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

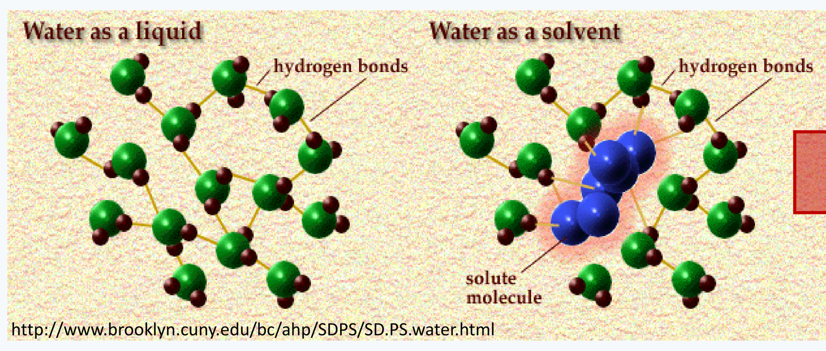
George Bázár,[1,2,*] Zoltán Kovács,[1,3] Mariko Tanaka,[1] Roumiana Tsenkokva [1,*]
[1] Biomeasurement Technology Laboratory, Graduate School of Agriculture, Kobe University, Japan
[2] Institute of Food and Agricultural Product Qualification, Faculty of Agricultural and Environmental Sciences, Kaposvár University, Hungary
[3] Department of Physics and Control, Faculty of Food Science, Corvinus University of Budapest, Hungary

INTRODUCTION

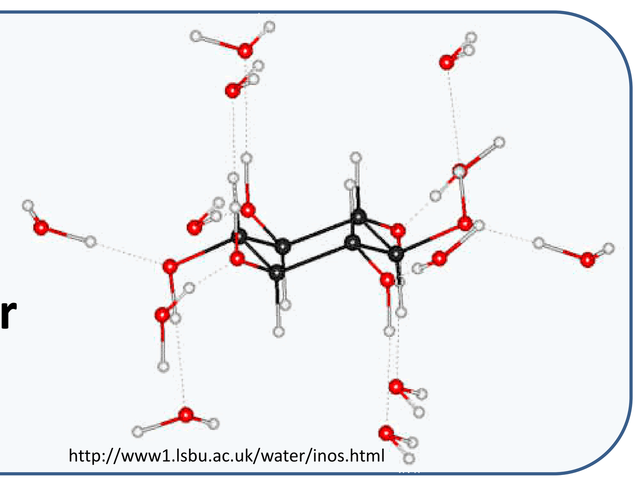
Low concentration aqueous solutions → low spectral intensity of solutes

BUT!

The molecular changes of the water solvent caused by the solute can be detected by NIR spectroscopy and used for qualitative and quantitative analyses [1]



Measuring low concentration of sugar in aqueous solutions based on the molecular changes of water [2]

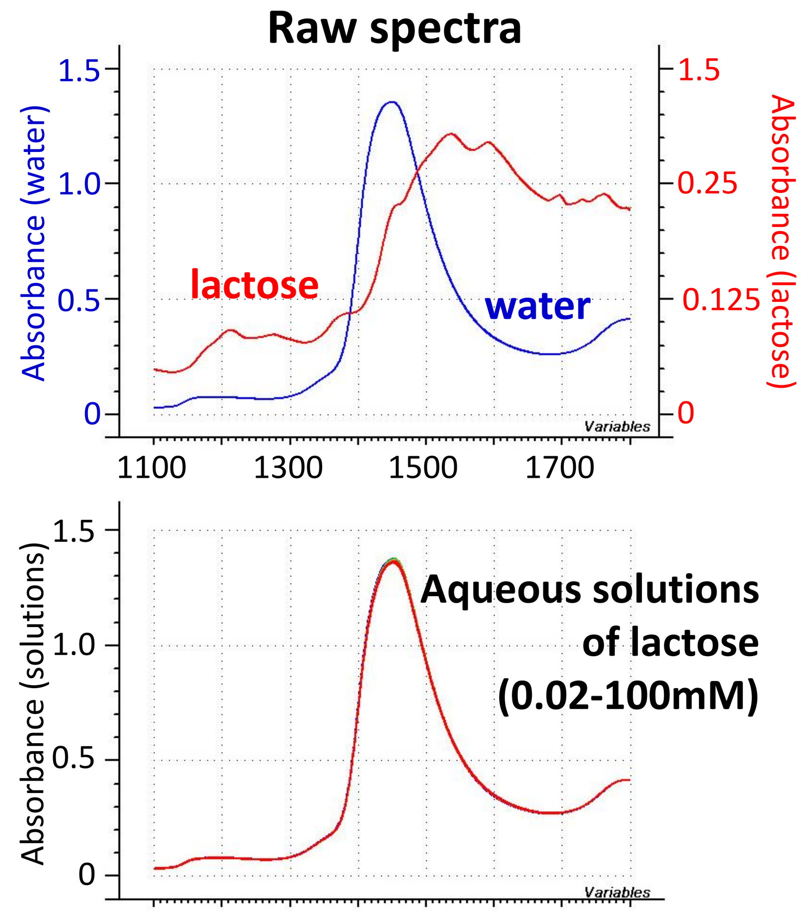


MATERIALS AND METHODS

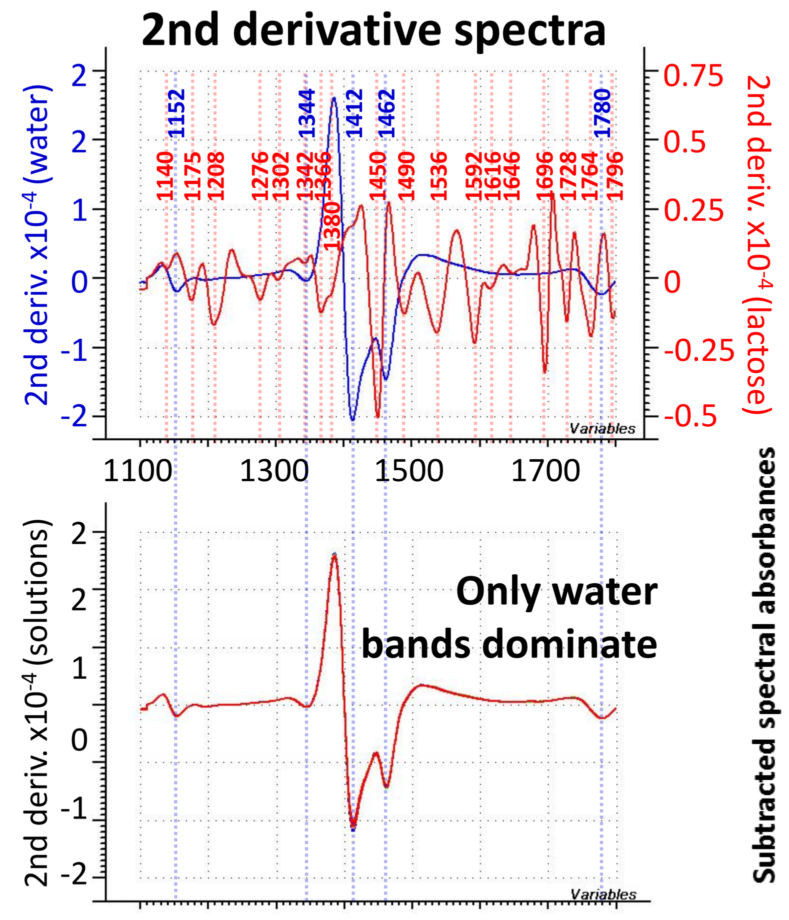
- Analytical grade lactose → diluted in Milli-Q water
  - 0.02-0.1mM range, with 0.01mM steps
  - 0.1-1mM range, with 0.1mM steps
  - 1mM-10mM range, with 1mM steps
  - 10mM-100mM range, with 10mM steps
- Four independent replicates were prepared for each concentration range
- FOSS XDS spectrometer (FOSS NIRSystems, Inc., Hoganas, Sweden) with RLA module and 1mm cuvette → transmittance spectra ($\log T^{-1}$) at 1100-1800nm with 0.5nm spectral step
- R Project (www.r-project.org), The Unscrambler v9.7 (CAMO Software AS, Oslo, Norway), Pirouette 4.0 (Infometrics, Inc., Woodinville, WA, USA)

RESULTS

Raw spectra

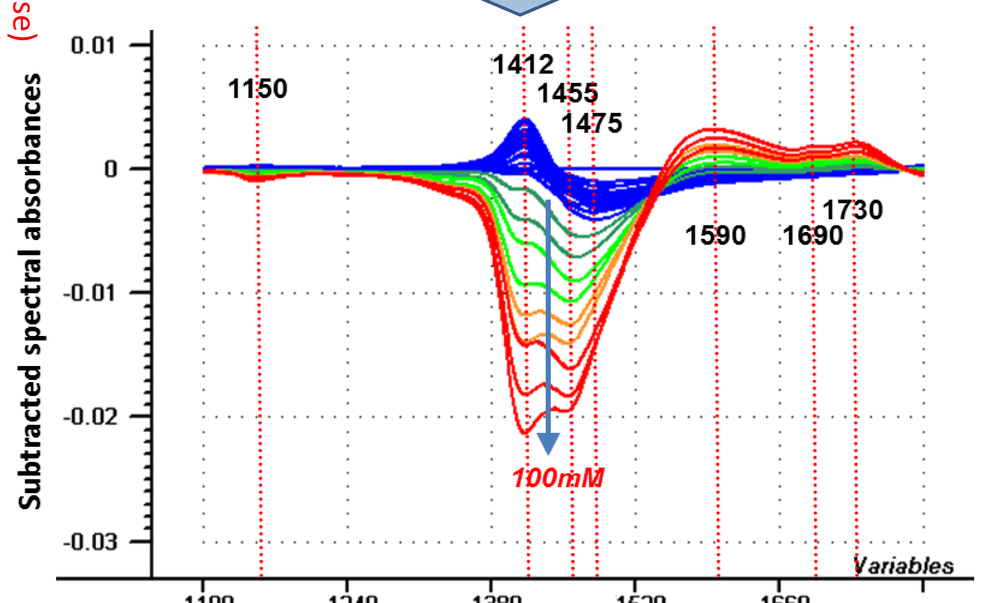


2nd derivative spectra



Signals of lactose can hardly be detected in low concentration solutions.

Subtraction of water spectrum from those of the lactose solutions reveals the spectral differences of the different concentrations.



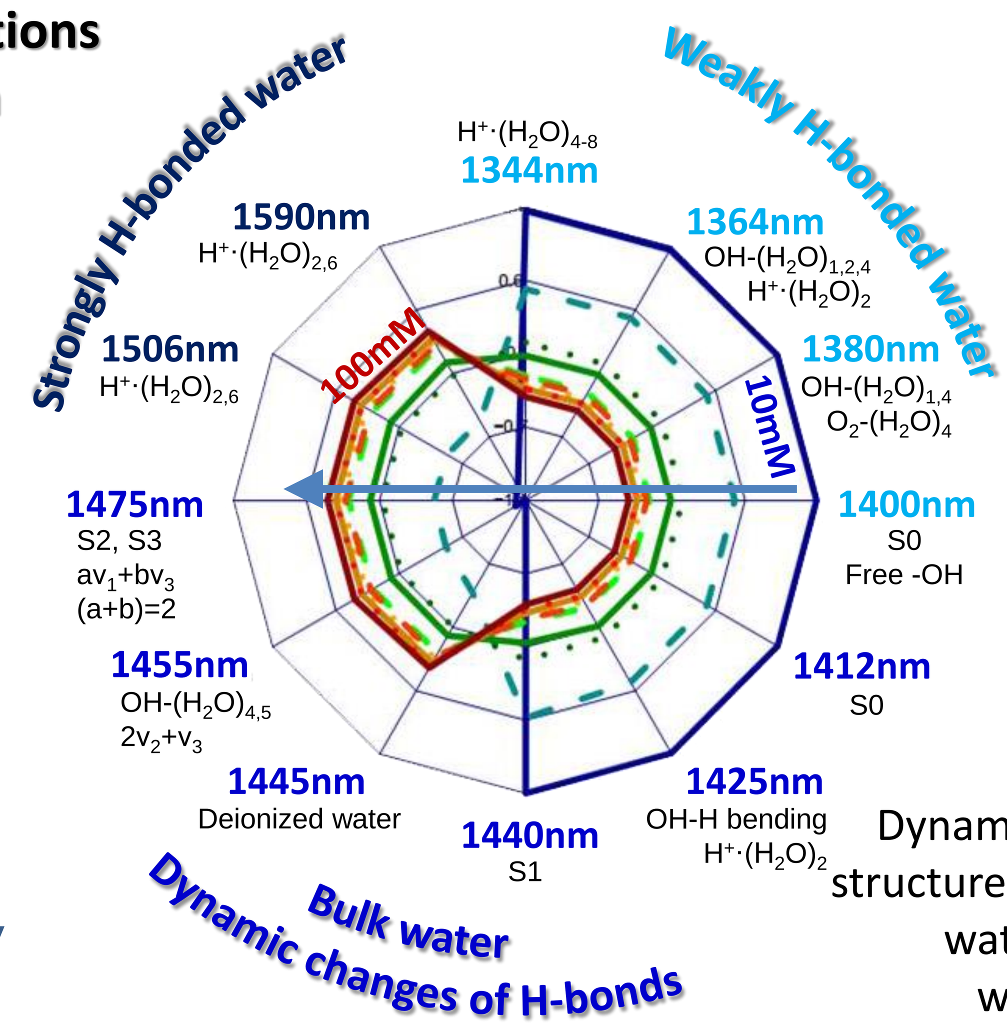
Characteristic changes at water matrix coordinates describe the water spectral pattern of lactose.

Visualization on aquagram [3]:

$$A = \frac{a - \mu}{\sigma}$$

A = Aquagram value
a = absorbance after MSC
μ = average of all spectra
σ = SD of all spectra

Structural changes of water in sugar solutions presented on aquagram



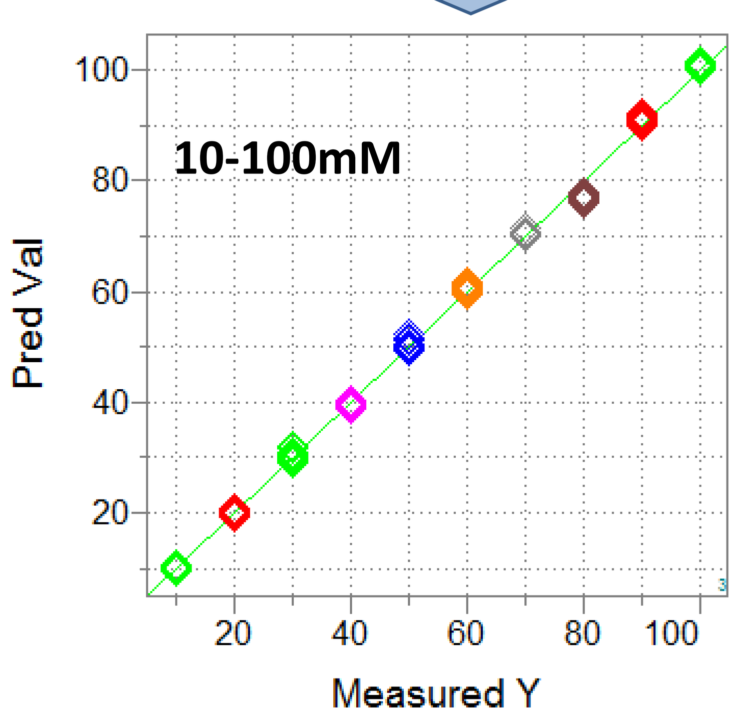
Dynamic changes of structure maker and structure breaker characteristics of sugar in water [2]. Breaker is dominant in low, while maker in high concentrations.

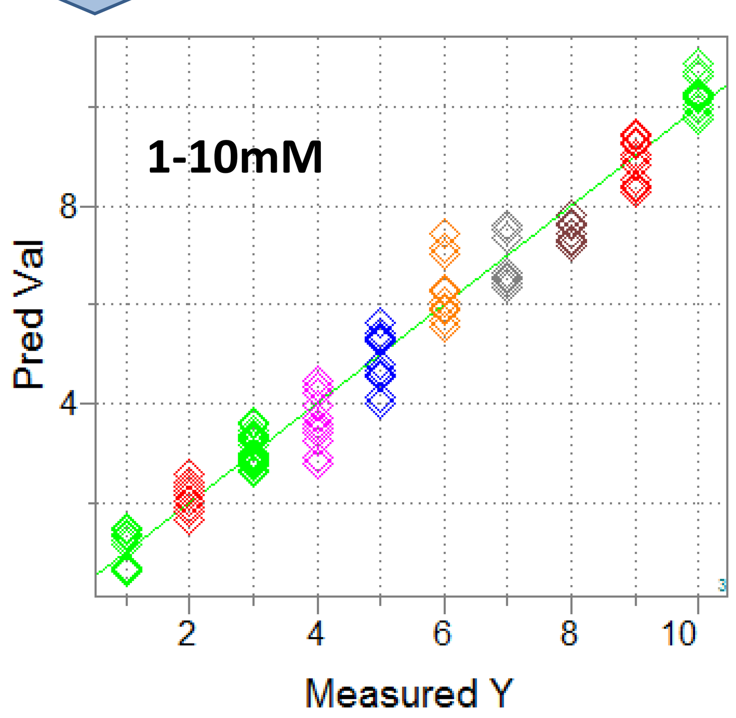
Means and standard deviations of PLSR results on lactose concentration in the four replicate solutions (n = ca.30) at the different concentration ranges, applying different spectral regions

		10-100mM	1-10mM	0.1-1mM	0.02-0.1mM
1100-1800nm	factor#	3	3	4	1.75±1.5
	R^2_{Cal}	**0.99±0.00**	**0.99±0.01**	**0.84±0.12**	0.72±0.09
	RMSEC	**0.99±0.06**	**0.34±0.06**	**0.11±0.04**	0.02±0.01
	R^2_{CV}	**0.99±0.00**	**0.97±0.02**	**0.48±0.27**	-1.17±0.46
	RMSECV	**1.34±0.22**	**0.48±0.13**	**0.19±0.05**	0.03±0.00
	RPD_{CV}	***22.63***	***6.33***	***1.56***	*1.05*
1300-1600nm	factor#	3	3	3.75±0.5	1.75±1.5
	R^2_{Cal}	**0.99±0.00**	**0.99±0.01**	**0.80±0.15**	0.68±0.09
	RMSEC	**0.99±0.07**	**0.34±0.07**	**0.13±0.07**	0.02±0.01
	R^2_{CV}	**0.99±0.00**	**0.97±0.01**	**0.33±0.33**	-0.91±0.70
	RMSECV	**1.34±0.23**	**0.48±0.12**	**0.22±0.05**	0.03±0.00
	RPD_{CV}	***22.59***	***6.37***	***1.37***	*1.07*

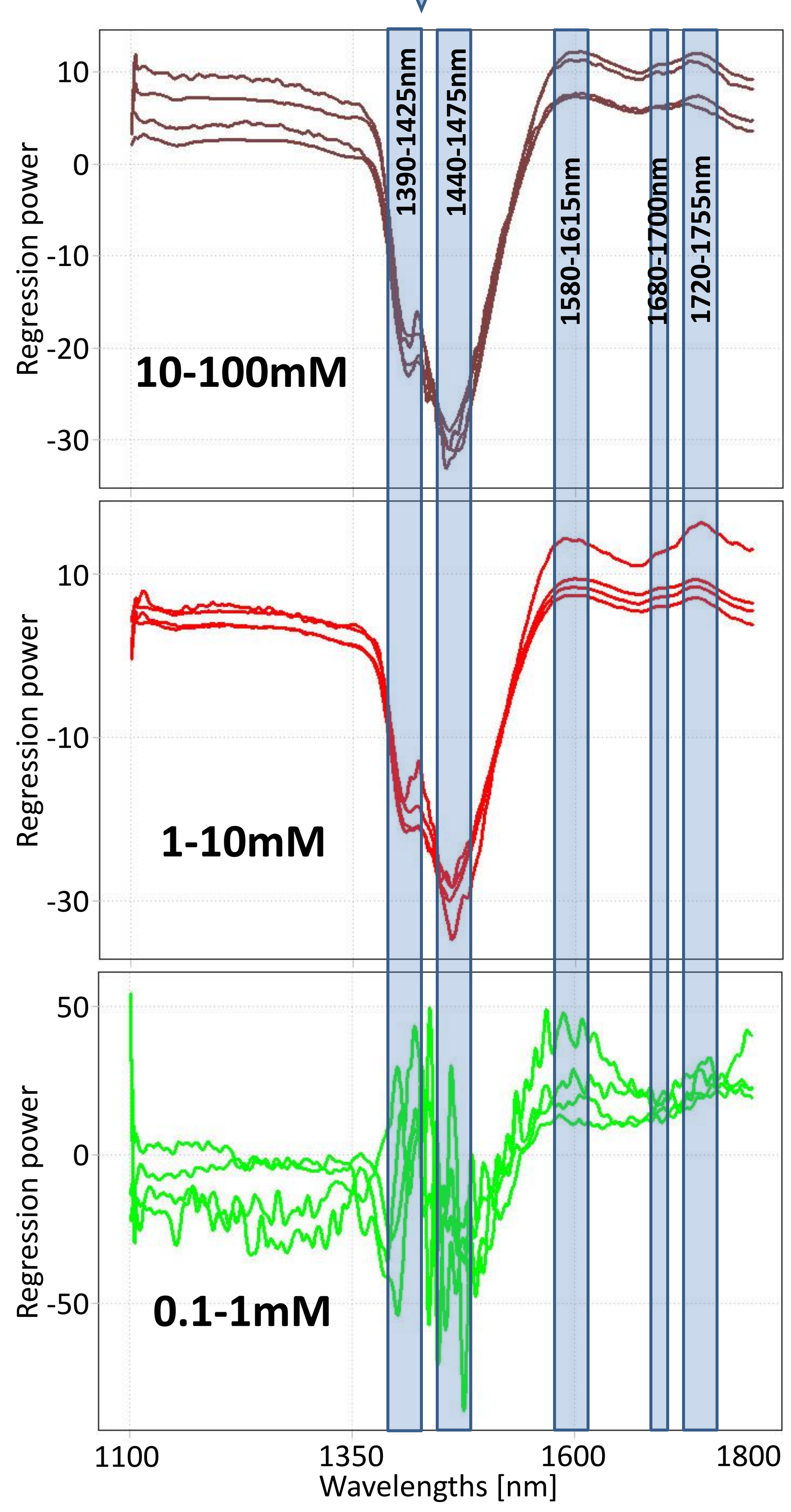
PLSR results on lactose concentration at the different concentration ranges using the four replicate solutions together (n = ca.120), applying different spectral regions and 'leave one replicate out' cross-validation

		10-100mM	1-10mM	0.1-1mM	0.02-0.1mM
1100-1800nm	factor#	3	3	3	1
	R^2_{Cal}	**0.99**	**0.98**	0.35	0.07
	RMSEC	**1.03**	**0.40**	0.23	0.03
	R^2_{CV}	**0.99**	**0.98**	0.24	-0.1
	RMSECV	**1.08**	**0.42**	0.25	0.03
	RPD_{CV}	***27.94***	***7.19***	*1.23*	*1.15*
1300-1600nm	factor#	3	3	3	1
	R^2_{Cal}	**0.99**	**0.98**	0.33	0.05
	RMSEC	**1.04**	**0.40**	0.23	0.03
	R^2_{CV}	**0.99**	**0.98**	0.23	-0.04
	RMSECV	**1.08**	**0.42**	0.25	0.03
	RPD_{CV}	***28.04***	***7.13***	*1.22*	*1.15*





Regression vectors of calibration models built on the subtracted spectra of water and lactose solutions show stability among replicate measurments, and accentuate the dominant water regions.



CONCLUSIONS

NIR technique coupled with aquaphotomics concept is useful method for quantification of the investigated carbohydrate solutes at millimolar level.

Lactose causes gradual changes in the water molecular matrix, thus, performance of calibration on lactose concentration does not decrease when only the characteristic spectral region of water 1st overtone (1300-1600nm) is applied.

In the contrary, it has been demonstrated in the present study that the absorption regions of water provide 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 provide a quick and accurate alternative for classical analytical measurements even at very low (1-10mM) concentration levels.

REFERENCES & ACKNOWLEDGEMENTS

[1] Tsenkova, R., 2009. Journal of Near Infrared Spectroscopy, 17, 303-314. [2] Giangiacomo, R., 2006. Food Chemistry, 96, 371-379. [3] Tsenkova, R., 2010. Spectroscopy Europe, 22, 6-10.

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*** To whom correspondence should be addressed**
E-mail: bazar@agrilab.hu (G.B.); rtsen@kobe-u.ac.jp (R.T.)