Multi-spectral assessment of ingredients and physical properties of apricot

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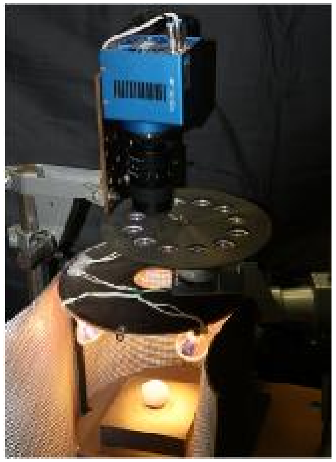


About us

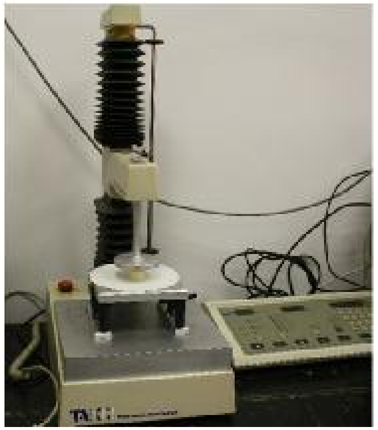
At the Corvinus University of Budapest (physics.uni-corvinus.hu)

- •Faculty of Horticulture
- •Faculty of Food Science
  - •**Department of Physics and Control**

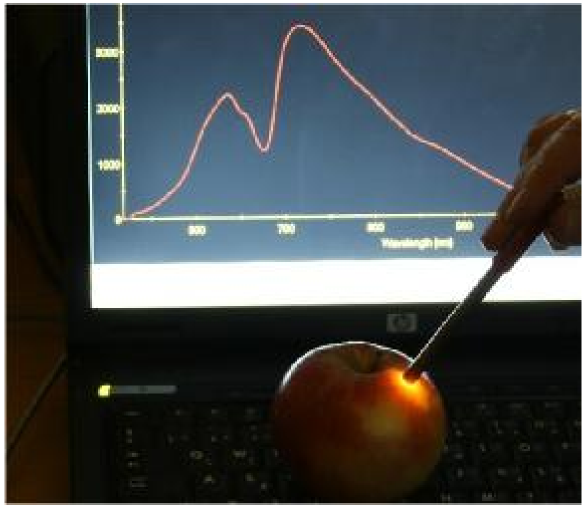
physical properties of food, their raw materials, fruits and vegetables are investigated:

- •Rheological by static and dynamic methods
- •Dielectric, chemical (e-tongue)
- •Optical by image processing, scattering, spectroscopy, multi- and hyperspectral imaging methods

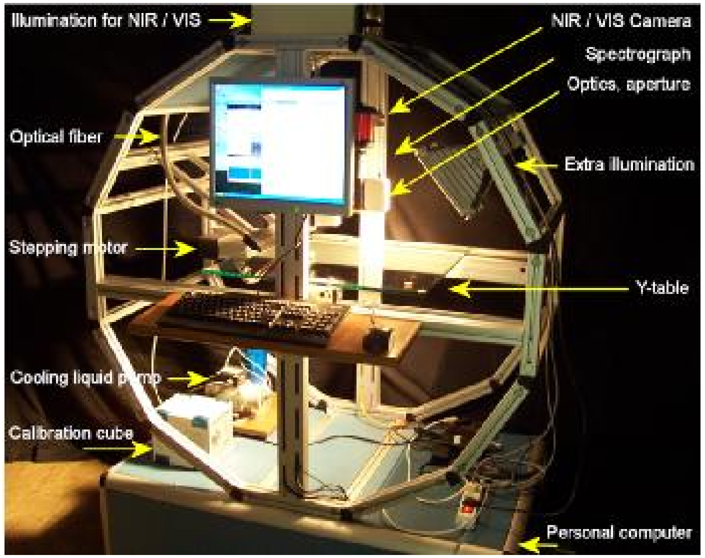
for basic research and industrial quality control, automation purposes.



Penetrometer (static method)



Scattering at multiple wavelength



Zeutec hyperspectral measurement setup

NIR and apricot

Some quality-related internal parameters of apricot can be predicted by the reflected NIR spectrum. According to the recent publications, using 800-2500nm range, the **soluble solids content (SSC, Brix)** and the **titratable acidity (TA)** can be predicted properly, but other quality traits, like malic and citric acid, individual sugars, ethylene production and firmness were not satisfactory modeled.

1. Prediction of other quality traits ?

2. For non-homogeneous surface ?

==> **Multispectral imaging** as non-contact method

References

•Sylvie Bureau, David Ruiz, Maryse Reich, Barbara Gouble, Dominique Bertrand, Jean-Marc Audergon, Catherine M.G.C. Renard (**2009**) Rapid and non-destructive analysis of apricot fruit quality using FT-near-infrared spectroscopy. *Food Chemistry 113 pp 1323–1328.*

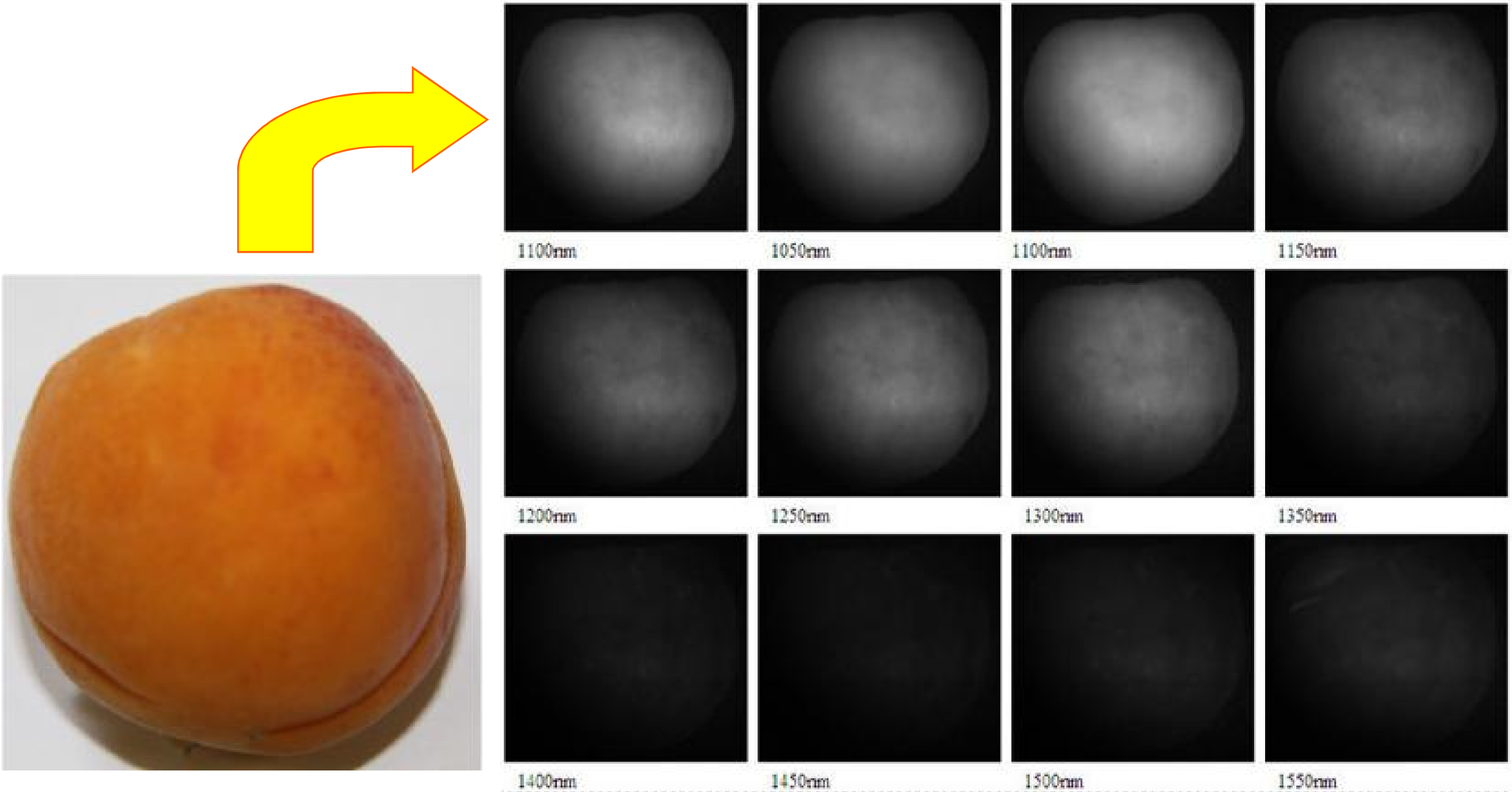
•C. Camps*, D. Christen (**2009**) Non-destructive assessment of apricot fruit quality by portable visible-near infrared spectroscopy. *Food Science and Technology 42 pp 1125–1131.*

Multispectral imaging combines the advantages of **spectroscopy** and **imaging**:

Obtain the spatial distribution of spectral properties on non-homogeneous surfaces

Non-contact method good for industrial, automation purposes

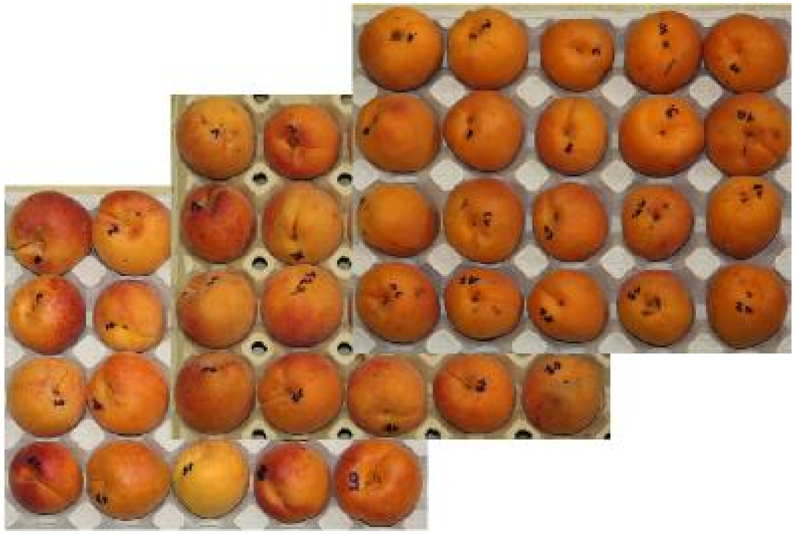
but have much less spectral information in noisy environment



Multispectral images of defected Bergarouge sample

Need to test the feasibility of multispectral sensing of internal properties

Materials and method



Bergeron, Bergarouge and Zebra cultivars

Bergeron cultivar in three ripeness state

Samples of **Bergeron, Bergarouge and Zebra** apricot cultivars were tested grouping in three ripeness category (**1. immature, 2. ripened for processing, 3. ripened for consumption**).

The second category was stored for one week (**4. category**) and two weeks (**5. category**).

20 samples in each group.

All the measurements were taken on both **blushed and un-blushed** side as well.

Optical	• **RGB Imaging System** (RGB images using diffuse illumination): average value and variance of XYZ colour components of segmented areas • **Pigment Analyzer** (400-1090 nm range, 3.25nm resolution): reflected spectra, Normalized Difference Vegetation Index, Normalized Anthocyanin Index • **ColorLite sph850 spectrophotometer** (400-700 nm range, 10nm resolution): reflected spectra, CIE Lab, Luv and XYZ coordinates • **PCM Spectralyzer 10-25** (1000-2500 nm range, 2nm resolution) (Figure 5): the average reflectance on a 25mm diameter area • **NIR Multispectral Imaging system** (12 images at 1000-1050-…-1550 nm) (Figure 8): average value and variance of intensity values on segmented areas
Mechanical	• **acoustic resonance method**: measured: resonance frequency (**f,** Hz) and width of the resonance peek at -3 dB (**bw**, Hz) calculated: $\mathbf{s_1} = f^2*m^{2/3}$ and $\mathbf{s_2} = f^2*d_1^2$ acoustic stiffness coefficients • **impact method**: measured: time of deceleration of the impact hammer (**dT**, ms) calculated: $\mathbf{D} = 1/dT^2$ impact stiffness coefficient • **Sinclair Internal Quality tester** measured: Sinclair firmness coefficient on 1-100 scale (**IQ**)
Destructive	• **pH** of the apricot flesh (Vaiseshika pH-conductivity TDS+DO meter and inserted flesh probe) • **SSC (Brix)** of the apricot juice (Atago digital refractometer PAL-1) • **Sugar-content** of groups (fructose, glucose, saccharose, xylose, raffinose) (HPLC) • **Titratable acid content** of groups (titration)



Pigment Analyzer, Color Lite; Acoustic method, Impact method, Sinclair IQ tester; Brix tester, pH-meter

Data analysis

•The correlation between **NIR spectrophotometer measurement** and different quality traits was investigated by **Partial Least Squares (PLS)** linear regression method. Since randomly selecting two third of whole dataset as calibration subset did not resulted reliable prediction, finally the first (immature) and third (ripened for consumption) groups were used as calibration set having a wide distribution of internal properties. The optimal number of latent variables was determined on the base of the minimal value of **RMSEV** and the maximal value of **Relative Performance Determinant (RPD)**. RPD is defined as the standard deviation of the reference values of all samples devided by the standard deviation of the error of the validation set. The overfitting of regression was checked by the values of **B-vector**.

•The **multispectral images** were segmented, than the average spectra of investigated area were compared with spectrophotometer measurements. The variance of spectra on investigated area was also checked. The prediction model was also the PLS method calculating the correlation, the RPD, RMSEC and RMSEV values and the B-vector. **Multi-linear regression (MLR)** method was used to determine the significant wavelengths of given internal properties. All, the statistical algorithm were developed in Mathcad software package (version 14.0, MathSoft, USA).

Results

Almost all the measured parameters were changed monotonically by the ripeness state and by the storage time as well.

		Geometric				Stiffness					
cultivar	ripeness / storage categories	Mass, g		Volume, cm3		Sinclair		Impact		Acoustic	
		avg	std	avg	std	avg	std	avg	std	avg	std
Bergeron	immature (1)	55,4	4,9	52,1	4,3	14,0	2,5	0,140	0,028	2050093	475643
	processing (2)	57,8	6,6	54,7	6,6	12,1	1,3	0,133	0,017	2135610	370329
	consumption (3)	65,9	6,6	61,5	7,1	9,8	1,3	0,092	0,017	1672507	294066
	processing (2)	57,8	6,6	54,7	6,6	12,1	1,3	0,133	0,017	2135610	370329
	1 week (4)	59,4	7,8	54,4	6,9	10,3	7,2	0,073	0,020	1011637	465146
	2 weeks (5)	44,2	8,8	37,7	8,6	-	-	0,039	0,016	186192	107327
Bergarouge	immature (1)	64,7	8,3	60,6	7,7	14,9	2,5	0,141	0,027	2955759	1117284
	processing (2)	64,3	9,8	58,9	8,9	11,2	2,6	0,110	0,022	2085061	847019
	consumption (3)	62,0	11,7	57,2	11,0	8,2	2,0	0,073	0,016	956134	315487
	processing (2)	64,3	9,8	58,9	8,9	11,2	2,6	0,110	0,022	2085061	847019
	1 week (4)	51,4	5,0	46,2	4,9	13,5	12,4	0,066	0,012	461506	202062
	2 weeks (5)	45,4	7,3	39,4	7,0	-	-	0,034	0,011	186482	131904
Zebra	immature (1)	51,3	5,2	46,6	4,9	21,8	3,1	0,228	0,041	4262904	1238783
	processing (2)	56,3	5,0	52,2	4,4	20,3	4,1	0,181	0,030	3339701	1033934
	consumption (3)	57,1	10,0	51,5	8,4	13,2	4,2	0,123	0,027	1608299	554808
	processing (2)	56,3	5,0	52,2	4,4	20,3	4,1	0,181	0,030	3339701	1033934
	1 week (4)	57,6	7,6	50,5	7,3	12,3	3,1	0,092	0,019	928187	282781
	2 weeks (6)	52,0	6,1	43,7	6,0	-	-	0,067	0,011	621339	168562

		Reflectance in visible range							
		un-blushed		blushed side		un-blushed		blushed side	
cultivar	ripeness / storage categories	NDVI				Normalized Anthocyanin Index			
		avg	std	avg	std	avg	std	avg	std
Bergeron	immature (1)	-0,07	0,20	0,06	0,21	0,77	0,15	0,56	0,16
	processing (2)	-0,10	0,18	-0,02	0,20	0,90	0,07	0,78	0,12
	consumption (3)	-0,30	0,10	-0,24	0,21	0,92	0,06	0,80	0,08
	processing (2)	-0,10	0,18	-0,02	0,20	0,90	0,07	0,78	0,12
	1 week (4)	-0,46	0,06	-0,48	0,07	0,84	0,13	0,61	0,18
	2 weeks (5)	-0,47	0,07	-0,51	0,04	0,90	0,05	0,75	0,12
Bergarouge	immature (1)	-0,11	0,15	-0,08	0,19	0,69	0,23	0,35	0,33
	processing (2)	-0,29	0,11	-0,27	0,11	0,89	0,11	0,71	0,15
	consumption (3)	-	-	-	-	-	-	-	-
	processing (2)	-0,29	0,11	-0,27	0,11	0,89	0,11	0,71	0,15
	1 week (4)	-0,46	0,06	-0,47	0,07	0,84	0,09	0,60	0,16
	2 weeks (5)	-	-	-	-	-	-	-	-
Zebra	immature (1)	0,22	0,28	0,21	0,27	0,83	0,10	0,76	0,10
	processing (2)	-0,08	0,19	0,10	0,25	0,83	0,09	0,79	0,11
	consumption (3)	-0,32	0,11	-0,31	0,15	0,91	0,08	0,77	0,14
	processing (2)	-0,08	0,19	0,10	0,25	0,83	0,09	0,79	0,11
	1 week (4)	-0,39	0,06	-0,43	0,07	0,86	0,04	0,65	0,17
	2 weeks (6)	-0,49	0,02	-0,51	0,03	0,88	0,07	0,74	0,07

		Reflectance in visible range											
		un-blushed						blushed side					
cultivar	ripeness / storage categories	L*		a*		b*		L*		a*		b*	
		avg	std	avg	std	avg	std	avg	std	avg	std	avg	std
Bergeron	immature (1)	57,8	2,7	6,7	1,9	41,0	2,7	49,5	4,8	15,4	5,3	31,3	5,4
	processing (2)	51,5	1,3	11,5	1,6	40,3	1,7	46,5	1,7	14,0	2,0	31,9	2,0
	consumption (3)	56,3	2,4	14,2	2,8	40,8	2,1	45,5	3,9	22,1	2,5	26,5	6,6
	processing (2)	51,5	1,3	11,5	1,6	40,3	1,7	46,5	1,7	14,0	2,0	31,9	2,0
	1 week (4)	49,3	2,8	12,5	3,6	33,7	2,8	41,1	4,9	19,4	4,1	23,5	5,5
	2 weeks (5)	45,8	4,2	11,8	2,9	33,0	4,0	36,0	4,0	19,2	2,8	19,6	6,1
Bergarouge	immature (1)	58,1	1,7	7,2	2,7	41,5	2,4	49,7	4,2	14,9	5,6	31,6	5,5
	processing (2)	56,0	2,5	12,1	2,2	40,1	3,0	43,0	5,3	22,8	4,4	24,1	6,2
	consumption (3)	54,1	1,8	14,7	2,7	39,5	1,9	41,2	4,0	23,6	3,5	22,5	4,7
	processing (2)	56,0	2,5	12,1	2,2	40,1	3,0	43,0	5,3	22,8	4,4	24,1	6,2
	1 week (4)	47,7	2,7	10,5	3,4	31,6	1,8	41,6	3,8	16,9	3,9	23,1	4,4
	2 weeks (5)	45,9	2,0	11,2	2,1	33,1	2,1	37,3	3,4	17,0	2,9	21,9	4,9
Zebra	immature (1)	55,5	1,9	15,4	2,9	40,5	2,4	44,4	5,4	23,7	3,4	26,4	7,1
	processing (2)	50,6	1,9	13,8	1,6	42,6	2,0	45,1	2,8	17,5	2,8	34,5	4,0
	consumption (3)	50,6	1,5	16,1	1,2	39,4	2,3	45,1	2,3	20,4	1,7	31,5	3,2
	processing (2)	50,6	1,9	13,8	1,6	42,6	2,0	45,1	2,8	17,5	2,8	34,5	4,0
	1 week (4)	47,3	1,0	15,2	1,1	36,3	1,6	42,9	2,2	18,2	1,5	28,8	3,7
	2 weeks (6)	45,6	1,0	18,2	1,0	36,7	1,2	41,3	2,0	19,9	1,4	28,6	3,3

Average and standard deviation of quality traits

The chemical properties, however, behave irregularly.

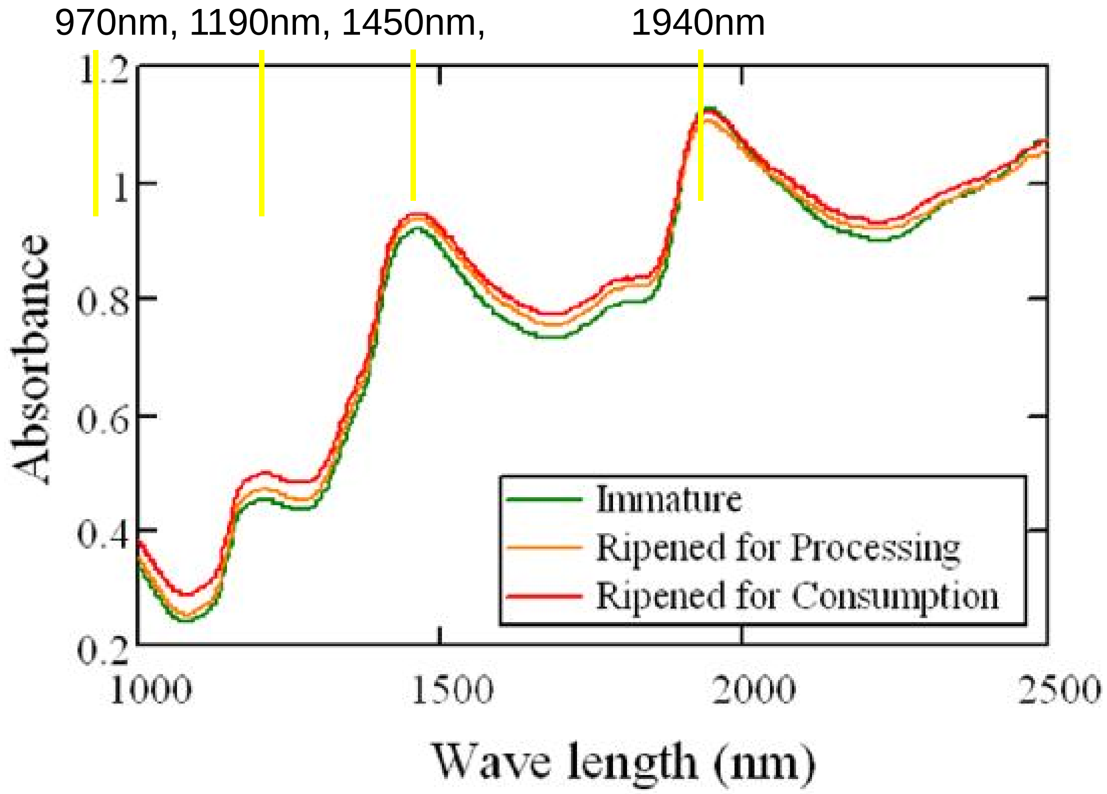
- The **pH** increased during ripening, but it grown significantly only at the first week of storage.
- The soluble solids content (**Brix**) increased during ripening, but has not changed during storage.
- The change of **sugar-content** (fructose, glucose, saccharose, xylose, raffinose) and titratable acid (**TA**) was not commonly monotonous by ripeness state, neither by storage time.

This paper will focus on the prediction of **pH** and **Brix**.

		Chemical				Chemical measurement on groups of samples					
cultivar	ripeness / storage categories	Brix, % avg	Brix, % std	pH avg	pH std	Acid %	Fructose mg/g	Glucose mg/g	Saccharose mg/g	Xylose mg/g	Raffinose mg/g
Bergeron	immature (1)	**14,8**	1,3	**3,46**	0,24	1,75	10506,207	9845,568	21569,182	96,198	819,391
	processing (2)	**15,5**	1,4	**3,92**	0,23	1,40	9411,198	11443,192	21658,131	50,830	863,158
	consumption (3)	**17,1**	1,2	**4,28**	0,22	2,45	13778,566	11396,893	21225,966	102,499	752,355
	processing (2)	**15,5**	1,4	**3,92**	0,23	1,40	9411,198	11443,192	21658,131	50,830	863,158
	1 week (4)	**15,1**	1,3	**5,29**	0,21	1,75	11703,572	10738,349	22068,284	65,112	539,058
	2 weeks (5)	**15,6**	1,5	**5,11**	0,35	1,75	13129,465	11340,238	21588,050	129,805	891,967
Bergarouge	immature (1)	**13,8**	1,5	**3,6**	0,4	3,50	9243,476	9778,556	11996,406	137,786	587,812
	processing (2)	**16,5**	1,0	**4,2**	0,3	1,75	10449,962	8579,653	18680,144	86,116	644,875
	consumption (3)	**17,6**	1,1	**4,4**	0,3	1,75	10207,753	9904,356	19122,192	43,688	749,584
	processing (2)	**16,5**	1,0	**4,2**	0,3	1,75	10449,962	8579,653	18680,144	86,116	644,875
	1 week (4)	**15,5**	0,9	**5,2**	0,4	5,25	9701,039	8035,943	22119,048	117,622	754,017
	2 weeks (5)	**15,7**	1,2	**5,0**	0,5	1,75	10483,405	9323,789	18574,124	189,456	581,163
Zebra	immature (1)	**13,4**	1,2	**2,8**	0,1	3,50	820,492	2475,184	4245,206	50,649	-
	processing (2)	**14,2**	1,0	**2,9**	0,2	4,20	444,131	1337,115	2787,826	-	-
	consumption (3)	**14,6**	1,1	**3,6**	0,5	5,60	1048,810	2878,175	6610,912	211,109	236,838
	processing (2)	**14,2**	1,0	**2,9**	0,2	4,20	444,131	1337,115	2787,826	-	-
	1 week (4)	**16,1**	1,3	**5,2**	0,2	1,75	737,394	1792,188	3533,094	44,265	11,894
	2 weeks (5)	**16,8**	1,0	**5,1**	0,5	2,80	1181,121	2529,844	5859,953	180,890	181,564

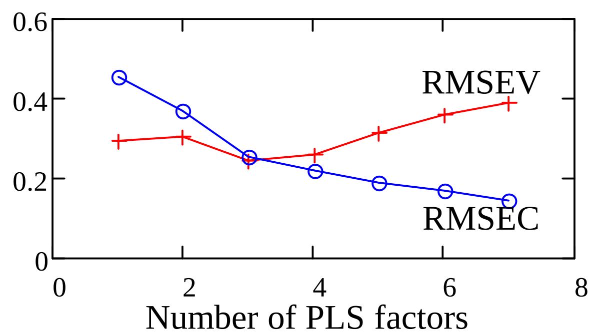
1. Spectrophotometer data analysis:

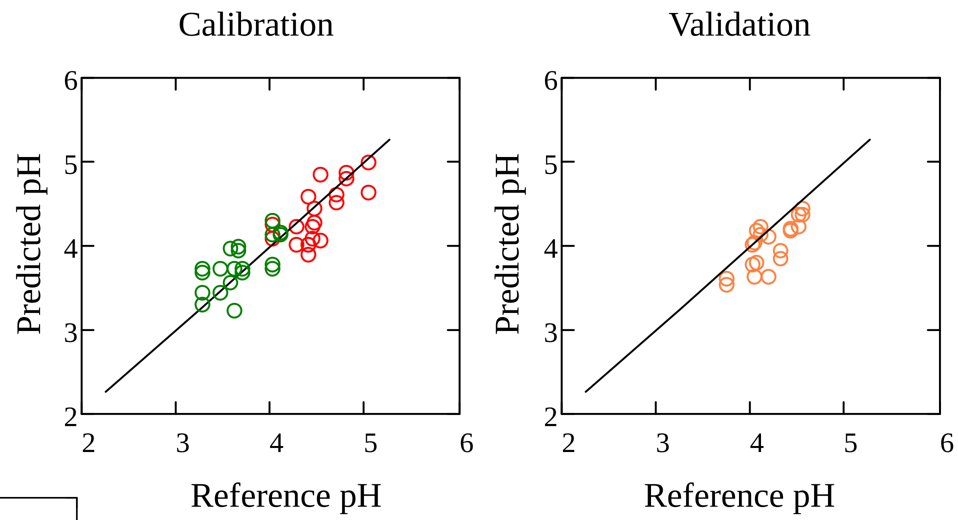
PCM Spectralyzer 10-25

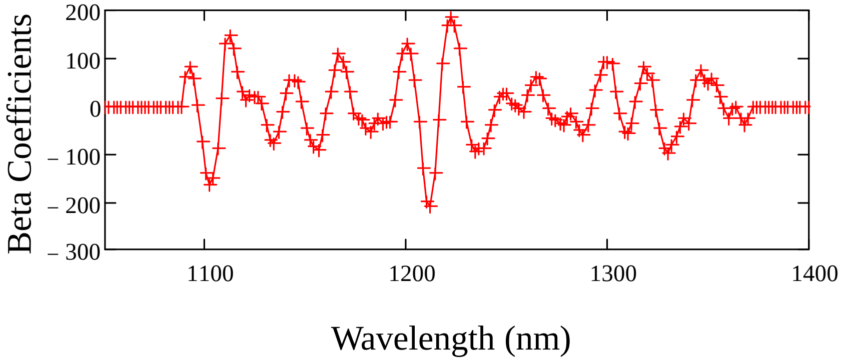


Typical spectra of different ripeness states
(averages for all cultivars, items and sides)

Prediction of pH:





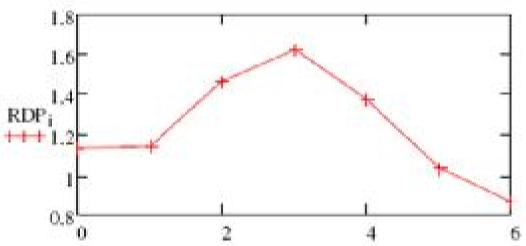


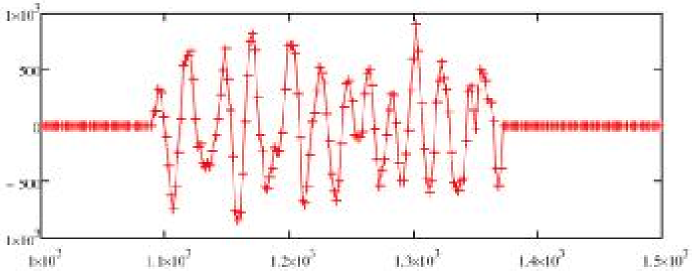
LV=3	Cal	Val
RPD	1.69	**2.45**
RMSE	0.26	0.24
R^2	0.74	**0.58**

A.) Determination of LV, B.) Checking overfitting, C.) Calibration and validation set, D.) Result

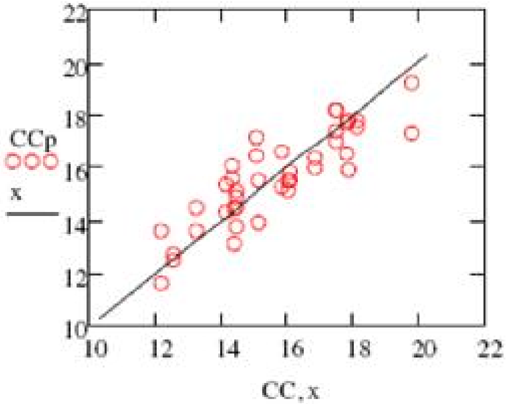
- The optimal number of factors was found to be 3 (A).
- The diagram of B-coefficients appears smooth enough (B).
- The diagram of calibration and validation shows relationship (C).
- High RPD and small RMSEV values sign, that this model is encouraging, despite of sample set contained both the spectra measured on blushed and un-blushed side.

Prediction of Brix:





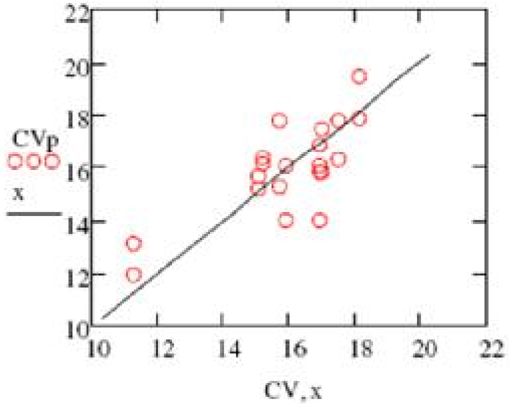
LV=3	Cal	Val
RPD	1.98	1.58
RMSE	0.97	1.22
R^2	0.76	**0.58**



$$\frac{\mathrm{stdev}(CC, CV)}{\mathrm{stdev}(CCp - CC)} = 1.984$$

$$\sqrt{\frac{\sum (CCp - CC)^2}{\mathrm{rows}(CC)}} = 0.975$$

$$\mathrm{corr}(CC, CCp)^2 = 0.758$$



$$\frac{\mathrm{stdev}(\mathrm{stack}(CC, CV))}{\mathrm{stdev}(CVp - CV)} = 1.582$$

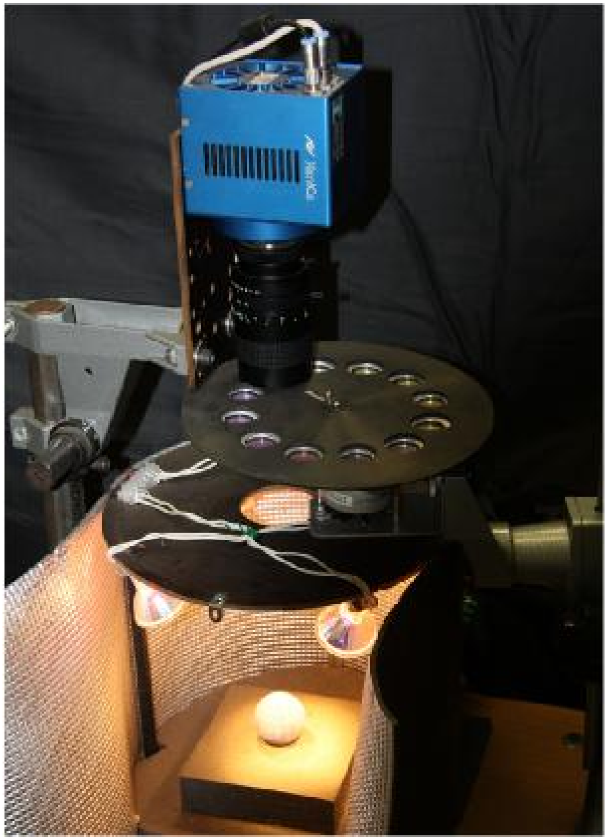
$$\sqrt{\frac{\sum (CVp - CV)^2}{\mathrm{rows}(CV)}} = 1.222$$

$$\mathrm{corr}(CV, CVp)^2 = 0.582$$

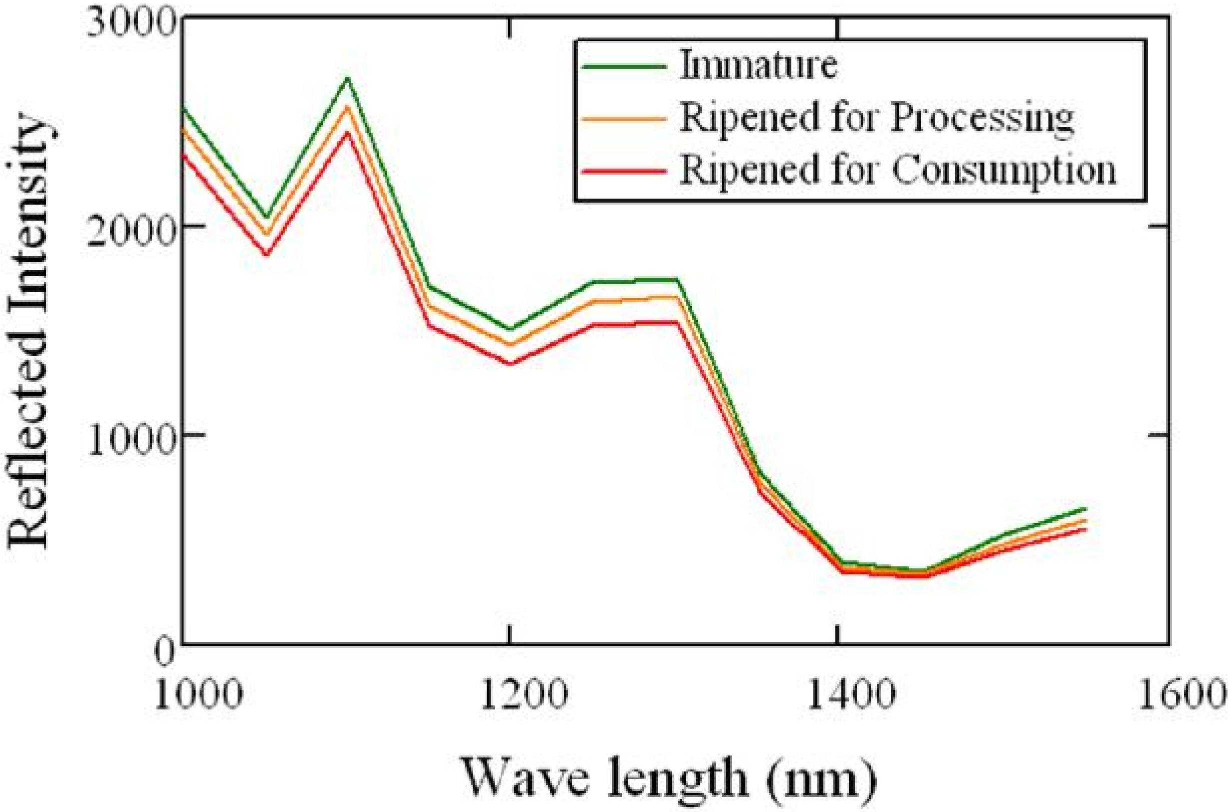
A.) Determination of LV, B.) Checking overfitting on B-values, C.) Result
D.) Calibration and validation set

RPD=1.58 is less, RMSV=1.22 is higher, but the validation has the same correlation.

2. Multispectral data analysis:

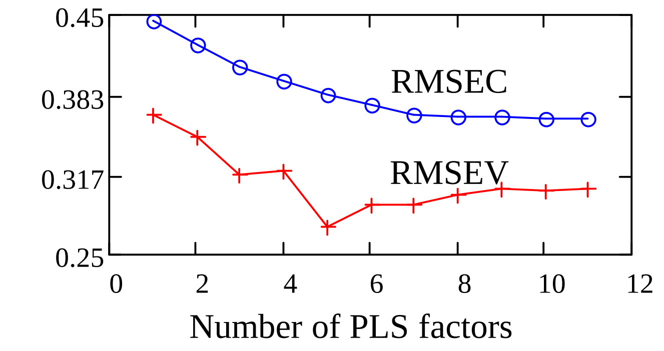


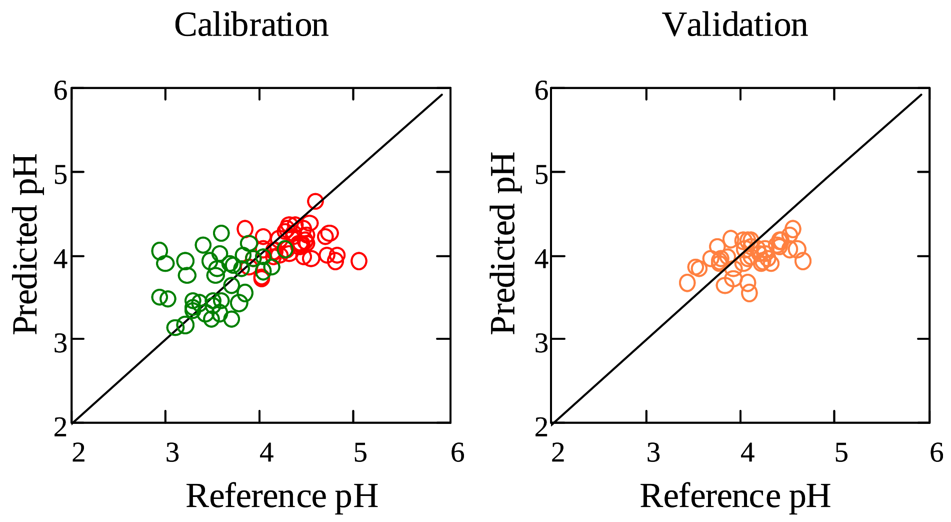
Multispectral setup

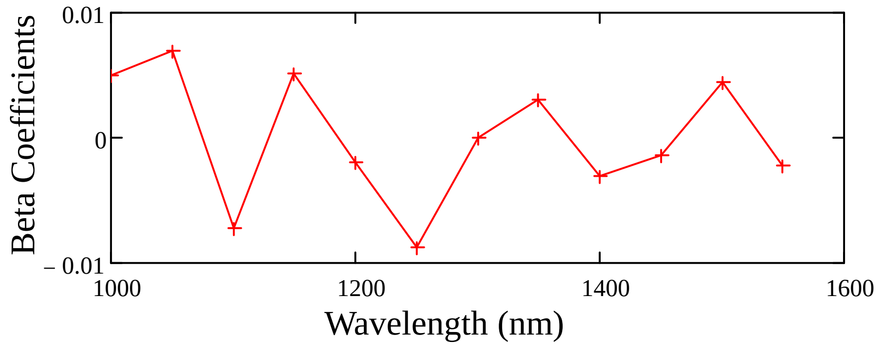


Typical spectra of different ripeness states
(average for all cultivars, items and sides)

Prediction of pH:







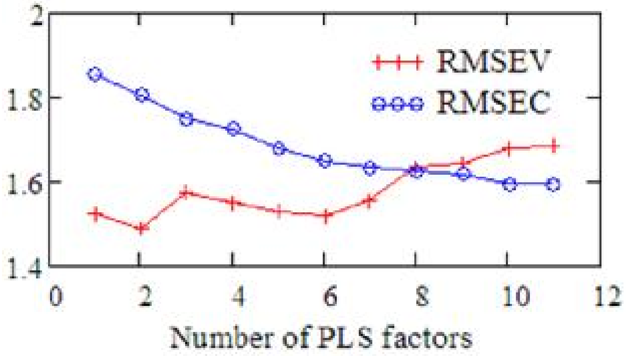
LV=5	Cal	Val
RPD	1.19	1.73
RMSE	0.38	0.27
R^2	0.44	0.24

Determination of LV, B.) Checking overfitting, C.) Calibration and validation set

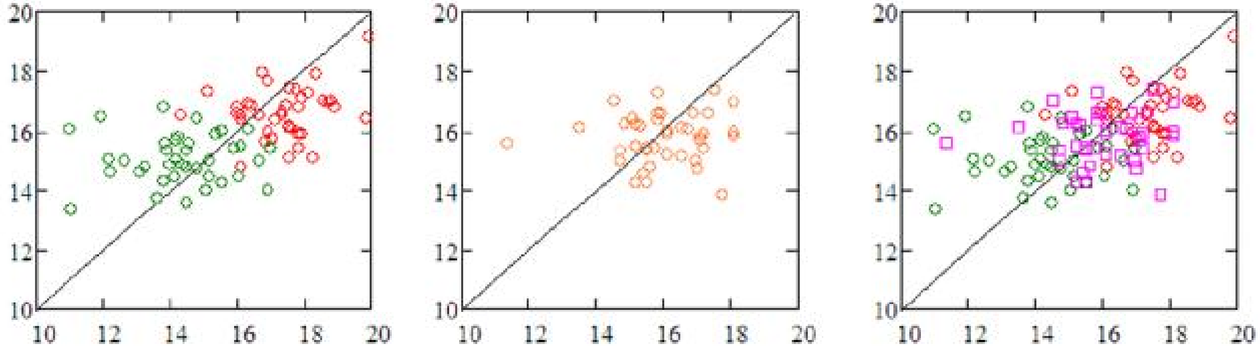
Using multiplicative scatter correction, the RPD and the small RMSEV show acceptable relation. R^2 is small, because the cultivars have different behaviour on these wavelengths. Building the model for given cultivar (e.i. Bergeron), the results were better.

Without multiplicative scatter correction, only 2 factors resulted RPD=1.38 and RMSEV=0.37 values. The significant wavelengths were calculated by MLR method.

Prediction of Brix:



LV=6	Cal	Val
RPD	1.09	1.20
RMSE	1.65	1.52
R^2	0.32	**0.01**



A.) Determination of LV, B.) Result
C.) Calibration and validation set

The RPD is bigger than 1, the RMSEV is acceptably small, but the R^2 is almost zero, signing that using these wavelengths, the soluble solids content can not be predicted.
Significant wavelengths of this property must be studied by hyperspectral method.

Conclusion

The multispectral assessment of ingredients seems to be encouraging, but:

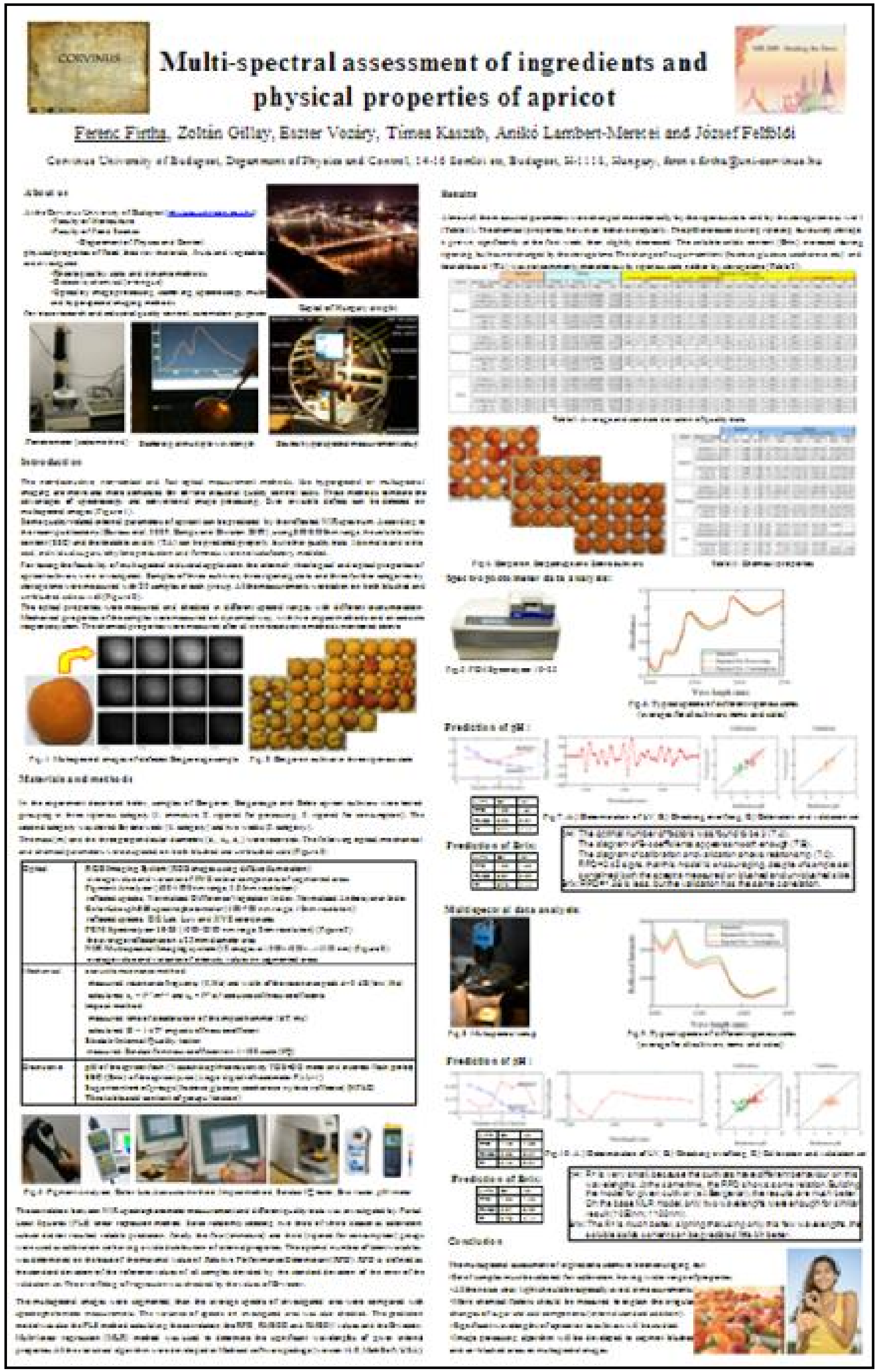
•Set of samples must be selected for calibration, having wider range of properties.

•All the noise, stray light should be especially excluded at measurements.

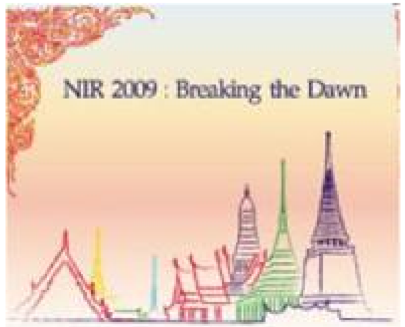
•More chemical factors should be measured to explain the irregular changes of sugar and acid components (internal standard addition).

•Significant wavelengths of investigated properties will be studied by hyperspectral method.

•Image processing algorithm will be developed to segment blushed and un-blushed areas on multispectral images to improve efficiency.


Multi-spectral assessment of ingredients and physical properties of apricot

Ferenc Firtha, Zoltán Gillay, Eszter Vozáry, Tímea Kaszab, Anikó Lambert-Meretei and József Felföldi



Köszönöm a figyelmet!

NIR Klub, 2009. november 3. $14^{\underline{00}}$