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TILIA HONEY'S FRUCTOSE, GLUCOSE AND SUCROSE CONTENT PREDICTION USING FT-IR SPECTRA WITH PARTIAL LEAST SQUARES REGRESSION

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Abstract: *The aim of this study was to assess the usefulness of Fourier transform infrared (FT-IR) spectroscopy coupled with partial least squares regression (PLS-R) to predict the fructose, glucose and sucrose content of tilia honeys. In order to achieve the aim of this study, 22 samples of tilia honey were purchased from Suceava, Neamt and Iasi County in the year of 2020. The fructose, glucose and sucrose content was determined prior the PLS-R prediction using high-performance liquid chromatography coupled with refractive index detector (HPLC-RID). The fructose content of tilia honeys ranged from 31.94 to 35.22%, the glucose content ranged between 26.76 and 33.15%, while sucrose content ranged between 0 and 2.20%. For the prediction of fructose, glucose and sucrose it was used the 3000 - 2800 + 1700 - 1600 +1540 - 700 cm^{-1} spectral range. The spectral data was submitted to different mathematical pretreatments in order to reduce the noise and to improve the prediction of results. For the prediction of fructose content the suitable pretreatment was Multiplicative Scatter Correction – MSC, for glucose prediction the suitable pretreatment was Standard Normal Variate – SNV, while for the prediction of sucrose the suitable pretreatment was 1st derivate.*

Keywords: *tilia honey, fructose, glucose, sucrose, FT-IR, prediction*

1. Introduction

Honey is the oldest sweetener used by humankind and is worldwide known by its taste, color, aroma, and medicinal and nutritional properties as antioxidant, antiinflamatory, antitumor, anticancer and antimicrobial [1]. It is considered that honey has more than 200 substances as: sugars, organic acids, proteins, aminoacids, enzymes, vitamins, minerals, phenolic compounds and some solid particles (e.g. wax, pollen or other particles originating from its harvesting) [2,3].
The sugar composition of honey is a complex mixture of mono-, di-, tri-, oligo- and polysaccharides, but the main sugars present are fructose and glucose [4]. The main method used to determine the sugar composition of honey is high-performance liquid chromatography coupled with refractive index detector (HPLC-RID) [5].
Fourier transform infrared (FT-IR) spectroscopy presents information from frequencies of fundamental molecular vibrations and mostly reveals sharp peaks and different spectral characteristics [6,7].
Fourier transform infrared spectroscopy was used in many non-destructive methods for the characterization of honey and to determine different parameters, as follows: moisture content, sugar composition, free acidity, authentication of the botanical origin of honeys or to estimate the phenolic compounds and antioxidant capacity [7-10].
Partial least squares regression (PLS-R) is a multivariate regression method used for the complex data (e.g. FT-IR spectra, Raman

spectra, large number of data, UV-VIS spectra) and physicochemical data [11-13]. The PLS-R models are able to provide reduced models constructed on the original data in order to reduce data complexity [13, 14].

In this study is presented the prediction of fructose, glucose and sucrose from tilia honeys using FT-IR data with partial least squares regression (PLS-R).

2. Materials and methods

Materials

22 samples of tilia honeys were collected from Suceava, Neamt and Iasi County from 2020 production.

Methods

The fructose, glucose and sucrose content were determined using a high-performance liquid chromatography (HPLC) method based on the protocol of Bogdanov & Baumann [4].

FT-IR analysis

An ATR-Nicolet iS-20 spectrometer (Thermo Scientific, Karlsruhe, Dieselstraße, Germany) was used for honey spectra acquisition in the mid-infrared region of 4000-650 cm^{-1} with a resolution of 4 cm^{-1}. The sample was placed on the ATR crystal and the spectra were collected using OMNIC software (version 32, Thermo Scientific).

Statistical analysis

Partial least squares regression (PLS-R) was realized using the Unscrambler X 10.1 software (Camo, Norway).

3. Results and discussion

Sugar content

In Table 1 are presented the mean, minimum and maximum concentrations of fructose, glucose and sucrose from the analyzed tilia honey samples. As it can be observed, the fructose concentration was higher in all samples, while sucrose content ranged between 0 and 2.20 %. The concentrations of fructose + glucose were higher than 60% in all the honey samples therefore meeting the threshold established by the EU legislation [15]. The fructose/glucose ratio was higher than 1 which confirmed the liquid state of the analyzed samples.

Table 1.
Fructose, glucose and sucrose content in tilia honeys

Parameter	Mean	Min	Max
Fructose (%)	33.14	31.94	35.22
Glucose (%)	28.79	26.76	33.15
Sucrose (%)	0.36	0	2.20
F/G		1.15	

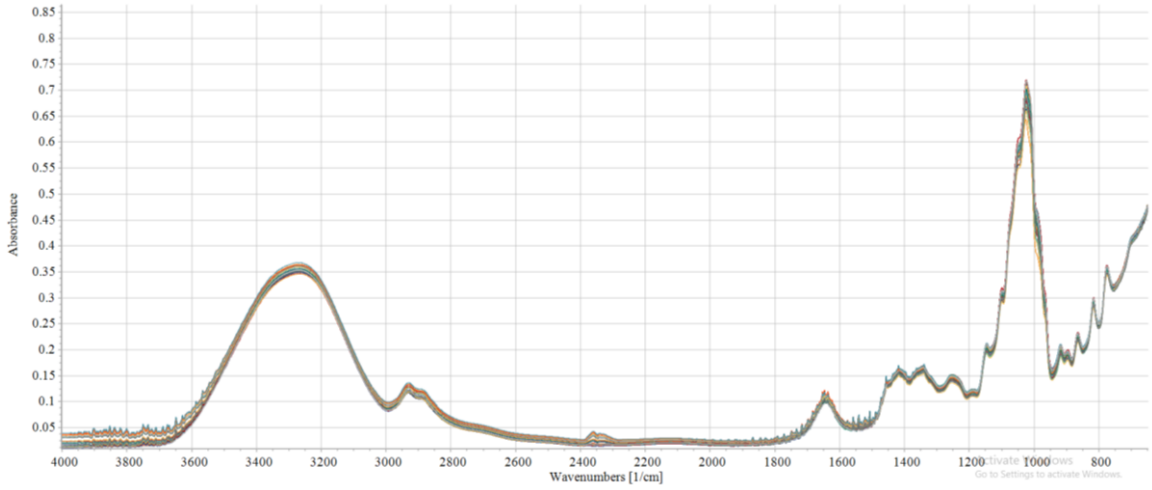
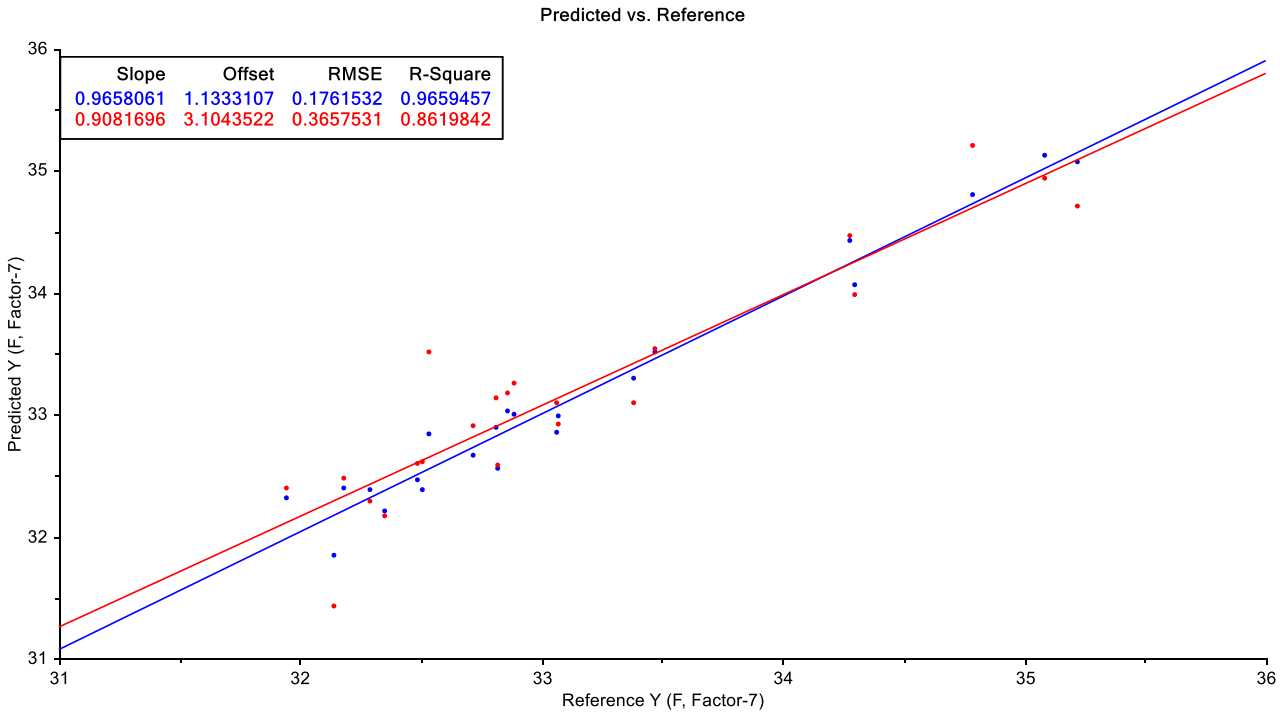


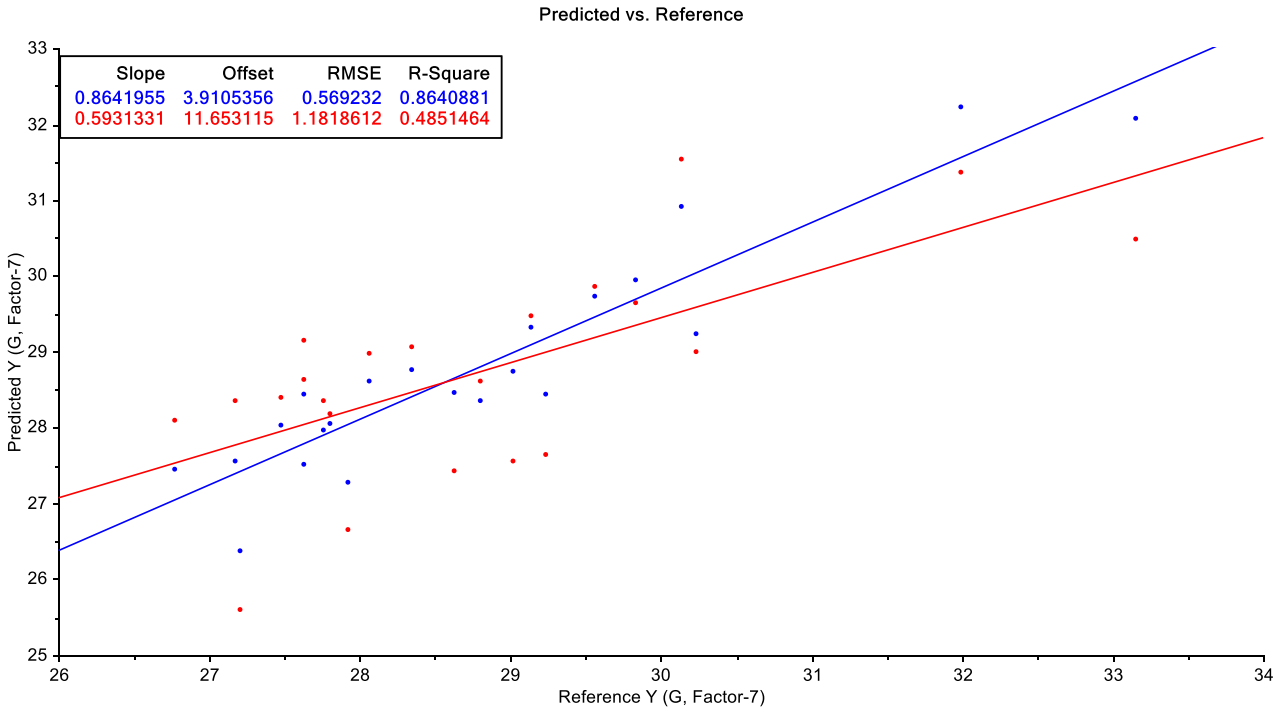
Fig. 1. FT-IR spectra of tilia honeys

Table 2.

Regression parameters of the calibration and validation procedure calculated for the FT-IR spectral data submitted to partial least square regression (PLS-R) analysis in order to predict glucose, fructose and sucrose in tilia honey

Parameter	Treatment	No factors	Spectral range (cm^{-1})	Calibration				Validation			
				Slope	Offset	RMSE	R^2	Slope	Offset	RMSE	R^2
Fructose	NON	7	3000-2800 + 1700-1600 +1540-700	0.892	3.561	0.312	0.892	0.739	8.586	0.493	0.762
Glucose		7		0.790	6.040	0.707	0.790	0.489	14.492	1.862	NA
Sucrose		7		0.954	0.016	0.121	0.954	0.906	0.017	0.194	0.905
Fructose	MSC	7		0.965	1.133	0.176	0.965	0.908	3.104	0.365	0.861
Glucose		7		0.833	4.802	0.630	0.833	0.476	15.267	1.471	0.142
Sucrose		7		0.953	0.016	0.122	0.953	0.832	0.088	0.222	0.855
Fructose	SNV	6		0.747	8.355	0.479	0.747	0.546	14.966	0.822	0.336
Glucose		7		0.864	3.910	0.569	0.864	0.593	11.653	1.181	0.485
Sucrose		7		0.830	0.170	0.392	0.530	0.167	0.226	0.717	NA
Fructose	Baseline	7		0.972	0.926	0.159	0.972	0.849	4.930	0.473	0.811
Glucose		6		0.765	6.759	0.748	0.765	0.474	15.357	1.523	0.124
Sucrose		6		0.953	0.017	0.124	0.953	0.961	0.022	0.181	0.907
Fructose	Normalization	6		0.913	2.854	0.279	0.913	0.761	7.907	0.461	0.779
Glucose		6		0.754	7.058	0.764	0.754	0.505	14.320	1.325	0.323
Sucrose		7		0.949	0.018	0.128	0.949	0.877	0.041	0.209	0.877
Fructose	1st derivate	4		0.888	3.700	0.318	0.888	0.602	13.166	0.541	0.719
Glucose		4		0.628	10.685	0.940	0.628	0.306	20.102	1.478	0.186
Sucrose		7		0.964	0.012	0.107	0.964	0.847	0.051	0.173	0.917
Fructose	2nd derivate	7		0.974	0.842	0.151	0.974	0.061	31.073	0.971	0.093
Glucose		7		0.991	0.240	0.141	0.991	0.010	28.524	1.660	NA
Sucrose		7		0.960	0.014	0.113	0.960	0.400	0.192	0.453	0.427
Fructose	Smoothing	7		0.892	3.561	0.312	0.892	0.852	4.872	0.456	0.796
Glucose		6		0.747	7.284	0.776	0.746	0.407	17.232	1.510	0.202
Sucrose		7		0.954	0.016	0.121	0.954	0.873	0.056	0.202	0.885


Predicted vs. Reference
Slope Offset RMSE R-Square
0.9658061 1.1333107 0.1761532 0.9659457
0.9081696 3.1043522 0.3657531 0.8619842
Predicted Y (F, Factor-7)
Reference Y (F, Factor-7)
31
32
33
34
35
36


Predicted vs. Reference
Slope Offset RMSE R-Square
0.8641955 3.9105356 0.569232 0.8640881
0.5931331 11.653115 1.1818612 0.4851464
Predicted Y (G, Factor-7)
Reference Y (G, Factor-7)
25
26
27
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31
32
33
34

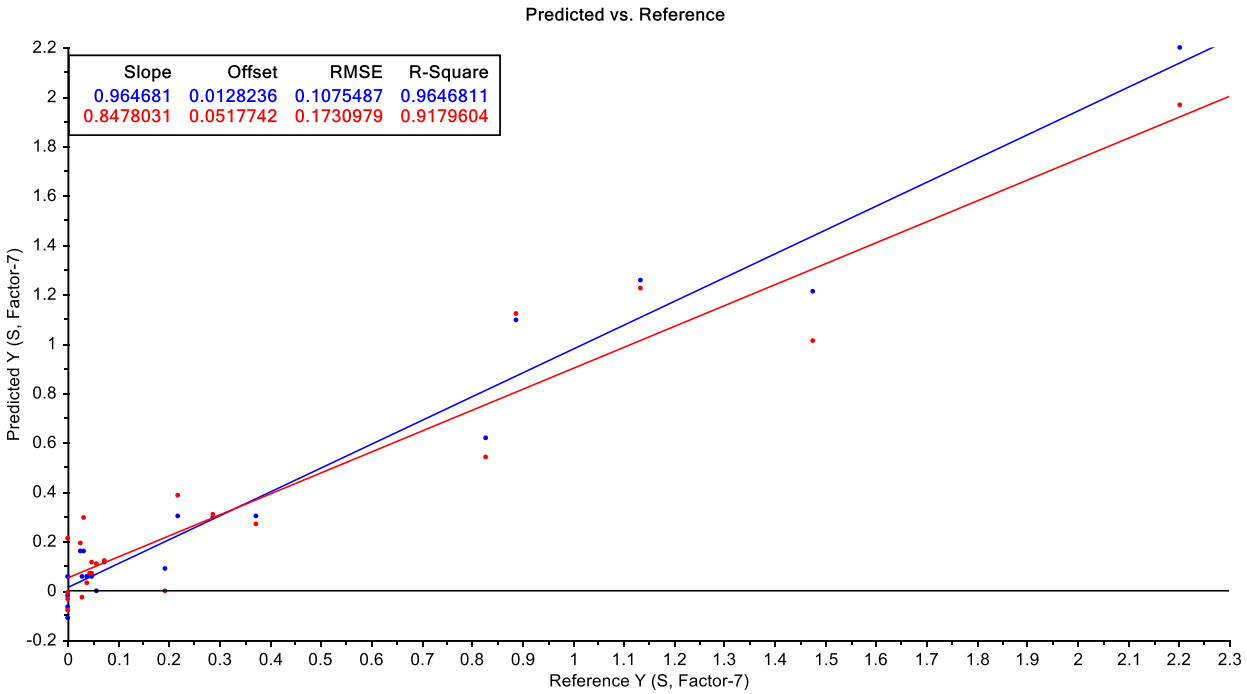

Fig. 2. Reference vs predicted fructose, glucose and sucrose content using FT-IR spectra and PLS-R

FT-IR spectra

The FT-IR spectra collected for the analyzed honey samples are shown in Figure 1.
According to the scientific literature, the spectral range typical for sugars in honeys are

3000-2800 + 1700-1600 +1540-700cm^{-1}

As it can be observed in Figure 1, the signal for the spectral range presented above is high in the tilia honey samples that were analyzed in this study.

PLS-R prediction

The PLS-R model was used for the prediction of fructose, glucose and sucrose based on FT-IR spectral data. As it can be seen in Figure 1, the noise recorded for the honey samples was high and to reduce it the spectra must be submitted to different mathematical procedures, as follows: Multiplicative Scatter Correction – MSC, Standard Normal Variate – SNV, baseline, normalization, 1st derivate, 2nd derivate, smoothing (Table 2). As it can be observed in Table 2, each parameter predicted has a different pretreatment: fructose – Multiplicative Scatter Correction – MSC, glucose – Standard Normal Variate – SNV and sucrose – 1st derivate. The suitable model for each parameter is highlighted in Table 2 with different colours. The calibration and validation coefficients for the fructose and sucrose were higher than 0.861 proving the suitability of the proposed models, and in the case of glucose, the calibration parameters have a good magnitude, however, the validation parameters cannot be considered satisfactory.

For improving the correlation coefficients of the glucose prediction it would be necessary a higher number of samples. In Figure 2 is presented the evolution of reference and predicted values for fructose, glucose and sucrose.

4. Conclusion

In this study it was determined the concentration of fructose, glucose and sucrose in 22 samples of tilia honeys from Suceava, Neamt and Iasi County.

As it was observed, the concentration of fructose was higher than that of glucose in all the samples, while the concentrations of fructose + glucose met the threshold established by the UE legislation. The FT-IR spectra of the tilia honey samples were used for the prediction of glucose, fructose and sucrose content. The pretreatment of the FT-IR spectra increased the values of the prediction parameters. The fructose and sucrose prediction and validation parameters were satisfactory ($R^2 > 0.860$), while the glucose parameters where not satisfactory in the validation step. For improving the correlation coefficients of the glucose prediction, a higher number of samples would be necessary.

5. Acknowledgment

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