Aquaphotomics: Introduction

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水と光

Water and Light

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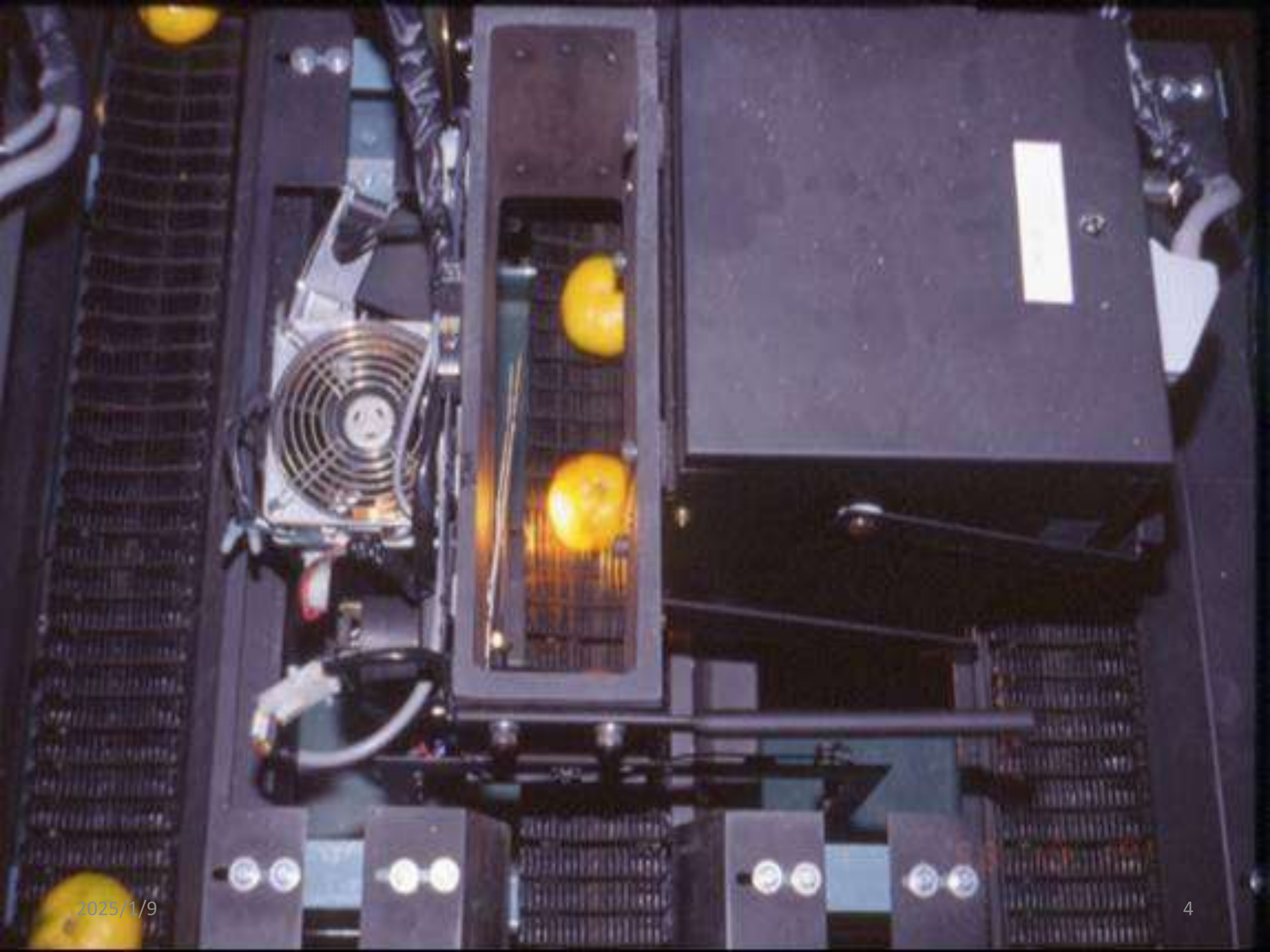
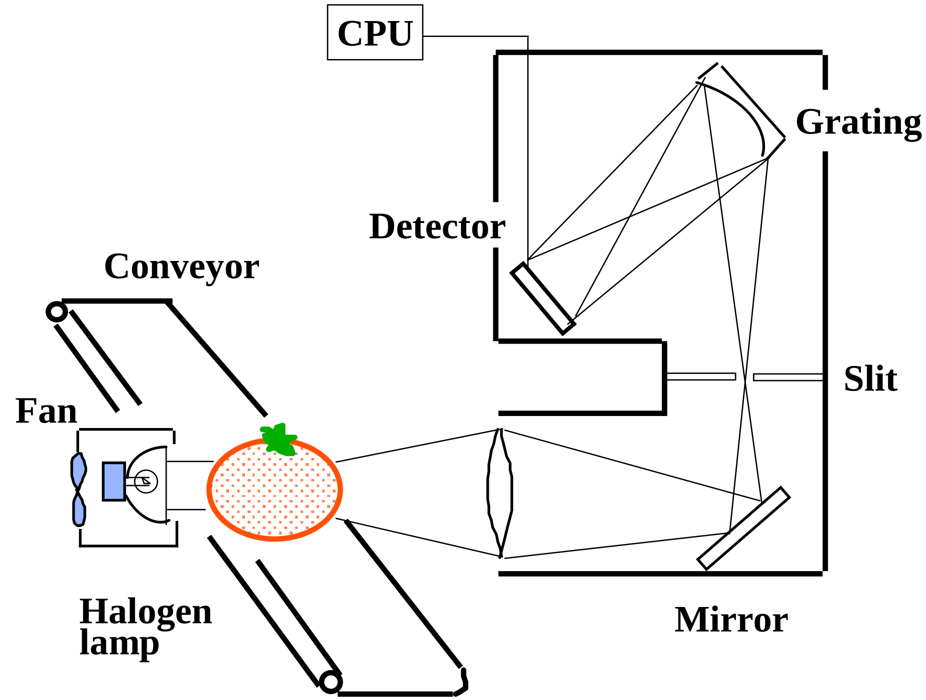
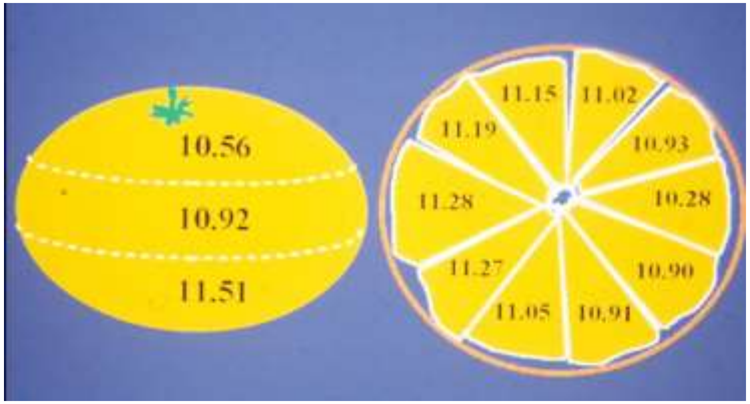
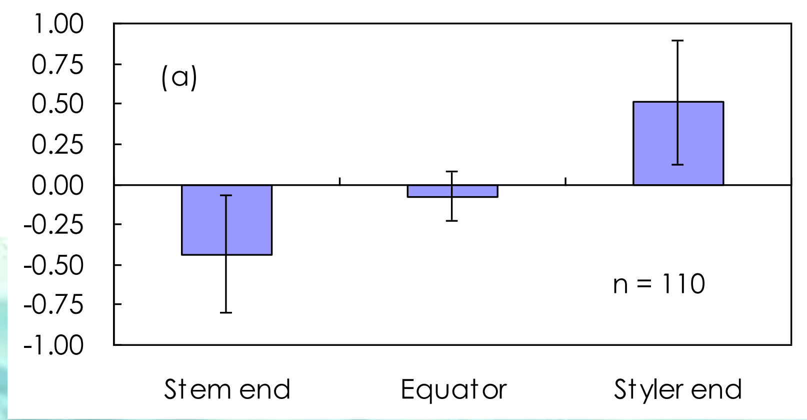
04
05
06
07

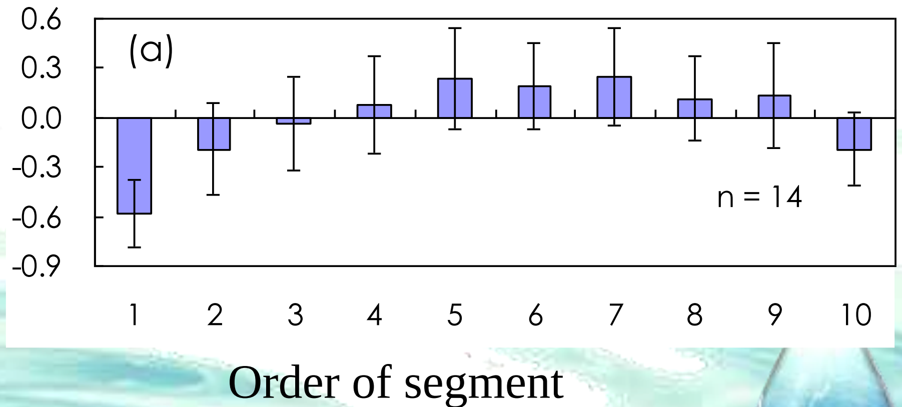






NIR grader's structure for satsuma mandarin





Distribution of the difference from the average sugar content in a whole fruit

Aquaphotomics concept

Water as matter and energy mirror

AQUAPHOTOMICS

Aqua - : water

Photo - : light

Omics - : all about,

complement of something

LIGHT *"turns on"* the **mirror**,

LIGHT *"turns on"*

the **water in to 4 - dimensional molecular mirror**

LIGHT as a

source of perturbation
(electromagnetic field)

and a probe
(the spectrum)

1

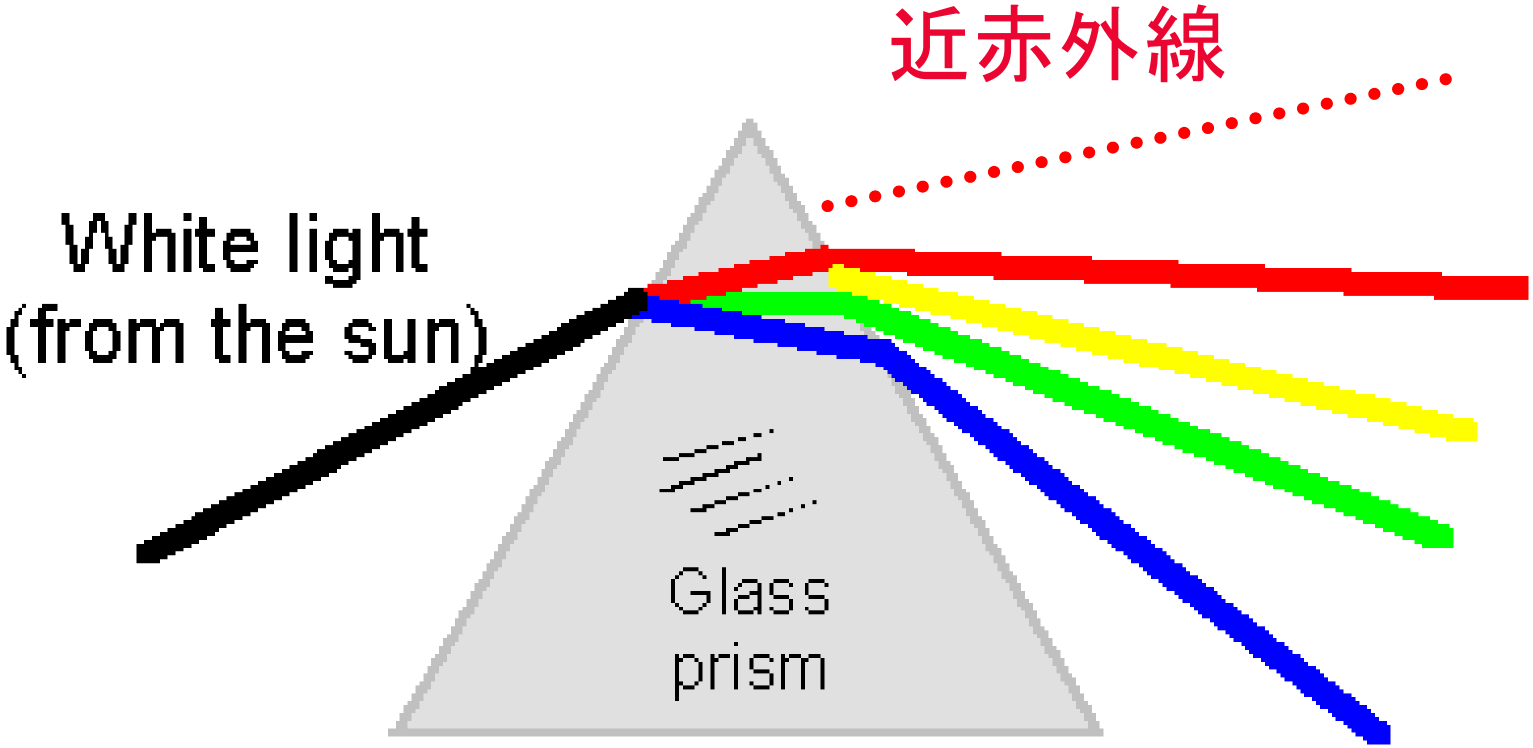
Aquaphotomics Concept

Current approach in biology:
X – Omics

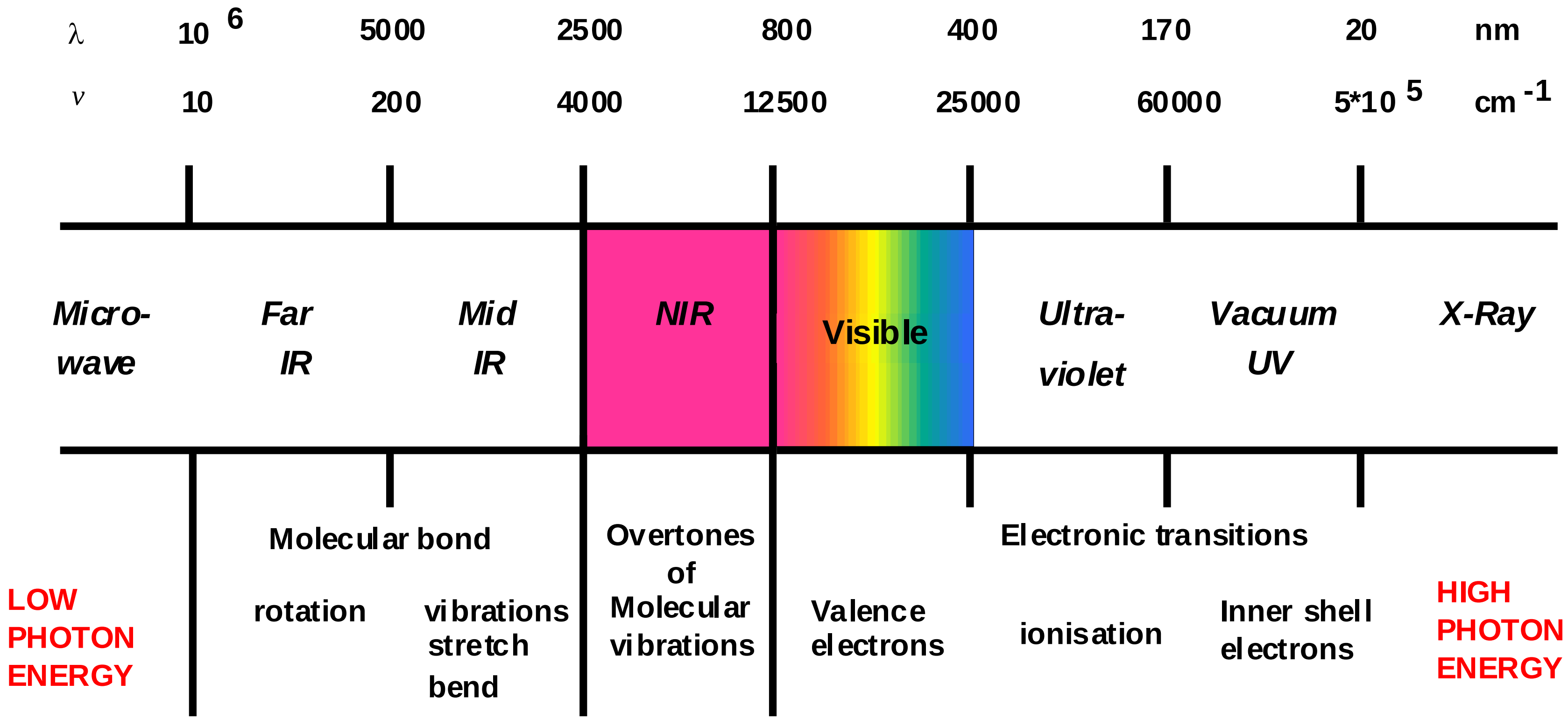
Newly proposed Aquaphotomics:
Water as Molecular and Energy Mirror Holistic Approach

single components analysis (genomics, proteomics, metabolomics, …)

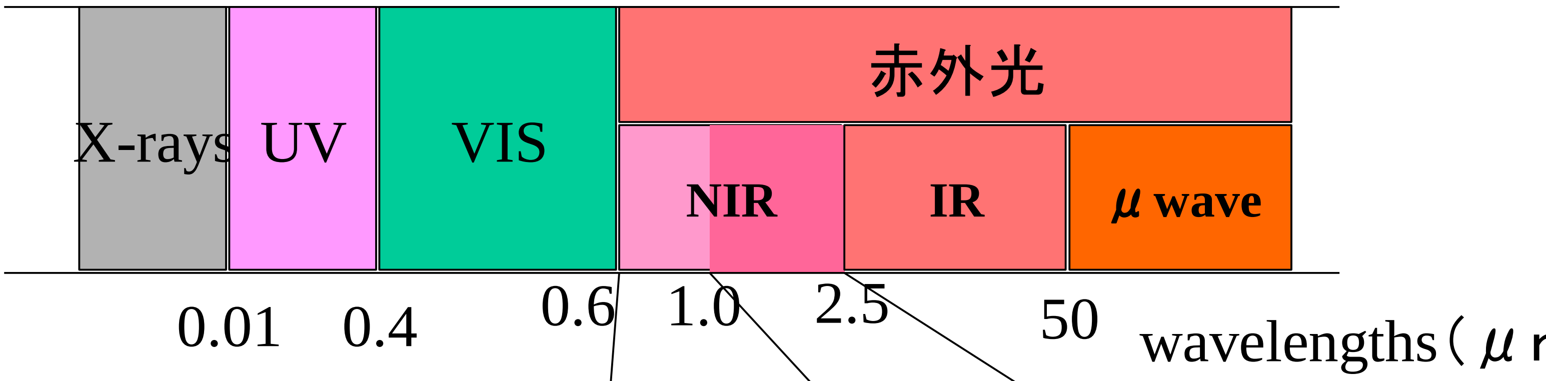
water molecular system multivariate spectral analysis directly related to system functionality


近赤外線
White light
(from the sun)
Glass
prism

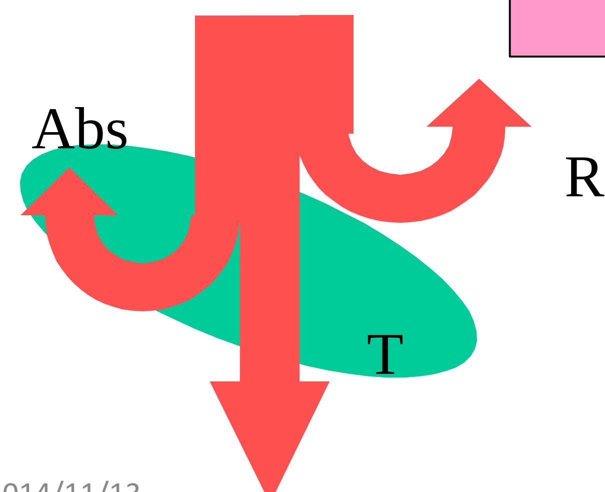
The Electromagnetic Spectrum



$\lambda\nu = c = 3 \times 10^{8}\ m\ s^{-1}$ $E_{photon} = h\nu$ $h = 6.6 \times 10^{-34} Js$

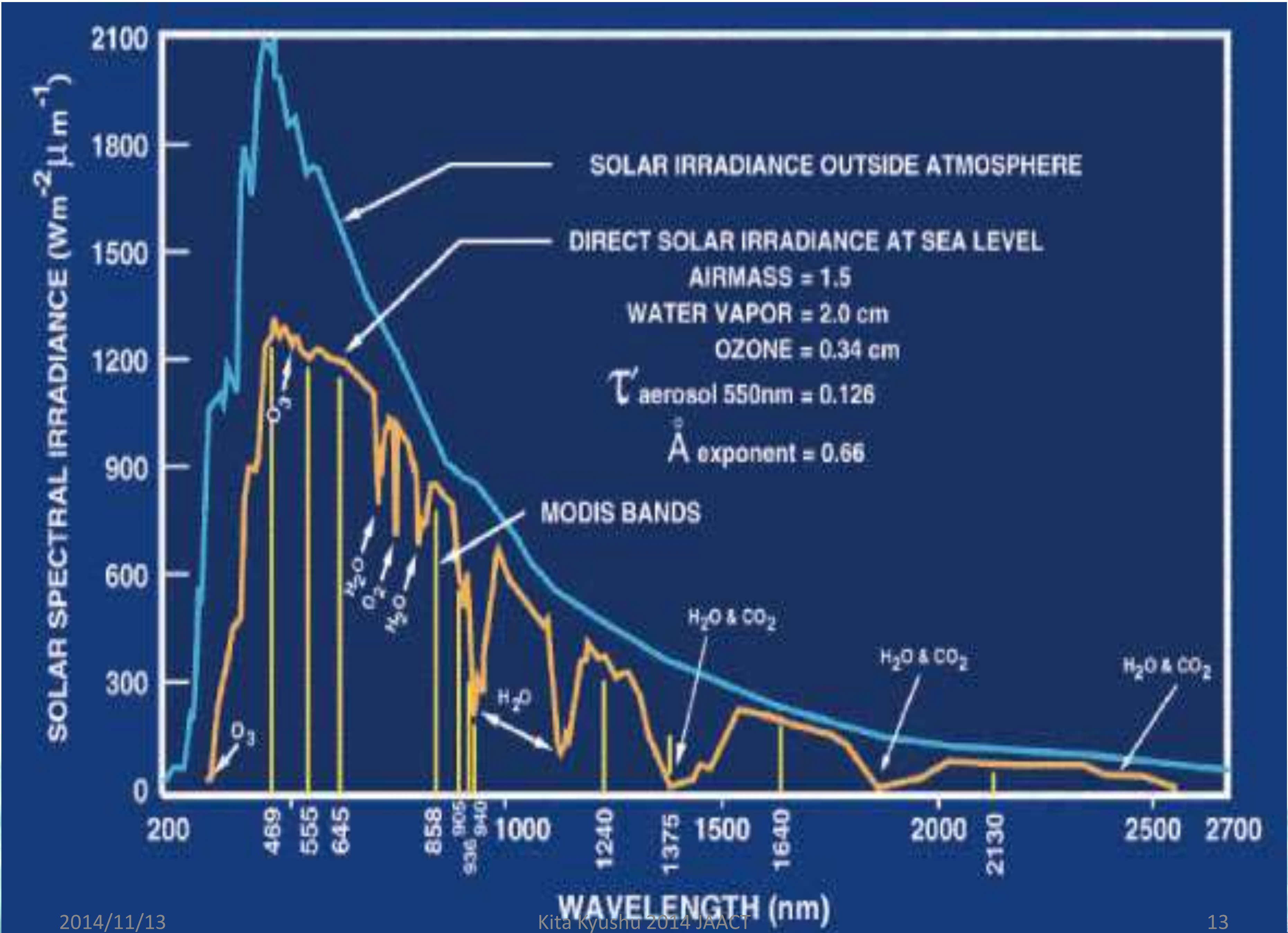


R	small	big
Abs	small	small
T	big	small

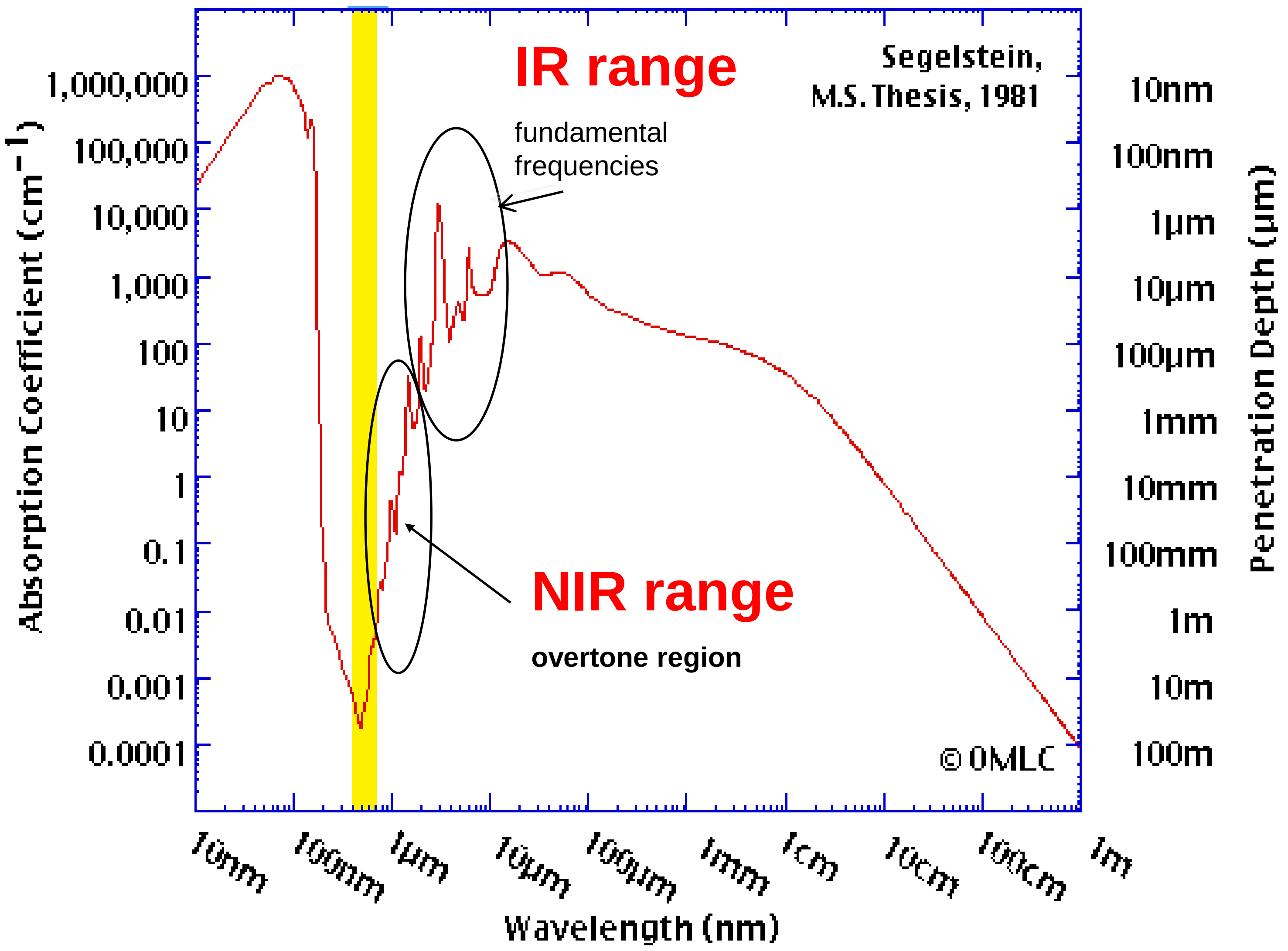


NIR range

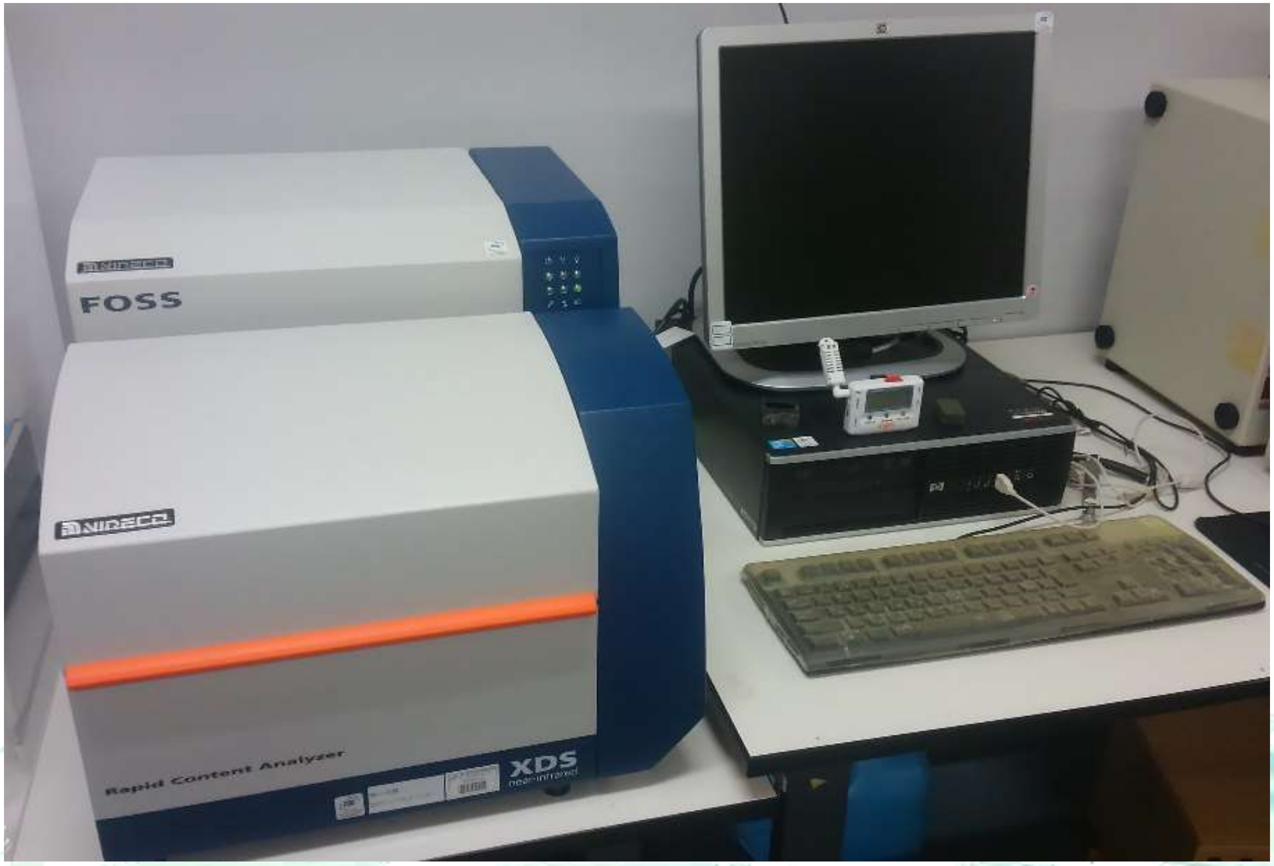
1-2


SOLAR SPECTRAL IRRADIANCE ($Wm^{-2}\mu m^{-1}$)
SOLAR IRRADIANCE OUTSIDE ATMOSPHERE
DIRECT SOLAR IRRADIANCE AT SEA LEVEL
AIRMASS = 1.5
WATER VAPOR = 2.0 cm
OZONE = 0.34 cm
$\tau'_{aerosol\ 550nm}$ = 0.126
Å exponent = 0.66
MODIS BANDS
O_3
O_3
H_2O
O_2
H_2O
H_2O
H_2O & CO_2
H_2O & CO_2
H_2O & CO_2
2100
1800
1500
1200
900
600
300
0
200
469
555
645
858
905
936
940
1000
1240
1375
1500
1640
2000
2130
2500
2700
WAVELENGTH (nm)

WATER SPECTRUM



NIRS Bench Type Instrument

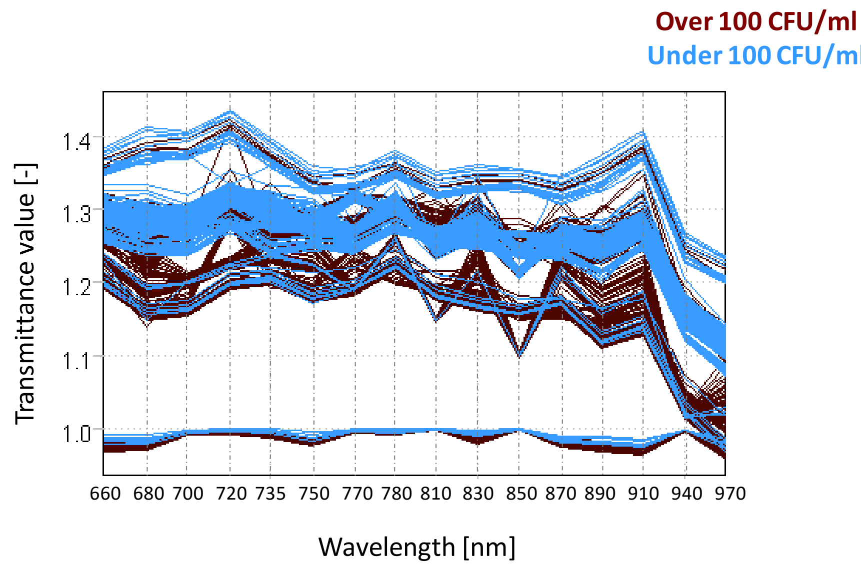


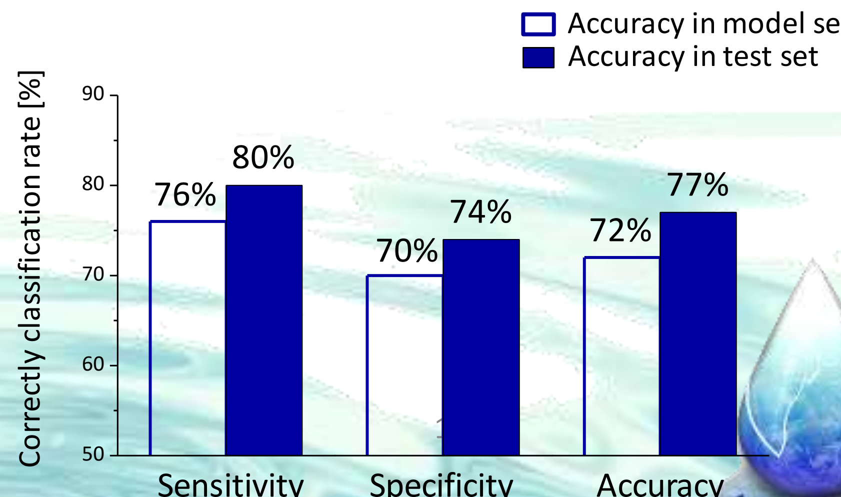
BIO MONITORING AND

BIO DIAGNOSIS

PORTABLE FIBER PROBES FOR TISSUE MEASUREMENTS

LED SENSOR for Bacteria Count Measurement in Milk





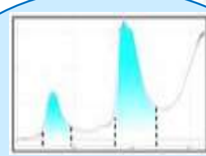
LED at 660, 680, 700, 720, 735, 750, 770, 780, 810, 830, 850, 870, 890, 910, 940, 970 nm

AQUAPHOTOMICS:
WATER as a
MOLECULAR MIRROR

Perturbations

Bio・
Aqueous
System

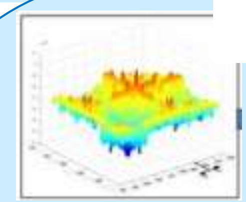
Spectral
Data Base

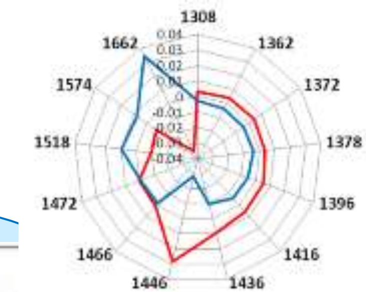


NIR spectrum

WAMACS

Activated Water
Absorbance Bands





Water Absorbance
Spectral Pattern,
WASP

WAMACS = Water Matrix Coordinates, i.e. water absorbance bands in VIS-NIR range

Contents

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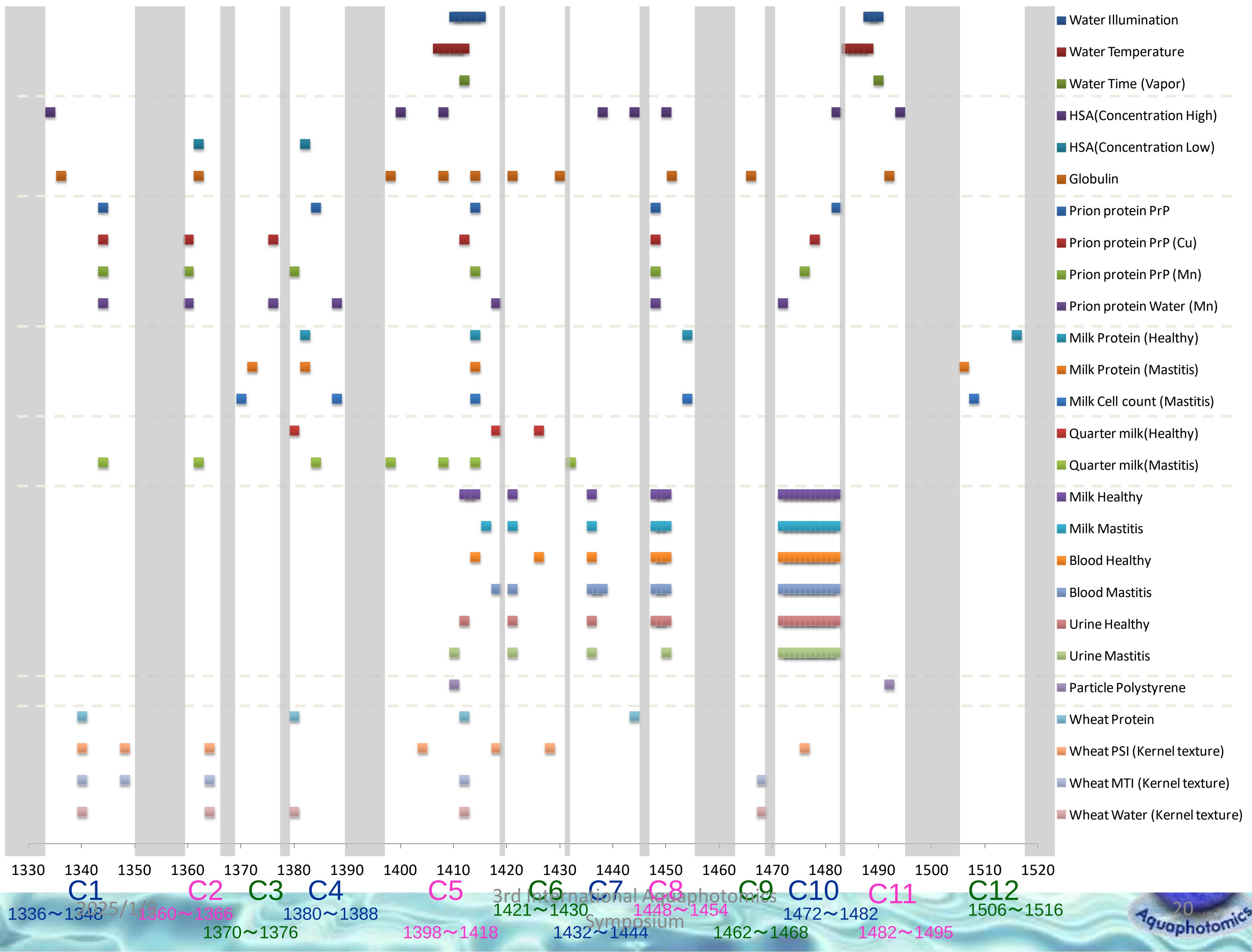
2. Water shaped by:
   - Environment
   - Single molecule
   - Cells (bacteria)



Water Illumination
Water Temperature
Water Time (Vapor)
HSA(Concentration High)
HSA(Concentration Low)
Globulin
Prion protein PrP
Prion protein PrP (Cu)
Prion protein PrP (Mn)
Prion protein Water (Mn)
Milk Protein (Healthy)
Milk Protein (Mastitis)
Milk Cell count (Mastitis)
Quarter milk(Healthy)
Quarter milk(Mastitis)
Milk Healthy
Milk Mastitis
Blood Healthy
Blood Mastitis
Urine Healthy
Urine Mastitis
Particle Polystyrene
Wheat Protein
Wheat PSI (Kernel texture)
Wheat MTI (Kernel texture)
Wheat Water (Kernel texture)
1330 1340 1350 1360 1370 1380 1390 1400 1410 1420 1430 1440 1450 1460 1470 1480 1490 1500 1510 1520
C1
1336～1348
C2
1360～1366
C3
1370～1376
C4
1380～1388
C5
1398～1418
C6
1421～1430
C7
1432～1444
C8
1448～1454
C9
1462～1468
C10
1472～1482
C11
1482～1495
C12
1506～1516

1345.5	H17O8+, 1st overt.	Wei and Salahub 1997: The Journal of Chemical Physics, 106: 6086.				
1346.3	H9O4+ free OH stech, 1st overt.	Mizuse and Fijii 2012: The Journal of Physical Chemistry, 116: 4868.				
1346.3	H17O8+ free OH stech, 1st overt.	Mizuse and Fijii 2012: The Journal of Physical Chemistry, 116: 4868.				
1346.6	H15O7+, 1st overt.	Wei and Salahub 1997: The Journal of Chemical Physics, 106: 6086.				
1347.0	aqueous proton [H+·(H2O)5] - AD-type H2O free-OH strech, 1st overt.	Headrick et al. (Mark Johnson) 2005: Science, 308: 1765.				
1347.0	H15O7+ free OH stech, 1st overt.	Mizuse and Fijii 2012: The Journal of Physical Chemistry, 116: 4868.				
1347.7	H13O6+ free OH stech, 1st overt.	Mizuse and Fijii 2012: The Journal of Physical Chemistry, 116: 4868.				
1348.1	H11O5+ free OH stech, 1st overt.	Mizuse and Fijii 2012: The Journal of Physical Chemistry, 116: 4868.				
1351	H502	Tsenkova				
1351.35	1st overtone (OH-(H2O)5)	Science28				
1351.35	OH-(H2O)5 (free RTs)	Tsenkova				
1351.4	-OH free streching, 1st overt.	Shin et al. (Mark Johnson) 2004: Science, 304: 1137.				
1353.0	high correlation with combined single salt solution data (NaCl and KCl)/overall salinity	R. Peters and S. Nobles, University of Saskatchewan				
1353.2	nonbonded -OH steches, 1st overt.	Headrick et al. (Mark Johnson) 2005: Science, 308: 1765.				
1353.2	1st overtone free OH stretch (OH-(H2O)3)	Science28				
1354	1st overtone free OH stretch (OH-(H2O)2)	Science28				
1355	1st overtone Superoxide Tetrahydrate O2-.(H2O)4	Weber, Science 2000				
1356.8	Water - n1+n3+n	Choppin and Violante 1972: The Journal of Chemical Physics, 56: 5890.				
1357.6	H17O8+ free OH stech, 1st overt.	Mizuse and Fijii 2012: The Journal of Physical Chemistry, 116: 4868.				
1357.93	1st overtone H2O (1%) - n3	Ozaki 1982				
1358.3	H17O8+, 1st overt.	Wei and Salahub 1997: The Journal of Chemical Physics, 106: 6086.				
1359.1	H15O7+ free OH stech, 1st overt.	Mizuse and Fijii 2012: The Journal of Physical Chemistry, 116: 4868.				
1359.4	H15O7+, 1st overt.	Wei and Salahub 1997: The Journal of Chemical Physics, 106: 6086.				
1360.55	1st overtone free OH stretch (OH-(H2O)4)	Science28				
1362	1st overtone free wather OH stretch (OH-H2O)	Xantheas, 1995				

C1 - **1336-1348 (1342)nm – ν_3**

*1344nm H2O - 2** ν_3 (*Siesler, Ozaki, Kawata, & Heise, 2001)*

1340nm liquid water/moisture (Williams, 2009)

$\nu_1 + \nu_2$ $\nu_1 + \nu_3$ $\nu_1 + \nu_2$ $2\nu_{OH}$ (v)II 2*v2+v3

$OH\text{-}(H_2O)_{I\ \ i=1\ldots}$

H15O7+ free OH strech

H13O6+ free OH strech, 1st overt

$O2\ \text{-}(H_2O)_{I\ i=1\ldots}$

'-OH strech in fully hydrated hydronium, 2nd overt.

$H+\ \text{-}(H_2O)_{I\ i=1\ldots}$

DD stretch (OH-(H2O)4)

1st overtone free OH stretch (OH-(H2O)4) - 3675cm^{-1}

(*Robertson, Diken, Price, Shin, & Johnson, 2003)*

H bond 18=<n=<24, 1st overt.

aqueous proton [H+·(H2O)5] - AD-type H2O free-OH strech, 1st overt

degenerate asymmetric OH strech, 2nd overt.

aqueous proton [H+·(H2O)4] - H3O+ symmetric stretch, 1st overt.

Dangling -OH (non-hydrogen-bonded), 1st overt.

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Assignment

<u>C1</u> - 1336-1348 (1342)nm – ν_3
1344nm H2O - 2 ν_3 (Siesler, Ozaki, Kawata, & Heise, 2001)*
1340nm liquid water/moisture (Williams, 2009)

<u>C2</u> - 1360-1366 (1364)nm – $OH\text{-}(H_2O)_1$, $OH\text{-}(H_2O)_2$, $OH\text{-}(H_2O)_4$
1360nm 1st overtone free OH stretch (OH-(H2O)4) - 3675cm^{-1} (Robertson, Diken, *Price, Shin, & Johnson, 2003)*
1366nm 1st overtone OH- stretch (OH-(H2O)2) - 3660cm^{-1} (Robertson et al., 2003)

<u>C3</u> - 1370-1379 (1374)nm – $\nu_1 + \nu_3$
1379.3nm H2O - v1 + v3 – 7250cm^{-1} (Siesler et al., 2001)
1379.3nm overtone of stretching vibration – 7250cm^{-1} (Kuroda, Hamano, Mori, Yoshikawa, & Nagao, 2000)
1373 nm first overtone of $2v_{OH}$ (Lakshmi Reddy, Padma Suvarna, Udayabhaska Reddy, Endo, & Frost, 2014)

<u>C4</u> - 1380-1388 (1384)nm – $OH\text{-}(H_2O)_1$, $OH\text{-}(H_2O)_4$, $O_2\text{-}(H_2O)_4$
1383.15nm 1st overtone interwater / DD stretch (OH-(H2O)4) - 3615cm^{-1} (Robertson et al., 2003)
1381nm H2O-v_{1+} v_3 (Cattaneo, Cabassi, Profaizer, & Giangiacomo, 2009)

WAMACS

Water Matrix Coordinates:

Water absorbance bands corresponding to pools of water molecules with the same vibration frequency

1

AQUAPHOTOME

is

the entire complements of

water matrix coordinates

found under

various perturbations

over the whole EMS [1]

Water Absorbance Pattern, WAP

AQUAGRAM

Aquagram was devised to **visualize the WASP.**

The aquagram displays **normalized absorbance values at specific water** bands on the axes originating from the center of the graph.

Absorbance values at the WAMACs are placed on the respective radial axes.

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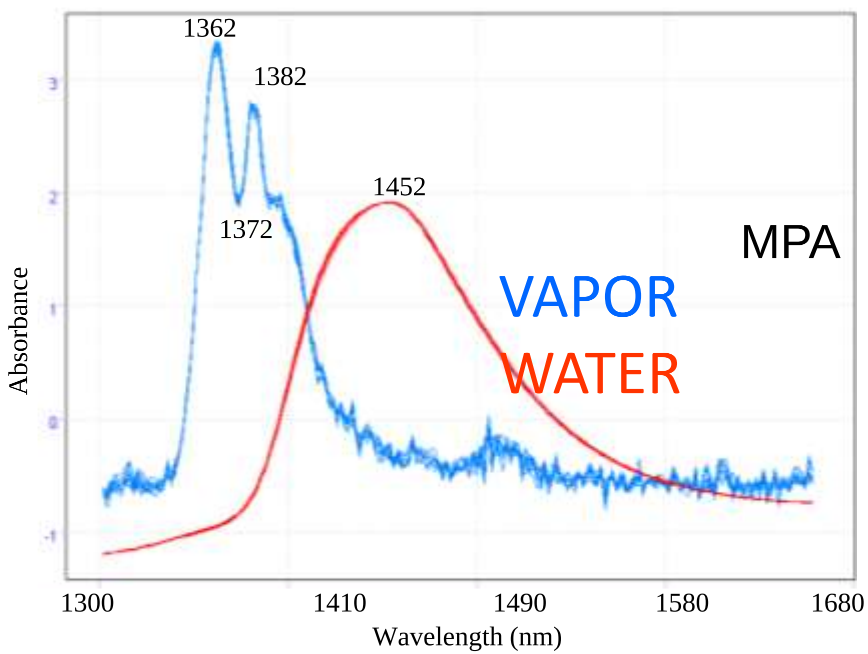
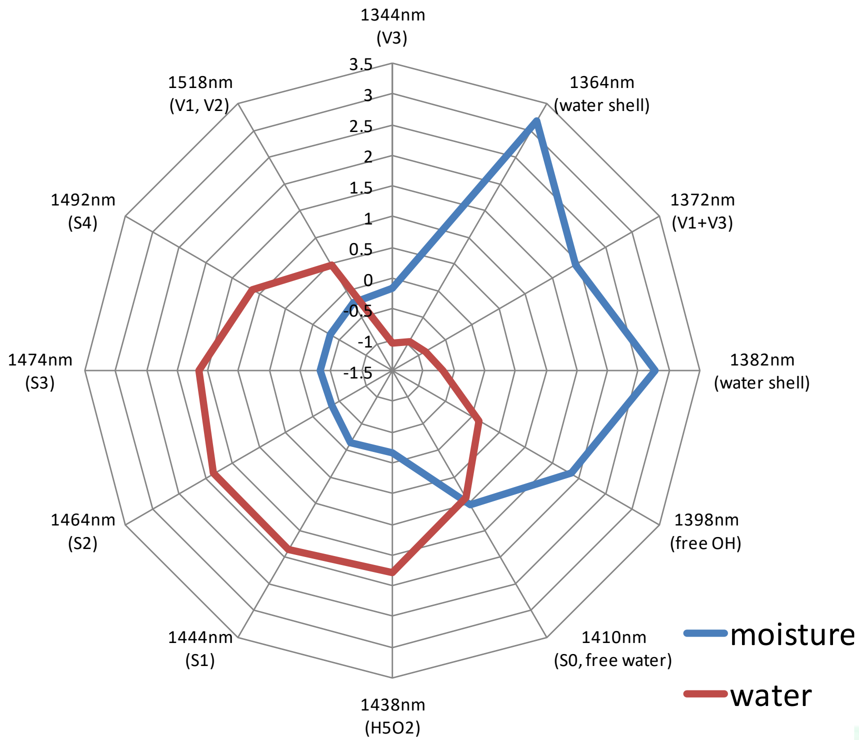
WATER and VAPOR SPECTRA AQUGRAM

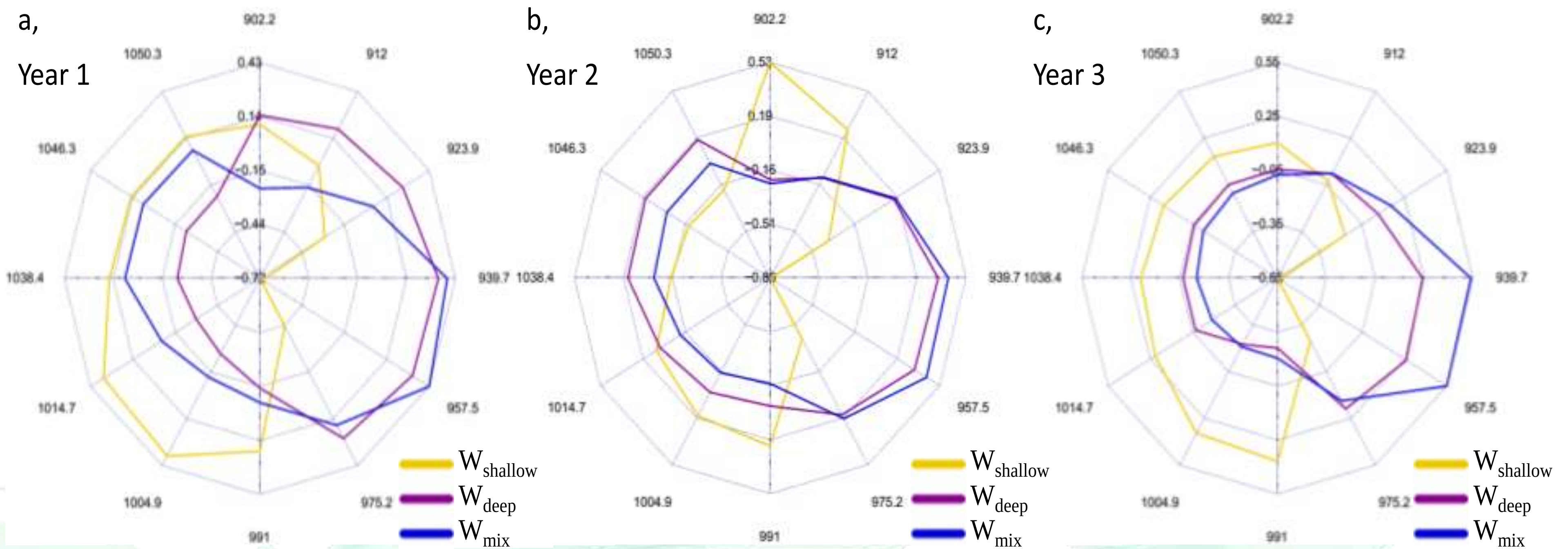




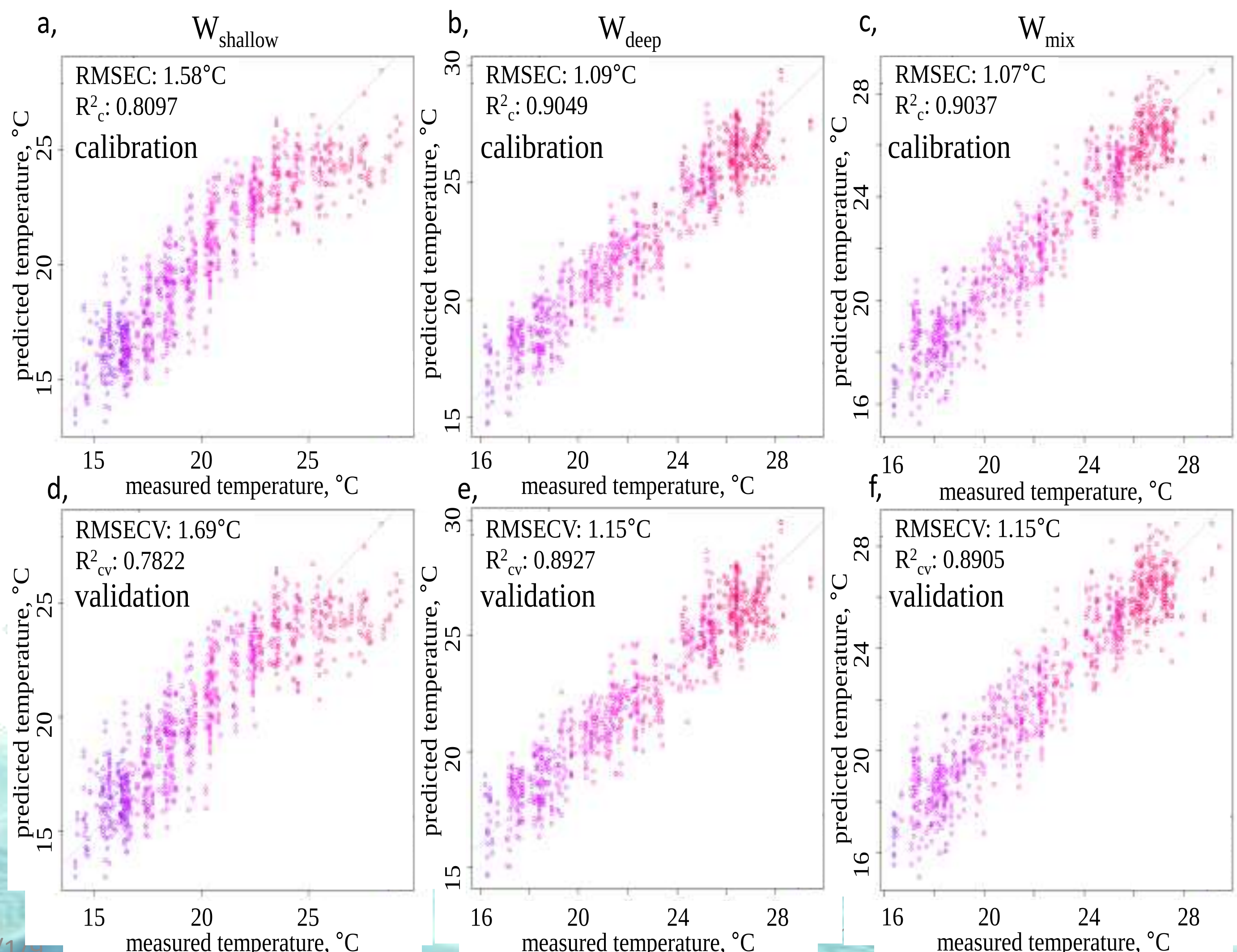
$$A'_\lambda = \frac{A_\lambda - \mu}{\sigma}$$

A : Absorbance after EMSC (1300-1600 nm)
μ : Mean of Averaged spectra
σ : SD of absorbance each wave length

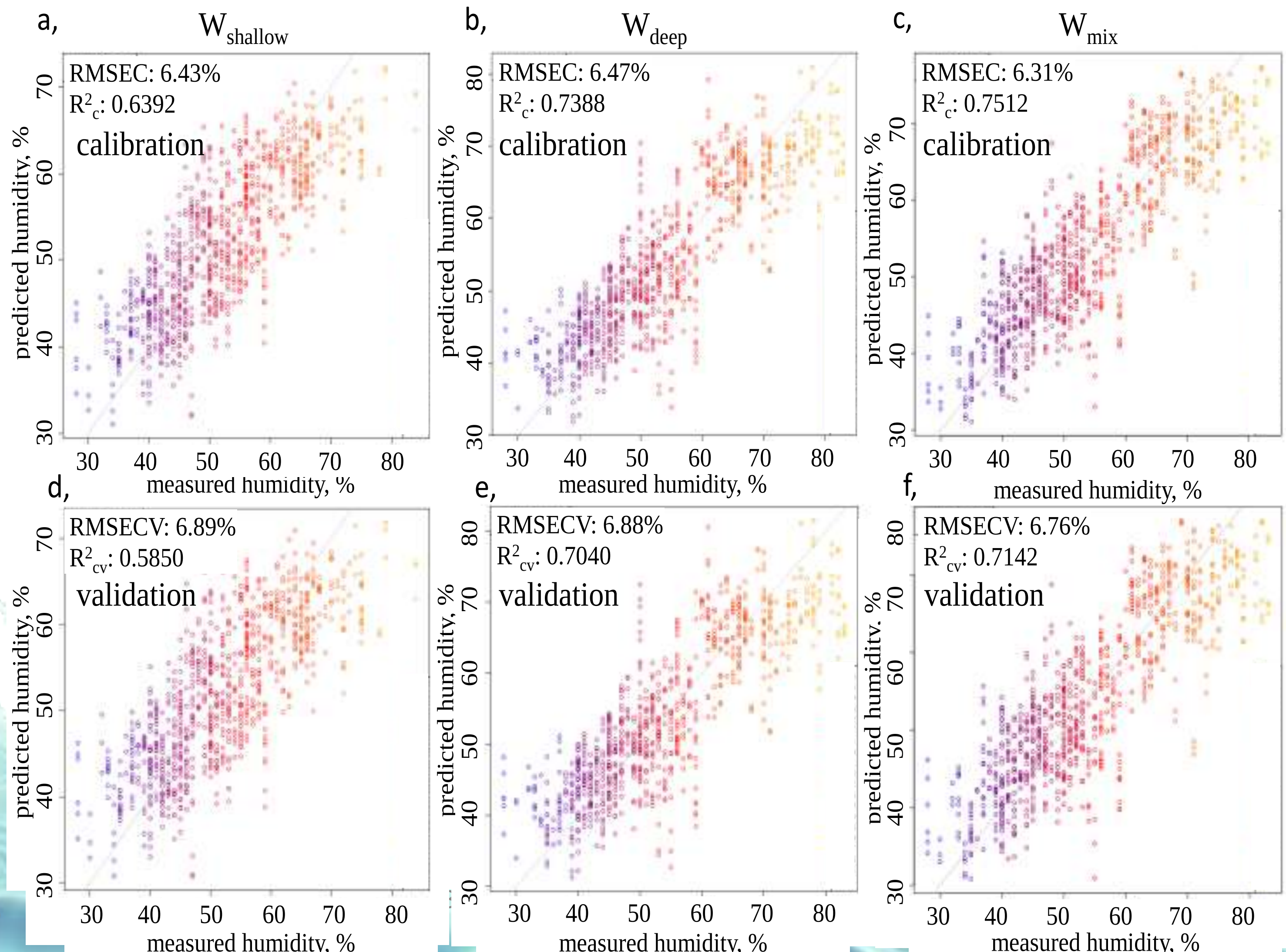
Aquagrams of ground water samples



PLSR Models on Water Temperature One Year Spectral Data



PLSR models on relative humidity One Year Spectral Data



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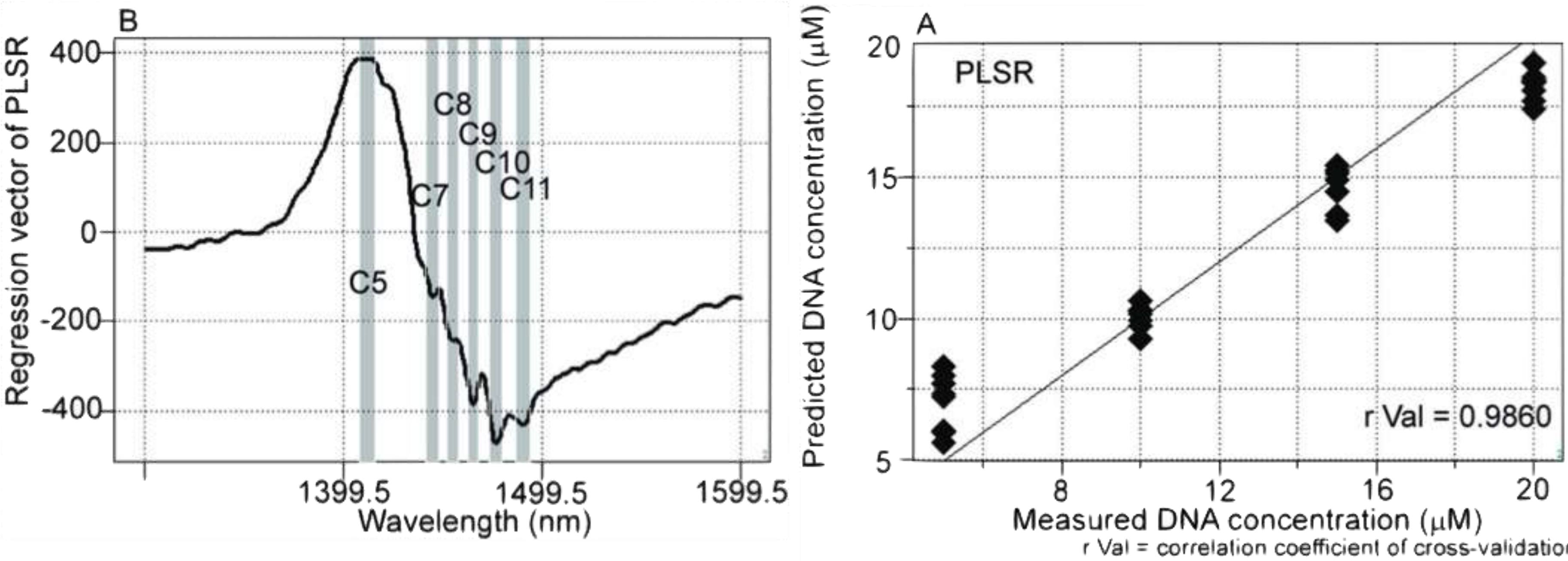

NIRS regression model according to DNA concentration. (**A**) Y-fit for DNA concentration of partial least squares regression (PLSR) with pretreatment by mean centering, smoothing (21 points), OSC (one component), and active class validation. N = 32, number of applied latent variables = 2, r Cal = 0.9978, SEC = 0.3882, r Val = 0.9860, SECV = 1.5131. (**B**) Regression vector of the PLSR calibration model for DNA concentration showing characteristic water peaks at the 1400–1500 nm spectral interval.

Detection of UV-induced cyclobutane pyrimidine dimers by near-infrared spectroscopy and aquaphotomics
N Goto, G Bazar, Z Kovacs, M Kunisada, H Morita… - Scientific reports, 2015

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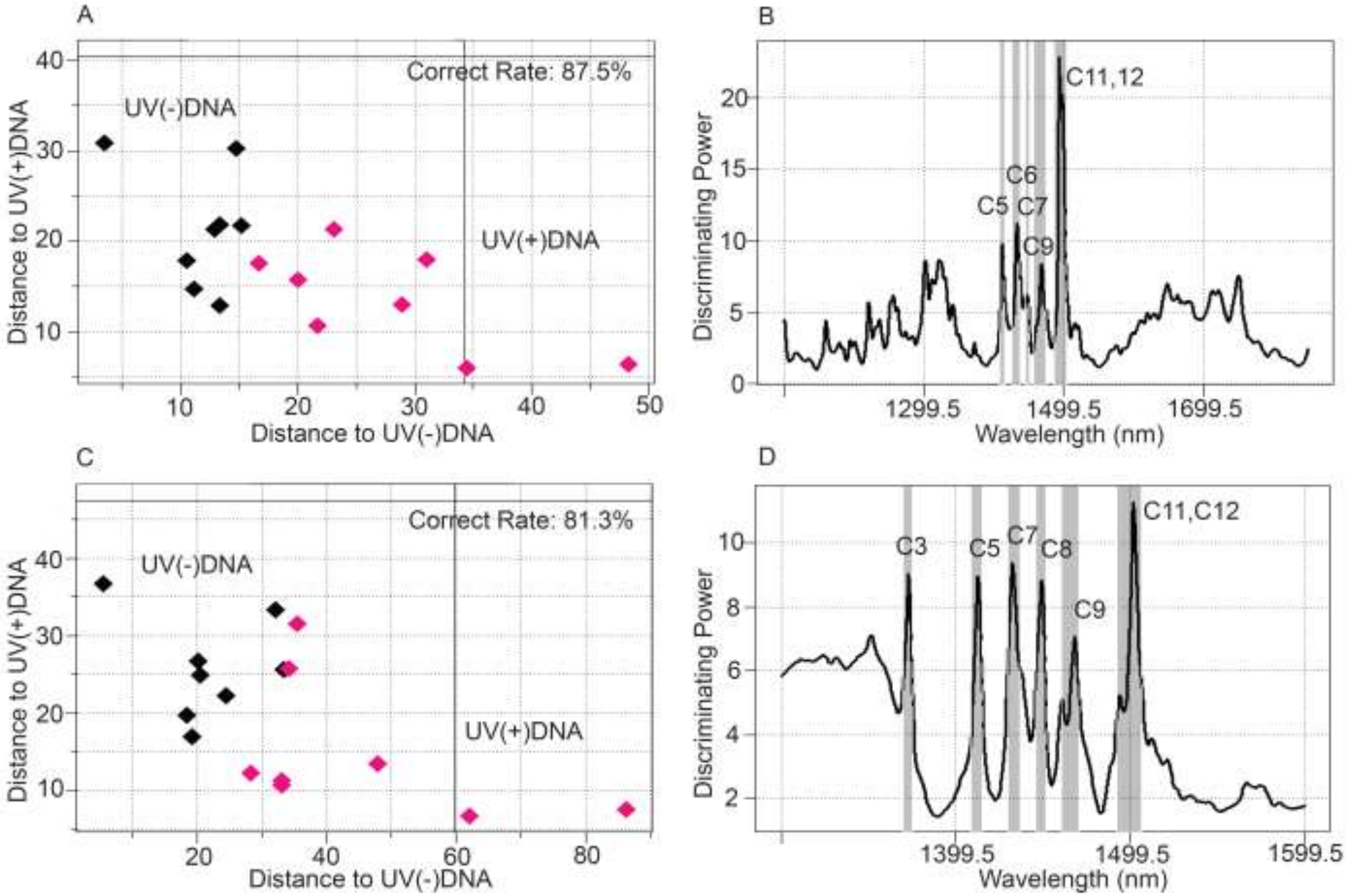

NIRS based discrimination of Milli-Q water and cis-syn T<>Ts solutions.

SIMCA using 1300-1600 nm interval of NIR spectra with mean-centering and smoothing (45 points). Factor # =2: samples of Milli-Q water and isolated cis-syn T<>Ts solutions form separate groups (ratio of correctly classified samples = 94.9 %).

C) PLS-DA using 1300-1600 nm interval of NIR spectra : 94.9 % of samples were classified correctly in cross-validation. Factor # =1.

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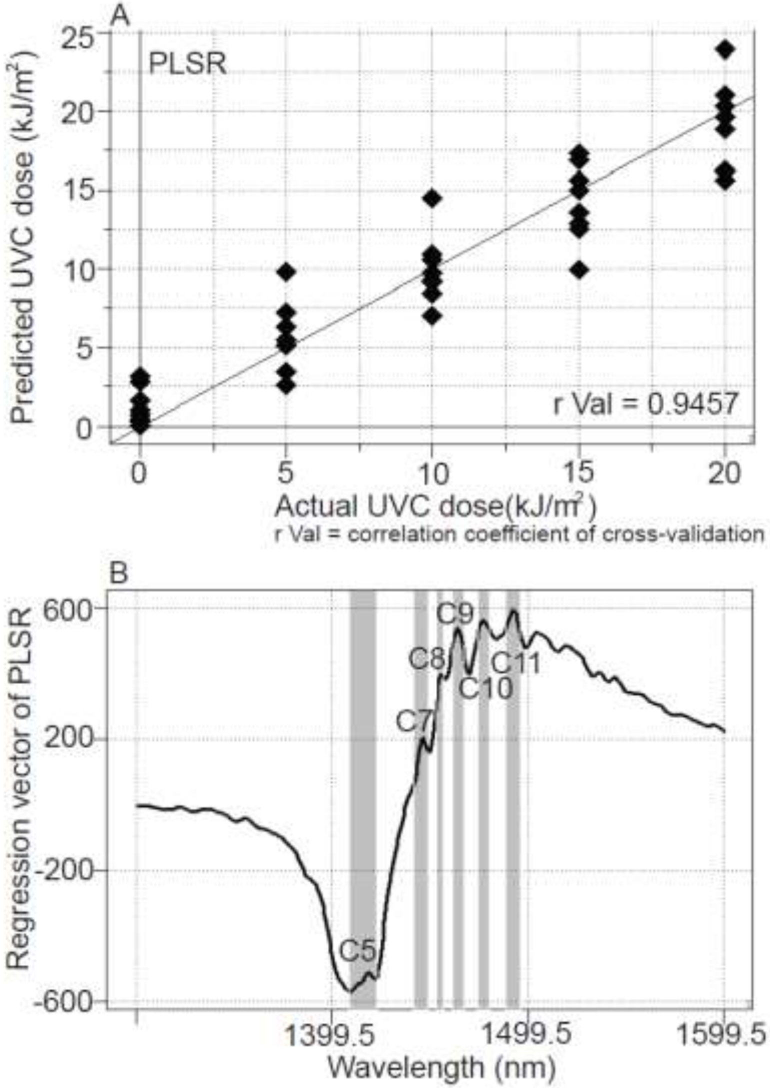
Detection of UV-induced cyclobutane pyrimidine dimers by near-infrared spectroscopy and aquaphotomics N Goto, G Bazar, Z Kovacs, M Kunisada, H Morita... - Scientific reports, 2015



Results of NIRS regression models dependent on the irradiated UVC doses show close correlation between the actually irradiated doses of UVC and the levels determined by the NIRS calibration model when DNA samples irradiated with UVC at doses of 0, 5, 10, 15 and 20 kJ/m^2 were measured in 20 µM aqueous solutions.

Detection of UV-induced cyclobutane pyrimidine dimers by near-infrared spectroscopy and aquaphotomics

N Goto, G Bazar, Z Kovacs, M Kunisada, H Morita… - Scientific reports, 2015

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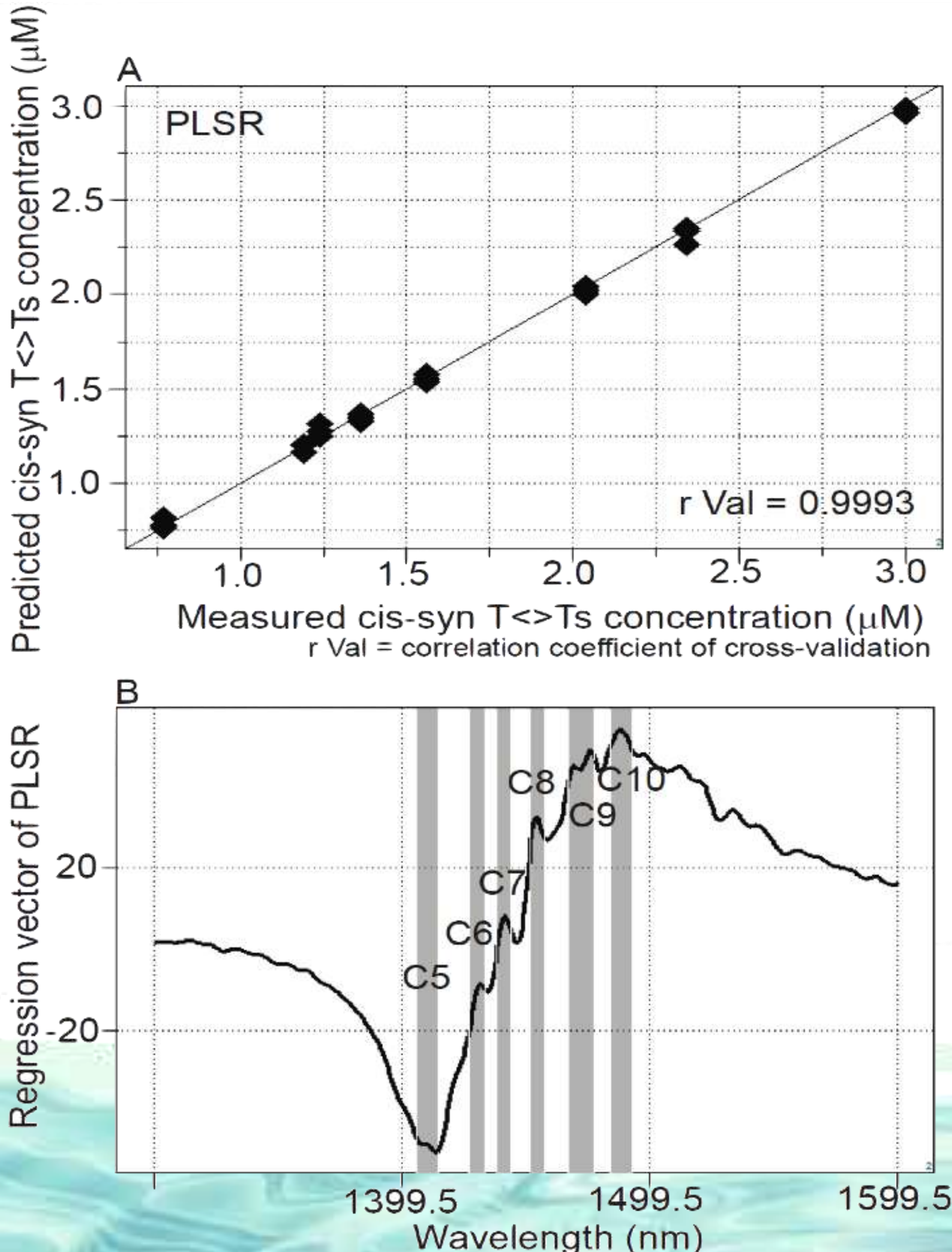


Quantitative analysis of isolated cis-syn T<>Ts using NIRS and HPLC data showing high correlation between cis-syn T<>Ts concentrations determined by the NIR calibration model and the laboratory reference values (0.77 μM -3.0 μM) determined by HPLC.

A) Y-fit for cis-syn T<>Ts concentration of PLSR with pretreatment of mean centering, smoothing (21 points), OSC (one component) and leave-one-out cross validation: N = 24, number of applied latent variables = 2, r Cal = 0.9993, SEC = 0.0267, r Val = 0.9993, SECV = 0.0308.

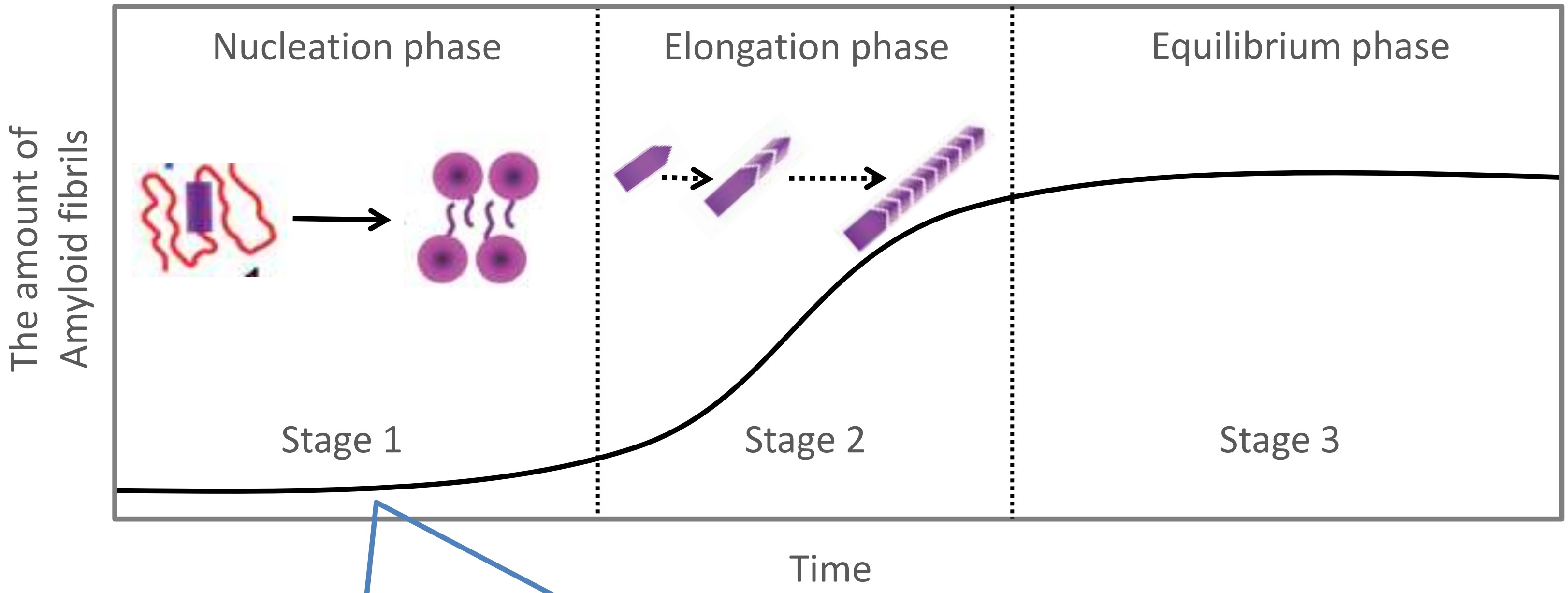
B) Regression vector of PLSR calibration model on cis-syn T<>Ts concentration revealed characteristic water peaks in 1400 nm-1500 nm spectral interval.

[Detection of UV-induced cyclobutane pyrimidine dimers by near-infrared spectroscopy and aquaphotomics]

N Goto, G Bazar, Z Kovacs, M Kunisada, H Morita... - Scientific reports, 2015

Unique transformations of water structure for the amyloidogenic nucleation

Chatani E, Tsuchisaka Y, Masuda Y, Tsenkova R (2014) Water molecular system dynamics associated with amyloidogenic nucleation as revealed by real time near infrared spectroscopy and aquaphotomics.PLoS ONE 9(7): e101997. doi:10.1371/journal.pone.0101997



If NIR could detect change with nucleation,
It is possible to diagnose amyloidosis!!

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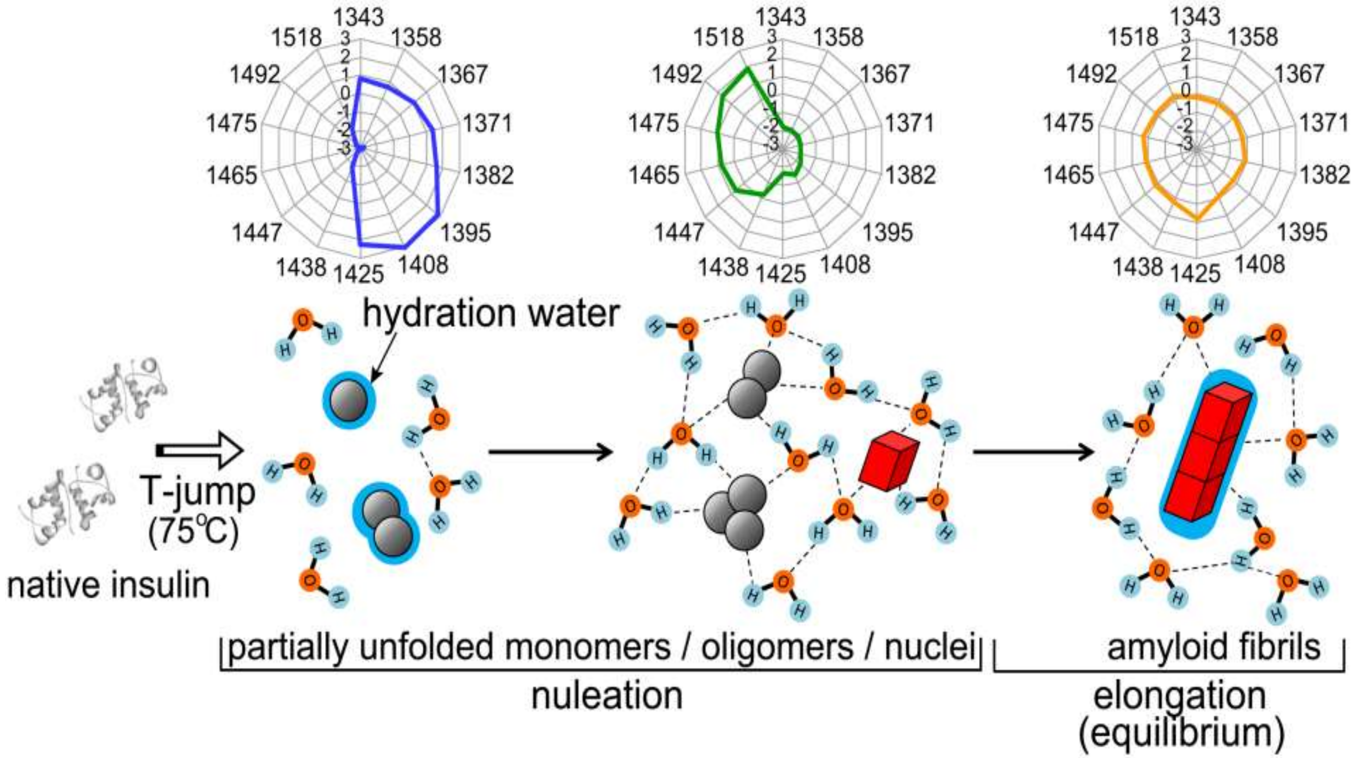


Figure: Schematic illustration representing multi-step transformation of water structures during the fibril formation.

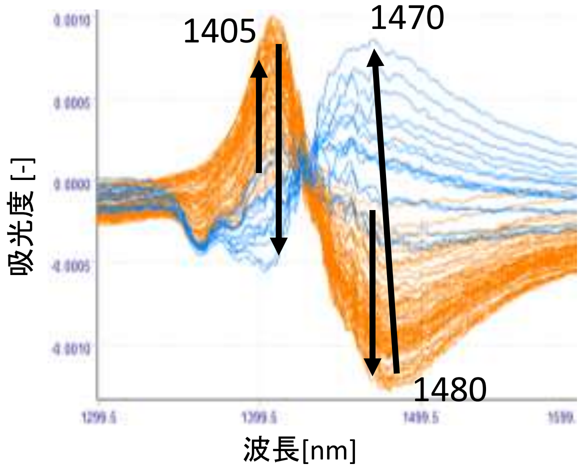
In the **nucleation phase**, **free water molecules and hydrating water** onto protein molecules are dominated initially, but **afterwards hydrogen-bonded water networks are developed**, which is considered essential for nucleation by interlinking protein molecules softly. In the **elongation phase**, the **hydrogen bonds were decayed** gradually towards the state observed in bulk water, and **slight increasing of hydrated water onto amyloid fibrils** was also observed.

Chatani E, Tsuchisaka Y, Masuda Y, Tsenkova R (2014) Water molecular system dynamics associated with amyloidogenic nucleation as revealed by real time near infrared spectroscopy and aquaphotomics.PLoS ONE 9(7): e101997. doi:10.1371/journal.pone.0101997 1

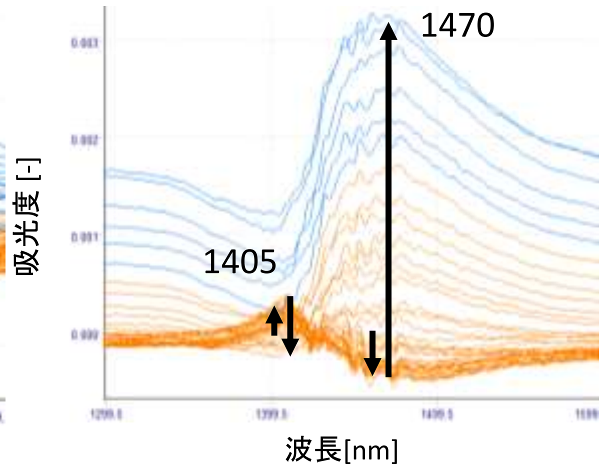
核形成期 伸長期

アミロイド線維形成サンプル
(NaCl)

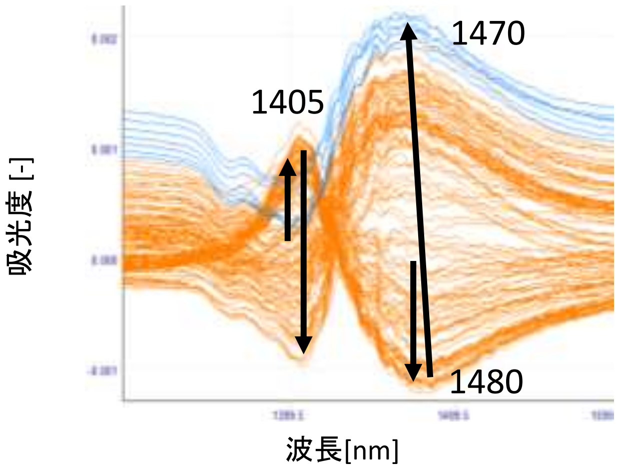
50 mM



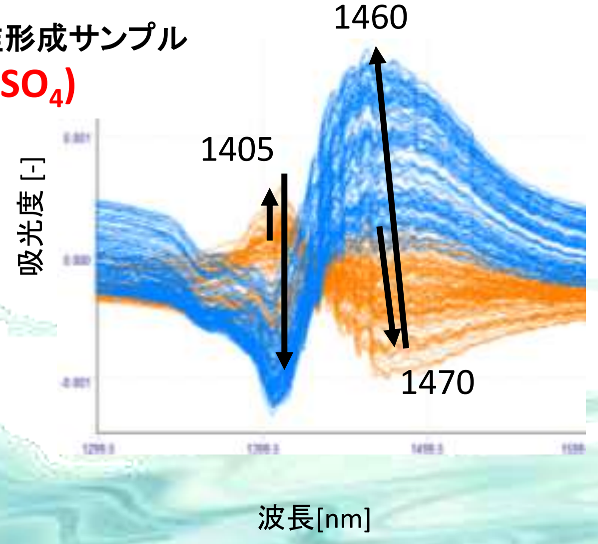
100 mM



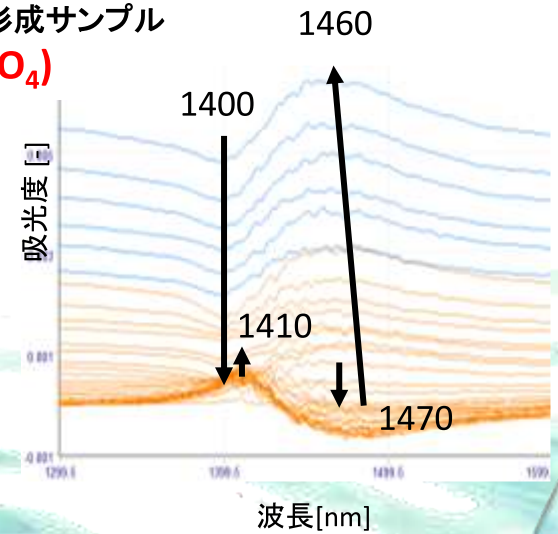
400 mM



アミロイド線維形成サンプル
(Na_2SO_4)



アミロイド線維形成サンプル
($NaClO_4$)



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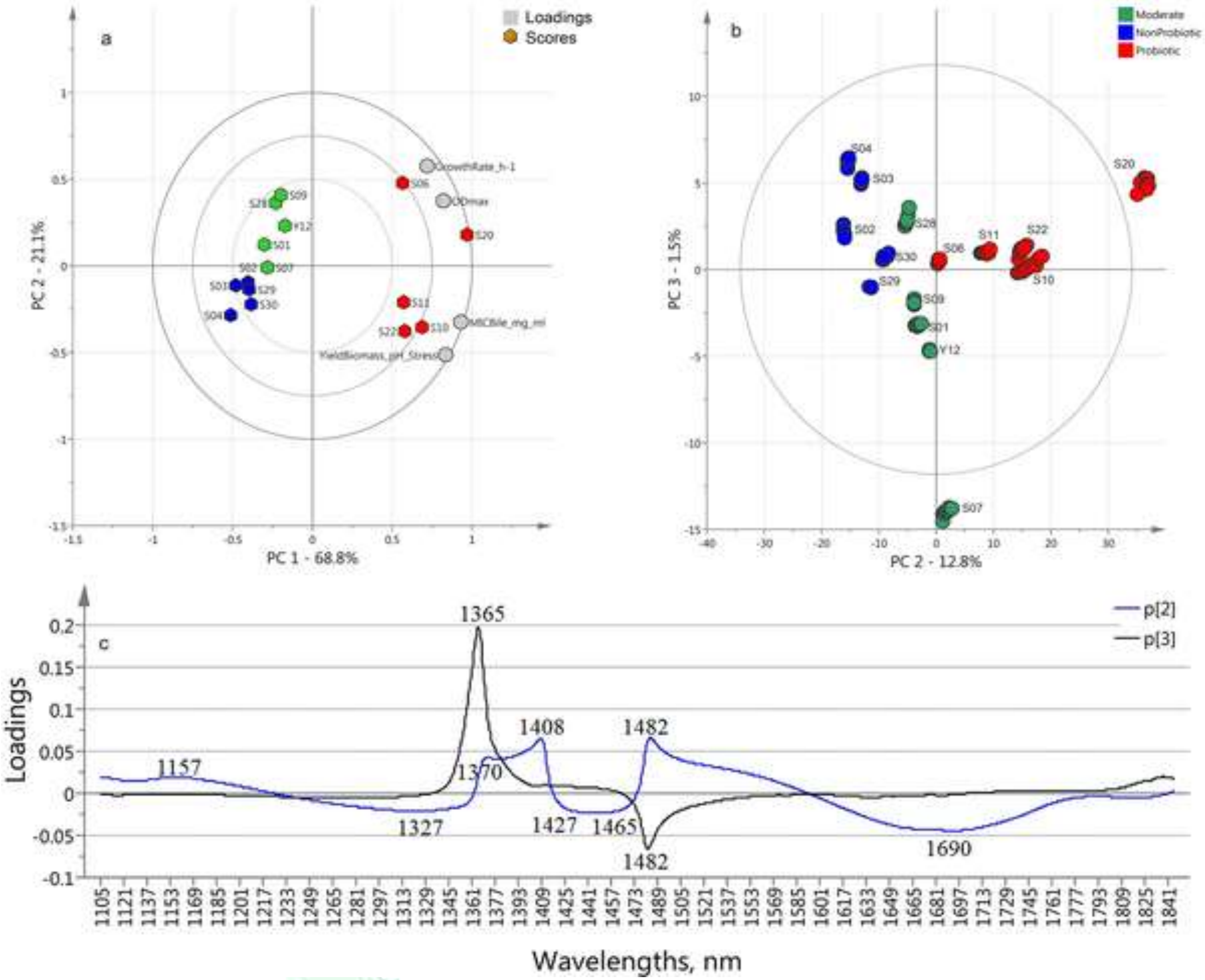
   - **Cells (bacteria)**

PLOS ONE



a) PCA Bi-plot calculated on the reference data (strains growth rates, maximal optical densities, bile MIC and the yield of biomass after three hours stay at pH 1.80 in presence of pepsin (9000 U/ml), reference data in Table 1); b) MW-PCA analyses using the 1100–1850 nm wavelength interval—Score plot calculated on spectral data (n = 150) at the cultivation time of 11.4–12 h.

Slavchev A, Kovacs Z, Koshiba H, Nagai A, Bázár G, et al. (2015) Monitoring of Water Spectral Pattern Reveals Differences in Probiotics Growth When Used for Rapid Bacteria Selection. PLoS ONE 10(7): e0130698. doi:10.1371/journal.pone.0130698
http://127.0.0.1:8081/plosone/article?id=info:doi/10.1371/journal.pone.0130698

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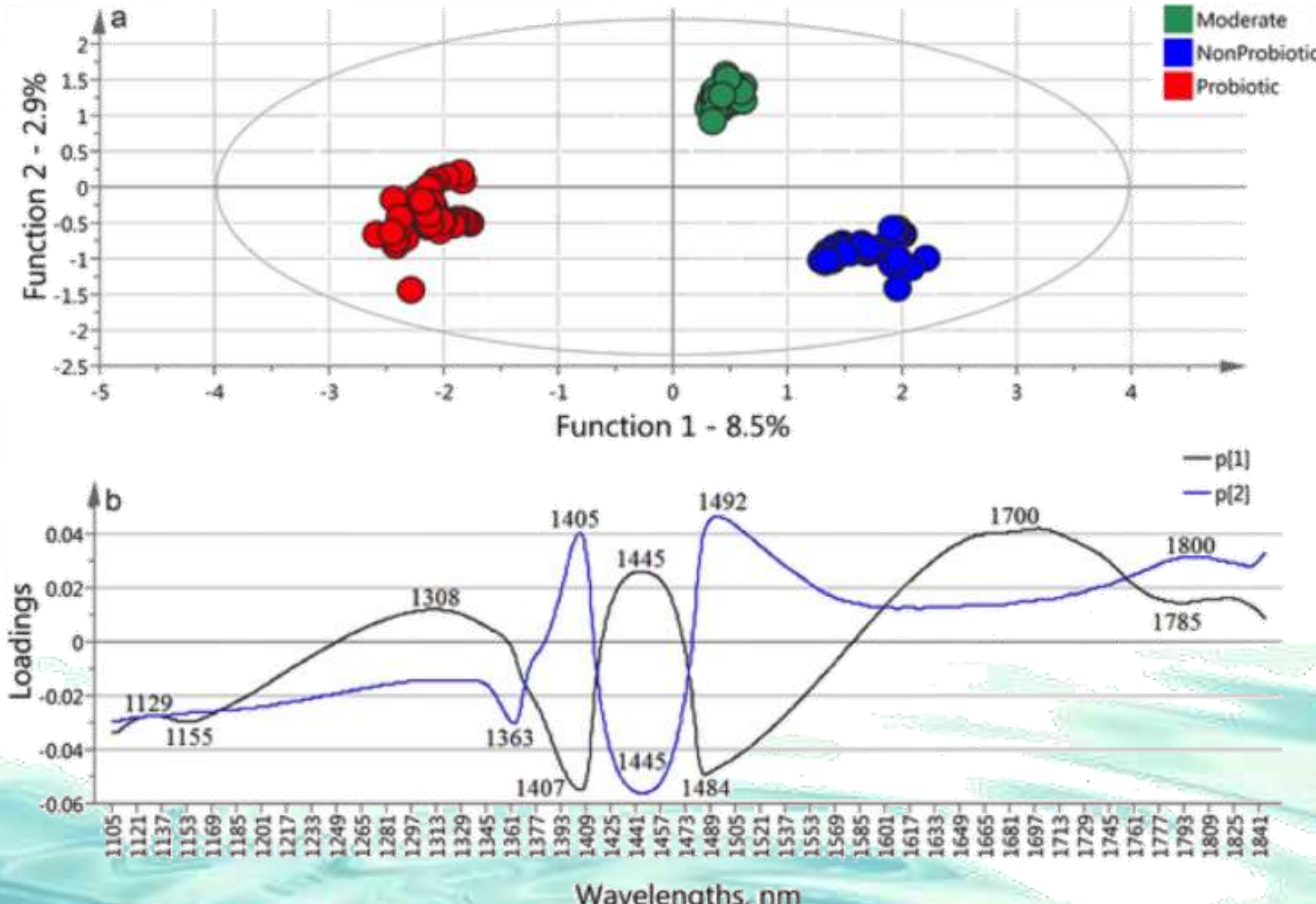
OPLS-DA model built on the spectral data of the 15 strains in the monitoring time between 11.4–12 h (n = 150) using the 1100–1850 nm wavelength interval to classify the probiotic, moderate and non-probiotic groups a) score plot and b) loadings plots.



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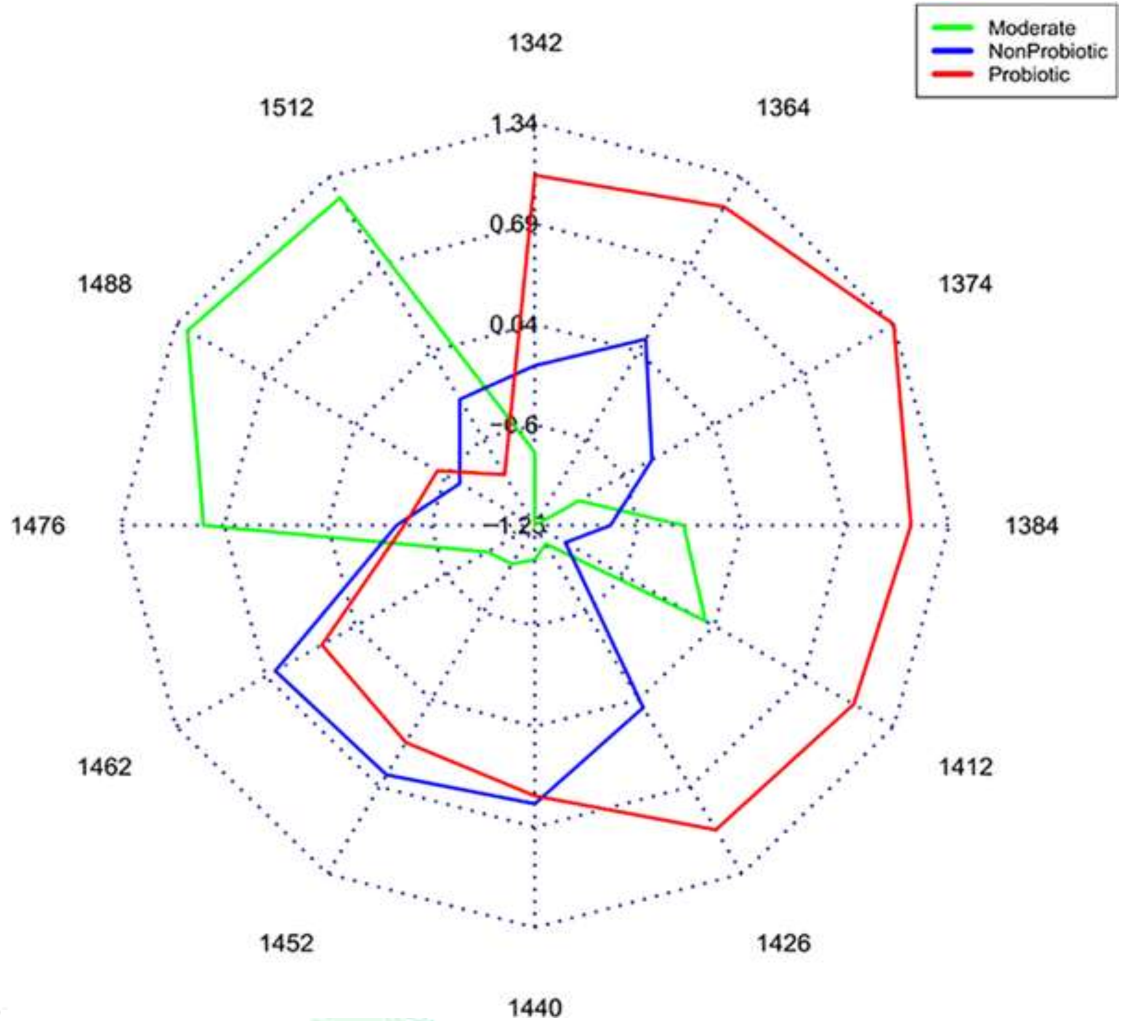

Aquagram on the spectra of culture media of groups of probiotic, moderate and non-probiotic strains

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Measured wave-length (nm)	Calculated wave-number (cm^{-1})	Calculated fundamental wavenumber (cm^{-1})	Assignment	Ref
1155		-	Combination overtone of free water (S_0)	-
1365	7326	7326/2 = 3663	OH, 1st overtone, aqueous proton [H+·$(H_2O)_2$]—H_2O asymmetric stretch	[40]
			OH, 1st overtone, Dangling-OH (non-hydrogen-bonded	[41]
			OH, 1st overtone, H_2O v1	[42]
			OH, 1st overtone, $H_{15}O_7$+	[43]
1386	7215	7215/2 = 3607.5	OH, 1st overtone, Superoxide Tetrahydrate O_2-·$(H_2O)_4$	[44]
			OH, 1st overtone, H+$(H_2O)_{10}$	[40]
			C–H stretching, sucrose	[45]
			OH, 1st overtone, OH^- stretching mode	[46]
1408	7100	7100/2 = 3550	OH, 1st overtone, H-bonded OH stretch	[47]
			O–H, 1st overtone, glucose bonds	[48]
			OH, 1st overtone, OH stretching in alcohols	[49]
			OH, 1st overtone, hydrogen-bonded dimers	[50]
1450	6895	6895/2 = 3447.5	OH, 1st overtone, deionized water	[51]
			OH, 1st overtone, O-H stretch	[52]
			combination of antisymmetric and symmetric stretching modes of water	[53]
1485	6735	6735/2 = 3367.5	OH, 1st overtone, $H_{17}O_8$+	[43]
			OH, 1st overtone, $H_{15}O_7$+ H-bonded OH stretch	[47]
			NH, 1st overtone, amid	[54]
			NH/OH, 1st overtone, N–H/O–H stretching	[55]
1492	6700	6700/2 = 3350	OH, 1st overtone, hydrogen-bonded (S_4)	[34]
			OH, 1st overtone, $H_{15}O_7$+	[43]
			OH, 1st overtone, strongly H-bonded	[56]
			NH, 1st overtone, N–H stretching	[57,58]
			NH, 1st overtone, NH_2's asymmetric stretch	[59]
1698	5890	5890/2 = 2945	OH 1st overtone, Superoxide Tetrahydrate O_2-·$(H_2O)_4$	[44]
			C–H vibration	[60]
			CH/CH2 combination band	[61]
			H–O–H/O–H bending and translation/rotation combinations	[62]
1819	5500	5500/2 = 2750	1st overtone IHB stretch (OH-$(H_2O)_3$)	[63]
			combinationv(C–H) + v(O–D)free	[64]

doi:10.1371/journal.pone.0130698.t002

Measured wavelength and calculated wavenumbers of the bands found with PCA, SIMCA, OPLS-DA and PLSR methods and their assignment based on the corresponding references.

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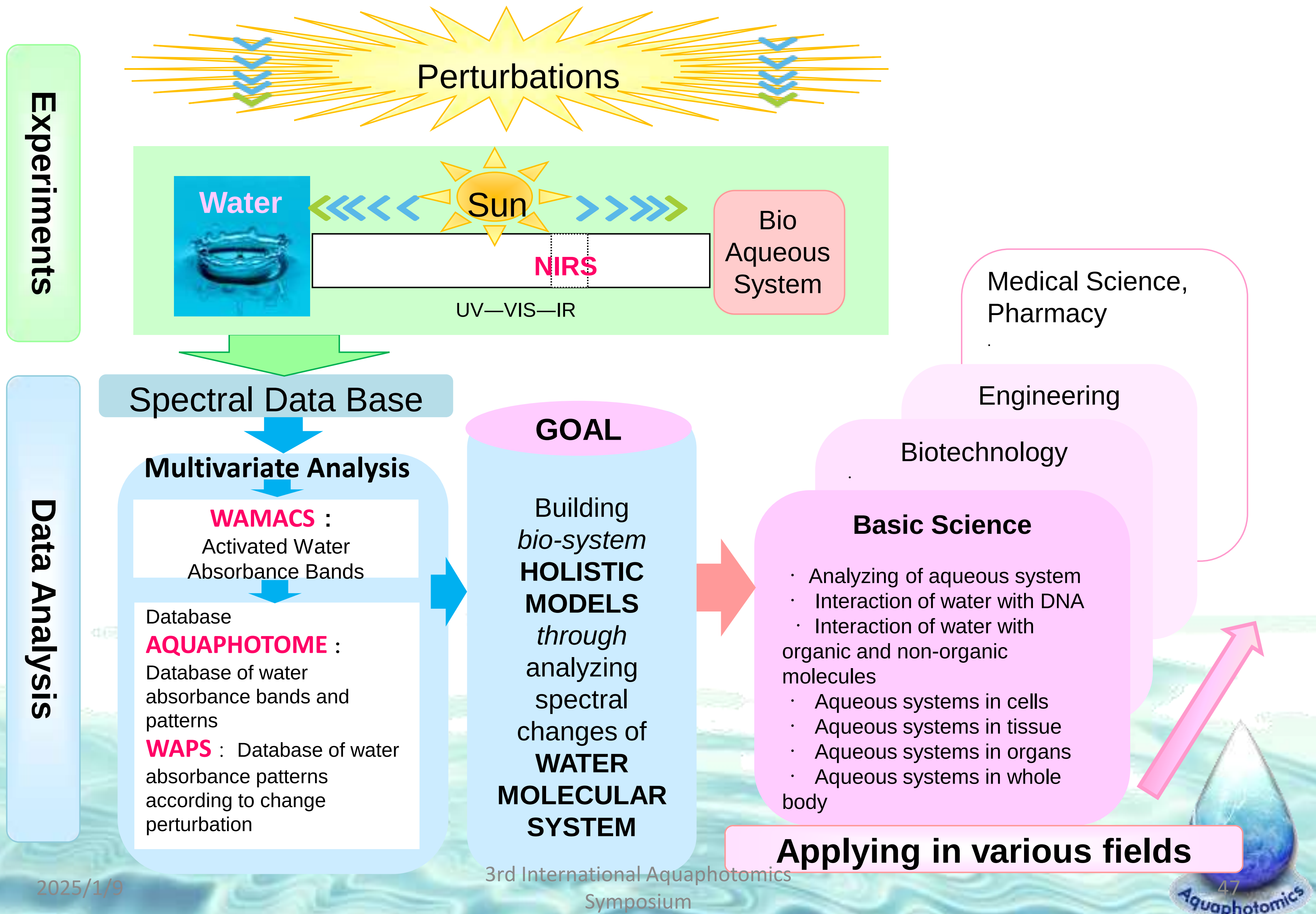
http://127.0.0.1:8081/plosone/article?id=info:doi/10.1371/journal.pone.0130698

FUTURE

- Water Vocabulary: letters (water bands), words (spectral patterns), sentences (water functionality)
- Basic well known phenomena and reactions should be explained with added knowledge about water
- Education about water on a large scale


Experiments
Perturbations
Water
Sun
NIRS
UV—VIS—IR
Bio Aqueous System
Data Analysis
Spectral Data Base
Multivariate Analysis
WAMACS : Activated Water Absorbance Bands
Database
AQUAPHOTOME : Database of water absorbance bands and patterns
WAPS : Database of water absorbance patterns according to change perturbation
GOAL
Building bio-system HOLISTIC MODELS through analyzing spectral changes of WATER MOLECULAR SYSTEM
Medical Science, Pharmacy
Engineering
Biotechnology
Basic Science
· Analyzing of aqueous system
· Interaction of water with DNA
· Interaction of water with organic and non-organic molecules
· Aqueous systems in cells
· Aqueous systems in tissue
· Aqueous systems in organs
· Aqueous systems in whole body
Applying in various fields
Aquaphotomics

水の音
光の遊び
生きている

Sound of a stream,
Sunlight dancing on waters,
Life wakes up again.

1

R. Tsenkova, 2004