Measurements of inherent optical properties of pure water

Technical note

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1. Introduction

Knowledge of the inherent optical properties of pure water is important for many optical application related to natural waters. Despite many measurements of pure water absorption the variations in published values are large especially in the UV spectral region where absorption by organic compounds is orders of magnitude higher than that of water. Errors by contamination with organic compounds can therefore be large, either because purification of water to an optically pure state is
difficult or/and contamination after purification is difficult to avoid.

The temperature and salinity coefficients of pure water absorption have been measured several times to enable in situ measurements with optical instruments under conditions of varying temperatures and salinities. Measurements with a higher spectral resolution are rare, and values for the NIR/SWIR spectral region are not yet published.

This technical notes describes new measurements of pure water absorption in the UV/VIS spectral region and measurements of the temperature and salinity coefficient of pure absorption for the whole spectrum of 300 to ~3000 nm.

2. Light absorption of pure water

The accuracy for measurements of light absorption of pure water is still limited. Large discrepancies between different published measurements exists in the shorter VIS and UV spectral region. A major reason for the discrepancies in UV is a possible contamination with organic compounds of the purified water used for these measurements, in case the purification is not sufficient or the water is again contaminated after been taken from the purification system.

Measurements of Smith and Baker (1981) were performed in situ in the clearest natural waters. It can be assumed that this natural water contained significant amounts of light absorbing compounds (CDOM) and that purified water has a lower light absorption in the UV. If this assumption is true data of Smith and Baker (1981) set an upper limit for the pure water absorption at wavelength < 600 nm. Published values below this upper limit are those of Quickenden and Irvin (1980), Sogandares & Fry (1997), Pope and Fry (1997), Lu (2006), Wang (2008), and Cruz et al. 2009.

2.1. Methodological approach

Measurements with a PSICAM are made to verify pure water absorption in the UV/VIS spectral region and to examined a possible contaminations of the purified water in detail. Purified water was taken from a high quality purification system. The absorption of this water was measured against air in a large integrating sphere using a slightly altered PSICAM set-up.

2.2. Quality of the purified water

The water was taken from a Millipore MilliQ Advantage A10 purification system that was connected to a Millipore ELIX pre-treatment system. In short the ELIX produces purified water of medium quality (15 MΩ cm–1), the water is stored in a 30 l tank for >12 h under anti-bacterial UV treatment for degassing. Purified water (18.2 MΩ cm–1, < 6ppm TOC) is taken from a Millipore MilliQ Advantage A10 system that takes pre-treated water from the 30 l tank. This water is filled into clean glass bottles that were washed before with purified water several times. The water is cooled in a water bath to bring it to ~20.0°C in a short time and measured less than 30 min after being taken. Several test were performed to control water quality and examine different contamination source by performing measurement in a 2m liquid capillary system (LWCC, WPI) at wavelengths < 300 nm. The test confirmed that the manipulation of the purified water during one measurements in the PSICAM does not introduced a significant contamination by organic compounds. It also showed that the optical water quality from the purification system was constant and was comparable to purified water from other purification systems. E.g. water recirculating several times through the MilliQ A10 system (18.2 MΩ cm–1, < 4ppm TOC) did not show a
significant lower absorption than water taken without a recirculation in the system. On the other hand water used several times in the PSICAM showed an increasing absorption in the UV.

2.3. PSICAM measurements

Measurements were performed in a large PSICAM cavity (diameter 130 mm). The lamp source of the PSICAM was shifted to the top of the cavity and the PSICAM was filled to just below the light source to avoid that the light source and the detector are submersed in water. A submersion would lead to larger deviations in the overall measures light intensity as the change in refractive index (air vs. water) influences the light reflection on both fibre-optic tips. Two light sources were used 1) a tungsten halogen lamp (spectral output: 350 – 750 nm) and a Xe-UV lamp (spectral output 280 – 600 nm). The light intensity inside the cavity is measured for large wavelength regions (polychromatic) with a RAMSES (TRIOS) spectrometer. The spectral output of the lamps was restricted to narrow regions using several type of short-pass and long-pass filters to avoid problems 1) with inelastic Raman scattering of water and 2) due to second order effects of the radiometer used. The absorption spectrum was measured several times but separately with different cut-off filter for spectral regions of 300 – 340 nm, 360 - 390 nm, 380 – 440 nm, 350 – 600 nm and 400 – 720 nm. The results were combined to a single spectrum.

The PSICAM was calibrated for the different spectral regions using a solution of the dye Nigrosin with known absorption. The absorption of the dissolved Nigrosin was measured with a 10 cm cuvette in a Perkin-Elmer Lambda 950 spectrophotometer against purified water. The accuracy of the final PSICAM measurement directly depends on the accuracy of the spectrophotometer's calibration. This is regularly done using NIST certified neutral density filters with an accuracy of ca. 2%. The precision of the PSICAM measurement is in the range of 0.0008 m⁻¹ (see Röttgers & Doerffer 2007). During this calibration the wall reflectivity of the PSICAM cavity is determined by measuring purified water against the Nigrosin solution. The reflectivity is calculated from these measurements with an assumed pure water absorption (Pope & Fry 1997, Lu 2006, Wang 2008) and the measured absorption by Nigrosin (see Röttgers et al. 2005). The influence of an error in the

![Fig. 1: Uncorrected absorption spectra of purified water. Shown are measurements in different wavelength regions. Some spectra showed artefacts at ~350, ~420 and ~470 nm induced by Raman scattering of water by lamp peaks at ~ 300, ~360, and ~410 nm.](image)
absolute values of pure water absorption in the UV/VIS (300-500 nm) is negligible as the Nigrosin absorption is two orders of magnitude higher than that of pure water. The following measurements of pure water absorption are based on the assumption that the wall reflectivity is not different from the measured reflectivity (filled with water) when the cavity is empty (filled with air).

2.4. Results

The raw spectra showed a strong influence by Raman scattering induced by strong intensities peak in the lamp spectrum (Fig. 1). These were avoided by using several cut-off filter in the UV and construction the complete spectrum from measurements with these different filter in front of the light source. Measuring the same purified water several time by filling it several times in the PSICAM cavity showed that the absorption at shorter wavelengths increased, probably by contamination of the water during this severe handling (Fig. 2). The obtained pure water absorption spectrum was very similar to published values in the range of 500 to 750 nm (see Fig.3). At shorter wavelengths it deviates significantly, showing higher values around the absorption minimum and lower values at even shorter wavelengths. Measuring the same purified water several time by filling it several times in the PSICAM cavity showed that the absorption at shorter wavelengths increased, probably by contamination of the water during this severe handling (Fig. 2). The discrepancies at the absorption minimum can be explained by the not perfect optical setup as we did not use a isotropic light field and reflection on the water surface inside the cavity would induce several kinds of artefacts. Indeed the same measurements done with a more isotropic light field (using an additional scattering sphere in front of the fiber optics) resulted in lower absorption value at < 500 nm (data not shown). In this case the absorption at 400 – 450 nm are very similar to the data of Pope and Fry 1997, but the absorption at shorter wavelengths is even lower. As the real error induced by non-isotropic light field can not be quantified the values below 500 nm are not reliable and, hence, are not comparable in accuracy with the data of Fry and co-workers. However, the large deviations in the UV cannot be completely explained by this error.

Fig. 2: Pure water absorption: uncorrected data of different experiments showing variations due to a contamination of the purified water.
2.5. Conclusions

As shown in Fig. 3 the conducted measurements reproduced former results of other published work at wavelengths >500 nm, but gave higher absorption coefficients in the range of 400 – 500 nm. (The data of Smith and Baker (1981) are for natural waters not pure water). This higher coefficients can be explained by methodological errors done with our setup, as filling the PSICAM's sphere with water changes the optical pathways inside the sphere due to the higher refractive index (real part) of water compared to air. Considering this error the data suggest that measurements of Fry & Co-workers in the range of 420-500 nm are correct, as e.g. the position of spectral shoulders are reproduced. However, the absorption coefficients at <400 nm are below those of Fry and co-workers and closer to data of Quickenden & Irvine (1980). Considering that there is still an overestimation by the refractive index error, the absorption of pure water at <400 nm remains questionable. The main error source here might be contamination of the pure water by handling during the experiments (see Fig. 2).
3. Temperature and salinity dependence of pure water absorption

The accuracy for measurements of the temperature and salinity coefficients of pure water absorption is better than that for pure water alone but measurements were only performed for the VIS and NIR spectral region (300 – 900, respectively 400 - 830 nm). Measurements with integrating sphere are more accurate but discrepancies between these and spectrophotometric measurements exist at some wavelength regions (e.g. 600 -740 nm). No measurements exists for the longer NIR and SWIR spectral region (~830 – 3000 nm). However, several temperature-dependent absorption measurements were done for the longer wavelengths (>3000 nm) (e.g. Larouche et al.

![Figure 4: Published data of the salinity coefficient of pure water absorption as a function of wavelength](image1)

![Figure 5: Different spectra of the temperature coefficient of pure water absorption, showing the available published data with higher spectral resolution.](image2)
Fig. 6: Uncorrected spectra of the salinity coefficient of pure water absorption determined with cuvettes of different pathlength 0.2 – 100 mm.
2008), and some absorption measurements of inorganic solution exist, e.g. NaCl (Max & Chapados 2001).

3.1. Spectrophotometric measurements of $\Psi^S$ in the VIS/NIR/SWIR spectral region.

The salinity coefficient $\Psi^S$, was determined by measuring the difference in optical density (OD) between pure water and a 100gL$^{-1}$ NaCl (99.5%, combusted) solution. The measurements were done in a Lambda 950 UV/VIS/NIR spectrophotometer (Perkin Elmer) in cuvettes of different pathlengths (0.2, 1, 2, 5, 10, 50, and 100 mm). Due to the strong absorption of water the pathlength has to be reduced with increasing wavelengths allowing light to reach the detector and, thus, to perform an accurate transmission determination.

Cuvettes with following pathlengths were used, each for a specific wavelengths region:

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<tr>
<th>Pathlength (mm)</th>
<th>Wavelengths (nm)</th>
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<tbody>
<tr>
<td>100</td>
<td>300 - 800</td>
</tr>
<tr>
<td>50</td>
<td>600 - 1300</td>
</tr>
<tr>
<td>10</td>
<td>900 - 1350</td>
</tr>
<tr>
<td>5</td>
<td>950 - 1850</td>
</tr>
<tr>
<td>2</td>
<td>1300 - 2300</td>
</tr>
<tr>
<td>1</td>
<td>1350 - 2400</td>
</tr>
<tr>
<td>0.2</td>
<td>1750 - 2700</td>
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The spectrophotometer's baseline was recorded by filling two cuvettes with purified water and placing one in the sample and one in the reference beam. Measurements were done with the reference cuvette filled with purified water and the sample cuvette filled with a 100.0 or 200.0 g L$^{-1}$ NaCl solution. Spectral resolution was set to 1 nm, scan speed was variable and between 60 and 200 nm min$^{-1}$, it was adjusted individually for specific wavelength regions to have a good signal to noise ratio over the whole spectrum measured. The slit width was set to “servo” to allow automatic light intensity adjustments by the spectrophotometer. For regions outside of the absorption maxima the slit width was < 4 nm, in the absorption maxima at ~1950 and > 2300 it was up to 20 nm. The measurements are adversely affect be two factors, 1) the increase of pure water scattering by the salt theoretically leads to an overestimation of the OD, 2) the increase in refractive index of salt water compared to pure water leads to an underestimation of the measured OD as it changes the reflection at the glass/water and water/glass boundary. The effect of 1) is significant only at shorter wavelengths as scattering of water decreases strongly with increasing wavelength. The effect of 2) is significant at all wavelengths and was corrected by calculating the Fresnel reflections by

$$R(\lambda) = \left[\frac{(n_1(\lambda) - n_2(\lambda))}{(n_1(\lambda) + n_2(\lambda))}\right]^2$$

where $n_1$ is the index of refraction of the glass material and $n_2$ that of the water sample (either pure water or salt water [NaCl]).

The real transmission in the sample ($T_r$) is the quotient of the effective transmission in the reference sample ($T'$) and that in the sample ($T$) as $T_r = T/T'$. The reflection of the water/glass (or glass/water) boundary of the reference cuvette, R and that for the sample cuvette, $R'$ are used to correct the
measured transmission $T_m(\exp(-OD))$ and to calculate the real transmission in the sample cuvette:

$$T_r(\lambda) = T(\lambda)/T'(\lambda) = T_m(\lambda) \times (1-R'(\lambda))/(1-R(\lambda))$$

All measured spectra were corrected for this refractive index influence (see figure 5). This correction included only the change in reflection at the first cuvette window. Some visible offsets remain between spectra measured with different path length. Taking the spectrum measured with a 100 mm cuvette as given the other spectra were step by step adjusted with a constant offset to have the same values in the overlapping regions. The difference in scattering between pure water and the salt solution was not corrected. Theoretically its influence is only significant at the shortest wavelengths. These spectra were then combined to a single spectrum of the salinity coefficient, $\Psi_s [m^{-1} \text{ PSU}^{-1}]$(see Figure 6). This was calculated as

Fig. 7: Salinity coefficient of pure water absorption for different wavelength regions.
\[ \Psi^6 = -\ln(1 - T_r) / l / [\text{NaCl}], \]

with \( l \) being the pathlength in meter, and \([\text{NaCl}]\) the PSU equivalent salt concentration.

3.2. Measurements of \( \Psi^6 \) in the UV spectral region.

Measurements of \( \Psi^6 \) in the UV are difficult. As water absorption is very low, the salinity coefficient is expected to be below the detection limit of the PSICAM. To increase sensitivity high NaCl concentration have to be used. Even the optical pure NaCl salt contains traces of organic compounds as well as traces of bromide, both absorbing strongly in the UV. The absorption of the organic compounds can be reduced by combustion of the salt at temperatures of 400 - 500 °C. However absorption by bromide is significant at < 350 nm. For these experiments NaCl of high purity is needed (99.99 to 99.999 %) to reduce absorption by bromide.

It was impossible to prepare NaCl solution without a significant absorption at 300 – 400 nm. Either the absorption of contaminants or of the salt itself made it impossible to determine the salinity coefficient of the water absorption in the UV.
3.3. Spectrophotometric measurements of $\Psi_T$ in the VIS/NIR/SWIR spectral region

The temperature coefficient, $\Psi_T$, was determined by measuring the difference in optical density (OD) between two water samples of different temperatures. The measurements were done in a Lambda 950 UV/VIS/NIR spectrophotometer (Perkin Elmer) in cuvettes of different pathlengths (0.1, 0.2, 1, 2, 10, and 100 mm). Due to the strong absorption of water the pathlength has to be reduced with increasing wavelengths allowing light to reach the detector and, thus, to perform an accurate transmission determination. The cuvettes used (type Helma 165) were surrounded by flow-trough cooling mantels. The mantels of the two cuvettes (reference and sample) were individually connected to two thermostated water bath (Haake, DC1 and Haake DC 50) and the temperature inside the cuvettes was controlled with a precision of 0.1°C. The baseline was recorded when both cuvettes were filled with freshly made purified water and set to 19.0 °C. Afterwards the temperature of the sample cuvette was increased to up to 60°C (range: 25 – 60 °C) and the measurement started. Several replicated (n = 3 - 6) were conducted for each temperature and path length. Cuvettes with following pathlengths were used, each for a specific wavelengths region:

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<tbody>
<tr>
<td>100</td>
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<tr>
<td>0.2</td>
<td>1750 - 2700</td>
</tr>
<tr>
<td>0.1</td>
<td>1800 - 2000</td>
</tr>
</tbody>
</table>

The obtained ODs were not further corrected as the influence by the differences in refractive index (e.g. see Max & Chapados 2009) and scattering between water of different temperatures are insignificantly small (see Trabjerg and Hoyerslev 1996) at most wavelengths (but see below). Only in the UV the influence of the change in refractive index is significant, leading to an overestimation of the measured coefficient. Because of the experimental setup, corrections could only be made for the changes in reflections at the first cuvette window using the known refractive index of water at different temperatures and that of the glass material of the cuvette window. The theoretically calculated change was wavelength-independent in the range of 300 – 1000 nm and lower than the obtained standard deviation for the measurement of the coefficient. However, ignoring this offset would give positive values for the temperature coefficient in the range of 300 – 700 nm, that would give significant error in the region were water absorption is very low (300 – 500 nm). The temperature coefficient is then calculated using the obtained transmission, the cuvette path length, $l$, and the temperature difference, $\Delta T$, as follows

$$\Psi_T = -\ln(1-T_r)/l/\Delta T.$$  

It is further considered that the temperature coefficient at <450 nm should be very near to zero because of the low absolute water absorption. As a small adjustment for the difference in refractive index (see above) an offset of 0.0001 m$^{-1}$ °C$^{-1}$ was subtracted from all data to bring the averaged spectrum of the temperature coefficient to zero in the range of 300 to 400 nm.
Fig. 8: Uncorrected data of the temperature coefficient of pure water absorption.
3.4. Conclusions

The obtained spectra of $\Psi^T$ and $\Psi^S$ showed basically the same spectral signatures in the VIS range as spectra published by others (Langford et al. 2001, Sullivan et al. 2006). However, there are significant differences at specific wavelengths, e.g. at 600 – 700 nm for $\Psi^T$, and at 700- 800 nm for $\Psi^S$. Some difference might be due to differences in the optical resolution, e.g. the additional trough at ~738 nm in the spectrophotometric measurements compared to the ACS and PSICAM measurements (this trough is commonly observed in photometric measurements of CDOM in seawater and is smoothed out in instruments with a coarser optical resolution). The discrepancies in the absolute values at some wavelengths can be explained by measurement errors and missing corrections for changes in scattering by water and the refractive index with temperature and salinity. At UV wavelengths the absolute values of the coefficients are considered to be very low as the pure water absorption is very low, and deviation from zero is most likely due to measurement errors. In case of $\Psi^T$ the absolute value is not significantly different from zero due to relatively low signal to noise levels. In case of $\Psi^S$ the measured OD in the UV is strongly increasing with shorter wavelengths and is likely to be due to absorption by organic contaminants in the NaCl solution. In both cases the exact coefficients for these wavelengths cannot be determined, but are considered to be very low and can be neglected as the absorption by non-water material (e.g. CDOM) is very high at these wavelengths.

![Fig. 9: Comparison of different published measurements of the temperature coefficient for the UV/VIS spectral region. Data from Röttgers & Doerffer 2007 are considered as instrument correction factor only!](image-url)
4. Final spectra of the salinity and temperature coefficients of pure water absorption.

4.1. Salinity coefficient:

The measured data (300 – 2600 nm) were combined with data from J. J. Max (2600 – 14000 nm). The latter were calculated from measured spectral data of NIR/SWIR - FTIR absorption of NaCl solutions (Max & Chapados 2001). The values at <450 nm were set to zero as the absolute values were not significantly different from zero or could not be determined due to contamination problems of the NaCl solutions used (see above).
Fig. 12: Final spectrum of the salinity coefficient (red). Different spectral regions are enlarged by linear factors (see legend) to show the spectral distribution in these regions. Uncertainty is indicated by 2 times the standard deviation of the measurement error.

Fig. 13: Relative change in pure water absorption per PSU salinity.
4.2. Temperature coefficient:

The measured data (300 – 2600 nm) were combined with data from J. J. Max (2600 – 4000 nm) and data measured earlier using a PSICAM (“Röttgers unpublished” in Fig. 11, 380 – 700 nm). The values of J.J. Max were calculated from measured spectral data of NIR/SWIR - FTIR absorption of pure water at different temperatures (Larouche et al. 2008).

At < 380 nm the values measured here were not significantly different from zero and were, hence, set to zero to avoid artefacts in the water absorption spectrum when temperature are strongly deviating from 20 °C.

Fig. 14: Final spectrum of the temperature coefficient in the UV/VIS spectral region

Fig. 15: Final spectrum of the temperature coefficient (red). Different spectral regions are enlarged by linear factors (see legend) to show the spectral distribution in these regions. Uncertainty is indicated by 2 times the standard deviation of the measurement error.
Fig. 16: Relative change in pure water absorption per °C.
5. References:


