Temperature-dependent absorption of water in the red and near-infrared portions of the spectrum

Abstract—We looked at the influence of temperature and salinity on the absorption coefficient of water with emphasis on the red and near-IR portions of the spectrum. The absorption coefficient of pure water was found to have a strong dependence on temperature and little dependence on salinity near the harmonics of the O-H bond-stretching frequency. We found an increase in the absorption coefficient of 0.009 m$^{-1}$°C$^{-1}$ at 750 nm and 0.0015 m$^{-1}$°C$^{-1}$ at 600 nm.

The absorption of water is a fundamental property that influences the passage of light through the water column. Changes in the absorption coefficient will alter measured light properties such as irradiance and reflectance. It has long been known that temperature affects the absorption coefficient of water at the harmonics of the stretching of the O-H bond (Collins 1925; Luck 1963; Tam and Patel 1979). Effects of salinity on the O-H bond are manifested in the reflectance (Hirschfeld 1985) and Raman scattering (Georgiev et al. 1984). Sullivan (1963) showed that salinity affects the absorption of water in the near-IR. The influence of temperature and salinity on the absorption of water in regions of the harmonics are related to formation of tetrahedral-shaped hydrogen-bonded macromolecules of water (Walrafen 1967; Whetsel 1968). Increasing temperature and salinity break up the hydrogen-bonded water macromolecules. Changes in the proportion of the water macromolecules with temperature or salinity are then seen as changes in the absorption of water at harmonics of the O-H bond-stretching frequency. Although it is understood that environmental parameters modify the absorption of water, there has been little effort to quantify the modification.

The role of temperature in determining the absorption properties of water has been re-examined. Højerslev and Trabjerg (1990) recently reported a $\Delta a$ of $+0.003$ m$^{-1}$°C$^{-1}$ from 10 to 30°C for wavelengths between 400 and 600 nm. Apparent changes, as a function of temperature, of the in situ absorption coefficient measured at 750 nm with a reflecting tube absorption meter developed by Sea Tech, Inc., prompted our study of temperature effects on the absorption coefficient at longer wavelengths.

Our study combines shipboard and laboratory experimental data to investigate the dependence of the absorption coefficient on variations in temperature and salinity. Using our results and interpreting the results of others (Collins 1925; Højerslev and Trabjerg 1990), we estimate the size of the change in absorption at the 750-nm absorption maximum and the 600-nm absorption shoulder. We also identify other regions of the spectrum that may have variations in absorption with changes in environmental parameters.

In situ absorption was measured with a reflecting tube absorption meter developed by Sea Tech (Zaneveld et al. 1990). The filter used in the absorption meter had a peak value of 750±2 nm and a full-width, half-maximum bandpass of 10 nm. A Sea Tech transmissometer was used to measure beam attenuation at 660 nm in conjunction with the absorption measurements. These measurements were made from the eastern boundary of the central gyre of the North Pacific Ocean to the Oregon coastal region.

In the laboratory we used a dual-beam Cary 118 spectrophotometer to carry out investigations of the temperature and salinity dependence of the absorption spectrum of water. The spectrophotometer was modified to allow a computer to control the scanning wavelengths and record the measurements. The computer was programed to measure transmittance in...
l-nm intervals between 800 and 700 nm and in 5-nm intervals from 700 to 405 nm. Samples were placed in one beam and the reference path was left empty. A diffuser plate was placed in front of the photomultiplier tube to measure forward-scattered light as well as the attenuated direct beam. A nitrogen purge was connected to the sample box to prevent condensation.

Optically clean freshwater was obtained with a reverse osmosis filter. Samples of 400 ml were placed in a covered beaker in a temperature-controlled bath. A 10-cm quartz cuvette was then filled with sample water and analyzed with the spectrophotometer. Another set of samples was obtained by heating the filtered water to near boiling and mechanically removing bubbles that formed as the sample cooled. The removal of bubbles in the second set of samples provided filtered water that was not contaminated by gasses and microbubbles. Comparisons of the absorption of the two sample waters at identical temperatures showed that microbubbles affected the measured absorption in the blue portion of the spectrum but not in the red. To be able to use both data sets we do not consider the shorter wavelengths in the visible spectrum where effects of microbubble contamination were significant.

A salt-water sample with a salinity of ~29‰ was prepared with an aquarium salt mix. The artificial seawater sample was passed through a 0.3-μm Nuclepore filter before being placed in the sample cuvette.

Temperature was measured before and after each scan to determine the temperature drift during the sampling period. The spectrophotometer took 1 min to scan the 800–700-nm range and another 1.25 min to scan the 700–400-nm range. The temperatures listed on all figures are ±0.5°C for measurements at 21°C and ±1.0°C for every 10°C above or below 21°C.

To ensure that changes in absorption measured were not due to changes in the absorption of the sample cuvette, we measured the absorption of the empty quartz cuvette at two temperatures. Absorption was measured for a cuvette at room temperature and again after the cuvette had been in a freezer (−10°C) for 2 h. The cuvette’s absorption coefficient did not display a discernible temperature dependence.

Højerslev and Trabjerg (1990) suggested a nearly uniform increase in absorption with temperature in the range between 400 and 600 nm. Our results (Fig. 1) and previous work (Collins 1925; Tam and Patel 1979) indicate that absorption at 685 nm is invariant with changes in temperature. Because there was no evidence of a uniform increase with temperature, we have adjusted all curves to the value of absorption at 685 nm as given by Tam and Patel (1979). Correction to this value allows changes in the shapes of the curves to be studied easily. It should be noted that we did not determine the absolute value of the absorption coefficient of water. We searched for changes in the absorption coefficient as displayed by changes in the shape of the spectral absorption curve of water. There was no evidence that the quartz cuvette was responsible for changes in measured absorption, so the changes must be due to changes in the absorption coefficient or index of refraction of water. The changes in the index of refraction would have to be much larger than published values (Austin and Hakiki 1976) to account for the observed effects. Changes in the index of refraction with wavelength thus contribute very little to the measured changes in absorption.

The apparent correlation between temperature and absorption at 750 nm observed during an oceanographic cruise off Oregon (Fig. 2) was our motivation. The correlation of absorption with temperature indicated a temperature response that was too rapid to be accounted for by temperature drift. We therefore
performed a multiple regression with absorption at 750 nm \( [a(750)] \) as the dependent variable with temperature and \( c(660) \) (a proxy measure of the scattering error) as the independent variables. At stations in oligotrophic waters the regression analysis gave values of \( \Delta a(750)/\Delta T \) ranging from 0.0122 to 0.0142 for regressions with an \( r^2 \) value >0.97. For coastal stations the values of \( \Delta a(750)/\Delta T \) ranged from 0.0063 to 0.0091 with \( r^2 \) values >0.97. The experimental design was not to test the temperature dependence of absorption at 750 nm, so we suspect uncontrolled factors caused the differences in the ranges of \( \Delta a(750)/\Delta T \) in the two water types. The consistent and significant dependence of the \( a(750) \) measurements on temperature observed at sea prompted the laboratory portion of this study.

In laboratory experiments at the 750-nm absorption maximum, absorption increased significantly with temperature (Fig. 3). Our results for this region are in good agreement with those of Collins (1925). In both cases the absorption maximum shifts toward 745 nm with increasing temperatures. In both studies there appears to be a crossover region at -775 nm where there is little or no temperature effect. At wavelengths between 775 and 800 nm an increase in temperature causes a decrease in absorption. At 750 nm both studies show an increase in the absorption coefficient of ~0.25 m\(^{-1}\) for a 25°C temperature shift within the range of 0–30°C—the range of oceanographic interest. We found that at a given wavelength the change in the absorption coefficient with temperature is nearly linear (Fig. 4). The magnitude of the slope of the linear regression changes with wavelength which represents the shift in the absorption peak.

The value of the temperature dependence determined in the laboratory is in good agreement with in situ values, with laboratory results \( [\Delta a(750)/\Delta T] \approx 0.009 \text{ m}^{-1} \degree C^{-1} \) being within the range found by in situ measurements. The \( \Delta a(750)/\Delta T \) of 0.009 m\(^{-1}\) degree\(^{-1}\) implies that for a 1° temperature change there is
a 0.36% change in the absorption coefficient at 750 nm.

Tam and Patel (1979) reported that absorption is temperature-dependent at the fifth (600 nm) and sixth (510 nm) harmonics of the O-H bond-stretching frequency. Because of scattering by contaminants such as microbubbles, it is hard to observe these lower harmonics with any certainty. Our results do suggest that the absorption shoulder at 600 nm is raised with increasing temperature. There is also a suggestion of a temperature-dependent shoulder at 660 nm. The work of Højerslev and Trabjerg (1990) also shows the change in the shape of the curve of the absorption coefficient at 600 nm. Their figure 1 furthermore hints at temperature-dependent changes in the shape of the absorption spectrum at 515 and possibly 550 nm. From our measurements and interpretations of their figure 1, we estimate that there is a $\Delta a$ of 0.01 m$^{-1}$ per 6–7°C at 600 nm, or $\Delta a(600)/\Delta T \approx 0.0015$ m$^{-1}$°C$^{-1}$. Using the value of the absorption coefficient from Smith and Baker (1981) at 600 nm (0.245 m$^{-1}$) gives a 4% change in absorption with a 7°C change in water temperature.

An example of environmental parameters affecting measurements is the apparent negative values of the absorption coefficient for some Gelbstoff measurements. Figure 5 is a portion of two Gelbstoff measurements made recently at Lake Pend Oreille, Idaho. For these measurements water samples were collected and filtered through a GFF filter. The filtered water was placed in a dual-beam spectrophotometer with a pure water sample in the reference path. The collected water had temperatures as low as 4°C and the pure water reference was at room temperature. When the Gelbstoff absorption measurements were made, the difference in the absorption of water caused an apparent negative absorption of Gelbstoff in the near-IR. Allowing the Gelbstoff samples to reach room temperature removed the apparent negative absorption. Measurements of Gelbstoff in a water sample is one of the applications of optical measurements in which one needs to take account of the influence of environmental parameters on the measurement itself.

Sullivan (1963) showed artificial seawater absorbed more strongly than distilled water with a $\Delta a$ of 0.04 m$^{-1}$ for wavelengths >735 nm. Our results for the near-IR portion of the spectrum indicated the change in the absorption coefficient between fresh and saline water is about a quarter of that found by Sullivan. Because the artificial seawater that we used was not passed through a reverse osmosis filter we have reason to suspect that there may have been some very small particles in the sample that increased the backscattering error in the measurements at shorter wavelengths preventing us from making observations of the effects of salts in the 600-nm region.

The greatest effect of temperature on the absorption coefficient of water occurs at frequencies near the harmonics of the O-H bond-stretching frequency. The region of the fourth harmonic’s (750 nm) absorption maximum has the largest temperature effect in the portion of the spectrum between 500 and 800 nm. The absorption shoulder in the 600-nm (the fifth harmonic) region also has a significant temperature dependence. Our analysis indicates that temperature may also affect the absorption coefficient at 515, 550, and 660 nm. Our results indicate that the effect of temperature on absorption is much greater than that of salinity.

With the development of in situ measuring devices for absorption and the increased use of remote sensing, it becomes imperative that we understand the influence of environmental
properties on absorption in the waters being measured. Our work attempted to identify portions of the spectrum that may be affected by environmental parameters. We have given estimates of the effects of temperature on absorption at the 750-nm absorption peak and 600-nm absorption shoulder. Further research is needed to identify wavelengths at which the absorption coefficient is influenced by environmental parameters and to quantify the magnitude of these effects. The studies of temperature effects on absorption have been restricted to pure water, so the effect of temperature on the absorption of saline solutions is still to be studied. When the effects of environmental parameters are understood we will be able to better interpret measurements of absorption and related optical properties.

W. S. Pegau
J. R. V. Zaneveld

School of Oceanography
Oregon State University
Corvallis 97331-5503

References


