

Temperature influence on the 1.2 μm band of water

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Introduction

Near infrared (NIR) spectroscopy is rapidly establishing itself as a valuable technique in quantitative analysis.¹ Due to the fact that often no sample manipulation is required, NIR spectroscopy is well-suited for process analysis. Furthermore, the transparency of silica in the NIR range also makes the use of conventional SiO₂ optical fibres for *on-line* measurements possible.²⁻⁴

The precision of the measurements can be quite high⁵⁻⁷ but to obtain this, precautions have to be taken in order to control all the parameters that might influence the spectra.

Temperature variations are the first perturbation source of spectral measurements. A rather conventional approach is to take them into account by including the temperature change in the calibration set.⁸ By measuring the spectra at different temperatures, comprised in the expected variation range and running a multivariate calibration algorithm, it is possible to obtain a robust, albeit complicated, calibration model.^{8,9} However, when H-bonds are present, as in the case of water, alcohols and their mixtures, a temperature change causes non-linear wavelength shifts and the net result is a loss in measurement precision. Therefore, if a high degree of precision is required, the temperature of the sample has to be stabilised.^{5,6}

In a laboratory instrument it is relatively easy to have a very good thermal stabilisation, but this is problematic for process controls, especially when *on-line* measurements have to be carried out. In this case, it would be of great advantage if it were possible to mathematically model the influence of the temperature on the spectra to correct them before calibration.

The starting point to build a mathematical model is to understand the origin of the wavelength shifts in water. The presence of H-bonds provokes the formation of molecular clusters,¹⁰⁻¹² even if isolated molecules also seem to be present.¹³ This point is debatable, as some authors have reported finding that very few isolated molecules existed.¹⁴

Two models of the structure of the water are proposed in the literature; the continuous model¹⁵ that considers the water as a continuous network of H-bonds where distortion of the H-bonds results in a continuous distribution of bonding distance, angles and geometry and the mixture one^{10,16-18} that considers the water as a mixture of discrete species differing in their structural arrangement. In both cases

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the change of the temperature has the effect of altering the lengths and energies of H-bonds causing the observed shifts.

If the mixture model were the correct one, from the molecular point of view, the size of the cluster should not be relevant, since the local deformation of the H-bond will be more or less the same for the same state of polymerisation of the molecules, the difference being limited to the outer boundary of the cluster. The absorbance bands will, therefore, convolute a discrete number of bands whose central wavelength should be independent from the temperature. However, the relative balance of the cluster is expected to vary as a function of the temperature, the larger clusters being favourite at low temperature and the smallest ones at higher temperature. In this case, only the wavelength shift turns are apparent, reflecting the different distribution of the cluster sizes. Under these hypotheses, it should be possible to establish a mathematical model of the water spectra at different temperatures by fitting the amplitudes and peaks of the sub-bands and convoluting the resulting gaussians.

In this paper, this approach has been followed for water. Even if the conclusions are not directly applicable in real applications, it will provide information on the validity of the method.

Materials and methods

Demineralised water ($\rho \approx 17 \text{ M}\Omega \text{ cm}^{-1}$) was used throughout all the measurements. The spectra in the range 850–1350 nm were collected with a Perkin–Elmer Lambda 9 spectrometer at the Department of Experimental Physics of the Technical University, Graz. The noise is estimated in

$dT/T \approx 25 \times 10^{-3}$ where T is the transmittance. The spectra of the band at 1.2 μm have been collected with a single-beam double-monochromator (Oriel Instruments) equipped with cooled InGaAs detectors (Telcom Devices Corporation) on both the measurement and the reference channels. The photocurrent has been measured with two digital lock-in amplifiers (Stanford Research Systems SR830). The spectrometer was driven by a custom software written in Labview (National Instru-

ments). The noise of the measurements is estimated in $dT/T \approx 2 \times 10^{-4}$. All the spectra have been corrected for density change at the different temperatures.

All the other computations were carried out by using GRAMS/32 (Galactics Corp.) and Origin 5.0 (Microcalc Software Inc.).

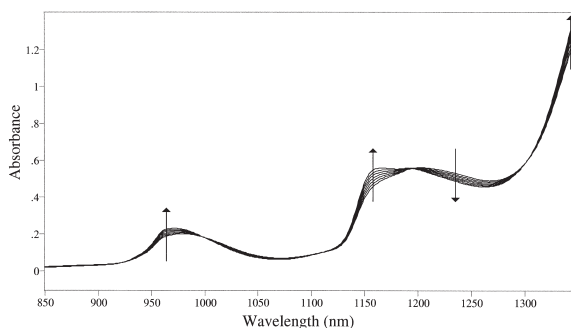


Figure 1. Density-corrected water spectra in the range 850–1350 nm when the temperature is changing from 10 to 40°C in steps of 5°C. The arrows show the behaviour of the spectra when the temperature is changing.

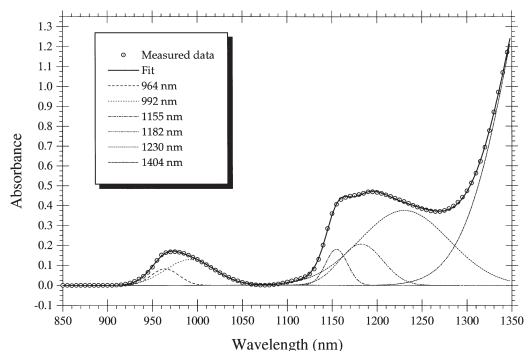


Figure 2. Deconvolution of the spectrum at $T = 25^{\circ}\text{C}$ after the subtraction of a linear baseline.

Results and discussion

We initially verified our hypothesis by trying to deconvolve water spectra collected with the Lambda 9 spectrometer in the range 850–1350 nm (Figure 1). The data have been compensating for baseline by subtracting the straight line obtained by fitting the points in the range 850–900 nm and 1065–1075 nm, where the first absorbance minima are observed, with a least-squares routine.

The spectrum at $T = 25^{\circ}\text{C}$ has been considered first and it has been found that a good fit was obtained by using six gaussian peaks (Figure 2). At this stage, all the parameters of the gaussians have been kept free. The spectra at the other temperatures have been fitted by using the same number of peaks and by fixing the central wavelengths. Only the amplitudes and widths of the peaks were allowed to change. Of these peaks, two account for 960 nm band, three for the 1200 nm band and one for the tail of the 1450 nm band. The number of components found for the 1200 nm band agrees with what is reported in the literature.¹⁹ The position is, however, different but we observed that the central wavelength of the peaks is strongly dependent on the baseline correction. Since Andaloro and co-workers have used a double-exponential baseline, the difference in the position of the peaks should not be overemphasised.

The next step has been to search for a correlation between the observed variations in amplitude and width. Figure 3 shows the results of the least-squares fittings of these parameters of the three peaks obtained by the deconvolution of the 1200 nm band as functions of the temperature and Table 1 reports the numerical values of the parameters. It is very interesting to observe how

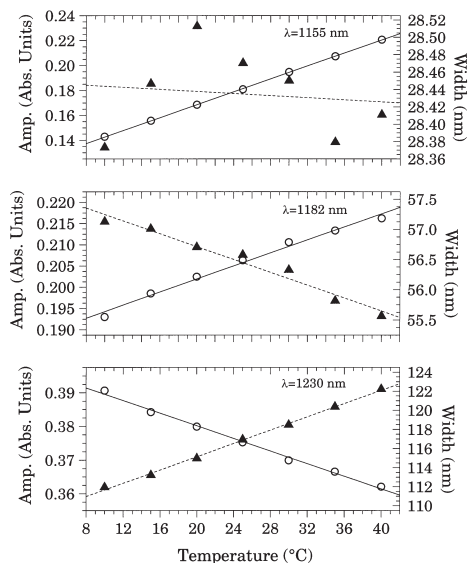


Figure 3. Linear fits of the amplitudes and widths of peaks 3–5 of Table 1 v. sample temperature. R_A and R_W are the correlation coefficients of the fits for amplitudes and widths, respectively. Circles: amplitude. Triangles: width.

Table 1. Gaussian bands used in the deconvolution of the spectrum of Figure 2.

	Central wavelength (nm)	Amplitude ($a_{i1}T + a_{i2}$) (absorbance units)	R_A	Width ($b_{i1}T + b_{i2}$) (nm)	R_w
Peak 1	964	$0.0436 \pm 0.0004 +$ $(0.00158 \pm 0.00001)*T$	0.99983	$32.6 \pm 0.2 +$ $(0.15 \pm 0.02)*T$	0.94668
Peak 2	992	$0.1303 \pm 0.0004 -$ $(0.00004 \pm 0.00002)*T$	-0.75931	$68.7 \pm 0.2 -$ $(0.146 \pm 0.008)*T$	-0.99236
Peak 3	1155	$0.1167 \pm 0.0003 +$ $(0.00259 \pm 0.00001)*T$	0.99995	$28.45 \pm 0.05 -$ $(0 \pm 0.002)*T$	-0.12943
Peak 4	1182	$0.18659 \pm 0.00096) +$ $(0.00077 \pm 0.00004)*T$	0.9946	$57.78 \pm 0.12) -$ $(0.053 \pm 0.004)*T$	-0.98263
Peak 5	1230	$0.3988 \pm 0.0008 -$ $(0.00093 \pm 0.00003)*T$	-0.99744	$108.2 \pm 0.2 +$ $(0.347 \pm 0.007)*T$	0.99979
Peak 6	1404	$1.771 \pm 0.003 +$ $(0.0118 \pm 0.0001)*T$	0.99979	$133.6 \pm 0.1 -$ $(0.221 \pm 0.004)*T$	-0.99934

the variation of both parameters with the temperature is linear. The only exception is the width of the peak centred at $\lambda = 1155$ nm, but this may be expected for the very small variation of this parameter on the considered temperature range. Moreover, the absorbance at other wavelengths appears to vary in a linear fashion as a function of the temperature (data not shown).

Since all the peaks share the same linear behaviour as functions of the temperature, it is possible to write the following relation:

where $S_w(\lambda, T)$ is the water spectrum with explicit temperature and wavelength dependence, λ_{i0} is the central wavelength of the i -th peak, $\alpha_{i1}T + \alpha_{i2}$ and $\beta_{i1}T + \beta_{i2}$ are the amplitude and width coefficients

$$S_w(\lambda, T) = \sum_i S_i(\lambda, T) = \sum_i (\alpha_{i1}T + \alpha_{i2}) \cdot e^{\left(\frac{\lambda - \lambda_{i0}}{\beta_{i1}T + \beta_{i2}} \right)^2} \quad (1)$$

for the i -th peak, respectively. An estimation of how good this model is can be obtained by computing the residuals:

$$R(\lambda, T) = S_w(\lambda, T) - S_w^e(\lambda, T) \quad (2)$$

where $R(\lambda, T)$ are the residuals and $S_w^e(\lambda, T)$ is the experimentally measured water spectrum. The values of $R(\lambda, 10)$ and $R(\lambda, 35)$, i.e. at the extremes of the temperature range are reported in Figure 4. In both cases, all the values fall in the interval ± 0.01 absorbance units, a factor of 4 larger than the noise of the Lambda 9 spectrometer used for collecting the data.

The result of these measurements indicates that the amplitude of the short-wavelength peaks increases with the increase in temperature, whilst the amplitude of the longer amplitude peak decreases.

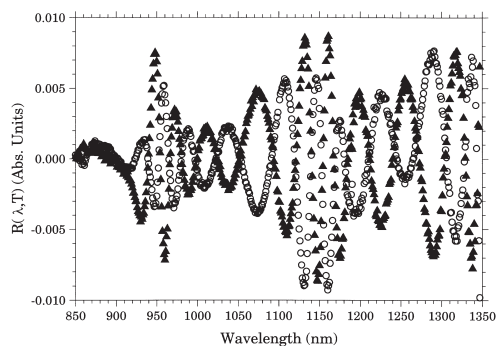


Figure 4. $R(\lambda, T)$ computed at the extremes of the temperature range. Circles: $T = 10^\circ\text{C}$. Triangles: $T = 35^\circ\text{C}$. For the definition of $R(\lambda, T)$ see text.

From the physical point of view, our interpretation is that the first two peaks are correlated with the low H-bonded water molecules, whose concentration should increase with the temperature and the third with the high H-bonded water molecules. Furthermore, since the change in the spectra can be explained with a fixed set of peaks, we can conclude that only the shift is apparent, only being related to the equilibrium of few species.

It is rather obvious that the precision of the correction depends strongly on the precision of the data, so we further investigate the behaviour of the 1200 nm band of the spectrum by collecting the spectra between 15 and 35°C with the Oriel spectrometer. A quadratic baseline was subtracted before deconvolving the spectra.

As before, the spectrum collected at $T = 25^\circ\text{C}$ was first deconvoluted to find the optimal number and position of the peaks. It turned out that five peaks were necessary to fit the band properly (Figure 5) but, as before, it was possible to find reasonable fits of all the spectra at the other temperatures, fixing the position of the peaks. Again, the parameters of the fittings were found to change linearly with the temperature, as shown in Table 2. The residuals are all within ± 0.001 absorbance units if one neglects the last points where the baseline was not completely compensated by the baseline subtraction (Figure 6).

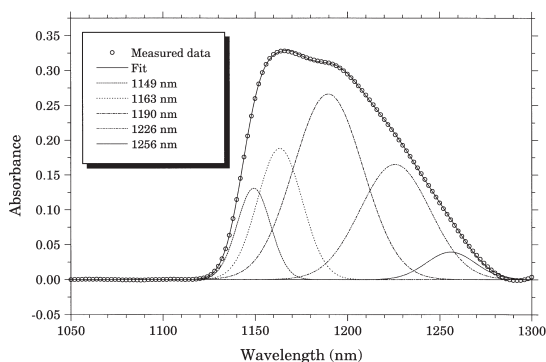


Figure 5. Deconvolution of the spectrum at $T = 25^\circ\text{C}$ after the subtraction of a quadratic baseline.

Table 2. Gaussian bands used in the deconvolution of the 1200 nm band of the water spectra.

	Central wavelength (nm)	Amplitude (a_iT+ai_i) (absorbance units)	R_A	Width ($b_{i1}T+b_{i2}$) (nm)	R_w
Peak 1	1149	$0.0785 \pm 0.0012 + (0.00205 \pm 0.00005)*T$	0.99925	$20.37 \pm 0.22 + (0.031 \pm 0.008)*T$	0.90213
Peak 2	1163	$0.131 \pm 0.001 + (0.00233 \pm 0.00004)*T$	0.9995	$28.75 \pm 0.11 - (0.011 \pm 0.004)*T$	-0.82525
Peak 3	1190	$0.250 \pm 0.006 + (0 \pm 0.0002)*T$	0.7228	$45.57 \pm 0.45 - (0 \pm 0.017)*T$	-0.931
Peak 4	1226	$0.185 \pm 0.003 - (0.0009 \pm 0.0002)*T$	-0.97532	$46.67 \pm 0.44 - (0.067 \pm 0.017)*T$	-0.91515
Peak 5	1256	$0.0474 \pm 0.0056 - (0.0005 \pm 0.0002)*T$	-0.81803	$34.1 \pm 2.3 - (0.185 \pm 0.089)*T$	-0.77019

Conclusions

Our computation showed that the water spectrum and in particular the 1200 nm band, can be deconvoluted by a set of gaussian of fixed central wavelength. Since the amplitudes and widths of the peaks vary linearly with the temperature, two conclusions may be drawn. First, it is possible to mathematically model the water spectrum with a relatively high degree of precision, so that a unique calibration model may be used. Since a high degree of precision can be attained, this model may be applied in critical experimental conditions such as *on-line* process control.

Second, only the wavelength shift of the water band is apparent, being provoked by a mere redistribution of the single spectral contributions. Also, it is possible to tentatively assign the short wavelength contributions with the molecules with a low number of H-bonds, since the number of bonded molecules increases with the decrease of the temperature due to the formation of larger clusters. This might support the polymeric model of the water structure, since the number of small clusters (and con-

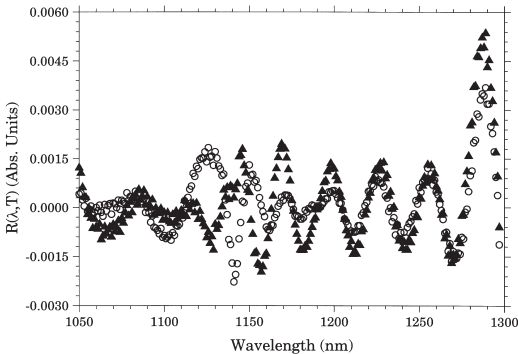


Figure 6. $R(\lambda,T)$ computed at the extremes of the temperature range. Circles: $T = 10^{\circ}\text{C}$. Triangles: $T = 35^{\circ}\text{C}$. For the definition of $R(\lambda,T)$ see text.

sequently the number of low H-bonded molecules) is expected to increase as the temperature increases. However, this conclusion is not unambiguous and further investigations are needed to clarify this point.

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