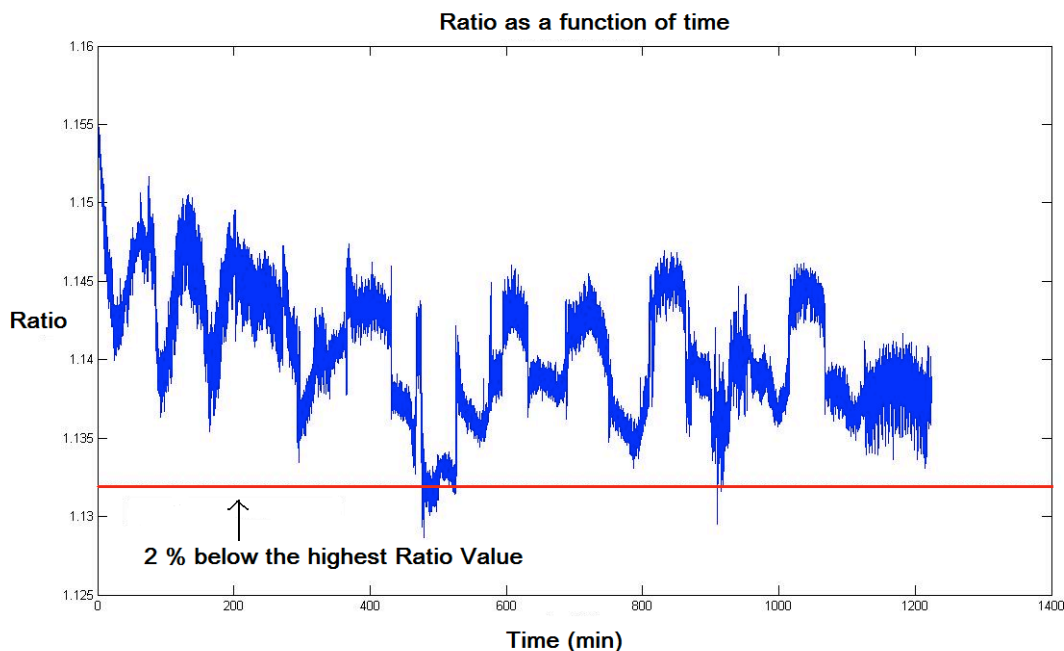


Figure 21. Plot showing ratio of voltage detected by photodiode measuring transmitted light and voltage detected by photodiode measuring the reflected light for a 20-hour period. The variability has a range between 1.13 and 1.15. The lowest value is about 2 % lower than the highest value.

The figure shows the ratio of the voltage detected by a photodiode measuring the transmitted light over the voltage detected by a photodiode measuring the reflected or incoming light. It is clear from this ratio, which ideally should not change, that fluctuations do exist. The ratio oscillated between 1.13 and 1.15, or about 2 % of the largest observed value. From these observations, it became clear that we had to allow 2 % error in the experimental observations. Thus, it was important that the amount of RhoB used in this experiment was large enough to differentiate real change from experimental error within this 2 % range.

With this condition in mind, a set of experiments was conducted to determine the optimum RhoB concentration to use. In these tests, a ratio value (i.e., ratio of transmitted signal to reflected signal) from de-ionized water was initially calculated. Then, ratio

values from solutions containing de-ionized water and a certain amount of RhoB were calculated (Figure 22). In the figure, a ratio value from de-ionized water is normalized to one and repeatedly plotted as blue squares with error bars. These ratio values do not change as they are not a function of RhoB but are plotted repeatedly as a reminder that the values are compared to ratio values from solution containing RhoB (referred as RatioRhoB). The ratio values, RatioRhoB, are plotted as red squares. A horizontal line showing the value that is 2 % below the ratio is also included in the figure.

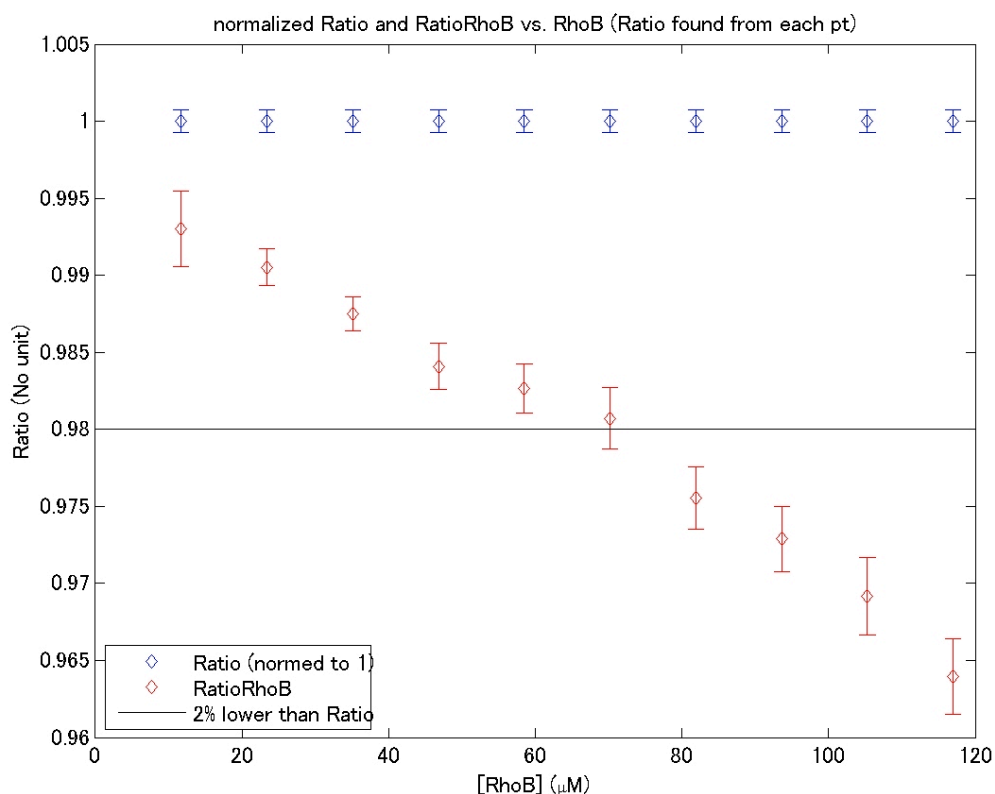


Figure 22. Plot showing both Ratio (normalized to 1) of de-ionized water (blue squares) and Ratio from solution containing RhoB (shown as RatioRhoB) as a function of RhoB concentration (red squares). A line indicating the value that is 2 % below the ratio (i.e., Ratio) has also been added. Note that the error bars represent ± 1 standard deviation about the mean of data acquired from 10 minutes of observations.

The error bars represent ± 1 standard deviation about the mean of data acquired from 10 minutes of observations. This figure reveals that, in order to have 2 % difference from the ratio value, a minimum concentration of 70 μM of RhoB is required. Based on this analysis, it was decided that 93.6 μM of RhoB (8 mL of available RhoB concentrate) would be suitable and easy to prepare for the experiments.

2.2.2.2 Study of varying the rotational speed of the glass disk

To study the effect of different glass-disk rotational speeds on the film thickness, a number of experiments were conducted using, firstly, de-ionized water followed by the same runs using RhoB dye. At first, 4500 ± 1.4 mL of de-ionized water was prepared in the solution container. Using this water, readings of transmission and reflection signals were obtained. During each reading, which lasted about 10 minutes, the rotational speed was varied from 2.5 RPM to 15 RPM. This set of readings was used as the standard and compared with other sets of readings taken from dyed solution to calculate thickness of the adsorbed solution layer.

After the reading, the RhoB dye was added to the solution to make it to the desired concentration (i.e., 93.6 μM) and stirred for 10 minutes to dissolve all the crystals. Following this process, another set of readings was made by again varying the rotational speed of the glass disk from 2.5 RPM to 15 RPM. Once the set of readings was collected, part of the sample solution (2.0 mL) was collected from the solution container and used for absorbance measurement ($A_{0.2}$) made on a spectrophotometer (Varian, Cary 50 Scan UV-Visible Spectrophotometer).

2.2.2.3 The effect of changing salinity

In order to investigate the effect of different salinities on the thickness of the film adsorbed to the rotating glass plate, another study was conducted to collect thickness as a function of salinity. Two different scientific approaches were used during this study.

The first approach was designed to obtain data concerning only the effect of salinity. By omitting the process of varying the rotational speed and simply changing the salinity, the procedure would be faster and a large number of data could be obtained. At first, a calculated mass of NaCl was added to water in a large beaker to make the overall volume exactly 4500 ± 1.4 mL. This mixture was stirred until all the salt dissolved. This solution was transferred to the solution tank and the laser beam was turned on to get a reading of transmitted and reflected beam strengths. Then, RhoB was added to a final concentration of $93.6 \mu\text{M}$. This was stirred for 10 minutes. Another reading was made. This set of readings was then used to calculate the thickness using the approach discussed in Section 2.2.1.1. This procedure was repeated for different concentrations of NaCl.

The second approach was to expand on the study done on varying the rotational speed (Section 2.2.2.2) by adding salt. The set of measurements collected in that section was used as the set to determine the thickness of 0 parts per thousand (ppt) of NaCl. Measurements (Section 2.2.2.2) were then repeated after 10 ppt of NaCl was added. Again, 2 mL of solution was collected from the solution containers for absorbance measurements. The salt concentration was then increased to 20 ppt before the measurements were repeated. Finally, the concentration was increased to 40 ppt before a final set of measurements was made. It is worth noting that because the volume of the solution decreased by 2 mL each time, the resulting salinities were not quite 10, 20, and

40 ppt. The actual salinities were 0, 9.90, 19.62, and 38.51 ppt, respectively.

Nevertheless, the rounded numbers will be used in the subsequent discussion.

2.2.2.4 The effect of changing the concentration of Surface-active substances

Similarly, a study was done to investigate dependence of thickness on Surface-active substances (SAS) by using sodium dodecyl sulfate (SDS) as representing a typical SAS. Here, SDS concentrate of a certain volume was added to 4500 ± 1.4 mL (0.03 %) of de-ionized water in the solution tank. This was stirred for about 10 minutes before the laser beam was turned on and readings of transmitted and reflected beam strengths were made. Then, RhoB was added to the solution and stirred to make its concentration $93.6 \mu\text{M}$. A new set of readings was made and used to obtain thickness estimates. This whole procedure was repeated for SDS concentrations of $500 \mu\text{g L}^{-1}$, 5 mg L^{-1} , and 50 mg L^{-1} .

2.3 Field Data

2.3.1 Santa Barbara Channel Sampling, September 2008

One of the first opportunities to test and the use the microlayer sampler was as part of a large international study called Radiance in a Dynamic Ocean (RaDyO) that took place in Santa Barbara Channel, California in September 2008 (Figure 23). The main objective of this multi-year study was to investigate the physical and chemical processes that control light propagation in the upper ocean.

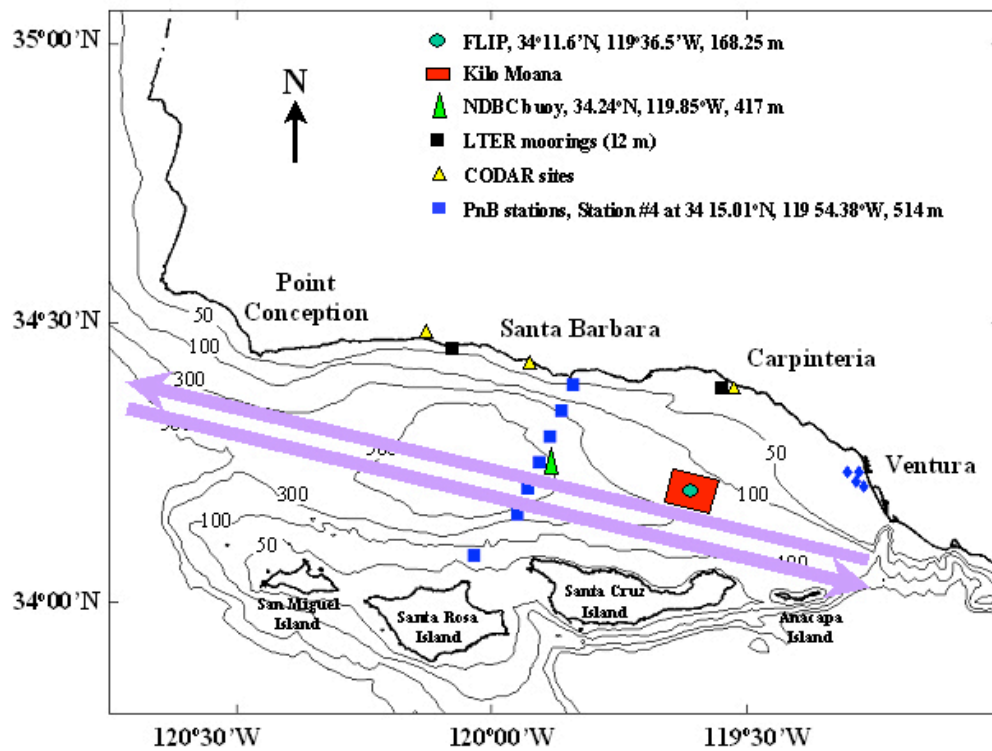


Figure 23. Location of RaDyO experiment in Santa Barbara channel. The light-purple arrows indicate the movement of R/V Kilo Moana, a research ship used as mother ship for this experiment.

The R/V Kilo Moana (KM) is an oceanographic research ship owned by the US Navy, but operated by the University of Hawaii, and was used as the base for this experiment. A Small Waterplane Area Twin Hull (SWATH) vessel, R/V Kilo Moana, was designed to provide a stable platform from which to deploy oceanographic instrumentation (Figure 24).

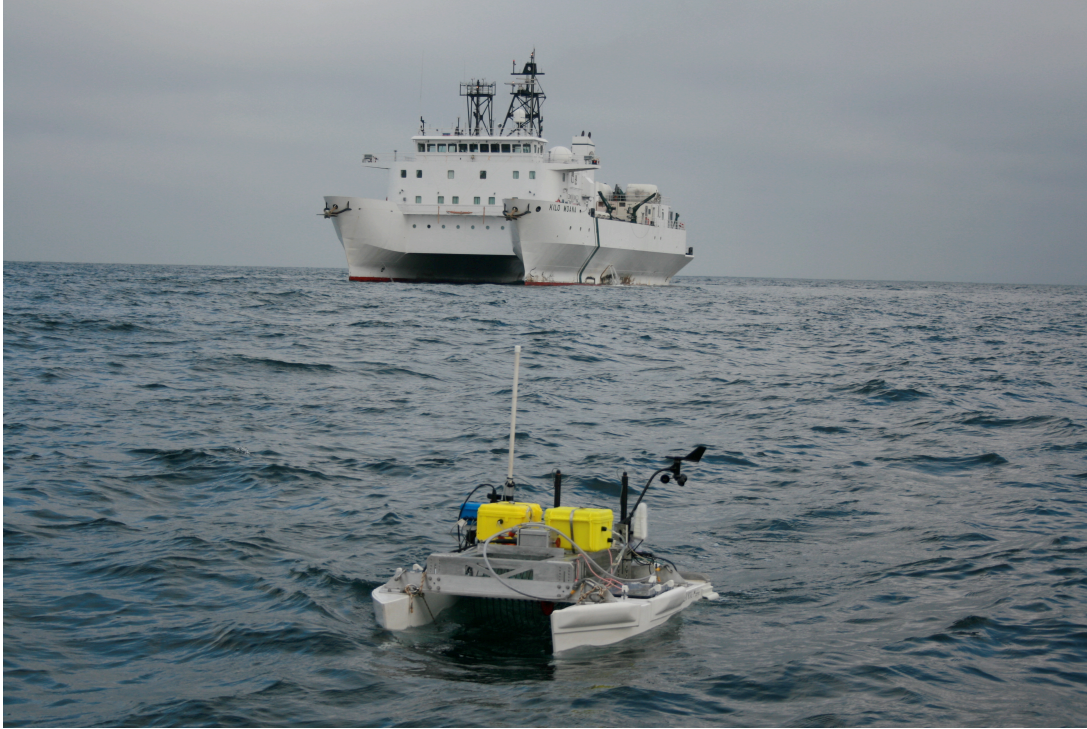


Figure 24. R/V Kilo Moana (KM) and the microlayer sampler.

During the day, KM was stationed near 34 13.3N, 119 37.7W (173 m depth) and she kept moving back and forth in the Santa Barbara Channel (Figure 23). KM collected oceanographic data from September 9 to 25, 2008. During this period, the skimmer was deployed from the KM a number of times to evaluate its capability.

2.3.2 Saanich Inlet sampling, February – April 2009

In addition to the Santa Barbara channel experiment, a series of tests of the skimmer were conducted in Saanich Inlet, British Columbia, between February and April, 2009 (Figure 25).



Figure 25. The microlayer sampler being towed from the dock and into Saanich Inlet for sea trials and sensor evaluations.

During this series of tests, manual collection of microlayer sample water was also conducted using a glass plate (Section 1.2.2).

To finalize the evaluation of the skimmer, a 24-hour continuous study was conducted in Saanich Inlet on April 29, 2009. The scientific objective of this study was to investigate the diurnal variability in surfactants and how this relates to other parameters, such as upper ocean temperature, stratification, and wind speed. In addition to the microlayer sampler, samples were collected using manual glass plate sampling.

The experiment took place from a small boat (Elvis) tied up to a meteorological buoy in Saanich Inlet from 09:00 April 28 to 09:00 April 29. In this experiment, scientific instruments including the skimmer were deployed off Elvis as shown in Figure 26.

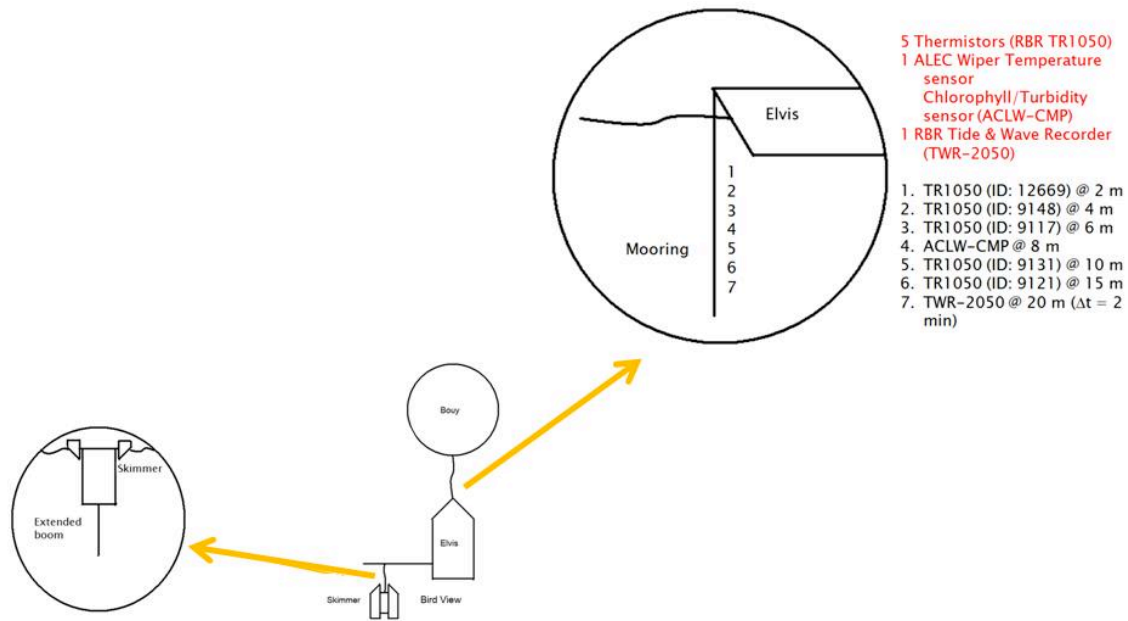


Figure 26. Experimental setup during the 24-hour Saanich Inlet trials during April 28-29, 2009. The circle on the right and text indicates the depth of an array of sensors deployed from the bow of the boat for the duration of the experiment. The sensors included five internally recording temperature loggers (RBR, TR-1050), one temperature and pressure logger (RBR, TR-2050), a Chlorophyll/Turbidity sensor (JFE Advantech Co. Ltd., ACLW-CMP), and a wave sensor (RBR, TWR-2050).

On the skimmer, three thermistors (RBR, TR-1050) were attached to the vertical leg (Figure 12) below the vehicle (Figure 27). In addition the leg was equipped with a dissolved oxygen sensor (JFE Advantech Co. Ltd., RINKO III) and one temperature and depth recorder (RBR, TDR-2050). Exact locations of these instruments are shown in Figure 27. The skimmer was also equipped with the two Wetlabs ECO fluorometers described in Section 2.1.3, but, because of technical problem, one of them did not work. The direction of the vehicle was controlled by an autotiller using an internal compass heading.

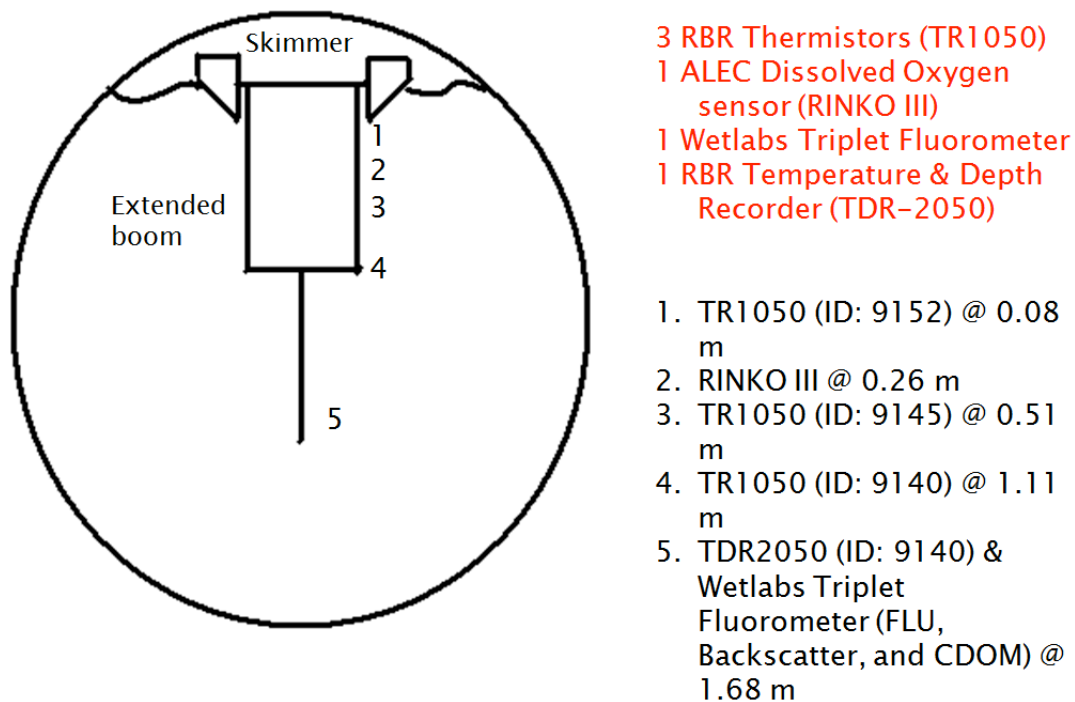


Figure 27. Vertical view of skimmer and its extended aluminum vertical leg. Summary of sensors used in red and exact location in black.

3 Results

3.1 The results of varying the rotational speed of the glass disk

Figure 28 shows a simple plot of thickness as a function of RPM for the data gathered from de-ionized water.

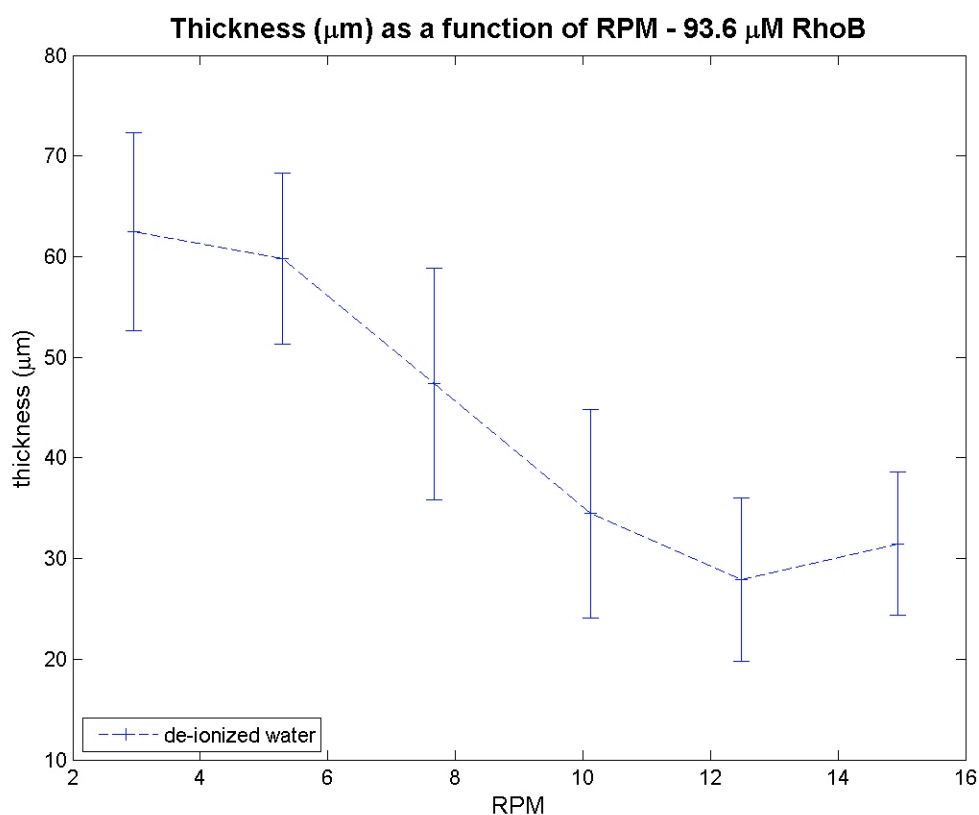


Figure 28. Thickness as a function of RPM for de-ionized water. Note again that the error bars represent ± 1 standard deviation about the mean of 10 minutes of data.

Again, the error bars represent ± 1 standard deviation about the mean of 10 minutes of data. This figure shows a decreasing behaviour of thickness up to 12.5 RPM. It is interesting to see that the thickness decreased from $62 \pm 10 \mu\text{m}$ at 3 RPM to $28 \pm 8 \mu\text{m}$ at

12.5 RPM, but then increased slightly to $31.5 \pm 7 \mu\text{m}$ as the disk rotational speed was increased slightly to 15 RPM. These results cannot reveal whether the thickness keeps increasing at speeds exceeding 15 RPM because the gear motor used for rotating the glass was operational only up to 15 RPM. No data are therefore available for those higher RPMs.

3.2 The effect of changing salinity

In the first experiment aimed to observe the effect of salinity, data were gathered to obtain thickness change as a function of salinity. Figure 29 shows the measured thickness change for a range of different salt concentrations.

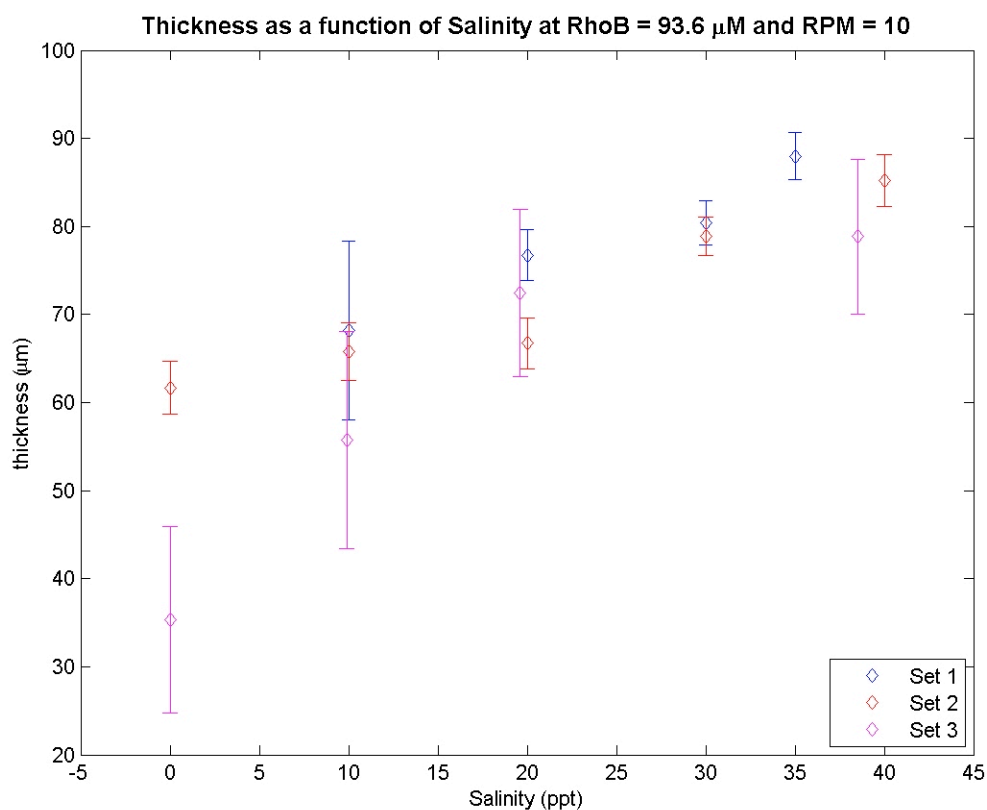


Figure 29. Plots of thickness as a function of salinity. The rotational speed was fixed at 10 RPM and the concentration of RhoB was $93.6 \mu\text{M}$.

It is noted that there are only two data points for 0 ppt of salinity (Set 2 and Set 3). Also note that error bars on Set 3 are much bigger than error bars of Set 1 and 2. This is because the integration time (i.e., time it takes to record an average of data points) was much shorter on Set 3. When the integration time was shorter, data showed more variability and thus bigger error bars are produced.

In all three different sets of data, there is a significant dependence of thickness on salinity. In general, the thickness increased almost linearly as a function of salinity. Overall, it is apparent that the more salt a solution contains, the thicker the adsorbed film becomes.

This behavior can be explained by changes in the viscosity of the fluid, since, as discussed before, an increase in viscosity results in a change in thickness. Adding salt increases the solution viscosity, and thus it is reasonable to witness the change in thickness.

The results of investigating changes in thickness from different rotational speeds have been summarized in Figure 30. Four sets of data have been plotted in this figure. One is from the data without any NaCl added to the water and shown in blue horizontal bar. This set is the same data used in the study of speed dependence as above in the Section 3.1. The other three datasets were obtained with increasing salinity from 10 ppt (red circle), to 20 ppt (black diamond) to 40 ppt (magenta square). The data are also summarized in Table 3.

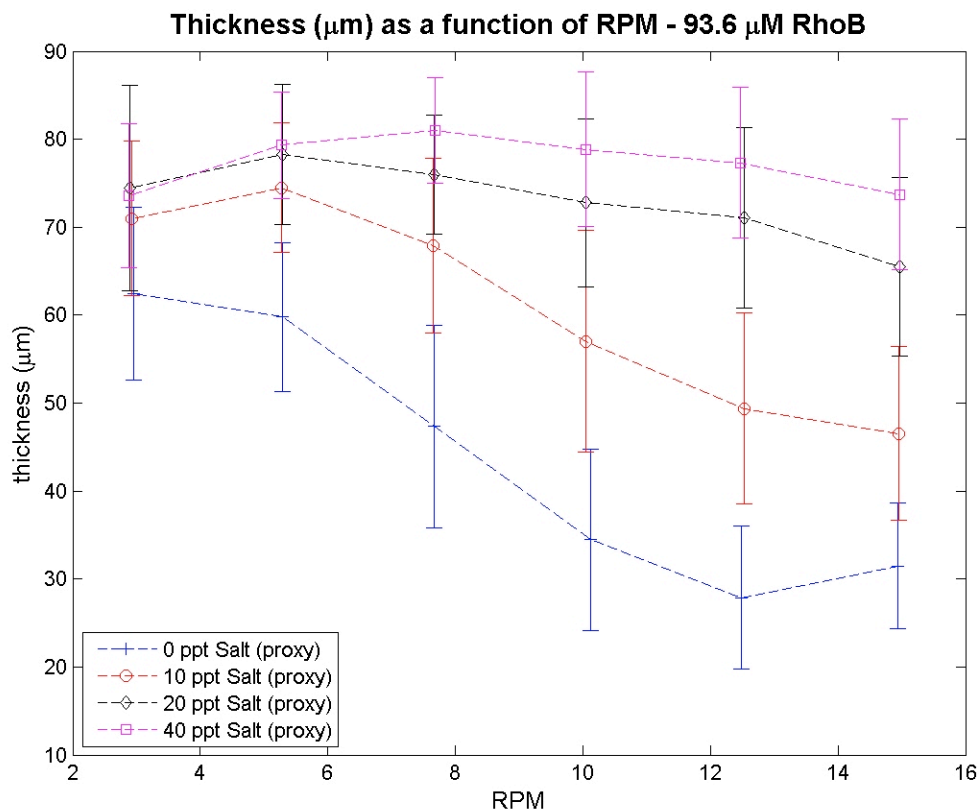


Figure 30. Thickness as a function of rotational speed (in RPM). There are four data sets shown here. One is from the result of solution without any salt (i.e., blue crosses). The other three are from solutions with increasing salinity. Open red circles represent data with 10 ppt, black diamonds represent data with 20 ppt and 40 ppt water is represented by magenta squares.

RPM	s (RPM)	h (μm) of 0 ppt Salt	s (μm)	h (μm) of 10 ppt Salt	s (μm)	h (μm) of 20 ppt Salt	s (μm)	h (μm) of 40 ppt Salt	s (μm)
2.92	0.03	62.5	9.8	71.0	8.8	74.4	11.7	73.6	8.2
5.28	0.01	59.8	8.5	74.5	7.3	78.2	8.0	79.3	6.1
7.67	0.01	47.3	11.5	67.9	10.0	76.0	6.8	81.0	6.0
10.07	0.03	34.5	10.3	57.0	12.6	72.8	9.5	78.9	8.8
12.50	0.03	27.9	8.1	49.4	10.9	71.0	10.2	77.3	8.5
14.96	0.01	31.5	7.1	46.6	9.9	65.5	10.2	73.7	8.6

Table 3. Thickness estimates at different rotational speeds in RPM at different NaCl concentrations. Here, h is the thickness of adsorbed solution and s is the standard deviation about the mean of either RPM or thickness.

Several interesting observations are apparent from these data. One is that the adsorbed fluid thickness decreases with decreasing salt concentrations. Another observation is that the change of thickness with increasing rotational speed becomes less obvious, especially as the salinity increases. For example, the thickness decreased from $62.5 \pm 9.8 \mu\text{m}$ at 3 RPM and became the smallest ($27.9 \pm 8.1 \mu\text{m}$) at 12.5 RPM in the no-salt case. In other words, the decreasing characteristic was quite obvious. In contrast, with a solution with 40 ppt salt, the thickness change does not seem obvious. The thickness increased from $73.6 \pm 8.2 \mu\text{m}$ to $81 \pm 6.0 \mu\text{m}$ as the rotational speed went from 3 RPM to 7.7 RPM and it peaked there and decreased from there down to $73.7 \pm 8.6 \mu\text{m}$.

These data are plotted together with the relationships derived from theoretical considerations discussed in Section 1.2.4 and Figure 6 (see Figure 31). Also included in this figure are the data values collected by Magnus Eek (personal communication) and discussed in Section 2.2.1.2 and Figure 10. These data are shown in black squares for de-ionized water and in red square for seawater collected in Patricia Bay, British Columbia, Canada.

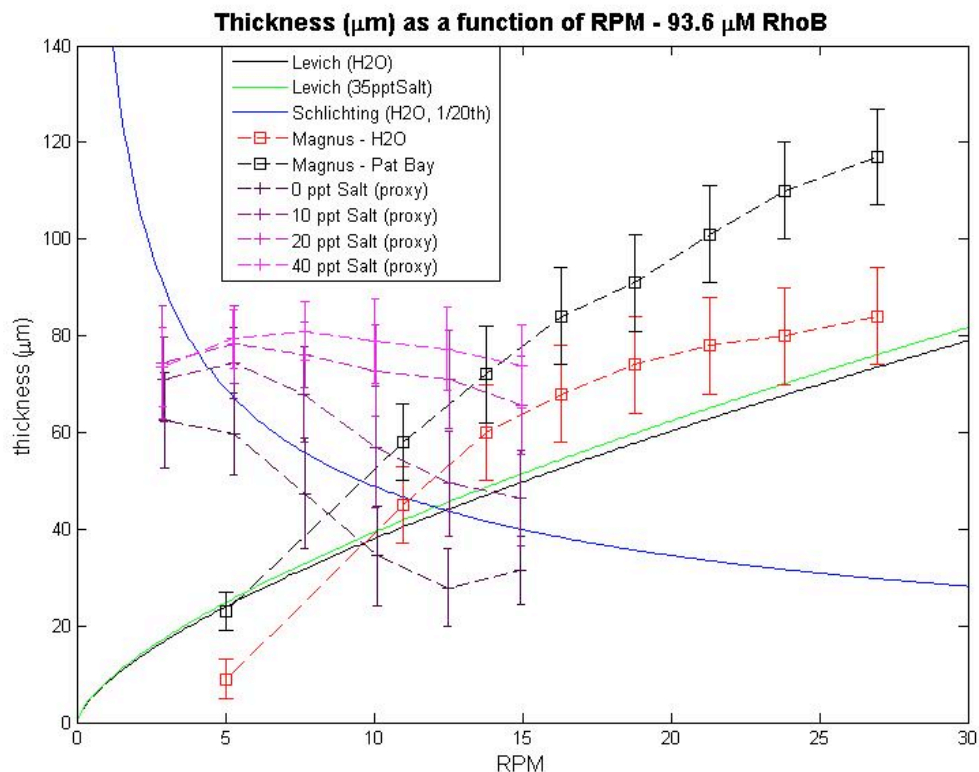


Figure 31. Plots of thickness as a function of RPM. The data from the present experiments are plotted together with two theoretical estimates from Levich (1962) and Schlichting (1987) and discussed in Section 1.2.4 and Figure 6. Also shown here are unpublished data collected by Magnus Eek (Section 2.2.1.2 and Figure 10).

The theoretical estimates from Levich (1962) seem to have similar values and trends to the data collected by Eek. In contrast, the data collected in this study do not follow the same trend, but rather have a decreasing trend, in agreement with Schlichting (1987). Unfortunately, we did not have access to a motor that could run faster than 15 RPM, making it impossible to make direct comparisons at higher speeds.

When we consider a centrifuge used commonly in a chemistry lab, it seems appropriate that a thin fluid layer on a rotating disk is a decreasing function of rotational speed, and thus the theory by Schlichting seems more plausible. However, the theory is only an approximation and does not allow for direct comparisons with experimental data.

Nevertheless, it is noteworthy that the theory suggests reduction of the film thickness with increasing rotational speed.

Average thickness of the adsorbed solution layer at 10 RPM with 40 ppt [NaCl] was $78.9 \pm 8.8 \mu\text{m}$ and little change occurred with increasing speed. To make the comparison between our result and other results easier, thickness of 40-ppt salt has been plotted as a function of rotational speed (equation (12) in Section 2.2.1.2), instead of RPM, in Figure 32.

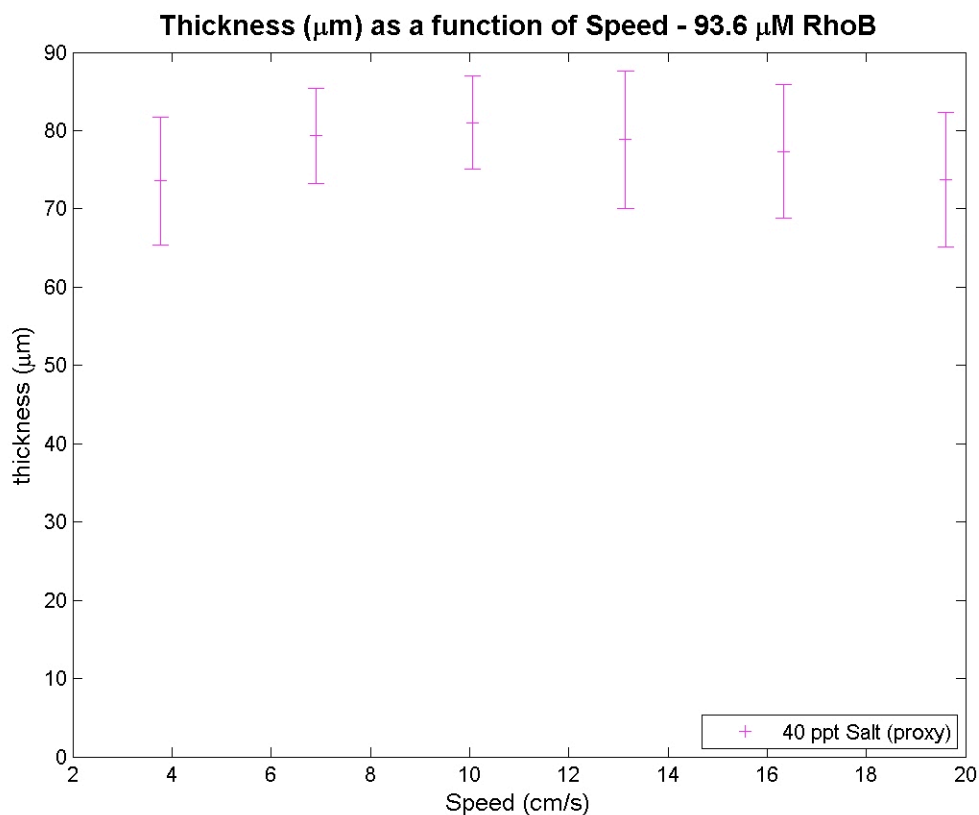


Figure 32. Film thickness as a function of speed at 40 ppt of salt. Note that, by extrapolating to a speed of around 5 cm s^{-1} , the corresponding film thickness will be around $80 \mu\text{m}$.

From equation (12) (Section 2.2.1.2), 4 RPM is equivalent to 5.23 cm s^{-1} and 10 RPM corresponds to a speed of 13.09 cm s^{-1} . According to these results, when the rotational speed was around 5 cm s^{-1} , the thickness would have been approximately $80 \text{ }\mu\text{m}$. This estimate is similar to the $90 \text{ }\mu\text{m}$ reported by Falkowska (1999), but significantly larger than the thickness determined by Carlson ($52 \pm 1.8 \text{ }\mu\text{m}$, 1982) and Guitart et al. ($40\text{-}60 \text{ }\mu\text{m}$, 2004). Accepting the variability above, our results with the rotating glass disks compare well with the results of others utilizing glass plates to sample the sea surface microlayer.

3.3 The effect of changing the concentration of SAS

Sodium dodecyl sulfate (SDS) is used as a proxy for naturally occurring SAS (Figure 33). Because SDS has been one of most extensively studied SAS and it is very safe to use (Myers 2006), it was chosen as a representative SAS.

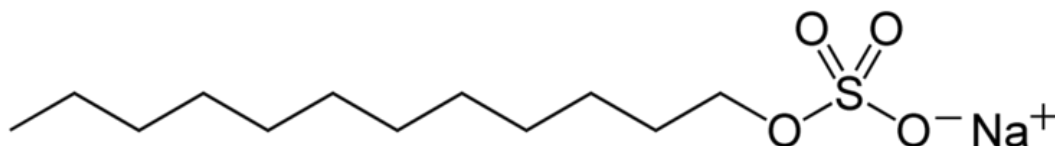


Figure 33. Chemical Structure of sodium dodecyl sulfate (SDS).

Figure 34 shows the thickness change as a result of adding different concentrations of SDS in solutions.

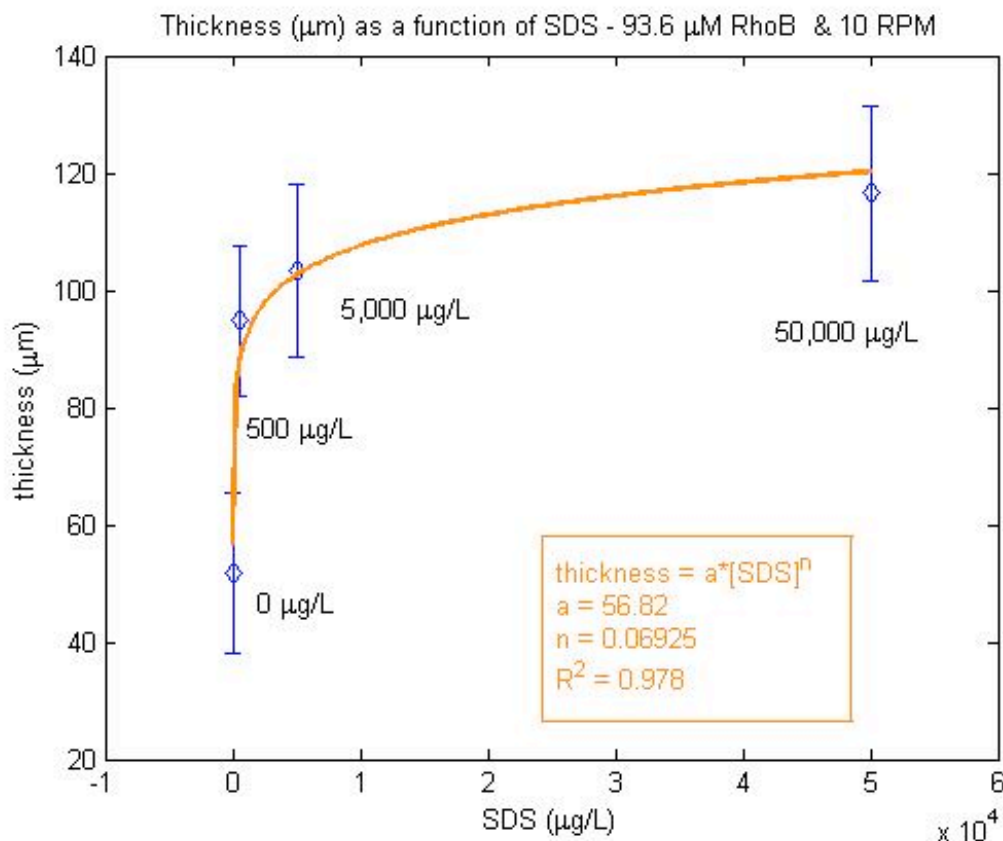


Figure 34. Plots of thickness as a function of sodium dodecyl sulfate (SDS). 500 $\mu\text{g L}^{-1}$, 5 mg L^{-1} and 50 mg L^{-1} of SDS was added before the collection of each ensemble. The concentration of RhoB was fixed at 93.6 μM and the rotational speed was 10 RPM. A curve was fitted to the data by guessing the power-law relation, thickness = $a[\text{SDS}]^n$. Note that, when the power law was used to plot the curve, 0 $\mu\text{g/L}$ of SDS concentration was changed to 1 $\mu\text{g/L}$ instead, to avoid a mathematical problem.

Four data points are plotted on the figure. Along the data points, a curve was fitted to the data by guessing the power-law relation, thickness = $a[\text{SDS}]^n$ where a and n are constants. The resulting numbers are $a = 56.82$ and $n = 0.06925$ and shown in the figure. The coefficient of determination, R^2 , is 0.978 and also seen in the figure. Note that, when the power law was used to plot the curve, 0 $\mu\text{g/L}$ of SDS concentration was changed to 1 $\mu\text{g/L}$ instead, to avoid a mathematical problem.

Addition of SDS, even at modest concentrations, immediately changed the observed thickness of the adsorbed layer. As soon as 500 $\mu\text{g L}^{-1}$ of SDS was added, the

thickness changed from $51.6 \pm 14 \mu\text{m}$ to $94.8 \pm 13 \mu\text{m}$. This SDS concentration of $500 \mu\text{g L}^{-1}$ is similar to the concentrations of SAS determined in coastal waters off of British Columbia (Oliver Wurl, Personal Communication). When 5 mg L^{-1} of SDS was added, the thickness increased to $103.0 \pm 15 \mu\text{m}$. When 50 mg L^{-1} of SDS was added, its thickness increased to $117 \pm 15 \mu\text{m}$, but the increase of thickness seems to reach saturation. In Figure 35 these same data have been plotted using a log scale.

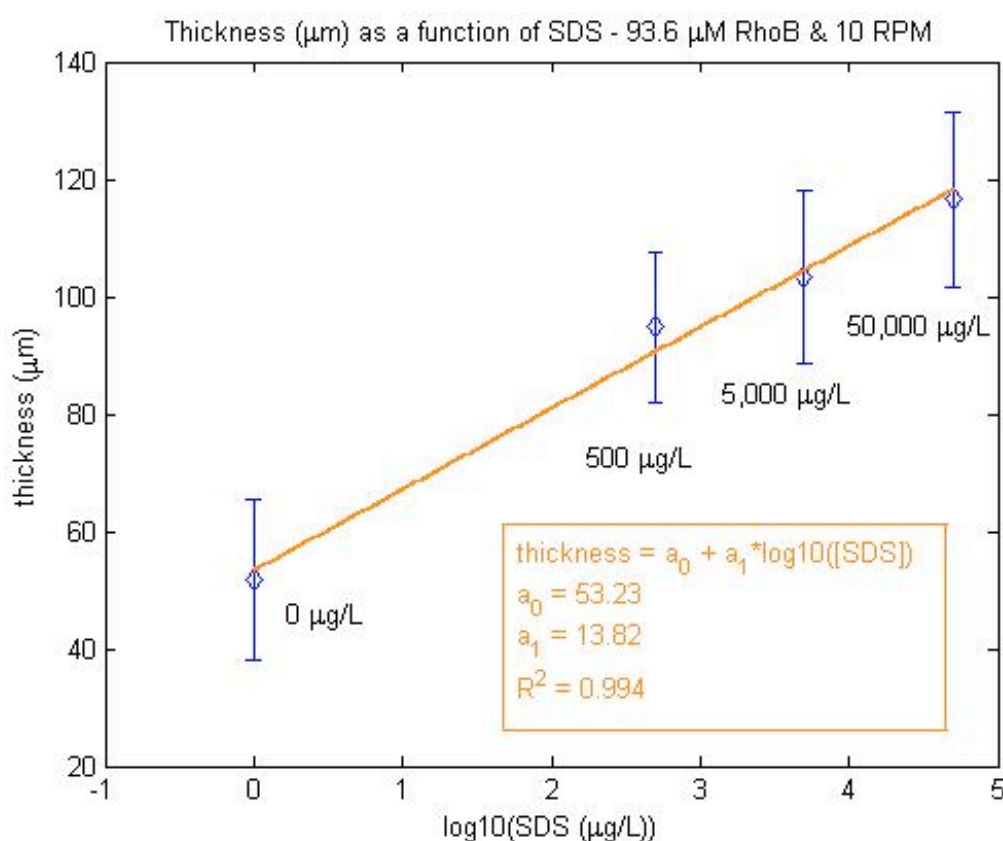


Figure 35. Adsorbed film thickness as a function of $\log_{10}(\text{SDS}(\mu\text{g L}^{-1}))$. A linear fit is added to the data. Note again that $0 \mu\text{g/L}$ of SDS concentration was changed to $1 \mu\text{g/L}$ instead, to avoid a mathematical problem.

In this log scale figure, a linear fit was added and the constants of the linear fit were estimated, along with R^2 value. The resulting linear fit is estimated as thickness = 53.23

+ $13.82 \times \log_{10}([\text{SDS}])$. The results in both Figure 34 and Figure 35 suggest a power law relationship between the thickness of the adsorbed liquid and SDS.

In summary, the addition of SDS increased the thickness of the adsorbed liquid on the glass plate, and it seems reasonable to assume that the presence of SAS in ocean water also will result in increases in the thickness.

3.4 Santa Barbara Channel Sampling, September 2008

Because the deployment of the skimmer during the Santa Barbara Channel RaDyO experiment was the first significant ocean deployment of the vehicle, many mechanical and electrical issues had to be dealt with. Also, because the experiment took place relatively far away from shore, replacement parts were impossible to get. The end result was that a number of issues could not be dealt with during the experiment. As a result, only data set, showing the capabilities of the skimmer, is presented here. During the experiment, the thermistors worked perfectly because they were independent of the computer and power supply on the skimmer. The ECO Triplet B worked during most of the deployments. The dissolved oxygen sensor had been programmed with the wrong calibration coefficients and did not produce useful data. The onboard Fluorescence spectrometer had a faulty electronics board that could not be fixed onboard the ship. Nevertheless, even with all these setbacks, the skimmer behaved nicely as a platform for microlayer sampling and near surface measurements. An example of a data set collected during one of the autonomous runs in Santa Barbara Channel is presented in Figure 36.

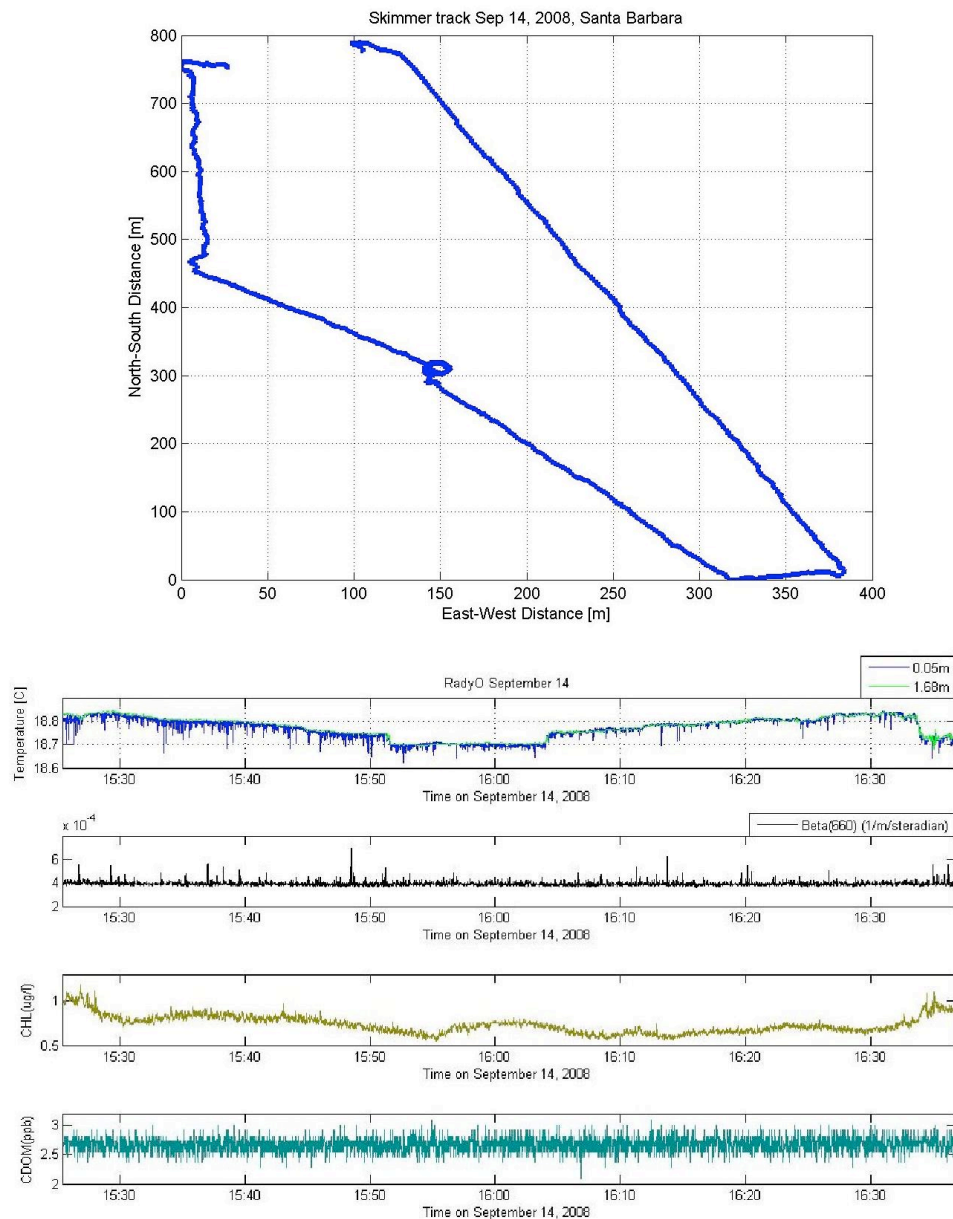


Figure 36. The skimmer track during the mission shown on the top panel. Plots of temperature (in °C), total volume backscattering (in $\text{m}^{-1}\text{steradian}^{-1}$), Chlorophyll concentration (in $\mu\text{g L}^{-1}$), and CDOM (in ppb) during a skimmer mission in Santa Barbara channel are shown on the bottom panel.

The spikes in the temperature data (shown as blue line in Figure 36) are caused by the thermistor moving from water into air due to platform motion.

3.5 Saanich Inlet sampling, February – April 2009

As an example of the type of data being collected during these trials, we have chosen the data from March 12, 2009. Figure 37 shows heading and speed over ground of the sampler during the run.

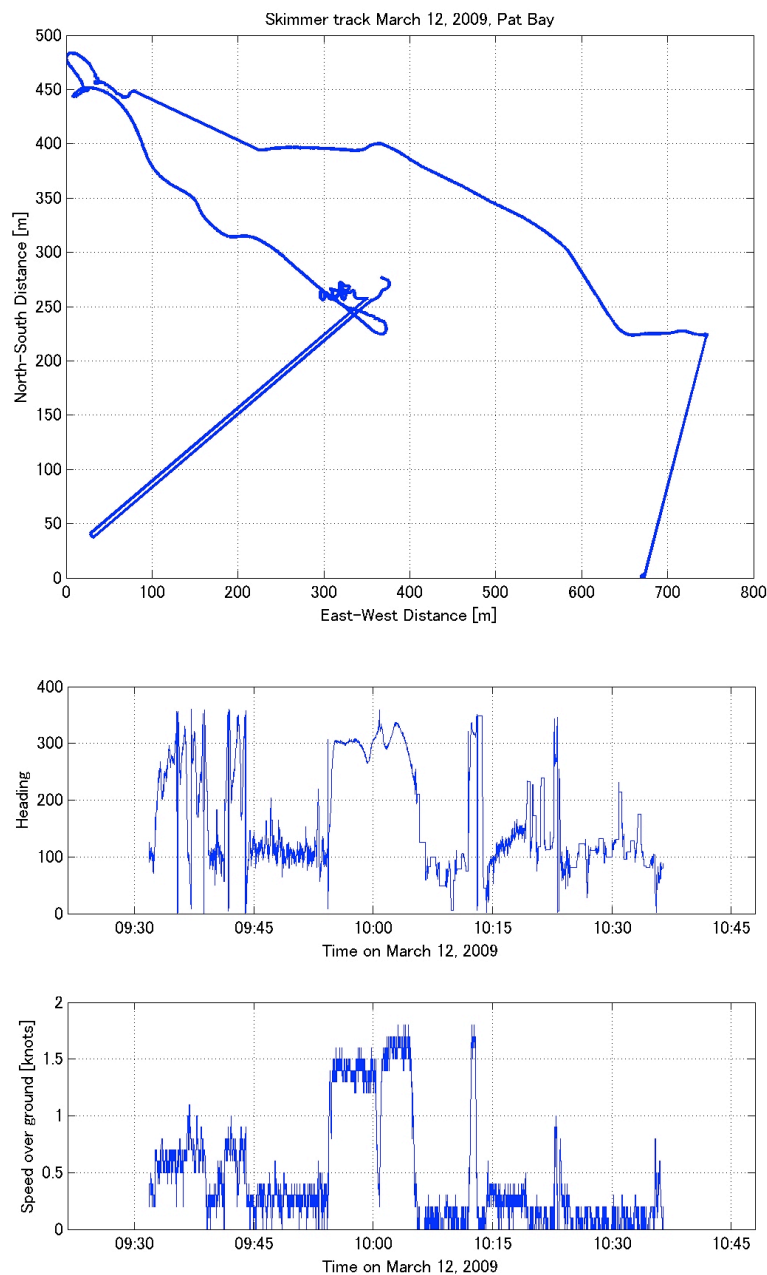


Figure 37. Skimmer movement (top panel), heading and speed over ground (bottom panels) on March 12th, 2009.

In addition to recording GPS position, speed, heading and different scientific sensor data, the skimmer records status information that allows for error checking and debugging following a given mission. As an example, some of these parameters are shown in Figure 38. The parameters plotted here are propeller speeds on both port and

starboard motors, rotational speed of the glass disks, and the status on when a given sampling bottle was being filled and the number of sample bottles filled.

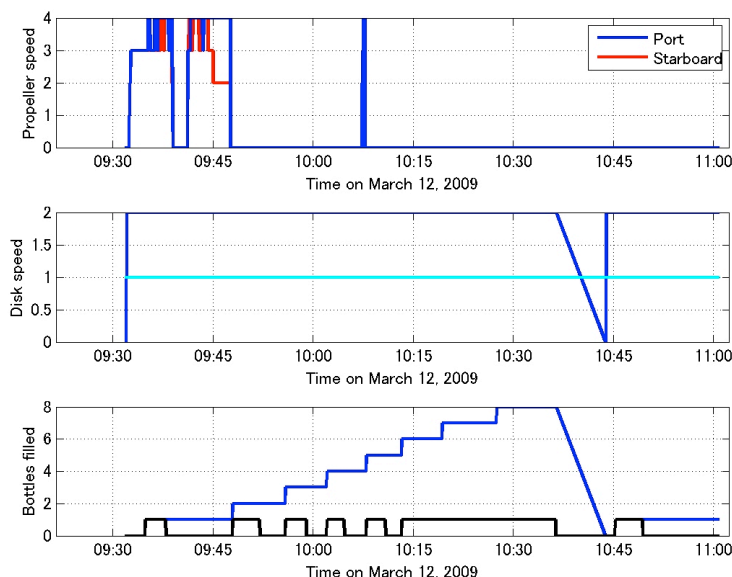


Figure 38. Example of skimmer status parameters being recorded by the onboard computer. The parameters plotted are (in order from top to bottom): Propeller speeds (port and starboard motors), glass disk speed, and sample bottle status during the mission of March 12th, 2009. On the top plot, blue and red lines are drawn to indicate which motors are in what speed. On the middle plot where the disk speed is plotted as the blue line, the line in cyan indicates whether the disk is operated or not, 1 being operated and 0 being not operated. On the bottom plot, states of sample bottles are plotted. The blue line indicates the number of bottles filled, while the black line goes zero or one to indicate if a bottle was filled or not, one being that a bottle was filled.

The propeller speed values range between 0 and 4, with 0 being stop and 4 being full power ahead. From the top of Figure 38, one can see that neither propeller worked very hard during this mission, except between 9:30 and 9:45 and at 10:12.

The rotational speed of the glass disks can be set between 0 and 7, with 7 being full speed. The equivalent rotational speed in RPM and cm s^{-1} was calibrated in the laboratory (Table 4). During the March 12th test, the rotational speed of the glass disks was set to 2 almost all the time, corresponding to a RPM of 3.75 (the middle of Figure

38). The line in cyan seen in the plot indicates whether the disk is operated or not, 1 being operated and 0 being not operated.

Speed on Skimmer Software	Time of one rotation	RPM	Rotational Speed of Disk (Outer Rim) (cm/s)
1	32.0	1.9	3.0
2	16.0	3.8	6.0
3	8.0	7.6	12.0
4	8.0	7.6	12.0
5	6.4	9.5	15.0
6	4.6	13.3	20.8
7	4.6	13.3	20.8

Table 4. Relationship between rotational glass disk speed and equivalent power setting.

The number of sample bottles filled is also recorded, and the start time and closing time of each bottle. To avoid the sample bottles from being filled more than once, it is important to keep track of the status of the bottles. The recorded data shown in Figure 38 (the third plot from top) has a blue line indicating the number of bottles filled. According to the data indicated by step-shapes of blue line, sample bottles were filled slowly from after 9:30 until after 10:30. The black line in the same figure shows zero or one to indicate if a bottle was filled or not, one being that a bottle was filled. As seen in the third plot, the black line went up and down the values between zero and one, indicating that sampling to a bottle was initiated.

Some data from the fluorescence spectrometer have been plotted versus time and wavelength in Figure 39. Although the plot is made without much meaningful information, it is plotted nonetheless to show the capability of the skimmer.

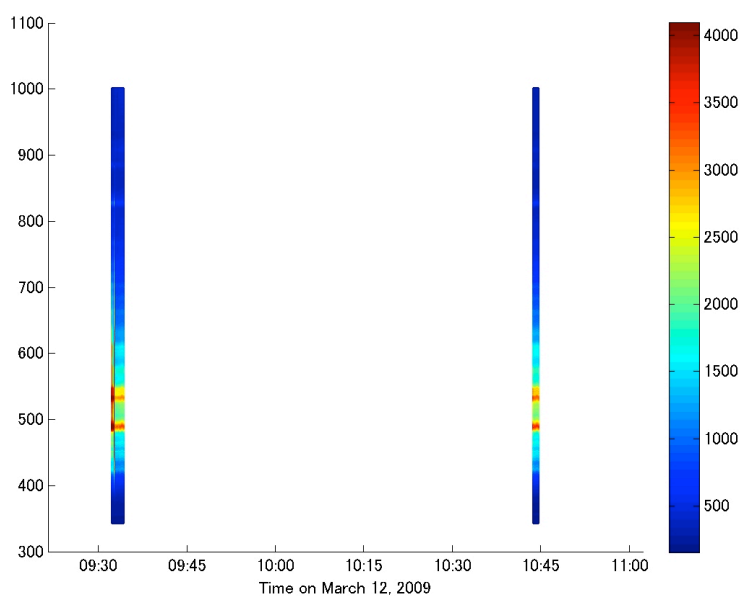


Figure 39. Fluorescence spectra onboard Ocean Optics spectrometer on March 12th, 2009. The colour bar corresponds to raw counts from the spectrometer.

O₂ concentration and temperature from RINKO III sensor are plotted in Figure 40.

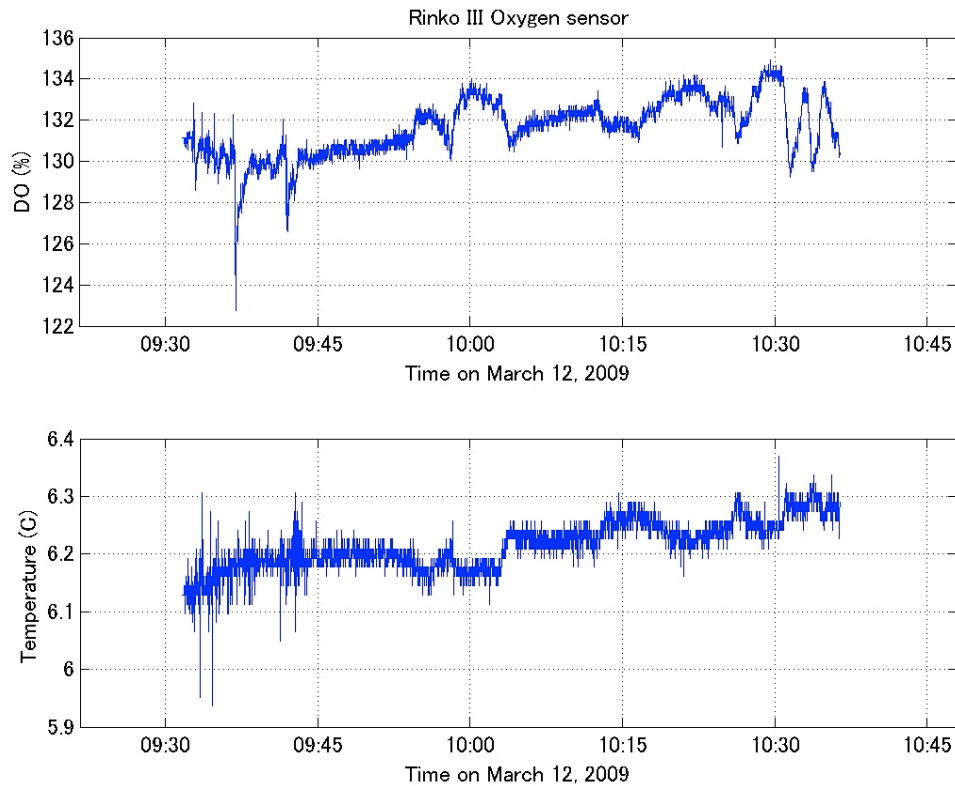


Figure 40. Plots of O₂ saturation level and temperature data from RINKO III sensor on March 12th, 2009.

During the mission on March 12th, the O₂ saturation level was very high throughout the sampling period. These high values clearly indicate the super-saturation of oxygen due to active oxygen production by phytoplankton. Codispoti et al. (2009) reported O₂ saturation levels above 190 %. Their observation was held at the Arctic region and it is true that, in general, the Arctic region has higher O₂ saturation. But, it is likely that the O₂ in Saanich Inlet was super-saturated resulting from phytoplankton blooms. A part of the observed high O₂ saturations may also be the result of diurnal warming of the upper few meters of the water column. By looking at the plots in Figure 40 and noticing the variability in both O₂ and temperature, one can see that the two parameters are clearly correlated.

Wetlabs' Triplet B sensor collects CDOM data, Chlorophyll-a concentration and optical backscatter at 660 nm. An example of these data is shown in Figure 41. The recorded voltage levels of each sensor were converted to physical parameters using calibration data supplied by the sensor manufacturer. The optical backscatter is plotted in $\text{meter}^{-1} \text{steradian}^{-1}$, Chlorophyll-a in $\mu\text{g L}^{-1}$, while CDOM is shown as parts per billion (ppb).

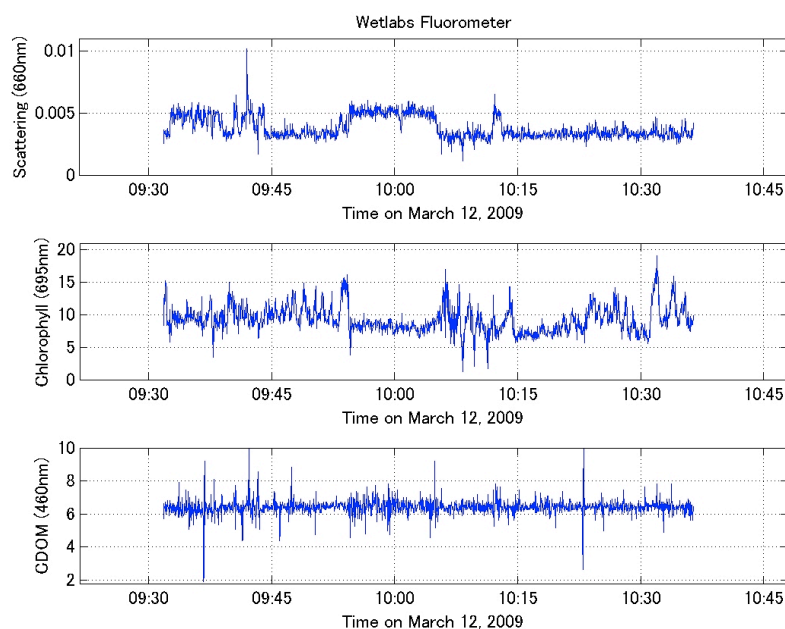


Figure 41. Plots of optical backscatter, Chlorophyll concentration and CDOM concentration on March 12th, 2009.

4 Discussion

When the absorbing dye was chosen to be RhoB, it was based on two reasons. One is that it was a reasonably good fit to the laser source available in the laboratory. The other is that RhoB is a very stable and safe dye and therefore easy to use outside of a fume hood. The laser source was a green laser operating at a wavelength of 532.07 nm at its peak. We looked for an absorbing dye that has a peak or near peak absorbance at this wavelength.

However, if we could design our dye, we might have chosen another set of dye and laser source because the absorbance of RhoB at 532.07 nm is not as strong as other dyes at peak wavelength. For example, RhoB itself has its maximum absorbance around 543 nm. If a laser source operating near this wavelength had been available, the amount of RhoB needed would have been reduced because the molar absorption at 532.7 nm is $81,954 \text{ cm}^{-1} \text{ M}^{-1}$, while it is $106,000 \text{ cm}^{-1} \text{ M}^{-1}$ at 543 nm (data from Oregon Medical Laser Center 2010).

Because it is very likely that a high concentration of dye affects viscosity of the solution just as Kim and Cho (2003) suggested, it is better to use as low a concentration of dye as possible. Therefore, although we used a certain combination of dye and laser in this study, there are better combinations available, which may have improved data quality.

Similarly, because the concentration of RhoB might have been too high and this might have caused a change in viscosity, there is possibly a significant unknown error in the measurements. This issue was carefully considered and the minimum required concentration of RhoB was investigated. Specifically, we observed the solution layer on

a glass disk and tried to halt the addition of dye before the layer started to show different behavior. However, because we did not have any apparatus to measure viscosity or any other instrumentation to reveal viscosity-related physical parameters, it may be that we had gone beyond an appropriate dye concentration. These issues might have resulted in errors that are larger than the errors reported in this thesis.

When the thickness from the laboratory is compared with the thickness estimated by Eek, we have to keep in mind that the thickness estimated by Eek probably underestimated the thickness. Two situations could be considered that would both have resulted in underestimation. These cases are illustrated in Figure 42.

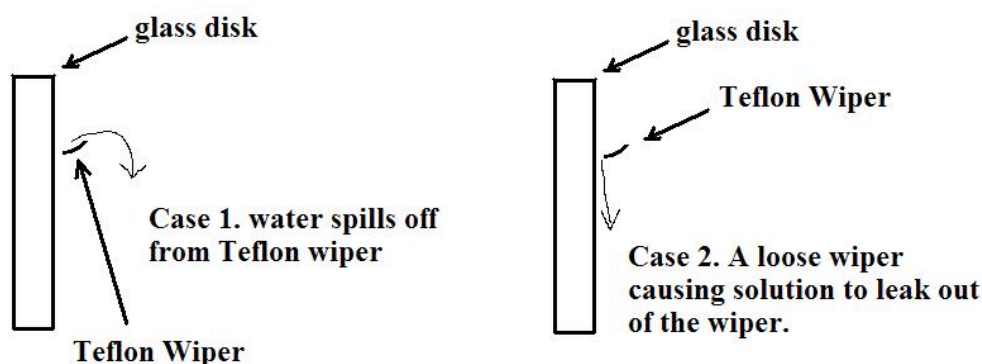


Figure 42. Illustrations of two cases where the thickness of adsorbed solution become underestimated.

One situation is where a solution spilled off of the Teflon wipers (i.e., the left illustration of Figure 42). Teflon wiper has only a certain surface area and if a volume more than the amount the wiper could hold was present, remaining solution would have spilt over the opening of the wiper. This would cause the volume of sample collected to be smaller than what actually was. This would occur more frequently when the rotational speed of glass disk is fast and collects sample more than the wiper could hold. The other situation

is where the contact between the wiper and glass disk was loose and some volume of the sample adsorbed on the glass disk was not scraped (i.e., the right illustration of Figure 42). Because the contact could not be perfectly tight and the wiper could not scrape off the solution completely, there was remaining solution on the disk after being scraped by the wiper. Again, this situation would potentially cause underestimation of the thickness using the method employed by Eek.

We can compare the estimate by collecting volume with the estimate of optical method we employed. The estimate such as that by Eek has the advantage in that it is easily operational, and thus it is a good way of quick estimation. In contrast, the approach we employed here requires laborious adjustment on the experimental setup and sensitive measurement.

Also, because the rotating glass disk is governed by centrifugal force, it is likely that the thickness would be different at any point along an imaginary line drawn between the center of glass disk and its outer rim. Thus, it is very important to know where the laser was aiming. Ideally, it would have been beneficial to collect thickness measurements from various points along the imaginary line. However, changing where the laser was aimed would demand a careful adjustment of the setup and there were also spatial constraints imposed by the optical bench in the laboratory.

In summary, this method is lot more difficult to operate, but it could be more precise and result in a range of thicknesses from points along the imaginary line. The volume estimate is very quick to operate, but can underestimate and would produce only one thickness, which is an average thickness.

5 Conclusions and suggestions for future work

Even though my thesis project started out as a study to finalize, evaluate, and use a new, novel, glass-plate microlayer sampling robot being constructed at the Institute of Ocean Sciences, Sidney, British Columbia, it became apparent very quickly that our scientific understanding of several key components of the sampler was lacking and required further study. Significant effort was required on the software side of the new instrument (not discussed in the thesis), as well as electrical and mechanical issues associated with making the sampler reliable in the harsh ocean environment. The desire to collect a number of individual microlayer water samples during a mission also added complexity to both instrumentation and the software members of the sampler. These problems were eventually overcome and we now have a functioning sampler, capable of self-contained open ocean missions.

The main scientific issue that had to be addressed before the skimmer could be used in more routine microlayer sampling missions was the fact that we did not fully understand the operation of the critical rotating glass plate module used to collect the microlayer samples on the skimmer. This question became the primary focus of the project leading to this thesis.

Using the Beer-Lambert Law, our experiments successfully estimated the thickness of adsorbed solution layer on a rotating glass disk with and without salt and surfactants. A simple extrapolation based on the experimental results showed that the thickness of a film of water with 40 ppt of salt and 5 cm s^{-1} of rotational speed would be about $80 \text{ }\mu\text{m}$ (see Figure 32). This result is comparable to results obtained by dipping a glass plate. A significant conclusion of this effort is that microlayer samples collected

with a rotating glass plate sampler are directly comparable to samples collected using a much slower and cumbersome dipping glass plate system.

This study also showed that the rotational speed of the glass disks significantly influences the thickness of the adsorbed solution layer, and thus it is very important that the speed is held constant unless there is a specific use. The study also showed that the adsorbed layer thickness is an increasing function of both salinity and SAS.

The work presented in this thesis shows that the microlayer sampler using rotating glass disks is a potential tool to collect interesting data from the surface microlayer.

The idea of adding an onboard fluorescence spectrometer to the microlayer sampler is a useful one and has the potential of giving instant feedback on the status of the microlayer where the sampler is being used. This information can, for example, be used to determine when and where to collect samples for further analysis back in the laboratory. However, the incorporation of the spectrometer into the overall system has not been successful. This should be rectified as soon as possible.

Although the addition of a weather station on the skimmer took place too late to make part of this project, such data are invaluable and will be a significant component in the analysis and interpretation of the microlayer data set.

Originally, it was planned that the skimmer should be able to operate in a completely autonomous mode. This would happen by integrating a programmable steering mechanism, such as a programmable tiller, with a GPS receiver and appropriate software. By downloading a suitable mission control file, the skimmer could be sent on repeat tracks, collecting samples at predetermined stations without direct human interaction. This would be useful for repeat studies of, for example, sewage outfalls or

pulp-mill effluents. But, this plan has not been put into effect due to the complexity of such integration. However, such an operating mode would be useful and expand the possible uses of the skimmer. Future investigations should also include the use of different materials on the disks, such as Teflon and different plastics, to collect specific chemicals and compounds.

More thorough testing of the skimmer is desirable. The work presented in this thesis shows that the skimmer demonstrated its capability under calm ocean conditions but cannot conclude anything about its ability in higher sea states. Only with use in a range of conditions can the overall capabilities be assessed.

The variability of adsorbed layer thickness in relation to the forward motion of the skimmer also needs to be evaluated to determine the optimum speed, and therefore spatial coverage, under a range of wind and wave conditions and with a range of SAS concentrations, or flume studies where the velocity of water passing the disks can be adjusted.

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Appendices

A. Derivation of thickness estimation by Schlichting

In this section, the expression to estimate thickness of solution layer resulted from analysis by Schlichting (1987) is derived. He examined fluid motion around a rotating disk that rotates with a uniform angular velocity, ω , as in the figure below.

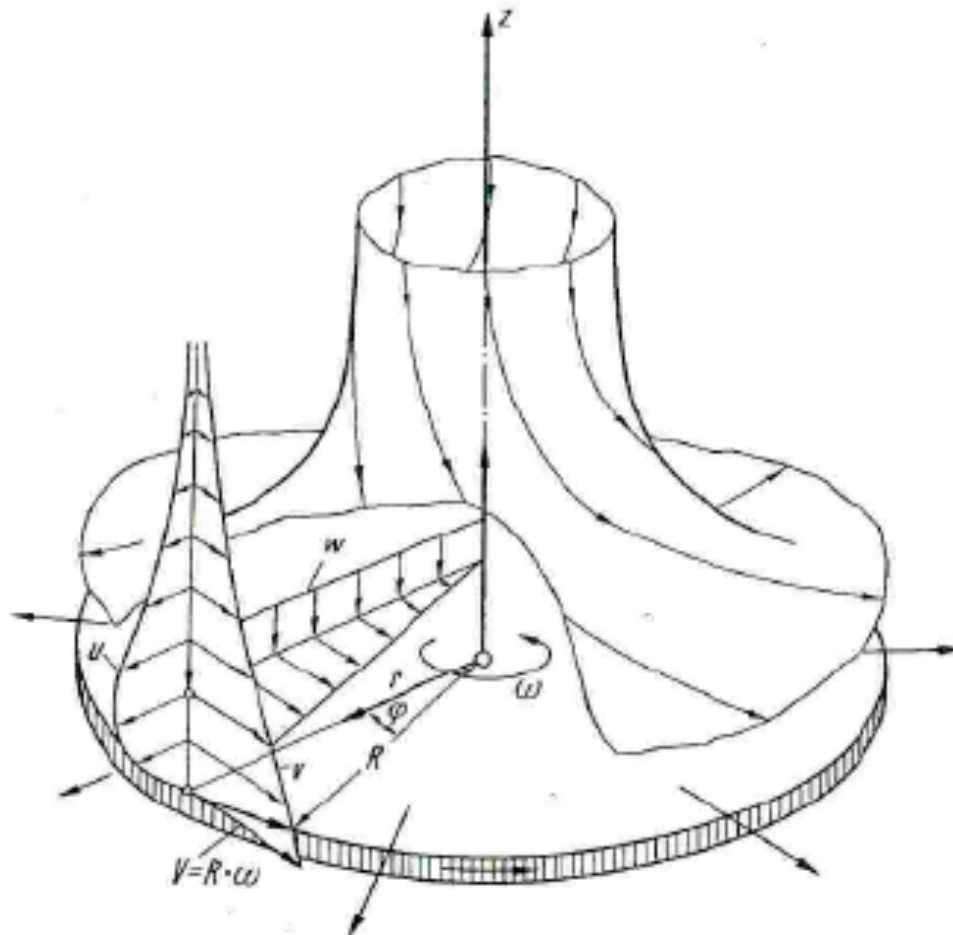


Figure A1. Diagram showing the geometry of a horizontal rotating disk and parameters (Schlichting 1987). The radial direction is r , the circumferential angle ϕ , and the vertical axial distance z . Velocity components are denoted as u , v and w , respectively. ω is the angular velocity. (This is the same as Figure 5.)

In the Schlichting's analysis, friction causes a solution layer near the disk to move along with the disk and is eventually carried radially outward in by the action of centrifugal forces. The outward movement of the solution layer is counterbalanced by a flow of particles towards the disk in axial direction along the z-axis. Thus, the situation has a full three-dimensional flow, as shown in Figure A1. The velocity components in the radial direction, the circumferential direction, and the axial direction are denoted as u , v and w . The Navier-Stokes equations for this case can be written as,

$$\begin{aligned}
 u \frac{\partial u}{\partial r} - \frac{v^2}{r} + w \frac{\partial u}{\partial z} &= -\frac{1}{\rho} \frac{\partial p}{\partial r} + \nu \left\{ \frac{\partial^2 u}{\partial r^2} + \frac{\partial}{\partial r} \left(\frac{u}{r} \right) + \frac{\partial^2 u}{\partial z^2} \right\}, \\
 u \frac{\partial v}{\partial r} - \frac{uv}{r} + w \frac{\partial v}{\partial z} &= \nu \left\{ \frac{\partial^2 v}{\partial r^2} + \frac{\partial}{\partial r} \left(\frac{v}{r} \right) + \frac{\partial^2 v}{\partial z^2} \right\}, \\
 u \frac{\partial w}{\partial r} + w \frac{\partial w}{\partial z} &= -\frac{1}{\rho} \frac{\partial p}{\partial z} + \nu \left\{ \frac{\partial^2 w}{\partial r^2} + \frac{1}{r} \frac{\partial w}{\partial r} + \frac{\partial^2 w}{\partial z^2} \right\}, \\
 \frac{\partial u}{\partial r} + \frac{u}{r} + \frac{\partial w}{\partial z} &= 0
 \end{aligned} \tag{A1}$$

where p = pressure and ρ = density.

If the wall is considered not slipping, then the following boundary conditions are appropriate:

$$\begin{aligned}
 z = 0 : \quad u &= 0, \quad v = r\omega, \quad w = 0, \\
 z = \infty : \quad u &= 0, \quad v = 0.
 \end{aligned} \tag{A2}$$

At a distance r from the axis, the centrifugal force per unit volume acting on a fluid particle is $\rho\omega^2$. When a unit volume enclosed by a length, dr , width, ds , and height, h , is considered, the centrifugal force is equal to $\rho\omega^2 h dr ds$. The shearing stress τ_w acts on the same fluid element, forming an angle θ with the circumferential velocity. The radial component of the shearing stress has to balance with the centrifugal force,

$$\tau_w \sin \theta dr ds = \rho r \omega^2 h dr ds \quad (\text{A3})$$

which is equal to

$$\tau_w \sin \theta = \rho r \omega^2 h. \quad (\text{A4})$$

In contrast, the circumferential component of the shearing stress has to be proportional to the velocity gradient of the circumferential velocity right at the glass disk. This can be written as,

$$\tau_w \cos \theta \sim \frac{\mu r \omega}{h} \quad (\text{A5})$$

where μ is the dynamic viscosity. By combining equations (A4) and (A5), one gets,

$$h^2 \sim \frac{\mu}{\rho \omega} \tan \theta. \quad (\text{A6})$$

By assuming that the angle of slip, θ , is small, the thickness of fluid carried along the disk is proportional to the dynamic viscosity of the fluid, μ , and inversely proportional to density, ρ , and angular velocity of disk, ω ,

$$h \sim \sqrt{\frac{\mu}{\rho \omega}}. \quad (\text{A7})$$

B. Derivation of the thickness expression by Levich

Here, the expression developed by Levich (1962) and presented in Introduction is derived in more detail. This considers a case where a solid plate is dipped into a solution and brought up vertically at a constant low velocity. Note that this case does not involve rotation. The forces that are of interest are transfer of kinetic energy from the plate to the viscous liquid, gravity causing the liquid to drop along the plate and capillary pressure

acting around the liquid surface (Cinbis 1992). Figure A2 shows the geometry associated with this case.

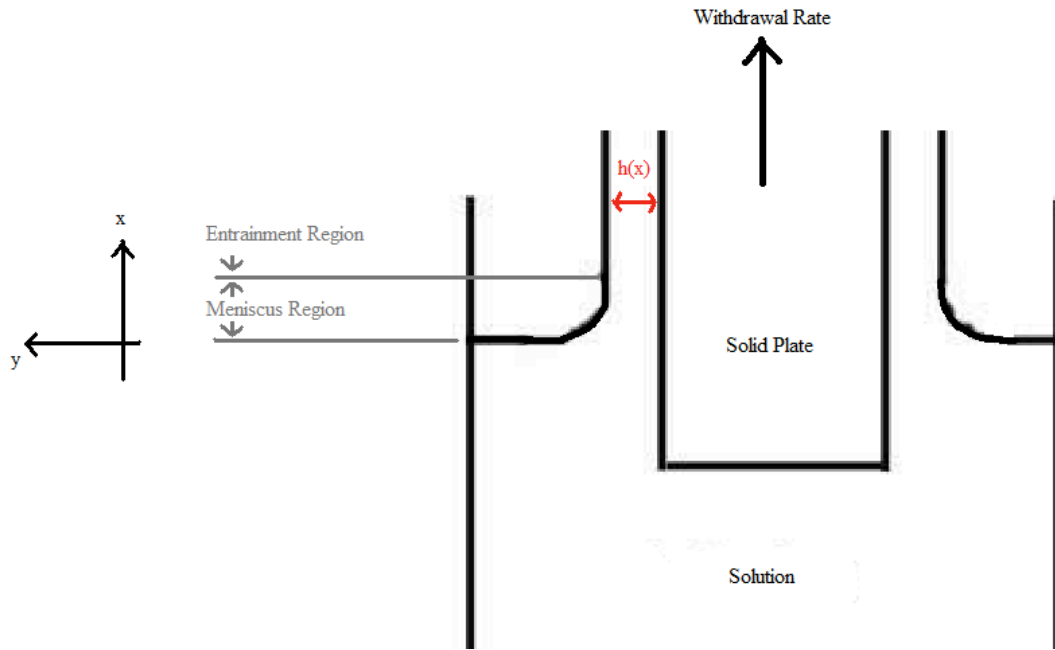


Figure A2. Schematic diagram showing a vertical plate being vertically pulled out of a solution.

The solid plate forms a meniscus on the solution surface where the shape of the meniscus remains static. This region is called the static meniscus region. Away from the solution surface and the meniscus region, the thickness becomes constant and this region is called the entrainment region. In this entrainment region, the thickness, h , becomes dependent of the height from solution surface, x .

Fluid dynamical analysis reveals that the capillary pressure balances the gravitational pull,

$$\sigma \frac{\frac{d^2 h}{dx^2}}{\left[1 + \left(\frac{dh}{dx}\right)^2\right]^{\frac{3}{2}}} = \rho g x \quad (\text{A8})$$

where σ = surface tension

ρ = density of fluid, and

g = gravitational acceleration.

Because the liquid surface far from the plate is required to be horizontal, the integrated solution becomes,

$$\sigma \frac{\frac{dh}{dx}}{\left[1 + \left(\frac{dh}{dx}\right)^2\right]^{\frac{1}{2}}} = \frac{\rho g x^2}{2\sigma} - 1. \quad (\text{A9})$$

When $dh/dx \rightarrow 0$, the static meniscus region and entrainment region show smooth transitions. Equation (A9) indicates that, as $dh/dx \rightarrow 0$, $x \rightarrow (2\sigma/\rho g)^{(1/2)}$. When this x is inserted into equation (A8), it becomes clear that $d^2h/dx^2 \rightarrow (2\rho g/\sigma)^{(1/2)}$. In other words, a solution of equation (A9) for the static meniscus region also becomes a solution for the entrainment region when the following conditions are all met:

$$\begin{aligned} h &\rightarrow 0 \\ \frac{dh}{dx} &\rightarrow 0 \\ x &\rightarrow \left(\frac{2\sigma}{\rho g}\right)^{\frac{1}{2}} \\ \frac{d^2h}{dx^2} &\rightarrow \left(\frac{2\rho g}{\sigma}\right)^{\frac{1}{2}}. \end{aligned} \quad (\text{A10})$$

Thus, the function $h(x)$ can be found from a solution that satisfies the boundary conditions above.

In the entrainment region, Levich showed that the equation for slow and steady-state motion is,

$$\frac{\sigma}{\rho} \frac{d^3 h}{dx^3} + \frac{\mu}{\rho} \frac{\partial^2 v_x}{\partial y^2} + g = 0 \quad (\text{A11})$$

where μ = dynamic viscosity

v_x = vertical velocity of the liquid.

The boundary conditions required here are,

$$\begin{aligned} v_x &= v_0 \text{ at } y = 0 \\ \mu \frac{\partial v_x}{\partial y} &= 0 \text{ at } y = h(x) \end{aligned} \quad (\text{A12})$$

The liquid consumption rate, Q , which represents the liquid flow in the film, can be written as,

$$Q = \int_0^{h(x)} v_x dy = \text{constant}. \quad (\text{A13})$$

When equation (A11) is integrated with the boundary conditions (i.e., equation (A12) and the solution is substituted into equation (A13), it becomes,

$$Q = v_0 h + \left(\rho g + \sigma \frac{d^3 h}{dx^3} \right) \frac{h^3}{3\mu}. \quad (\text{A14})$$

Because this is a third-order differential equation and, when integrated, three constants will appear as well as four unknowns including Q . Thus, four boundary conditions are required to solve this equation.

It is convenient to express x and $h(x)$ as dimensionless normalized forms, λ and L , respectively.

$$\lambda = \left(\frac{3\mu}{\sigma} \right)^{\frac{1}{3}} \frac{v_0^{\frac{4}{3}}}{Q} x$$

$$L = \frac{v_0 h(\lambda)}{Q} .$$
(A15)

Then, the dimensionless form of equation (A14) becomes,

$$\frac{d^3 L}{d\lambda^3} - \frac{1-L}{L^3} + \frac{\rho g Q^2}{3\eta v_0^3} = 0 .$$
(A16)

Because the film thickness becomes constant at large distances, the constant thickness, h_0 , can be written as,

$$h_0 = \frac{Q}{v_0} ,$$
(A17)

and because

$$h \rightarrow h_0 \text{ as } x \rightarrow \infty$$
(A18)

is true, the following holds true:

$$L \rightarrow 1 \text{ as } \lambda \rightarrow \infty$$

$$\frac{dL}{d\lambda} \rightarrow 0 \text{ as } \lambda \rightarrow \infty \text{ and}$$
(A19)

$$\frac{d^2 L}{d\lambda^2} \rightarrow 0 \text{ as } \lambda \rightarrow \infty .$$

Solving this set of equation shows that

$$Q \approx v_0^{\frac{5}{3}} .$$
(A20)

Therefore, at sufficiently small v_0 , the last term on the left hand side of equation (A16) becomes negligible and the equation is simply,

$$\frac{d^3 L}{d\lambda^3} - \frac{1-L}{L^3} = 0 .$$
(A21)

The matching boundary condition in dimensionless forms can be written as,

$$\left[\frac{d^2 L}{d\lambda^2} \right]_{L \rightarrow 0}^{Meniscus} = \left[\frac{d^2 L}{d\lambda^2} \right]_{L \rightarrow \infty}^{Entrainment} . \quad (A22)$$

The numerical solutions of equation (A21) and the last expression in the set of equation (A10) and yield the liquid flow per unit length

$$Q = 0.93 \frac{v_0^{\frac{5}{3}} \mu^{\frac{2}{3}}}{\sigma^{\frac{1}{6}} (\rho g)^{\frac{1}{2}}} \quad (A23)$$

where the limiting thickness h_0 is

$$h_0 = 0.93 \frac{(\mu v_0)^{\frac{2}{3}}}{\sigma^{\frac{1}{6}} (\rho g)^{\frac{1}{2}}} . \quad (A24)$$

To make the notation simpler, subscripts '0's are dropped from the equation above and equation (A24) can be written as,

$$h = 0.93 \frac{(\mu v)^{\frac{2}{3}}}{\sigma^{\frac{1}{6}} (\rho g)^{\frac{1}{2}}} \quad (A25)$$

where v = the withdrawal rate.

Note that when the equation (A21) was derived, v_0 was assumed small. When Q in equation (A23) is substituted into equation (A16), it indicates that this assumption is valid if

$$v \ll \frac{\sigma}{\mu} . \quad (A26)$$

For pure water at 20 °C, this means that $v \ll 73 \text{ m s}^{-1}$. Thus, as long as the withdrawal rate does not exceed 73 m s^{-1} , the derivation above holds true. This is a very fast rate and is never exceeded in any practical situation.