

The optical properties of pure water

H. Buiteveld

Institute for Inland Water Management and Waste Water Treatment, Ministry of Transport and Public Works, P.O. Box 17,
8200 AA Lelystad, The Netherlands.
tel:+31-3200-70737 fax:+31-3200-49218

J.H.M. Hakvoort and M. Donze

Delft University of Technology, Faculty of Civil Engineering, P.O. Box 5048, 2600 GA Delft, The Netherlands

ABSTRACT

The optical properties of pure water are basic input data for many geophysical investigations such as remote sensing of surface water and underwater radiative transfer calculations. Knowledge of the spectral properties of components in surface water is required for accurate interpretation of measured reflection and attenuation spectra in terms of their concentrations. Also the sources and sizes of errors in the basic data must be known.

Absorption measurements were done with a submersible absorption meter in the temperature range 2.5 till 40.5 °C. The scattering of pure water is recalculated using the Einstein-Smoluchowski equation. The input for this equation is evaluated and the temperature dependency is included. New values for the absorption coefficient are given based on these results and analysis of data from the literature. Absorption in the wavelength range 300-550 nm is lower than presently used values. In the wavelength range above 700 nm the spectrum has a different shape. A formulation of the effect of temperature on the absorption spectrum is given.

1. INTRODUCTION

From reflectance spectra and attenuation spectra measured in the optical window concentrations of aquatic humus and suspended matter such as algae and silt in surface water are derived. Decomposition of measured spectra in terms of concentrations requires knowledge of the inherent optical properties of these components. Also the sources and sizes of errors in these basic data must be known. The inherent optical properties of pure water can be used to test and apply algorithms to decompose reflectance spectra and to calibrate instruments.

The inherent optical properties of surface water are the absorption coefficient a , the scattering coefficient b and the volume scattering function β . The beam attenuation c is the sum of the absorption and scattering coefficients. These properties depend only on dissolved and suspended matter in the water and water itself and not on the geometry of the light field. The coefficients are defined for an infinitesimally thin layer of medium, illuminated at right angles by a narrow parallel beam of monochromatic light. The fraction of the incident flux that is absorbed, divided by the thickness of the layer, is the absorption coefficient. The fraction of the incident flux that is scattered, divided by the thickness of the layer, is the scattering coefficient. The angular distribution of the scattered light is specified by the volume scattering function. The diffuse attenuation coefficient is an apparent optical property which depends on the geometry of the light field, it specifies the attenuation of solar irradiance in natural waters.

The optical properties of pure water were reviewed by Morel ¹, Smith and Tyler ² and Smith and Baker ³. Several methods were used to determine these properties. The beam attenuation coefficient of water can be measured by spectrophotometry and the absorption coefficient then is calculated by subtraction of the scattering coefficient from the beam attenuation coefficient. Optoacoustic measurements ⁴ yield absorption directly. Another way to derive the absorption coefficient of pure water is from measurements of the diffuse attenuation coefficient in very clear natural water ³. Smith and Baker ³ presented diffuse attenuation and absorption coefficients of water that are in common use now. These data were based on measurements from several sources and sound judgement as to what source to use. They arrived at the absorption spectrum in the following way:

1. At wavelengths smaller than 380 nm the spectrum was calculated from direct measurements of the diffuse attenuation coefficient.
2. At wavelength between 380 and 700 nm the spectrum was based on beam attenuation measurements of Morel and Prieur ⁵. In the wavelength range 600-700 nm these authors shifted their measured spectra in a vertical direction to obtain the same

3. values as found by Sullivan ⁶. So from 600 to 700 nm the results of Smith and Baker are based on Sullivan's work. At wavelengths above 700 nm the average of beam attenuation data measured by Curcio and Petty ⁷, James and Bridge ⁸, Clark and James ⁹ and Sullivan ⁶ are used, as was done by Smith and Tyler ².

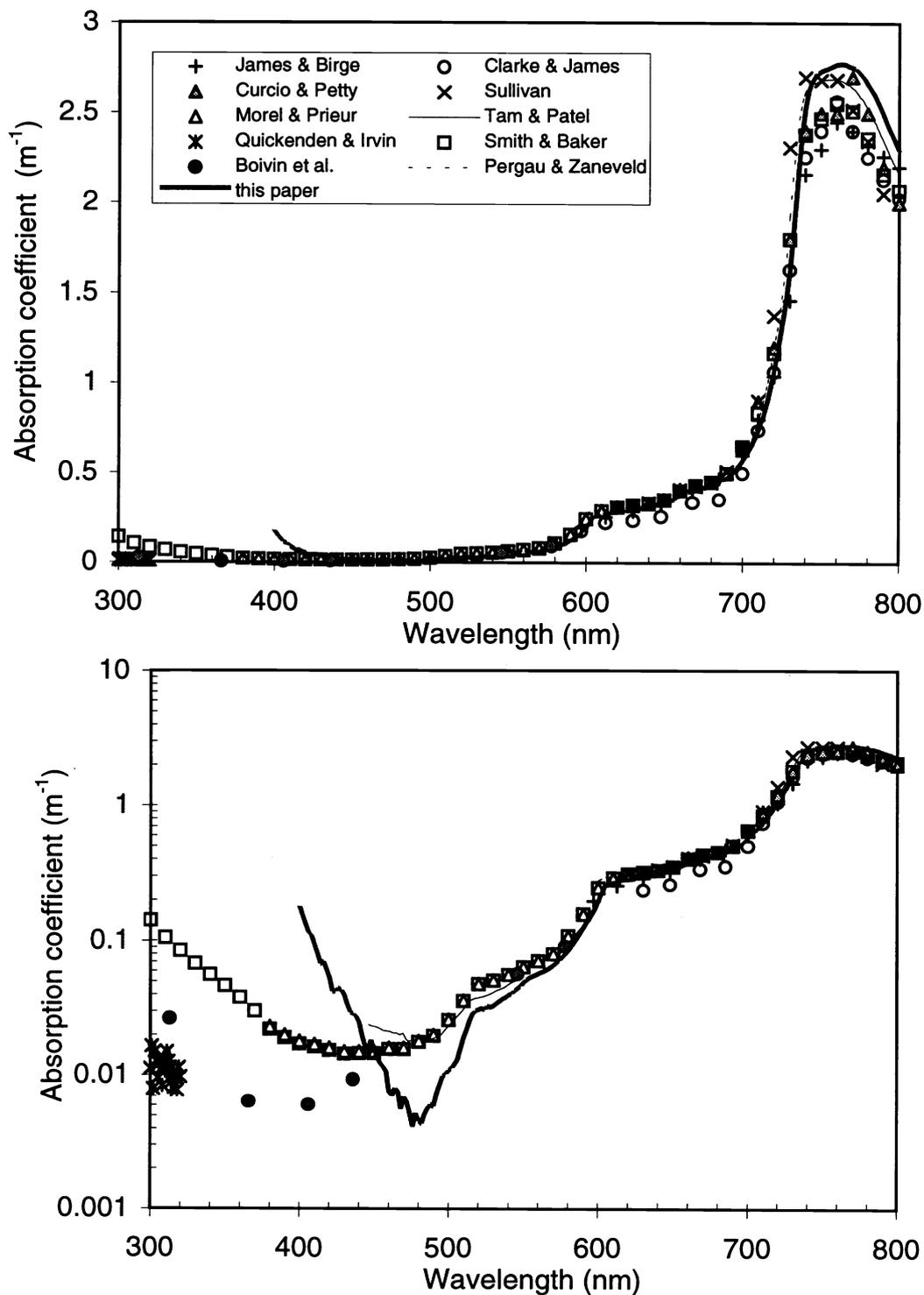


Figure 1 a and b. Absorption spectra (logarithmic and linear scale) used by Smith and Baker³ including our measurement and other resent measurements.

The shape of the water absorption spectrum in the visible wavelength range has the following characteristics. In the 300-700 nm wavelength range absorption is low. Published spectra show minima at 490 nm⁵, 480 nm⁴ or 380 nm¹⁰. This variation occurs due to impurities of the water as explained further on. The absorption increases with increasing wavelength and has shoulders at 510 nm, 600 nm and a small one at 660 nm. From 690 nm absorption increases rapidly until approximately 740 nm. At still higher wavelength the absorption decreases again. In Figure 1a and 1b the absorption spectra from Smith and Baker³ are shown together with our measurements and the values measured by Tam and Patel⁴, Boivin *et al.*¹⁰ Quickenden and Irvin¹¹ and at 21°C by Pegau and Zaneveld¹². Our values are the average of 16 absorption spectra between 10° and 40.5°C with a mean temperature of 20.1°C.

Among different authors differences between the absorption spectra are significant in the complete visible wavelength range. These must be explained by combinations of several possible errors:

1. False reflections of light in the optical equipment cause problems in the accurate determination of low attenuation coefficients. An extensive analysis of such errors is given by Quickenden and Irvin¹¹. Over a limited wavelength region this error results in a vertical shift of the spectrum, which may be positive or negative.
2. The values can be too high due to scattering by dust and micro air bubbles. Large particles lead to a vertical upward shift of the spectrum, small particles to an exponential increase which decreasing wavelength.
3. Absorption by other molecules than water also leads to overestimation of absorption. Large and complicated organic molecules, generally summarized as aquatic humus, begin to absorb significantly below 600 nm. This absorption increases in first approximation exponentially with lower wavelength, the exponent varies between 0.010 nm⁻¹ and 0.021nm⁻¹¹³. Contamination of the water by significant concentrations of specific organic molecules and several ions leads to specific broad absorption bands in the ultra violet part of the spectrum.
4. Højerslev and Trabjerg¹⁴ observed that water absorption depends on temperature and Pegau and Zaneveld¹² found that this effect was especially large in the wavelength range 700-800 nm. This temperature effect was however until recently not identified as important. The spectral shape of this effect is one of the subjects of this paper.

In practice it is usually impossible to ascribe observed errors and differences among published spectra to these single causes. Boivin *et al.*¹⁰ and Quickenden and Irvin¹¹ measured attenuation coefficients in the 300-600 nm wavelength range which are significantly lower than the values reported before. This can probably be attributed to better purification of the water used¹¹. Højerslev and Trabjerg¹⁴ and Pegau and Zaneveld¹² measured the temperature dependence of the absorption coefficient. This effect increases with the absorption coefficient and it is strongest at the harmonics of the stretching of O-H bonds. In the range 400-600 nm Højerslev and Trabjerg¹⁴ found a temperature dependency of 0.0015 m⁻¹°C⁻¹. Pegau and Zaneveld¹² found a temperature dependency of 0.0071, 0.0092 and 0.0113 m⁻¹°C⁻¹ at respectively 755, 750 and 745 nm.

In this paper absorption measurements made with a submersible absorption meter¹⁵ in the temperature range 2.5 till 40.5 °C are given. The scattering of pure water is recalculated using the Einstein-Smoluchowski equation¹⁶. The input for this equation is evaluated and the temperature dependency is included. New values for the absorption coefficient are given based on these results and analysis of data from the literature.

2. ABSORPTION MEASUREMENTS

2.1 Materials and methods

Twenty five spectra of the sum of absorption and backscattering of pure water were measured with a submersible absorption meter¹⁵ in the temperature range from 2.5°C to 40.5°C. This submersible absorption meter measures radiance attenuation spectra in a Lambertian diffuse light field. If measured close to the light source the radiance forwardly scattered out of the normal direction is replaced by path radiance. The radiance attenuation approaches the sum of absorption and backscattering. In clear samples the radiance attenuation is equal to the absorption.

The sample compartment of the submersible absorption meter was filled with pure water. This was obtained by reversed osmosis followed by distillation. Conductivity of this water was 1.5 µS. A series of temperature was made from 2.5° to 40.5°C. Temperature was measured with an accuracy 0.05°C. Light reflection from the water surface into the sample compartment was prevented by a black absorption panel behind the radiance detector. Absorption spectra were measured over a path length of

0.120 m. At each temperature three spectra were averaged. Repeated measurements at a single temperature had a standard deviation of 0.03 m⁻¹.

2.2 Results

In Figure 1a and 1b the average of the spectra measured between 10 and 40.5 is shown. Averaging reduced noise; it is allowed since the dependence of absorption on temperature is linear (see below). This spectrum shows the general characteristics as described in the introduction. Most unsolved problems occur below 500 nm, considered in more detail in the discussion. In the 500-700 nm wavelength range good agreement occurs with the data of Tam and Patel. In the 700-800 nm wavelength range the measured spectra were up to 20 percent higher than the spectra of Smith and Baker³, here the temperature dependence is important.

The absorption spectrum of water as a function of temperature is shown in Figure 2. Absorption increases with temperature in the 400-780 nm wavelength range and decreases in the 780-800 nm range. The absorption maximum shifts towards a lower wavelength at increasing temperature. Absorption was linearly fitted to temperature at all wavelengths.

$$a(T) = a(20.1) + A(T - 20.1) \quad (1)$$

where $a(T)$ is the absorption at temperature T and A is the absorption increment due to temperature. The temperature dependency of absorption is plotted in Figure 3 along with the correlation between absorption and temperature.

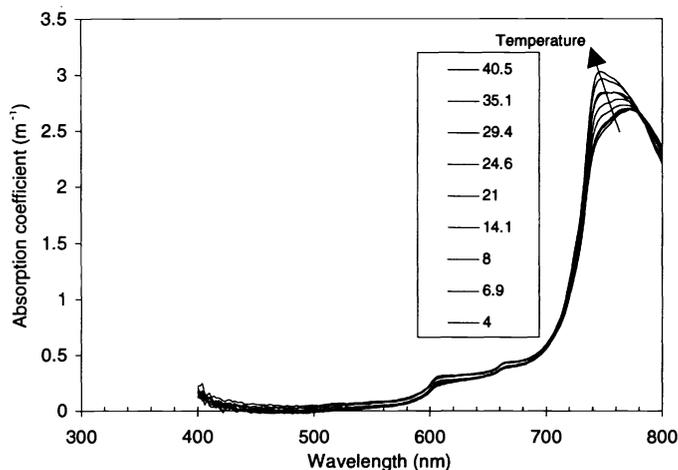


Figure 2. Absorption spectra of pure water measured with the submersible absorption meter for different temperatures.

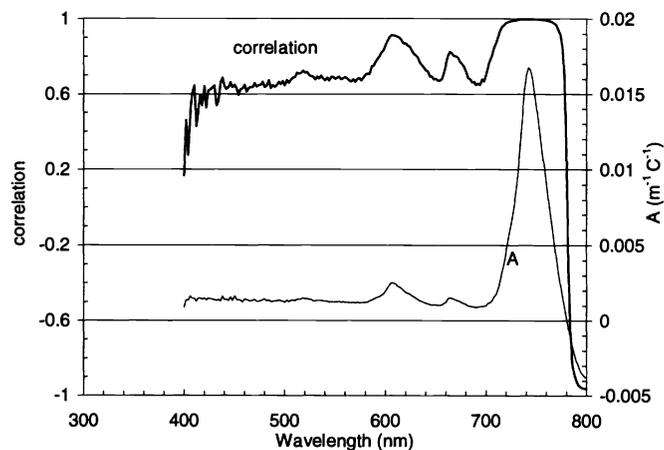


Figure 3. Spectrum of the temperature dependency (A) of the absorption coefficient of pure water and the correlation between the absorption coefficient and temperature

A has peaks in the same wavelength ranges where the shoulders and maximum absorption are found; 520, 606, 664 and 742 nm. At wavelengths below 580 nm the slope coefficient A is nearly constant at 0.0012 m⁻¹°C⁻¹ and in agreement with Højerslev and Trabjerg¹⁴. A small peak around 520 nm can be seen, where A increases to 0.0015 m⁻¹°C⁻¹. No peak was found at 550 nm as was predicted by Pergau and Zaneveld¹². Around the absorption maximum at 740 nm our measured absorption values are higher than those reported by Pergau and Zaneveld¹². Part of this difference may have been caused by their correction procedure; the spectra were adjusted in the vertical direction to the absorption at 685 nm as measured by Tam and Patel⁴. In doing so part of the temperature effect was discarded. However this does not completely explain the difference, because at 685 nm A is only 0.001 m⁻¹°C⁻¹. Compared to Pergau and Zaneveld¹² our values for A are higher. Irvin and Pollard¹⁷ reported a value of A at 750 nm of 0.014 m⁻¹°C⁻¹ which is in agreement with our results.

3. PROPOSED ABSORPTION SPECTRUM.

We arrived at an improved estimate for the absorption spectrum of pure water in the following way:

1. In the 300-394 nm wavelength range the spectrum according to Boivin *et al.*¹⁰ is used. Their measured data were interpolated to obtain absorption coefficients at fixed wavelength intervals.
2. In the 394-520 nm wavelength range the shape of the spectrum according to Smith and Baker³ is used, but the absolute values are changed by vertically shifting the spectrum such as to obtain a smooth fit at the lower wavelength with the data of Boivin *et al.*¹⁰ At the higher wavelength at 520 nm the constraint for a smooth fit is met by shifting the next section.
3. In the 520-604 nm wavelength range our measurements were used. The absorption coefficients were 0.01 m^{-1} shifted to obtain a smooth fit with the data of Tam and Patel⁴.
4. In the 604-800 nm wavelength range the unmodified absorption spectrum as measured with the submersible absorption meter was used.

The results are given in Table 1 and in Figure 4. The measurements of Boivin *et al.*¹⁰ at 546 and 478 nm agree within a few percent. These values were not used in the numerical analysis. In the range below 400 nm we can choose between the values of Quickenden and Irvin¹¹ and Boivin *et al.*¹⁰ because both used highly purified water. Quickenden and Irvin¹¹ demonstrated the effect of subsequent purification steps on the water absorption spectrum. Probably a general feature visible in Figure 1 is that the absorption minimum in the spectrum shifts towards the ultra violet region with a higher degree of purification. Contamination causes exponentially increased attenuation coefficients towards the lower wavelengths. This criterium must be judged in combination with the value of the absorption. Absorption spectra with minima near 500 nm must be rejected for the low wavelength range. This also applies to our measurements in the 400-500 nm wavelength range.

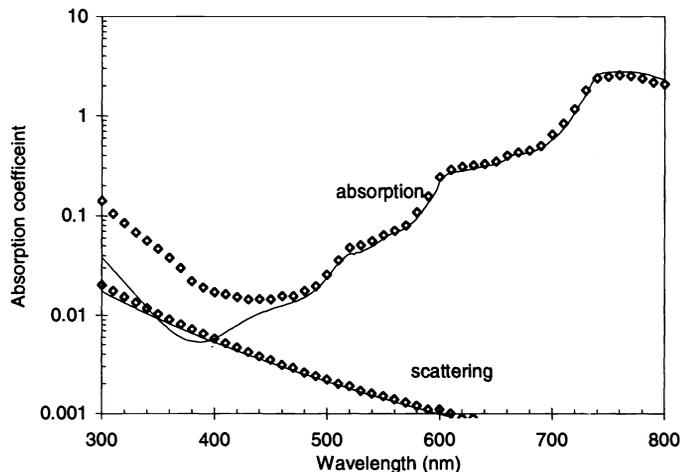


Figure 4. Spectra of absorption and scattering coefficient. The solid lines are the new values proposed and diamonds are the values given by Smith and Baker³

The data of Boivin *et al.*¹⁰ were selected because they used a longer cuvette than Quickenden and Irvin¹¹ and because they also made measurements in the visible part of the spectrum. Values for the attenuation coefficient were calculated for fixed wavelength intervals using fifth degree polynomial interpolation.

Our absorption measurements correspond well with the data of Tam and Patel⁴ between 600-700 nm. Therefore it is believed that these measurements are also accurate above 700 nm. Between 500 and 600 nm a small systematic difference remains.

Above 600 nm noise in a small wavelength region is generally much smaller than the systematic errors; the shape of water absorption spectra measured by different authors are very similar here. In contrast absolute values at single wavelength show larger differences. Boivin *et al.*¹⁰ arrived at an absolute error in their measurements of 0.007 m^{-1} by direct experimental analysis of correction factors of their instrument. From our measurements we estimated the error in the absorption at 0.02 m^{-1} .

To align measurements from different sources it appears sometimes necessary to apply a vertical shift to the spectra, this may be

Table 1. Proposed values for absorption and scattering coefficients at 20 °C. The temperature dependence A derived from new measurements is included. Symbols: λ = wavelength (nm), a = absorption coefficient (m^{-1}), A = absorption increment due to temperature ($m^{-1}C^{-1}$) and b = scattering coefficient (m^{-1}).

λ	a	A	b	λ	a	A	b	λ	a	A	b	λ	a	A	b
300	0.0382	-	0.0174	438	0.0102	0.0016	0.0036	576	0.0858	0.0012	0.0012	714	0.8445	0.0026	0.0005
302	0.0361	-	0.0169	440	0.0104	0.0014	0.0036	578	0.0896	0.0012	0.0012	716	0.9109	0.0032	0.0005
304	0.0341	-	0.0165	442	0.0106	0.0014	0.0035	580	0.0952	0.0012	0.0011	718	0.9871	0.0039	0.0005
306	0.0323	-	0.0160	444	0.0108	0.0013	0.0034	582	0.1008	0.0012	0.0011	720	1.0724	0.0046	0.0005
308	0.0305	-	0.0156	446	0.0110	0.0016	0.0034	584	0.1079	0.0013	0.0011	722	1.1679	0.0053	0.0005
310	0.0288	-	0.0152	448	0.0112	0.0013	0.0033	586	0.1159	0.0014	0.0011	724	1.2684	0.0061	0.0005
312	0.0272	-	0.0148	450	0.0114	0.0016	0.0033	588	0.1253	0.0014	0.0011	726	1.3719	0.0068	0.0004
314	0.0257	-	0.0144	452	0.0116	0.0014	0.0032	590	0.1356	0.0015	0.0011	728	1.4870	0.0077	0.0004
316	0.0242	-	0.0140	454	0.0118	0.0014	0.0031	592	0.1459	0.0016	0.0010	730	1.6211	0.0086	0.0004
318	0.0228	-	0.0137	456	0.0120	0.0014	0.0031	594	0.1567	0.0016	0.0010	732	1.7872	0.0098	0.0004
320	0.0215	-	0.0133	458	0.0122	0.0012	0.0030	596	0.1700	0.0017	0.0010	734	1.9917	0.0114	0.0004
322	0.0203	-	0.0130	460	0.0124	0.0014	0.0030	598	0.1860	0.0018	0.0010	736	2.2074	0.0133	0.0004
324	0.0191	-	0.0126	462	0.0126	0.0014	0.0029	600	0.2224	0.0020	0.0010	738	2.3942	0.0152	0.0004
326	0.0180	-	0.0123	464	0.0128	0.0013	0.0029	602	0.2366	0.0022	0.0010	740	2.5319	0.0163	0.0004
328	0.0170	-	0.0120	466	0.0130	0.0013	0.0028	604	0.2448	0.0024	0.0010	742	2.6231	0.0168	0.0004
330	0.0160	-	0.0117	468	0.0133	0.0014	0.0028	606	0.2587	0.0025	0.0009	744	2.6723	0.0166	0.0004
332	0.0151	-	0.0114	470	0.0135	0.0014	0.0027	608	0.2653	0.0025	0.0009	746	2.7021	0.0161	0.0004
334	0.0142	-	0.0112	472	0.0138	0.0013	0.0027	610	0.2691	0.0024	0.0009	748	2.7216	0.0152	0.0004
336	0.0134	-	0.0109	474	0.0141	0.0013	0.0026	612	0.2715	0.0023	0.0009	750	2.7334	0.0143	0.0004
338	0.0127	-	0.0106	476	0.0144	0.0013	0.0026	614	0.2740	0.0022	0.0009	752	2.7413	0.0132	0.0004
340	0.0119	-	0.0104	478	0.0148	0.0014	0.0025	616	0.2764	0.0021	0.0009	754	2.7478	0.0122	0.0004
342	0.0113	-	0.0101	480	0.0152	0.0014	0.0025	618	0.2785	0.0020	0.0009	756	2.7542	0.0111	0.0004
344	0.0107	-	0.0099	482	0.0157	0.0013	0.0024	620	0.2810	0.0019	0.0009	758	2.7628	0.0102	0.0004
346	0.0101	-	0.0096	484	0.0162	0.0014	0.0024	622	0.2839	0.0018	0.0009	760	2.7710	0.0091	0.0004
348	0.0096	-	0.0094	486	0.0167	0.0013	0.0024	624	0.2868	0.0018	0.0008	762	2.7733	0.0081	0.0004
350	0.0091	-	0.0092	488	0.0174	0.0013	0.0023	626	0.2893	0.0017	0.0008	764	2.7742	0.0071	0.0004
352	0.0086	-	0.0090	490	0.0181	0.0013	0.0023	628	0.2922	0.0016	0.0008	766	2.7701	0.0061	0.0004
354	0.0082	-	0.0088	492	0.0189	0.0013	0.0022	630	0.2955	0.0015	0.0008	768	2.7610	0.0051	0.0004
356	0.0078	-	0.0086	494	0.0198	0.0014	0.0022	632	0.2988	0.0014	0.0008	770	2.7542	0.0042	0.0003
358	0.0075	-	0.0084	496	0.0209	0.0013	0.0022	634	0.3011	0.0013	0.0008	772	2.7482	0.0033	0.0003
360	0.0071	-	0.0082	498	0.0223	0.0013	0.0021	636	0.3038	0.0013	0.0008	774	2.7305	0.0025	0.0003
362	0.0069	-	0.0080	500	0.0238	0.0012	0.0021	638	0.3076	0.0012	0.0008	776	2.7097	0.0016	0.0003
364	0.0066	-	0.0078	502	0.0255	0.0014	0.0021	640	0.3111	0.0012	0.0008	778	2.6896	0.0009	0.0003
366	0.0064	-	0.0076	504	0.0273	0.0013	0.0020	642	0.3144	0.0011	0.0007	780	2.6590	0.0002	0.0003
368	0.0062	-	0.0075	506	0.0291	0.0014	0.0020	644	0.3181	0.0011	0.0007	782	2.6332	-0.0005	0.0003
370	0.0060	-	0.0073	508	0.0310	0.0014	0.0020	646	0.3223	0.0011	0.0007	784	2.6062	-0.0011	0.0003
372	0.0058	-	0.0071	510	0.0329	0.0013	0.0019	648	0.3263	0.0010	0.0007	786	2.5702	-0.0017	0.0003
374	0.0057	-	0.0070	512	0.0349	0.0014	0.0019	650	0.3315	0.0011	0.0007	788	2.5335	-0.0022	0.0003
376	0.0056	-	0.0068	514	0.0368	0.0014	0.0019	652	0.3362	0.0010	0.0007	790	2.4924	-0.0027	0.0003
378	0.0055	-	0.0067	516	0.0386	0.0015	0.0018	654	0.3423	0.0010	0.0007	792	2.4481	-0.0030	0.0003
380	0.0054	-	0.0065	518	0.0404	0.0015	0.0018	656	0.3508	0.0010	0.0007	794	2.4083	-0.0034	0.0003
382	0.0054	-	0.0064	520	0.0409	0.0014	0.0018	658	0.3636	0.0011	0.0007	796	2.3742	-0.0036	0.0003
384	0.0053	-	0.0063	522	0.0416	0.0015	0.0018	660	0.3791	0.0012	0.0007	798	2.3332	-0.0037	0.0003
386	0.0053	-	0.0061	524	0.0409	0.0014	0.0017	662	0.3931	0.0015	0.0007	800	2.2932	-0.0038	0.0003
388	0.0053	-	0.0060	526	0.0427	0.0014	0.0017	664	0.4019	0.0015	0.0006				
390	0.0054	-	0.0059	528	0.0423	0.0013	0.0017	666	0.4072	0.0015	0.0006				
392	0.0054	-	0.0058	530	0.0429	0.0013	0.0017	668	0.4098	0.0014	0.0006				
394	0.0054	-	0.0056	532	0.0445	0.0014	0.0016	670	0.4122	0.0014	0.0006				
396	0.0055	-	0.0055	534	0.0456	0.0013	0.0016	672	0.4150	0.0013	0.0006				
398	0.0056	-	0.0054	536	0.0470	0.0013	0.0016	674	0.4173	0.0013	0.0006				
400	0.0058	0.0009	0.0053	538	0.0480	0.0013	0.0016	676	0.4223	0.0012	0.0006				
402	0.0059	0.0014	0.0052	540	0.0495	0.0013	0.0015	678	0.4270	0.0011	0.0006				
404	0.0061	0.0014	0.0051	542	0.0503	0.0013	0.0015	680	0.4318	0.0011	0.0006				
406	0.0063	0.0016	0.0050	544	0.0527	0.0012	0.0015	682	0.4381	0.0010	0.0006				
408	0.0065	0.0015	0.0049	546	0.0544	0.0013	0.0015	684	0.4458	0.0010	0.0006				
410	0.0067	0.0015	0.0048	548	0.0564	0.0012	0.0014	686	0.4545	0.0009	0.0006				
412	0.0069	0.0013	0.0047	550	0.0588	0.0013	0.0014	688	0.4646	0.0010	0.0006				
414	0.0072	0.0015	0.0046	552	0.0611	0.0012	0.0014	690	0.4760	0.0009	0.0006				
416	0.0074	0.0015	0.0045	554	0.0631	0.0013	0.0014	692	0.4903	0.0009	0.0005				
418	0.0076	0.0014	0.0044	556	0.0646	0.0012	0.0014	694	0.5071	0.0009	0.0005				
420	0.0079	0.0015	0.0043	558	0.0658	0.0013	0.0013	696	0.5244	0.0010	0.0005				
422	0.0082	0.0014	0.0042	560	0.0672	0.0012	0.0013	698	0.5470	0.0009	0.0005				
424	0.0084	0.0015	0.0042	562	0.0686	0.0012	0.0013	700	0.5722	0.0010	0.0005				
426	0.0087	0.0015	0.0041	564	0.0699	0.0012	0.0013	702	0.5995	0.0012	0.0005				
428	0.0089	0.0015	0.0040	566	0.0718	0.0012	0.0013	704	0.6303	0.0012	0.0005				
430	0.0092	0.0014	0.0039	568	0.0734	0.0012	0.0012	706	0.6628	0.0013	0.0005				
432	0.0094	0.0013	0.0038	570	0.0759	0.0012	0.0012	708	0.6993	0.0016	0.0005				
434	0.0097	0.0014	0.0038	572	0.0787	0.0012	0.0012	710	0.7415	0.0018	0.0005				
436	0.0099	0.0013	0.0037	574	0.0819	0.0012	0.0012	712	0.7893	0.0021	0.0005				

due to differences in correction for specular reflection in the apparatus and to the presence of large particulate impurities. But also large differences occur in the shape of measured spectra. In practice it is usually impossible to ascribe observed errors and differences among published spectra to single causes.

4. THE SPECTRUM OF THE SCATTERING COEFFICIENT

The scattering of light by water is described by the Einstein - Smoluchowski equation¹¹. In this theory the scattering of light is attributed to fluctuations in the dielectric constant, caused by the random motion of molecules. It is therefore also known as the fluctuation theory. The spectra of the total scattering and the volume scattering are given by the following equations:

$$\beta(90) = \frac{2\pi^2 kT}{\lambda_m^4 \beta_T} n^2 \left(\frac{\delta n}{\delta p}\right)_T^2 \frac{6+6\rho}{6-7\rho} \quad (2)$$

$$\beta(\theta) = \beta(90) \frac{(1+\rho)+(1-\rho)\cos^2(\theta)}{1+\rho} \quad (3)$$

$$b = \frac{8\pi}{3} \beta(90) \frac{2+\rho}{1+\rho} \quad (4)$$

$$\frac{\delta n}{\delta p_T}(\lambda, T_c) = \frac{\frac{\delta n}{\delta p}(\lambda, 20) \cdot \frac{\delta n}{\delta p}(633, T_c)}{\frac{\delta n}{\delta p}(633, 20)} \quad (5)$$

Table 2 List of notations used in the Einstein-Smoluchowski equation.

b	total scattering coefficient, m^{-1}
k	Boltzmann constant; $1.38054 \cdot 10^{23} \text{ JK}^{-1}$
$n(\lambda, T_c, S)$	refractive index; $1.3247 + 3.3 \cdot 10^3 \cdot \lambda^{-2} - 3.2 \cdot 10^7 \cdot \lambda^{-4} - 2.5 \cdot 10^{-6} \cdot T_c^2 + (5.2 \cdot 10^{-2} \cdot T_c) \cdot 4 \cdot 10^{-5} \cdot S$
S	salinity 0/00
T	absolute temperature, K
T_c	temperature, °C
$\beta(90)$	volume scattering function at right angle Rayleigh ratio, $m^{-1} \text{ sr}^{-1}$
$\beta(\theta)$	volume scattering function, $m^{-1} \text{ sr}^{-1}$
β_T	isothermal compressibility, Pa^{-1} ; $(5.062271 - 0.03179 \cdot T_c + 0.000407 \cdot T_c^2) \cdot 10^{-11}$
θ	angle between the direction of the incident beam and the direction of observation, sr^{-1}
λ	wavelength, nm
λ_m	wavelength, m
ρ	depolarization ratio; 0.051
$\delta n / \delta p_T(\lambda, T_c)$	pressure derivative of n , Pa^{-1}
$\delta n / \delta p_T(\lambda, 20)$	pressure derivative of n at 20 °C as a function of wavelength, Pa^{-1} ; $(-0.000156 \cdot \lambda + 1.5989) \cdot 10^{-10}$
$\delta n / \delta p_T(\lambda, T_c)$	pressure derivative of n at 633 nm as a function of temperature, Pa^{-1} ; $(1.61857 - 0.005785 \cdot T_c) \cdot 10^{-10}$

The temperature dependence of the isothermal compressibility between 5°C and 35°C is given as a quadratic fit to the data of Lepple and Millero¹⁸. The refractive index of water is a function of wavelength, temperature, salinity and pressure. Empirical equations for this dependency are given by Mcneil¹⁸ and Matthäus²⁰. The formula given by Matthäus is reliable between 400 and 650 nm. We use the approximation given by Mcneil because it covers the greater wavelength range 350-800 nm. Values

calculated with this formula agreed within 0.01 percent with the values tabulated by Sager ²¹. For remote sensing applications only atmospheric pressure needs to be considered, and the equation reduces to the form given above.

The depolarization ratio is taken from Farinato and Roswell ²² who measured at 515 nm and 20°C. No discussion of the dependence of the polarization ratio on temperature and wavelength was found in the literature. The wavelength and temperature dependency of the pressure derivative of the refractive index are given by two independent linear approximations. The temperature influence was fitted to the data tabulated by O'Conner ²³ between 5°C and 35°C for 633 nm. The wavelength dependency is a linear approximation to the data of Evtushenkov and Kiyachenko ²⁴ measured at 20°C. The temperature and wavelength dependencies are combined to describe $\delta n/\delta p$ permitting a better representation.

Table 3. Rayleigh ratio calculated using Equation 2 for $T_c=20^\circ\text{C}$, measurement and calculation by Morel ¹ using a depolarization ratio of 0.09.

Wavelength (nm)	Rayleigh ratio ($\times 10^4 \text{ m}^{-1}$)		
	Equation 2	Morel	
		measured	calculated
366	4.67	4.53	5.32
405	3.07	2.90	3.42
436	2.26	2.12	2.49
546	0.89	0.83	0.94
578	0.71	0.66	0.73
633	0.48		0.49

Some spectral measurements of the Rayleigh ratio ($\beta(90)$) are given by Morel ¹ and shown in Table 2. The measured Rayleigh ratio is about 4 percent lower than described by Equation 2. Also the measurements of Pike *et al.* ²⁵ at 633 nm and at 22 °C agree well.

A consequence of this input into the Einstein-Smoluchowski equation is that in the temperature dependence of the total scattering a maximum at 15°C appears. From 15 till 30 °C the scattering coefficient decreases by 2.4 percent. The influence of salinity on the scattering is not studied here. According to Morel ¹ the scattering of sea water is 30 percent higher as compared with fresh water. Result of the calculations for fixed wavelength intervals are given in Table 2. The spectrum of the scattering coefficient is shown in Figure 4.

Relative errors in the input parameters of the scattering coefficient were estimated as follows:

1. 0.1 percent in the isothermal compressibility according to Lepple and Millero ¹⁸.
2. 2 percent in the pressure derivative of the refractive index.
3. less than 0.1 percent in the refractive index
4. 20 percent in the depolarization ratio.

This results in an relative error of about 6 percent in the total scattering coefficient and in the volume scattering function.

Morel ¹ used the Einstein-Smoluchowski equation with different input parameters, this result was adopted by Smith and Baker ³. Below 680 nm the numerical results of our interpretation are lower, above 680 nm they are higher. The difference is about 10 percent at 400 nm and 3 percent at 800 nm.

5. DISCUSSION

The inherent optical properties of pure water and the accuracy with which they are known have been reviewed here. Difficulties due to the recently discovered temperature dependence have been removed. It is seen that remaining systematic errors increase with decreasing wavelength. This leads to a problem in choosing the best values in practical applications, requiring a combination of measurements from several sources and sound judgement as to what source to use, a problem that becomes more difficult with decreasing wavelength.

It is arbitrary to choose a spectrum in the low wavelength range. Since impurity of the water sample is the largest source of error, it may be expected that the lowest spectrum measured is more or less automatically the best choice. Additionally the place of minimum absorption can be used to select. This minimum shifts toward lower wavelengths with less contaminations. The measurements of Boivin *et al* were adapted in this region because they found a minimum absorption at the lowest wavelength. However in the region between 300 nm and 500 nm these very low absorption may not be important in most practical problems because other components will be present even in clear ocean waters. The values given by Smith and Baker³ below 500 nm may therefore be the lowest which can be found in clear natural waters.

At wavelengths above 600 nm the absorption of water has a significant temperature dependency. Beyond 700 nm the differences between literature values increase up to 20 percent. The temperature effect on absorption is part of the explanation for these differences. But also other differences must be present since the difference spectra do not correspond accurately to the spectrum of the temperature effect.

The consequences of these proposed absorption coefficients must be evaluated in the various fields where the optical properties of water are used. Especially the temperature dependency of the absorption coefficient on the remote sensing signal in the red and near infra-red requires attention, such as procedures in remote sensing signal processing that may be sensitive to different water temperatures, atmospheric corrections using the darkest pixel method and chlorophyll determination from passive chlorophyll fluorescence.

In this study we used reversed osmosis water. There is however a general need for knowledge on absorption and scattering coefficients of sea water. The absorption coefficient and the temperature effect in sea water have to be studied.

6. ACKNOWLEDGEMENTS

The authors thank J. Krijgsman, G.B.J. Dubelaar and G.N.M Stokman for their comments and suggestions, Pegau and Zaneveld for supplying their original measurements and A.E.R. Beeker for assistance during the measurements.

7. REFERENCES

1. A. Morel, "Optical properties of pure water and pure sea water," in *Optical aspects of oceanography*, N.G. Jerlov and E. Steenman Nielsen, Eds, Acad. Press, London and New York, 1974.
2. R.C. Smith and J.E. Tyler, "Transmission of solar radiation into natural waters," in *Photochemical and photobiological reviews* Vol. 1. K.C. Smith Ed. Plenum Press, New York, 1976.
3. R.C. Smith and K. Baker, "Optical properties of the clearest natural water (200-800 nm)," *Applied Optics* **20**, 177-184, 1981.
4. A.C. Tam and C.K.N. Patel, "Optical absorption of light and heavy water by laser optoacoustic spectroscopy," *Applied Optics* **18**, 3348-3358, 1979.
5. A. Morel and L. Prieur, "Analysis of variation in ocean color," *Limnology and Oceanography* **22**, 709-722, 1977.
6. S.A. Sullivan, "Experimental study of the absorption in distilled water, artificial sea water, and heavy water in the visible region of the spectrum," *J. Opt. Soc. Am.* **53**, 962-968, 1963.
7. J.A. Curcio and C.C. Petty, "The near infrared absorption spectrum of liquid water," *J. Opt. Soc. Am.* **41**, 302-304, 1951.
8. H.R. James and E.A. Bridge, "A laboratory study of the absorption of light by lake water," *Trans. Wisconsin Acad. Sci.* **31**, 1-150, 1938.

9. G.L. Clark and H.R. James 1939, "Laboratory analysis of selective absorption of light by sea water," J. Opt. Soc. Am. **29**, 43-55, 1939.
10. L.P. Boivin, W.F. Davidson, R.S. Storey, D. Sinclair and E.D. Earle, "Determination of the attenuation coefficient of visible and ultraviolet radiation in heavy water," Applied Optics **25**, 877-882, 1986.
11. T.I. Quickenden and J.A. Irvin, "The ultraviolet absorption spectrum of liquid water," J. Chem. Phys. **72**, 4416-4428, 1980.
12. W.S. Pergau and J.R.V. Zaneveld, "Temperature-dependent absorption of water in the red and near-infrared portion of the spectrum," Limnology and Oceanography **38**, 188-192, 1993.
13. J. Krijgsman, "Optical remote sensing of water quality parameters," Thesis Delft University of Technology, Delft University Press, Delft, 1994.
14. N.K. Højerlev and I. Trabjerg, "A new perspective for remote sensing measurements of plankton pigments and water quality," Univ. Copenhagen Inst. Phys. Oceanogr. rep. 51. 1990.
15. J.M.H. Hakvoort, A.E.R. Beeker and J. Krijgsman, "An instrument to measure *in situ* visible light absorption in natural waters," in Ocean Optics XII, Proc SPIE 2258, 1994.
16. See, for example, M. Kerker, *The scattering of light and other electromagnetic radiation*. Acad. Press, New York and London, 1963.
17. W.M. Irvine and J.B. Pollack, "Infrared optical properties of water and ice spheres," Icarus **8**, 324-360 (1968).
18. F.K. Lepple and F.J. Millero, "The isothermal compressibility of seawater near one atmosphere," Deep Sea Research **18**, 1233-1254, 1971.
19. G.T. McNeil, "Metrical fundamentals of underwater lens systems," Optical Engineering **16**, 128-139, 1977.
20. W. Matthäus, "Empirische Gleitungen für den Brechungsindex des Meerwassers," Beiträge zur Meereskunde **33**, 73-78, 1974.
21. G. Sager, "Zur Refraction von Licht im Meerwasser," Beiträge zur Meereskunde **33**, 63-72, 1974.
22. R.S. Farinato and R.L. Roswell, "New values of the light scattering depolarization and anisotropy of water," J. Chem. Phys. **65**, 593-595, 1975.
23. C.L. O'Conner and J.P. Schlupf, "Brillouin scattering in water: The Landau-Paszek ratio," J. Chem. Phys. **47**, 31-38, 1967.
24. A.M. Evtushenkov and Yu.F. Kiyachenko, "Determination of the dependence of liquid refractive index on pressure and temperature," Opt. Spectrosc. **52**, 56-58, 1982.
25. E.R. Pike, W.R.M. Pomeroy and J.M. Vaughan, "Measurement of Rayleigh ratio for several pure liquids using a laser and monitored photon counting," J. Chem. Phys. **62**, 3188-3192, 1975.