

Effects of filtration processes on aqueous nanostructures by near infrared spectroscopy

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Introduction

Water is a universal solvent and, for this reason, it has been the subject of many investigations. Many of the unique properties of water, such as its very high boiling point, its density variation with temperature and its heat capacity at constant pressure, have been interpreted as the result of the strong intermolecular attractions essentially represented by hydrogen bonds. Nevertheless, it is not yet possible to believe that all properties of water are known.

Recent studies of extremely dilute solutions (with a concentration of solute lower than 10^{-7} M) and pure water, analysed after the application of physical pre-treatments, have highlighted the existence of physicochemical properties of the solvent (water) which require an in-depth knowledge of the liquid solvent structure to be explained. Some examples may clarify this statement: extremely dilute solutions, perturbed by mechanical treatments and analysed with a calorimetric technique, showed anomalous behavior when mixed with solutions containing sodium hydroxide and hydrochloric acid;¹ evaporation at room temperature and atmospheric pressure of NaCl solutions with a concentration 10^{-7} M leads to the formation of stable clusters of water molecules with dimensions from tens of nanometres to several microns.²

In recent years, NIR spectroscopy has been applied to the study of water properties and structure as evidenced by the research carried out for the monitoring of structural changes induced into the water matrix by the presence of solutes³⁻⁵ or temperature changes.⁶⁻⁹ Different theories regarding the structure of liquid water have been put forward.¹⁰⁻¹¹ Temperature studies of the band centred near 6900 cm^{-1} have shown that separate peaks correspond to different states of hydrogen-bonded water molecules. Results obtained appeared so important as to suggest the creation of a field of study dedicated to water, called aquaphotomics, which recently led to a special issue of the Journal of Near Infrared Spectroscopy.¹²

During filtration variations occur in conductivity distinctly greater than those due to the presence of pollutants normally present in distilled water alone. The formation of aqueous nanostructures has recently been suggested to explain this observation.^{13,14} The aim of the present study was to investigate changes induced in pure water by different filtration processes using NIR spectroscopy.

Materials and Methods

Samples

Water samples, purified and deionised to a high degree, with resistivity equal to $18.2\text{ M}\Omega\cdot\text{cm}$ (MilliQ-Millipore, Vimodrone, Milan, Italy) were analysed before and after iterated processes of filtration. The filters used in all the experiments were sintered glass with porosity $15 - 40\ \mu\text{m}$ (R3). The sample set consisted of 61 samples: 10 samples of MilliQ water not filtered belonging to the same stock, 38 samples divided into two sub-sets of respectively 17 (set A1) and 21 (set A2) samples filtered with the same protocol but obtained in two different experiments, and 13 samples processed with a different protocol (set B).

Near infrared spectroscopy

NIR spectra were collected in transmission mode (optical length = 1 mm, 32 scans, resolution 8 cm^{-1} , 3 replicates) in the NIR range from 5500 to 10000 cm^{-1} using NIRFlex N500 (BÜCHI Italia, Assago, Milano, Italy) spectrometer at constant temperature ($40 \pm 1^\circ\text{C}$).

Data processing

NIR data were processed using The Unscrambler (v. 9.2; Camo Inc., Oslo, Norway). A principal components analysis (PCA) was performed on spectral data pre-treated with standard normal variate (SNV), Savitzky – Golay second derivative (15 points, polynomial order 2) and mean centering.

Origin Pro 7.5 (OriginLab Corporation, Northampton, MA, USA) was used to curve fit an average spectrum of unfiltered MilliQ water. To calculate the curve fit, the baseline was approximated by a straight

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line between two points (5950 and 7750 cm^{-1}) of the band envelope in the non-absorbing region and subtracted from the spectrum. The baseline-corrected spectrum was fitted with a multi-peak Gaussian fit which assumes Gaussian band envelopes for the resolved components. The three parameters of each band (peak position, height and half width at half maximum) were allowed to float during the computation.

ANOVA statistical analysis was performed with Minitab 15.1.0.0 (Minitab Inc., State College, PA, USA) to identify differences between the maxima of spectra which were calculated by subtracting the average spectrum of not filtered water samples from all the spectra acquired. The p -value was calculated at the level of significance of 0.05.

Results and discussion

NIR spectra of water in the analysed range are characterised by three bands centred near 5600, 6900 and 8700 cm^{-1} , assigned respectively to the combination bands $\nu_2+\nu_3+\nu_L$, $\nu_1+\nu_3$, and $\nu_1+\nu_2+\nu_3$, where ν_1 is the symmetric stretching mode of the water molecule, ν_2 the bending mode, ν_3 the asymmetric stretching mode and ν_L an intermolecular mode.¹⁵

In particular, the observed changes in the second derivative of the water spectrum, varying with temperature variations and detectable on the broad downward band at 6090, on the signal at 6640 and on the minima at 6870, 6948, 7094 cm^{-1} have been tentatively assigned to water species with four, three, two, one and no hydrogen bonds respectively (marked by arrows in Figure 1 for a spectrum acquired at $40 \pm 1^\circ\text{C}$). Another downward band at 7440 cm^{-1} was assigned to a combination of symmetric stretching, bending and rotational modes of water molecules.⁶⁻⁹

The multiple Gaussian fit of an average spectrum of unfiltered MilliQ water collected at $40 \pm 1^\circ\text{C}$, (obtained with a trial and error method) is shown in Figure 2. The determination coefficient (R^2) obtained for this curve was 0.9999 and the wavenumbers corresponding to the maxima of the Gauss functions that approximate the curve were identified at: 6569 ± 47 , 6735 ± 84 , 6855 ± 41 , 6978 ± 15 , 7092 ± 24 and 7143 ± 71 cm^{-1} . They can be, respectively, assigned to water species with four, three, two, one and no hydrogen bonds plus the band due to the combination of symmetric stretching, bending and rotational mode.

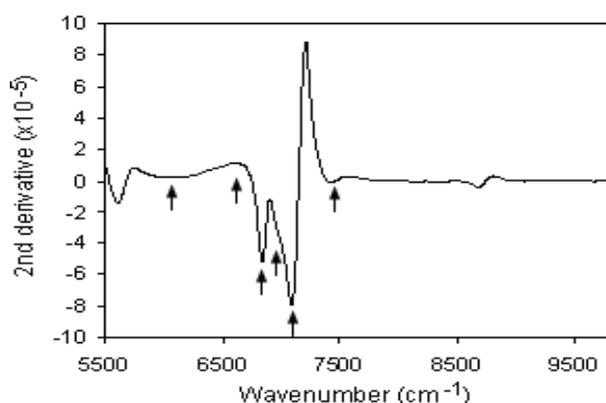


Figure 1. The second derivative of a NIR spectrum of water ($T = 40 \pm 1^\circ\text{C}$).

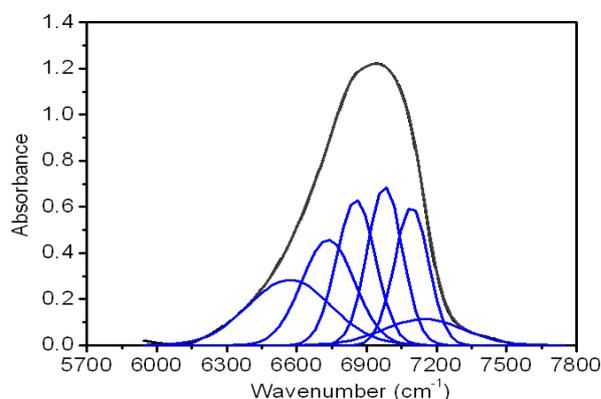


Figure 2. Results of curve fitting for the range from 6000 to 7500 cm^{-1} for the average spectrum of not filtered water samples acquired at $40 \pm 1^\circ\text{C}$.

Comparing the obtained values with those reported in literature⁶⁻⁹ they seemed to be sometimes in good agreement and sometimes very different. The main differences in wavenumber assignments were found for Gaussian function in the second derivative ranges corresponding to broad bands. The peak assignments presented in this study are supported by the decreasing full width at half maximum (FWHM) of the Gaussian functions: the FWHM decreased from 355, 227, 166, 149 to 144 cm^{-1} as the number of hydrogen bonds associated with the peak decreased. It has previously been shown that peak intensities and widths are affected by “internal” anharmonicity; molecules bonded to more adjacent molecules will have less anharmonicity and therefore be associated with broader and weaker peaks.¹⁵

The peak shift observed within the range 5900 – 7600 cm^{-1} when water is perturbed in some way, e.g. varying temperature, is not due to a shift in component bands but rather reflects changes in the intensity ratios of the component bands. For example, decreasing temperature produces species with many hydrogen bonds while increasing temperature produces species with few hydrogen bonds.⁶⁻⁹

A redistribution of water species with different numbers of hydrogen bonds was also expected in water samples subjected to different filtration processes. To prove this theory, a PCA was performed on the NIR

spectra of 61 water samples; SNV and second derivative were applied as pre-treatments. The plots obtained are shown in Figures 3 and 4. The principal component one (PC1) versus PC2 score plot (Figure 3) highlighted the presence of three well defined groups of samples distributed along the PC1 axis that was able to explain 61% of the total variance. The first group, with negative PC1 and PC2 values, corresponded to the 10 samples of MilliQ water before filtration, and the remaining two sets of samples were assigned to samples treated with an increasing number of filtration processes (up to 580).

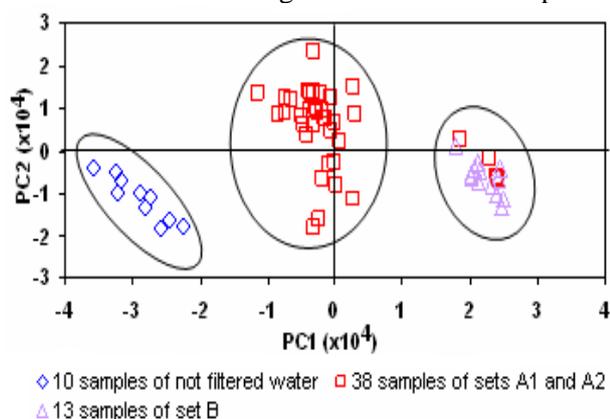


Figure 3. Plot of sample scores obtained from the PCA analysis performed on all 61 water samples.

at positive values of the PC1 axis (Figure 3); this set of samples was associated with the positive signals of the PC1 loading at 6790 and 7184 cm^{-1} (Figure 4a). The first signal, 6790 cm^{-1} , corresponded to water species with three hydrogen bonds, but it could be not well resolved and contained two bands, one centred at 6735 and the other centred at 6855 cm^{-1} . The second signal, detected at 7184 cm^{-1} , did not depend on the number of hydrogen bonds; it was due to a water combination band of symmetric stretching, bending and rotational modes. Following the same approach, the distribution of unfiltered water samples was associated with the negative peaks of the PC1 loading at 6880 and 7076 cm^{-1} (Figure 4a). These bands corresponded to water species with two and no hydrogen bonds respectively.

In order to formulate a theory able to explain the structural nature of set A1 and A2 samples the PC2 loading plot was examined (Figure 4b); two positive signals were detected at 6736 and 7110 cm^{-1} that can be assigned to water species with three and no hydrogen bonds, respectively.

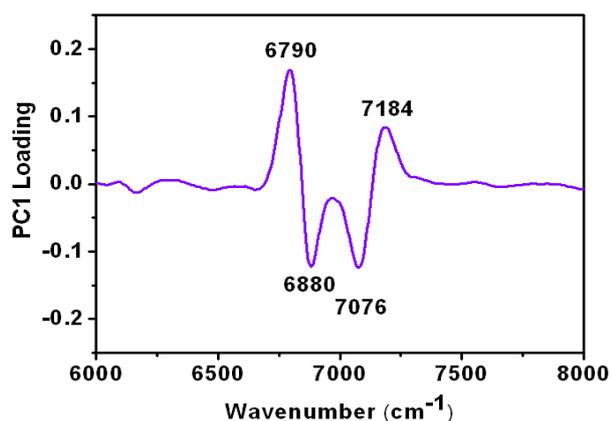


Figure 4a. Plot of PC1 loadings obtained from PCA performed on all 61 samples.

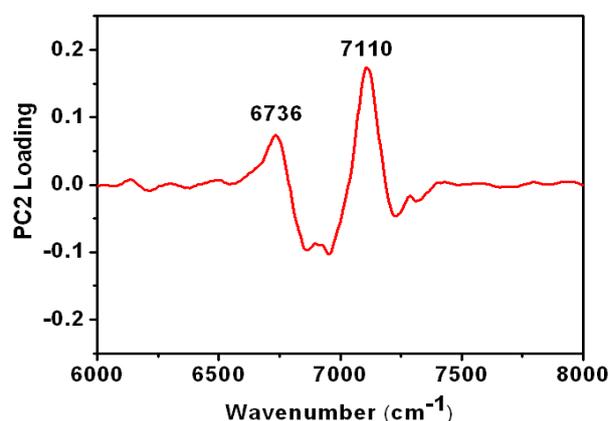


Figure 4b. Plot of PC2 loadings obtained from PCA performed on all 61 samples.

It was clear that sets A1, A2 and B, in comparison with unfiltered water samples, contained a greater number of water species with a high number of hydrogen bonds. In particular, samples of sets A1 and A2 contained the greatest number of water species with three hydrogen bonds.

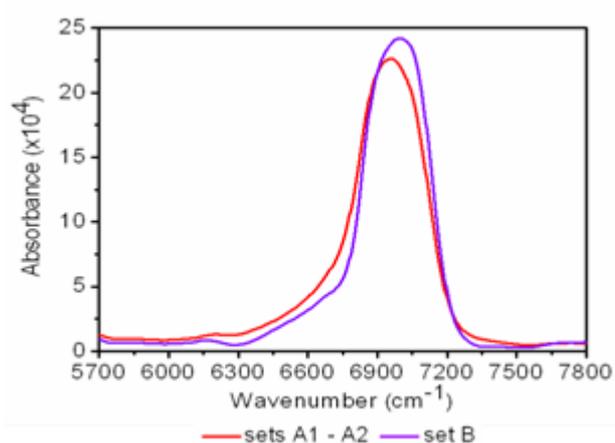


Figure 5. Difference spectra were calculated by subtracting the average spectrum of unfiltered water samples from the average spectra of samples in sets A1-A2 and of set B.

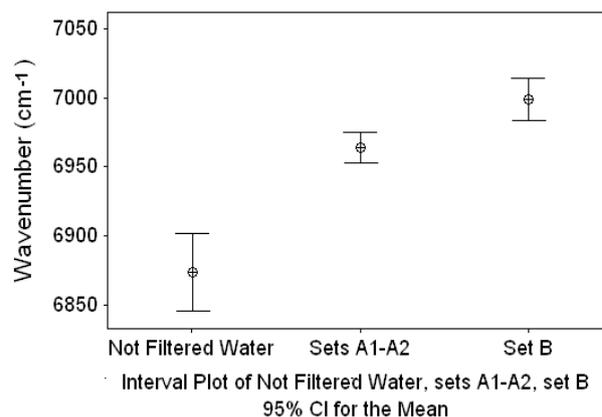


Figure 6. Interval plot of unfiltered water, sets A1-A2 and set B.

“Difference spectra” were calculated by subtracting the average spectrum of unfiltered water samples from the average spectra of samples in sets A1-A2 and set B (Figure 5). A greater intensity and the presence of additive signals in the range from 6300 to 7350 cm^{-1} were highlighted. Significant differences between the two “difference spectra” were observed in the same range as the signals observed in PC1 and PC2 loading plots. It was furthermore interesting to observe that the tail of the “difference spectra” had greater intensity for sets A1-A2, as expected from the presence of the signal at 6736 cm^{-1} in the PC2 loading.

The average spectrum of water was subtracted from all 61 spectra to verify the presence of significant differences between filtered and unfiltered water samples. The wavenumbers corresponding to the maxima of the “difference spectra” and, in the case of unfiltered water, also to the minima of the “difference spectra”, were statistically processed by applying ANOVA, with the probability level fixed at 5%. The ANOVA indicated that the “null hypothesis, which declares that different protocols do not influence water structure, was rejected. Moreover, the application of Tukey method demonstrated that the 95% confidence intervals did not intersect among the intervals of maxima values for the three sample sets, confirming the presence of significant differences between sets.

Conclusions

It is difficult to establish which physical processes, such as iterated filtrations, lead to the formation of water nano-structures. AS observed in this paper, after applying statistical analyses, iterated filtrations induced significant NIR spectral differences between filtered and unfiltered samples. It seemed that filtration processes could induce the formation of water clusters which were detectable in the NIR region by the presence of an increasing number of water species with a high number of hydrogen bonds.

The relationship between NIR spectra and variables that can influence the filtration process, for example filter porosity, number of iterations or some indices that vary with the number of filtration cycles (e.g. conductivity) is not yet clear. Further experiments are required for a greater understanding of the influence of these variables on the NIR spectral response and on water structure.

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