



Faculty of Food Science

THESES OF THE DOCTORAL DISSERTATION

**Development of the controlled atmosphere
storage technology of apricot**

Géza Hitka

**Corvinus University of Budapest,
Faculty of Food Science,
Department of Postharvest Science and Technology**

**Budapest
2011**

PhD School / Program

Name: PhD School of Food Science

Field: Food Science

Head: Prof. Péter Fodor, D.Sc.
Corvinus University of Budapest

Supervisor: Associate Prof. Csaba Balla, Ph.D.
Department of Refrigeration and
Livestock Products' Technology
Faculty of Food Science
Corvinus University of Budapest

The applicant met the requirement of the PhD regulations of the Corvinus University of Budapest and the thesis is accepted for the defence process.

.....
Signature of Head of School

.....
Signature of Supervisor

1. Background and aims of the work

In order to make apricot a successful fruit of the Hungarian fruit-growing sector, it is essential to re-define the quality and develop the sequential systems of production, storage, processing and sales. This essentially requires wide range collaboration between the sector-participants and the researchers of horticulture, food science and commercial disciplines. New ideas, professionally cared and designed plantations created at the best growing lands, modern harvest- and storage technologies and coordinated marketing concepts are needed to exploit the capabilities of our country and to export marketable commodity in the global fruit market.

In my Ph.D. work, a section of the above mentioned complex development concept, and the postharvest and storage possibilities of apricot were studied with the aim of a good quality product and thus a longer marketing period (season). Harvest time of apricot allows to take advantage of the controlled-atmosphere storage capacity built up for apple. The current domestic practice did not use these storehouses for other fruits, but considering the economic aspects they might be worth to use. With the modern and prevailing controlled-atmosphere storage we could preserve the quality of the Hungarian apricot for a longer term, but the application of this technology requires great caution and care, since a wrong gas composition or temperature setting may result in complete spoilage of fruits.

The main aim of the PhD work was to investigate the biological activity of apricot, the effect and kinetics of low oxygen storage conditions. Research tasks:

1. Application of non-destructive investigation methods for determination of apricot ripening.
2. Analysis of the respiration kinetics of apricot. Develop a testing method and to construct a measuring system for the detection of the respiratory process. Investigation of temperature and gas concentration (O_2 , CO_2) dependence of respiration.
3. Method development for the determination of optimal gas content during controlled atmosphere storage of apricot.
4. Method development for the detection of components present in the gas atmosphere of apricot which indicate the quality.
5. Making storage experiments with apricots under normal and controlled atmosphere storage conditions.

2. Materials and methods

In my doctoral work 'Ceglédi bíborkajszi', 'Gönci Magyar kajszi' and 'Pannónia' apricot cultivars were investigated which came from Pomáz, Hungary. I picked the fruits myself to ensure the highest homogeneity of the sample set.

Based on visual judgement (coloration) apricot fruits were ranked into three groups according to their ripeness: 1 – unripe (ripeness less than 75%); 2 – ripe for storage (80-85% ripe); 3 – table ripe (above 95% ripeness). In the color measurements the greenest point of the ground color and the reddest point of the skin color were chosen. Color measurements were carried out by a Minolta CR-200 type (Minolta Co., JPN) tristimulus chroma meter. SMS TA.XTPlus texture analyzer (Stable Micro Systems Ltd., GBR) was used for the non-destructive texture measurements and the so called mechanical hysteresis was measured. Acoustic and impact texture analyses were performed by AFS texture analyzer (JT28-01-09, AWETA BV., NED), while NIR spectra of fruits were recorded in the 700-1700 nm wavelength range in 2 nm steps by a MetriNIR 1017 PR type instrument (MetriNIR Kutató, Fejlesztő és Szolgáltató Kft., HUN).

A 2-chamber open system respirometer which could be transformed to a closed one as well, fitted with high sensitivity (0-9999ppm) infrared CO₂ sensors (ALMEMO 3290, Ahlborn Mess- und Regelungstechnik GmbH., GER) was used for the analysis of the respiration kinetics of apricot. Temperature and oxygen concentration dependence of respiration were examined.

Photosynthetic activity was measured by a portable, pulse-amplitude modulated (PAM) Plant Efficiency Analyser (PEA) fluorescence detector (FMS-2, Hansatech Ltd., GBR), while for the determination of lower oxygen limit Moni-PAM (Heinz Walz GmbH, GER.) chlorophyll fluorometer was used.

For the determination of the lower oxygen limit solid phase microextraction (SPME) sampling was involved to detect the volatile compounds resulting from the anaerobic respiration of apricot at low oxygen level. Perichrom 2100 type gas chromatograph (Perichrom, FRA) was used for the measurements and a DB-WAX type column (SGE Analytical Science Pty Ltd., USA) was used for the separation. The SPME fiber was a PDMS-DVB copolymer with 65 µm film thickness (Supelco Inc., USA).

Stock-solution and dilution series were prepared by sterile physiological saline for microbiological examinations. Mesophilic aerobic cell count was determined on Nutrient agar by streak plate method. Yeast and mould counts were determined on DRBC (dichloran rose

bengal chloramphenicol) agar also by streak plate method. For the detection of volatile compounds developing during microbiological spoilage processes gas chromatography coupled with mass spectrometric identification and SPME sampling (SPME-GC-MS) was chosen. PR2100 type gas chromatograph (Perichrom, FRA), Agilent 5975 B VL type mass spectrometer (Agilent Technologies Inc., USA) and for the separation BPX5 column (SGE Analytical Science Pty Ltd., USA) were used in the measurements. The SPME fiber was again a PDMS-DVB copolymer with 65 µm film thickness (Supelco Inc., USA).

Normal and controlled-atmosphere storage experiments on fruits were also carried out based on the information obtained during preliminary experiments. Effects of increased carbon dioxide levels and reduced oxygen levels were examined by instrumental (weight loss, respiration, firmness, shelf-life tests) and sensory tests during storage.

3. Results

Mathematical and statistical models have been made from the results of the color measurements, the acoustic and impact test and the precision texture analysis to discern the different stages of apricot ripeness. With the application of the near-infrared spectroscopy and using the canonical discriminant analysis method I created a model to identify the cultivar and determine the ripeness of apricots.

I determined that the respiration of the investigated apricot cultivars had exponential relationship with the temperature and determined the activation energy requirements of each cultivar by the Arrhenius kinetic equation based on statistical thermodynamic representation of the $\ln(LI) - 1/T$ slope of linear fit.

For determining the lower oxygen limit the testing method of fruit photosynthetic activity, the determination of anaerobic metabolites over the fruit airspace by application of GC, and the measurement method for the respiratory effects of oxygen concentration were developed. I found and proved that the lower oxygen limit of 'Ceglédi bíborkajszi', the 'Gönci magyar kajszi' and the 'Pannonia' apricot cultivars was between 1.1 and 1.2 vol% oxygen concentration.

I found that the air space above the micro-biologically contaminated apricot has different volatile compounds like over the intact, uninfected apricots. Clearly identified the compounds, which characterized the microbiologically contaminated apricots.

Fruits showed an increased tendency of internal flesh browning when 8 vol% CO₂ concentration was used during storage therefore it should be avoided. Application of

extremely low oxygen concentrations (0.9 vol%) can be unfavorable for the taste and smell of the fruit by the accumulation of anaerobic metabolites. Results of the instrumental and sensory tests have proved that the investigated apricot cultivars could keep good quality for 28 days in controlled atmosphere with 1.2% O₂ and 4% CO₂ concentrations, 1°C temperature and 95% relative humidity.

4. New scientific results

1. Mathematical statistical models were created by near infrared spectroscopy (NIR) for the identification and species-independent determination of ripeness stage of 'Ceglédi bíborkajszi', 'Gönci Magyar kajszi' and 'Pannónia' apricot cultivars.
2. Temperature dependence of respiration intensity of 'Ceglédi bíborkajszi', 'Gönci Magyar kajszi' and 'Pannónia' apricot cultivars was determined. I proved that respiration changes exponentially with temperature and I determined the activation energy requirement of each cultivar.
3. Methods were developed for the determination of the lower oxygen limit of apricot by applying respiration intensity measurement, chlorophyll fluorescence measurement technique and gas chromatography combined with solid phase microextraction (SPME) sampling.
4. I determined and proved that the lower oxygen limit of 'Ceglédi bíborkajszi', 'Gönci Magyar kajszi' and 'Pannónia' cultivars is at 1,1-1,2 vol% oxygen level.
5. I determined that storage of 'Ceglédi bíborkajszi', 'Gönci magyar kajszi' and 'Pannónia' apricot cultivars in an atmosphere with 1.2vol% O₂ and 4vol% CO₂ concentrations, at 1°C temperature and 95% relative humidity does not cause any detrimental physiological changes. Results of instrumental and sensory tests proved that the produce could keep good quality for 28 days by the suggested controlled atmosphere storage technology.

5. Conclusions and suggestions

A basic condition of apricot storage is the proper ripeness of the fruit. Its determination is done typically by visual judgement. In the course of my investigations I created a multivariate mathematical statistical model by the use of non-destructive test methods that affords possibility to sort out apricot fruits on a sorting line based on their ripeness. Beside ripeness, selection of the investigated cultivars could be attained by the use of near infrared (NIR) spectroscopy. I think it's worthy to test the adaptability of this method on other cultivars as well and further refine the model.

I could develop three different measurement methods for the determination of lower oxygen limit of apricot. Possibility of the measurement of oxygen dependence of respiration intensity and the use of gas chromatography provide new opportunities to determine the optimal gas composition, however, precise measurement of the lower oxygen limit is time-consuming, can be less automated, and results can be obtained only by indirect measurements. Whereas chlorophyll fluorescence measurement technique is rapid, can be well automated, requires only slight control, reaction of the fruit is immediate that makes precise determination of the lower oxygen limit possible. Measurement of photosynthetic activity permits us to intervene in conformity with the physiological state of fruits during controlled atmosphere storage (dynamic control) when the instrument and the method is integrated into the monitoring system of storage and control of oxygen limit is related to the change in F_0 basic fluorescence value. Amount of acetaldehyde and ethanol produced during anaerobic respiration and measured in the airspace around fruits is a good indicator value. It might be worth to use a target instrument for the detection of these two compounds since its investment costs are much lower and requires less technical skills than the nowadays still expensive gas chromatography. Such an ethanol/acetaldehyde sensor might be suitable for the optimization of gas composition during controlled atmosphere storage. I intend to test the three methods with other fruit and vegetable species and to develop their practical use.

Optimal gas composition of the controlled atmosphere storage technique was determined up to now mostly based on positive empirical research results. Determination of lower oxygen limit provided possibility for longer preservation of quality, however, some physiological changes (e.g. flesh browning) occur even in spite of the optimization of oxygen concentration. Thus empirical research is still justified. More thorough knowledge of biochemical and physiological changes taking place in fruits during storage and their non-destructive monitoring and early detection of undesirable processes determine my research work and the future direction of this area of science.

6. Publications related to the thesis

Publications in journals:

IF publications:

Kantor D. B., **Hitka G.**, Fekete A., Balla Cs. (2008): Electronic Tongue for Sensing Taste Changes with Apricots during Storage. *Sensors and Actuators B: Chemical*, 131 pp. 43–47 (IF:2,331)

Non IF publications:

Hitka G., Balla Cs. (2010): Új vizsgálati módszerek kajszifajták oxigénküszöb értékének meghatározására. *Élelmiszer Tudomány Technológia LXIV. évf. 1. Különszám* pp.27-28.

Hitka G., Balla Cs.(2010): Kajszai szabályozott légterű tárolási technológiájának fejlesztése. *Értékálló aranykorona, Országos Mezőgazdasági Szaklap*, 10 (8), pp. 15-16.

Balla Cs., **Hitka G.** (2009): Élelmiszertudományi Kutatások a Corvinus Egyetemen – A szabályozott légterű hűtőtárolás új vizsgálati módszere. *Gazdasági Tükörcső Magazin*. 2009/5. p 40

Books, textbooks, chapters:

Balla Cs., **Hitka G.**, Horti K., Dalmadi I., Polyákné Fehér K., Árva J., Apali Szabó J., Csukáné Nemes M., Jónás G., Pásztorné Huszár K., (2008): Az alma és a kajszai környezet kémiai természetének, szüret utáni kezelésének és feldolgozásának fejlesztése a hevesi térségben. In: Tóth Magdolna (szerk): *Kajszai és alma szabályozott légterű tárolási technológiájának fejlesztése*. Magyar Mezőgazdaság Kft., Budapest. 37-42. o. ISBN 978-963-06-6487-5

Publications in conference proceedings:

Hitka G., Balla Cs., Gyepes A. (2009): Early detection of storage disorders of apricots and japanese plums. *Environmentally Friendly and Safe Technologies for Quality of Fruits and Vegetables*. COST 924 action, Portugal, Faro, 14-16 January 2009. Book of abstract, p. 43

Hitka G., Balla Cs., Csobanczi A., Saska T., (2008): Determination the lower oxygen limit of 'granny smith' apples by application of solid phase microextraction. *CIGR - International Conference of Agricultural Engineering. XXXVII Congresso Brasileiro de Engenharia Agrícola*. Brazil, August 31 to September 4, 2008, Conference CD: ISSN 1982-3797

Hitka G., Balla Cs., Csobanczi A., Saska T. (2008): New methods to determine the level of low oxygen limit. *Postharvest Unlimited 2008, COST 924 action*, Germany, Berlin, 4-7. November 2008. Book of Abstract, *Bornimer Agartechnische Berichte*, Heft 64, Potsdam-Bornim (ISSN 0947-7314) p. 152

Hitka G., Balla Cs. Fodor P., Gyepes A. (2008): Studying postharvest processes in fruits by application of solid phase microextraction (SPME) *The 2008 Joint Central European Congress, 4th Central European Congress on Food 6th Croatian Congress of Food Technologist, Biotechnologists, and Nutritionists*, Cavtat, Croatia, 14-17. May. 2008, Book of Abstract, p. 98.

Hitka G., Balla Cs. (2007): Klorofil fluoreszcencia változásának vizsgálata oxigénküszöb meghatározása céljából. (Investigation of changes in chlorophyll fluorescence in order to determinate the level of low oxygen limit) *Lippay János - Ormos Imre - Vas Károly Tudományos Ülésszak*, Budapest, 2007.11. 7-8. pp. 262-263

Balla Cs. **Hitka G.**, Fodor P., Gyepes A. (2007): Szilárd fázisú mikroextrakciós eljárás (SPME) alkalmazása gyümölcsök posztharvest folyamatainak tanulmányozására (Application of solid phase microextraction (SPME) for studying postharvest process in fruits) *Lippay János - Ormos Imre – Vas Károly Tudományos Ülésszak*, Budapest, 2007. november 7-8. pp. 264-265

Citations (without self-citations):

- Oliveri, P., Casolino, M.C., Forina, M. (2010): Chemometric Brains for Artificial Tongues. In *Advances in Food and Nutrition Research*. Academic Press ISSN: 10434526 Vol. 61 pp. 57-117.
- del Valle, M. (2010): Electronic tongues employing electrochemical sensors. *Electroanalysis* 22, (14): 1539-1555,
- Gutiérrez, J. M., L. Moreno-Barón, M. I. Pividori, S. Alegret, and M. del Valle. (2010): A voltammetric electronic tongue made of modified epoxy-graphite electrodes for the qualitative analysis of wine. *Microchimica Acta* 169, (3): 261-268,
- Escuder-Gilabert, L. & Peris, M. (2010): "Review: Highlights in recent applications of electronic tongues in food analysis", *Analytica Chimica Acta*, vol. 665, no. 1, pp. 15-25.
- Javanmard, M., F. Garousi. (2009): Shelf-life of whey protein concentrate-gellan coated apricots (*prunus armeniaca* L.). 5th International Technical Symposium on Food Processing, Monitoring Technology in Bioprocesses and Food Quality Management: 1250-1262,
- Gatti, E., B. G. Defilippi, S. Predieri, and R. Infante. (2009): Apricot (*prunus armeniaca* L.) quality and breeding perspectives. *Journal of Food, Agriculture and Environment* 7, (3-4): 573-580,
- Ali Batu (2009): Storage Suggestion of Apricot In Modified Atmosphere Packaging. *Electronic Journal of Food Technologies* Vol: 4, No: 1, pp. 9-19