Aquaphotomics and its extended water mirror concept explain why NIRS can measure low concentration aqueous solutions

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Abstract

NIR spectroscopy is regarded as a quick method that provides analytical solutions for components that represent approximately 1% or more of the total mass of the investigated composite samples. Aquaphotomics is a concept that presents water spectrum as a molecular mirror which represents the dissolved solutes. Here, NIR technique and aquaphotomics are applied for quantification of solutes at concentration level less than 1%, that has been considered unachievable with NIR spectroscopy. According to the results, the applied method based on the extended water mirror concept offers a quick and accurate alternative for classical analytical measurements of mono- and di-saccharides even at millimolar concentration levels, and provides an insight into the water molecular structure when perturbed with saccharides at low concentrations.

Keywords: NIRS, aquaphotomics, sugar, limit of detection

Introduction

Aquaphotomics is a concept in near infrared (NIR) spectroscopy that aims the evaluation of spectral data of water as a mirror which represents the dissolved solutes, and offers the possibility for disentanglement of information remaining hidden in the spectra during the mostly applied chemometrics approaches.[1] Since low concentrations of solutes can result in considerable changes of the molecular structure of water, looking at the water can amplify the information on solutes and even very low concentrations of solutes can be measured and characterized. NIR spectroscopy does not require derivatization or other labor-intensive time consuming sample preparations which are common in classical analytical methods of measuring micro-compounds, like thin-layer chromatography, HPLC, GC, GC-MS.[2,3,4] The precision and accuracy of NIR technique might be lower in some applications than those of the above mentioned analytical methods, but the simplicity of the measurements, the ability to be used in sample non-destructive monitoring provide a big advantage and a good alternative in many cases. The goal of this study was to apply NIR technique and aquaphotomics for quantification of lactose at millimolar concentration in aqueous solutions.

Materials and methods

Sample

Analytical grade lactose (Hirose Chemicals Co., Ltd., Kobe, Japan) was diluted in water (Millipore, Molsheim, France) for definite concentrations between 0.02-100mM, at 0.01, 0.1, 1 and 10mM steps in the 0.02-0.1, 0.1-1, 1-10 and 10-100mM concentration ranges, respectively. Four independent replicates were prepared for each concentration.

NIR spectral collection

Samples were scanned in the range of 400-2500nm with 0.5nm spectral step, using a FOSS XDS spectrometer (FOSS NIRSystems, Inc., Hoganas, Sweden). Transmittance spectra of MQ and lactose solutions were recorded with Rapid Liquid Analyzer module and 1mm cuvette. Acquisition of absorbance values ($\log T^{-1}$) was performed with the VISION 3.5 software (FOSS NIRSystems, Inc., Hoganas, Sweden).

Data analysis

Pirouette 4.0 spectral analytical program (Infometrics, Inc., Woodinville, WA, USA) was applied for data transformations, evaluations and visualizations.

Results and discussion

Quantitative partial least squares regression (PLSR) models were fitted on the spectral data and reference concentration values of lactose solutions in the four range, using 1100-1800nm spectral interval. Applying the four replicate series of dilutions together, highly accurate models were developed in the 10-100 and 1-10mM concentration ranges, R^2_{CV} = 0.99 and 0.98, SECV = 0.96 and 0.42, respectively, using only four PLSR factors in each case (Figure 1). During cross-validation, data of one replicate of four was left out from the calibration model and this retained set was used for testing. Then, another replicate was left used for test until all of the replicates were used as validation samples. To check the stability of the quantitative models, PLSR calibrations were made on the four separate replicates of dilutions in each concentration range (n = 30 per replicates). Data analysis was performed on 1100-1800nm and 1300-1600nm spectral intervals, the latter representing the 1st overtone region of water. Results of the two spectral intervals were very similar. Table 1 summarizes the readout data of the 1300-1600nm interval, where the mean values of the performance indicators are shown with the standard deviations achieved for the four replicate solutions. Further data evaluations accentuated characteristic changes at the same regions highlighted in Figure 1, showing that the most information is provided by the solvent water.

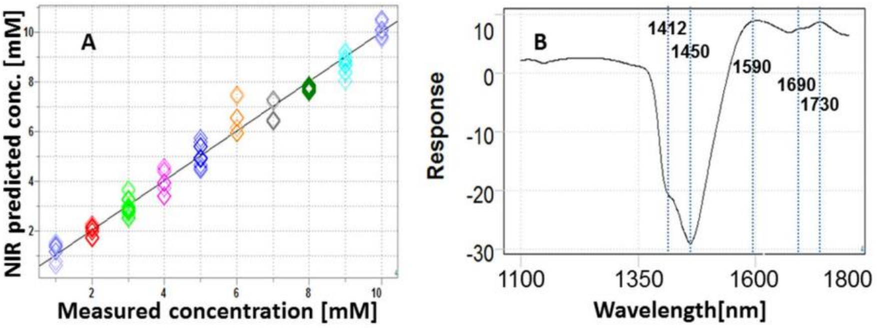

Figure 1. (A) PLSR cross-validation Y-fit of lactose in the 1-10mM concentration range using 1100-1800nm NIR spectra of all the four replicate solutions together (n = 120, R^2_{CV} = 0.98, SECV = 0.42); (B) the regression vector of the calibration model showing dominant characteristic peaks in the 1st overtone region of water (1300-1600nm), namely at 1400-1470nm spectral interval

Table 1. Means and standard deviations of PLSR results on lactose concentration for the four replicate solutions at the different concentration ranges, using 1300-1600nm spectral interval ($RPD_{CV}=SD_Y/SECV$)

	10-100mM	**1-10mM**	**0.1-1mM**	**0.02-0.1mM**
factor#	3	4	5	1
R^2_{Cal}	0.99±0.00	0.99±0.01	0.88±0.07	0.05±0.02
SEC	1.32±0.11	0.34±0.15	0.11±0.03	0.03±0.00
R^2_{CV}	0.99±0.00	0.97±0.02	0.49±0.26	0.33±0.18
SECV	1.69±0.23	0.47±0.17	0.21±0.06	0.03±0.00
RPD_{CV}	17.91	6.40	1.44	0.91

Conclusion

NIR technique coupled with aquaphotomics concept is useful method for quantification of the investigated carbohydrate solutes at millimolar level. It has been demonstrated in the present study that the absorption regions of water provide the most useful information on the solutes in case of highly diluted aqueous solutions. Accordingly, the molecular changes of water caused by the solute can be traced and used for describing the amount of dissolved material. NIR technique and aquaphotomics based on the extended water mirror concept may provide a quick and accurate alternative for classical analytical measurements even at very low concentration levels.

References

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