A New Hyperspectral Spherical-Cavity Absorption Meter

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INTRODUCTION

How do you measure spectral light absorption by ocean water-or any other liquid? How do you accurately determine the spectral absorption coefficient, in inverse meters (1/m), over the full spectrum? The only widely accepted method is to use an integrating sphere. An integrating sphere with high diffuse reflectivity overpowers the scattering by suspended solids in the liquid, and also increases the absorption path length, thereby increasing the instrument sensitivity and accuracy. There simply is no better approach for measuring the absorption coefficient of any liquid. Yet until now this approach has not been available in a commercial instrument. The engineering challenge has been in how to implement this approach in a practical instrument. The scientific challenge has been in how to calibrate such an instrument.

HOBI Labs has developed an integrating sphere absorption meter for both in-water (depths to 600 m) and laboratory applications. This revolutionary instrument is called the I-Sphere. The laboratory version, which has additional spectral capabilities, is called the HyperSphere. Moreover, we have developed an accurate and scientifically verifiable calibration methodology.

BACKGROUND

Absorption Measurement Methods

Laboratory Spectrophotometers typically use a very small measurement volume, or dried samples deposited on filter paper. In some cases a solid or encapsulated liquid sample is placed in an integrating sphere acting as an uncalibrated light collector. To achieve adequate sensitivity the samples must be concentrated after being collected in the field. The necessary procedures are cumbersome, time-consuming, subject to contamination and chemical degradation, and obviously inappropriate to in-situ use.

Finally, the results are typically expressed in terms of absorbance or absorptance, quantities that are not applicable to geometries other than the measurement apparatus.

Reflecting Tube

This variation on an in-situ transmissometer attempts to minimize scattering errors by enclosing the sample in a highly reflecting tube, and using a wide-angle receiver that collects both direct and scattered light. However a significant portion of the scattered light is still lost, and the amount lost must be estimated and corrected for.6 Also, the absorption over the typical 25 cm path is still small enough in clear water that some users find it necessary to bring a source of highly purified water into the field for frequent comparison measurements.

I-Sphere Approach: Integrating Sphere

An integrating sphere has walls with high diffuse reflectivity. Light entering through an aperture reflects off the wall many times, distributing the light uniformly over the internal surface. More importantly for absorption measurements, the multiple reflections in an integrating sphere cause photons to traverse a total distance much greater than the dimensions of the cavity. This greatly increases the effective path length and therefore the sensitivity of the measurement. The I-Sphere's 10 cm sphere gives effective path lengths of up to 2 meters, as shown in Figure 1.

At the same time, the integrating cavity's sensitivity to scattering is very low, because the cavity captures and reflects scattered photons just as efficiently as unscattered ones. The only error introduced by scattering is a slight increase in the total path length traversed by scattered photons, but this error is not significant in most practical cases. Figure 2 shows I-Sphere's negligible scattering sensitivity.

Earlier Integrating Cavity Absorption Measurements

Fry, Kattawar and Pope first demonstrated the viability of using a non-spherical integrating cavity for absorption measurements in the laboratory.[1] Pope and Fry refined this approach to measure the absorption of pure water.[2,3] However their apparatus was developed specially for those measurements and is not suitable for use outside the laboratory. Kirk has extensively modeled the performance of integrating cavities and concluded that optimum performance is obtained with an isotropic light source in the center of a sphere.[4,5] However that approach entails major engineering challenges, and our work indicates it is not necessary for practical purposes.

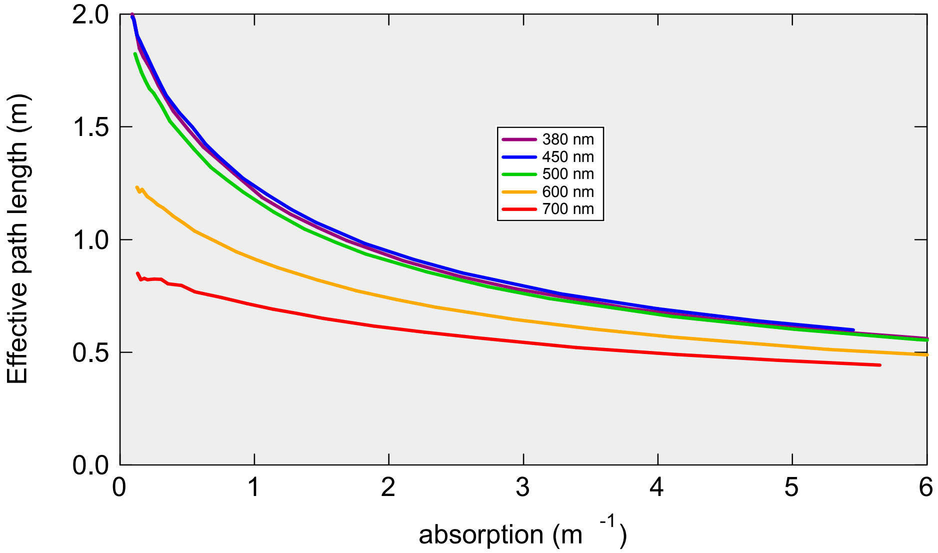

Figure 1. Effective Path Length — Sensitivity to absorption is directly proportional to path length. The integrating sphere's reflecting properties multiply its effective path length to provide much higher sensitivity than a transmissometer approach. At higher absorptions, the effective path length decreases, but this has a beneficial effect: reducing the dynamic range required to measure high absorption values. Path length also varies by wavelength, but is highest for the wavelengths where water's absorption is lowest.

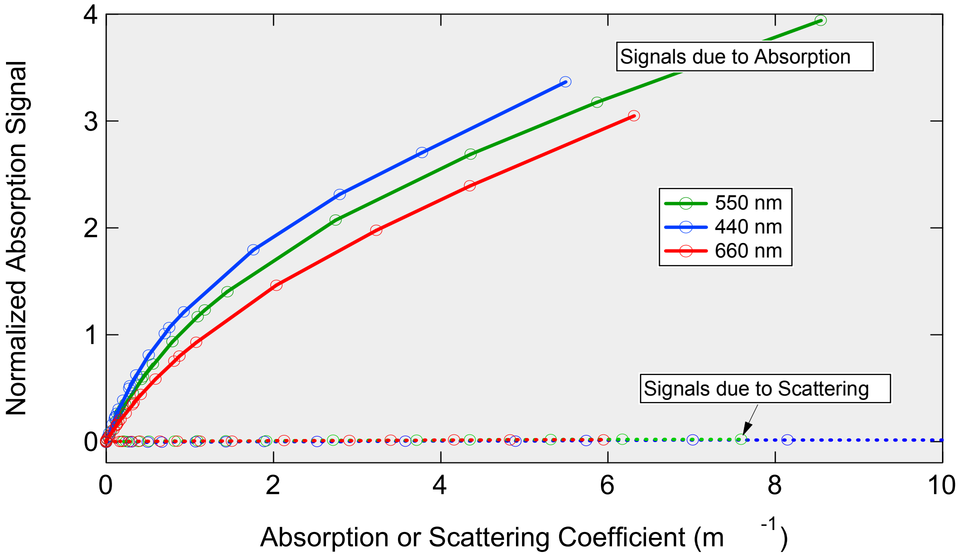

Figure 2. Scattering Sensitivity: No Correction Required — This plot shows the actual measured response to 1) a dye with high absorption, and 2) highly scattering particles with negligible absorption. The I-Sphere shows no significant response to the scattering particles. In contrast, measurements using a reflecting tube would show 10 to 20% scattering error.

INSTRUMENT DESCRIPTION

The in-situ I-Sphere and the bench-top HyperSphere have the same essential features, which are shown in Figure 3.

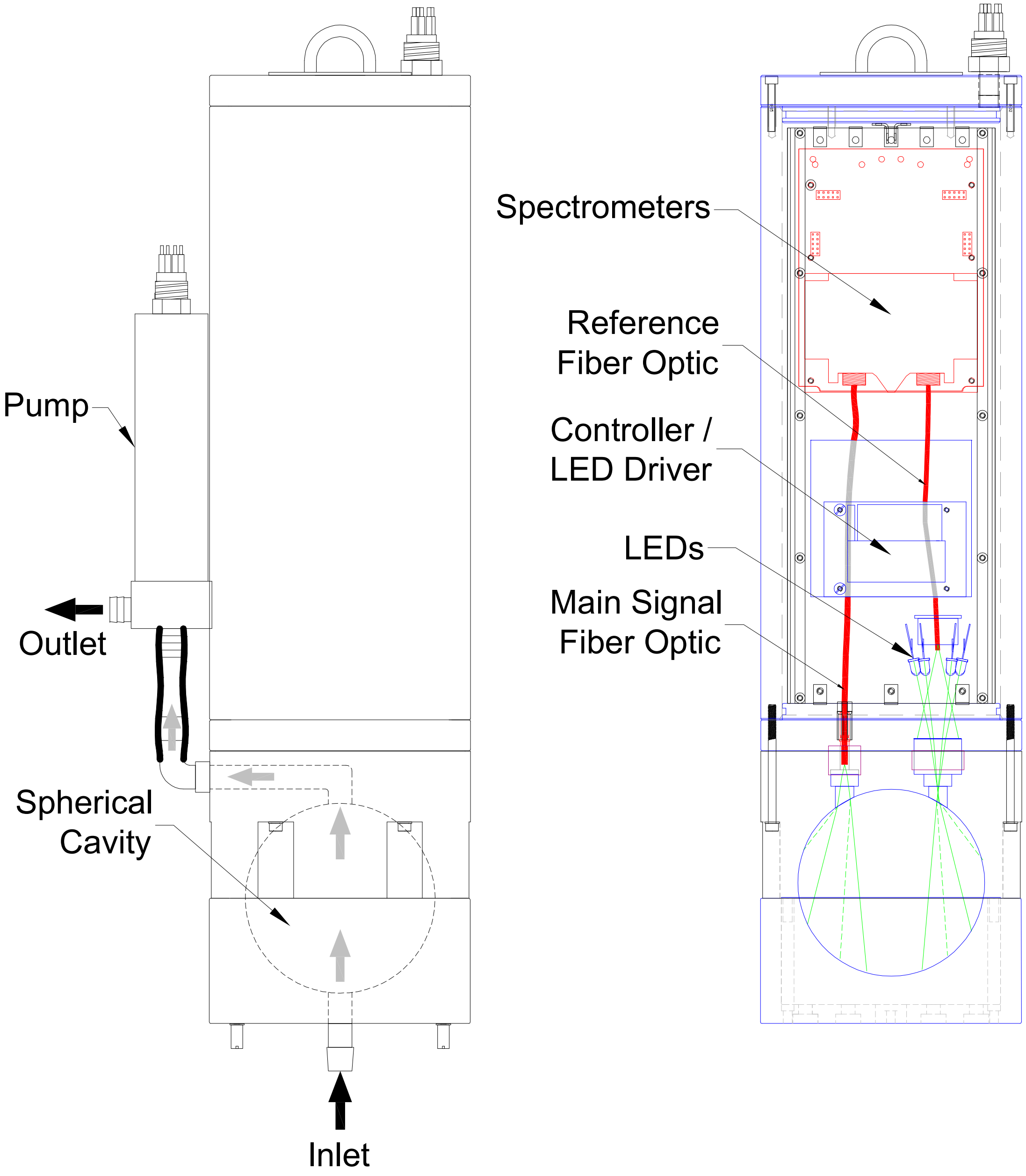

Figure 3. Schematic View — The water flow path is shown at left; at right, the major internal components.

Integrating Sphere

The sphere, key to the I-Sphere's performance, is made of a solid plastic that has high diffuse reflectivity. But unlike materials such as Spectralon, it is impervious to water and other substances, so the fluid under test can be pumped directly into the sphere (Figure 4). The sphere is shielded against external light by an opaque shell, and divided into two hemispheres, one of which is removable for easy cleaning (Figure 5). The fluid inlet and outlet are configured for easy connection to a submersible pump, and a streamlined flow path prevents trapping of bubbles.

Figure 4. **Flow-through Design** — A prototype integrating sphere, without its opaque outer shell, is shown during testing in the laboratory. Unlike typical integrating spheres that must be kept dry, the I-Sphere cavity is impervious to moisture and contamination, and is designed for flow-through use.

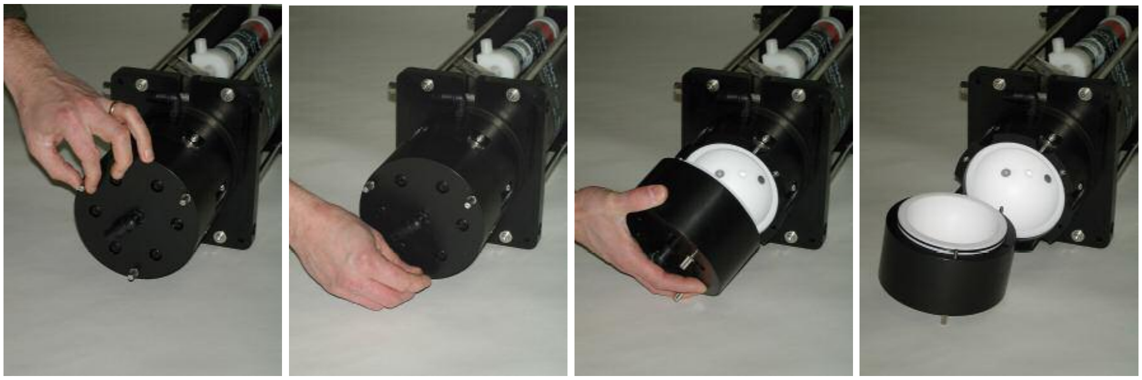

Figure 5. **The split sphere opens easily for cleaning and drying.**

Light Source

The I-Sphere is also distinguished by its solid-state light source. An array of light-emitting diodes provides efficiency, reliability, and ease of electronic control. By carefully selecting a set of LEDs and adjusting their drive, we balance the spectral output to complement the response of the detector, leveling the response over the full 360 to 850 nm range. The LEDs can be switched on and off under instrument control to measure and compensate for dark offsets, or for special applications including fluorescence measurement.

The HyperSphere offers an optional deuterium light source that extends the wavelength range down to 200 nm.

Optics

The light source illuminates the sphere interior through a 1 cm aperture with a sealed fused silica window. The received signal is sensed by an optical fiber looking through a second, similar window. A second fiber views the output of the light source before it enters the sphere, to provide a reference measurement.

Detectors

A sensitive CCD spectrometer measures the radiance in the sphere with spectral resolution of about 0.3 nm per pixel from 200 to 850 nm. A second, identical spectrometer measures the light source output, to correct for any changes in its output. Variable integration time allows the spectrometers to accommodate a very wide range of signals. Typical integration times in most natural waters are 100 ms or less.

Electronics

An intelligent controller regulates the light source(s), controls the signal and reference spectrometers, and receives and interprets commands. The command interpreter can execute arbitrary sequences of commands stored in files, including timed sequences for scheduled data collection over long periods. Data can be stored in high-capacity flash memory, transmitted in real time, or both.

CALIBRATION

We calibrate the I-Sphere by measuring its signal $S(a,\lambda)$, while it is filled with a fluid whose absorption is known from independent measurements. The fluid is a solution of Nigrosin dye in water. We start with the dye in a concentration high enough to be measured with a spectrophotometer. This produces a measurement of $a^*(\lambda)$, the dye-specific absorption coefficient. Knowing $a^*(\lambda)$, we can calculate the absorption coefficient, $a^*(\lambda)$, of more dilute solutions that are suitable for I-Sphere's sensitivity.

Measuring *S*(*a*,λ)

Varying the dye concentration over a wide range while recording the I-Sphere output, we acquire a set of $S(a,\lambda)$ values like that shown in Figure 6. Typical curves of $S(a)$ for individual wavelengths were shown in Figure 2.

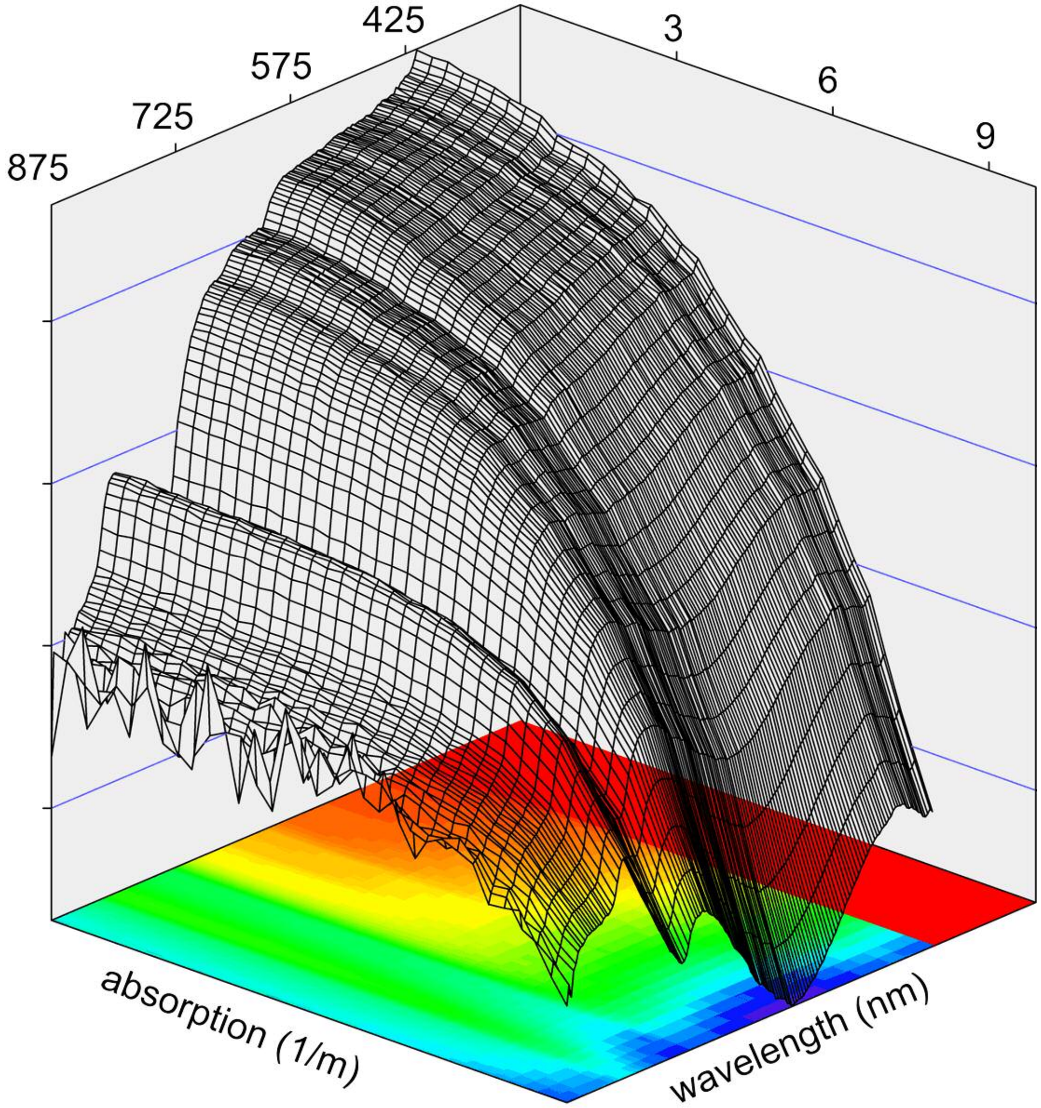

Figure 6. Calibration Data Matrix — Calibration is based on complete measurements of the instrument response to fluids representing a wide range of known absorption values, at all wavelengths. This produces a matrix of values like that shown here.

Calibration Functions

From the $S(a,\lambda)$ dataset we can observe the inverse function, $a(S,\lambda)$. For each wavelength we fit a polynomial to $a(S)$. These fitting functions can then be used to convert measured values of S to calibrated absorptions.

Calibration Maintenance: No Pure Water Required

I-Sphere calibration values are normalized by $S_d(\lambda)$, the output of the instrument when its sphere is empty and dry. Because of the properties of the integrating sphere, small changes in instrument response have proportional effects on "dry" and "wet" readings. Therefore the calibration can be easily maintained in the field or laboratory by periodically recording and normalizing by the dry-sphere response. This is vastly easier than transporting and maintaining a source of pure water. I-Sphere's split-sphere design makes it especially easy to clean and dry.

LABORATORY TESTS

In addition to extensive testing related to calibrations, we measured absorption spectra such as the one shown in Figure 7. The I-Sphere was used to measure a suspension of plant leaf extracts, whose chlorophyll dominates the absorption spectrum. In contrast to spectrophotometer measurements, no special preparation of the sample is required for measurements like these. Scattering from suspended particles did not affect the measurement, and the results are provided in transferable units of inverse meters (m^{-1}) rather than dimensionless absorbance.

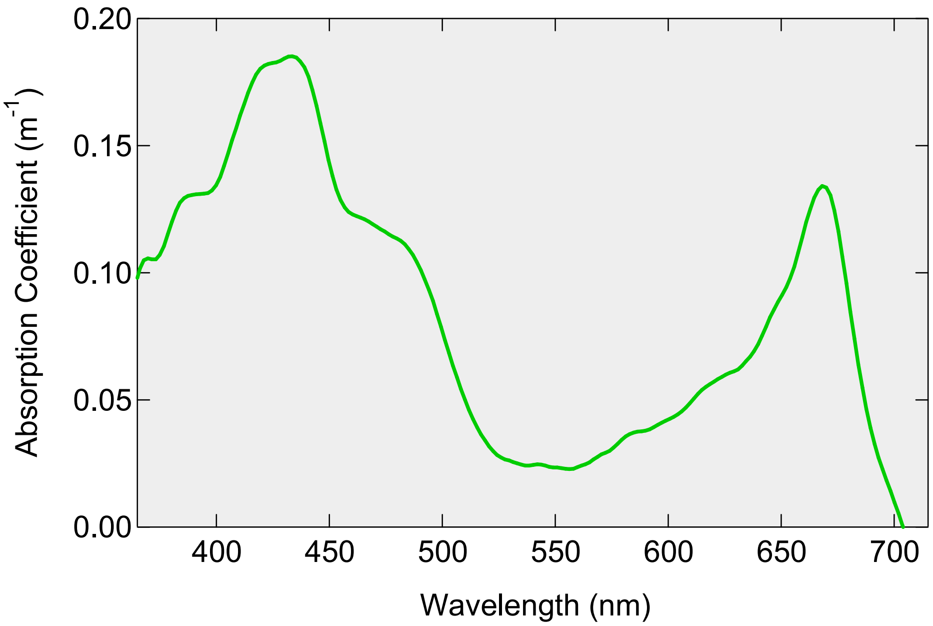

Figure 7. Calibrated spectral absorption of leaf extracts rich in chlorophyll.

FIELD DEPLOYMENTS

We deployed the I-Sphere in Puget Sound and Lake Washington. In the Puget Sound deployment, the I-Sphere was held at a constant depth while collecting a time series of the spectral absorption coefficient. In Lake Washington, it collected depth profiles.

Lake Profiles

Figure 8 shows I-Sphere being deployed in Lake Washington, and Figure 9 shows a typical absorption spectrum. The lake is high in dissolved organic matter, which dominates the absorption.

Figure 8. Deployment — I-Sphere is shown in a profiling cage with pump. For this cast, a filter was mounted on the water inlet, at right, to remove particles.

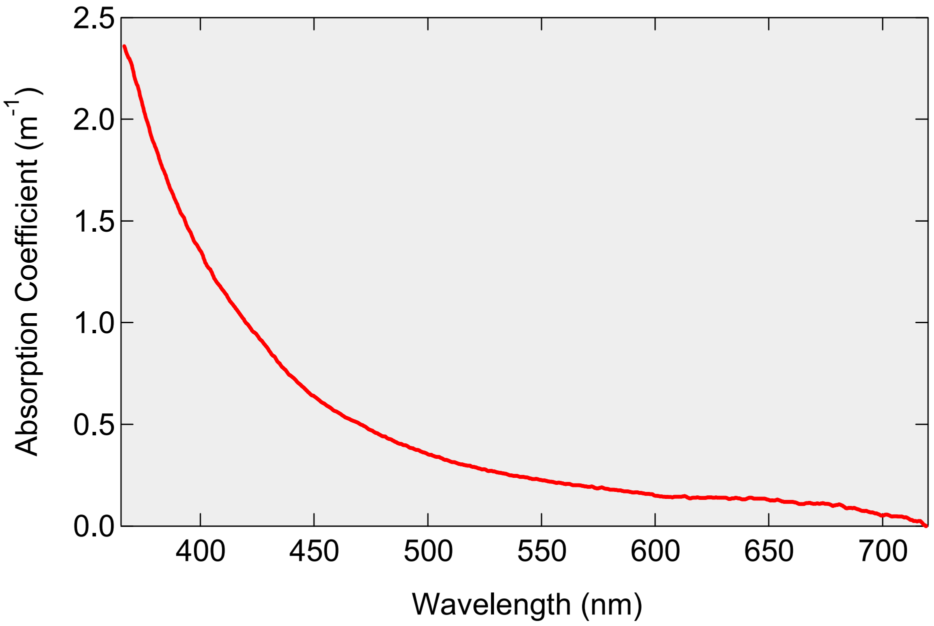

Figure 9. Absorption Spectrum from Lake Washington — I-Sphere was used for profiles in water 65 m deep, with water continuously pumped through it for measurement. The Lake water was not stratified, and the absorption spectrum remained as shown throughout the entire profile.

Salt Water Time Series

We deployed an I-Sphere, simultaneously with a HydroScat-6 spectral backscattering sensor/fluorometer, in Puget Sound for a 5-hour time series, shown in Figure 10, Figure 11, and Figure 12. Although the water changed only slightly during this time, the I-Sphere clearly detected the changes.

Over the course of the experiment there was a slight increase in absorption at short wavelengths. Figure 10 shows one spectrum measured at high tide, at which point the absorption was near its minimum, and one near the end of the experiment, after the tide had lowered about 1.5m. The absorption spectrum indicates a large amount of colored dissolved organic matter, which increased as the tide drew water from shallower areas of the Sound.

Figure 11 shows absorption versus time at four wavelengths in the UV-blue region since those wavelengths showed the greatest variation. These data show a small but steady rise in absorption. This corresponds to a similar rise in scattering and fluorescence recorded by the HydroScat-6, shown below in Figure 12. Note the small events at 13.7 and 15.5 hours, which also appear in the scattering data. Though very small, they are well within the measurement capability of the I-Sphere. With other absorption meters, one would need to consider whether these small absorption events were simply caused by scattering interference. I-Sphere's immunity to scattering allows us to conclude that they are genuine.

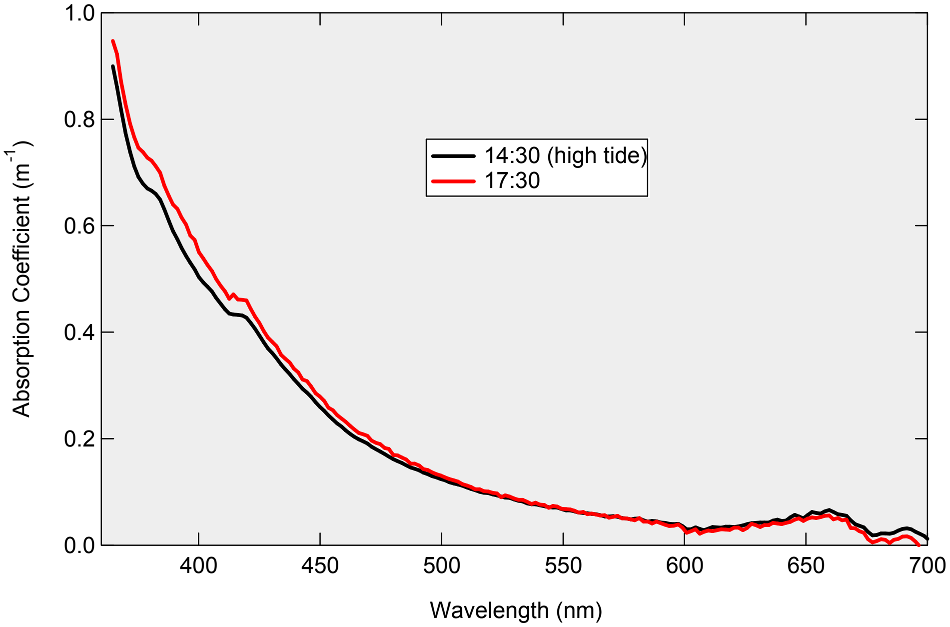

Figure 10. Puget Sound Absorption Spectra — The red trace shows that absorption in UV-blue range increased as the tide went out, drawing water from shallower parts of Puget Sound.

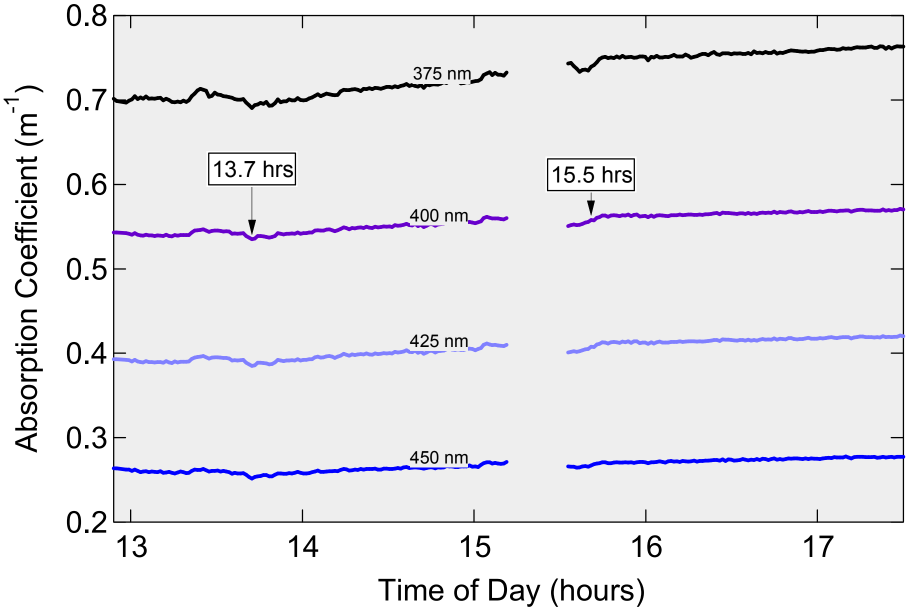

Figure 11. Absorption Time Series — The overall increase in UV-blue absorption correlates with a similar increase in chlorophyll fluorescence, shown in Figure 12. Also note correlation between absorption and scattering at 13.7 and 15.5 hours. (The gap in data between 15 and 16 hours is due to an interruption by the laptop computer used to acquire the data.)

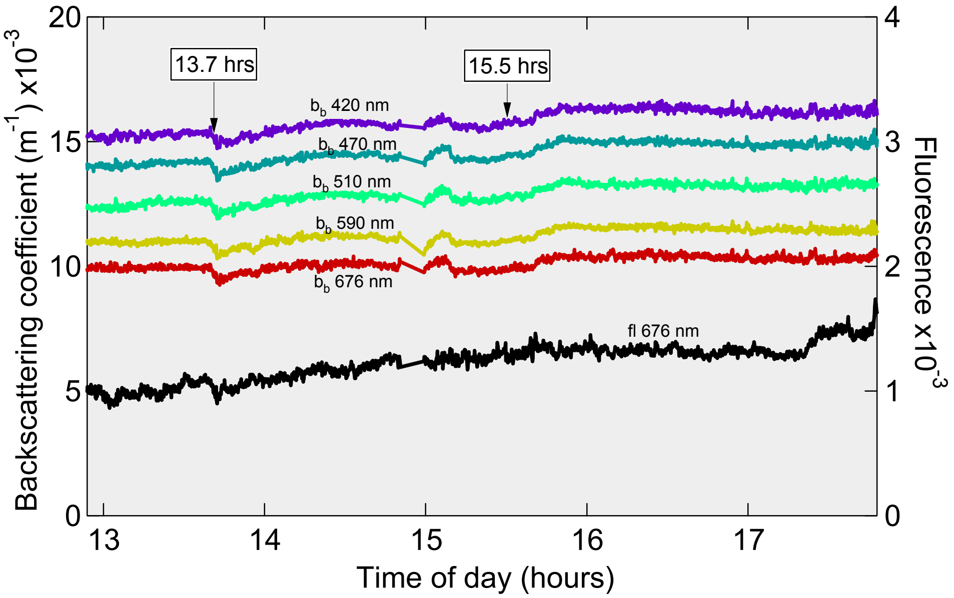

Figure 12. Scattering and Fluorescence Time Series — Data recorded by a HydroScat-6 spectral backscattering & fluorescence sensor, simultaneous with the I-Sphere data shown in Figure 11 and discussed above.

CONCLUSIONS

I-Sphere and HyperSphere offer major improvements over existing absorption instruments for measuring absorption of liquids, either in-situ or in the laboratory:

- No scattering correction required
- Calibration can be monitored and corrected with air readings — pure water is not required
- The integrating sphere is easy to clean and maintain
- Easy flow-through operation
- Wide wavelength range up to 250 - 850 nm
- High spectral resolution (0.3nm per pixel)
- In-situ version rated to 600 m depth.
- Data output in real time, or stored in onboard flash memory
- Supplied software provides real-time processing and display of raw or calibrated data, and control.

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ACKNOWLEDGEMENT

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