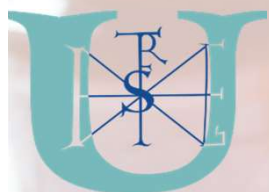


International Symposium on Bee Products
5th edition Sliema, Malta, 2019

DETECTION OF HEAT TREATMENT OF HONEY BY RAPID CORRELATIVE TECHNIQUES



Zsanett Bodor^{1,2}, John-Lewis Zinia Zaukuu², Csilla Benedek¹,
Zoltan Kovacs²

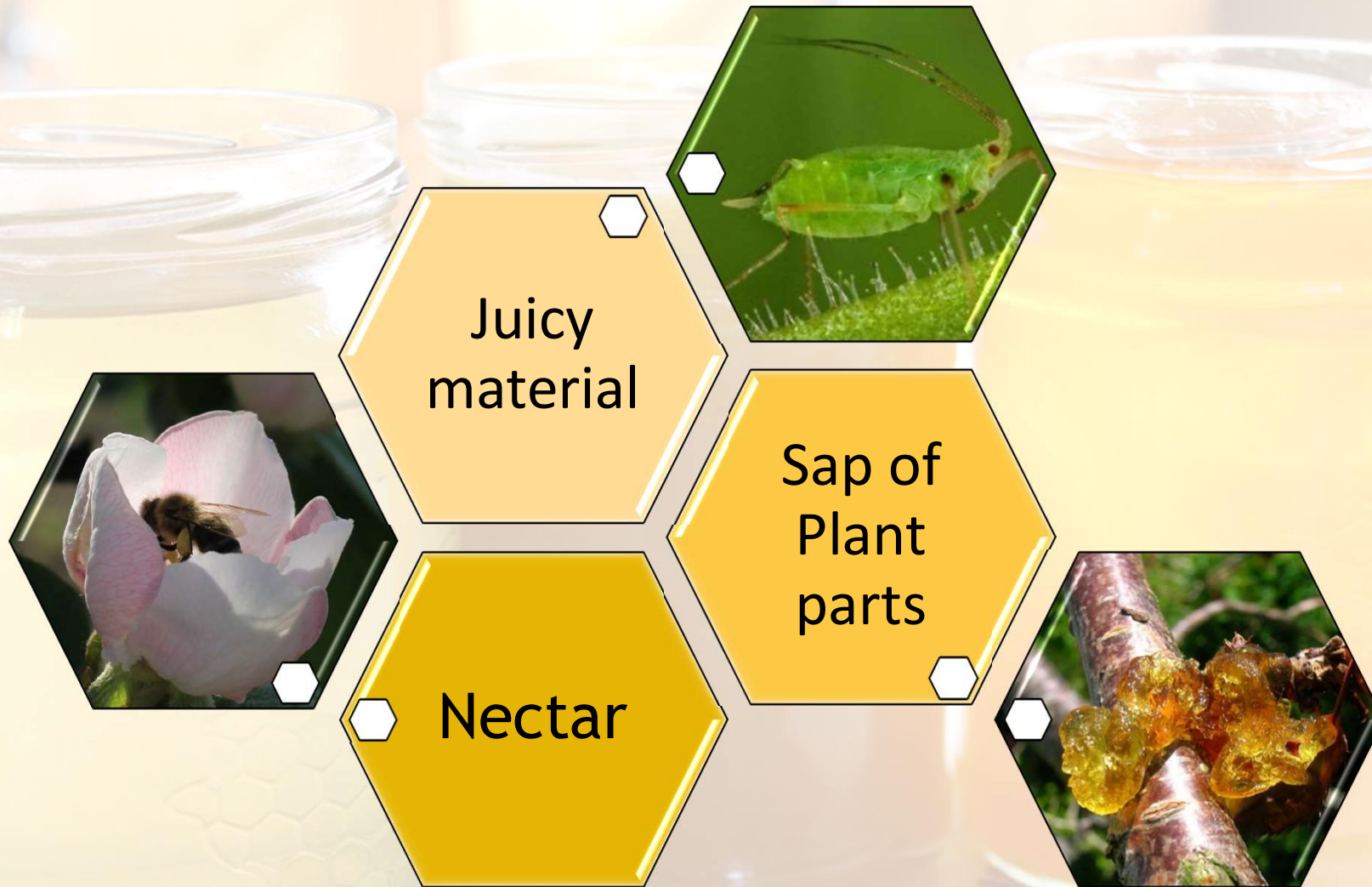
¹Szent István University, Faculty of Food Science, Department of Physics and Control,
14-16 Somloi str., 1118 Budapest, Hungary

²Semmelweis University, Faculty of Health Sciences, Department of Dietetics and Nutrition,
17 Vas str., 1088 Budapest, Hungary



Supported by the Hungarian National Excellence Program of Ministry of Human Capacities (Zoltan Kovacs, Zsanett Bodor), the Doctoral School of Food Science, Szent István University. (Zsanett Bodor, John-Lewis Zinia Zaukuu). The Project is supported by the European Union and co-financed by the European Social Fund (grant agreement no. EFOP-3.6.3-VEKOP-16-2017-00005)

INTRODUCTION - HONEY



ACTUALITY



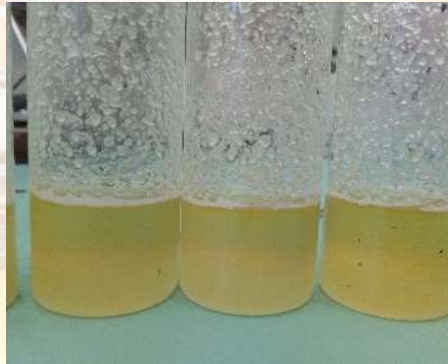
Importance of botanical
and geographical origin

Adulteration

- Direct (adding syrups)
- Indirect (feeding bees with syrup)
- Others (heating, evaporation)



ACTUALITY



Heat treatment of honey

- The reason:
 - Crystal elimination, easier handling
- Consequences → changes in honey
 - Hydroxymethyl-furfural (HMF) (max. 40 mg/kg)
 - Enzymes, antioxidants
 - aroma, color

OUR AIMS

Monitoring the changes during heat treatment in honey in:

Parameters previously described in the literature

- hydroxymethyl-furfural content (HMF),
- Antioxidant properties

Not reported in the literature before for heat

- Near infrared spectroscopy (NIR),
- Electronic tongue (ET)

The image shows three glass jars with lids, arranged in a row. The jar on the left contains a light yellow liquid and has a textured, honeycomb-like pattern on its surface. The middle jar contains a pale pink liquid. The jar on the right contains an orange liquid. A semi-transparent yellow banner is overlaid across the middle of the image, containing the text 'MATERIALS AND METHODS' in a bold, black, sans-serif font.

MATERIALS AND METHODS

HONEYS



Minimal heat treatment

- Honey types
 - Acacia
 - Sunflower
 - Linden
 - Multiflora
- 120 samples
 - Control (not heated)
 - 40°C, 50°C, 60°C
 - 30, 60, 120 minutes



Extended experiment

- Honey types
 - Sunflower
- 15 samples
 - Control (not heated)
 - 40°C, 60°C, 80°C, 100 °C
 - 120 minutes

PHYSICO-CHEMICAL METHODS - QUALITY INDICATORS



Total soluble dry matter content

- Abbé-type refractometer



pH

- Testo 205 portable pH meter



Electrical conductivity

- Mettler Toledo

PHYSICO-CHEMICAL - UV/VIS SPECTROPHOTOMETRY

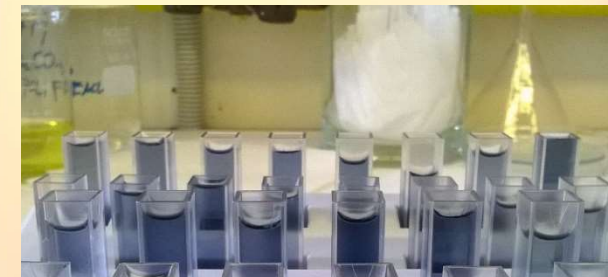
Helios α spectrophotometer



Hydrodymethyl-
furfural (Winkler
method)
550 nm



ABTS antioxidant
capacity
734 nm



Total polyphenol
content
750 nm

RAPID METHODS

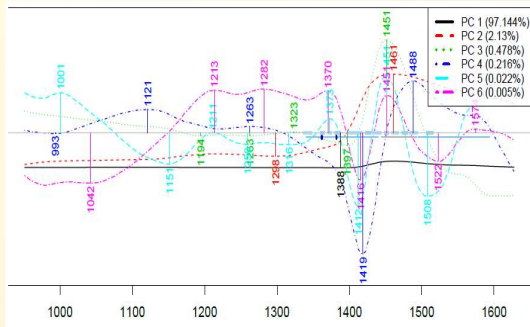


αAstree Electronic tongue

Potentiometric (Ag/AgCl,
7 CHEMFET electrode)

Based on human sensory organs

- 10 g honey -> 100 ml (distilled water)



Near infrared spectroscopy (NIRs)

- 900-1700 nm
- 0.4 mm layer thickness of cuvette
- ~ 2 g honey

STATISTICS

Univariate for the physico-chemical methods


- Descriptive statistics
- ANOVA – Variance analysis followed by pairwise comparison

Multivariable for rapid methods

- Data pre-treatments
 - ET (drift correction, outlier detection)
 - NIR (smoothing, baseline shift correction, outlier detection)
- Principal components analysis (PCA)
- Linear discriminant analysis (LDA) - Three-fold cross validation

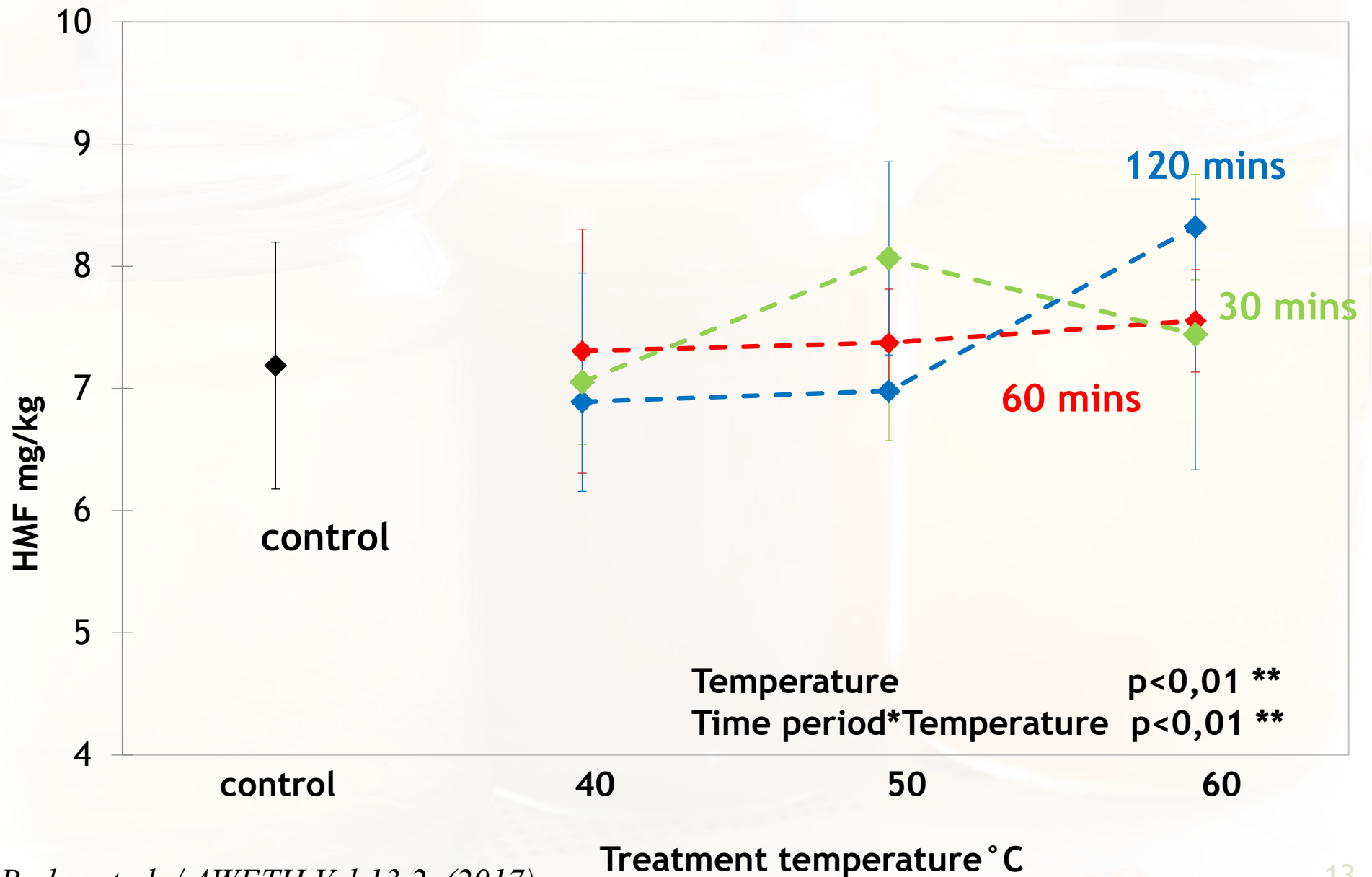
Softwares

- MS Excel 2016
- R-studio 3.4.1

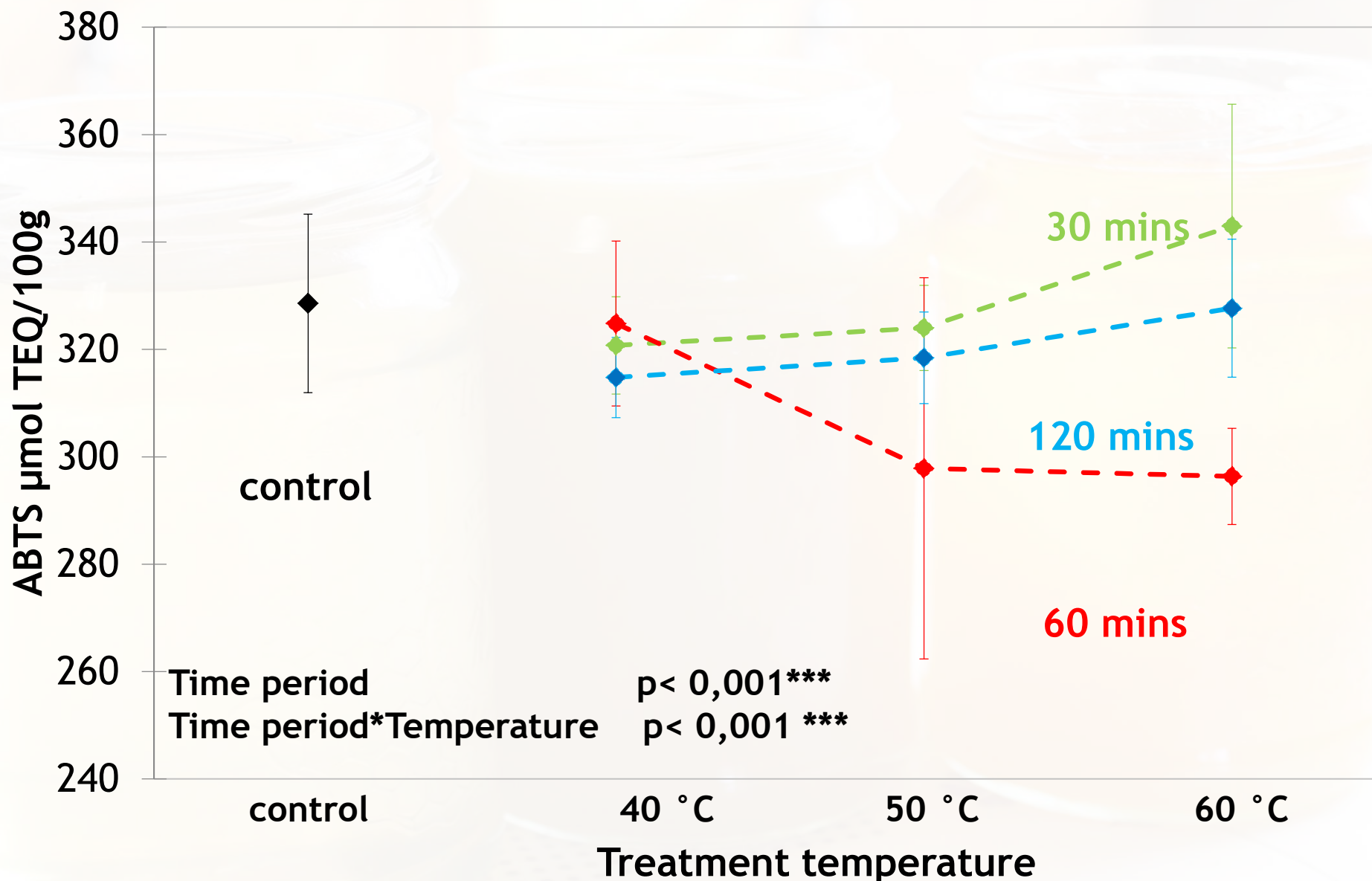
The image shows three glass jars with lids, arranged in a row. The jar on the left contains a pale yellow liquid. The middle jar contains a light brown liquid. The jar on the right contains a dark orange liquid. A semi-transparent orange banner is overlaid across the middle of the jars, containing the word "RESULTS" in bold black text. The jars are sitting on a white surface with a brown polka-dot pattern.

RESULTS

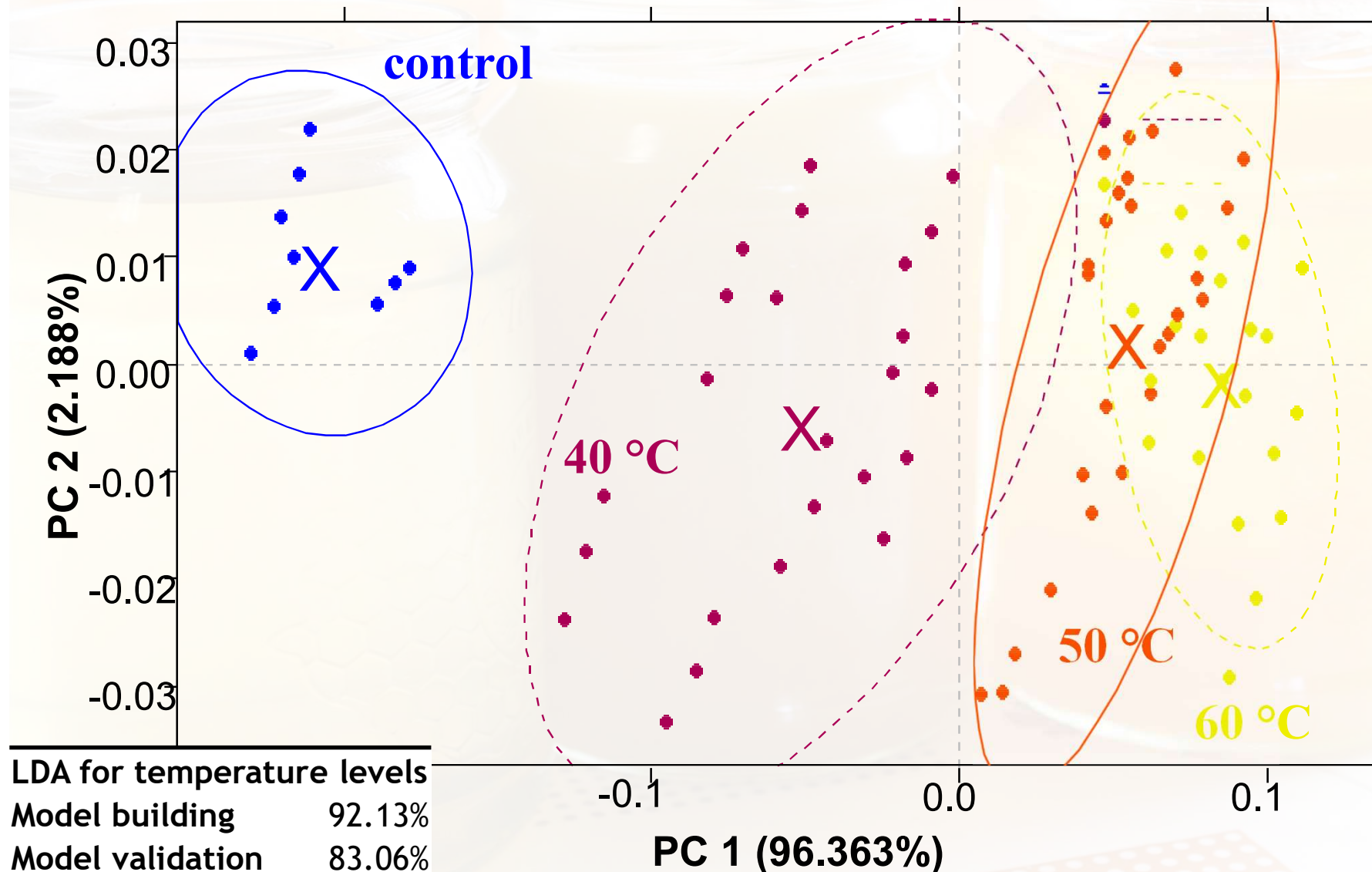
Means and SD of HMF content of Linden honeys by heat treatment level (n=90)



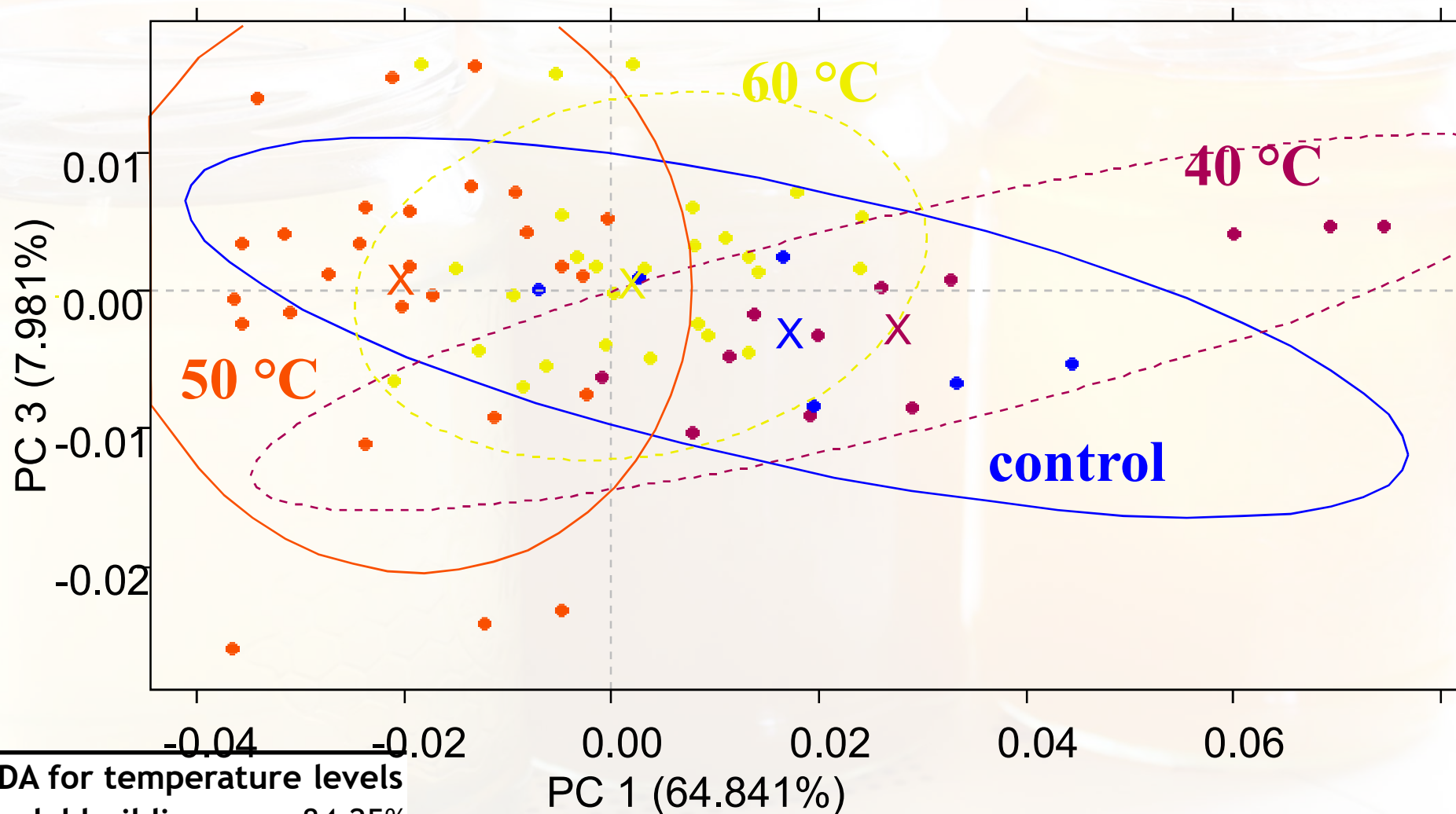
Means and SD of ABTS antioxidant capacity of linden honeys by heat treatment level (n=90)



PCA results of NIR spectra of **linden** honeys after Savitzky-Golay smoothing, MSC and outlier detection by temperature groups (n=80)

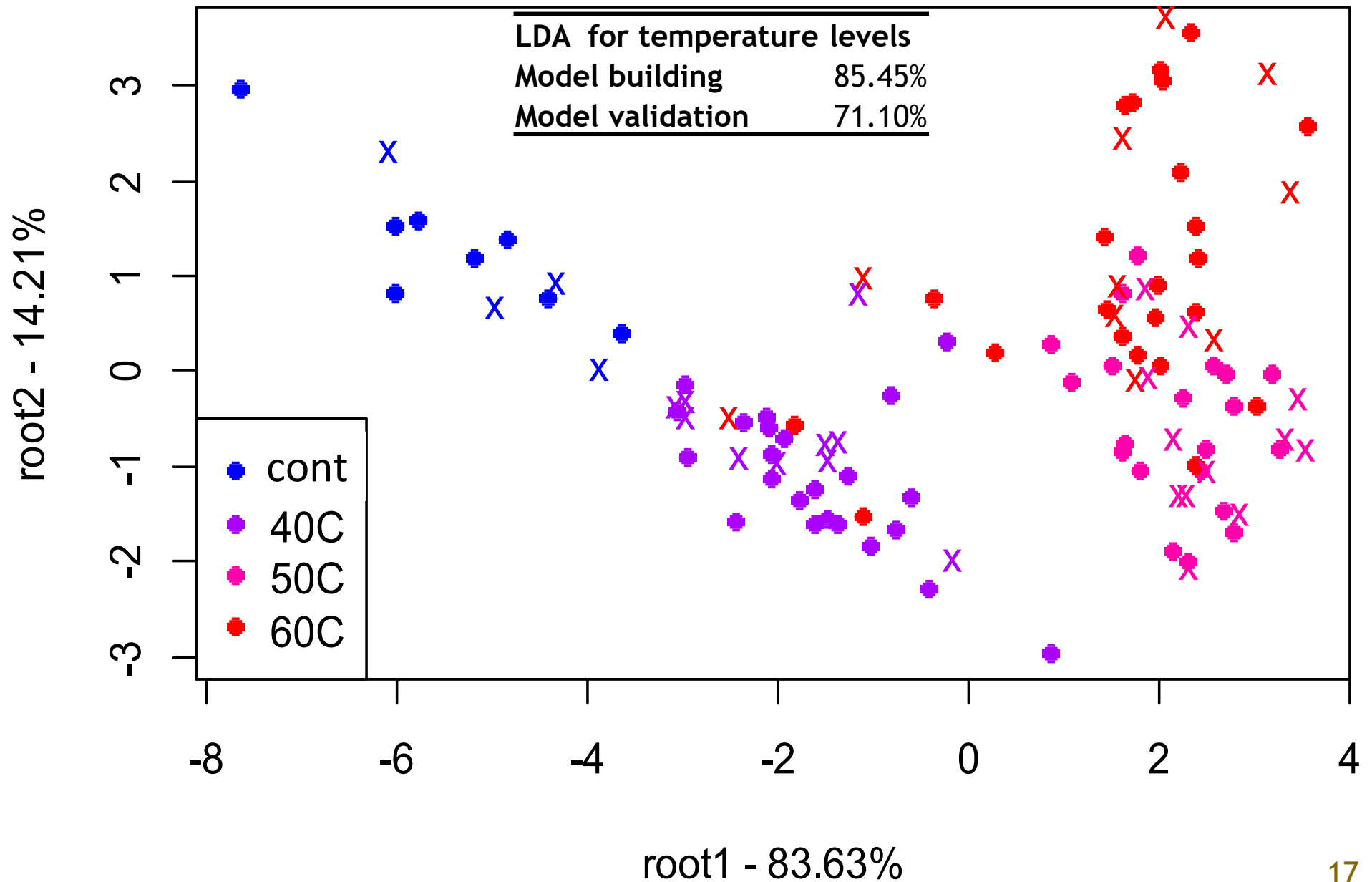


PCA results of NIR spectra of acacia honeys after Savitzky-Golay smoothing, MSC and outlier detection by temperature groups (n=78)

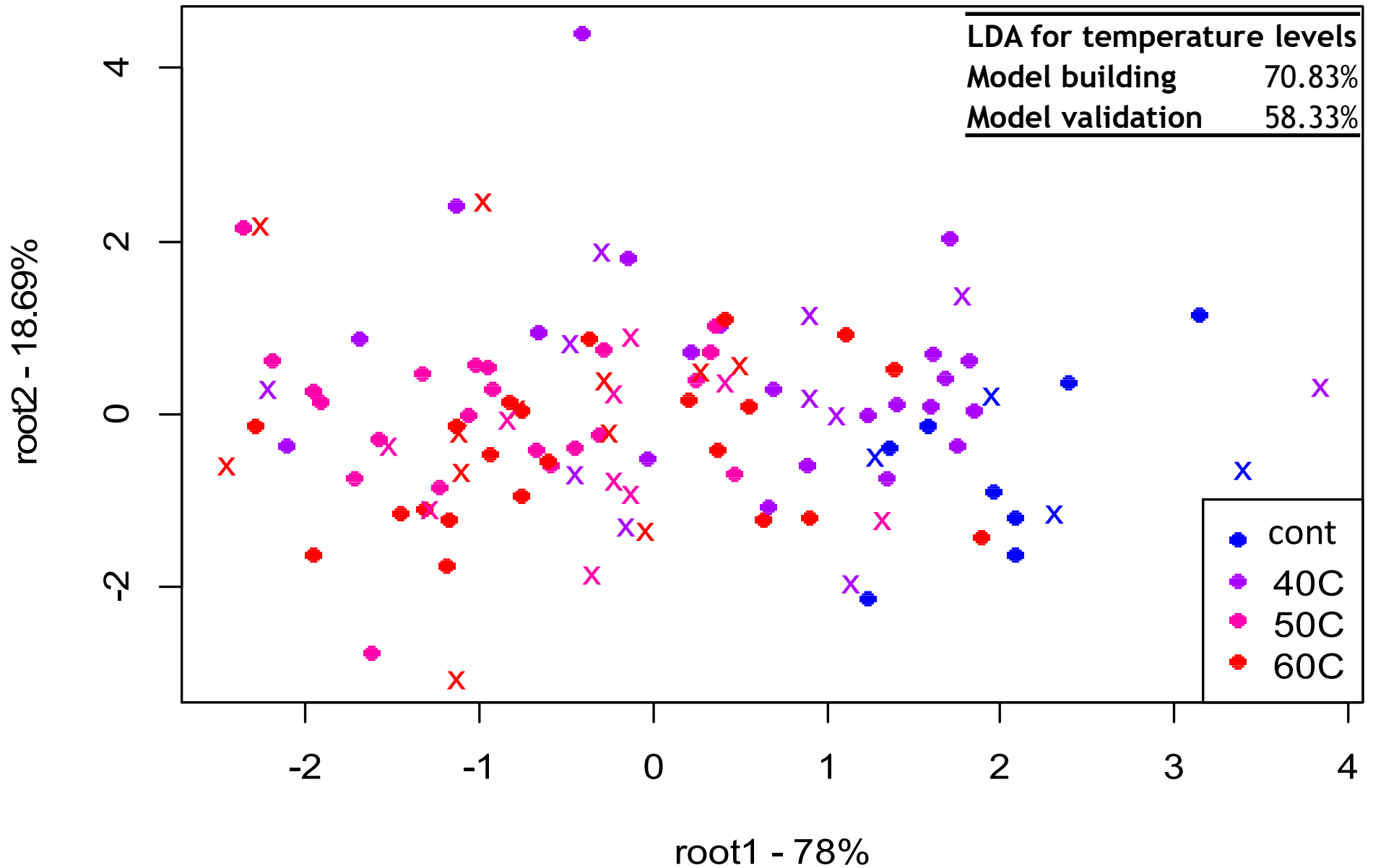


LDA for temperature levels	
Model building	84.25%
Model validation	59.99%

LDA results of electronic tongue data of multiflora honeys by temperature levels (n=110)



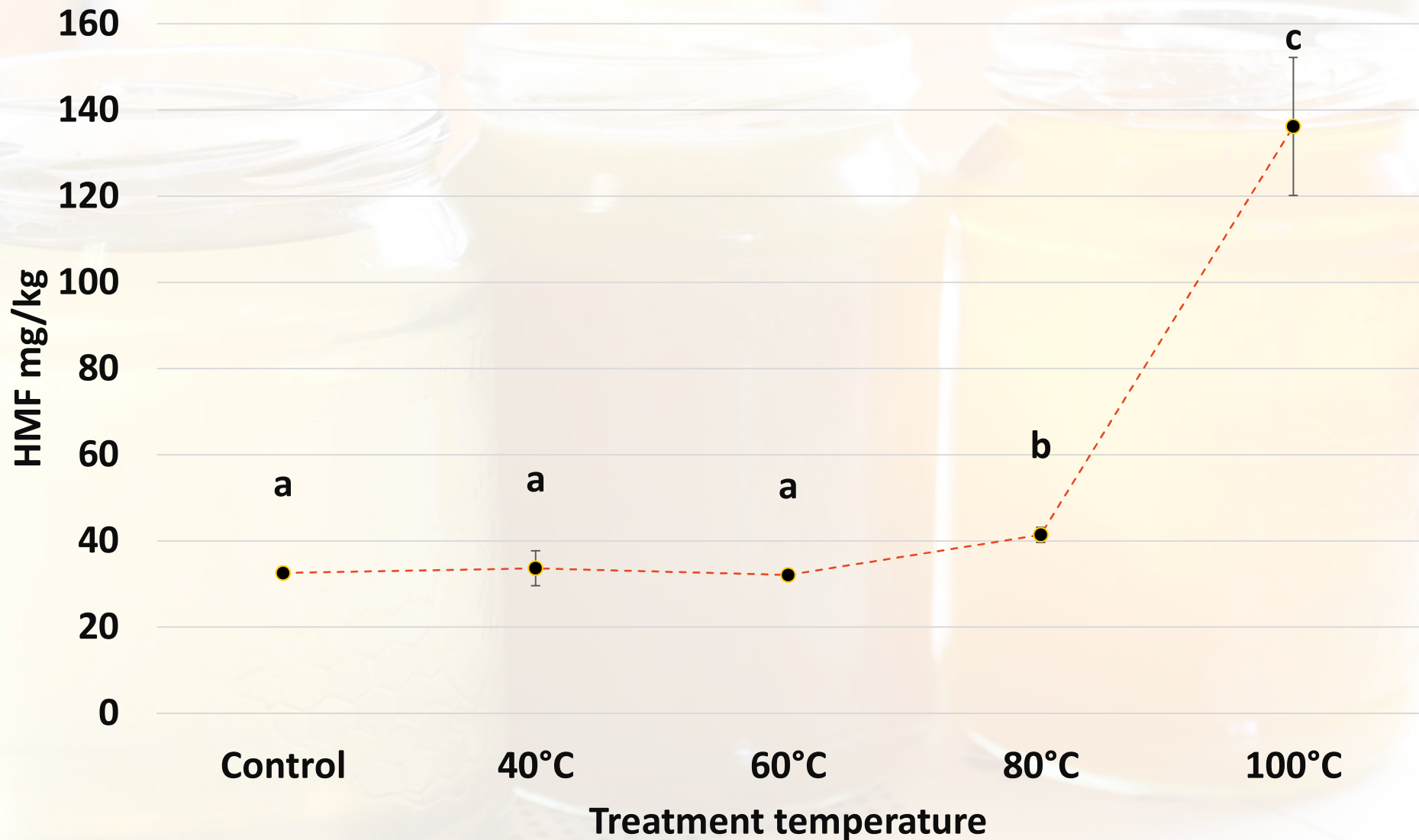
LDA results of electronic tongue data of acacia honeys by temperature levels (n=111)



The image shows three glass jars with lids, arranged in a row. The jar on the left contains a light yellow liquid. The middle jar contains a pale pink liquid. The jar on the right contains an orange liquid. A semi-transparent yellow banner is overlaid across the middle of the image, containing the text 'EXTENDED EXPERIMENT'.

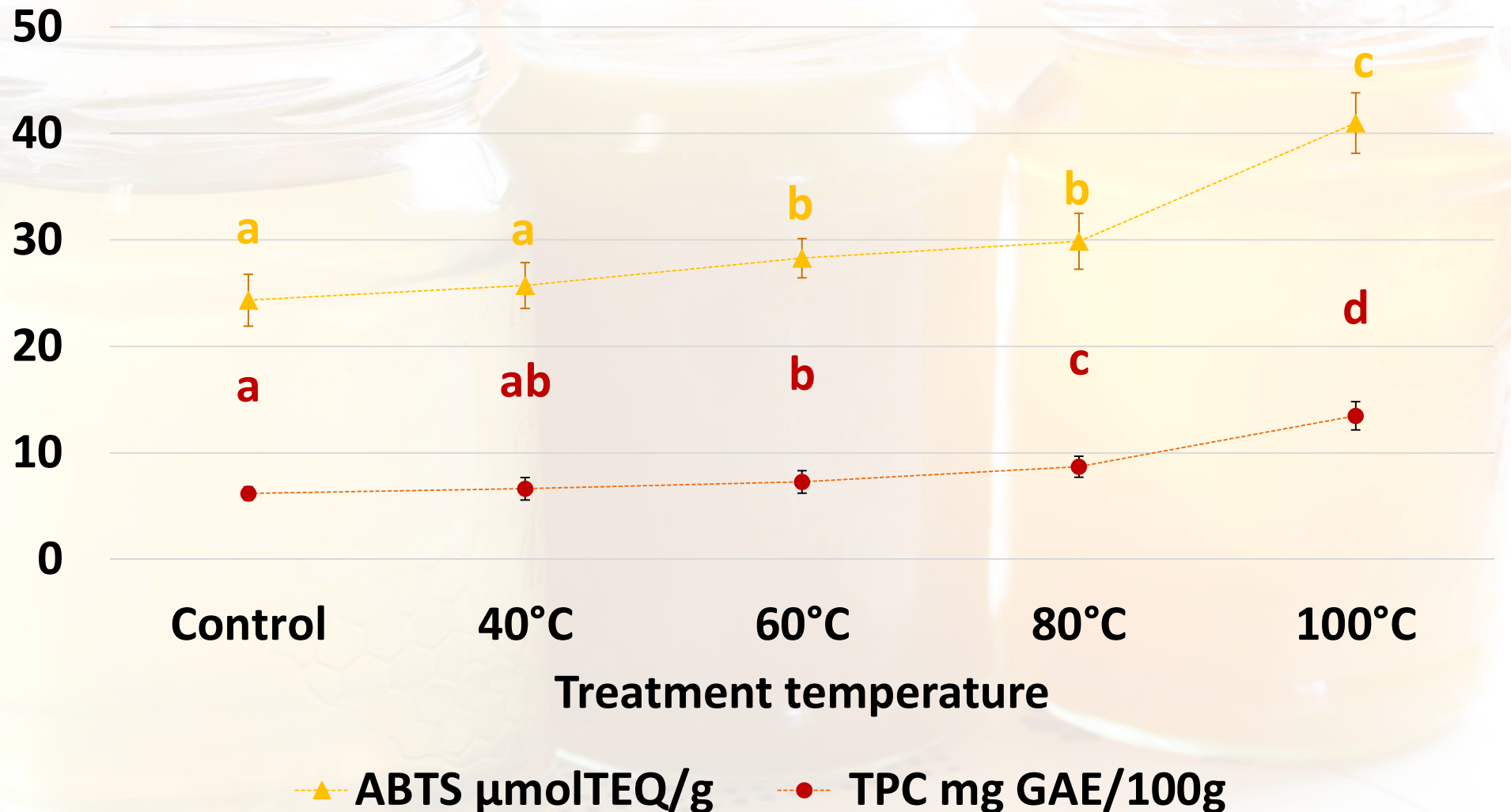
EXTENDED EXPERIMENT

HMF CONTENT OF HEATED SUNFLOWER HONEYS AT DIFFERENT TEMPERATURES FOR 120 MINUTES n=45



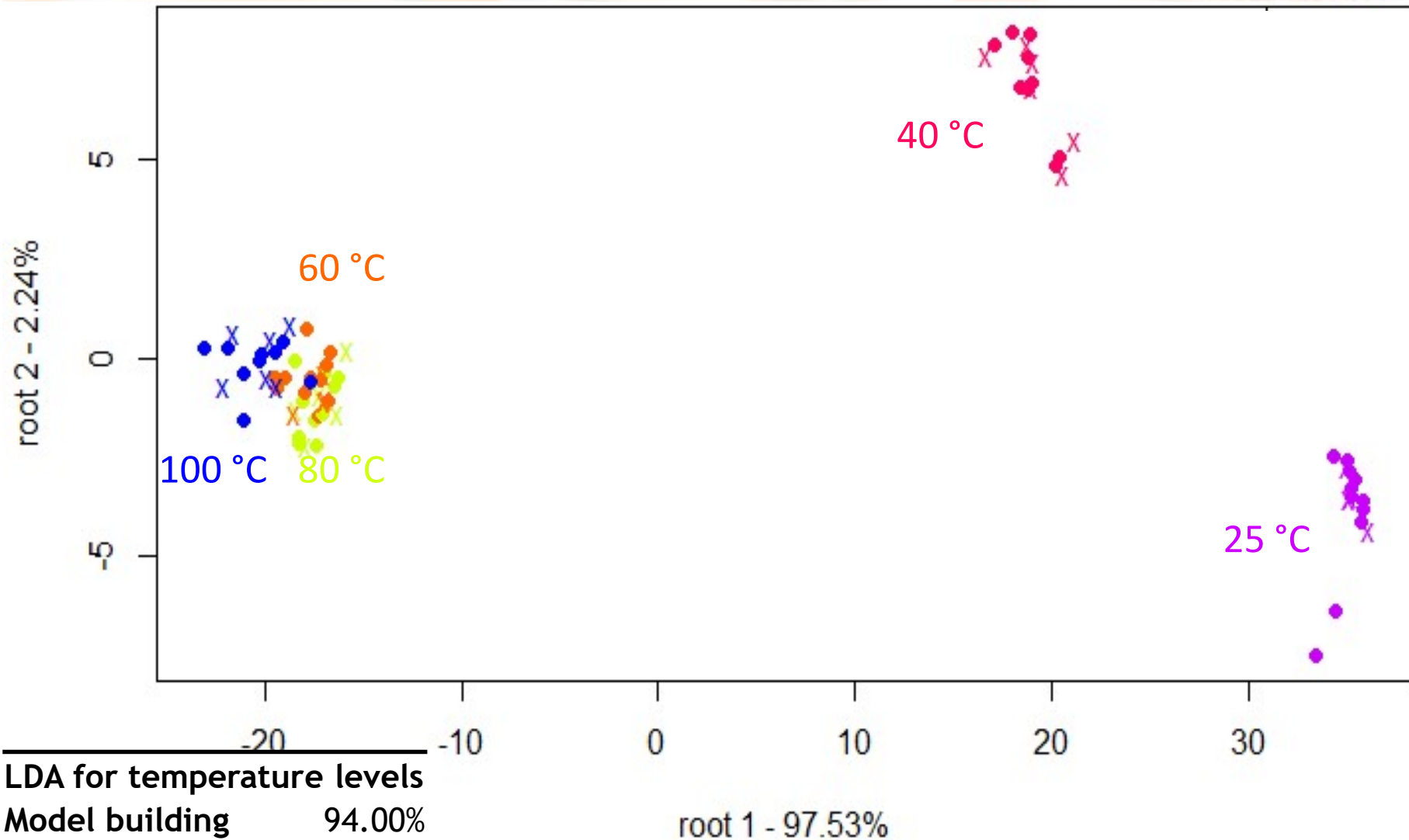
Letters mean the significant differences $p < 0.05$

ABTS ANTIOXIDANT CAPACITY AND TPC CONTENT OF SUNFLOWER HONEY AT THE DIFFERENT HEATED LEVELS FOR 120 MINUTES (n=75)



Letters mean the significant differences $p < 0.05$

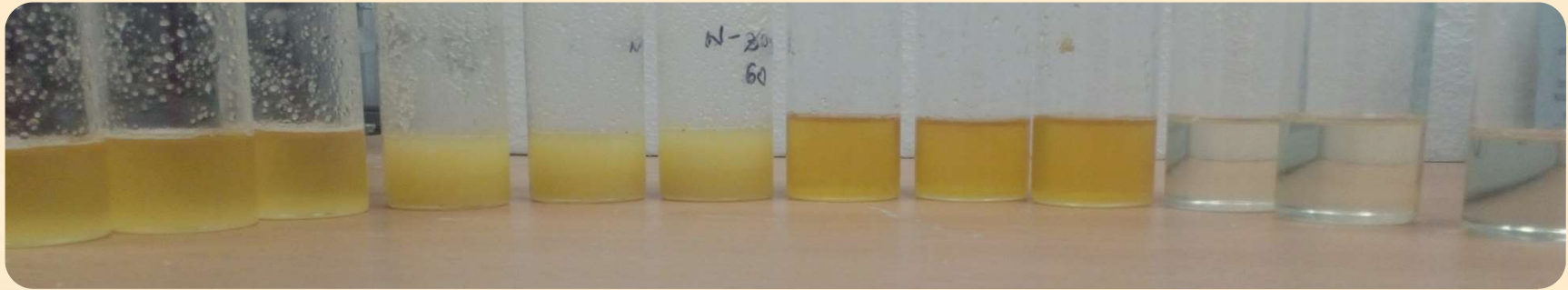
LDA results of NIR (METRI) spectra of sunflower honeys after Savitzky-Golay smoothing, MSC and outlier detection by temperature groups (n=75)



LDA for temperature levels
Model building 94.00%
Model validation 90.68%

root 1 - 97.53%

CONCLUSION



For the detection of minimal heat treatment:

- The HMF and antioxidant capacity measuring assays are not sensible enough
 - HMF at 60°C 120 min not showing significant increase
 - Antioxidant capacity is increasing
- NIR and ET were capable in of separating heated honeys from control
 - **linden**, **multiflora** and **sunflower** honeys

ACKNOWLEDGEMENT



My co-authors and our research group

- Zoltan Kovacs
- Csilla Benedek
- John Lewis Zinia Zaukuu
- Tímea Kaszab
- István Kertész

The Honey Providers

- Zoltan Sipos
- Gyula Gacsal
- Péter Tóth
- János Nagy



Supported by the Hungarian National Excellence Program of Ministry of Human Capacities (Zoltan Kovacs, Zsanett Bodor), the Doctoral School of Food Science, Szent István University. (Zsanett Bodor, John-Lewis Zinia Zaukuu). The Project is supported by the European Union and co-financed by the European Social Fund (grant agreement no. EFOP-3.6.3-VEKOP-16-2017-00005)

REFERENCES I.

1. Anklam, E. (1998). A review of the analytical methods to determine the geographical and botanical origin of honey. *Food Chemistry*. [https://doi.org/10.1016/S0308-8146\(98\)00057-0](https://doi.org/10.1016/S0308-8146(98)00057-0)
2. Bázár, G., Romvári, R., Szabó, A., Somogyi, T., Éles, V., & Tsenkova, R. (2016). NIR detection of honey adulteration reveals differences in water spectral pattern. *Food Chemistry*, 194, 873-880. <https://doi.org/10.1016/j.foodchem.2015.08.092>
3. Bodor, Z., Koncz, F. A., Rashed, M. S., Kaszab, T., Gillay, Z., Benedek, C., & Kovacs, Z. (2016). Application of Near Infrared Spectroscopy and classical analytical methods for the evaluation of Hungarian Honeys. In *1st International Conference on Biosystems and Food Engineering CD of Full Papers*. Retrieved from <http://physics2.bc.szie.hu/biosysfoodeng/cdrom/pdf/E108.pdf>
4. Bogdanov, S. (2002). *Harmonised methods of the International Honey Commission. International Honey Commission (IHC)*. Swiss Bee Research Centre, FAM, Liebefeld. Cimpoiu, C., Hosu, A., Miclaus, V., & Puscas, A. (2013). Determination of the floral origin of some Romanian honeys on the basis of physical and biochemical properties. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 100, 149-154. <https://doi.org/10.1016/j.saa.2012.04.008>
5. Czipa, N. (2010). *Különböző eredetű mézek összehasonlító vizsgálata és a gyártmánykialakítás hatása a minőségre*. Hankóczy Jenő Növénytermesztési, Kertészeti és Élelmiszertudományok Doktori Iskola. Retrieved from <https://dea.lib.unideb.hu/dea/bitstream/handle/2437/99459/ertekezes.pdf?sequence=5>
6. Csóka, M., Tolnay, P., & Szabó S, A. (2014a). Hársmez diasztázaktivitásának változása hőkezelés hatására, illetve a tárolás során = Changes in the diastase activity of linden honey due to heat treatment, and during storage. *Élelmiszervizsgálati Közlemények*, 60(3), 270-277. Retrieved from http://epa.oszk.hu/03100/03135/00257/pdf/EPA03135_elelmiszervizsgalati_kozlomenyek_2014_03_270-277.pdf
7. Csóka, M., Tolnay, P., & Szabó S, A. (2014b). Hársmez színjellemzőinek változása hőkezelés hatására, illetve a tárolás során = Alteration in linden honey colour properties by storage and heat treatment. *Élelmiszervizsgálati Közlemények*, 60(1), 44-49. Retrieved from http://epa.oszk.hu/03100/03135/00255/pdf/EPA03135_elelmiszervizsgalati_kozlomenyek_2014_01_044-049.pdf
8. FAOSTAT. (2017). *Food balance sheets* (Vol. 34). <https://doi.org/http://faostat.fao.org/>

REFERENCES II.

9. Fekete, Róbert, T., Tamás, P., Antal, Á., & Décsei-Paróczy, A. (2014). A CIE féle színmérő rendszer. Retrieved October 17, 2017, from http://www.tankonyvtar.hu/en/tartalom/tamop412A/2011-0042_3d_megjelenitesi_technikak/ch02s04.html
10. Karabagias, I. K., Badeka, A. V., Kontakos, S., Karabournioti, S., & Kontominas, M. G. (2014). Botanical discrimination of Greek unifloral honeys with physico-chemical and
11. chemometric analyses. *Food Chemistry*, 165, 181-190. <https://doi.org/10.1016/j.foodchem.2014.05.033>
12. Kertész, P. (OGYÉI). (2014). Közel infravörös spektrószkópia. Retrieved October 17, 2017, from https://www.ogyei.gov.hu/dynamic/2_2014_sz_kozlemenyehez/2_2014_kozlemenypdf_jei/2_2_40_8_0_kesz_Jutka_Szilvi.pdf
13. Kesić, A., Zaimović, I., Ibrišimović-Mehmedinović, N., & Šestan, A. (2017). The Influence of Thermal Treatment on the Concentration of HMF in Honey. *Http://www.sciencepublishinggroup.com*, 2(1), 1. <https://doi.org/10.11648/J.IJEC.20170201.11>
14. Kiss, T., & Tóth, G. (1987). A méhészeti termékek. In A. Nikovitz (Ed.), *A méhészet kézikönyve I.* (1., pp. 383-490). 1987: Állattenyésztési és Takarmányozási Kutatóközpont.
15. Koncz, F. A., Bodor, Z., Kaszab, T., Kertész, I., Zaukuu, J.-L. Z., Benedek, C., ... Kovacs, Z. (2017). Prediction of Main Analytical and Physical Parameters of Honey with Electronic Tongue. In *Synergy 2017 - CD of PAPERS of the V. International Conference of CIGR Hungarian National Committee and the Szent István University, Faculty of Mechanical Engineering and the XXXVIII R&D Conference of Hungarian Academy of Sciences* (p. Paper 04-6-138). Gödöllő.
16. Koncz, F. A., Bodor, Z., Rashed, M. S., Kaszab, T., Gillay, B., Kovacs, Z., & Benedek, C. (2016). Floral and geographical origin identification of Hungarian honeys with electronic tongue and classical analytical methods. In *1st International Conference on Biosystems and Food Engineering*. Retrieved from <http://physics2.bc.szie.hu/biosysfoodeng/cdrom/pdf/E124.pdf>
17. Kovács, Z. (2012). *Módszer elektronikus nyelvvel végzett méréseknél fellépő zavaró hatások csökkentésére*. Budapesti Corvinus Egyetem. Retrieved from http://phd.lib.unicorvinus.hu/642/1/Kovacs_Zoltan.pdf

REFERENCES III.

18. Központi Statisztikai Hivatal. (2017). Agrár idősorok és censzusok 1857-2015. Retrieved October 16, 2017, from https://www.ksh.hu/docs/hun/agrar/html/tab1_5_3_4.html Magyar Élelmiszerkönyv. (2002). 1-3-2001/110 számú előírás Méz. (Codex Alimentarius 44 Hungaricus, Ed.). Magyar Élelmiszerkönyv Bizottság. Retrieved from http://elelmiszerlanc.kormany.hu/download/b/15/b1000/132001110_2009.pdf
19. Magyar Élelmiszerkönyv. (2009). 2-100 számú irányelv Megkülönböztető jelöléssel ellátott mézfélék. (Codex Alimentarius Hungaricus, Ed.) (1.). Magyar Élelmiszerkönyv Bizottság. Retrieved from http://elelmiszerlanc.kormany.hu/download/d/65/50000/2100_2009.pdf
20. Nicoli, M. ., Anese, M., & Parpinel, M. (1999). Influence of processing on the antioxidant properties of fruit and vegetables. *Trends in Food Science & Technology*, 10(3), 94-100. [https://doi.org/10.1016/S0924-2244\(99\)00023-0](https://doi.org/10.1016/S0924-2244(99)00023-0)
21. OMME Cegléd. (2017). A Méz története. Retrieved October 16, 2017, from <http://ommecegléd.hu/mez/>
22. Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M., & Rice-Evans, C. (1999). Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radical Biology and Medicine*, 26(9-10), 1231-1237. [https://doi.org/10.1016/S0891-5849\(98\)00315-3](https://doi.org/10.1016/S0891-5849(98)00315-3)
23. Tosi, E. A., Ré, E., Lucero, H., & Bulacio, L. (2004). Effect of honey high-temperature shorttime heating on parameters related to quality, crystallisation phenomena and fungal inhibition. *LWT - Food Science and Technology*, 37(6), 669-678. <https://doi.org/10.1016/j.lwt.2004.02.005>
24. Tosi, E., Martinet, R., Ortega, M., Lucero, H., & Ré, E. (2008). Honey diastase activity modified by heating. *Food Chemistry*, 106(3), 883-887. <https://doi.org/10.1016/j.foodchem.2007.04.025>
25. Turkmen, N., Sari, F., Poyrazoglu, E. S., & Velioglu, Y. S. (2006). Effects of prolonged heating on antioxidant activity and colour of honey. *Food Chemistry*, 95(4), 653-657. <https://doi.org/10.1016/j.foodchem.2005.02.004>
26. Zábrowská, B., & Vorlová, L. (2014). Adulteration of honey and available methods for detection - a review. *Acta Veterinaria Brno*, 83(10), S85-S102. <https://doi.org/10.2754/avb201483S10S85>