

COMMODITY SCIENCE IN RESEARCH AND PRACTICE

FOOD PRODUCTS' QUALITY



EDITED BY MAŁGORZATA MIŚNIAKIEWICZ & STANISŁAW POPEK

**COMMODITY SCIENCE
IN RESEARCH AND PRACTICE**

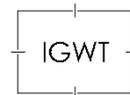
FOOD PRODUCTS' QUALITY

**Edited by
Małgorzata Miśniakiewicz, Stanisław Popek**

**Polish Society
of Commodity Science**



**International Society
of Commodity Science and Technology**



**Faculty of Commodity Science
Cracow University of Economics**



Editors: Małgorzata Miśniakiewicz, Stanisław Popek

All published papers have been reviewed before publishing

Reviewers of Commodity Science in Research and Practice series:

Jadwiga Adamczyk, Waclaw Adamczyk, Andrzej Chochół,
Agnieszka Cholewa-Wójcik, Joanna Dziadkowiec, Tadeusz Fijał, Dariusz Firszt,
Andrzej Gajewski, Marta Gollinger-Tarajko, Łukasz Jabłoński, Piotr Kafel,
Agnieszka Kawecka, Małgorzata Lisińska-Kuśnierz, Małgorzata Miśniakiewicz,
Paweł Nowicki, Stanisław Popek, Anna Prusak, Joanna Ptasińska-Marcinkiewicz,
Renata Salerno-Kochan, Grzegorz Suwała, Jerzy Szakiel, Jarosław Świda,
Paweł Turek

The monograph has not been amended or proofread and editors are not responsible for the language used by chapter's Authors (in chapters).

Suggested citation:

Author A., 2014, Title of the paper, in: M. Miśniakiewicz, S. Popek (eds.)
Commodity Science in Research and Practice – Food products' quality, Polish
Society of Commodity Science, Cracow, pp. xx-xx. ISBN: 978-83-938909-3-4

© Copyright by Polish Society of Commodity Science, Cracow University
of Economics, Cracow 2014

ISBN 978-83-938909-3-4 (printed version)

ISBN 978-83-938909-7-2 (html)

Year of publishing: 2014

Number of pages: 184

Publisher

Polish Society of Commodity Science
Sienkiewicza 4, 30-033 Cracow, Poland

Contents

Foreword	5
Ludmila Eliseeva, Irina Makhotina, Petr Gorozhanin INDUCED AUTOLYSIS AS A WAY TO IMPROVE THE QUALITY OF LUPINE PROTEIN PREPARATIONS	7
Bożena Garbowska, Monika Radzymińska, Dominika Jakubowska FACTORS AFFECTING SELECTED WHEY PROTEINS CONTENT IN UHT MILK	13
Justyna Głaz, Władysław Kędzior THE QUALITY OF TRADITIONAL AND CONVENTIONAL MEAT PRODUCTS	25
Michał Halagarda THE QUALITY OF CONVENIENCE FOODS ON THE EXAMPLE OF SOUP CONCENTRATES AVAILABLE ON THE POLISH MARKET ...	35
Władysław Kędzior, Aleksandra Zuba – Wróbel THE QUALITY OF NATURAL YOGHURTS	47
Vladimir Kiselev, Tatyana Kiseleva, Elena Bastron, Ragima Kerimova FACTOR ANALYSIS OF CUSTOMER VALUE SPIRITS.....	57
Vladimir Kiselev, Elena Zubareva, Tatyana Ponkratjeva QUALIMETRIC APPROACH TO OPTIMIZING CONSUMER CHOICE OF SPIRITS	69
Elżbieta Kondratowicz-Pietruszka ASSESSMENT OF OXIDATIVE STABILITY OF RAPESEED AND SUNFLOWER OILS.....	77
Jolanta Król, Anna Litwińczuk, Monika Kędzierska-Matysek, Aneta Brodziak QUALITY EVALUATION OF ACID CURD CHEESES (TVAROGS) AVAILABLE ON LUBLIN MARKET.....	91
Ewa Marjańska, Maria Szpakowska INVESTIGATION OF SWEET SUBSTANCES OF DIFFERENT MOLECULAR STRUCTURE BY POTENTIOMETRIC TASTE SENSOR WITH ALL SOLID STATE ELECTRODES.....	103
Lidia Ostasz CHANGES IN PHYSOCOCHEMICAL PARAMETERS OF ARGAN OIL DURING MICROWAVE HEATING.....	115
Agnieszka Palka EVALUATION OF CHANGES IN MELTING AND OVERRUN OF FAMILY ICE CREAM DURING LONG-TERM STORAGE	127

Monika Radzymińska, Bożena Garbowska, Dominika Jakubowska, Ewa Siemianowska	
MINERAL CONTENT IN TRADITIONAL AND CONVECTIONAL PORK MEAT AND PRODUCTS	137
Anna Sylwia Tarczyńska	
PERCEPTION OF PORK QUALITY BY STUDENTS.....	149
Elwira Tymoszuć, Maria Szpakowska	
INVESTIGATION OF ACIDIC SOLUTIONS BY POTENTIOMETRIC TASTE SENSOR WITH ALL SOLID STATE ELECTRODES	161
Aleksandra Wilczyńska, Piotr Przybyłowski	
INFLUENCE OF EXTREME HEATING ON COLOUR AND ANTIOXIDANT ACTIVITY OF DIFFERENT TYPES OF HONEY..	173

„...only high quality is worthy of homo sapiens, it is the measure of human dignity and should be the source of success for those who achieve it.”

Tadeusz Kotarbiński

An increasingly growing globalization process and intense market competition cause that the quality becomes more and more significant issue in all areas of life. The quality of food is one of non-price competition components. It became, along with innovativeness, the most important factor influencing the demand. In addition, with technological progress more and more attention has been focused on the quality in the entire food chain (from suppliers to consumers, the final food chain link).

The quality of food products covers an extremely large area containing its various properties – chemical, physical, biological, microbiological, utility and any other features deciding on the extent to which the consumer’s needs and expectations are met. Commodity science as the science of quality being faced with the current economic situation is predisposed to propagate this idea in many areas of economic life.

Monograph entitled **“Food Products’ Quality”** is a part of “Commodity Science in Research and Practice” series. It is aimed at the presentation of commodity science achievements within the scope of widely understood the problem of food quality.

Monograph contains 16 chapters written by the Authors being scientists from the European commodity science centres.

In particular monograph chapters the Authors deal with problems related both to the quality and its determinants pertaining to food of plant or animal origin as well as consumer’s criteria for food quality assessment.

The monograph is published to present the capacity of commodity science to create the quality of food products and can be a valuable source of knowledge for practitioners and theorists of economic life as well as economics students.

*Małgorzata Miśniakiewicz
Stanisław Poppek*

INDUCED AUTOLYSIS AS A WAY TO IMPROVE THE QUALITY OF LUPINE PROTEIN PREPARATIONS

Ludmila Eliseeva, Irina Makhotina, Petr Gorozhanin

*Plekhanov Russian University of Economics,
eliseeva@rambler.ru*

Introduction

All countries of the world consider human needs in a safe and adequate nutrition as one of most important international and national problems. Forecasts of modern scientists show that in the coming decades the problem of lack of food and its quality will rank first in the world. Currently, more than half of the world's population feels a shortage of food protein in their nutrition. World production of animal protein is four times less than the demand or it. The total deficit of protein on the earth is 10-25 million tons a year.

In the nutritional status of the population in Russia the proportion of plant proteins is increasing, most of which has unbalanced amino acid composition (such as grains, potatoes, vegetables). The important direction in solving this problem is the development and application of modern biotechnology production of new sources of vegetable protein with the most balanced amino acid composition.

The best way to solve the problem is to construct a protein deficient food by protein enrichment of traditional foods with herbal components; this path includes the main features of traditional and new ways of producing food protein (Hall, Johnson, Baxter, Ball 2005).

Vegetable proteins are characterized by high biological value, good digestibility, unique functional properties and the ability to use traditional and new processes with giving semi-finished and finished products of high consumer qualities. Seeds of legumes (soybeans, peas, beans, lupins, lentils, vetch, chickpeas, grass, peanuts, etc.) play an important role in decreasing of the protein deficit. According to the nutritional value and chemical composition these proteins are the closest to the sources of animal protein - meat, fish, milk. Legumes have high nutritional qualities due to the ability to accumulate and retain several times more high quality protein than other types of plants (Turnbull, Baxter, Johnson 2005).

Typically, legumes contain 20-30% protein. Legume proteins have better balance of essential amino acids, as compared with cereal proteins.

Soya beans are the main source of vegetable protein in the world. They have a monopoly position in the world as a raw material for the production of protein products.

Besides the low cost and high nutritional value, close to the proteins of animal origin, soya protein has a high functional properties, which allows to consider it as a reference standard in the study of new plant proteins, and also facilitates and reduces the cost of its processing in the production of composite food products (Braudo, Danilenko 2001).

Nevertheless, soya has a number of disadvantages - the content of anti-nutritional substances such as protease inhibitors, haemagglutinin, etc.

Lupine is on the second place after the soya by the content and the ability to accumulate protein. The prospect of lupine seeds as raw material for food industry is determined, first of all, by chemical composition and biological value. Table 1 shows the chemical composition of different grades of lupine.

Table 1. Chemical composition of different varieties of lupine

Varieties of lupine	Content, %						
	water	protein	lipid	cellulose	ash	nitrogen-free extractives	alkaloids
Lupinus albus	9.6	43.4	11.3	7.2	3.4	25.1	0.029
Lupinus luteus	10.4	41.1	5.7	10.3	4.7	27.8	0.10
Lupinus angustifolius	9.9	36.6	5.8	9.9	3.6	33.9	0.34

Source: Charles, 1986

The carbohydrate content in the lupine seeds varies slightly. Dietary fibers are mainly contained in the shell of the seed, kernel number is not greater than 1%.

The hallmark of lupine flour is the complete absence of prolamins (alcohol-soluble proteins), including gliadin and gluten, which is especially important for people with digestive disorders caused by celiac disease (no ability to digest gluten and gliadin component) (Catassi, Fanciulli, 2001). Lupine may be a raw material for creating ungluten foods in the form of cookies, cakes, etc.(Charles, 1986).

Modern technology of protein isolates allows to achieve the maximum fractionation feedstock, to inactivate or remove antinutritive factors, depersonalized negative organoleptic characteristics (taste and smell of raw beans). This allows the direct use of vegetable protein isolate in food production.

However, the principle of maximum fractionation of plant protein has several negative consequences. In the process of deep fractionation many biologically active components are lost and biological value of the isolates reduces.

We have suggested that the method of induced autolysis of vegetable protein preparations can achieve better results than limited enzymatic hydrolysis, proteolytic enzymes of own raw materials will be involved and the processes occurring during germination can be reproduced.

Induced autolysis is the method of processing of agricultural or microbial raw materials under its own hydrolytic enzymes (hydrolases), whose activity is initiated by an external inductor. The essence of the method is the initiation of the enzyme system "working" during germination, imitating the action of key endogenous enzyme synthesized de novo in the beginning of germination.

Using the method of induced autolysis meets the needs of modern food biotechnology in the best way. First, this is due to the fact that the raw material which is used is not fractionated, it means that it contains all the original biologically active components. Secondly, there is a decrease in the content of anti-nutritional factors and to improve the functional properties of flour. This technology is waste-free and profitable from an economic and environmental points of view.

Material and methods

We used the lupine flour variety "Crystal". Protein, fat and carbohydrates were determined by standard methods.

Results and discussion

The flour was suspended in water (1:5). This provides the desired viscosity, which allows to perform all the technological manipulations with the suspension, on the other hand, the ratio of lupine flour and water is the lowest possible and requires less time and energy for drying the final product.

Chicken pepsin was selected as an acid protease (endoenzymes), since, according to some researchers (Papastoitsis G., Wilson K., 1991) the germination begins with the action of acid proteases, which include pepsin.

After sample preparation, the proteolysis was carried out within 60 minutes. Optimum pH was determined by the increase in free amino groups. Most active chicken pepsin was observed in the range of pH 2,5-4,0. As the optimum the value of pH 4.0 was chosen.

The next step was to determine the duration of the hydrolysis of proteins, in order to identify the time interval after which the process of proteolysis of this raw material slows or stops. At this point it was necessary to inactivate the enzyme, in order to enable its own enzymes to activate the process of raw autolysis.

Hydrolysis of lupine flour was conducted for 5 hours, periodically (every 30 minutes) taking samples. For the duration of hydrolysis and the degree of

influence of the ratio enzyme / substrate of the process of hydrolysis was monitored by the increase in free amino groups in the samples.

Therefore, the most complete research objective corresponds to the ratio E / S equal to 1/50, where the rate exceeds the rate of proteolysis in the ratio of 1/100, recommended by several authors (Fontana, Polverino, 1999, 2004) to work with isolates and concentrates.

The data on the growth of free amino groups during five hours hydrolysis allow to say that the most optimal duration of hydrolysis, irrespective of the ratio enzyme / substrate, is 180 minutes. Further hydrolysis does not lead to a significant change in the concentration of amino groups, so it is advisable to limit the duration of proteolysis to 3 hours.

We establish the following optimal conditions for limited proteolysis of lupine flour: 1. Ratio of lupine flour: water - 1:5; 2. For the implementation of proteolysis, it was recommended to use chicken pepsin; 3. pH for the most intensive process of proteolysis is 4.0; 4. Duration of limited proteolysis is three hours; 5. Ratio enzyme: substrate in the reaction medium should be 1:50.

According to the literature, for the process of autolysis was selected room temperature, which is within 72 hours autolysis maintained constant at 22 ± 1 °C.

Choice of pH was based on the optimum enzyme action. At a pH of 7.0 chicken pepsin stops working, so it is possible to eliminate its influence on the processes occurring in the slurry of flour lupine seeds.

The growth of TCA-soluble peptides, characterizing the dynamics of protein hydrolysis, showed that it was not only due to the action of chicken pepsin, because at pH 7,0 introduced enzyme was inactivated. These data suggest that the lupine flour hydrolytic protein changes occur not only by the action of exogenous acid protease, but by activating of the endogenous lupine seed flour enzyme (Shutov, Vaintraub, 1987).

In order to characterize the change in protein content induced autolysis process and compare them with the data obtained from germination, we determine protein concentration.

Determination of protein was carried out before autolysis and at 24, 48 and 72 hours autolysis. In parallel with the experience of control implemented similar experience, but without making the suspension of lupine flour chicken pepsin.

The data obtained allow to ascertain a higher rate of hydrolysis of protein in the samples experience, as compared to the control.

The lupine seed flour contains an average of 4 % oligosaccharides, which reduces their nutritional value and digestibility, and therefore our task was to determine how the process of the induced autolysis will affect on the contents of this group of carbohydrates. Therefore, the process of changing of the

content of reducing sugar, which concerns the α - galactosides, was used to compare the germination process and induced autolysis .

Changes taking place with oligosaccharides during induced autolysis, we judged by the dynamics of the formation of reducing sugars in the flour lupine. In parallel with the experience of control implemented similar experience, but without making the suspension of lupine flour chicken pepsin.

In the first phase of induced autolysis (proteolysis) the change in absorbance of solutions containing reducing sugars was equal to 0, i.e. samples and control experience and the same values were obtained by optical density. This is due to the fact that an endogenous enzyme, we used was chicken pepsin, which leads to hydrolysis of proteins, but does not affect carbohydrate and exoenzymes lupine bean flour in the first step of induced autolysis.

These data show that the autolysis process is an increase in the optical density of samples experience, as compared to control samples. These results can be interpreted as follows, in the process of autolysis under the action of its own enzymes flour lupine seeds hydrolysis reducing sugar, which resulted in the increase in the content of reducing sugars.

It should also be noted that during induced autolysis changes are setted, i.e. capacity optical density, which indicates the increase in the concentration of the hydrolysis products of sugars that occur after 40 hours of autolysis.

The modification of lupine flour by induced autolysis allows to eliminate the imperfections of taste and aroma (“bean-taste”), due to inactivation of lipoxygenases. It was established that autolysis leads to the hydrolysis of complexes between polypeptides and cellulose, and this causes the liberation of access of digestive enzymes to their substrates. As a result, the degree of protein digestion increases, the partial hydrolysis of reserve globular proteins and polysaccharides occurs, and these processes lead to the increase of functional properties of the flour. Modified lupine flour contains more vitamins of B-group and tocopherols, and the content of antioxidants in it increases more than twice as much. The content of anti-nutritional substances – raffinose polysaccharides and phytates – decreases significantly, and the degree of potential mutagenicity does not increase. All our data obtained allow to establish that consumer properties of modified lupine flour make it a competitive analogue of soybean flour.

Conclusions

On the basis of our data, we can conclude the feasibility of using the process-induced autolysis in order to improve consumer properties of flour lupine seeds. As a result, we propose the following technological scheme of main steps of induced autolysis of lupine seeds' flour:

1. Limited proteolysis of lupine flour by exo-enzyme – chicken pepsin;
2. Neutralization of flour suspension to inactivate the introduced enzyme;
3. Autolysis of lupine flour by endogeneous enzymes;
4. Freeze drying of suspension.

Acknowledgments

We express our heartfelt thanks to Braudo E. (Doctor of science, prof.) and Danilenko A. (Doctor of science, prof.).

References

- Braudo E., Danilenko A., 2001, *Alternative approaches to the manufacture of plant protein products from grain legumes*, *Nahrung/Food*, 6, 405-407.
- Catassi C., Fanciulli G., 2000, *Antiendomysium versus antigliadin antibodies in screening the general population for coeliac disease*, *Am. J. Gastroenterol.*, 95 (7), 732-736.
- Charles W. P., 1986, *The return of the legendary lupin*, *The Saturday evening post*, November, 16-17.
- Fontana A., Polverino de Laureto P., 2004, *Probing protein structure by limited proteolysis*, *Acta Biochimica Polonica*, 51(2), 299–321.
- Fontana A., Polverino de Laureto P., De Filippis V., 1999, *Limited proteolysis in the study of protein conformation*, in: *Proteolytic enzymes: tools and targets* (ed. by Sterchi E., Stocker W.), Springer-Verlag, Berlin, Heidelberg, pp 257–284.
- Hall R., Johnson S., Baxter A., Ball M., 2005, *Lupin kernel fibre-enriched foods beneficially modify serum lipids in men*, *European Journal of Clinical Nutrition*, 59, 325–333.
- Papastoitsis G., Wilson K., 1991, *Initiation of the degradation of the soybean Kunitz and Bowman-Birk trypsin inhibitors by a cysteine protease*, *Plant Physiology*, 96, 1086-1092.
- Shutov A., Vaintraub I., 1987, *Degradation of storage proteins in germinating seeds*, *Phytochemistry*, 26 (6), 557-1566.
- Turnbull C., Baxter A., Johnson S., 2005, *Water-binding capacity and viscosity of Australian sweet lupin kernel fibre under in vitro conditions simulating the human upper gastrointestinal tract*, *International Journal of Food Sciences and Nutrition*, 56(2), 87-94.

FACTORS AFFECTING SELECTED WHEY PROTEINS CONTENT IN UHT MILK

**Bożena Garbowska, Monika Radzymińska,
Dominika Jakubowska**

*Chair of Commodity Science and Food Research, Faculty of Food Sciences,
University of Warmia and Mazury in Olsztyn,
bozena.garbowska@uwm.edu.pl*

Introduction

Milk is a product of a very complex, which consists of about 250 components. The most important of them are fat, protein, lactose and mineral salts (Donato et al. 2007).

Milk protein content ranges from 3.05% to 3.85 %. Milk protein fraction is divided into casein and whey proteins. Assuming proper amount of protein in the milk casein as 100% of 78 %. Besides milk contains casein, whey protein, of which:

- albumin - α -lactalbumin β -lactoglobulin A and B and blood serum albumin,
- globulin : immunoglobulins,
- proteozes and peptones (Fox, Mulvihill, 1982).

Whey protein does not contain phosphorus and are characterized by a high content of sulfur amino acids - methionine and cystine. About 50 % of the whey protein is β -lactoglobulin. Unlike typical albumin is not soluble in water (which is commonly referred pseudoalbumin), while freely soluble in dilute solutions of neutral salts (Farrell, Douglas 1983).

Blood serum albumin and α -lactalbumin, is a typical water-soluble whey proteins. Their characteristic feature is the high content of cystine. Immunoglobulins (proteins immune) account for about 10 % of whey protein. Inflammatory conditions of the udder to significantly increase the content of immunoglobulins in the milk. (Fox, Mulvihill , 1982; Parris, Baginski, 1991 Recio, Olieman, 1996).

Raw milk is a product unstable and therefore it is subjected to heat treatment. The most common method of preservation of the milk is heating UHT in the system, resulting in a product with stability up to six months.

Thermal treatment causes partial denaturation of the milk whey protein, of which the most resistant to the sterilization temperature is α -lactalbumin and most thermo-labile is immunoglobulin and β -lactoglobulin B. However, the treatment temperature is not the only factor affecting content the fraction of whey proteins in the milk subjected to UHT sterilization system. Therefore, the aim of this study was to evaluate the influence of selected factors such as fat content, temperature and storage time on the content of selected non-denatured soluble at a pH of 4,6 – 4,7 whey protein (α -lactalbumin, β -lactoglobulin A and B) in commercial UHT milk.

Material and methods

The experimental materials comprised commercial UHT milk aseptically packaged in 1 liter cartons from the same supplier. Experimental samples were collected from three different batches of UHT milk 0,5% fat content, as declared by the supplier, and from three different batches of milk 3,2% fat content from winter and summer production. The experiment involved analyses of UHT milk immediately after production (no later than a week since production date) and analyses of milk stored at temperatures of 4 ± 2 and $22\pm 2^\circ\text{C}$: after 2, 4 and 6 months of storage.

Whey protein content

The content of the non-denatured soluble at pH 4.6 - 4.7 whey protein : α -lactalbumin, β -lactoglobulin A and B was determined by HPLC (Visser et al. 1991).

Chromatographic separation of the soluble whey proteins after the precipitation of casein thereof isoelectric point was performed by high performance liquid chromatography HPLC liquid chromatograph using a Hewlett Packard 1050 computer coupled to the chromatographic software Chem -Station, version A.00.33. The chromatographic column used was BIO - RAD HI- Pore reversed Phase RP - 304 , length 250 mm, internal diameter 4.6 mm; mobile phase: buffer A: 0.1 % trifluoroacetic acid in deionized water, buffer B: 0.1% trifluoroacetic acid in acetonitrile; mobile phase flow rate of 1 cm³ / min.; temperature separation 40°C; UV spectrophotometric detection system $\lambda = 210$ nm; reverse phase chromatography in the gradient system was used, gradient separation conditions : 0 min . - 80 % A; 1min. - 80% A , 16 min . - 58 % A , 20 min . - 54 % A , 22 min . - 50 % A , 22.5 min . - 0 % A , 30 min . - 80% A , 38 min . - 80% A.

Interpretation of results

Qualitative and quantitative interpretation of the obtained chromatographic separations were carried out by comparing the amount of the

peak α -lactalbumin , β -lactoglobulin A, β - lactoglobulin B and quantitative samples of standard solutions and test their integration designated by taking the concentration of protein in the samples assayed standard. Standard samples were prepared from weighed amounts α -lactalbumin , β -lactoglobulin A, β -lactoglobulin B Sigma.

Acidity (pH)

Measurements of pH were conducted with laboratory pH-meter AD130.

Statistical analysis

The data obtained were statistically analysed with the use of basic statistics. Differences in determined whey protein content between the examined categories (fat content and storage conditions) were marked on the basis of a one-factor variation analysis (ANOVA). The significance of differences was tested at the significance level of 0,05.

Results and discussion

The content of the non-denatured whey protein in milk is a one of the factors characterizing the marks of quality change during heating and storage of the final product. The results of studies on the content of selected fractions non-denatured whey protein and acidity are shown in Figures 1 - 4 and Tables 1 – 3.

In the milk, not heat-treated the greatest concentration of the whey protein fraction occurs β -lactoglobulins (in an amount of 0.30% on average) and to a lower amount of α -lactalbumin (average 0.18%) (Pellegrino, 1994). Based on the survey and the results it can be concluded that in all the tested samples immediately after the milk production in the greatest concentration is present α -lactalbumin fraction (Figures 1 - 4, Table 1). The results show that this fraction is the most resistant to heating, which confirmed the literature data (Fareel, Duglas, 1983; Miralles et al. 2000, 1996 Buffoni et al. 2011).

Table 1 shows the results of studies on the content of α -lactalbumin and β -lactoglobulin A and B in the samples of UHT milk tested immediately after the production derived from winter and the summer period, of a fat content 0,5% and 3,2%. Based on a statistical analysis of the results obtained it can be concluded that the contents of all fractions non-denatured whey protein of UHT milk with a fat content of 0,5% differed significantly from those of the content in 3,2% milk fat. Comparing the concentration of the milk fraction derived from a different production period, had higher contents of all assayed in the milk whey protein derived from winter period of production, but statistically significant differences have only been demonstrated in the case of

the concentration of fraction α -lactalbumin and β -lactoglobulin A in milk containing 0,5% fat (Table 1).

Table 1. The content of selected fractions of the non-denatured whey protein UHT milk immediately after production with 0,5% and 3,2% fat content of derived from winter and summer production period (mean value)

Whey protein	UHT milk from winter production		UHT milk from summer production	
	UHT milk 0,5% fat content	UHT milk 3,2% fat content	UHT milk 0,5% fat content	UHT milk 3,2% fat content
α -lactoalbumin [%]	0,151a	0,111b	0,132c	0,114b
β -lactoglobulin B[%]	0,098a	0,080b	0,092a	0,053b
β -lactoglobulin A[%]	0,122a	0,067b	0,080c	0,066b
sum of fractions [%]	0,371a	0,258b	0,304c	0,233b

Source: results of own research, [Notes: statistically high significant differences between averages marked with the same letters in rows a, b, c ($p \leq 0,05$)]

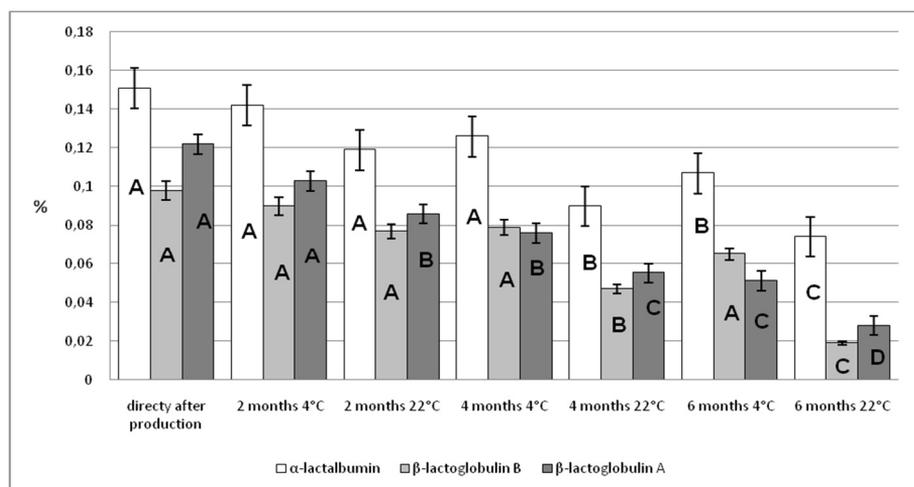
Pellegrino (1994) showed that in UHT milk heated using direct system β -lactoglobulins content was at the level of 0 to 723mg /l, and α -lactalbumin at a level of 0 to 700 mg/l. Research conducted by Lopez - Fandino et al (1993) showed that in the direct system heated UHT milk range of denaturation α -lactalbumin and fraction β -lactoglobulins was similar in milk with a fat content of 1,5% and 3,2%. The average content of α -lactalbumin was at 60,40 mg/100ml level and β -lactoglobulins level 57,60 mg/100 ml (Lopez – Fandino et al. 1993).

The Figures 1 - 4 presents the results of research on the influence of time and storage conditions on the content of the selected fraction of non-denatured whey protein in the tested samples of UHT milk.

Figure 1 presents data on the content of α -lactalbumin and β -lactoglobulin B and A in the commercial UHT milk with a fat content of 0,5% originating from the winter period of production .

On the basis of the study it can be concluded that the storage time and temperature conditions have an influence on the concentration of selected fractions of whey proteins in the test samples of commercial sterilized milk. Storage of samples of the product at refrigeration ($4 \pm 2^\circ\text{C}$) for 6 months resulted in a reduction in α -lactalbumin non-denatured with an initial concentration of 0,151% to 0,107 % on average , while in room temperature ($22 \pm 2^\circ\text{C}$) to 0,074 % on average. While, the concentration of β -lactoglobulin B and A (the initial concentration, respectively 0.098% and 0.122%) in samples of milk after 6 months of storage was reduced accordingly to the

value of 0,065% and 0,051% at $4\pm 2^{\circ}\text{C}$, and 0,019% and 0,028% at $22\pm 2^{\circ}\text{C}$ (Figure 1). Wherein a statistically significant difference was found after four months of storage of samples of the milk at a temperature of $22\pm 2^{\circ}\text{C}$. Only in the case of β -lactoglobulin A significant differences from a statistical point of view, it was found after a two-month period of storage at room temperature (Figure 1).



Notes: statistically high significant differences between averages marked with the same letters in series A, B, C ($p\leq 0,05$)

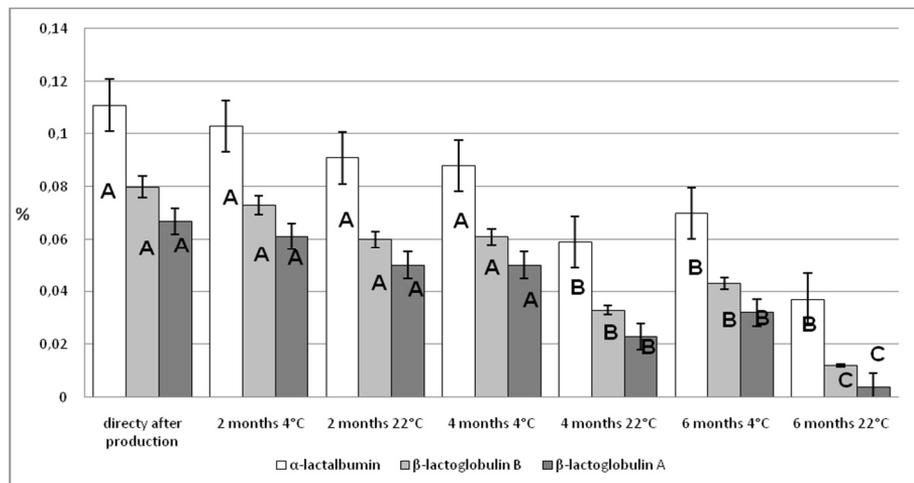
Figure 1. The content of selected fractions of the non-denatured whey protein in UHT milk directly after production and stored at different times and temperatures conditions with a fat content of 0,5% derived from winter production period

Source: results of own research.

The results regarding the effect of time-temperature conditions on the content of the tested fractions in UHT milk derived from the winter production period, of a fat content of 3,2% is shown in Figure 2. In the samples of fresh milk α -lactalbumin amount reached the level an average of 0,111% and β -lactoglobulin B and A respectively 0,080% and 0,067%. Storage of samples of the milk resulted in a lowering of all protein fractions.

It was found that in samples stored at refrigeration conditions ($4 \pm 2^{\circ}\text{C}$) at the end of shelf-life, the concentration of α -lactalbumin and β -lactoglobulin B and A was reduced to 0,070%, respectively, 0,043 and 0,032% on average. However, in the milk samples incubated at $22 \pm 2^{\circ}\text{C}$ number of α -lactalbumin reached an average of 0,037%, β -lactoglobulin B – 0,012%, and β -lactoglobulin and A – 0,004% (Figure 2). On the basis of statistical analysis demonstra-

ted that significant differences in the concentrations of the selected whey protein fraction were in the samples stored at $22 \pm 2^\circ\text{C}$ after four and six months of storage and in samples stored for six months in refrigeration (Figure 2).

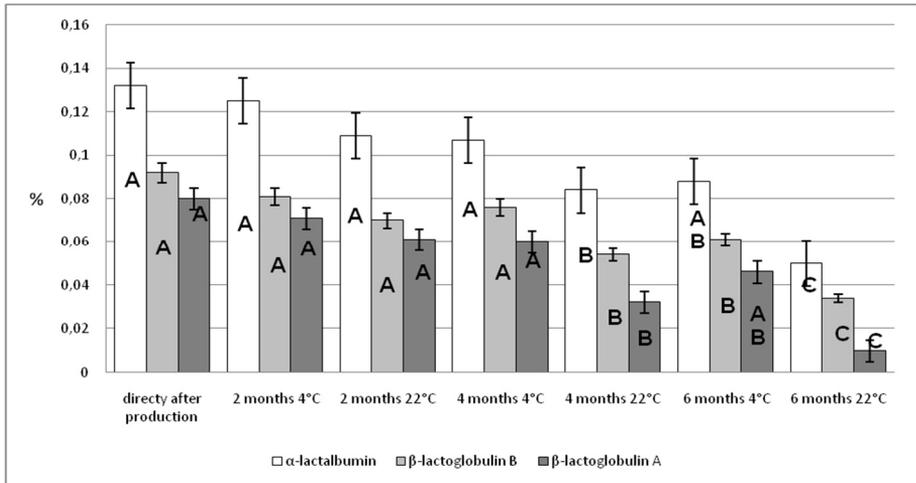


Notes: statistically high significant differences between averages marked with the same letters in series A, B, C ($p \leq 0,05$)

Figure 2. The content of selected fractions of the non-denatured whey protein UHT milk immediately after production and stored at different times and temperatures conditions with a fat content of 3,2% derived from winter production period

Source: results of own research.

Figure 3 presents the results of research on the content of the three fractions of whey proteins in samples of commercial UHT milk with a fat content of 0,5% derived from the summer production period. That milk samples were also stored for six months at various time-temperature conditions. The initial concentration of the analyzed proteins were as follows: 0,132% - α -lactalbumin, 0,092% - β -lactoglobulin B and 0,080% - β -lactoglobulin A (Figure 3). Storage of samples of milk resulted in a decrease the content of studied non-denatured protein fractions. It has been shown that at the end of the shelf life of the samples stored at $4 \pm 2^\circ\text{C}$ and $22 \pm 2^\circ\text{C}$ content of α -lactalbumin stood at, respectively, 0,088% and 0,050%, β -lactoglobulin B: 0,061% and 0,034% and β -lactoglobulin a: 0,046% and 0,010%. Statistical analysis of the results showed that the differences were statistically significant only after the 4-month storage of the samples at a temperature of $22 \pm 2^\circ\text{C}$ (Figure 3).

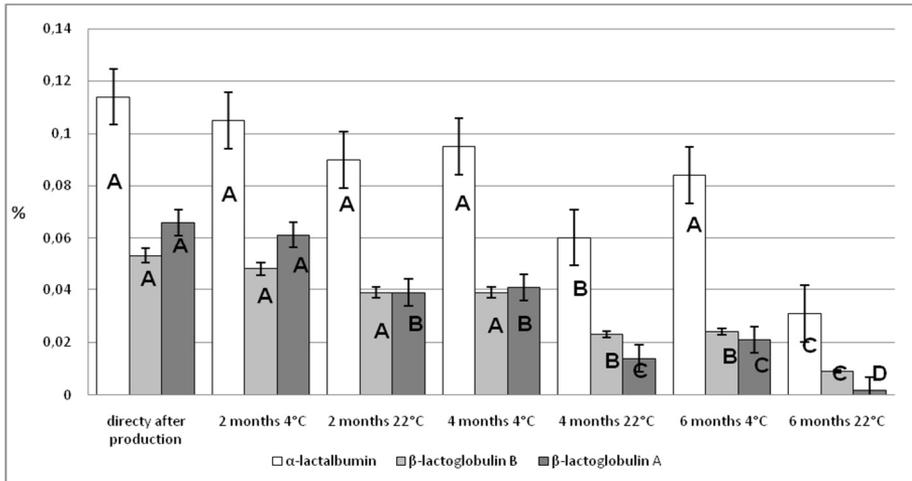


Notes: statistically high significant differences between averages marked with the same letters in series A, B, C ($p \leq 0,05$)

Figure 3. The content of selected fractions of the non-denatured whey protein UHT milk immediately after production and stored at different times and temperatures conditions with a fat content of 0,5% derived from summer production period

Source: results of own research.

On the Figure 4 presented the results of research on the content of selected non-denatured whey protein fraction of UHT milk with a fat content of 3,2% originating the summer production period. In the milk immediately after production α -lactalbumin concentration was on average 0,114%, β -lactoglobulin 0,053%, while β -lactoglobulin A – 0,066%. Storage of samples of milk for six months at $4 \pm 2^\circ\text{C}$ increased the extent of denaturation of tested protein fractions, thereby lowering their content in the product: α -lactalbumin to an average value of 0,084%, β -lactoglobulin B to 0,024%, and a β -lactoglobulin A 0,021%. The milk samples incubated at room temperature ($22 \pm 2^\circ\text{C}$) had a significantly greater decrease in the level of the assayed compounds on average to: α -lactalbumin – 0,031%, β -lactoglobulin B to 0,009%, and β -lactoglobulin A – 0,002% (Figure 4). Statistically significant differences were found for β -lactoglobulin A after two months of storage of the milk samples at room temperature ($22 \pm 2^\circ\text{C}$) and after four months at refrigeration (Figure 4).



Notes: statistically high significant differences between averages marked with the same letters in series A, B, C ($p \leq 0,05$).

Figure 4. The content of selected fractions of the non-denatured whey protein UHT milk immediately after production and stored at different times and temperatures conditions with a fat content of 3,2% derived from summer production period

Source: results of own research.

The loss of selected fractions of the non-denatured whey proteins during six months storage samples of UHT milk are presented in Table 2. On the basis of obtained results it can be concluded, in the case of α -lactalbumin, factor that influencing the significance of differences was only a storage temperature of UHT milk samples. At room temperature the loss of the protein content was significantly higher than in milk stored for the same period at a temperature of refrigeration (Table 2).

Observing the loss content of β -lactoglobulin B and β -lactoglobulin A, it can be concluded that the important factor, in addition to the storage temperature, is also the fat content of milk and the production period. However, on the basis of the results can not clearly determine how these factors determine the loss of analyzed whey protein fractions. Only in the case β -lactoglobulin A in UHT milk the derived from the winter production period can be concluded that the reduction of the protein content was significantly lower in the UHT milk with a fat content of 3.2% (Table 2).

On the relationship between temperature and storage time and the content of non-denatured whey protein also indicate other authors. Renner and Dorguth (1980) showed that the UHT milk whey protein albumin content could be lowered by approximately 36 - 56% depending on storage conditions.

Also Corzo et al. (1994) and Miralles et al. (2000) reported that with the increase of storage temperature of the product increases, the degree of denaturation of whey protein. In a similar direction changes also indicate other authors [Farrel, Douglas, 1983; Leonil i in., 1997; Panfil-Kuncewicz, Kuncewicz, 1997].

Table 2. The loss of selected fractions of the non-denatured whey protein in UHT milk with 0,5% and 3,2% fat content of derived from winter and summer production period after six months of storage in various temperature conditions (mean value)

Whey protein	UHT milk from winter production				UHT milk from summer production			
	UHT milk 0,5% fat content		UHT milk 3,2% fat content		UHT milk 0,5% fat content		UHT milk 3,2% fat content	
	4°C	22°C	4°C	22°C	4°C	22°C	4°C	22°C
α -lactalbumin [%]								
β -lactoglobulin B[%]	0.044a	0.077b	0.041a	0.074b	0.044a	0.082b	0.030a	0.083b
β -lactoglobulin A[%]	0.033a	0.079b	0.037a	0.068b	0.031a	0.058c	0.029a	0.044a
sum of fractions [%]	0.071a	0.094b	0.035c	0.063a	0.034c	0.070a	0.045c	0.064a
	0.148a	0.250b	0.113c	0.205d	0.109c	0.210d	0.104c	0.191d

Notes: statistically high significant differences between averages marked with the same letters in rows a, b, c, d ($p \leq 0,05$)

Source: results of own research.

The reason for decrease in the content of soluble at pH 4.6 – 4.7 of whey proteins during storage of test samples are probably the UHT milk further reactions to varying degrees of denatured whey protein in the process for producing UHT milk casein micelles mainly casein and especially near the obtained the results of non-denatured whey protein content in the analyzed samples of UHT milk can be assumed that the interaction between these proteins and casein micelles proceed further during storage, although no longer operates direct causative agent of these reactions or heating. In a similar direction of the non-denatured whey protein fraction of milk during storage revealed among other Recio et al. (1996). These authors showed that, during the storage of samples of UHT milk undenatured whey protein content decreased, probably due to formation of complexes of α -lactalbumin and β -lactoglobulin from the other constituents of milk. In contrast, Oldfield et al. (1998) and Corredig and Dalgleish (1999) found that these proteins fall within the k-casein complexes can not be excluded their participation in the formation of compounds of proteolysis - although the major lipid protein molecules to react with the fat proteins are casein fractions (Vasbinder, de

Kruif, 2003; Ye et al, 2004; Safon et al. 2014). Lowering of the content of the soluble form of whey proteins during UHT milk storage cannot be limited only can be slow by keeping the final product under refrigeration. These changes do not affect the biological value of the product because the whey proteins do not precipitate from the milk and interact with the casein micelles and remain in the milk.

The results of the active acidity UHT milk samples are shown in Table 3. The average pH of UHT milk samples 0.5% and 3.2% fat content, determined directly after production, was 6,69 and 6,66 (milk from winter period), respectively, and 6,60 and 6,61 (milk from summer period) and it was consistent with Polish Standard (1996) requirements for products of the type. Even after 6 months of storage at a temperature of 22±2°C, changes in the acidity of milk samples were minor. Despite statistically significant differences observed in the mean values of active acidity during the storage of UHT milk, all values determined corresponded to requirements stipulated in the Polish Standard (1996) (Table 3).

Table 3. pH values in UHT milk with 0,5% and 3,2% fat content of derived from winter and summer production period directly after production and after six months of storage in various temperature conditions (mean value)

	UHT milk from winter production				UHT milk from summer production			
	UHT milk 0,5% fat content		UHT milk 3,2% fat content		UHT milk 0,5% fat content		UHT milk 3,2% fat content	
Directly after production	6,69a		6,66a		6,60a		6,61a	
After six months of storage	4°C	22°C	4°C	22°C	4°C	22°C	4°C	22°C
	6.53a	6.31b	6.50a	6.25b	6.51a	6.42b	6.52a	6.46b

Notes: statistically high significant differences between averages marked with the same letters in columns a, b (p≤0,05)

Source: results of own research.

Conclusions

Fat content of UHT milk affect significantly the level of whey protein fractions in product, while the impact of the production period is not unequivocal. It was found that for all samples of UHT milk the content of selected whey proteins fractions is higher in milk from winter production period, but not always, these differences were statistically significant.

Conditions of UHT milk storage exert a significant effect on the extent of denaturation whey proteins fractions. The greatest extent of changes is observed during the storage of UHT milk at a room temperature ($22\pm 2^{\circ}\text{C}$), as compared to the changes proceeding in milk stored at a refrigerating temperature ($4\pm 2^{\circ}\text{C}$).

References

- Buffoni J.N., Bonizzi I., Pauciullo A., Ramunno L., Feligini M., 2011, Characterization of the major whey proteins from milk of Mediterranean water buffalo (*Bubalus bubalis*), *Food Chemistry* 127, 1515 – 1520.
- Corredig, M., Dalgleish D. G., 1999, The mechanisms of the heat-induced interaction of whey proteins with casein micelles in milk, *International Dairy Journal*, 9, 233 – 236.
- Corzo N., Lopez-Fandino R., Delgrado T, Ramos M., Olano A., 1994, Changes in furosine and proteins of UHT-treated milks stored at high ambient temperatures, *Lebensmittel Untersuchung und Forschung*, 198, 302-306.
- Donato L., Guyomarc'h F., Amiot S., Dalgleish DG., 2007, Formation of whey protein/ κ -casein complexes in heated milk: Preferential reaction of whey protein with κ -casein in the casein micelles, *International Dairy Journal*, 17, (10), 1161-1167.
- Farrell H.M., Douglas F.W. 1983, Effect of ultra-high-temperature pasteurization on the functional and nutritional properties of milk proteins, *Milch-wirtschaftliche Forschung* 35, 365 – 56.
- Fox P. F., Mulvihill D.M., 1982, Milk proteins: molecular, colloidal and functional properties, *Journal of Dairy Research*, 49, 679 – 693.
- Leonil, J., Molle D., Fauquant J., Maubois J. L., Pearce R. J., Bouhallab S., 1997, Characterization by ionization mass spectrometry of lactosyl β -lactoglobulin conjugates formed during heat treatment of milk and whey and identification of one lactosebinding site, *Journal of Dairy Science*, 80, 2270 – 2281.
- Lin S., Sun J., Cao D., Cao J., Jiang W., 2010 Distinction of different heat-treated bovine milks by native-PAGE fingerprinting of their whey proteins *Food Chemistry*, 121, (3), 803-808.
- Lopez – Fandino R., Olano A., San Jose C., Ramos M., 1993, Application of reversed-phase HPLC to the study of proteolysis in UHT milk. *Journal of Dairy Research*, 60, 111 – 116.
- Miralles B., Bartolomé B., Amigo L., Ramos M., 2000, Comparison of Three Methods to Determine the Whey Protein to Total Protein Ratio in Milk, *Journal of Dairy Science* 83(12), 2759 – 2765.

Oldfield D.J., Singh H., Taylor M.W., Pearce K.N., 1998, Kinetics of determination and aggregation of whey proteins in skim milk heated in an ultra-high temperature (UHT) pilot plant, *International Dairy Journal*, 8, 311 – 318.

Panfil-Kuncewicz H., Kuncewicz A., 1997, Ocena wybranych wyróżników jakości mleka UHT, *Przegląd Mleczarski* 11, 359 – 364.

Parris N., Baginski M.A., 1991, A rapid method for the determination of whey protein denaturation, *Journal of Dairy Science* 74, 58 – 64.

Pellegrino L., 1994, Influence of fat content on some heat-induced changes in milk and cream, *Netherlands Milk & Dairy Journal* 48, 71 – 80.

Polish Standard PN-A-86003:1996, Milk and dairy products. Drinking milk (in polish).

Recio I., de Frutos M., Olano A., Ramos M., 1996, Protein changes in stored ultra-high-temperature-treated milks studied by capillary electrophoresis and high performance liquid chromatography, *Journal of Agriculture and Food Chemistry*, 44, 3955-3959.

Recio, I., Olieman C., 1996, Determination of denatured serum proteins in the casein fraction of heat-treated milk by capillary electrophoresis, *Electrophoresis* 17, 1228–1233.

Renner E., Dorguth H., 1980, Untersuchungen zur eiweissqualitaet, *Deutsche Milchwirtschaft*, 14, 505-508.

Safon M., Jiménez-Flores R., Britten M., Pouliot Y., 2014 On the use of buttermilk components as aggregation nuclei during the heat-induced denaturation of whey proteins *Journal of Food Engineering*, 132, 21-28.

Vasbinder A.J., de Kruif C.G., 2003, Casein-whey protein interactions in heated milk: the influence of pH, *International Dairy Journal*, 13, 669 – 677.

Visser S., Slangen C., Rollema H., 1991, Phenotyping of bovine milk proteins by Reversed Phase High Performance Liquid Chromatography, *Journal of Chromatography* 548, 361 – 370.

Ye A., Sinhg H., Oldfield D.J., Anema S., 2004, Kinetics of heat-induced association of β -lactoglobulin and α -lactalbumin with milk fat globule membrane in whole milk, *International Dairy Journal*, 14, 389 – 398.

THE QUALITY OF TRADITIONAL AND CONVENTIONAL MEAT PRODUCTS

Justyna Głaz, Władysław Kędzior

*Department of Food Commodity Science,
Cracow University of Economics,
kedziorw@uek.krakow.pl*

Introduction

In recent years, there has been a growing demand for traditional and regional food. The interest in this food is a response to the global production and unification of products. It is conducive to the sustainable development of rural areas and small and medium-sized enterprises. Production, protection and promotion of traditional and regional foods are becoming more popular in the countries of the European Union. National and EU regulations, among others, the Regulation of the European Parliament and of the Council (EU) No 1151/2012 (Regulation 2012) stimulate development of the food market.

The European Union, since the early 90s of the twentieth century, has been supporting omni-directional rural development. It has been trying to create proper conditions for producers, allowing them to compete on world markets. For this purpose, instruments have been developed to help protect manufacturers who produce goods using traditional methods, ensuring their unique organoleptic characteristics (Halagarda, Kędzior and Pyrzyńska, 2013).

Poland has a large possibility of producing traditional and regional products due to its traditional agriculture, family farms, workforce in rural areas, clean environment, and rich and varied cultural heritage. Products whose unique quality or characteristics and properties result from the use of traditional methods of production may be added to the list of traditional products of the Ministry of Agriculture and Rural Development. The products at the same time promote the region and are part of the cultural heritage and increase consumer awareness. Buyers are convinced of their higher nutritional values and better quality, especially the sensory quality of the products manufactured traditionally, often without or with a minor contribution of additional substances (Domaradzki and Florek 2012). Among traditional products, processed meat products are of particular interest to consumers.

Production of meat and meat products in Poland is remarkably similar to production under natural conditions. Producer groups are formed to be organized and see their chances of development in promoting brands and traditional products. An increasing number of consumers are willing to pay much more for traditional products with relevant certificates, which, in addition to their health benefits, are characterized by unique and specific taste (Olszańska 2007).

Traditional and regional foods raise understandable interest (Dolatowski and Kołożyn-Krajewska 2008).

The aim of this study was to compare the quality of traditional processed meat products included in the list of traditional products, processed meat products declared by their manufacturers to be traditional and conventional processed meat products – large-scale production.

Material and methods

The subjects of sensory and chemical tests were processed meat products belonging to the two groups of hams and sausages. Two products of three manufacturers were selected for the study. They were the products of companies A, B and C.

Products of the first manufacturer (ham - A1 and sausage A2) were added to the list of traditional products of the Ministry of Agriculture and Rural Development. Products from the B manufacturer (ham - B1 and sausage - B2) are products with the word *traditional* included in their name, but are not included in the list of traditional products. Products from the C manufacturer (ham – C1 and sausage - C2) are conventional products.

Analyses were performed at the Department of Food Commodity Science of the Cracow University of Economics.

The study consisted of two parts: sensory analysis and determination of the chemical composition of processed meat products. The first part of the study was made by the five assessors using a five-point rating scale: 1 - the lowest rating, 5 - the highest rating. They evaluated: the smell, color, structure and consistency and taste.

Chemical tests included determination the content of:

- water according to the Polish Standard PN-ISO-1442,
- protein, using the Kjeldahl method (Kędzior 2009),
- fat, using the Soxhlet method (Kędzior 2012),
- salts, using the Mohr method (Kędzior 2012),
- phosphorus, according to the Polish Standard PN-ISO-13730.

Results and discussion

Analysis of the results of sensory evaluation

Analysis of the results of sensory evaluation was made with a division into two groups of products: hams and sausages. Ratings obtained for individual quality differentiator are shown in Tables 1 and 2.

In the assessment of the structure and consistency of individual of hams, there were no significant differences (Table 1). Similarly, the color of the hams A1 and B1 was rated (respectively 4.40 and 4.47). Differences occurred while assessing other characteristics. The smell of ham A1 was top-rated (4.10). The conventional ham C1, among hams, was rated as the worst in terms of its smell, color and taste, respectively, 3.80; 3.93; 3.90. The best results were those of ham B1, in terms of its taste (4.47)

Table 1. Assessment of individual sensory characteristics of hams

Quality differentiator	Coefficient of importance	Evaluation of hams, scale 1-5		
		Ham A1	Ham B1	Ham C1
Smell	0.30	4.10	4.40	3.80
Structure and consistency	0.25	4.12	4.20	4.40
Color	0.15	4.40	4.47	3.93
Taste	0.30	4.30	4.47	3.90

Source: own research

Analyzing individual sensory characteristics of sausages (Table 2) there were no significant differences in the evaluation of color. Evaluation of other quality features differed. The highest assessment in terms of smell was that of sausage A2 (4.50) and the lowest, sausage C2 (4.10). The structure and consistency of sausages A2 and C2 were evaluated equally (3.92). Definitely the best taste characterized sausage A2 (4.60). The taste of sausage C2 was assessed as the worst (3.60).

Table 2. Assessment of individual sensory characteristics of sausages

Quality differentiator	Coefficient of importance	Evaluation of sausages in points, scale 1- 5		
		Sausage A2	Sausage B2	Sausage C2
Smell	0.30	4.50	4.30	4.10
Structure and consistency	0.25	3.92	3.32	3.92
Color	0.15	4.13	4.07	4.13
Taste	0.30	4.60	3.77	3.60

Source: own research

On the basis of partial assessments of individual quality features, including the coefficient of importance (Table 1 and 2) the overall sensory evaluation of processed meat products was calculated. The results are shown in Figure 1.

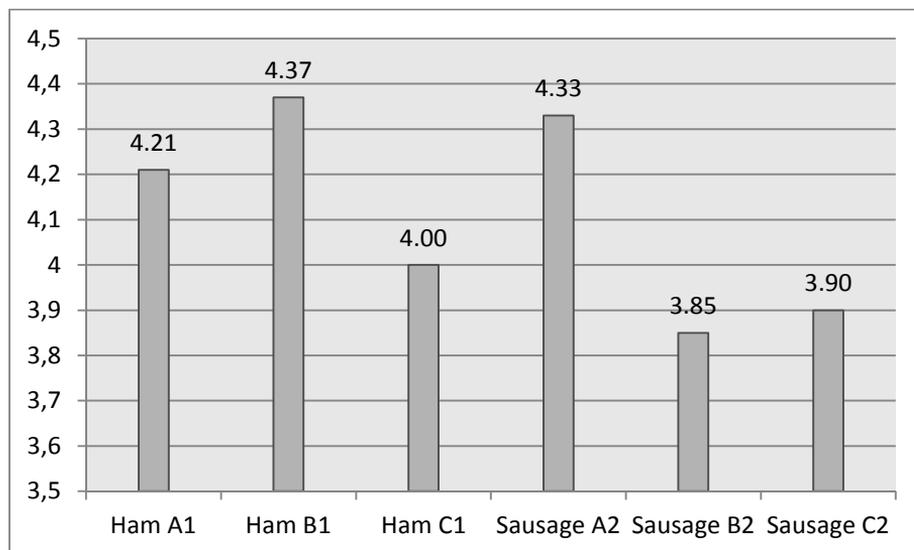


Figure 1. Overall sensory evaluation processed meat products

Source: own research

Among hams, the highest overall sensory evaluation was received by ham B1 (4.37), while the lowest – by ham C1 (4.00). In the case of sausages, the best rated sausage was A2, while B2 (3.85) and C2 (3.90) were much worse. The evaluation of sausages can be concluded with a statement that traditional products (included in the list of traditional products) have better organoleptic characteristics than the conventional products.

Analysis of the results of chemical determinations

The results of chemical tests are presented in Tables 3 and 4 with a division into hams and sausages. Chemical tests included determination of water, protein, fat, salt and phosphorus content in the products.

Between the A1 ham chemical composition, which is a conventional processed meat product, and the composition of C1, which is a conventional ham, there are clear differences in the content of each ingredient (Table 3). Ham C1 contains much more water and salt than ham A1. The content of these ingredients in ham C1 is: 75.70% of water and 2.48% of salt, while in the case of ham A1, it is, respectively, 62.95% and 1.91%. Conventional processed

meat products contain much less of the most valuable ingredient, protein. Its content is only 16.76%, while in the case of traditional processed meat products – A1 contains 10 percentage units more of it, 26.70%. Ham C1 contains on average of 3.40% of fat, and it ham A1 contains twice as much of it (average 6.80%). There are also differences in the content of phosphorus. Conventional processed meat products contain as much of it as 0.437%, whereas conventional products contain as much as 0.746%, indicating an additive of polyphosphates in the production conventional ham.

Table 3. Chemical composition of hams

Ingredient	Determined value			Value according to the Polish Standard
	Ham A1	Ham B1	Ham C1	
Protein (%)	26.70	20.16	16.76	Not less than 16.0%
Water (%)	62.95	64.25	75.70	Not more than 80.0%
Fat (%)	6.80	10.75	3.40	Not more than 10.0%
Salt (%)	1.91	2.39	2.48	Not more than 4.0%
Phosphorus (g/kg)	4.37	4.34	7.46	-

Source: own research

Table 4. Chemical composition of sausages

Ingredient	Determined value			Value according to the Polish Standard
	Sausage A2	Sausage B2	Sausage C2	
Protein (%)	17.98	16.82	13.14	Not less than 13.0%
Water (%)	53.05	54.45	61.20	Not more than 70.0%
Fat (%)	26.20	25.40	19.95	Not more than 35.0%
Salt (%)	1.89	1.60	2.46	Not more than 3.0%
Phosphorus (g/kg)	4.38	3.53	6.39	-

Source: own research

As in the case of hams, sausages are characterized by apparent differences within their chemical composition (Table 4). Sausage A2 (traditional) comprises of 53.05% of water, while C2 contains 61.20%. Salt content in the conventional sausage (C2) is also higher than in the traditional one and was at a level of 2.46%. Sausage A2 contains 1.89%. Fat and protein content is lower than in sausage C2, respectively 13.14% and 19.95%. In the case of conventional sausages, the content of these components is significantly higher, 17.98% of protein and 26.20% of fat. It should be emphasized that fat content of sausage A2 is much higher than in the case of sausage C2. The phosphorus content in sausage C2 is high and amounts to 0.639%, while in the case of sausage A2 it is lower – 0.438%.

To sum up, differences in the chemical composition of the tested traditional and conventional processed meat products should be assessed.

In order to determine whether the chemical composition of traditional processed meat products and the one declared by the manufacturer as traditional are significantly different, the results of ham A1 (traditional) and ham B1 (declared by the manufacturer as traditional) and sausage B1 (traditional) and sausage B2 (declared as a traditional) were compared. Water content in hams A1 and B1 are similar and, respectively 62.95% and 64.25%. Phosphorus content in both sausages is virtually identical and amounts to 0.437% in ham A1 and 0.434% in ham B1. The content of the other ingredients is visibly different. Traditional processed meat products contain far more protein (26.70%) and processed meat products declared to be traditional contain less of it (20.16%). Traditional ham contains less fat and salt than the ham declared to be traditional. The content of these ingredients is as follows: A1 ham – 6.80% of fat and 1.91% of salt; B1 ham – 10.75% of fat and 2.39% of salt.

Table 4 shows chemical composition of traditional sausages and those declared by the manufacturer to be traditional to be similar. Sausages A2 and B2 contained, respectively, 53.05% and 54.45% of water, 17.98% and 16.82% of protein, 26.20% and 25.40% of fat, 1.89% and 1.60% of salt, 0.438% and 0.353% of phosphorus.

Thus, it can be concluded that there were no significant differences in the chemical composition of traditional processed meat products and those declared by the manufacturer to be traditional.

Another issue dealt with is a comparison of the chemical composition of processed meat products declared to be traditional and those conventional. The composition of hams belonging to these groups showed significant differences (Table 3 and 4). Water content in ham C1 (76.40%) is much higher than in the B1 ham (64.25%). Conventional processed meat products (C1) also contain much less protein – 16.91%, and those declared to be conventional (B1) contain 20.16%. Fat content in ham B1 was 10.75%, while C1 ham contained 3.43% of fat. It is worth mentioning that phosphorus content in ham

C1 is much higher than in B1 and amounts to 0.753%, while the product declared to be traditional contains 0.434%. Salt content of both of the processed meat products is comparable and amounts: 2.39% - ham B1 and 2.50% - ham C1.

There are also differences in the chemical composition of the sausage declared to be traditional (B2) and the conventional (C2), though they are smaller than in the case of hams. Sausage B2 contains less water, salt and phosphorus than sausage C2. The contents of those amounts to, respectively, in the case of sausage B2 – 54.45%, 1.60% and 0.353%, while in the case of sausage C2 – 61.20%, 2.46%, 0.639%. The content of protein and fat is higher in B2 and amounts to, respectively, 16.82% and 25.40%. The C2 sausage contains 13.14% of protein and 19.95% of fat.

In order to determine the addition of polyphosphates, Figure 2 shows the content of phosphorus as P_2O_5 in all of the tested processed meat products. The lowest phosphorus content was found in sausage B2. The contents of it in the product amounted to 0.353%. Phosphorus content in hams A1 and B1, and in the A2 sausage (0,434-0,438%) was slightly higher than in the B2 sausage. Ham C1 and sausage C2 (conventional processed meat products) contain much more phosphorus than the previously mentioned traditional sausages. In summary, it can be stated that both the products included in the list of traditional products and products declared to be traditional contain much less phosphorus than conventional processed meat products. This indicates the addition of polyphosphates in conventional production.

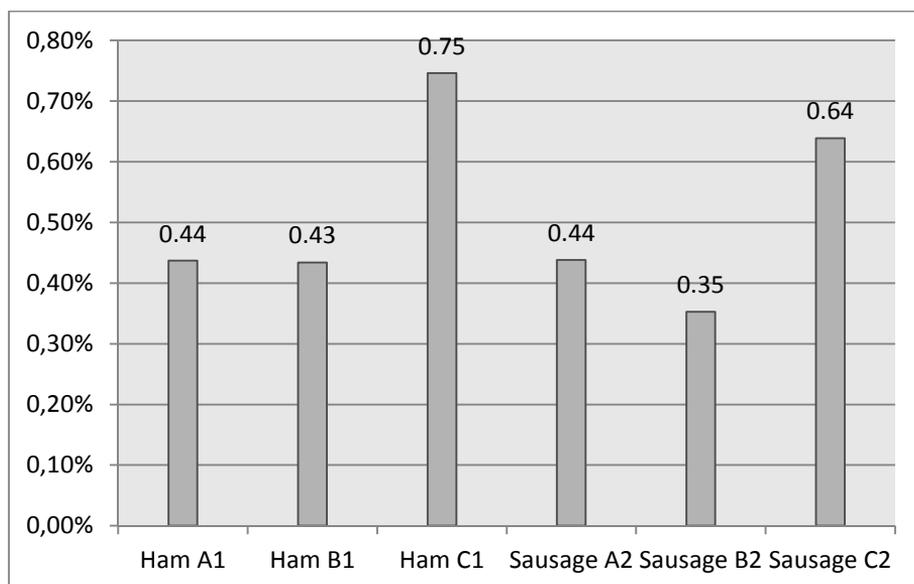


Figure 2. Phosforus content (%) in processed meat products

Source: own research

Tables 3 and 4 show the requirements on the content of protein, water, fat and salt, according to the Polish standard PN-A-82007. *Processed meat products*. Virtually all of the tested hams and sausages meet their requirements.

Summary and conclusions

Traditional hams and hams declared to be traditional by manufacturers received similar sensory assessments. Evaluators did not show significant differences between these products. As part of the observed differences, ham B1 received the highest rating (4.37). Ham A1 was rated slightly lower with a note at the level of 4.21. In the group of sausages the highest rating was the one of sausage B1, which is a traditional product. The score was 4.33. Other sausages achieved a rating of less than 4.00. Generally, the lowest organoleptic assessment was received by conventional processed meat products, and assessments of other meats were comparable.

Comparing the chemical composition of traditional processed meat products with the composition of those conventional, differences were found in the content of individual ingredients. It is worth emphasizing that conventional processed meat products contain less protein when compared to traditional processed meat products. In addition, conventional processed meat products contained a large amount of water, which contributes to a reduction in product life. A large difference was also observed in fat content.

Between the chemical composition of traditional processed meat products and those declared to be traditional, no large differences were observed. The largest differences were observed in the case of hams and they were related to the content of protein and fat. The A1 ham contains more protein and less fat than ham A2. The contents of other ingredients were similar. In the case of sausages, differences in the contents of individual ingredients were small and did not exceed 1.5% .

Analyzing the chemical composition of smoked processed meat products declared to be traditional and conventional smoked ones, differences in the content of individual ingredients were found. Only salt content of these products was similar. In the case of sausages belonging to these groups, differences were found, although they were smaller than in the case of hams. Processed meat products declared to be traditional contain more protein and fat and less water and phosphorus than those conventional ones.

In summary, it can be stated that the greatest differences in chemical composition were observed between the traditional and conventional processed meat products.

In examining the content of phosphorus in individual sausages, it was demonstrated that the products belonging to the group of traditional products

contain much less phosphorus than the conventional products. There were no significant differences in phosphorus content between processed meat products inscribed on the list of traditional products of the Ministry of Agriculture and Rural Development and the ones declared to be traditional.

On the basis of the study the following conclusions have been formulated:

1. Organoleptic characteristics of traditional processed meat products and those declared to be traditional are similar.
2. Conventional products have slightly worse organoleptic quality than traditional products.
3. The chemical composition of traditional and conventional processed meat products are significantly different. Favorable chemical composition exists in the case of traditional processed meat products. They contain significantly more protein than conventional processed meat products.
4. There are no significant differences in the chemical composition of traditional processed meat products and those declared to be traditional.
5. Traditional products contain less phosphorus in their composition than conventional products.
6. Not all of the products available on the market meet their requirements.

References

Dolatowski Z. J., Kołożyn-Krajewska D. (ed.), 2008, Tradycyjne i regionalne technologie oraz produkty w żywieniu człowieka, Wydawnictwo Naukowe Polskiego Towarzystwa Technologów Żywności, Kraków, pp. 5-121.

Domaradzki P., Florek M., 2012, Regionalne i tradycyjne produkty mięsne, in: Litwińczuk Z. (ed.), Towaroznawstwo surowców i produktów zwierzęcych z podstawami przetwórstwa, Powszechne Wydawnictwo Rolnicze i Leśne, Warszawa, pp. 386-391.

Halagarda M., Kędzior W., Pyrzyńska E., 2013, Ochrona i zasady rejestracji produktów regionalnych i tradycyjnych, Zeszyty Naukowe UEK. Towaroznawstwo, Uniwersytet Ekonomiczny w Krakowie, Kraków, in print.

Kędzior W., 2012, Badanie i ocena mięsa i przetworów mięsnych, in: Kędzior W. (ed.), Badanie i ocena jakości produktów spożywczych, Wydawnictwo Uniwersytetu Ekonomicznego w Krakowie, Kraków, pp. 145-155.

Kędzior W., 2009, Oznaczanie białek, in: Cichoń Z. (ed.), Towaroznawstwo żywności. Podstawowe metody analityczne Wydawnictwo Uniwersytetu Ekonomicznego w Krakowie, Kraków, pp. 35-40.

Olszańska A., 2007, Traditional products on the meat market in Poland – their chances and possibilities of sale on the foreign and domestic markets, Folia Universitas Agriculturae Stetinesis, Oeconomica, 256 (48), 283-290.

PN-A-82007:1996. Przetwory mięsne. Wędliny.

PN-ISO 13730: 1999. Mięso i przetwory mięsne. Oznaczenie zawartości fosforu całkowitego. Metoda spektrofotometryczna.

PN-ISO 1442: 2000. Mięso i przetwory mięsne. Oznaczenie zawartości wody (metoda odwoławcza).

Rozporządzenie Parlamentu Europejskiego i Rady (UE) nr 1151/2012 z dnia 21 listopada 2012 w sprawie systemów jakości produktów rolnych i środków spożywczych, Dziennik Urzędowy Unii Europejskiej z 14.12.2012, L 343/1-29.

THE QUALITY OF CONVENIENCE FOODS ON THE EXAMPLE OF SOUP CONCENTRATES AVAILABLE ON THE POLISH MARKET

Michał Halagarda

*Department of Food Commodity Science, Faculty of Commodity Science,
Cracow University of Economics,
michal.halagarda@uek.krakow.pl*

Introduction

Demand for food that would be safe and easy to cook in various situations connected with people's activities forced human to seek such methods of food processing that would enable preserving food for long time and its fast preparation. The first examples of convenience food were seeds and nuts as well as sun-dried meat (Kowalczyk 2004). Nowadays, convenience food market is one of the most dynamic segments of food processing and that is why consumers have many convenience products to choose from.

Convenience food products are very popular among Polish consumers. Their consumption in Poland accounts for approximately 40 million kilograms per year (Nadolski 2012). The reasons for that are: fast pace of life, little time spent at home, women's professional work, increasing number of single- or double-person households, economic growth, greater proportion of elderly people in the population, rising popularity of food snacks and more frequent travelling (Suwała 2011, Kowalczyk 2004, Adamczyk 2010, Drzewicka, Grajeta & Kleczkowski 2012, Kociszewski 2007).

As a consequence people have little time for cooking and they choose food that is simple and fast for preparation. Convenience food also allows to save time needed for cleaning and contributes to more rational use of food. Consumers can use spare time for work or relax and that is why the interest in such food products is on a relatively high level (Babiczyk-Zielińska, Jeżewska-Zychowicz & Laskowski 2010, Presha *et al.* 2008, Kociszewski 2007).

Research by Adamczyk (2010) showed that 97% of the respondents used convenience food. The most popular products were frozen foods (48%) and soup concentrates (16%). Their reasons for using convenience food products were mainly: ease of preparation and little time required (51% and 44% respondents accordingly). Almost 40% use those types of products because of

time absorbing job. According to the respondents, convenience foods represent 28% of food products used in households. Pentor Institute Report (2006) proved that food concentrates are frequently bought mostly by professionally active people, who spend most of the time out of their homes, as well as by youngsters and not wealthy pensioners.

According to almost half of the respondents surveyed by Babicz-Zielińska, Jeżewska-Zychowicz and Laskowski (2010) convenience food has more pros than cons and is safe. For a quarter of those participating in the survey the nutritional value and safety of convenience products was not a matter of concern. Although for 75% of the surveyed people nutritional value was important, the respondents could not comment on actual nutritional value of convenience foods. Positive attitudes towards convenience foods were presented by over 50% of the respondents, mainly by young people. The main advantage of using this type of food was its easy and time saving preparation.

Soup concentrates are widely consumed, especially during cold days, and therefore play an important role in human nutrition. They are used in households, in tourism and even in catering. Their main advantages are as follows: large variety, ease of cooking, low weight, long shelf-life and relatively low price (Jeżewska, Kulczak & Błasińska 2011, Sylwiak 2006).

Soup concentrates can be purchased in the form of concentrated liquid, cubes, granules or the most popular – powder (Krejčová, Černohorsky & Meixner 2006, Sylwiak 2006, Dawiec 2010).

Each year billions of soup concentrates are consumed. In 2010, statistically each human on earth ate 13 packages of soup. However, Chinese consumed 42% of the total concentrates produced in the world (Nadolski 2012). The results of the survey performed by MillwardBrown SMG/KRC Institute between April 2009 and March 2010 showed that 38,7% of the consumers declared eating soups made from concentrates. The most frequently chosen brands were: Winiary (43,7%), Knorr (29,5%) and Amino (18,9%). 31,1% of the respondents consumed this type of food two or three times a month. The results of MillwardBrown SMG/KRC research also show that every year Poles eat 41 thousand kilograms of soups that need cooking (Dawiec 2010).

While choosing ready-made dishes consumers have little or no influence on their nutritional value. That is why they have to trust information presented by the manufacturer on the label of packaging. Knowing the nutritional value of the food is essential for constructing a proper diet, especially taking into account the fact that right amounts of particular nutrients are important to ensure proper functioning of human body and prevent chronic diseases (Krejčová, Černohorsky & Meixner 2006).

However, thanks to education and promotion of healthy life style, consumers are now more aware of the importance of proper nutrition. That is

why more and more people are choosing products of good nutritional value without the addition of preservatives and other artificial ingredients (Kowalczyk 2004, Kuśmierczyk & Szepieniec-Puchalska 2008, Kociszewski 2007). In Poland and other well-developed countries consumers spend little part of their income on food. That is why they seek products that will not only satisfy their hunger but also fulfill other needs as safety, organic origin, convenience, high nutritional value, eco-friendliness (Kuśmierczyk & Szepieniec-Puchalska 2008, Żywność wygodna... 2013). Consumers expect natural flavorings, colorings, aromas and spices as well as low contents of sodium chloride and fat (Słowiński and Remiszewski 1997). For some of the producers consumer satisfaction is their top priority and that is why they try to meet these expectations (Tarczyńska 2013). They alter products they make to fulfill consumers' needs. They produce soup concentrates using natural ingredients and high meat stocks. Some of them are supplemented with vitamins (Świdorski & Waszkiewicz-Robak 2006).

The aim of this study was to assess the quality of soup concentrates available on the Polish market as an example of convenience food products. According to Dawiec (2010) Polish consumers prefer traditional tastes of soups. Therefore a pea soup concentrates were chosen as a research material.

Materials and methods

The research was conducted on 7 varieties of pea soup concentrates, produced by 6 different manufacturers, available on the Polish market. The samples were bought in supermarkets in Cracow. All the analyzed samples had original and tight packaging. The material comprised of four production batches and was collected in 2013 and 2014. The samples were coded with letters A-G. During the research one of the producers changed the composition of the concentrate. The results of the examinations from two batches of old composition are coded with letter D and two batches of new one with D'.

The research program was prepared on the basis of Polish standard PN-A-79011:1998 "Food concentrates – testing methods" and was divided into two stages.

The first stage of the study involved determination of chemical composition of the soup powder and calculation of energy value. It included examinations of: water - according to the oven-drying method, fat - according to Soxhlet method, salt - according to Mohr's method, protein - according to Kjeldahl's method and total ash - by incineration in 600°C with prior carbonization. Carbohydrates' contents were then calculated and with a use of Atwater's coefficients energetic values of the products in kcal units were estimated. To compare the obtained data, the results were converted to grams that should be dissolved in 100ml of water to prepare a ready-to-eat soup. The

exception was the water content which was presented as a part of the concentrates' powder.

In the second phase of the research, sensory analyses were performed by a team of selected assessors. The assessors were chosen according to the method presented by Turek (2011). They assessed appearance, color, odor, texture and taste. Importance coefficients were determined on the basis of attribute relevance analysis and Sensory Quality Indicators were calculated.

Thus obtained data went through statistical analysis. Empirical distributions of continuous variables were summarized using means and standard deviations. The hypothesis of equality of two means was tested by Student's t-test. No correction for multiple testing was applied. Clustering was performed on standardized group averages using Ward's hierarchical method with Euclidean distance. All data processing and statistical calculations were performed in Statistica 10.

Results and discussion

According to Douglas (1976) convenience foods are products that allow consumers spare some time needed for preparation of meals. Gawęcki (2002) on the other hand perceives convenience foods as ready-to-eat or requiring little culinary processing, portioned and packaged products that are particularly convenient for the consumer.

Soup concentrates are made from concentrated, dehydrated or processed plant or animal material or mixtures of them, with or without an addition of natural spices, flavoring agents, flavor enhancers, substances improving products' structure and colorings (PN-A-94050). They are produced by dehydrating a cooked soup or by mixing dry ingredients in appropriate proportions (Kowalczyk 2004).

The main ingredients used in production of soup concentrates include: dried vegetables, legume seeds, salt, fats, starch, flour, groats, dried meat, meat extracts, flavourings, protein hydrolysates, glutamates, yeast extracts (Świdorski & Waszkiewicz-Robak 2006).

The analysed soup concentrates comprised mainly of pea flour, potato starch, sodium glutamate and/or yeast extract, salt, sugar, wheat flour, vegetable and/or pork fat, vegetables, spices and in one case bacon.

Soup concentrates are believed to have low nutritional value due to the use of high temperature. However, some of the producers lyophilize ingredients so that they retain some of the vitamins. Moreover, they contain the proper levels of mineral salts. Consumers can increase their nutritional value simply by adding fresh vegetables (Dawiec 2010, Świdorski & Waszkiewicz-Robak 2006).

The results of physicochemical analyses are presented in Table 1.

Table 1. The results of the physicochemical analyses

Product	A	B	C	D	D'	E	F	G
Water, (%)	7.92 (0.52) ^a	10.2 (0.31) ^{abcdefg}	8.18 (0.28) ^{bhijk}	7.21 (0.24) ^{ch}	7.09 (0.30) ^{di}	7.61 (0.32) ^{ejl}	7.15 (0.32) ^{fk}	8.18 (0.13) ^{glm}
Protein, (g/100ml)	1.08 (0.29) ^{abcdef}	0.67 (0.04) ^{ghijkl}	1.96 (0.07) ^{ijmno}	1.72 (0.00) ^{phm}	1.82 (0.11) ^{ci}	1.60 (0.18) ^{djn}	1.88 (0.17) ^{ek}	1.70 (0.11) ^{lo}
Fat, (g/100ml)	0.08 (0.03) ^{abcde}	0.05 (0.02) ^{fghij}	0.10 (0.07) ^{klmno}	1.05 (0.03) ^{apqrst}	0.63 (0.06) ^{bslpu}	0.72 (0.02) ^{chmrv}	1.19 (0.03) ^{dinswx}	0.57 (0.11) ^{ejotxs}
Carbohydrates, (g/100ml)	4.34 (0.36) ^{abcdefg}	2.96 (0.03) ^{ahijklm}	9.12 (0.22) ^{bhnoprs}	5.47 (0.08) ^{cintu}	5.80 (0.18) ^{djo}	4.89 (0.14) ^{ekpt}	4.96 (0.18) ^{lr}	5.33 (0.61) ^{sms}
Total ash, (g/100ml)	1.14 (0.02) ^{abcde}	0.81 (0.02) ^{afghijk}	1.66 (0.06) ^{bilmnop}	1.04 (0.03) ^{qrs}	1.03 (0.02) ^{chmtuxy}	1.13 (0.07) ^{jmwx}	1.25 (0.07) ^{djortuy}	1.34 (0.12) ^{ekpuw}
Energy value, (kcal/100ml)	22.4 (0.16) ^{abcdef}	15.0 (0.14) ^{ghijkl}	45.3 (0.22) ^{bgmnopr}	38.2 (0.10) ^{chmstu}	36.2 (0.27) ^{dinswx}	32.4 (0.30) ^{ejotwy}	38.1 (0.34) ^{fkpxyz}	33.3 (2.91) ^{lmuz}
NaCl, (g/100ml)	1.05 (0.10) ^{ab}	0.77 (0.06) ^{acdef}	1.86 (0.37) ^{bcdghijk}	1.01 (0.13) ^g	1.03 (0.27) ^h	0.94 (0.05) ^{dil}	1.11 (0.07) ^{ejl}	1.29 (0.24) ^{fk}

Letter symbols were used to mark statistically significant differences

Source: own research

Water content in soup concentrates is one of the factor influencing product's quality. It should be on the optimum level. Low water activity of soup concentrates allows their long shelf-life (Jeżewska, Kulczak & Błaśńska 2011, Świdorski & Waszkiewicz-Robak 2006) However, too little water in a product causes hardening of the powder and facilitates fats' oxidation. Too much water, on the other hand, can lead to negative physical, chemical and microbiological changes in the soup concentrate (Ruszkowska & Ociecek 2005, Świdorski & Waszkiewicz-Robak 2006).

In this study the statistically significant highest water content was noted in product B – 10.2%. All other pea soup powders contained from 7.09% to 8.18% of water. Water content in pea soups examined by Ruszkowska and Ociecek (2005) varied between 5.23% and 6.63%.

Proteins play an important role in human nutrition as they perform various, essential functions within the human body. The main source of protein in analysed material was pea flour. According to Martinez-Villaluenga *et al.* (2008) pea is a source of valuable proteins.

Statistically, significantly lowest protein concentrations were detected in products B (0.67 g/100ml) and A (1.08 g/100ml). In other samples protein levels ranged from 1.6 g/100ml (product E) to 1.96 g/100ml (product C). The results are similar to those received by Suwała (2011). Protein concentrations in various soup concentrates fluctuated between 0.59 g/100ml and 1.8 g/100ml.

Vegetable or animal fat is added to soup concentrates to enhance their sensory properties. Fat contents in analysed soups ranged from 0.05 g/100ml

(product B) to 1.19 g/100ml (product F). Almost all of the differences between products were statistically relevant. In research by Suwała (2011) fat levels varied from 0.4 to 1.89 g/100ml.

Carbohydrates are the main source of energy for human body. In case of soup concentrates, they mainly affect the energy values of the products. The highest contents was noted in product C (9.12 g/100ml) and the lowest in product B (2.96 g/100ml). The differences in concentrations of carbohydrates between analysed products were, however, significant in most off the cases (see Table1). Similarly, soups of various tastes analyzed by Suwała (2011) contained from 3.71 to 7.84 g/100ml of carbohydrates.

Similar situation was observed in case of energy value of examined samples. Again the highest value in this research was represented by product C (45.3 kcal/100ml) and the lowest by product B (15 kcal/100ml). In the study by Suwała (2011) energy value of examined products ranged between 23.84 and 46.58 kcal/100ml.

Minerals are a crucial element of human diet and play an important role in the functioning of the human body. Total ash contents enable an estimation of their concentration in food product. Total ash concentration in analysed research material varied between 0.81 g/100ml (product B) and 1.66 g/100ml (product C). Only in some cases the differences between obtained values were statistically insignificant (see Table 1).

Sodium is one of the macro-elements that are essential for human's life. It plays an important role in ensuring proper blood pressure and osmotic balance in body fluids, regulates acid-base balance and takes part in transportation of amino acids (Jeżewska, Kulczak & Błasińska 2011). Too much salt, however, can cause excessive blood pressure. It can also accelerate the processes of fats becoming rancid and increase water absorption that results in powder agglomeration .

A daily intake of salt should be lower than 6 g. Snacks analyzed by Vardavas *et al.* (2007) had a very high salt content, ranging from 0.8 to 3.9 g per 100 g of a product. Some of the Asian noodle soup concentrates contain as much as 8 g of sodium chloride in one packaging (Nadolski 2012).

In this research, the statistically significantly highest concentration of sodium chloride was detected in sample C (1.86 g/100ml). Other soup concentrates contained from 0.77 g/100ml (product B) to 1.29 g/100ml (product G).

Soup concentrates tested by Jeżewska, Kulczak and Błasińska (2011) contained from 8.87% to 18.14% of sodium chloride, depending on taste. The average concentration of NaCl in soup powder in this study fluctuated from 10.01% (product D) to 15.38% (product B).

According to Zandstra, de Graaf and van Staveren (2001) taste is the most important factor influencing consumption of food. In other words, consumers will not eat food products that they evaluate as not tasty.

According to female respondents surveyed by Kowalczyk (2004), the most important reasons for eating food prepared from concentrates were: little time needed for their cooking (91%) and convenience (78%). Taste was pointed out only by 18% of respondents and nutritional value by 3%. The results of that research also showed that the older the female in the survey was, the more appreciated was the taste of the meal. The main factors influencing selection of food concentrates were: producer or brand (71%), taste (65%) and preparation method (55%). The price (39%), nutritional value (18%) and promotion (13%) were less important in the opinion of surveyed. As many as 66 % of the respondents declared that they oftentimes cooked soups from concentrates. Older women, however, were less inclined to use them in their kitchen.

The results of the sensory analysis are presented in Table 2.

Table 2. The results of the sensory analysis

Product	A	B	C	D	D'	E	F	G
Parameter								
Appearance	3.89 (0.47) ^a	3.01 (0.40) ^{abcd}	3.23 (0.52) ^{efg}	4.47 (0.28) ^{beh}	4.52 (0.02) ^{efi}	4.15 (0.88) ^d	4.30 (0.48) ^{ej}	3.05 (0.60) ^{hij}
Color	4.00 (0.08) ^{ab}	3.03 (0.67) ^{ac}	2.99 (0.62) ^{bdef}	4.33 (0.64)	4.53 (0.21) ^{cdg}	3.98 (0.47) ^{eh}	4.26 (0.38) ^{fi}	3.03 (0.44) ^{ghi}
Odor	4.03 (0.29) ^{abc}	2.58 (0.58) ^{adefg}	2.92 (0.41) ^{bhijk}	3.88 (0.01) ^{dhi}	4.00 (0.18) ^{eim}	3.77 (0.43) ^{fn}	3.80 (0.41) ^{gko}	2.24 (0.54) ^{lmno}
Texture	3.72 (0.61)	2.92 (0.84)	3.82 (0.50)	4.18 (0.54)	4.39 (0.20)	3.84 (0.58)	4.04 (0.47)	3.56 (0.44)
Taste	3.77 (0.27) ^a	2.32 (0.88)	2.90 (0.60) ^b	4.27 (0.57)	3.78 (0.21) ^c	3.88 (0.15) ^{bd}	3.72 (0.15) ^c	2.12 (0.26) ^{acde}
SQI	3.88 (0.24) ^a	2.60 (0.71) ^b	3.04 (0.49) ^{cde}	4.17 (0.38) ^{bf}	4.06 (0.18) ^{cg}	3.88 (0.23) ^{dh}	3.89 (0.22) ^{ei}	2.49 (0.35) ^{afghi}

Source: own research

Product D and its modification - product D' were of the highest sensory quality. They received the best scores in all of the analysed parameters, except texture. It is worth noting that the change in product's recipe resulted in better appearance, color, odor and texture but worse taste. Products C and G were assessed as being of the worst sensory quality.

However, in sensory analysis relatively large standard deviations were observed. The result of the analysis is, though, the average rating for the team, not the individual. Even in a properly trained team the variability of evaluation results exists. It is associated with individual sensual reaction, being an inherent feature of the sensory apparatus of individual members of the research group (Baryłko-Pikielna and Matuszewska, 2009). Therefore in this

research only some statistically significant differences regarding analysed sensory qualities were observed.

According to research by Kozłowska *et al.* (2006) Polish older consumers regard soups made from concentrates as less tasty and healthy than their traditionally made equivalents. They also express neo-phobic behaviors towards new tastes and retail packaging forms of soups.

Nutritional value of soup concentrates varies, depending on ingredients used. In comparison to traditionally cooked soups they are less healthy due to necessity of drying ingredients and using food additives. On the other hand, soup concentrates are rich in mineral salts (Świderski & Waszkiewicz-Robak 2006).

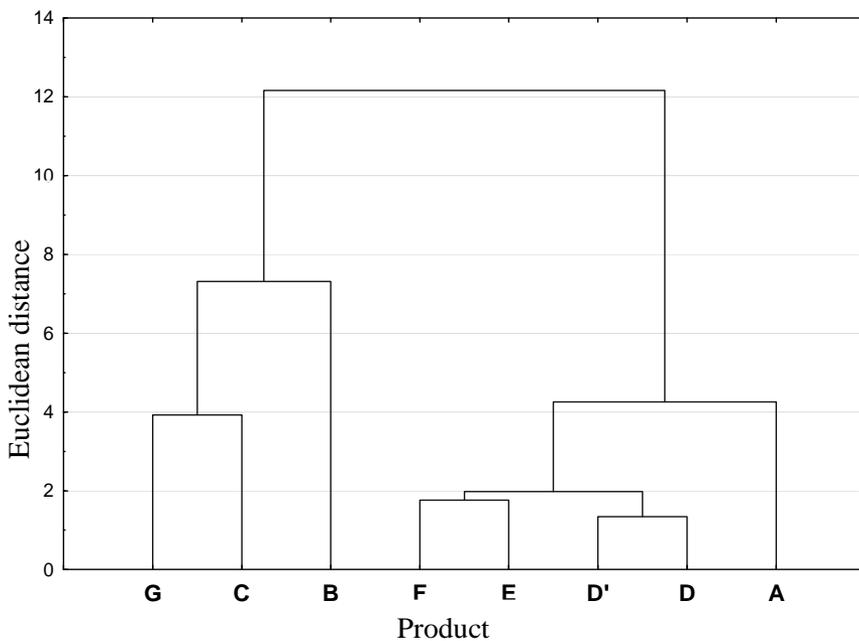


Figure 1. Visualisation of hierarchical clustering results with a use of dendrogram

Source: own research

Comparing nutritional value of soups made from concentrate to the traditionally cooked pea soup analysed by Kunachowicz *et al.* (2005) it can be stated that all examined commercial products have less than half of the amount of nutrients that can be found in a self-made soup. There was one exception. Product C had similar carbohydrates' content.

The results of hierarchical clustering prove that the analysed research material can be divided into two groups of similar products (see Figure 1.).

The first cluster consists of products B, C and G and the second of products A, D, D', E, F. The differences between these two groups are mainly affected by their sensory properties. The first group stands for the least expensive soup concentrates in the research material. The cheapest product B has also the lowest nutritional value.

Conclusions

In today's world consumers choose food that brings tangible benefits. Soup concentrates are certainly very convenient and time saving. However, the results of this research prove that all analysed pea soups made from concentrates have lower nutritional value than traditionally cooked meals. Yet, among commercially available products differences regarding quality, nutritional value and sensory properties are to be found. The worst sensory properties represent products of the lowest prices. The nutritional value varies among products. Most certainly, products of well-known manufacturers are of the highest quality among analysed samples. One of the producers, in order to enhance the nutritional value of the product, changed the recipe lowering the content of fat and increasing concentration of protein. The modification caused, however, some negative changes in taste. Unfortunately, all soup concentrates contained large amounts of salt. One portion - 250ml in almost all cases accounted for over 50% of maximum daily intake of sodium chloride.

References

- Adamczyk G., 2010, *Popularność żywności wygodnej*, Journal of Agribusiness and Rural Development, 4(18), pp. 5-13.
- Babicz-Zielińska E., Jeżewska-Zychowicz M., Laskowski W., 2010, *Postawy i zachowania konsumentów w stosunku do żywności wygodnej*, Żywność, Nauka. Technologia. Jakość., 4 (71), pp. 141-153.
- Baryłko-Pikielna N., Matuszewska I., 2009, *Sensoryczne badania żywności. Podstawy, metody, zastosowania*, Wydawnictwo PTTŻ, Kraków.
- Dawiec M., 2010, *Zarobkowy instant*, Hurt & Detal, 6 (52), pp. 32-35.
- Douglas S., 1976, *Cross-national comparisons and consumer stereotypes: a case study on working and non working wives in the US and France*, Journal of Consumer Research, 3, pp. 226-231.
- Drzewicka M., Grajeta H., Kleczkowski J., 2012, *Zawartość tłuszczu i skład kwasów tłuszczowych w wybranych produktach żywności wygodnej*, Roczniki Państwowego Zakładu Higieny, 2 (63), pp. 199-205.
- Dukaczewski M., 2006, *Dania instant*, Hurt i Detal, nr 6(8), pp. 39.

- Gawęcki J., 2002, *Żywność nowej generacji a racjonalne żywienie*, *Żywność. Nauka. Technologia. Jakość*, 4 (33), pp. 5-14.
- Jeżewska M., Kulczak M., Błasińska I., 2011, *Zawartość soli w wybranych koncentratów obiadowych*, *Bromatologia i Chemia Toksykologiczna*, 3, pp. 585-590.
- Kociszewski M., 2007, *Rynek żywności wygodnej w Polsce*, *Przemysł Spożywczy*, 10, pp. 24-29.
- Kociszewski M., 2007, *Rynek żywności wygodnej w Polsce*, *Przemysł Spożywczy*, 10, pp. 24-26.
- Kowalczyk I., 2004, *Uwarunkowania konsumpcji koncentratów spożywczych*, *Acta Scientiarum Polonorum Technologia Alimentaria*, 3(1), pp. 187-198.
- Kozłowska K., Szczecińska A., Roszkowski W., Brzozowska A., Saba A., Raats M., Lumbers M., 2006, *Perception of convenience food by older people living in Warsaw (on the example of vegetable soups)*, *Polish Journal of Food and Nutrition Sciences*, 2 (15/56), pp. 227-233.
- Krejčová A., Černohorský T., Meixner D., 2007, *Elemental analysis of instant soups and seasoning mixtures by ICP-OES*, *Food Chemistry*, 105, pp. 242-247.
- Kunachowicz H., Nadolna I., Przygoda B., Iwanow K., 2005, *Tabele składu i wartości odżywczej żywności*, Wydawnictwo Lekarskie PZWL, Warszawa.
- Kuśmierczyk K., Szepieniec-Puchalska D., 2008, *Globalizacja rynku i nowe wzorce spożycia. Zmiany w konsumpcji żywności w Polsce*, *Przemysł Spożywczy*, 12, pp. 6-13.
- Martinez-Villaluenga C., Gulewicz P., Frias J., Gulewicz K., Vidal-Valverde C., 2008, *Assessment of protein fractions of three cultivars of Pisum sativum L.: Effect of germination*, *European Food Research and Technology*, 226 (6), pp. 1465-1478.
- Nadolski K., 2012, *Czego nie wiecie o zupkach w proszku?*, <http://technowinki.onet.pl/aktualnosci/czego-nie-wiecie-o-zupkach-w-proszku/c8fkc>, accessed 24.04.2014.
- Pentor Institute Report, Koncentraty obiadowe*, 2006, *Poradnik Handlowca*, 4, pp. 50-70.
- Prescha A., Grajeta H., Pieczyńska J., Wróbel A., 2008, *Produkty należące do żywności wygodnej jako źródło wapnia, magnezu i żelaza*, *Bromatologia i Chemia Toksykologiczna*, 3, pp. 243-248.
- PN-A-79011:1998 "Food concentrates –testing methods".
- PN-A-94050:1996 "Food concentrates. Lunch concentrates".
- Słowiński W., Remiszewski M., 1997, *Koncentraty spożywcze – żywność wygodna i szybka*, *Przegląd Piekarski i Cukierniczy*, 1 (45), pp. 6-7.
- Suwała G., 2011, *The accuracy of the information relating to nutritional value of ready-made dishes exemplified by soup concentrates*, *Polish Journal of Commodity Science*, 1 (26), pp. 63-69.

- Sylwiak A., 2006, *Dania instant*, Hurt & Detal, 6 (8), pp. 39.
- Świdorski F., Waszkiewicz-Robak, 2006, *Koncentraty obiadowe i desery w proszku*, in: ed. Świdorski F., *Żywność wygodna i żywność funkcjonalna*, Wydawnictwa Naukowo-Techniczne, Warszawa.
- Tarczyńska A., 2013, *Projektowanie żywności wygodnej z wykorzystaniem metody QFD*, *Żywność. Nauka. Technologia. Jakość.*, 3 (88), pp. 187-199.
- Turek P., 2011, *Study of water quality fragrances. Possibilities of differentiation of genuine and counterfeit products*, Monographs: Doctoral dissertation, 12, WUEK, Kraków.
- Vardavas, C. I., Yiannopoulos, S., Kiriakakis, M., Poulli, E., & Kafatos, A., 2007, *Fatty acid and salt contents of snacks in the Cretan and Cypriot market: A child and adolescent dietary hazard*, *Food Chemistry*, 101, pp. 924-931.
- Zandstra E., de Graaf C., van Staveren W., 2001, *Influence of health and taste attitudes on consumption of low- and high-fat foods*, *Food Quality and Preference*, 12, pp. 75-82.
- Żywność wygodna – tendencje i perspektywy*, 2013, *Przegląd Piekarski i Cukierniczy*, 9, pp. 64-65.

THE QUALITY OF NATURAL YOGHURTS

Władysław Kędzior, Aleksandra Zuba - Wróbel

*Department of Food Commodity Science, Cracow University of Economics,
kedziorw@uek.krakow.pl*

Introduction

Consumer interest in fermented milk beverages is based on their sensory qualities, high nutritional and dietary value. These very common food products are characterized by nutrient content similar to the one of milk, but due to the fermentation processes, their digestibility increases and health-oriented substances are produced.

Under the effect of microorganisms, proteins are decomposed to become easily digestible, low-molecular peptides and free amino acids. Lactose content is reduced, it is decomposed into simple sugars, lactic acid and other components (Jurczak 2003). Milk fermentation also contributes to an increase in the bioavailability of calcium, phosphorus and iron, increase in the content of certain vitamins, especially group B vitamin, and also the production of antibacterial substances, such as lactic and acetic acids (Flaczyk, Górecka, Korczak 2011). The support of human intestinal microflora and pro-health impact of lactic acid bacteria are especially important (Zmarlicki 2010).

The quality of milk fermented beverages raises understandable interest (Jakubczyk, Kosikowska and Skarżyńska 2004, Kudełka 2008, Stankiewicz 2009, Rój and Przybyłowski 2012).

Among fermented beverages, yogurts are the ones characterized by high consumption. The choice of natural yoghurts on the Polish market is great (Piekut 2011). Brand (manufacturer) strongly influences the assessment and acceptance of yoghurts (Kabacińska and Babicz-Zielinska 2009).

The aim of this study was to determine the organoleptic quality and basic physicochemical properties of natural yoghurts available on the Polish market from different manufacturers.

Material and methods

The material consisted of natural yoghurts on the market, made by twelve manufacturers, from three different batches. In the paper, company names were replaced by numbers from 1 to 12. All the tested yogurts have a valid

expiry date. Thirty-six yoghurt samples were collected for analysis, and each of them was analyzed with a parallel repetition. The arithmetic mean of the two measurements of all three tested batches (test series) were assumed to be the final results. Yogurts were purchased in retail in Krakow. Analyses were performed at the Department of Food Commodity Science at the Cracow University of Economics.

Table 1. Organoleptic evaluation sheet of yoghurts

Quality differentiator	Coefficient of importance	Number of points				
		5	4	3	2	1
Structure	0.3	uniform, dense, no grittiness, no whey seep out	uniform, less dense, no grittiness, almost not visible whey seep out	uniform, a bit visible grittiness, slightly tangled, slight whey seep out	uniform, too thin, chewy, visible grittiness, visible whey seep out	not uniform, thinned, large grittiness, very strongly visible whey seep out
Color	0.15	typical, characteristic, intensely white	typical, white to light cream	slightly yellow, not very typical	changed, not too typical	Strongly changed, not typical
Taste	0.4	typical of a natural yogurt, refreshing, slightly sour, slightly astringent, highly pure and harmonized	typical of a natural yogurt, less perceptible, pure, harmonized	typical, slightly less pure, less harmonized	unusual, too sour, too astringent, or empty, impure with a foreign flavor	clearly changed and impure an unusual example of the strongly bitter, salty, sour or other foreign
Flavor	0.15	perceptible, characteristic, pure	slightly perceptible, distinctive pure	imperceptible	slightly impure, changed	unusual, impure, modified, strange

Source: own elaboration

The samples were properly packaged and labeled. Information on the wrapping contained:

- manufacturer's name and address,
- average nutritional value per 100 g, including: energy; protein, carbohydrates, fat, and calcium (% of the recommended daily intake),
- ingredients: milk, skimmed milk powder, milk protein, live bacterial cultures
- manner and conditions of storage,
- expiry date,
- net weight [g],
- suggested price for yogurts no. 2, 6, 7 and 12.

Designations of qualitative characteristics of natural yoghurts were made in accordance with the Polish Standard PN-A-86130: 1975. Organoleptic evaluations of smell, taste, color, structure and consistency were performed using a model sheet (Table 1)

Physicochemical studies included determining:

- color ($L^* a^* b^*$) in the CIELAB system, with Minolta Spectrophotometer CM - 3500 d,
- fat content using Gerber method,
- dry matter content by drying in the oven,
- acidity by titration,
- pH using a pH meter.

Results and discussion

The results are shown in Table 2 and Figures 1 - 7.

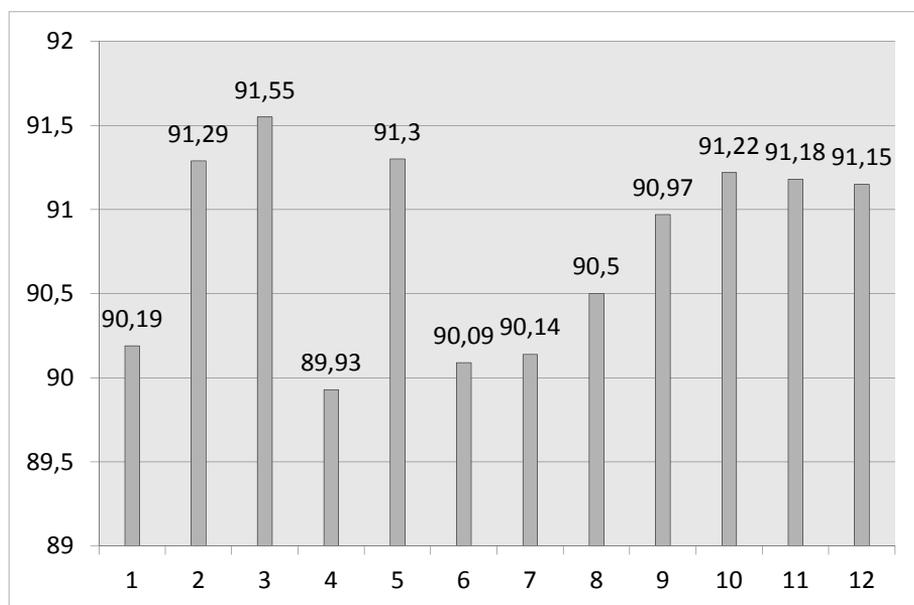


Figure 1. Value the L^* parameter of natural yoghurts from different manufacturers

Source: own research

Color is an important differentiator of consumer assessment, it has a significant impact on the feelings of organoleptic properties of the finished product. Dyes are compounds susceptible to various factors and indicate

unfavorable processes. Analysis of $L^* a^* b^*$ allows to conclude that individual yogurts varied in terms of brightness. The greatest value of the L^* parameter was shown by yoghurt No. 3 (91.55) and the lowest brightness was observed in yoghurt No. 4 (89.93) - Table 2, Figure 1]. Another feature of the test was the share of green in color samples (parameter a^*). The greatest tone was observed in the case of yoghurt No. 7 (-3.24) and the lowest in the case of yoghurt No. 4 (-1.25). The share of yellow was defined using parameter b^* . The smallest value of the b^* parameter was obtained in the case of yoghurt No. 10 (9.75) and the largest in the case of yoghurt No. 7 (13.01).

Organoleptic properties of food products are considered to be the main determinant of consumer choices. Yoghurt No. 10 was best rated by respondents assessing natural yoghurts, its average rating was 4.53. Yoghurt No. 2 was slightly less popular among the participants with the assessment of 4.31 and yoghurts No. 3, 8 and 9 were rated at the level 4.21. The lowest score (3.54) was granted to yoghurt No. 12 (Table 2, Figure 2). The best-rated yoghurt was above all characterized by its correct structure and consistency and taste. The yoghurt assessed as the worst was mostly characterized by wrong flavor. Natural yoghurts, the consistency of which is more dense are characterized by a greater degree of desirability among consumers than yoghurt being not very dense (thin).

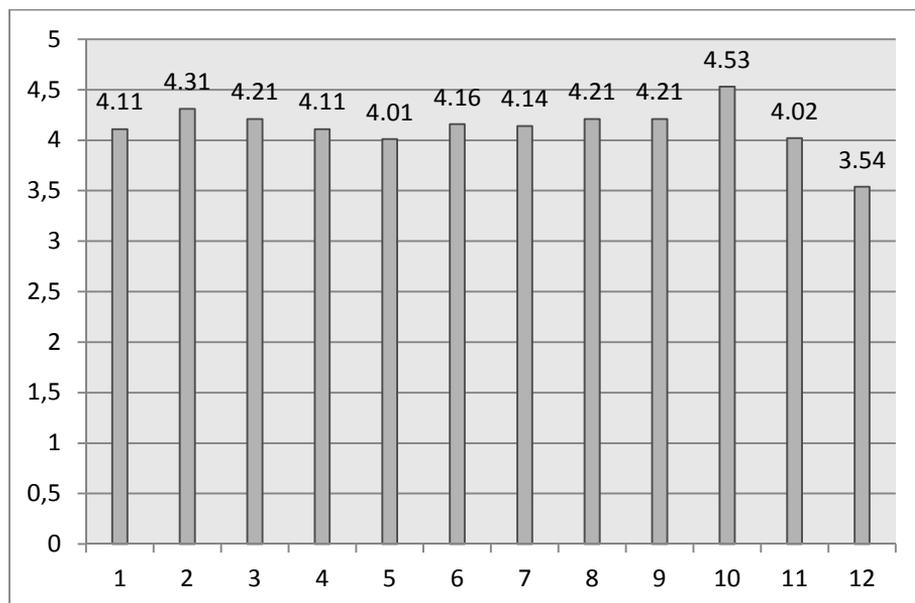


Figure 2. Average values of organoleptic evaluation of natural yoghurts from different manufacturers

Source: own research

Fat content of milk fermented beverages should be normalized in accordance with the manufacturer's declaration and according to Polish Standard (PN-A-86061: 2002), it should not exceed 10%. Yogurt made from skimmed milk (thin) should contain a maximum of 0.5% fat, partly skimmed yoghurt should contain a maximum of 0.5 - 3% of and yoghurt with a normal fat content – a minimum of 3%. On the market there are also cream and Greek type yoghurts, their fat level reaches about 10%. Fat content declared by the manufacturers of the tested yoghurts ranged between 0 and 2.81%. The highest fat content was observed in yoghurt No. 11 (2.81%) and the lowest in the case of yoghurts No. 7, 8, 9 (0%) (Table 2, Figure 3). The conducted analysis showed that most of the products contained a slightly lower percentage of fat than the declared by the manufacturers (Table 2.). The differences were within the tolerance of the Polish standard (PN-A-86061: 2002).

Table 2. Average values of organoleptic evaluation and physicochemical characteristics of natural yoghurts from different manufacturers

Characteristics	Manufacturers											
	1	2	3	4	5	6	7	8	9	10	11	12
Organoleptic evaluation	4.11	4.31	4.21	4.11	4.01	4.16	4.14	4.21	4.21	4.53	4.02	3.54
L*	90.19	91.29	91.55	89.93	91.30	90.09	90.14	90.50	90.97	91.22	91.18	91.15
a*	-2.61	-2.39	-2.12	-1.25	-2.40	-2.22	-3.24	-3.06	-2.04	-1.64	-1.76	-2.14
b*	12.15	11.45	10.79	12.59	11.44	12.34	13.01	12.38	10.72	9.75	11.11	11.65
Fat (%)	1.52	1.68	2.23	1.78	2.02	1.54	0	0	0	2.50	2.81	2.57
Declared fat (%)	1.5	2	2.50	1.8	2.5	1.5	0	0	0	2.50	3.00	2.5
Acidity (% of lactic acid)	0.90	0.72	0.90	0.99	1.01	1.02	1.11	0.92	1.15	1.01	1.04	0.85
pH	4.41	4.70	4.58	4.56	4.48	4.39	4.52	4.47	4.39	4.41	4.23	4.41
Dry matter (%)	14.47	14.57	15.60	14.93	15.55	14.43	12.09	13.14	12.98	15.85	16.00	15.90
Acidity (°SH)	40.00	31.80	39.93	43.93	44.80	45.40	49.33	40.73	51.20	44.67	46.07	37.80
Price/100g	0.34	0.56	0.41	0.50	0.46	1.29	0.47	0.43	0.61	0.51	0.65	0.50

Source: own research

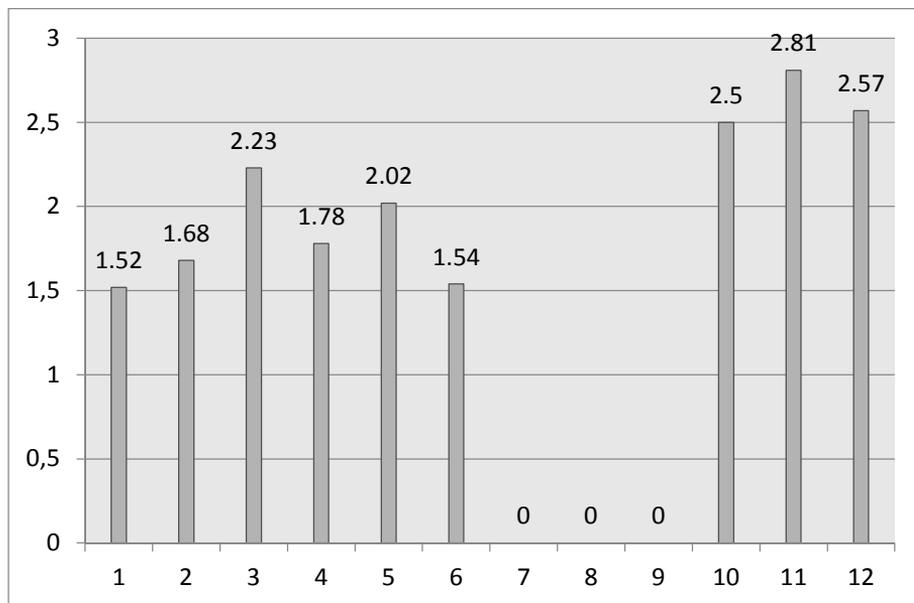


Figure 3. Fat content (%) in the natural yoghurts from different manufacturers

Source: own research

The tested yoghurts were varied with respect to values of titratable acidity. According to the Polish Standard [PN-A-86061:2002] acidity of milk fermented beverages shall not be less than 0.6% of lactic acid. Yoghurt No. 2 was characterized by the lowest titratable acidity (31.80°SH, 0.72% of lactic acid) and yoghurt No. 9 by the highest (51.20°SH; 1.15% of lactic acid) - Table 2; Figure 4.). According to the literature, titratable acidity of yoghurts is 36-48°SH, and the pH should be kept within the range of 4.4 - 4.6. Active acidity (pH) of commercial yoghurts ranged from 4.23 to 4.70. The lowest value was the pH of yoghurt no. 11 and the yoghurt with the highest value was no. 2 (Table 2, Figure 5.).

Currently, the Polish standard does not specify the correct dry matter content or non-fat dry matter in milk fermented beverages. The most important component of dry matter is protein. The level of dry matter in milk fermented beverages is within fairly wide limits, from about 9 to over 20%, with a minimum content of non-fat dry matter from milk to be at the level of 8.2%. However, the most favorable level of dry non-fat matter in natural yoghurts is 13 - 14%. (Dzwolak et al., 2000). The obtained results are generally within the ranges. The lowest dry matter content was observed in the case of nonfat yoghurts nos. 7, 8 and 9, it was, respectively, 12.10%, 13.15% and 12.98%, while the highest dry matter content was noted in the case of yoghurt no. 11 - 16.00% (Table 2, Figure 6).

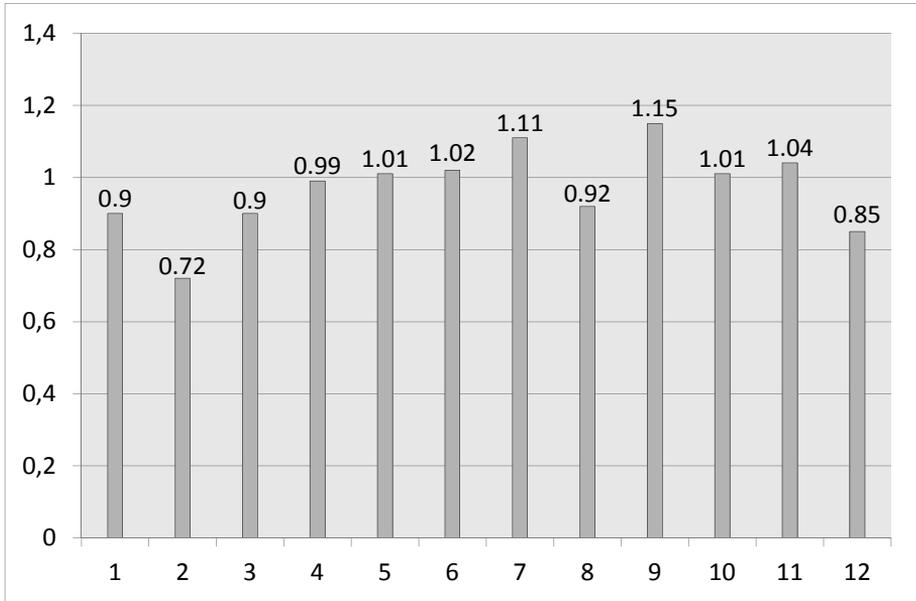


Figure 4. Titratable acidity (% of lactic acid) of natural yoghurts from different manufacturers

Source: own research

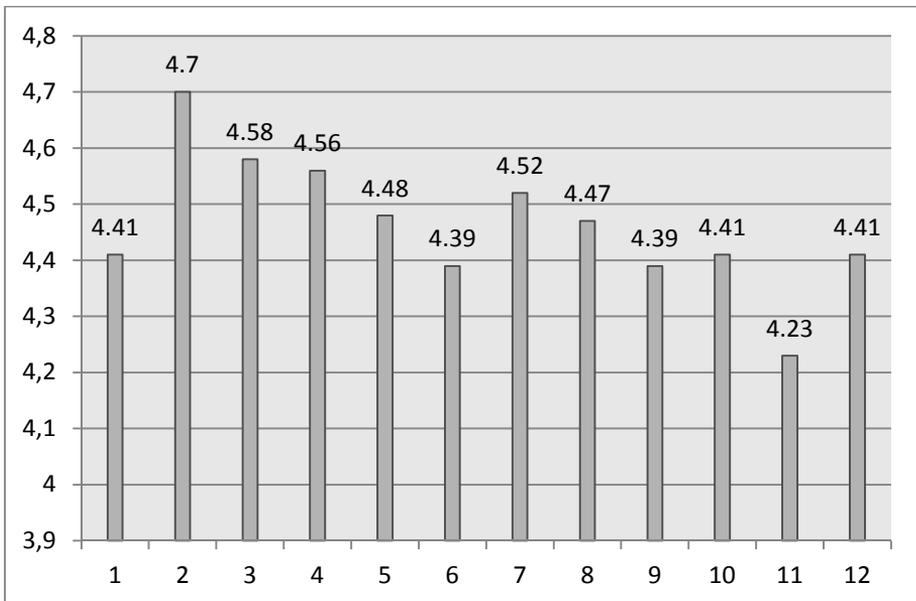


Figure 5. Value the pH of natural yoghurts from different manufacturers

Source: own research

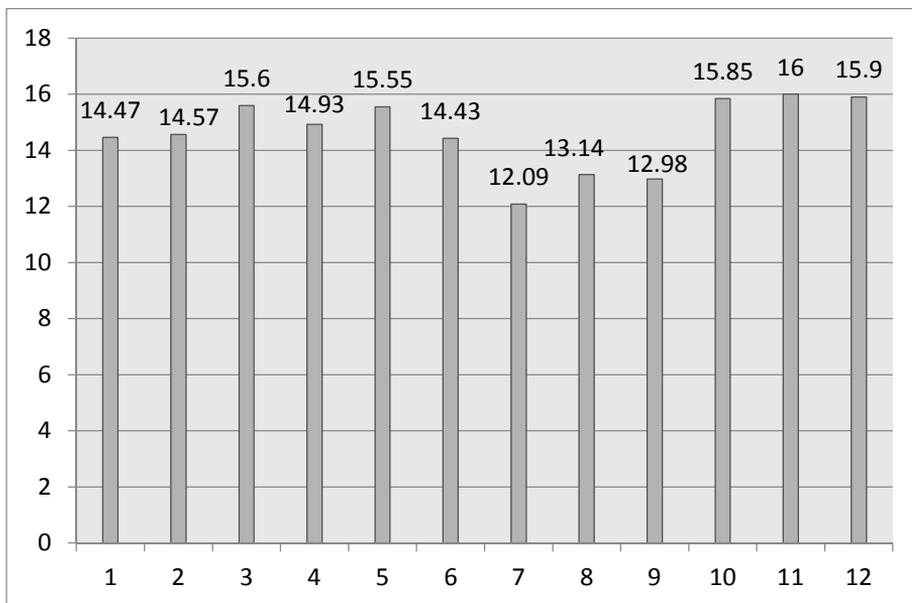


Figure 6. Dry matter content (%) in the natural yoghurts from different manufacturers

Source: own research

Price of the tested natural yoghurts calculated for 100 g of the product ranged from PLN 0.34 for the cheapest yogurt (no. 1) to PLN 1.29 for the most expensive yogurt (no. 6). Comparing the ratio of the price to the organoleptic evaluation (Table 2; Figure 7), none of the yoghurts matched their highest and lowest assessment. High price of the product is not adequate to the assessment of quality, as exhibited by consumers.

Conclusions

1. The quality of natural yoghurts available on the market is at an appropriate level.
2. Analyses of yoghurts of different manufacturers on the market have shown differences with respect to physicochemical properties.
3. The tested yoghurts meet the requirements for the content of dry matter and fat content and titratable acidity
4. It has been shown that, in some samples, fat content was not in accordance with the manufacturer's declaration set out on the packaging.
5. Average assessment of organoleptic properties of the tested yoghurts was between 3.54 - 4.53 in a 5-point scale.

6. Comparing the value for money of the tested yoghurts, it was found that the price of yoghurts is not always adequate to their quality. There was no distinctive highest quality among the most expensive yogurts, as well as the cheapest ones were not characterized by the lowest quality.

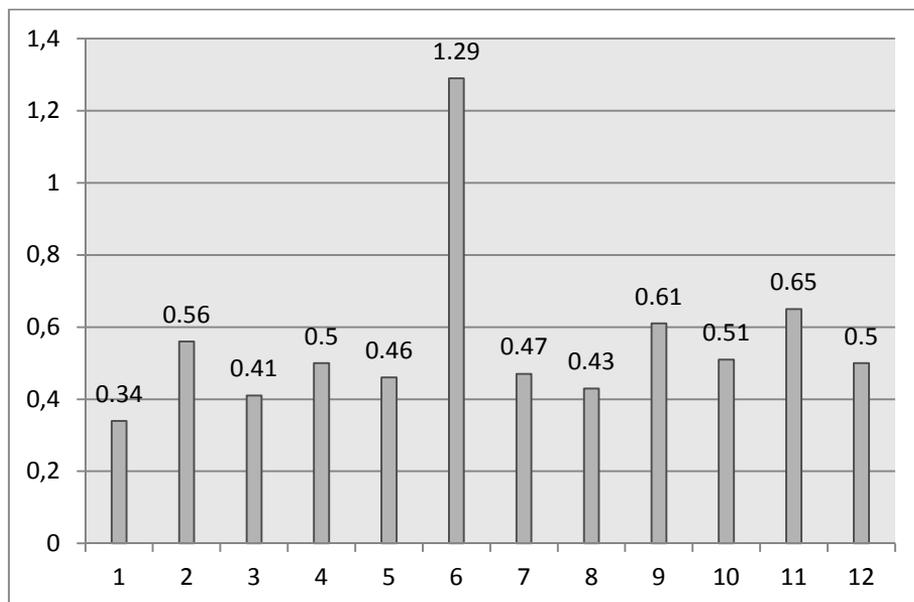


Figure 7. Price per 100 g of individual natural yoghurt (PLN) from different manufacturers

Source: own research

References

Dzwołak W., Ziajka S., Chmura S., Baranowska M., 2000, Produkcja mlecznych napojów fermentowanych, Oficyna Wydawnicza Hoża.

Górecka D., Cais-Sokolińska D., Pikul J., Flaczyk E., 2011, Mleczne napoje fermentowane, in: Flaczyk E., Górecka D., Korczak J., (ed.), Towaroznawstwo żywności pochodzenia zwierzęcego, Wydawnictwo Uniwersytetu Przyrodniczego w Poznaniu, Poznań, pp. 101-102.

Jakubczyk E., Kosikowska M., Skarżyńska M., 2004, Jakość jogurtów produkowanych w Polsce, Przemysł Spożywczy, 10, 31-35.

Jurczak M. E., 2005, Mleko. Produkcja, badanie, przerób, Wydawnictwo SGGW, Warszawa, pp. 190-194.

Kabacińska A., Babicz-Zielińska E., 2009, Wpływ marki na akceptację cech sensorycznych jogurtów, Żywność, Nauka. Technologia. Jakość., 4 (65), 388-394.

Kudelka W., 2008, Możliwości modelowania mlecznych napojów fermentowanych w czasie przechowywania, Wydawnictwo Uniwersytetu Ekonomicznego w Krakowie, Kraków, pp. 41-148.

Piekut M., 2011, Rynek jogurtów w Polsce, Przegląd Mleczarski, 10, 44-49.

PN-A-86061:2002. Mleko i przetwory mleczne. Mleko fermentowane.

PN-A-86130: 1975. Mleko i przetwory mleczne. Napoje mleczne. Metody badań.

Rój A., Przybyłowski P., 2012, Ocena barwy jogurtów naturalnych, Bromatologia i Chemia Toksykologiczna, XLV, 3, 813-816.

Stankiewicz J., 2009, Jakość mlecznych napojów fermentowanych suplementowanych dodatkami pochodzenia roślinnego, Zeszyty Naukowe Akademii Morskiej w Gdyni, 11 (61), 39-44.

Zmarlicki S., 2010, Mleczne napoje fermentowane. Wybrane aspekty zdrowotne, Przemysł Spożywczy, 4 (64), 30-33

FACTOR ANALYSIS OF CUSTOMER VALUE SPIRITS

**Vladimir Kiselev, Tatyana Kiseleva,
Elena Bastron, Ragima Kerimova**

*Plekhanov Russian University of Economics. Kemerovo Branch.
University Food Science & Technology. Kemerovo.
kisselev.vm@gmail.com*

Introduction

The beginning of vodka production in Russia dates back to the late 15th century. Commercial production of vodka's in Russia began in 1861. Aimed at removal of contaminants and, more importantly, fusel oil, it was at this time that mandatory dilution of distilled grain alcohol with water took root. Russian feature is the careful separation of pure ethanol from impurities in the cleaning process distilled spirits (separated head and tail fractions of distillate). It is because of this important technological operation that the traditional Russian alcoholic beverage produced from grain alcohol was called vodka (from Russian “voda”, which means water). In light of both historical and cultural traditions and the technical backwardness of the country at that time, it was this particular technological element common only to Russian vodka manufacturers that indirectly established vodka as a uniquely Russian alcoholic beverage.

Material and methods

Objects of research included:

- factual data for the period 2000-2011 reflecting spirits production and consumption volume in Russia and its regions, price levels, trademarks, and peculiarities of ingredients and composition (Kazantcev, 2008);
- buyer preferences in spirits consumption among a select target buyer audience in supermarkets (Kazantcev, 2008);
- spirits distribution channels as well as individual members scoring high in the factors most influencing consumer demand (Mazanjkov, 2009);

- assortment lists of spirits retailers experiencing the largest consumer demand (Kazantcev, 2008);
- spirits consumers in integrated product distribution channels (Mazanjkо, 2009);
- samples of the most popular spirits brands purchased in retail networks supermarkets during the 2011 (Kazantcev, 2008).

Research methods

Market research was based on the following methods: quota, selective, standardized, structured (based on a number of features), combined and personal observation of spirits retailers (Mazanjkо, 2006).

Study of the product supply structure among homogeneous product groups was conducted by market auditing of sales statistics, including product turnover in physical and monetary terms, quantity of items (SKUs), and retail prices. Output data analysis was based on techniques suggested in our earlier studies (Kiselev, 2005).

Qualitative marketing research into consumer preferences was conducted by means of focus groups and panel discussions among the target buyer audience in Novokuznetsk and Kemerovo (Kazantcev, 2008).

Analysis of theoretical data was conducted using methods for registration, systematization, grouping, classification, comparative analysis, and summation of scientific and methodological publications, regulatory documents, statistics digests, periodicals, and Internet resources.

Statistical processing of experimental data was conducted through use of standard methods for statistical and correlation analysis (SPSS, MS Excel software).

Results and discussion

Product availability for the target consumer group is one of the factors affecting the product selection. This property, in our opinion, includes two major aspects: physical and economic availability.

With respect to the product group under consideration, these aspects can be described by: the volume and quantity of the product supply (spirits assortment), the variety of consumer properties capable of satisfying the diverse needs of the target buyer group (spirits assortment structure), and finally, the product price levels.

Product Volume

Today the global market for vodka is estimated at 4.5 billion liters per year. Most of this consumption volume is consumed by Russians (57%). The current status of vodka consumption, beginning in the first year of the 21 century, is characterized by a steady decline (Figure 1).

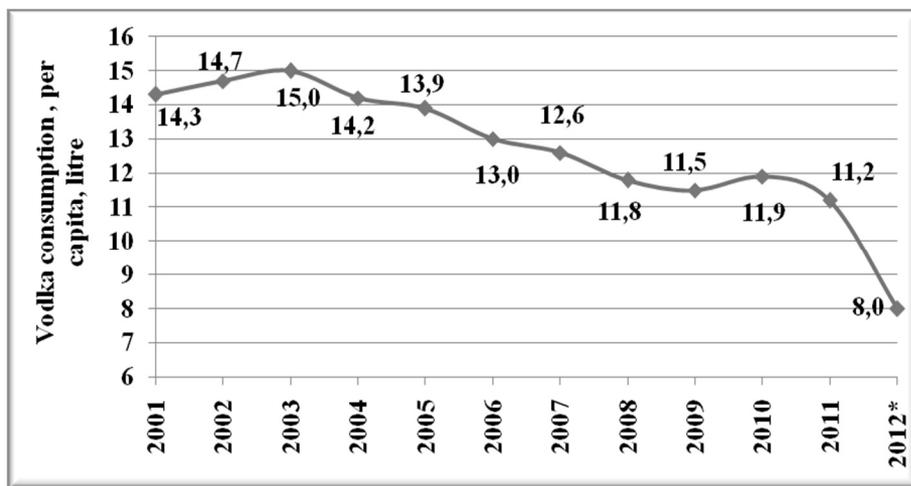


Figure 1. Vodka's consumption, per capita, liters

Source: Rosstat, 2011

The function of per capita consumption is a regressive form (1):

$$y = -0,005x^4 + 0,148x^3 - 1,291x^2 + 3,909x + 11,32 \quad (1)$$

where: x- is the serial number of the calculation period, from 2001.

The tendency to reduce the consumption of vodka per capita has been observed in Russia since 2004. According to Rosstat, this figure declined over the past seven years by 26%, from 15 to 11.1 liters of vodka per year for each person, including women, children and the elderly. At the same time, market experts say that the actual decrease in consumption of alcohol by Russians did not happen - the changes only affected the structure of consumption. Part of consumers switched to beer and wine.

The growth period in spirits consumption coincides with the overall trend in Russian economic development of the time. Increase in the commercial production of vodka corresponded to a growing consumer demand, which, in its turn, was supported by a growth in the real income of the population. Today, personal income growth rates among the Russian population remain high, supported by a combination of varying sources of income including wages, social benefits, income from property and entrepreneurial activities, etc. At the same time, there is a noticeable downward trend in spirits

consumption in Russia, mirroring reduced demand for the product. Several non-economic factors have contributed to this phenomenon in modern Russian history:

- The overall trend in consumer preferences away from spirits with high alcoholic content towards lighter alcoholic beverages (wine, beer, low-alcohol carbonated drinks), a tendency common not only in Russia but in other developed countries.
- Unique to Russia, a growing mistrust of spirits quality (after a 2005 mass poisoning that occurred through consumption of counterfeit alcoholic beverages and resulted in an outbreak of toxic hepatitis in a number of regions of Russia). These events occurred as a result of the distribution of low cost spirits containing polyhex-amethylguanidin hydrochloride and capable of causing instantaneous damage to the liver. In response to this, a number of preventive measures were taken geared to shut down illegal spirits manufacturers in these regions.
- Increased consumer demand for expensive, brand-name spirits with a stronger alcohol content (cognac, tequila, whiskey, etc.) and manufactured by reputable licensed producers.

Despite growth in sustainable income among the Russian population, the short-term prospective through 2012 is that of continued decline in consumer demand for spirits. This tendency may be adequate to satisfy current governmental policies geared toward reduction of spirits consumption in the Russian population.

The development of the uniquely Russian trend of spirits quality distrust can be largely explained by the large degree of fragmentation in the product supply within the spirits market in Russia. According to the study, the 10 largest producers of spirits account for only 50% of the product supply in the Russian spirits market. The remaining 310 producers provide the other half. This makes quality control a challenge. This issue is dramatically illustrated by the fact that one half of the consumed volume consists of illegally produced spirits, unaccounted for by state control agencies. Since its packaging is marked with official excise stamps, this spirits, despite its illegal nature, is still included in the overall product supply structure of traditional product distribution channels (stores licensed by local authorities to sell spirits).

The authoritative American trade magazine *Impact* has summed up the results of 2011 for the alcohol market, recognizing his year of «big return» of the world's leading brands after the crisis of 2008-2009 (World statistics, 2011). Five of the world's leading manufacturers of distilled spirits in the most prestigious premium category, which includes the company Diageo, Pernod Ricard, Baccardi, Brown-Forman and Beam Global, showed sales growth in 2010, although the year before their values were in the negative zone.

Absolute market leader in the premium segment is a group Diageo to 85.8 million 9-liter cases, an increase of 1.6% over the previous year. The greatest

growths in sales have shown Beam Global (6,5%) and Moët Hennessy (9,5%). Has Russian roots SPI Group (owner of the Stolichnaya vodka brand in most international markets) entered the 20 largest international manufacturers of premium alcohol, despite falling rates by 3% to 3.1 million cases. This allowed the company to take 19th place in the list of leading manufacturers.

Five of the most successful premium spirits brands remain unchanged over the last few years. Is still the undisputed leader is vodka Smirnoff (Diageo) from 24.8 million cases in 2010, followed by spirits, Absolut (Pernod Ricard - 10,9 million).

In the top 50 best-selling premium vodka were two Russian brands. But if Stolichnaya (SPI Group) is gradually losing ground, having fallen for two years from 31 th to 27 th place, «Russian Standard» every year shows more and more steady growth and is located on the 39th place (44th place two years ago) with a score of 2.5 million cases, an increase of 13.4% over the previous year. If this growth trend continues, «Russian Standard», claiming to be «a major Russian vodka» on the international market will be able to get ahead of their historic rival Stolichnaya in the current 2012.

The most impressive growth over the last two years of premium vodkas demonstrated French vodka brand Pinnacle (the company White Rock Distilleries), vodka Eristoff (Bacardi), Svedka (Constellation).

In the top 25 fastest growing vodka brands no premium got the only Russian vodka brand «Yamskaya», an increase of sales in 2010 to 21%, reaching 2.6 million cases.

Representation of Russia in the ranking of the top 100 best-selling vodkas in the world, regardless of the price range has decreased significantly. In this list there are no vodka brands of «Synergy» («Belenkaya» and «Mjagkov», «Beluga»), previously occupied space in the middle of the rankings, as well as the brand «Slavic» (GK «Gross»), due to financial problems the company - holder, and «Zhuravli» (CEDC).

The most popular of Russian brands for two years, down from 11th to 15th place in the rankings, helped by a drop in sales in 2010 to 4.6%. «Green Mark» gave way to his 2nd fastest growing Ukrainian brand «Hlebnyj Dar» (company «Bajadera»), which has increased over the year is up 20.7% to 12.3 million cases, despite the fact that last year experts predicted that this brand has reached the ceiling of growth. All presented in the ranking of domestic vodka brands in 2010 showed a negative trend.

Emerging trends of spirits production in Russia are mirrored in its regions. Buyer preferences established during Soviet times are still quite strong in favor of local vodka manufacturers. As exemplified by vodka production in the Kuzbass region local producers manufacture over half of the total volume sold in the region.

Numerous findings by independent reviews geared towards assessing critical quality indicators suggest that all companies produce high quality spirits. In this case it is important to recognize that consumer demand is influenced not so much by the producer's geographical location, as it is by the image established by the company and its business reputation. Take for example a nationwide consumer poll conducted in 2007 where consumers rated the following brands of spirits as being reliable (based on a scale of 1 to 5): Absolut (4.5), Nemiroff (4.4), Russian Standard (4.4), Finlandia (4.3), Soft (4.2). Ranked as unreliable were such brands as Poltina (2.3), Istok (2.5), and Capital Doctor (2.5). This observation should be recognized as one of the factors perceived by the target consumer group to be an indicator of spirits quality.

Analysts estimate that existing production facilities are largely underutilized, with only 35% of available production capacity actually in use. However, the abovementioned trends toward repartitioning of the Russian vodka market among global and domestic producers, including aggressive product distribution through regional channels and acquisition of local producers, significantly impact the perception of the product supply by the target buyer group. This situation also becomes one of the factors of quality and value from the consumer standpoint.

Thus, our analysis of product distribution factors allowed us to make the following generalizations conclusive to the goals of this research, namely developing an integrated model for spirits quality:

- A trend has been recognized that reveals movement in consumer preferences away from spirits towards drinks of lower alcoholic content (wine, beer, low-alcohol carbonated drinks).
- A tendency peculiar to Russia, there is growing distrust toward spirits quality.
- A trend has developed toward increased consumer demand for expensive, brand-name vodka labels manufactured by reputable, licensed producers.
- The product supply structure for vodka will significantly change in the short-term prospective: 80% of Russia's spirits sales volume will be manufactured by 10 of the largest manufacturers by means of aggressive product distribution via regional Distribution channels and takeovers of local producers.
- A spirits producer's geographical location has been noted to be influential to consumer demand.
- There is a push in Russian society toward lowering per capita spirits consumption to 2 liters per year (in absolute alcohol equivalent), a level considered to be safe.

- Further in-depth study is needed in order to develop state policy adequate to regulate alcohol consumption levels, including spirits, and geared towards improvement of the quality of life and health of Russian citizens.

Quantity of Product Supply (Vodka Assortment)

Saturation of product assortment is a crucial factor in customer value perception. It can be clearly seen in the analyzed product group. Saturation can be evaluated based on the number of items, or stock keeping units (SKUs) within an analyzed homogeneous product grouping. With this in mind, we examined the vodka selection within the retail sales network.

As shown by our study, the average saturation of alcoholic beverage product assortment is 117 SKUs. For comparison, non-alcoholic beverage saturation, which is 154 SKUs. At the same time, figures for the primary members in the analyzed distribution channel for alcoholic beverages are 874 SKUs for the market leader and an average of 546 SKUs for the closest contenders. By comparison, the non-alcoholic beverage assortment saturation of the channel leader is only 560 SKUs, with contenders averaging 379 SKUs, i.e. 1/3 less compared to the group of non-alcoholic beverages.

Comparison of the most frequently encountered product assortment saturation values for alcoholic and non-alcoholic beverages reveals a similar difference (1/4). This illustrates the significance of alcoholic beverages for product distribution channel members and should be noted as one of the factors in the comprehensive model for spirits valuation by suppliers and retailers. This indicator can also be indirectly applied consumers.

Based on study of product assortment saturation values it bears mentioning that the most realistic value for this parameter in the comprehensive model for spirits quality should be the average value of 275 SKUs.

It should be noted that the analyzed indicator reveals an expressed dependence on amount of sales floorspace (the correlation coefficient is $r = 0.6$ for the cumulative distribution channel and $r = 0.58$ for the integrated channel) and the price of the average receipt ($r = 0.6$ and $r = 0.45$, respectively). The largest channel members have an even greater correlation factor ($r = 0.89$ and $r = 0.81$, respectively, for floorspace and receipt value). This last observation is crucial for the purposes of this research, as it indirectly reflects the value of the assortment saturation factor to the target consumer group. For the non-alcoholic beverage assortment these coefficients are likewise meaningful: $r = 0.64$ and $r = 0.7$ respectively, which indirectly confirms the validity of our conclusions.

These correlation coefficients illustrate the high level of dependence between the customer flow indicator and assortment saturation indicator.

Thus, the higher the value of assortment saturation, the more it attracts buyers (correlation factor between these indicators is $r = 0.61$). For comparison, the value of this indicator for non-alcoholic beverages is $r = 0.56$, which indirectly confirms the validity of our findings and conclusions drawn from our study of spirits assortment saturation in the retail channels.

Spirits assortment values for the largest members of the analyzed distribution channel substantially exceed the averaged value used as a basis for the development of the integrated model for spirits quality (275 SKUs).

Retailers have cumulative alcohol product assortment saturation values of 784 to 3764, i.e. from 261 to 376 SKUs per retail outlet. This generally meets the required conditions and supports the validity of the calculated value of alcoholic beverage assortment saturation, 2/3 of which includes spirits, that is, over 180 SKUs of spirits. This value has been adopted for the purposes of this research, namely for the development of a comprehensive model for spirits quality.

Thus, our study of the product assortment saturation indicator for the analyzed product group enabled us to define the most important characteristics of this indicator to the purposes of our re-search – namely, the development of a comprehensive model for spirits quality:

- Alcoholic beverages are significant to members of the distribution channel: the higher the value of the indicator, the more buyers are attracted.
- There is a direct correlation between this indicator and both floorspace and the average price of a retail outlet sales receipt.
- The value of this indicator should be more than 180 SKUs for one point of sale.
- There is high physical availability of spirits in the distribution channels.

Product Price Levels

The retail price of vodka is an important factor influencing product value as perceived by the target consumer group. In the context of our research it is one of the most important factors influencing the quality of life of Russian citizens since it impacts overall national health.

The question of the price of vodka is a historical one since many milestones in Russian history are associated not only with major geopolitical events but with the price of a bottle of spirits. Thus, the price of a bottle of vodka during the Soviet era (forty years ago) was 3.62 rubles; the minimum monthly wage was 70 rubles and average monthly wage 125 rubles. Consequently, the correlation between the price of a bottle of vodka and monthly wages at the time was 1:19 (minimum) and 1:35 (average). Minimum

monthly wage today is 4 611 rubles (as of June 1, 2011) and average salary of employees of the federal budget institutions is 30 474.6 rubles (Press Service of the Russian Federation Ministry of Public Health, 2011), while the minimum retail price for a bottle of vodka (From 1 January 2012) is the cheapest bottle of vodka legally produced is estimated at 130 rubles. Therefore, the current ratio is estimated at 1:35 (minimum) and 1:234 (average). These results clearly illustrate the fact that, over the last forty years of Russia's development, vodka has become at least twice as affordable, and for the average wage earner - six and a half times more affordable. Needless to say, this inevitably effects overall national health.

We evaluated the influence of both sales floorspace and average receipt price on consumer behavior at points of sale. As illustrated by the results, these factors have no effect on vodka retail prices (the correlation coefficients were $r = -0.06$ and $r = -0.14$, respectively). A similar conclusion can be drawn regarding the correlation between vodka retail price and customer flow ($r = -0.01$). We recorded the indifference price for buyers of cheap spirits.

At the same time it is worthwhile noting that the same manufacturers produce vodka for different price categories. This is an indirect confirmation of the desire on the part of the most active members in the Russian spirits market to increase their market share by attracting customers with differing vodka price demands. Characteristic also is the presence of only one producer in the "people's vodka" segment (130 rubles), the Federal State Enterprise "Rosspirtprom." This is considered important to the purposes of our work, namely, the modeling of a comprehensive consumer appraisal of spirits quality and the respective impact of other members of the product distribution system on that appraisal.

Buyers in the low-price level demonstrate high indifference, in other words, these consumers choose spirits within this price segment without regard to emotive qualities of the product, but based on their own experience and the particular purchase occasion.

Level of indifference in other price segments declines with an increase in the absolute value of the retail price for spirits. The lowest level of consumer indifference is observed in the highest retail price segment. In developing a comprehensive model for spirits quality, this observation should be taken into account in response to customer needs.

The estimated weighted average of the average market price for vodka is 167 rubles.

Based on the study of spirits price levels in product distribution channels, the following conclusions can be drawn, each related to the goals of our research:

- Over the last forty years, economic affordability of spirits increased by an average of 6.6 times, a factor negatively effecting national health.

- Consumer indifference to spirits price has been observed. As a result, customers often make purchases at prices 28,5% greater than the lowest price for the exact same spirits sold elsewhere in the same city.
- Neither sales floor space nor average receipt price has an effect on spirits retail prices.
- Spirits retail price, in its turn, has no impact on customer flow.
- Spirits producers supply product to different price categories thus attracting buyers with different spirits price preferences.
- Buyers of low price vodka make their purchase decision without consideration as to the emotive qualities of the particular brand, but based on their own experience and particular purchase occasion. Buyers preferring the premium vodka segment, on the contrary, exhibit price indifference in favor of other factors unrelated to the price of the product.
- The average weighted price of spirits in integrated product distribution channels has been estimated at 167 rubles (\$5,35).

Diversity of Consumer Properties (Spirits Assortment Structure)

As a food product spirits does not have a complex formula. However, consumers tend to attribute a specific set of unique properties to their favorite type of spirits; these properties are integrated into their particular preferences toward specific product brands and manufacturers. In order to investigate these preferences we studied the spirits sales structure (in monetary and physical terms) in Russia.

The structure of spirits consumption in the remote regions of Russia is different from that of the central regions. The most significant difference concerns so-called «local patriotism», implying consumer preference to locally manufactured spirits (Kiselev, 2006). It is a well-known fact that consumers give their preference to locally produced food products. Over 40 % of the regional consumer demand for spirits is met by Siberian producers. In all other aspects the list of leading regional spirits producers is similar to that of the national.

The above-mentioned consumer preference to regional brands remains a strong factor in competitive market conditions. This appears to be an important factor influencing consumer selection of spirits and should be taken into account in the development of a comprehensive model for spirits value (Erchak, 2004).

As mentioned before, local producers possess a number of psychological advantages. They help buyers appreciate their local way of life and also promote responsibility of regional vodka producers for the quality of their product. In addition, regional producers possess significant logistical advantages that are manifested in the economic affordability of the regional

product distribution channels. This factor has a positive impact on the structure and size of their spirits assortment (Kiselev, 2006).

It is a well-known fact that there is an inverse relationship between the size of the product assortment and its efficiency (salability of SKUs constituting the assortment). This means that effective sales management can only be achieved through limiting product diversity. In order to analyze the efficiency of the spirits assortment we studied sales data of different spirits brands in Russia.

Understanding the relevance of taste and of other useful spirits properties is crucial to understanding consumer vodka preferences. For this purpose, we conducted a study of consumer demand for vodka with various flavoring and physiologically active ingredients as compared to spirits without additives (vodka).

Consumer demand for spirits with flavoring is estimated to be 19% of the total cumulative demand in monetary terms and 23% in physical terms. It points to the significant consumer interest in the taste properties and variety of spirits, as well as the presence of physiologically active ingredients. It is worthwhile mentioning that spirits producers have also taken this into account. Thus, 28.4% of the product selection consists of flavored spirits.

Study of the consumer demand for flavored spirits revealed that the highest consumer demand in monetary terms is associated with vodka containing pine tree extract (4.1%), birch tree buds, etc. (2.4 %), honey (1%), lemon and blackcurrant (each 0.8%). The structure of demand in physical terms (number of purchases) includes the same components, except for black currant, which gave place to pantoheumatogen. In terms of the number of distinct SKU items, among flavored vodkas birch tree bud spirits leads (4%), followed by spirits with honey (3%), and then lemon, pine nut, and black currant (each 2%). This indicates that consumer demand for flavored vodka is adequate to the product supply and directly dependent on the producers.

Conclusions

The following conclusions have been made based on the results of the study:

- Compared to Russia as a whole, vodka production in the regions of Russia has greater consolidation and higher competitiveness in the product supply structure due to the presence of a large number of non-regional brands.
- Spirits consumption in the outlying regions of Russia differs from that of the central regions due to "local patriotism," reflecting consumer preference to locally produced spirits.

- Consumer preference to the regional vodka brands is stable in the context of competitive market conditions.
- Regional producers possess a logistical advantage that positively affects the size and structure of the spirits assortment and likewise influences consumer choice.
- A significant buyer interest has been observed in regard to the variety and flavor of spirits, as well as the use of physiologically active ingredients, all of which have been taken into account by producers.

Acknowledgments

The authors are grateful for the participation at various stages of this study Andrey Kazantsev and Elena Mazanko, who worked at the Department of Commodity and Quality Management in the Kemerovo University Food Science & Technology as candidates for a degree.

References

Ерчак, А.И., 2004. О взаимосвязи цены и качества товаров в розничной торговле и обоснованности ее учета со стороны потребителей. Маркетинг в России и за рубежом, 5: 107-116.

Киселев, В.М., 2005. Методология ассортимента товаров, PhD thesis, КемТИПП, Кемерово.

Киселев, В.М., Е.И. Мазанько, 2006. Управление ассортиментом товаров. Москва-Кемерово: Объединенное издательство «Российские университеты».

Казанцев, А.А., 2008. Разработка модели потребительской оценки качества водки с развертыванием его функции, PhD thesis, КемТИПП, Кемерово.

Мазанько, Е.И. Региональные аспекты государственного регулирования товародвижения и качества алкогольной продукции, 2009. PhD thesis, КемТИПП, Кемерово.

Мировой водочный рейтинг. Date Views 3.03.2011 www.rbcdaily.ru.

QUALIMETRIC APPROACH TO OPTIMIZING CONSUMER CHOICE OF SPIRITS

Vladimir Kiselev, Elena Zubareva, Tatyana Ponkratjeva

*Plekhanov Russian University of Economics. Kemerovo Branch.
University Food Science & Technology. Kemerovo.
kisselev.vm@gmail.com;*

Introduction

Consumer assessment of spirits' quality is done directly in the points of sale of alcoholic beverages. This assessment is not accompanied by mathematical calculation or comparison of the results, obtained from various stock-keeping units. Such an assessment is empiric in its nature for the most part.

It is not a coincidence that primary attributes that impact consumer choice are external attributes, some of which could be rational (retail price) and may correlate with irrational (non-price quality attributes) in the ratio of 1:9. Such correlation is considered fair from the point of view of the contemporary theory of the "system of balanced indicators", which was developed by the specialists of Stockholm School of Economics Kaplan R.S. and Norton D.P. (Kaplan and Norton, 1996).

The importance of external attributes of product value and the necessity of their consideration by manufacturers and retailers was also noted in the research of Kiselev V.M (Kiselev, 2005). The fact of consumer selection of specific spirits stock items from diversified family of similar products in essence means a much higher assessment of this product compared to the others, as observed by Savchuk S.I. (Savchuk, 2004).

In light of this, the process of spirits quality assessment in points of sale involves identification of sum-total of exterior attributes, which allow to compare aggregate estimates of various stock keeping units of the same price level in view of their ability to satisfy the most significant requirement in each specific situation. In this context the requirements are defined as diverse life values: security, comfort, and hedonism (satisfaction), dominancy (image support), sociality (demonstration of your identification with a specific social group), cognitivity (knowledge of the world) and, finally, cost effectiveness. Satisfaction of these requirements in its essence is the degree of usefulness of

spirits. The appropriateness of this statement has been tested during the focus group, which constituted of respondents representing various price segments, as reported earlier. This data agrees very well with earlier published materials regarding this subject (Voronov and Gusjkov, 2005).

Thus, multi-attributive model of spirits quality, which implies quality function deployment, involves its ability to satisfy not only individual requirements, but also the social activity of the consumer, in other words, activity carried out in specific social environment. In this case, the economic components of the suggested quality model, as well as its other attributes, change their significance on various price levels of the perceived consumer value.

For consumers of the lowest price level economic attributes will have a much higher significance in their choice of spirits, as compared to the non-price attributes. And on the contrary, for consumers choosing a high price level during their spirits quality assessment the importance of economic attributes will be significantly less, as compared to the non-price attributes (image etc.). Price levels of consumer evaluation of vodka quality are not directly related to consumer income level. To a large degree they are determined by the psychic archetype, which has been addressed in several researches related to the subject (Russian Consumer Study, 2003).

Material and methods

A survey has been conducted to evaluate the significance of various factors which impact consumer choice of specific trade marks, types, modifications and stock keeping units. The case study was based on spirits, as the most popular product among Russians, especially men, on the one hand, and the most contradictory product in terms of customer assessment and evaluation of public healthcare specialists. For this purpose a customer survey was conducted in order to determine the significance of the following factors: grade of alcohol, which was used for spirits production, mildness, flavor, color, trade mark and retail price.

Results and discussion

The results of the case study demonstrated a big significance of the analyzed factors for vodka consumers. The largest impact on consumer perception of spirits quality is produced by the grade of alcohol: 60 % of respondents noted that they closely study the information regarding the grade of alcohol during their selection of each specific stock item.

The next significant factor is organoleptic assessment of spirits quality. 40 % of respondents noted that their choice of each specific item was based on the previous purchase experience. In cases when consumption of a well-known article allowed consumers to determine the mildness of the selected vodka, the choice was considered to be a good one. At the same time, in case of spirits, mildness is not considered to be the primary determining quality factor: 60 % of respondents were indifferent to this attribute. This is especially particular of Russian consumers who often prefer not the mild but rather strong flavor of spirits. This is well supported by the structure of consumer demand for spirits with various additives, among which there is pepper, horse radish etc. (For example the most popular flavor is Gorilka with pepper).

Based on the case study of consumer preferences of spirits qualities the following conclusions can be made:

- There is an evident connection between consumption and knowledge of spirits quality. Correlation ratio between this two indicators is estimated at 2.3;
- Size and volume of packaging does not impact consumer perception of spirits quality;
- The largest impact on consumer perception is rendered by the grade of alcohol;
- The choice of a particular stock item is based on the previous purchase experience of the consumer;
- The mildness of spirits is not an essential attribute of spirits quality;
- The label on the bottle should contain all information necessary for the preparation of cocktails.

As a result of the case study we may identify the following list of various requirements of distribution channels participants (product manufacturers, retailers, consumers, regulatory government agencies supervising alcohol production and consumption etc.):

- Reputation of the trade mark;
- Loyalty to spirits quality;
- Consumer experience based on the previous purchase;
- Reliability of the manufacturer;
- Geographic location of the manufacturer;
- Reduced volume of one-time spirits consumption;
- Size of the floorspace of the point of sale;
- Economic affordability of spirits (average weighted price vodka is 167 rubles);
- Various price categories of spirits;

- Factors of non-price selection;
- Quantity of stock keeping units of spirits;
- Flavor variations of spirits;
- Presence of physiologically active ingredients;
- Grade of the alcohol;
- Availability of the necessary information on the label.

It is reasonable to systematize these requirements in a short list of factors related to product distribution channels:

Point of sale factors: deep assortment, positive experience, retail price, purchase conditions (floor-space of the point of sale of alcoholic beverages, economic affordability, quantity of stock keeping units, flavor variations, various price categories, factors of non-price selection).

Spirits production factors: counterfeit proof (loyalty to spirits quality, reliability of the manufacturer), packing exterior (factors of non-price selection, reduced volume of one-time consumption), image of the trade mark (reputation of the trade mark, geographic location of the manufacturer).

Spirits consumption factors: no harm to human body (grade of the used alcohol, availability of necessary information on the label), health benefit (presence of physiologically active ingredients), taste, color, aroma, (consumer experience with the previous purchase).

As it has been noted earlier, the interests of distribution channel participants are often in conflict: the interests of one of the participants are ensured through the infringement of interests of the others. For example, availability of flavor varieties forces spirits retailers and manufacturers to reduce the economic efficiency of the production.

In order to model the parity of requirements of various distribution channel participants we have offered an expert evaluation of the significance of the abovementioned factors for each category of the participants (Table).

As it is obvious from the table, consumers are concerned with all listed spirits attributes. As a platform for the model we suggested compensational model of quality deployment in which the lack of one of the attributes is compensated by the advantages of another attribute.

$$Q = \sum_{i=1}^{i=n} k_i * q_i \quad (1)$$

where: Q – comprehensive assessment of spirits quality; score;
 n – number of attributes of spirits quality;
 ki – ratio of significance of the i- attribute;
 qi – consumer assessment of the i- attribute; score.

At the same time the important feature of this model is that the variety of attributes may be differentiated based on their significance for consumers. While evaluating the significance for consumers of analyzed attributes, respondents were asked to evaluate each of these attributes based on the 5-score scale. Respondents were selected from the target consumer audience. Further on, consumer preferences were processed via mathematic statistical methods in order to determine their significance ratio.

Suggested model of spirits quality is, on the one hand, multi-attributive, and, on the other hand, it has a deployed quality function. Quality function deployment is carried out through all of the levels of quality formation and assessment: product manufacturing, spirits distribution and sales, spirits purchase and consumption. The influence of government regulatory agencies supervising spirits production, sales and consumption is one of the internal limitations for many of the attributes such as retail price, purchase conditions, counterfeit proofness, absence of harm for human health, health benefits, exterior packing, information value of the label, flavor, color and spirits aroma. The last statement shows that interests of the government and society are considered in this model indirectly.

As it can be seen from the suggested model, the most impact on consumer quality assessment is done by such factors as deep assortment, positive experience of previous purchases, retail price, purchase conditions, absence of adverse effects on the human body, exterior packing and flavor. Significance ratios of these attributes are the most high.

Despite the empirical nature of spirits quality assessment provided by consumers in various points of sale of alcoholic beverages, the value of the developed model also includes its ability to forecast consumer demand for specific types, varieties, and stock items based on consumer assessment conducted during the focus group. Combination of focus group methods and the multi-attributive quality model with quality function deployment allows manufacturers and retailers to forecast consumer evaluation of spirits quality in various points of sale.

Estimated compensational model of consumer assessment of spirits quality must also consider the interests of other participants of integrated distribution channel. For this purpose a mathematical model of comprehensive assessment of vodka quality with quality function deployment was calculated based on the parity of requirements.

It should be accepted that there is one and the best point of view, which allows parity of the requirements of various participants of distribution channel (manufacturers, retailers, buyers, consumers, society, government etc). In this particular point the expenses of each participant are minimal, as compared to the expenses of these participants in any other point. Thus, optimal spirits quality is defined for this point in view of the opinion of all abovementioned participants of the parity requirements. Calculations are made on the bases of the formulas 2-9.

$$Q = \sum_{i=1}^{j=n} k_i * q\tilde{a}_{ij} \quad (2)$$

where: \bar{Q} – integral quality indicator at the point of requirements parity;
 n – number of participants for whom parity of requirements is formed;
 i, j – indices corresponding to the attributes and participants;
 \tilde{a}_{ij} – criterial vector of the i -attribute and j -participant;
 k_i – coefficient of the significance of criterial vector.

A_{κ} ($\kappa=1 \dots m$) – alternatives of the participants

$$A\{A_1 \dots A_m\} \quad (3)$$

Suppose, there is a set of criterial vectors which should be used to select the alternatives that satisfy the point of requirements parity based on the defined target function \tilde{a}_{ij}

$$\{\tilde{a}_1 \dots \tilde{a}_m\} \quad (4)$$

$$A * A \quad (5)$$

\tilde{a}_{ij} is accepted as functional of the total weighted loss $P_i^{\tilde{a}}$

$$P_i^{\tilde{a}} = \sum_{i=1}^{i=n} \tilde{a}_{ij} * p_{ij} \quad (6)$$

where: p_{ij} ($p_1 \dots p_m$) - loss of the j - participant having reached requirements parity

As the best solution that alternative A^* is chosen which corresponds to the minimal functional value of the total weighted loss $P_i^{\tilde{a}}$

$$A^* = \operatorname{argmin} P_i^{\tilde{a}}(A_i) \quad (7)$$

$$\text{z\textit{o}de: } i \{1 \dots m\} \quad (8)$$

Similarly to this, usefulness function is calculated $Q^k = \{Q^k_1 \dots Q^k_m\}$ of the criteria \tilde{a} for the alternative $A \{A_1 \dots A_m\}$. With that, the aggregation of the basic criteria \tilde{a}_{ij} is done according to the formula 1.

For the purpose of planning of optimal decisions of distribution channels participants, the following formula is used (9):

$$A^* \rightarrow A_{\text{проект}}^* = f(A_{\text{исх}, \tau, \varphi, \omega}^*) \quad (9)$$

where: $A_{\text{проект}}^*$ - projected alternative;

$A_{\text{исх}}^*$ - initial alternative;

τ, φ, ω – time and financial resources, etc.

With the help of formula 9 it is possible to design requirements parity for the near future, for example, if one of the participants intends to significantly change the vector of his interest.

Conclusions

The following conclusions can be made as a result of the case study:

- Spirits quality attributes that are considered by consumers during the evaluation of available variety of purchase options have been identified and systematized; coefficients of their significance have been estimated;
- The largest impact on consumer evaluation of product quality is rendered by such factors as deep assortment, positive experience of the previous purchase, retail price, purchase conditions, lack of adverse impact on the human body, packing exterior, flavor etc;
- A multi-attributive model of consumer assessment of vodka quality has been developed with quality function deployment in which rational attributes (retail price) are combined with irrational (non-price quality attributes) in 1:9 ratio. This being said, external value attributes of spirits dominate over internal. Appraisal of the model was done during the case study;
- The fact of consumer choice of specific stock keeping unit of spirits from the sum-total variety of similar proposal in its essence implies a higher consumer evaluation of its quality as compared to other market alternatives;
- The process of consumer assessment of vodka quality in the point of sale involves identification of some aggregate of external attributes, which allows to compare cumulative assessment of various stock keeping units of the similar price level based on their capacity to satisfy the most significant current requirement;
- Satisfaction of these requirements which include various life values such as security, comfort, hedonism, (satisfaction), dominancy (image support), sociality (demonstration of belonging to the specific social group), cognitivity (knowledge of the world) and, finally, cost effectiveness, in essence illustrates usefulness degree of spirits;
- Multi-attributive model of spirits quality which implies quality function deployment from the consumer point of view, describes not only the satisfaction of individual consumer requirements, but also consumer self-identification in specific social environment;
- Combination of multi-attributive model with quality function deployment and a focus group method will allow manufacturers and retailers to forecast consumer assessment of spirits quality in points of sale;

- The interests of various channel participants are often in conflict – the interests of one of the participants are ensured at the expense of the infringement of interests of the others;
- Model of requirements parity of various participants of the distribution channel has been developed. The model took into consideration various diverse requirements of manufacturers, agents, vodka sellers as well as consumers, society and government;
- Introduction of the multi-attributive model of consumer assessment of spirits quality in points of sale with quality function deployment allows to enhance consumer integral evaluation of spirits quality, while retailers will experience the increase of turnover, if measured in monetary units, and decrease – in case of the physical count with growth of profitability of sales.

Acknowledgments

The authors are grateful for the participation at various stages of this study Andrey Kazantsev and Elena Mazanko, who worked at the Department of Commodity and Quality Management in the Kemerovo University Food Science & Technology as candidates for a degree.

References

- Kaplan, R.S. and D.P. Norton, 1996. The Balanced Scorecard: Translating Strategy into Action. Boston (Ma., USA): Harvard Business School Press.
- Киселев, В.М., 2005. Конкурентоспособность продовольственных товаров. Пищевая промышленность, 1: 10-11.
- Савчук, С.И., 2004. О смешении понятий качества и конкурентоспособности продукции в теории конкуренции и экономике качества. Маркетинг в России и за рубежом, 3: 131-139.
- Воронов, А. и К. Гусько, 2005. Брэнд и качество продукции в модели принятия решения о покупке коньяка. Практический маркетинг, 8: 24-29.
- Russian Consumer Study: Купцы, 2003. Индустрия рекламы, 18: 14-17.
- Russian Consumer Study: Казак, 2003. Индустрия рекламы, 19: 12-14.
- Russian Consumer Study: Бизнесмен, 2003. Индустрия рекламы, 20: 26-29.
- Russian Consumer Study: Студент, 2003. Индустрия рекламы, 21: 20-22.
- Russian Consumer Study: Русская душа, 2003. Индустрия рекламы, 22: 16-18.

ASSESSMENT OF OXIDATIVE STABILITY OF RAPESEED AND SUNFLOWER OILS

Elżbieta Kondratowicz-Pietruszka

*Department of Chemistry, Faculty of Commodity Science,
Cracow University of Economics,
kondrate@uek.krakow.pl*

Introduction

Fats are one of the key nutrients and perform a number of various roles in a human body, inter alia, they are a source of energy for tissues and organs, improve taste qualities of food, and build cell membranes. Fats are indispensable in a diet; however, their impact on human health varies. Vegetable oils are rich in various fatty acids, including monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) (Ostasz, Kondratowicz-Pietruszka 2011).

For health reasons, it is recommended to consume oils with low content of saturated fatty acids (SFA) and high content of unsaturated fatty acids (UFA). It has been determined that saturated fatty acids contribute to the increase of the amount of cholesterol in blood and that they increase the risk of atherosclerosis and of cardiovascular diseases. Unsaturated fatty acids (UFA), both monounsaturated (MUFA) and polyunsaturated (PUFA), protect humans from cardiovascular diseases (Amaral et al. 2003). Depending on the type of oil, the ratio between the content of PUFA polyene acids and MUFA monoene acids vary (Kondratowicz-Pietruszka 2010).

Edible vegetable oils are produced from various plants. The most common oil plants in Poland are rape and sunflower. The quality of vegetable oils depends on various factors, including their chemical composition. It is affected by the type of oil plant, conditions of cultivation, and technological processes deployed (Mińkowski, Grzeńkiewicz, Jerzewska 2011). Oils are traded either as refined or cold pressed. Due to cold pressing, without access of light and air, oils retain their qualities and biological activeness. Necessary unsaturated fatty acids are not subject to decomposition, while oils retain in full their nutrition values (Kondratowicz-Pietruszka 2012).

Edible oils are a source of necessary unsaturated fatty acids. A basic form of necessary UFA of the n-3 series is α -linoleic acid (18:3, n-3) while of the

n-6 series - gamma-linoleic acid (18:2, n-6). Since α -linoleic and linoleic acid are synthesised by plants, they must be ingested by humans in food.

The proportion between necessary fatty acids of the n-6 series and of the n-3 series in daily intake of food is important for human development and health. This proportion should approximate 1, although some authors claim that it should be between 4 and 1. Current publications on healthy nutrition give the border values between 4:1 and 1:1. The amount of the n-3 series fats in the present-day diet is limited, while of the n-6 series - excessive. This results in immunological imbalance and extensive tendency to develop inflammations.

The key factors affecting the dynamics of oxidation changes in oils include: fatty acids profile and contents of accompanying substances (Szukalska 2003). Oxidative stability of oils can be assessed in various ways (Wroniak, Łubian 2008, Zarena, Sankar 2009, Abramowic, Butinar, Nikolic 2007). Methods applied to analyse oxidation changes include, inter alia: gas chromatography, titration methods - including determination of peroxide value, anisidine value and Totox value. Stability of oils can be determined with the use of FRAP and of DPPH ratios (Kruszewski et al. 2013, Amaral et al. 2003).

The objective of the tests was to present acid profile of selected vegetable oils, their anti-oxidant activity, overall anti-oxidant power, and content of polyphenols.

Material and methods

The objects of the tests were the following oils: cold pressed rapeseed oil - from ecological and non-ecological cultivation and refined rapeseed oil; cold-pressed sunflower oil, from ecological and non-ecological cultivation and refined sunflower oil. The samples were marked as follows:

- A - cold-pressed rapeseed oil from ecological cultivation ECO, packaging: dark glass
- B - cold-pressed rapeseed oil, packaging: PET,
- C - refined rapeseed oil, packaging: PET,
- D - cold-pressed sunflower oil from ecological cultivation, packaging: clear glass,
- E - cold-pressed sunflower oil, packaging: PET,
- F - refined sunflower oil, packaging: PET.

Samples of oils for testing were taken after purchase of oils in shops. Chemical parameters, determined in line with the following PN/ISO standards were taken into account during testing of oils: The peroxide value, PV (PN-

EN ISO 3960:2010), The acid value, AcV (PN-EN ISO 660:2010), The iodine value, IV (PN-EN ISO 3961:2011), The anisidine value, AnV (PN-EN ISO 6885:2008), Totox value, ($\text{Totox}=2 \cdot \text{PV}+\text{AnV}$), (PN-93 A-86926:1996).

The peroxide value, PV. The value is determined by the reaction of peroxide in a fat sample with potassium iodide, KI, which is oxidised to free iodine. The liberated iodine is titrated with standard sodium thiosulphate (VI) $\text{Na}_2\text{S}_2\text{O}_3$ and the peroxide value is expressed in (mEq O_2/kg fat).

The anisidine value, AnV. This is determined based on the reaction of aldehydes present in a fat sample with a solution of p-anisidine and spectrophotometric measurement of absorbance of the solution at a wavelength of 350nm.

The acid value, AcV. Determination is based on the neutralisation of free fatty acids in a fat sample with a standard solution of potassium hydroxide, KOH. The acid value is expressed in (mg KOH/g fat).

The iodine value, IV. It is determined by binding halogens *IBr* to the double bonds of unsaturated fatty acids. Excess halogen causes the oxidation of potassium iodide, KI, to free iodine I_2 , which is titrated with standard sodium thiosulphate (VI) $\text{Na}_2\text{S}_2\text{O}_3$ sodium. Iodine number is expressed in (g $\text{I}_2/100$ g fat).

Based on the analysis of changes in peroxide value, oxidation changes were noticed, taking place in rapeseed and sunflower oils during storage for 33 days in the temperature of 24°C , with access of dispersed light. The intention was to create conditions resembling typical household storage conditions.

Acid profile of the tested oils was analysed. The content of fatty acids in all samples was determined by means of gas chromatography, in line with the norm (PN-EN ISO 5508:1996), in the form of methyl esters in samples prepared in line with the norm PN-EN ISO (12966-2:2011), with the use of BF_3 . The analysis was performed with the use of gas chromatograph SRI 9610C with Restek RTX-2330 column of a length of 105 m and diameter of 0.25 mm, with FID detector, using hydrogen as carrier gas. Used as a quantitative template was AOCS Standard #3 by Restek, Cat. No 35024. Additional template used for identification of components was *Food Industry FAME Mix Cat. No 35077* by Restek, being a mixture of methyl esters of 37 fatty acids from C:4 to C:24.

Antioxidant power was determined with the use of FRAM method (μmol Fe/g oil) (Ferric Reducing-Antioxidant Power) described by Benzi and Strain (Benzie, Strain 1996). The method is based on the reduction of ferric ions III, present in the combination with tripyridylostriasine (TPTZ) to ferric ions II. Methanol extracts were prepared for each of oils tested, by shaking samples for an hour. Double-stage extraction was used. Methanol extracts so obtained were poured into containers for storage until analysis. The results were

calculated, based on the template curve. The analyses were performed with the use of UV-VIS spectrophotometer by UNICAM.

To evaluate total anti-oxidative power of DPPH (% inhibition), the method using solution of a free radical 2,2-diphenylpicrylhydrazyl DPPH was used, described by Zych and co. (Zych, Krzepińko 2010). The analysis was performed with the use of UV-VIS spectrophotometer by UNICAM. The results were calculated based on the template curve.

In order to determine the total content of polyphenols by means of spectrophotometer, the method described by Singleton and Silinkard, with minor modifications, was used (Singleton et Rossi 1965). Folin-Ciocalteu reagent was used, being a mixture of phosphomolybdic acid ($H_3PMO_{12}O_{40}$) and phosphowoframic acid ($H_3PW_{12}O_{40}$). These components cause oxidation of phenols and simultaneous reduction to blue molybdenum oxides (Mo_8O_{23}) and wolfram oxides (W_8O_{23}), which absorb radiation of a wave length of $\lambda=760$ nm. The basis for determination is the ratio between the absorbency value and the concentration of polyphenols. The content of polyphenols is in direct proportion to absorbency measured at a wave length of $\lambda=760$ nm. The analysis was performed with the use of UV-VIS spectrophotometer by UNICAM. The results were calculated based on the template curve.

Results and discussion

Table 1 presents characteristic values, including the acid value AcV, iodine value IV, anisidine value AnV, peroxide value PV (PV 0, PV 33 – initial and after 33 days of storage peroxide value) and Totox value of the tested oils.

Table 1. Characteristic values of tested oils

oil	AcV mgKOH/g	IV g I ₂ /100g	AnV	PV 0 mEq O ₂ /kg	PV 33 mEq O ₂ /kg	Totox mEq O ₂ /kg
A	2.07	73	0.71	3.49	5.90	7.69
B	0.51	127	0.86	3.85	5.39	8.56
C	0.24	76	1.10	1.37	2.95	3.84
D	1.05	97	0.93	4.77	7.23	10.47
E	0.67	143	1.33	4.48	6.19	10.29
F	0.16	107	0.72	1.38	2.22	3.48

Source: own work.

Cold-pressed values are characterised by higher initial peroxide value than refined oils. During the storage of rapeseed and sunflower oil samples, the peroxide value was subject to acceleration and increase. These processes are characterised by low dynamics of changes and small increases of ΔPV .

Peroxide value in these conditions of storage of oils does not exceed the value of 5 mEq O₂/kg for refined oils (Oils marked C and F). In the case of cold-pressed oils PV exceeds 5 mEq O₂/kg. Also interesting is the fact that the type of oil does not significantly affect the oxidation processes in the tested oils. This is best depicted in the obtained curves presented in Fig. 1.

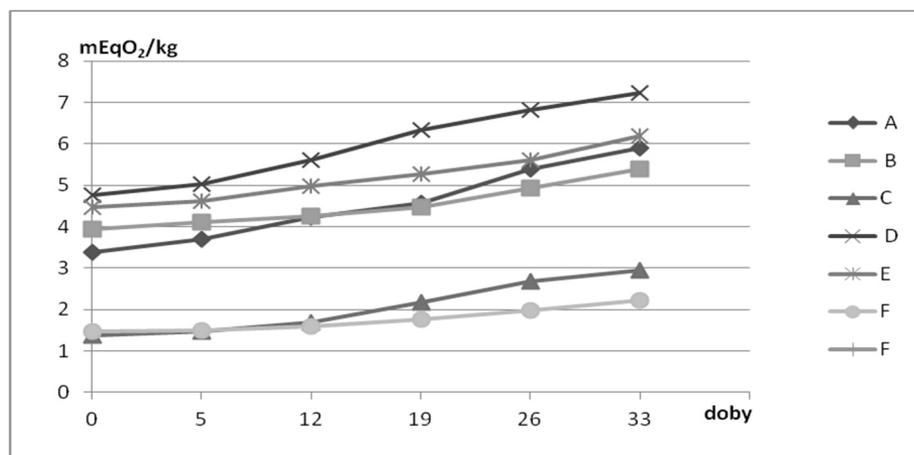


Figure 1. Contents of SFA acids in the tested oils

Source: own work.

Changes in the peroxide value during storage of all samples are described in the first approximation by means of aw-type first-order function. For the order $n=1$ aw, the formula for the rate constant of the change of peroxide value w_1 is as follows:

$$w_1 = \frac{1}{t} \ln \frac{PV(t)}{PV(0)} \quad (\text{PV} \cdot \text{t}^{-1})$$

where: t - time

$PV(0)$, $PV(t)$ – peroxide value - initial and after t time.

General form of the descriptive function, for all samples, is as follows:

$$P\hat{V}(t) = PV(0)e^{w_1 t} \quad (\text{mEq O}_2/\text{kg})$$

Matching error for the aw type function is expressed as e_m . E_m is the deviation of theoretical value $P\hat{V}(t)$ from the empirical $PV(t)$. It is assumed that when the value $e_m < 5\%$, the description of the set of empirical data by means of the proposed function is very precise.

$$e_m = \left| \frac{PV(t) - P\hat{V}(t)}{P\hat{V}(t)} \right| 100 \quad (\%)$$

The results of the calculations are presented in Table 2.

Table 2. The rate constant of the change of peroxide value w_1 and descriptive function

oil	w_1 (PV · t ⁻¹)	Descriptive Function (mEq O ₂ /kg)	e_m (%)
A	$14.823 \cdot 10^{-3}$	$P\hat{V}(t) = 3,49 e^{0,014823 \cdot t}$	2.23
B	$9.701 \cdot 10^{-3}$	$P\hat{V}(t) = 3,85 e^{0,009701 \cdot t}$	1.41
C	$21.054 \cdot 10^{-3}$	$P\hat{V}(t) = 1,37 e^{0,021054 \cdot t}$	4.23
D	$13.235 \cdot 10^{-3}$	$P\hat{V}(t) = 4,77 e^{0,013235 \cdot t}$	1.48
E	$8.287 \cdot 10^{-3}$	$P\hat{V}(t) = 4,48 e^{0,008287 \cdot t}$	1.40
F	$13,640 \cdot 10^{-3}$	$P\hat{V}(t) = 1,38 e^{0,013640 \cdot t}$	1.45

Source: own work.

The calculated e_m values reflect the fact that the function of the order $n=1$ law describes with high precision changes in the peroxide value of the oils stored. In order to compare the dynamics of the process of changes in the peroxide value, the rate constants of the processes in affine relation should be compared K_Y^X . The processes can be compared only if their respective w_n are identical. In the case of a common order, in this case $n=1$ law, the dynamics of the processes taking place can be compared.

$$K_Y^X = \frac{w_{1,X}}{w_{1,Y}}$$

The ratio K_Y^X defines how many times the process X is faster than process Y. The oxidation process was the fastest in the refined rapeseed oil C, which is confirmed by the value of reaction rate constant w_1 . Similar dynamics of the process was observed in the following oils: cold-pressed rapeseed oil from ecological cultivation A, cold-pressed sunflower oil from ecological cultivation D, refined sunflower oil F. The process of oxidation was the slowest in: cold-pressed rapeseed oil from non-ecological cultivation B, cold-pressed sunflower oil from non-ecological cultivation E. The process C was, on average, 1.5 times faster than the processes A, D, and F and 2-3 times faster than the processes B and E.

Determination of PV and AV enabled additional determination of Totox value which is used to assess oil oxidation level. The Totox value ranged considerably between the initial value of 3.48 for F sample to 10.47 for D sample. It is assumed that the border value of Totox for good quality edible oils is 10. As regards the tested oils, after 33 days of storage, the Totox value of 10 was exceeded in the samples D and E.

The chromatographic analyses performed produced fatty oils profile for the tested oils, presented in table 3.

Table 3. Fatty acids profile in the tested oils, % (m/m)

Kwasy tłuszczowe	A	B	C	D	E	F
C 16:0	5.51	4.81	6.31	8.20	9.80	9.94
C 16:1 (cis-9)	0.64	0.41	0.43	-	-	-
C 18:0	1.66	1.83	1.58	2.57	3.46	3.29
C 18:1 (cis-9)	65.74	66.14	61.20	32.60	22.80	23.02
C 18:2 (cis-9,12)	19.51	17.21	19.65	56.62	63.94	63.74
C 18:3 (cis-6,9,12)	0.45	0.47	0.36	-	-	-
C 18:3 (cis-9,12,15)	6.48	9.12	9.72	-	-	-
C 20:0	-	-	0.27	-	-	-
C 20:3 (cis-8,11,14)	-	-	0.27	-	-	-
C 20:3 (cis-11,14,17)	-	-	0.20	-	-	-

Source: own work.

All tested pressed and refined oils contain saturated acids C16:0 and C18:0. Their contents, however, vary depending on the type of oil. The chromatographic analyses confirmed low contents of saturated fatty acids SFA in rapeseed oils, ranging between 6.64% and 8.16%. Sunflower oils are slightly richer in saturated fatty acids SFA, with the contents between 10.77-13.26% (Fig. 2). Relative error in determining the contents of C:16 and C:18 acids was 3.7%.

The contents of monoene MUFA in the tested oils vary. Rapeseed oils containing 61.63 - 66.65% of MUFA are close in the classification to the group of oils with high degree of these acids. Currently, rapeseed oils intended for consumption are manufactured in Poland mainly from low erucic varieties, containing up to 2% of erucic acid (C22:1 (cis-13)), which was confirmed by the chromatographic analysis (0.0%) performed during the tests, with the

relative error of determination of 0.1%. As regards sunflower oils, they contain considerably less MUFA - between 22.80 and 32.60 % (Fig. 3).

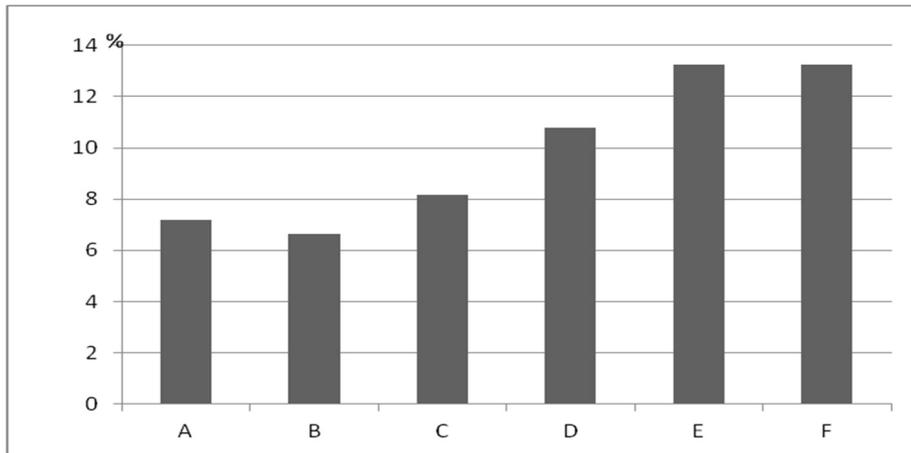


Figure 2. Contents of SFA acids in the tested oils

Source: own work.

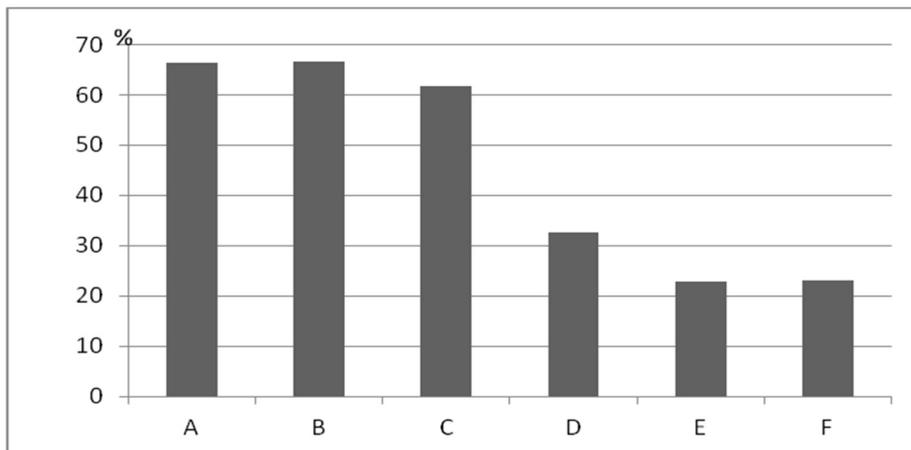


Figure 3. Contents of MUFA acids in the tested oils

Source: own work.

Acid C 18:2 (cis-9,12) affects the level of PUFA contents in the tested oils. The contents of PUFA vary considerably, from 17.21% for rapeseed oil to approx. 63.94% for sunflower oil (Fig.4). Average relative error in determination of the contents of PUFA was 1.6%.

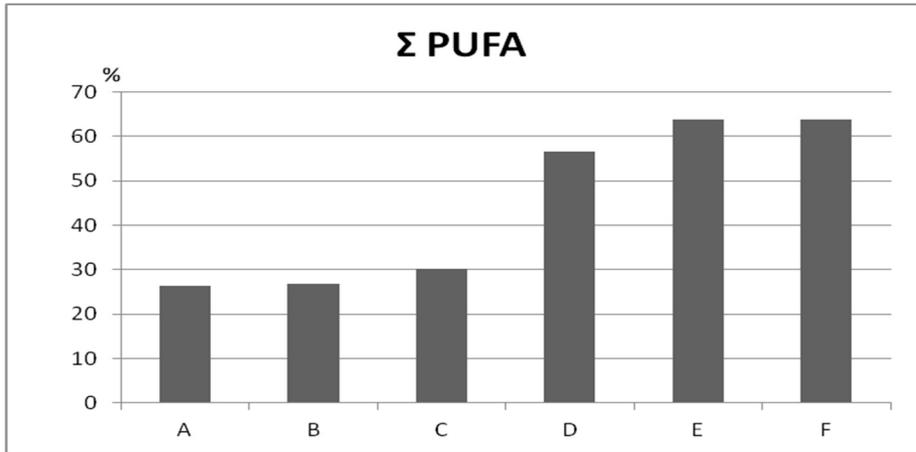


Figure 4. Contents of SFA acids in the tested oils

Source: own work.

As regards nutrition value of oils, the contents of unsaturated fatty acids UFA is important. The highest concentration of unsaturated fatty acids in the rapeseed oil is approx. 93%, while in the sunflower oils - approx. 87%. The calculated relations between unsaturated (UFA) and saturated (SFA) fatty oils in individual tested oils vary. They range from 11.25 for sample C sample to 14.06 for sample B. As regards sunflower oils, the UFA/SFA ratio was 6.54 to 8.28. This ratio does not allow for differentiating between pressed and refined oils or between ecological and non-ecological cultivation oils.

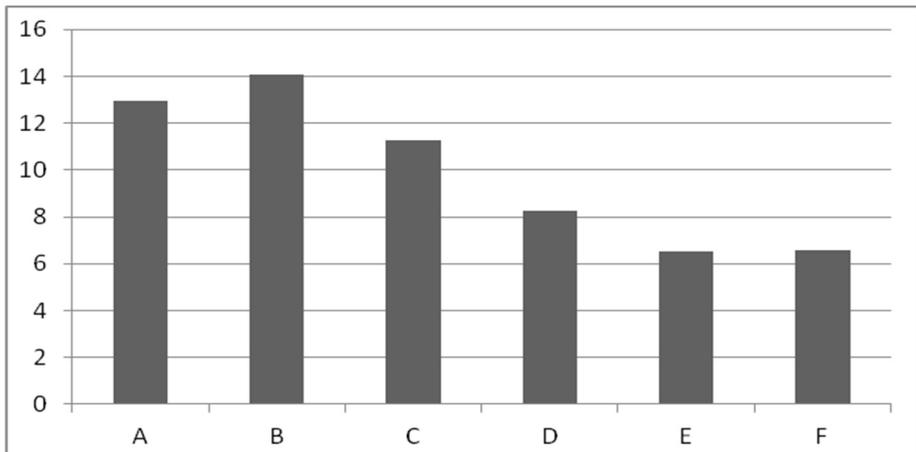


Figure 5. ΣUFA/ΣSFA ratio in tested oils

Source: own work.

Σ PUFA/ Σ MUFA ratio in tested oils ranges between 0.4 and 0.49. Greater diversity was observed in sunflower oils, ranging between 1.74 and 2.80. The calculated values for Σ PUFA/ Σ MUFA ratio are presented in (Fig.6).

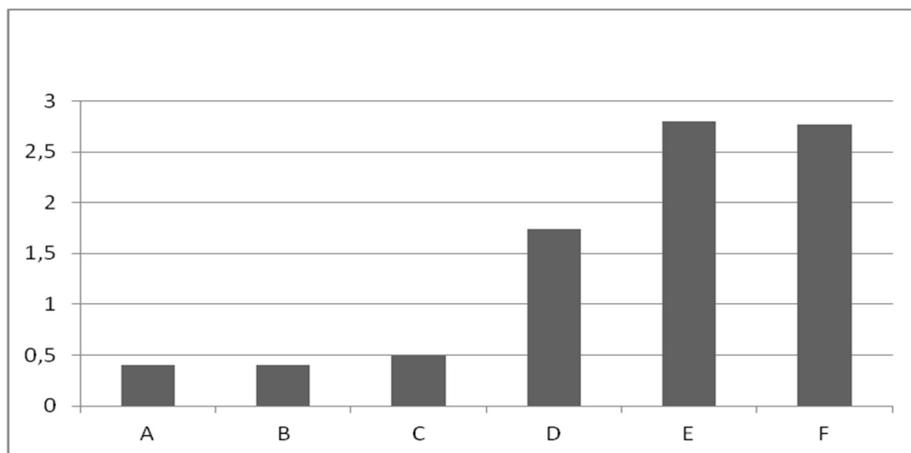


Figure 6. Σ PUFA/ Σ MUFA ratio in tested oils

Source: own work.

C 18:2 (cis-9,12)/ C 18:3 (cis-9,12,15) relation values can be calculated only for rapeseed oils. The values calculated for the n-6 and n-3 acids ratio are: A = 3:1, B = 2:1, C = 2:1, respectively.

DPPH values in the oils are similar. The highest value of 2.567(μ mol Fe/g of oil) for FRAP was calculated for sample C. This means that refined rapeseed oil has the greatest antioxidant power among all tested oils.

Table 4. Antioxidant power and concentration of polyphenols

oil	DPPH (% of inhibition)				FRAP (μ mol Fe/g)	Polyphenols g gallic acid /100 g
	15 min.	30 min.	60 min.	24 h		
A	0.615	0.596	0.593	0.380	1.002	0.160
B	0.619	0.599	0.589	0.385	0.350	0.120
C	0.587	0.569	0.544	0.362	2.567	0.346
D	0.622	0.595	0.576	0.381	0.683	0.117
E	0.623	0.612	0.598	0.405	0.800	0.122
F	0.610	0.611	0.590	0.398	0.430	0.162

Source: own work.

The content of polyphenols was determined with the use of spectrophotometer. The concentration of polyphenols is in direct proportion

to absorbency measured at a wave length of $\lambda = 760$ nm. The template curve was prepared using a solution of gallic acid at a concentration of 0.3 g/dm^3 . The relation between absorbency and concentration was described by means of the equation: $y = 0.1245x - 0.0024$, $R^2 = 0.9936$. The calculation results are the evidence of low content of polyphenols in the tested oils (Tab.4).

Conclusions

Changes in the peroxide value in the stored oils are very-well described by the function of the order $n+1$ law. This is confirmed by calculated error values as regards deviation of the empirical values from theoretical values $e_m =$ from 1.40% to 4.23%. The oxidation process was the fastest in the refined rapeseed oil, which is conformed in the value of reaction rate constant $w_1 = 21.054 \cdot 10^{-3}$. The process was, on average, 1.5 times faster than in the case of pressed rapeseed and sunflower oils from ecological cultivation and in the refined sunflower oil, and 2-3 times faster than in the case of presses rapeseed and sunflower oils from non-ecological cultivation.

As regards pressed sunflower oils, after 33 days of storage, the Totox value of 10 was exceeded, which is a sign of low resistance to oxidation characteristic for sunflower oils.

The contents of monoene acids in the tested oils varied considerably, from between 61.63% and 66.65% in rapeseed oils to between 22.80% and 32.60% in sunflower oils.

The calculated UFA/SFA ratio in individual types of oil vary. The values are higher (between 11.25 and 14.06) in rapeseed oils and slightly lower (between 6.54 and 8.28) in sunflower oils. This relation does not allow for differentiating between pressed and refined oils or between ecological and non-ecological cultivation oils.

The contents of polyene acids in sunflower oils are approximately two times bigger than in rapeseed oils. Sunflower oil is rich in linoleic acid while rapeseed oil contains both linoleic and α -linoleic acids in proportions very beneficial for humans, approximately 2:1.

Based on the results of the tests, it was determined that the oils are not rich in polyphenols, nor are they highly anti-oxidant.

References

Amaral J.S., Casal S., Pereira J.A., Seabra R.M., Oliveira B.P., 2003, Determination of sterol and fatty acid compositions, oxidative stability, and nutritional value of six walnut (*Juglans regia* L.) cultivars grown in Portugal, *Journal of Agricultural Food Chemistry*, 51, 7698 – 7702.

- Abramowic H., Butinar B., Nikolic V., 2007, Changes Occurring In Phenolic Content, Tocopherol Composition and Oxidative Stability of Camelina Sativa Oil during Storage, *Food Chemistry*, 104, 903 – 909.
- Benzie I.F., Strain J.J., 1996, The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power" the FRAP assay, *Anal Biochem*, 239(1), 70-76.
- Kondratowicz-Pietruszka E., 2012, *Kwasy tłuszczowe wybranych olejów roślinnych tłoczonych na zimno*, *Zeszyty Naukowe*, UEK, 899, 27 - 46.
- Kondratowicz-Pietruszka E., 2010, *Charakterystyka profilu kwasów tłuszczowych wybranych olejów roślinnych*, *Zeszyty Naukowe*, UEK, 841, 49 - 63.
- Kondratowicz-Pietruszka E., 2007, *The analysis of oxidative changes occurring in olive oil during storage*, *Polish Journal of Food and Nutrition Sciences*, 57, 4(B), 297-302.
- Kruszewski B., Fąfara P., Ratusz K., Obiedziński M., 2013, *Ocena pojemności przeciwutleniającej i stabilności oksydacyjnej wybranych olejów roślinnych*, *Zeszyty Problemowe Postępów Nauk Rolniczych*, nr 572, 43-52.
- Mińkowski K., Grześkiewicz S., Jerzewska M., 2011, *Ocena wartości odżywczej olejów roślinnych o dużej zawartości kwasów linolenowych na podstawie składu kwasów tłuszczowych, tokoferoli i steroli*. *Żywność. Nauka. Technologia. Jakość*, 2 (75), 124 – 135.
- Ostasz L., Kondratowicz-Pietruszka E., 2011, *Charakterystyka kwasów tłuszczowych omega – 3 oraz ocena poziomu wiedzy o ich działaniu zdrowotnym*, *Zeszyty Naukowe Towaroznawstwo*, UEK, 874, 139 - 161.
- PN-EN ISO 3960:2010, *Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby nadtlenkowej*;
- PN-EN ISO 6885:2008, *Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby anizydynowej*;
- PN-93 A-86926:1996 *Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby anizydynowej oraz obliczanie wskaźnika oksydacji tłuszczu Totox*;
- PN-EN ISO 660:2010, *Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby kwasowej*;
- PN-ISO 3961:2011, *Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby jodowej*;
- PN-EN ISO 5508:1996, *Oznaczanie składu kwasów tłuszczowych*;
- PN-EN ISO 12966-2:2011, *Analiza estrów metylowych kwasów tłuszczowych metodą chromatografii gazowej*.
- Singleton V.L., Rossi J.A., 1965, Colorimetry of total phenolics with phosphomolybdic acid reagents. *Am. J. Enol. Vitic.*, 16, 144-158.
- Szukalska E., 2003, *Wybrane zagadnienia utleniania tłuszczów*, *Tłuszcze Jadalne*, 38, 42-61.

Wroniak M., Łubian M., 2008, Ocena stabilności oksydacyjnej olejów rzepakowego i słonecznikowego tłoczonych na zimno z dodatkiem ekstraktu z oregano w teście Rancimat i termostatowym, 4(59), 80-89.

Zagrodzki P., Starek A., 2012, *Dietetyczne znaczenie olejów roślinnych*, Bromatologia. Chemia Toksykologiczna, XLV, 1175 – 1182.

Zarena A.S., Sankar K.U., 2009, *A study of antioxidant properties from Garcinia mangostana L. pericarp extract.*, Acta Sci.Pol., Technol. Aliment. 8 (1), 23-34.

Zych I., Krzepiło A., 2010, Pomiar całkowitej zdolności antyoksydacyjnej wybranych antyoksydantów i naparów metodą redukcji rodnika DPPH. Chem. Dydak. Ekol. Metrol., 15(1), 51-54.

QUALITY EVALUATION OF ACID CURD CHEESES (TVAROGS) AVAILABLE ON LUBLIN MARKET

**Jolanta Król¹, Anna Litwińczuk¹, Monika Kędzierska-Matysek¹,
Aneta Brodziak²**

*¹Department of Commodity Science and Processing
of Raw Animal Materials,*

*²Department of Breeding and Protection of Genetic Resources of Cattle,
University of Life Sciences in Lublin,
jolanta.krol@up.lublin.pl*

Introduction

Curd cheeses are recognized as one of the oldest dairy products. They were invented about 10000 years ago by Mesopotamian shepherds who poured milk into bags prepared from sheep stomachs. Accelerated by rennet milk divided itself into curd and whey (Górska 2014). In turn, Smithers (2008) reports that cheese was known about 3000 years ago in times when calf stomachs were used to store and transport milk and natural enzymes included in it (i.e. rennet) caused coagulation, thus turning the material into curd and whey. Curd cheese production dates back to about 3000 BC and its evidence can be found on Sumerian carvings which present particular stages of cheese production. It is said that curd cheese was also a renowned and valued product in Babylonia, yet because of its high prize it was available only to few connoisseurs. The beginnings of home production of cheese on a wider scale were connected with domestication and farming of horned animals (Górska 2014). Curd cheeses, known as tvarogs, include both acid cheeses and acid-rennet cheeses. The basis for the production of these cheeses is acid coagulation which results from oriented lactic acid fermentation, occurring after adding lactic acid fermenting bacteria or lactic acid-rennet fermenting bacteria to milk, accompanied by a simultaneous activity of lactic acid fermenting bacteria and the coagulating enzyme.

Acid curd cheeses, also called “white cheeses”, are highly popular among consumers due to a long tradition of their consumption, eating habits and a low price (Gołąbek 2011; Górska-Warsewicz 2005). Depending on fat content in dry matter tvarogs can be divided into: cream – containing 55±2% of fat in dry matter (14.5% in total) and up to 74% of water, full-fat – containing 42±2% of fat in dry matter (9.5% in total) and up to 77% of water, fat –

containing $30\pm 2\%$ of fat in dry matter (6.5% in total) and up to 79% of water, semi-skimmed – containing $15\pm 2\%$ of fat in dry matter (3% in total) and up to 82% of water and skimmed – containing not standardized fat content and up to 84% of water. In each group of cheeses we can distinguish wedge cheeses and sliced cottage cheeses. It is difficult to find an equivalent of “white cheese” in the world. To some extent the American farmers pressed cheese and the German quark can be treated as its equivalent (Siemianowski et al. 2011).

Similarly to milk, curd cheeses (tvarogs) are characterised by a high nutritional value but, unlike milk, they have a bigger concentration of nutritional ingredients. First of all, they contain concentrated protein, particularly casein (in the form of calcium phosphoparacaseinate), and amino acids, fatty acids and vitamins. They are also a source of mineral salts, mainly calcium of high bioavailability (Kolanowski 2000; Szpendowski et al. 2005; Marszałkowska-Jakubik 2011; Igras 2012). Unfortunately, compared with ripening cheeses tvarogs contain about 8 to 10 times less calcium. Losses arise due to draining of whey which absorbs this component. The calcium content can be increased by adding some enriching substances or introducing changes in the technology process. Moreover, the more skimmed the cheese is the more calcium it contains (Marszałkowska-Jakubik 2011).

Curd cheese market in Poland

Cheeses are now one of the most important groups of dairy products in Poland. For many years consumers have perceived tvarogs and curd cheeses as attractive products, therefore these cheeses have a firm position on the dairy products market. In recent years the national production of curd cheeses maintained at the level of over 300 thousand tons and showed a growing tendency which results from bigger supplies of this product to dairies and sustained demand for dairy products. This is proved by the increased production of curd cheeses throughout years 2006-2012 by 27.6 pp, that is the rise from 302,4 thousand tons in 2006 to 385,8 thousand tons in 2012. To produce cheeses, including tvarogs, almost half out of 12,7 million tons of the total amount of cow milk obtained in 2012 in Poland was used. In 2013 there was also an increase in the production of milk for consumption (i.e. by 4.9% as compared with the previous year) and cheeses (by 3.2%), including tvarogs – by 4.6% (Siemianowski et al. 2011, IERiGiŻ-PIB 2013). Tvarogs are offered by most of national dairies, therefore each producer has to monitor the market and adjust their product range to the needs of more and more demanding customers. Producers resign from traditional tvarogs sold by weight and focus on confectionery and introducing innovations connected both with the product (flavoured, ecological, functional and culinary tvarogs) and packaging (resealable packaging systems). According to IERiGiŻ-PIB

(2013) in Polish households the average annual consumption of curd cheeses in 2012 amounted to 6.60 kg per person and was lower by 1.8 pp as compared with the previous year. As quoted by Bohdziewicz and Śmietana (2007) and Bohdziewicz (2009) about 1/5 of all the expenses for dairy products purchased by an average household are connected with the purchase of curd cheeses. The biggest amount of cheese was consumed by pensioners (0.7 kg per person per month on average) (IERiGiŻ-PIB 2013). Uniqueness and a high quality of Polish dairy products resulted in 130 thousand tons of cheeses and 47 thousand tons of tvarogs being exported from Poland in 2012 (Śmigielska 2013).

Production technology

Acid curd cheeses are produced by proper processing of curd which is formed as a result of acidification of lactic acid fermenting bacteria up to the value of the isoelectric point of casein (pH=4.6). Particular stages of cheese production are presented in scheme 1.

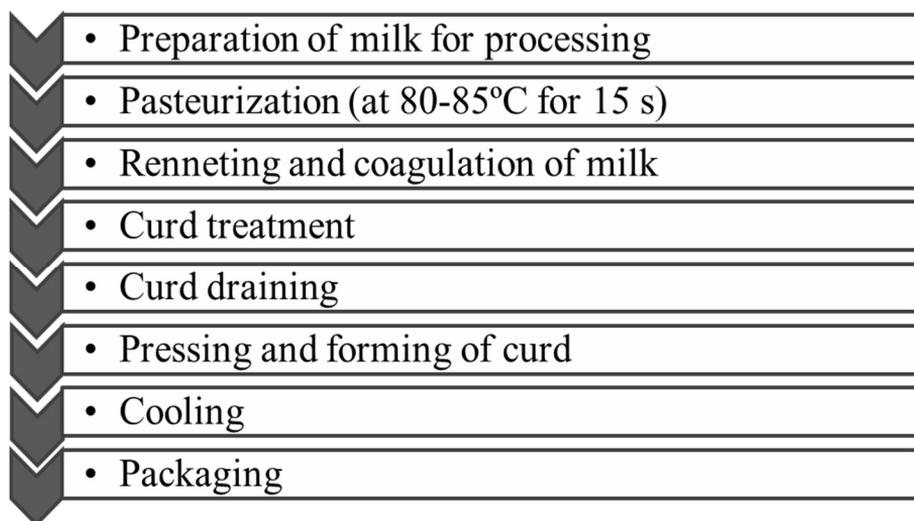


Figure 1. Production technology of acid curd cheeses

Source: own work based on Litwińczuk 2012

Raw material, compliant with applicable standards for milk purchasing, is subjected to pre-treatment. After heating up to 45°C the milk is centrifugated and standardized in order to obtain the required content of fat. After standardization it is subjected to pasteurization at 80-85°C for 15 s. Next, the thus prepared material is chilled to 20-26°C, then the sourdough of 0.5-2.5% of lactic acid producing cultures is added and the material is left for 12-16

hours for curd to be formed. Acid coagulation lasts until it reaches a pH of 4.5-4.6. In such conditions the electric charge of casein micelles equals zero, they no longer have the ability to bind water and lose their hydration shell, which in turn leads to aggregation and formation of curd. Mature curd should characterize by titration acidity of 32-34 °SH, jelly consistency, it should not have any cracks and slits or produce whey, whereas after bending it should form a fracture with smooth walls. The next step in processing of curd is cutting it into a cuboid of 12x12cm, stirring it delicately and breaking it into grain-sized granules of 1-5 diameter. While processing there is gradual draining of curd grain and separation of limp whey whose acidity should not exceed 28 °SH (Litwińczuk 2012; Siemianowski, Szpendowski and Bohodziewicz 2011). Draining of cheese mass is carried out with the use of filter materials and perforated forms. The next stage is moulding curd for the purpose of further drainage of cheese mass (Litwińczuk 2012; Siemianowski, Szpendowski and Bohodziewicz 2011). This process should be carried out at 20°C within 2 hours from obtaining cheese of quite firm consistency, moderately paste-like but not greasy, with uniform colour, without smudges and marks. Tvarog is shaped into proper blocks, then cut and cooled down to the temperature below 10°C. Currently there is a considerable progress in production engineering of curd cheeses (scheme 2).

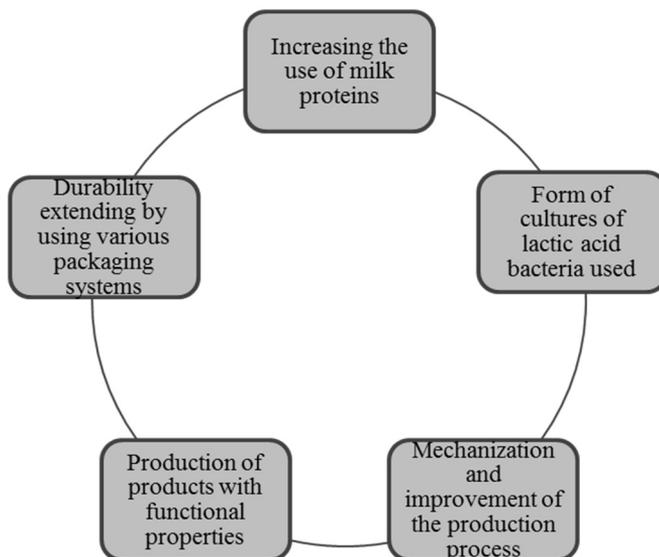


Figure 2. Progress in production technology of acid curd cheeses

Source: own work based on Siemianowski, Szpendowski and Bohodziewicz 2011

One of possible directions of the progress are solutions which allow to add whey proteins to cheese mass. It needs to be emphasised that in the traditional method of tvarog production these proteins come from whey. Thanks to the use of the ultrafiltration method, the serwitowa method (the calcium-thermal method, with the addition of CaCl_2 in the amount of 0.04%) and the addition of whey protein concentrate and transglutaminase it is possible to contain up to 100% of milk proteins in tvarog, as compared to 75% in the traditional method.

Quality requirements

Quality requirements for curd cheeses are specified by Polish Standard PN-A-86300:1991 (table 1). In the production practice most frequently the results of chemical analyses are documented, particularly the content of fat and dry matter. The organoleptic properties of tvarogs are also important, namely colour, structure, consistency, taste and smell. In most cases quality deviations of tvarogs are connected with a bad quality of the raw material or a defective technological process.

Table 1. Requirements for acid curd cheeses

Features	Acid curd cheeses			
	Full-fat	Fat	Semi-skimmed	Skimmed
Taste and smell	clean, mild, a bit sour, with pasteurization aftertaste			
Structure and consistency	uniform, firm, without lumps, a bit loose, a bit grainy is acceptable in the case of skimmed tvarogs			
Colour	White to a bit creamy, uniform in whole mass			
Water content - %, no more than	70	70	73	72-75
Fat content in dry matter - %, no less than	42±3	30±2	15±2	-
Acidity – °SH, not higher than	80	90	100	110

Source: PN-A-86300:1991

The aim of the research was to evaluate the physicochemical quality of acid curd cheeses available in retail sale in Lublin region.

Research material and methods

The research material was curd cheeses purchased in Lublin region, produced by 5 local milk producers associations. For the purpose of testing

they were marked anonymously with letters A, B, C, D and E. Three types of tvarogs were examined: skimmed, semi-skimmed and fat. The cheeses were vacuum packed with the use of parchment and foil paper. The producers declared first class quality on the packages of all the products. Table 2 gives information about the nutritional value of tvarogs which was stated on the labels of the analysed products.

Table 2. Nutritional value of tvarogs (in g/100g) as declared by the producers

Dairy	kJ/kcal	Protein	Carbohydrates	Fat
Skimmed				
A	366/86	18	4.2	0
B	419/98	18	3.5	0.5
C	366/86	18	3.5	0
D	419/98	19.8	3.5	0.5
E	366/86	18	3.5	0
Semi-skimmed				
A	515/122	17	4.6	4
B	517/123	18	3.7	4
C	517/123	18	3.7	4
D	544/129	18.7	3.5	4.5
E	474/113	15.5	3.8	4
Fat				
A	639/153	16	4.2	8
B	-	-	-	-
C	628/150	18	3.5	8
D	714/171	17.7	3.6	9.5
E	606/145	14.5	3.7	8

Source: own work

Three series of research in three types of acid curd cheeses from different production batches (two trials in each series) were performed. Analyses were done during the period of product shelf life. Contents of water (by drying method at temp. 102°C, according to PN-73/A-86232), fat (by Van Gulik's method, according to PN-73/A-86232) and protein (Kjeldahl's method, according to PN-EN/ISO 8968-1:2004) were determined in each samples.

Fat content in dry matter of cheese (X) was calculated according to the formula:

$$X = \frac{a \cdot 100}{100 - w}$$

where: a – percentage of fat, read on the scale of fat meter, w – water content in cheese (%).

The acidity of the acid curd cheeses was determined by measuring the total acidity (in Soxhlet-Hencle degrees – °SH) – by titration method (PN-73/A-86232) and active acidity (pH value) – using digital pH/conductometer CPC-501 (Elmetron) and combined electrodes ERH-12-6. Colour of tvarogs were determined using a portable Minolta Chroma Meter CR-310 (applying illumination D65, geometry 0 projection angle and 50 mm measure area). The results were given in the color space CIE (CIE 1976), where: L* – lightness; a* – redness and b* – yellowness.

The results obtained were analysed statistically using Statistica ver. 6 (Statsoft Inc. 2003), on the basis of one-way analysis of variances. Mean values and standard deviation for certain traits were given in the table. The significance of differences between means for analysed cheeses was estimated by NIR Fisher's test.

Results and discussion

All of the analysed cheeses were compliant with the standards specified by PN as regards distinguishing features of the organoleptic quality. In the produced cheeses with the higher amount of the declared fat content, lower amount of water was noticed (table 3). It needs to be emphasized that all cheeses, with the exception of the skimmed cheese from dairy B, were compliant with standards as regards the content of these two components, that is water and fat. The skimmed cheese from dairy B contained 1.58% of fat and 77.1% of water. Moreover, the tests showed that the majority of cheeses (fat and semi-skimmed cheeses and the skimmed cheese from dairy B) contained the inflated fat content in 100 g of the product as compared with the declared quantity on the label. The biggest “in plus” deviations were noted in products offered by dairies A (2.15 pp) and C (2.61 pp). Also the content of proteins was incompatible with the declared amount, though the highest amount of this component was in cheeses from dairy C (inflated even by 4.26 pp). Protein constitutes the basic ingredient of dry matter in tvarogs. Of all the analysed cheeses semi-skimmed products proved to be the richest in this component – 20.37% on average, with 28.06% of dry matter content. The smallest amount of protein was found in fat cheeses (18.56%), though they contained the biggest amount of dry matter (30.87%). It was connected with the highest percentage of fat in those tvarogs (29.92%). Similarly to our own research, in their analysis of cheeses offered in retail in Lublin region Litwińczuk *et al.* (2003) also obtained the lowest content of proteins in fat cheeses (18.76%), whereas in skimmed cheeses the amount of this component was the highest (19.76%). In turn, the research of Śmietana *et al.* (2003) showed that semi-skimmed tvarogs contained much less dry matter (24.6%), including proteins (17.71%), as compared with our own research. Indicating acidity is one of the basic chemical analyses which are conducted when evaluating the quality of

Table 3. Chemical composition and acidity of the analysed curd cheeses

Dairy		Water (%)	Protein(%)	Fat in dry matter (%)	Fat in 100g of cheese	pH value	Acidity (°SH)
Skimmed							
A	\bar{x}	72.63 ^A	19.23	0.00 ^a	0.00 ^a	4.74	74.10
	SD	0.30	1.72	0.00	0.00	0.08	4.12
B	\bar{x}	77.17 ^B	19.31	1.58 ^b	0.70 ^b	4.54	73.04
	SD	0.82	0.98	0.98	0.44	0.11	8.37
C	\bar{x}	72.58 ^A	20.80	0.00 ^a	0.00 ^a	4.79	72.00
	SD	0.21	1.52	0.00	0.00	0.10	5.82
D	\bar{x}	73.94 ^A	19.24	0.00 ^a	0.00 ^a	4.81	72.00
	SD	1.79	1.88	0.00	0.00	0.03	6.68
E	\bar{x}	74.77 ^{AB}	19.42	0.00 ^a	0.00 ^a	4.57	82.33
	SD	0.06	0.33	0.00	0.00	0.08	3.06
Total		74.80	19.51	0.47	0.21	4.63	74.78
Semi-skimmed							
A	\bar{x}	72.79	19.01 ^a	16.61 ^b	6.15 ^b	4.53	83.63
	SD	1.89	0.63	1.13	0.82	0.07	9.77
B	\bar{x}	72.88	19.21 ^a	17.15 ^c	6.32 ^c	4.62	78.56
	SD	1.26	2.36	1.21	0.25	0.22	6.68
C	\bar{x}	71.15	22.26 ^b	16.10 ^{ab}	5.58 ^{ab}	4.58	87.11
	SD	0.94	1.16	0.75	0.34	0.13	7.06
D	\bar{x}	72.47	19.40 ^a	16.30 ^b	5.92 ^{ab}	4.72	70.00
	SD	1.46	2.36	1.21	0.25	0.22	6.68
E	\bar{x}	71.50	19.32 ^a	14.04 ^a	4.93 ^a	4.48	89.33
	SD	0.51	0.10	0.25	0.18	0.03	3.21
Total		71.94	20.37	16.06	5.75	4.57	83.38
Fat							
A	\bar{x}	68.92	18.21 ^{ab}	30.65 ^B	9.88	4.52	83,24
	SD	1.24	1.63	0.21	0.38	0.11	4,12
B	\bar{x}	-	-	-	-	-	-
	SD	-	-	-	-	-	-
C	\bar{x}	69.05	20.98 ^b	32.83 ^B	10.61	4.64	80.00
	SD	0.84	2.33	0.10	0.28	0.00	0.10
D	\bar{x}	68.74	18.41 ^{ab}	29.26 ^A	9.41	4.80	78.00
	SD	1.81	1.21	1.43	1.00	0.13	10.03
E	\bar{x}	69.98	17.20 ^a	28.31	9.43	4.68	82.00
	SD	0.36	0.15	0.34	0.23	0.00	2.65
Total		69.13	18.56	29.92	9.71	4.73	75.75

a, b – differences significant at $p \leq 0.05$

Source: own work

Table 4. Colour (according to CIE L*a*b*) of analysed acid curd cheeses

Dairy		Colour		
		L*	a*	b*
Skimmed				
A	\bar{x}	90.54	1.51 ^{ab}	3.43 ^a
	SD	1.04	0.25	0.05
B	\bar{x}	91.54	1.26 ^{ab}	5.79 ^{ab}
	SD	1.18	2.37	2.78
C	\bar{x}	93.58	2.51 ^b	3.43 ^a
	SD	0.04	0.02	0.05
D	\bar{x}	93.20	0.92 ^{ab}	7.45 ^{ab}
	SD	3.61	1.91	3.38
E	\bar{x}	89.92	-2.20 ^a	10.45 ^b
	SD	0.16	0.09	0.32
Total		92.20	0.75	6.78
Semi-skimmed				
A	\bar{x}	91.38	1.37	6.67
	SD	1.31	2.53	3.15
B	\bar{x}	90.84	1.33	7.43
	SD	1.48	1.43	4.05
C	\bar{x}	91.91	1.80	4.92
	SD	1.59	2.15	2.26
D	\bar{x}	91.81	0.93	7.43
	SD	1.98	2.73	4.05
E	\bar{x}	89.45	-1.36	9.34
	SD	0.79	0.10	0.41
Total		91.48	1.15	6.43
Fat				
A	\bar{x}	90.15 ^{ab}	1.12 ^b	6.34 ^{ab}
	SD	0.25	0.14	0.13
B	\bar{x}	-	-	-
	SD	-	-	-
C	\bar{x}	93.25 ^b	3.17 ^c	4.55 ^a
	SD	0.03	0.02	0.08
D	\bar{x}	91.97 ^{ab}	0.29 ^{ab}	9.18 ^b
	SD	1.87	2.26	2.54
E	\bar{x}	89.28 ^a	-0.97 ^a	8.85 ^{ab}
	SD	0.47	0.03	0.18
Total		91.61	0.70	7.94

a, b – differences significant at $p \leq 0.05$

Source: own work

tvarogs. In all of the cases this indicator was within the standards PN-A-86300, ranging from 70.00 (semi-skimmed cheese) to 89.33 °SH (semi-skimmed cheese) (table 3). It was observed that cheese types and dairies did not influence acidity of the analysed cheeses, though regardless of their fat content cheeses from dairy E had the highest acidity (over 80 °SH). The research of Siemianowski et al. (2013) showed that the higher amount of dry matter there was the bigger titration acidity of curd cheeses was observed. Wiatr-Szczepaniak and Libudzisz (1997) explain the differences among acidity of the finished products by means of different levels of activity of starter cultures and the type of milk. According to Dmytrow et al. (2011) acidity is essentially connected with the duration of cheese storage and types of packaging.

One of the factors determining the choice of product by consumers is colour. Among all types of acid curd cheeses, the highest lightness (L^*) indicator and the highest share of red-green colour (a^*) were characteristic for dairy products from dairy C. However, skimmed and semi-skimmed acid curd cheeses from dairy E had the highest share of yellow-blue (b^*) colour (table 4). Similar results were obtained by Litwińczuk et al (2003) for cheeses available in Lublin region.

Conclusion

The general quality of curd cheeses available in retail sale in Lublin region is satisfactory, though – because of the occurring abnormalities – a systematic control should be conducted in order to check the quality of dairy products as well as some corrective measures should be taken to improve their quality.

References

- Analysis and Programming Office, 2014, Agricultural Market Agency (ARR). Milk Market, 02. (in Polish)
- Bohdziewicz K., 2009, Tvarog – the first fresh cheese in the world. Przegląd Mleczarski 2, 4–8. (in Polish)
- Bohdziewicz K., Śmietana Z., 2007, Tvarogs – the present and the future. Kalejdoskop Mleczarski 2, 32–35. (in Polish)
- Dmytrów I., Szczepaniak G., Kryża K., Mituniewicz-Matek A., Lisiecki S., 2011, Impact of polylactic acid packaging on the organoleptic and physicochemical properties of tvarog during storage. International Journal of Dairy Technology, 64 (4), 569-577.

- Gołabek J., 2011, Production of wedge tvarogs in a traditional method, allowing for new technological improvements and packing methods, *Przegląd Mleczarski* 11, 22-23. (in Polish)
- Górska J., 2014, Dairy Forum. Trade. I (62), February/March, 42-47. (in Polish)
- Górska-Warsewicz H., 2005, The development of dairy products market. *Przemysł Spożywczy* 10, 20-23. (in Polish)
- IERiGŻ-PIB 2013. Milk market – condition and perspectives. Warsaw, 45, September. (in Polish)
- Igras S., 2012, Characteristics of selected dairy milk products. *Journal of Nutrilife*, doi: <http://www.nutrilife.pl> (in Polish)
- Kolanowski W., 2000, Full-fat, fat and skimmed acid curd cheeses. *Przegląd Gastronomiczny*, 5, 10-11. (in Polish)
- Litwińczuk A., Barłowska J., Król J., Nowakowska J., Topyła B., 2003, The quality of curd cheeses available in retail in Kielce and Lublin. *Żywność. Nauka. Technologia. Jakość* 4 (37), 251-258. (in Polish)
- Litwińczuk Z. (red.) Commodity science of raw materials and animals products with the basis of processing industry. Wyd. PWRiL, Warszawa 2012. (in Polish)
- Marszałkowska-Jakubik J., 2011, Acid curd cheeses. *Przegląd Mleczarski* 11, 20-21. (in Polish)
- PN-73/A-86232: Milk and milk products. Cheeses. Reserach methods. (in Polish)
- PN-91/A-86300: Milk and dairy products. Unripening acid curd cheeses. (in Polish)
- PN-EN/ISO 8968-1:2004: Milk – determining nitrogen content – part 1: Kjeldahl's method. (in Polish)
- Sałaciński K., 2011, Ripening rennet cheeses. *Przegląd Mleczarski* 8, 40-41. (in Polish)
- Siemianowski K., Szpendowski J., Bohdziewicz K., 2011, Progress in acid curd cheese production. *Przegląd Mleczarski*, 11, 4-12. (in Polish)
- Siemianowski K., Szpendowski J., Bohdziewicz K., Kołakowski P., Pawlikowska K., Żylińska J., Bardowski J.K., 2013, Influence of dry matter content on composition and sensory features of acid curd cheese. *Folia Pomeraniae Universitatis Technologiae Stetinensis* 302 (25), 113-124. (in Polish)
- Smithers G.W., 2008, Whey and whey proteins – From 'gutter to gold'. *International Dairy Journal*, 18, 695-704.
- Szpendowski J., Kłobukowski J., Prokop E., 2005, Influence of calcium chloride additive and heating of milk on the chemical composition of curd cheeses. *Żywność. Nauka. Technologia. Jakość*, 3 (44), 36-45. (in Polish)
- Śmietana Z., Szpendowski J., Bohdziewicz K., 2003, Characteristic features of traditional Polish tvarog obtained according to own modern technique and technology. *Przegląd Mleczarski* 4, 126-129. (in Polish)

Śmigielska D., 2013, Milk market, III/2013. Polska Federacja Hodowców Bydła i Producentów Mleka. (in Polish)

Wiatr-Szczepanik A., Libudzisz Z., 197, Comparison of growth and acid activity of *Lb. acidophilus* strains in cow and goat milk. Przegląd Mleczarski 6, 173-175. (in Polish)

INVESTIGATION OF SWEET SUBSTANCES OF DIFFERENT MOLECULAR STRUCTURE BY POTENTIOMETRIC TASTE SENSOR WITH ALL SOLID STATE ELECTRODES

Ewa Marjańska, Maria Szpakowska

*Faculty of Management and Economics, Gdansk University of Technology,
ewam@zie.pg.gda.pl*

Introduction

Application of various taste sensors for the analysis of foodstuffs and beverages has been widely described in the literature. (Toko 2000; Ciosek et al. 2006, Szpakowska, Marjanska, & Lisowska-Oleksiak 2009, Winqvist, Wide & Lundström 1997). Among them taste sensors based on potentiometry have gained much attention. Potentiometric taste sensors are generally based on either ion selective electrodes (ISEs) containing inner electrolyte as electron transducer or on all solid state electrodes (ASSEs), where inner electrolyte is replaced by electroactive polymer. In both cases there are diverse lipophilic compounds immobilized in the plasticized polymeric matrix responsible for mimicking the taste sensing ability of the tongue of mammals. The output of such systems are different electric potential patterns obtained for chemical substances producing different taste qualities (Toko 2000).

A Japanese group has applied potentiometric multichannel taste sensors based on ISEs for discrimination of e.g. milk (Yamada et al. 1995), soy sauce (Iiyama, Yahiro., Toko, 2000), wine (Baldacci et. Al. 1998), sake (Iiyama et al., 1996). This scientific group has also investigated taste sensor potentiometric response for umami substances (e.g. monosodium glutamate) (Iiyama et al. 2003) and for astringent and pungent substances (e.g. tannic acid and piperine respectively) (Iiyama et al. 1995).

The collaborative research between Japanese scientists from Anritsu Corp. and Kyushu University has lead to development of the first commercial Taste Sensing System SA 401 in 1993. 10 units of this system were sold only in Japan and production was discontinued. The newest commercial taste sensor is called Taste Sensing System TS – 5000Z and is elaborated by the same scientific group. This model can be applied in quality control as well as in laboratory. Since 2007 there have been 100 units of TS – 5000Z introduced

to laboratories in Asia and Europe. Commercial taste sensing systems are based on ISEs with polymer membranes containing various lipophilic compounds (Insent Intelligent Sensor Technology, Inc. Web).

A Polish group lead by Szpakowska has applied taste sensors with ISEs as well as with ASSEs for discrimination and recognition of various beverages. Taste sensor with ISEs was successfully applied for tonic waters and orangeades (Szpakowska, Szwacki & Marjańska 2008). ASSE based taste sensing system was used for discrimination of various sour taste solutions (Szpakowska, Marjańska & Lisowska-Oleksiak 2009). Further investigations continued by this group concern taste sensor with ASSEs.

Another Polish group has a significant contribution to the knowledge and application of taste sensing systems. In 2004 this group has applied an electronic tongue based on an array of ion selective electrodes with polymeric membranes to qualitative analysis of milk, tonic and orange juice (Ciosek, Augustyniak & Wróblewski 2004). This group has also applied miniaturized ASSEs to develop flow – through electronic tongue. Its performance was tested with 83% of correct classifications in the qualitative analysis of various brands of beer (Ciosek, Wróblewski 2006). Some miniaturized taste sensing technology has been applied by Japanese scientists (Tahara et al. 2011, 2013).

The percentage of the population of highly developed countries that is overweight or obese is significant. In 2007 to 2008 in U.S. 68% of adults and 32% of children and adolescents were overweight or obese (Flegal et al. 2010). This in consequence lead to type 2 diabetes and cardiovascular diseases. WHO considers obesity as an epidemics of 21st century. The main causes of this epidemics are the change of life style and increasing consumption of food with high energy density including sugar sweetened beverages. There are many policies and proposals aimed to combat the obesity epidemic. There is a need to change the dietary habits of population especially in connection with sugar sweetened beverages. Polish Society of Obesity Research and Polish Diabetes Association have issued a document in which they recommend application of low calorie sweeteners instead of sucrose for persons with overweight or obesity problem. Hence, the market for sweeteners as alternative for sucrose is continuing to expand. Alternative sweeteners are successfully applied on the condition that they match perfectly the taste quality of sucrose The studies focusing on comparing the characteristics of various intense and bulk sweeteners with sucrose present dissimilar sensory profiles (Portman, Kilcast 1995). For example saccharin and acesulfame – K reveal bitter taste (Horne et al. 2002) whereas cyclamate reveals metallic aftertaste (Portman, Kilcast 1995). It was also proven that bulk and intense sweeteners (e.g. sucrose and aspartame) can be used in binary combinations bringing the benefits related to taste quality as well as calories and processing costs reduction (Hutteau et al. 1997). It is obvious that the type of sweetening substance used influences

the taste quality of the product, especially in case of beverages. As the market of artificially sweetened beverages is expanding there is need for further investigation on their influence on taste quality.

The attempts to relate chemical structure to the sour and salt tasting compounds have met success. However, attempts to relate chemical structure to the sweet taste have not been as successful. The minor stereochemical changes or the substitution of one atom for another in sugars may result in the changing of taste. The sugar α – D- mannose is sweet, but β – D- mannose, which is very similar in structure is distinctly bitter. The degree of sweetness is varying among different sugars. It is related to their chemical structure, especially to sugar hydroxyl groups bonding with intramolecular hydrogen. This kind of bonding has also been identified in some sweeteners as saccharin and cyclamates. (Shallenberger 1980). When hydroxyl groups, which are inducing sweet taste, are hydrogen bonded, the ability to elicit sweet taste is restricted (Shallenberger 2006). In literature there are many molecular theories relating chemical structure of compounds to sweet taste. The most comprehensive early attempt to relate chemical structure to taste is that associated with functional groups and structure of the saporous unit (Cohn 1914). Some of the chemical and physical properties of sweet tasting compounds have been related to their sweet taste, e.g. it was found that the relative sweetness of the sugars could be correlated with the ratio of the sum of a sugars' atomic volume to that of the molecular volume (Beck 1943). The hydrogen bond theory of sweet taste proposes that sugar sweetness is inversely related to the degree with which sugar hydroxyl groups are able to bind hydrogen intramolecularly (Shallenberger, Acree & Guild 1965). This thesis was developed into a general theory of sweet taste (Shallenberger, Acree & Guild 1967). Basing on those first, principal theories further research on that subject is being continued. One of the results of this research is the present knowledge of the structural mechanism of the sweet taste response.

In order to define how sweet a product is in relation to sugar an index of relative sweetness is applied. The relative sweetness can be measured by comparing the threshold values for various types of sugars and sugar substitutes. Sucrose is the usual standard compound for determining relative sweetness scores. Relative sweetness index of sucrose is usually taken to be unity or assigned a score of 100. Sucrose is used in sweet taste studies as a standard because it is easily crystallized and hence can be obtained in the high state of purity. However, it has been reported that even the taste of sucrose is "mixed". At the threshold levels sucrose yields a tactual sensation described as medicinal. As the concentration is increased, the taste becomes bitter, then bitter – sweet, and finally purely sweet (Beck 1956). The relative sweetness of sweetening compounds is estimated by a selected taste panel under defined set of conditions. However, it should be remembered, that many sweeteners potentiate others when used together and that usually sweetening compounds

are consumed in a variety of circumstances. Naturally occurring sugars have much lower relative sweetness than artificial sweeteners.

The aim of this work was to examine if any relationship between molecular structure of sweetening substances and the responses of ASSE taste sensor exists. Six sweetening substances were investigated: monosaccharides (glucose and fructose), disaccharides (sucrose and lactose) and artificial sweeteners (sodium cyclamate and aceulfame K). The patterns of potential responses of the sensor were discussed for each group of sweetening substances in relation to their molecular structure, providing a preliminary study on the actual mechanism of taste sensor response in relation to the chemical structure of sweet compounds. Principal component analysis (PCA) was performed in order to verify the discrimination ability of the taste sensor. The results of PCA were associated with the indexes of relative sweetness of studied compounds. This parameter is also somehow related to the stereochemical structure of sweetening substances.

Materials and methods

Lipophilic compounds: dodecyltrimethylammonium bromide, palmitic and stearic acids and phytol, plasticizing agent: dioctyl phenyl phosphonate (DOPP), the monomer 3, 4 – ethylenedioxythiophene (EDOT) and poly (sodium 4 – styrenesulfonate) (NaPSS, MM ~ 70,000) were from Aldrich. Anhydrous benzyldimethyltetradecylammonium chloride and high molecular weight PVC were from Fluka. Tetrahydrofuran was used as solvent. All the chemicals used were of analytical grade. Distilled water was used to prepare all tested solutions

PEDOT was deposited on GC working electrodes (area = 0.12cm²) by galvanostatic electrochemical polymerization from a deoxygenated solution of 0.01 M EDOT and 0.1 M NaPSS as supporting electrolyte at constant electric potential (850mV). Three - electrode electrochemical cell was used with GC working electrodes, platinum mesh auxiliary electrode and Ag / AgCl / Cl⁻ (0.1M KCl) reference electrode (Figure 1). GC working electrodes were polished with 0.05 μm alumina, rinsed with distilled water and cleaned ultrasonically prior to polymerization. Polymerization charge of 10mC was produced, which refers to 0.5μm thickness of PEDOT doped with PSS⁻ layer.

After deposition of PEDOT on the GC electrodes they were coated with the PVC membrane with embedded lipophilic compounds of the following composition: 150 mg PVC, 1.25 mg lipophilic compound, 242 mg DOPP in 5 mL THF. After drying electrodes were conditioned in 10⁻³M KCl for 24 hours before measurement.

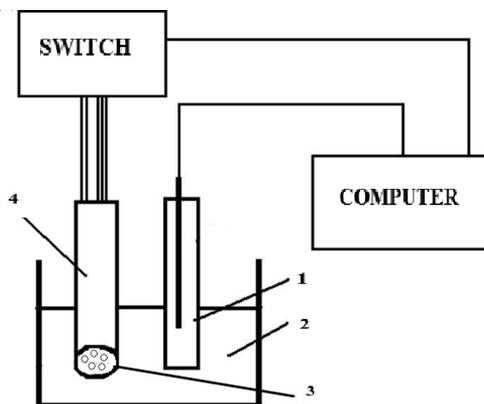


Figure 1. Experimental setup: 1 – reference electrode, 2 – tested solution, 3 – lipophilic compound / PVC membranes immersed in tested solution 4 – an array of 5 ASSE measuring electrodes.

Source: self elaboration

Results and discussion

The analysis of response pattern of taste sensor to all six sweet substances of different chemical structure (sucrose, lactose, fructose, glucose, sodium cyclamate and acesulfame K) (Figure 2) shows the evident difference between saccharides and artificial sweeteners. In particular, the responses provided by electrodes 1, 2 and 3 for sodium cyclamate are different from those for acesulfame K. Electrodes 4 and 5 do not reveal any special sensitivity for those two sweeteners. On the other hand, no clear difference between the patterns of mono and polysaccharides can be observed in Figure 2 – all tested sweet solutions show almost the same pattern.

In Figure 3 the radar plot in different than in Figure 2 scale is presented only for saccharides. It can be observed that disaccharides reveal almost exactly identical pattern for all five electrodes, whereas monosaccharides differ between each other. The greatest difference between fructose and glucose can be observed for electrode 2. The very similar response patterns for both analyzed disaccharides impedes discrimination between those to compounds. The response patterns of monosaccharides (Figure 3) differ from each other. This difference in response for glucose and fructose enables their identification and discrimination by taste sensor. Focusing on the general patterns presented in Figure 3 clear difference between monosaccharides and disaccharides can be observed. Because of this difference taste sensor has an ability to distinguish between monosaccharides and disaccharides.

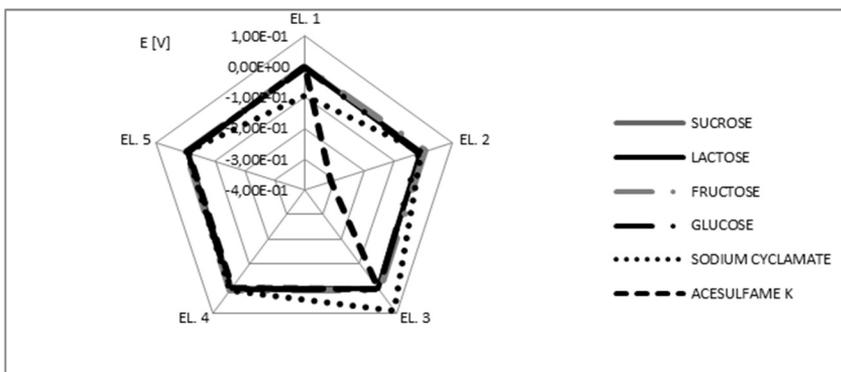


Figure 2. Radar plot of five ASSEs responses for all tested sweet substances of different chemical structure at concentration of 10^{-2}M ; electrodes: 1 - benzyldimethyltetradecylammonium chloride, 2 - dodecyltrimethylammonium bromide, 3 – palmitic acid, 4 – stearic acid, 5 – phytol.

Source: self elaboration

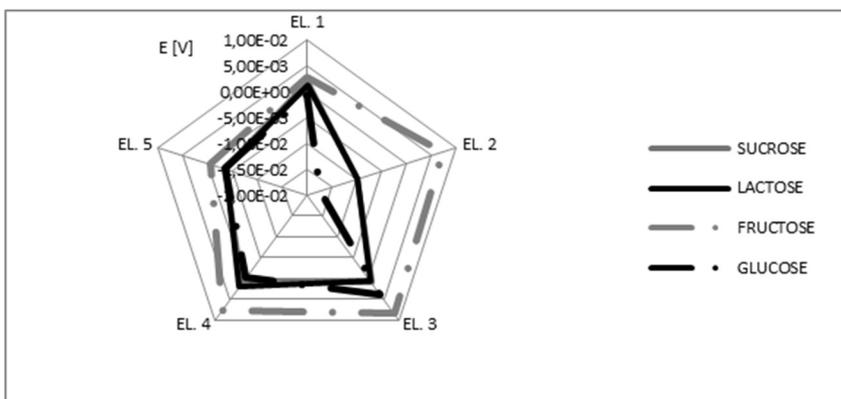


Figure 3. Radar plot of five ASSEs responses for monosaccharides (fructose, glucose) and disaccharides (sucrose, lactose) at concentration of 10^{-2}M ; electrodes: 1 – benzyldimethyltetradecylammonium chloride, 2 - dodecyltrimethylammonium bromide, 3 – palmitic acid, 4 – stearic acid, 5 – phytol.

Source: self elaboration

Since the sweet tasting saccharides are nonelectrolytes the mechanism of their interaction with the polymer membranes of taste sensor is not yet well known. The hydroxyl groups of sweet tasting sugars seem to play an important role in the interaction with human taste according to the AH – B model of sweet taste (Nofre, Tinti, 1996) and to studies on structure – activity relationships (SAR) (Meyers. Brewer 2008). The molecular structure (Figure

4) and the number of hydroxyl groups as well as distance between them in the particular molecule of sugar may also be important. Further investigations are conducted in order to verify if the same observation is valid for the interaction of sweet tasting sugars with ASSE taste sensor. According to one explanation, the interactions between the hydroxyl groups of sugars and the lipophilic compounds embedded in the polymer membranes of taste sensor influence the potential response. Probably those interactions appear at the surface of the lipophilic compound / polymer membranes of the taste sensor (Toyota et al. 2011). However, it is still unknown how this interaction with sugars being nonelectrolytes causes the potential change. Analyzing this concept the dimensions of the sugar molecules and the pores in polymeric membranes need to be taken into consideration. Another concept to be verified is based on the supposition that the mediating substance being electrolytes might act between the hydroxyl groups of sugars and the lipophilic compounds embedded in the polymer membrane of the taste sensor. More studies on this subject are still required.

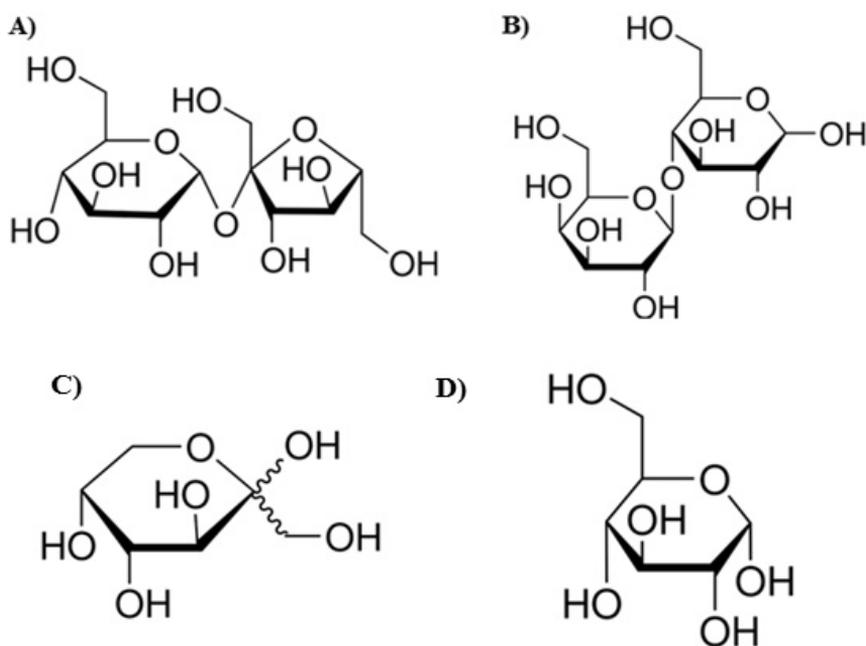


Figure 4 Molecular structure of analysed saccharides: A) sucrose, B) lactose, C) fructose, D) glucose

Source: Sigma Aldrich Web

Figure 5 presents response patterns for artificial sweeteners: sodium cyclamate and acesulfame K. It can be observed that those patterns are very

similar for electrodes no. 4, 5 and different for electrodes no. 1, 2 and 3. The most significant response difference is for the electrode 2. On the contrary to the analysed saccharides, both artificial sweeteners are present in the solution in the ionic form with small sodium or potassium cation and larger anions with carbon chains (Figure 6). To explain the mechanism of taste sensor response for such kind of substances hydrophobic and electrostatic interactions between ions in the solution and substances embedded in the polymer membrane should be considered. Those interactions are responsible for the changes in electric responses.

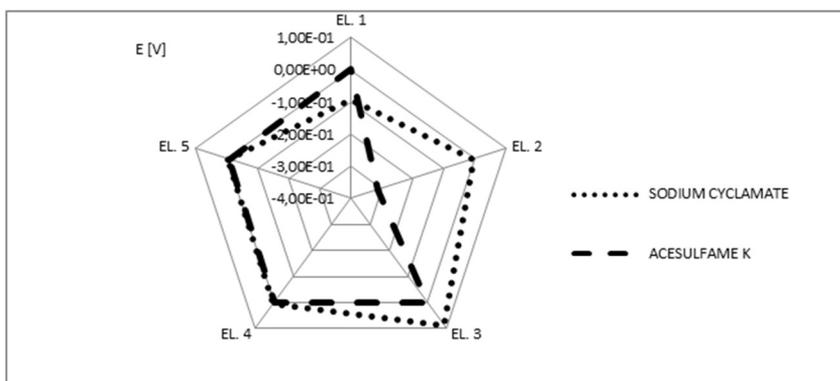


Figure 5. Radar plot of five ASSEs responses for artificial sweeteners: sodium cyclamate and aceulfame K at concentration of 10^{-2} M. Electrodes: 1 - benzyldimethyltetradecylammonium chloride, 2 - dodecyltrimethylammonium bromide, 3 – palmitic acid, 4 – stearic acid, 5 – phytol.

Source: self elaboration

Considering positively charged polymer membranes, i.e. electrodes 1 and 2 with benzyldimethyltetradecylammonium chloride and dodecyltrimethylammonium bromide respectively, artificial sweetener interacts with the positive charge of the lipid by electrostatic forces. Then hydrophobic interactions can be considered. Analysis of the negatively charged membranes requires to consider the change in the surface charge density caused by hydrophilic groups of the lipid embedded in the membrane that are in contact with the aqueous phase. The application of Gouy – Chapman theory of the electrical double layer is necessary to explain the influence of the charge density at the membrane surface on the taste sensor. The patterns received for artificial sweeteners differ significantly from those received for disaccharides. This enables discrimination between sugars and artificial sweeteners. Further investigations are continued to explain this mechanism.

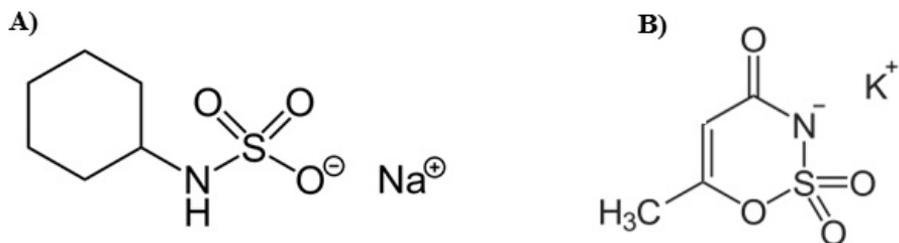


Figure 6. Molecular structure of artificial sweeteners: A) sodium cyclamate, B) acesulfame K.

Source: Sigma Aldrich Web

Although the exact mechanism of applied potentiometric taste sensor with all solid state electrodes response to sweet substance is not yet well known, it could be stated that this sensor is able to discriminate among sugars and artificial sweeteners. The results of PCA for investigated compounds in water solutions at concentration of $10^{-2}M$ are presented in Figure 7. First two PCs explain 99.93% of variability, which suggests existence of a distinct pattern.

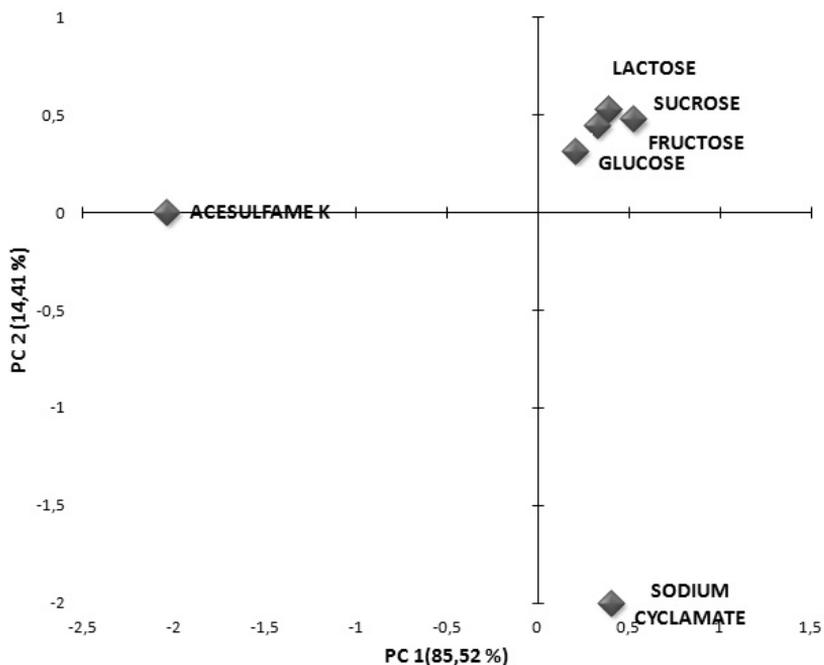


Figure 7. PCA plot after varimax rotation for tested sugars and artificial sweeteners by potentiometric taste sensor with ASSEs.

Source: self elaboration

Explicit grouping of saccharides can be observed. However, monosaccharides and disaccharides are grouped together. This does not enable discrimination between those two groups of sugars. Artificial sweeteners are not grouped. However, basing on these results it cannot be stated clearly that this taste sensor is not able to discriminate among artificial sweeteners.

Basing on results in Figure 7 it cannot be clearly concluded that taste sensor has an ability to discriminate sweetening substances with respect to their chemical structure. However, a convergence between the grouping of tested compounds in Figure 7 and their indexes of relative sweetness can be observed. Table 1 presents values of relative sweetness indexes.

Table 1. Relative sweetness indexes of tested substances

SWEETENING SUBSTANCE	RELATIVE SWEETNESS INDEX
Lactose	0.15
Glucose	0.75
Sucrose	1.00
Fructose	1.70
Sodium cyclamate	40.00
Acesulfame K	200.00

Source: Shallenberger, 1980

Tested natural sugars have relative sweetness indexes in the range of 0.15 – 1.70. Sodium cyclamate is almost 40 times and acesulfame K 200 times more sweet. Substances having similar relative sweetness indexes are grouped together (Figure 7). Sodium cyclamate and acesulfame K having index values in different ranges are located in different parts of PC plot.

Conclusions

There is a distinct difference of the taste sensor responses for saccharides and artificial sweeteners. The way the points in the PC plot are grouped converges with relative sweetness indexes of tested substances. It is known that there is a relation between sweet taste of a compound and its molecular structure. It seems that there is some relation between molecular structure of sweetening substances and the responses of ASSE taste sensor. However, further investigations on the mechanism of taste sensor responses are necessary. Obtained results show that the taste sensor with ASSEs is able to discriminate between natural sugars and artificial sweeteners.

References

- Baldacci S., Matsuno T., Toko K., Stella R., De Rossi D., 1998, Discrimination of wine using taste and smell sensors, *Sensors and Materials*, 10 (3), 185 – 200.
- Beck G., 1943, Sweetness and molecular volume, *Wien Chem.*, 46, 18 – 22.
- Beck S. D., 1956, A bimodal response to dietary sugars by an insect, *Biol. Bull.*, 110, 219 – 228
- Ciosek P., Augustyniak E., Wróblewski W., 2004, Polymeric membrane ion – selective electrode – based electronic tongue for qualitative analysis of beverage, *Analyst*, 129, 639 – 644.
- Ciosek P., Sobański T., Augustyniak E., Wróblewski W., 2006, ISE - based sensor array system for classification of foodstuffs, *Meas. Sci. Technol.*, 17, 6 – 11.
- Ciosek P., Wróblewski W., 2006, The recognition of beer with flow – through sensor array based on miniaturized solid state electrodes, *Talanta*, 69, 1156 – 1161.
- Cohn G., 1914, *Die organischen Geschmackstoffen*, Berlin, Siemerth.
- Flegal K. M., Carrol M. D., Ogden C. L., Curtin L. R., 2010, Prevalence and trends in obesity among US adults, 1999 – 2008, *Jama* 303, 3, 235 – 341.
- Horne J., Lawless H. T., Speirs W., Sposato D., 2002, Bitter taste of saccharin and acesulfame – K, *Chem. Senses.*, 27, 31 – 38.
- <http://www.insent.co.jp>
- Hutteau F., Mathlouthi M., Portman M. O., Kilcast D., 1997, Physicochemical and psychophysical characteristics of binary mixtures of bulk and intense sweeteners, *Food Chemistry*, 63, 9 – 16.
- Iiyama S., Ezaki S., Toko K., Matsuno T., Yamafuji K., 1995, Study of astringency and pungency with multichannel taste sensor made of lipid membranes, *Sensors and Actuators B*, 24 – 25, 75 – 79.
- Iiyama S., Kuga H., Ezaki S., Hayashi K., Toko K., 2003, Peculiar change in membrane potential of taste sensor caused by umami substances, *Sensors and Actuators B*, 91, 191 – 194.
- Iiyama S., Suzuki Y., Ezaki S., Arikawa Y., Toko K., 1996, Objective scaling of taste of sake using taste sensor and glucose sensor, *Materials Science and Engineering C4*, 45 – 19.
- Iiyama S., Yahiro M., Toko K., 2000, Measurements of soy sauce using taste sensor, *Sensors and Actuators B* 66, 205 – 206.
- Insent Intelligent Sensor Technology, Inc. Web
- Meyers B., Brewer M. S., 2008, Sweet taste in man : a review, *Journal of Food Science*, 73, 6, 81 – 90.

- Nofre C., Tinti J. M., 1996, Sweetness reception in man: the multipoint attachment theory, *Food Chemistry*, 56, 3, 263 – 274.
- Portman M. O., Kilcast D., 1995, Psychophysical characterization of new sweeteners of commercial importance for the EC food industry, *Food Chemistry* 56, 291 – 302.
- Shallenberger R. S., 1980, Predicting sweetness from chemical structure and knowledge of chemoreception, *Food Technology*, 34 (1), 65 – 66.
- Shallenberger R. S., 2006, Hydrogen bonding and the varying sweetness of the sugars, *Journal of Food Science*, 28 (5), 584 – 589.
- Shallenberger R. S., Acree T. E., Guild W. E., 1965, Configuration, conformation, and sweetness of hexose anomers, *J. Food Sci* 30, 560 – 563.
- Shallenberger R. S., Acree T. E., Guild W. E., 1967, Molecular theory of sweet taste, *Nature (Lond.)* 216, 480 – 482.
- Sigma Aldrich Web <http://www.sigmaaldrich.com>
- Szpakowska M, Marjanska E, Lisowska-Oleksiak A., 2009, Investigation of sour substances by a set of all-solid-state membrane electrodes, *Desalination*, 241, 236-43.
- Szpakowska M., Marjańska E., Lisowska – Oleksiak A., 2009, Investigation of sour substances by a set of All solid state membrane electrodes, *Desalination* 241, 236 – 243.
- Szpakowska M., Szwacki J., Marjańska E, 2008, Multichannel taste sensor with lipid, lipid like – polymer membranes, *Journal of Physics: Conference Series* 127, 012013.
- Tahara Y., Ikeda A., Maehara Y., Habara M., Toko K., 2011, Development and evaluation of a miniaturized taste sensor chip, *Sensors*, 11, 9878 – 9886.
- Tahara Y., Nakashi K., Ji K., Ikeda A., Toko K., 2013, Development of a portable taste sensor with a lipid / polymer membrane, *Sensors*, 13, 1076 – 1084.
- Toko K., 2000, Taste sensor, *Sensors and Actuators B*, 64, 205 – 215.
- Toyota K. Cui H., Abe K., Habara M., Toko K., Ikezaki H., 2011, Sweetness sensor with lipid / polymer membranes: Response to various sugars, *Sensors and Materials* 23, 8, 475 – 482.
- Winqvist F., Wide P., Lundström I, 1997, An electronic tongue based on voltammetry, *Analytica Chimica Acta* 357, 21 – 31.
- Yamada H., Mizota Y., Toko K., Doi T., 1995, Highly sensitive discrimination of taste of milk with homogenization treatment using a taste sensor, *Materials Science and Engineering C5*, 41 – 45.

CHANGES IN PHYSOCOCHEMICAL PARAMETERS OF ARGAN OIL DURING MICROWAVE HEATING

Lidia Ostasz

*Department of Chemistry, Faculty of Commodity Science,
Cracow University of Economics,
lidia.ostasz@uek.krakow.pl*

Introduction

Microwave heating of food products has been popular for many years. This way of heating is an alternative for other cooking methods, including traditional frying. Fats undergo adverse transformations during microwave heating, most importantly oxidation and hydrolysis. Oxidation and hydrolysis products formed during heating have adverse effect on human health (Caponio F. et al. 2002, Caponio F. et al. 2003). These transformations result in the formation of primary and secondary oxidation products: hydroperoxides, free fatty acids, ketones, aldehydes, in particular α -, β -alkenes, conjugated dienes and trienes, as well as of polymerisation products (El-Moneim M. et al. 2009, Lukešová, D. et al. 2009, Mińkowski K. et al. 2010, Mińkowski K. et al. 2011).

Oil in contact with atmospheric oxygen and high temperatures undergo qualitative changes. These changes in oils used as heating medium when using microwaves is the object of research of many authors. The results obtained show that the type and number of the product formed depends, in particular, on the type of fat, microwave power applied and duration of the process (Ostasz L., 2007, Ostasz L., Buczek B., 2007). The use of medium power microwaves (550W) for frying French fries in sunflower oil in several cycles over 20 minutes may be an alternative to traditional frying. The authors proved that in these conditions the degradation of oil is limited due to shorter exposure of oil particulars to hot temperature. The main products formed are peroxides; as regards changes in the structure of fatty acids - the concentration of saturated fatty acids increases. Furthermore, oil during heating in such conditions has longer induction period and lower contents of polar compounds (Gharachorloo M. et al. 2010, Tan C.P. et al. 2001, Vieira T., Regitano-d'Arce M., 2001).

In comparative analyses of qualitative changes in olive oil induced by conventional and microwave heating, higher degree of degradation was observed in the case of microwave heating. Microwave power of 1100 W was used and the heating time was 12-15 min. In these conditions higher concentration of primary and secondary oxidation products as well as polar compounds was observed. The differences observed are the consequence of the way the energy is transferred in the methods of heating used. Microwaves allow for achieving high volumetric density of energy, unachievable via other methods of heating. Heating energy from inside a product is distributed in all directions in a relatively short time, thus ensuring even warming (Ostasz L., Buczek B., 2006, Buczek B., Ostasz L. 2011). The likelihood of formation of radicals during microwave heating is larger than in the case of traditional heating. (Caponio F. 2002). When lower microwave power (500W) was used to heat up olive oil for 3 to 30 minutes, the resultant oxidation changes were much smaller than during traditional heating in 200°C (El-Moneim M. et al. 2009). Concurrently, research is conducted on achieving greater oxidation stability of microwave heated oils through the use of compounds such as grape seed extract (GSE) or butylated hydroxytoluene (BHT), which postpone the process of oxidation of lipids (Poiana M.A. 2012).

To determine the products of oxidation and fat degradation formed, chemical analyses methods may be used. Qualitative changes in oils induced by microwaves are assessed on the basis of changes in parameters, such as peroxide value, anisidine value, Totox value, contents of free fatty acids, of dienes and trienes, and of polar bondings (Cerretani, L. et al.2009, Dostalova J. et al. 2005).

The purpose of the research was to analyse oxidase changes in argan oil induced by microwave heating at a power of 200,400, 600 and 800 W.

Material and methods

The object of research was argan oil. It is a vegetable oil characterised by high content of tocopherols (vitamine E), phytosterols, NNKT omega-6 and omega-9. Argan oil comes from Morocco and is valued for its nutritional, pharmaceutical and cosmological qualities. The oil is derived from the seeds of argan tree fruit. Culinary argan oil, traditionally pressed from roasted seeds, has nutty smell and taste. The oil contains 92% of fats altogether.

Table 1 summarises the contents of fatty acids in fresh argan oil. It presents the values for Saturated Fatty Acids (SFA), Monounsaturated Fatty Acid (MUFA) and Polyunsaturated Fatty Acids (PUFA).

50 g samples of oils were being heated up in microwave reactor RM 800. Microwave power used was 200, 400, 600, 800 W. Heating times for individual oil samples were: 3, 6, 12, 18, 24, 30 minutes.

Table 1. Summary of contents of fatty acids in 100 g of argan oil

Composition	Content
Total fat, including:	92.0
SFA, g	18.0
MUFA, g	44.0
PUFA, g	30.0

Source: manufacturer's data on the product label.

Oxidase changes taking place in fresh and heated oils were assessed by means of the following parameters, determined on the basis of the PN/ISO standards: peroxide value, anisidine value, Totox value, acid value, and iodine value.

The peroxide value, *PV*, was determined according to ISO 3960:2010. The peroxide value is the quantity of peroxide in a sample of fat which oxidize iodide potassium to free iodine. Fat sample is dissolved in a solution of glacial acetic acid and chloroform. Derived iodine is titrated with a standard solution of sodium thiosulfate. Peroxide value is expressed in milliequivalents of active oxygen per kilogram of fat (mEq O₂/kg fat). Peroxide value is calculated according to the formula:

$$LN = \frac{(V_1 - V_0) \cdot C}{m} \cdot 1000 ,$$

where: *V*₀ - volume of sodium thiosulfate solution used for the blank sample, expressed in milliliters,
*V*₁ - volume of sodium thiosulfate solution used to determine the fat sample, expressed in milliliters,
C - the concentration of the sodium thiosulphate solution, expressed in moles /litre,
m - mass of the test sample, expressed in grams.

Anisidine value is a hundredfold increased value of the absorbance of the test solution, which is reacted with p-anisidine. Sample has been measured at 350 nm in a cuvette 10 mm. The principle of determination anisidine value is based on the reaction of aldehydes of fat present in the sample with a solution of p-anisidine. Then the spectrophotometric measurement of absorbance is execute in three solutions:

- reacted solution , that is, a solution of p-anisidine and fat sample; marked as *A*₁;
- unreacted solution, which is a solution of acetic acid and fat sample; marked as *A*₀.
- blind sample, that is, a solution of isooctane and p-anisidine; marked as *A*₂.

Anisidine value (LA) is calculated from the formula:

$$LA = \frac{25 \cdot [1,2(A_1 - A_2) - A_0]}{m}$$

where: A_1 = absorbance of reacted solution at 350 nm,
 A_0 = absorbance of unreacted solution at 350 nm,
 A_2 = absorbance of blind sample at 350 nm,
 m - mass of the test sample, expressed in grams.

The acid value is the number of milligrams of potassium hydroxide (KOH) needed to neutralize free fatty acids contained in 1 g of fat. The determination is based on titration of a standard solution of KOH of the free fatty acids contained in the fat sample dissolved in ethanol. The Indicator in the titration is phenolphthalein - in case of clear fats and thymolphthalein - in case of dark fats. The acid value, expressed as mg KOH/g of fat (mg KOH/g fat), is calculated from the formula:

$$LK = \frac{56,1 \cdot V \cdot C}{m}$$

where: V - volume of standard base used for the determination of the fat sample, expressed in milliliters,
 C - the concentration of the base solution, expressed in moles/litre,
 m - mass of the fat sample, expressed in grams.

The iodine value is the number of grams of halogen which was calculated to iodine. Halogens attach about 100 g of the tested fat. The determination consist in dissolving a fat sample in a mixture of glacial acetic acid and carbon tetrachloride and adding iodide bromide to it. In these conditions halogens attach/join to the double bond of unsaturated fatty acids. Excess halogen is determined by introducing to the mixture iodide potassium, which is oxidized to the free iodine. The released iodine is titrated with a standard sodium thiosulfate solution. Iodine value, expressed in grams $I_2/100$ g fat (g $I_2/100$ g fat), is calculated from the formula:

$$LI = \frac{12,69 \cdot C \cdot (V_0 - V_1)}{m}$$

where: V_0 - volume of sodium thiosulfate solution used to titrate the blank sample, expressed in milliliters,
 V_1 - volume of sodium thiosulfate solution used to titrate the test sample, expressed in milliliters,
 C - the concentration of the sodium thiosulphate solution, expressed in moles/litre,
 m - mass of the test sample, expressed in grams.

Results and discussion

The results of the experiments are presented in Figures 1 - 4 and Tables 2 - 4. During microwave heating of oil in time t oil temperature was measured; the results are presented in Fig. 1.

Maximum temperatures depended on the microwave power. The higher the microwave power, the higher the temperatures observed. In the oil heated at the power of 200 W, the highest temperatures recorded were 135-138°C. In the samples microwave heated at the powers of 400 W and 600 W, the maximum temperatures were 180-184°C and 198-202°C, respectively. While in the oil heated at the power of 800 W, the temperatures recorded were much higher and reached 226-230°C. The above-mentioned temperatures were observed after heating up the samples for 18 minutes.

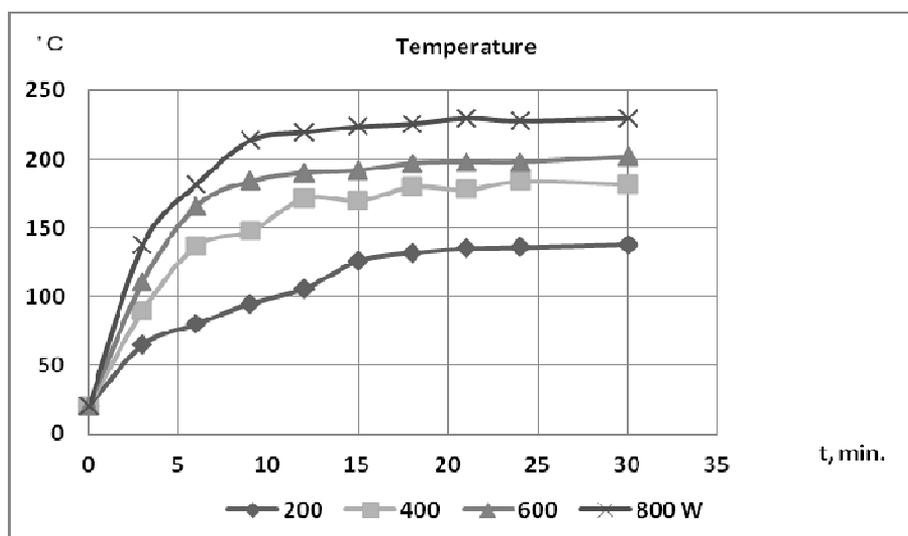


Figure 1. Temperatures of oils microwave heated at various powers

Source: own research.

The findings of the analyses of changes in peroxide value of microwave heated oils are presented in Fig. 2. This is the parameter enabling the assessment of initial oxidase changes taking place, namely the presence of primary products of oil oxidation, most importantly hydroperoxides.

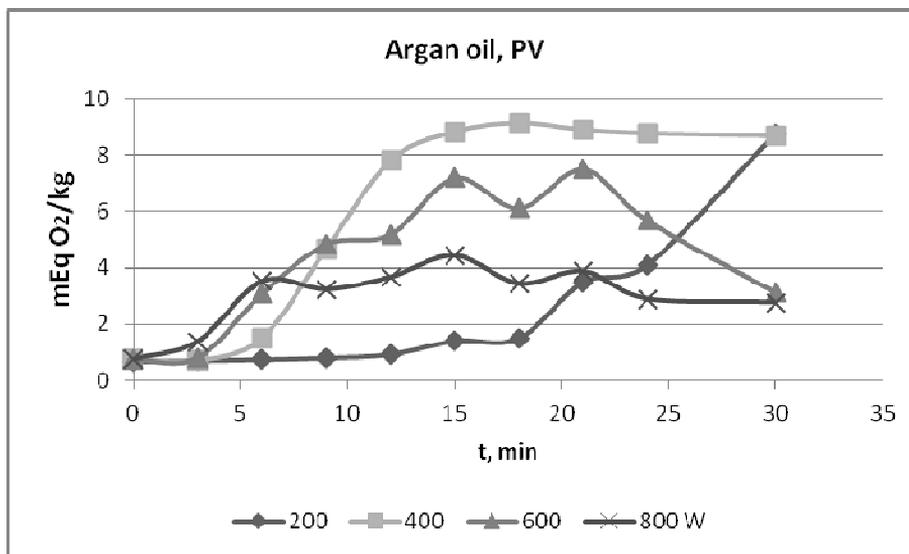


Figure 2. Changes of peroxide value in argan oil microwave heated at various powers

Source: own research.

As a result of microwave heating, peroxide values increased with time. In samples heated at the power of 200 W, the increase of peroxide value gave an upward convex curve. The parameter values grew gradually from the starting value of 0.68 mEq O₂/kg to 8.8 mEq O₂/kg after approx. 30 minutes of heating. The longer the heating time, the greater number of hydroperoxides formed.

In the oil microwave heated at the power of 400 W, the maximum values of this parameter were observed already after 12 minutes of heating. They equalled 7.8-9.1 mEq O₂/kg. In the samples microwave heated at the powers of 600 W and 800 W, lower hydroperoxide values were recorded. The lowest values of the parameter, equalling 2.8-4.4 mEq O₂/kg, were observed in oil microwave heated at the power of 800 W. The above-mentioned values were recorded already after 6 minutes of heating. Longer heating did not result in any considerable increase of the peroxide value. In samples microwave heated at the power of 600-800 W, hydroperoxides were produced during the first stage of heating, lasting up to 6 minutes. Heating for more than 6 minutes resulted in decomposition of hydroperoxides into secondary products.

Table 2 shows changes in anisidine values in the samples studied. This parameter is indicative of the presence of aldehydes - secondary products of oil oxidation. The values of the parameter increased with time in all analysed oil samples.

In the oil microwave heated at the power of 200 W, the changes of this parameter were the least observable. Only after 30 minutes of heating was the change in anisidine value of 3.0 recorded. Secondary products of oxidation were formed in samples microwave heated at the power of 400-800 W. Considerable increase in the parameter (25.3-48.6) was observed after 18 minutes of microwave heating at the power of 400 W. In the samples microwave heated at the highest power, the values of the parameter were even higher and equalled:

- 22.8-64.0 after 12 minutes (600 W),
- 23.1-69.5 after 9 minutes (800 W).

Table 2. Changes of anisidine value in argan oil microwave heated at various powers

t, min.	AV			
	200	400	600	800 W
0	0.62	0.68	0.63	0.88
3	0.64	0.80	1.18	12.61
6	0.66	1.04	4.81	14.73
9	0.67	1.72	14.49	23.07
12	0.73	6.41	22.81	34.37
15	0.87	12.93	27.82	41.12
18	1.12	25.28	37.47	43.65
21	1.47	31.69	46.93	50.00
24	1.97	35.98	52.89	58.65
30	3.04	48.56	64.02	69.46

Source: own research.

The amount of secondary products of oxidation formed depended on the microwave power. The higher the power, the shortest was the time after which the secondary oxidation products were formed; while their amount grew proportionally higher to the increase of the microwave power (Fig.3).

Fig. 4 presents changes in Totox value with time. The values of the parameter increased with time, similarly to the anisidine value.

The highest Totox values were recorded in oil samples microwave heated at the power of 800 W, equalling 75.0 mEq O₂/kg after 30 minutes. Slightly lower values of this parameter were observed in oil samples microwave heated at the power of 400 and 600W. They equalled:

- 22.0-65.9 mEq O₂/kg after 12 minutes. (400 W),
- 24.2-70.3 after 9 minutes (600 W).

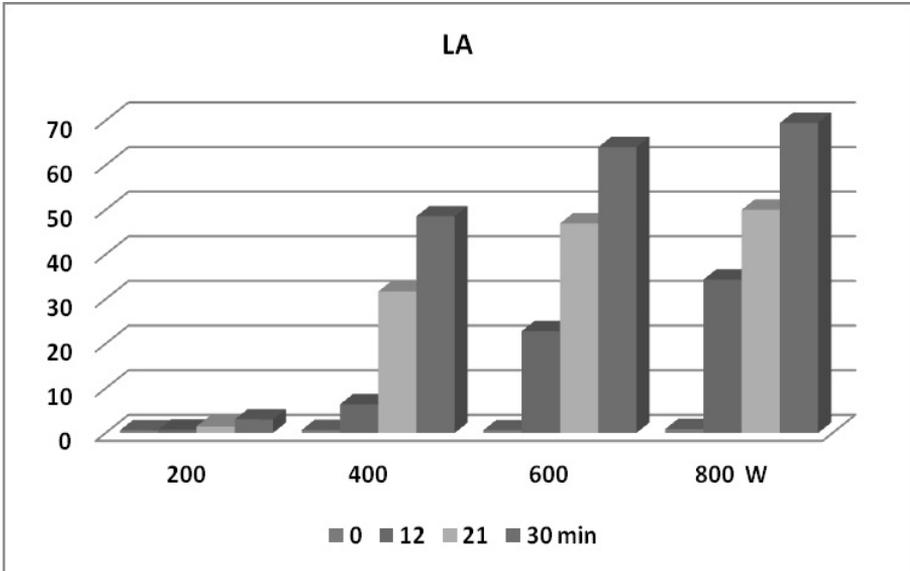


Figure 3. Anisidine values in argan oil after 12, 21, and 30 minutes of microwave heating at various powers

Source: own research.

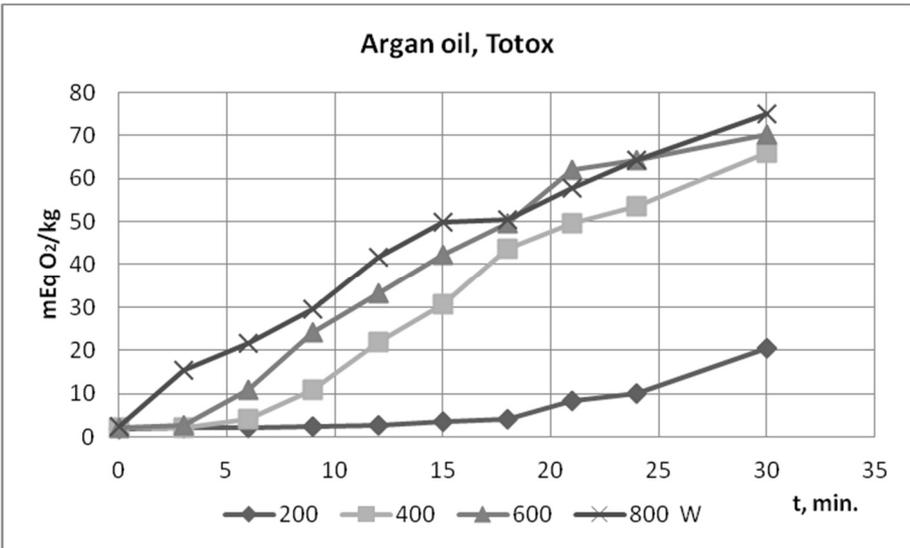


Figure 4. Changes Totox value in argan oil microwaved at various powers

Source: own research.

The nature of the changes was similar in oils microwave heated at the powers of 400, 600, and 800 W. In the oil microwave heated at the power of 200 W, oxidase changes were the smallest and increased with time, reaching 8.5-20.56 mEq O₂/kg after 21 minutes of heating.

Changes in Totox value with time in the oil microwave heated at the power of 200 W are described by means of the following 2nd degree polynomial:

$$y = b x^2 + c x + d.$$

The polynomial parameters *a*, *b*, *c* and the coefficient of determination R² were determined. As regards the argan oil microwave heated at the power of 200 W, the polynomial is:

$$y = 0.0346x^2 - 0.4828x + 2.9889.$$

The coefficient of determination R² equals 0.9784.

Changes in Totox value with time in the oil microwave heated at the power of 400-800 W are described by means of the following 4th degree polynomial:

$$y = ax^4 + bx^3 + cx^2 + dx + e.$$

The polynomial parameters *a*, *b*, *c*, *d*, and *e* as well as the coefficient of determination R² were determined. The values of individual parameters in this polynomial for oils heated at the powers stated above and the respective values of coefficient of determination R² are presented in Table 3.

Table 3. 4th degree polynomial representing changes in Totox value

Moc, W	$y = ax^4 + bx^3 + cx^2 + dx + e$	R ²
400	$y = 0,0003x^4 - 0,0207x^3 + 0,5335x^2 - 2,2854x + 2,9631$	0,9967
600	$y = 0,0002x^4 - 0,0166x^3 + 0,3961x^2 - 0,1048x + 1,4154$	0,9962
800	$y = 8E-05x^4 - 0,004x^3 + 0,0124x^2 + 3,3702x + 3,0415$	0,9933

Source: own research.

Another analysed parameters were: acid value and iodine value (Table 4). The acid value expressed as mg KOH/g indicates the degree of fat hydrolyse, resulting in the formation of free fatty acids subsequently undergoing oxidation processes. The value of this parameter during heating remained at a stable level of 0.7-0.8 mgKOH/g in the examined samples of argan oil .

The value of iodine number, expressed as I₂/ 100g in oils is, most importantly, indicative of the degree of unsaturation of fatty acids forming these oils. The parameter is also used to determine the effects of oxidation reactions taking place with the participation of mono- and polyene-fatty acids. In the samples of microwave heated argan oil, a slight decrease in the iodine value of 1-3 g I₂/ 100g was observed.

Table 4. Changes of acid value and iodine value in argan oil microwave heated at various powers

AcV, mgKOH/g				
t, min.	200	400	600	800 W
0	0.755	0.757	0.762	0.760
6	0.705	0.736	0.735	0.721
12	0.714	0.729	0.734	0.772
18	0.693	0.735	0.726	0.784
24	0.736	0.751	0.763	0.782
30	0.701	0.707	0.735	0.765
IV, g I ₂ / 100g				
t, min.	200	400	600	800 W
0	106.76	107.45	107.45	107.72
6	107.09	104.18	103.64	102.60
12	103.67	103.92	103.41	102.16
18	106.86	108.43	102.64	103.64
24	101.89	105.02	103.83	100.46
30	105.84	107.34	103.08	104.32

Source: own research.

Conclusions

1. Microwave heating of oil samples results in increase of the oil temperature. Maximum temperatures observed depended on the microwave power. The higher the microwave power, the higher the temperatures of oil samples. For example, 135-138°C (200W) and 226-230°C (800W).
2. As a result of microwave heating, peroxide values increased over time. The longer the time of heating, the larger the number of hydroperoxides formed in the samples microwave heated at the power of 200 W. The values recorded ranged between 0.68 and 8.80 mEq O₂/kg. Longer heating at higher powers (400-800 W) for a period exceeding 6 minutes did not

result in any considerable increase of peroxide value. This is due to the decomposition of hydroperoxides into secondary products.

3. The presence of secondary products of argan oil oxidation was determined on the basis of changes of the anisidine value. The amount of secondary products of oxidation formed depended on the microwave power. The higher the power, the shortest was the time after which the secondary oxidation products were formed; while their amount grew proportionally to the increase of the microwave power. Microwave heating at higher powers caused formation of secondary products of oxidation already after 6 to 12 minutes. In the oil microwave heated at the power of 200 W, the changes of this parameter were the least observable. Secondary products of oxidation were formed in samples microwave heated at the power of 400-800 W. The values of this parameter were much higher and equalled: 25.3-48.6 after 18 minutes. (400 W), 22.8-64.0 after 12 minutes. (600 W), 23.1-69.5 after 9 minutes. (800 W).
4. The Totox values increased with time, similarly to the anisidine value. The changes in Totox with time were described by means of the 2nd and 4th degree polynomial. The coefficient of determination for each sample ranged between 0.9784-0.9967.
5. The acid values and iodine values in the samples of argan oil changed insignificantly throughout the heating process.

References

- Buczek B., Ostasz L., Zmiany jakościowe i fizykochemiczne olejów roślinnych ogrzewanych mikrofalowo, *Przemysł Chemiczny*, 2011, t. 90, 6, 1245-1248.
- Caponio F. et al., Changes in the fatty acid composition of vegetable oils model doughs submitted to conventional or microwave heating." *International Journal of Food Science and Technology*, 2003, 38:481-486.
- Caponio F., Pasqualone A., Gomes T, Effects of conventional and microwave heating on the degradation of olive oil, *European Food Research and Technology*, 2002, 215, 114-117.
- Cerretani, L., Bendini, A., Rodriguez-Estrada, M.T., Vittadini, E., Chiavaro, E., 2009, Microwave heating of different commercial categories of olive oil: Part I. Effect on chemical oxidative stability indices and phenolic compounds, *Food Chemistry*, 115 (4), 1381-1388.
- Dostalova J., Hanzlik P., Reblova Z., Pokorny J., Oxidative Changes of Vegetable Oils during Microwave Heating, *Czech Journal of Food Sciences*, 2005, 23, 230-239;
- El-Moneim M, E.-A., Dostálová, J., Pokorný, J., Lukešová, D., Doležal, M. 2009, Oxidation of olive oils during microwave and conventional heating for fast food preparation, *Czech Journal of Food Sciences 27 (SPEC. ISS.)* , S173-S177.

- Gharachorloo, M., Ghavami, M., Mahdiani, M., Azizinezhad, R. (2010), The effects of microwave frying on physicochemical properties of frying and sunflower oils , JAOCS, Journal of the American Oil Chemists' Society, 87 (4), pp. 355-360.
- Lukešová, D., Dostálová, J., El-Moneim Mahmoud, E., Svárovská, M., 2009, Oxidation changes of vegetable oils during microwave heating, Czech Journal of Food Sciences 27 (SPEC. ISS.), pp. S178-S181.
- Mińkowski K., Grzeškiewicz S., Jerzewska M., *Ocena wartości odżywczej olejów roślinnych o dużej zawartości kwasów linolenowych na podstawie składu kwasów tłuszczowych, tokoferoli i steroli*, Żywność. Nauka, Technologia, Jakość, Wyd. Naukowe PTTŻ, Kraków, 2011, 2 (75), 124-135.
- Mińkowski K., Grzeškiewicz S., Jerzewska M., Ropelewska M., *Charakterystyka składu chemicznego olejów roślinnych o wysokiej zawartości kwasów linolenowych*, Żywność. Nauka, Technologia, Jakość, 2010, 6 (73), 146-157.
- Ostasz L., Buczek B., *Badania właściwości fizykochemicznych olejów jadalnych ogrzewanych mikrofalami*, Towaroznawcze Problemy Jakości, 2007, 1 (10), 44-54.
- Ostasz L. [2007], Changes in Physicochemical Parameters and Fatty Acid Composition of Vegetable Oils During Conventional and Microwave Heating, "Polish Journal of Food and Nutrition Sciences", Vol.57, No 4.
- Ostasz L., Buczek B., Influence of Different Heat Treatment on the Quality of Vegetable Oils, Priceedings of the 15th IGWT Symposium „Global Safety of Commodity and Environment. Quality of Life.” 2006, 757-761, KNIGA, Kyiv.
- Poiana, M.-A. Enhancing oxidative stability of sunflower oil during convective and microwave heating using grape seed extract, 2012, International Journal of Molecular Sciences 13 (7) , pp. 9240-9259.
- PN-EN ISO 3960:2010, Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby nadtlenkowej;
- PN-EN ISO 6885:2008, Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby anizydynowej;
- PN-93 A-86926:1996 Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby anizydynowej oraz obliczanie wskaźnika oksydacji tłuszczu Totox;
- PN-EN ISO 660:2010, Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby kwasowej;
- PN-ISO 3961:2011, Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby jodowej.
- Tan C.P., et al., Effect of microwave heating on changes in chemical and thermal properties of vegetable oils, Journal of the Americal Oil Chemists Society, 2001, 78:1227-1232.
- Vieira T. M. F. S., Regitano-d'Arce M. A. B., Canola Oil Thermal Oxidation During Oven Test and Microwave Heating, Lebensmittel-Wissenschaft und Technologie, 2001, 34:215-221.

EVALUATION OF CHANGES IN MELTING AND OVERRUN OF FAMILY ICE CREAM DURING LONG-TERM STORAGE

Agnieszka Palka

*Faculty of Entrepreneurship and Quality Science,
Gdynia Maritime University,
a.palka@wpit.am.gdynia.pl*

Introduction

Ice cream is a product obtained by freezing pasteurized and cooled liquid mixture, produced on the basis of milk or cream, or fruit juice-based with sugar, emulsifier, stabilizer, which also contains flavours. Such a mixture is usually aerated during freezing, with the result that the finished product in its volume has a rather large amount of air. Given the chemical composition of ice cream, one can say that they are a frozen mixture of: fat, non-fat solids derived from dairy products, sugars, water, stabilizer, emulsifier and flavoring additives. The amount of the individual components and their proportions depend on the type of ice cream (Grzezińska 2004, Marshall & Arbuckle 2000, Oziemkowski 1997).

Characteristic overrun of ice cream depends on the amount of air added to the mixture during the manufacturing process. Aeration and freezing of pre-mix is an important issue in the production of ice cream. Excessive or too low overrun are among the disadvantages of ice cream. In contrast, if there were no aeration, frozen dairy desserts would be hard, icy and tasteless (Campbell & Marshall 1982, Rakowska 1985).

The degree of aeration is essential not only for the organoleptic values of ice cream, but also the ease of heat transfer or cooling the interior of the ice cream. Air is a very good thermal insulator, which affects not only the rate of melting of the ice, but also on the rate of freezing.

Sweetening agents play an important role in ice cream, not only as constituents of suitable for sweet taste. They increase the viscosity of the mixture and the dry matter content and lower the freezing point to get soft and smooth product at low temperature (Polak 2005).

Fat is an important component of the ice cream, shaping their rheological properties, creating a coherent, stable consistency. Fat gives smoothness and

creaminess of ice creams, stabilizes small ice crystals formed during freezing. It facilitates aeration of mixture of ice, as increases the number of air bubbles in the ice. Optimal fat content in ice cream is about 8 percent, the addition of a smaller amount of fat increases aeration. Too large amount causes reduced aeration. By connecting to the proteins contained in the ice it forms molecular structures through which ice obtain a coherent and stable consistency. Furthermore, fat reduces the tendency of ice cream to melt, and increases the viscosity of the mixture (Czerwińska 2006, Dzwolak & Ziajka 1998, Polak 2005, Polak & Kałuziak 2000b, Soukoulis Ch. et al. 2010).

Milk proteins contained in the ice-cream mixture play an important role in ice cream technology, they bind free water, fulfilling a similar role that stabilizers play. Because of emulsifying properties the milk, they improve viscosity mixture of ice and facilitate aeration (Polak 2005, Polak & Kałuziak 2000a, Polak & Kałuziak 2000b).

An extremely important factor determining the quality of the ice cream is the selection appropriate stabilizers and emulsifiers. They increase the viscosity of the mixture of ice, facilitate the absorption of air, give the product a soft, firm texture resistant to melting, they prevent crystallization in the case of temperature fluctuations. Emulsifying agents in the process of homogenization allow for stable placement of the fat phase and to obtain a sustainable mixture with better taste (Polak & Kałuziak 2000b, Rakowska 1985).

Material and methods

Family ice cream with vanilla flavor in packs of 500 ml were examined. Purchased research material was stored for 360 days under the following conditions: variable temperature (-14 ÷ -22°C), temperature fluctuation in the cycle of 48 hours, constant temperature of -18°C, constant temperature of -30°C. In the studied ice cream after every 30 days of storage were determined: overrun (according to the method given in PN 67/A-86430) and melting behavior (melting resistance) - according to the method developed by the Central Laboratory of Refrigeration in Lodz (Bergamn-Szczepanik & Kałuziak 1988).

Results and discussion

Ice cream should have desirable characteristics: excellent flavor and aroma, smooth texture, moderately firm texture, smooth uniform throughout the mass, no ice crystals, the optimum overrun (air volume), resistance to changes in temperature, attractive appearance, ease of shaping and reaping, uniform appearance after melting, normal freezing point (melting), nutritional

and refreshing properties. They should be clean, with no signs of contamination, and a whole bunch evenly frozen. Good ice cream readily dissolve in the mouth, have a pleasant taste and aroma typical of the mix (Campbell & Marshall 1982, Hartel 1996, Rakowska 1985).

The primary direct indicators of the quality of ice cream include the structure and consistency. Ice cream should be characterized by the structure and consistency of fluffy, uniform throughout the mass, smooth, without noticeable crystals of frozen water or crystallized lactose and concise. The consistency of the ice cream with additives should be characteristic of these additives, and unaerated ice cream - smooth and compact.

Physicochemical features which greatly determine ice sensory impressions are overrun, viscosity and melting behavior. These features and their values are specific to particular types of ice cream and are mainly determined by the composition of the ice-cream mixture, and the course of the process. Ice cream as an article consists of water, air and solid components, and therefore the stability of the system is determined, inter alia, by the size of air bubbles and their stability. Too big bubbles cause deterioration of the structure and texture of ice cream.

Overrun of ice cream is important for their quality. A significant influence on the overrun of ice cream have mutual proportions of the individual components of ice-cream mixture, mainly fat and dry matter, the addition of stabilizers of a suitable amount and the addition of solid components, such as fruits, chocolate, etc. Overrun is one of the important quality characteristics of ice cream, since it determines the structure of the and the consistency of ice cream and has a significant impact on their organoleptic assessment.

Changes of overrun of vanilla ice cream during storage are shown in Figure 1. Over the entire storage period, these changes had a strong decreasing trend. Ice cream stored at the variable temperature characterized the highest dynamics of changes. Ice cream overrun was best preserved when stored at -30°C , because it remained at a level above 100%.

The initial a storage period the content of air was about 150%. In the final stage of storage different values of fluffiness were found, depending on the storage temperature. The overrun of vanilla ice cream reached after 360 days of storage of the value of 104.53% at -30°C , 84.11% at -18°C , and 66.82% in variable temperature. Ice cream stored in variable conditions of temperature characterized the greatest rate of overrun changes.

The air in ice cream provides a light and soft texture and affects the physical properties of ice cream such as hardness and melting. These parameters are influenced not only the amount of air, or the degree of aeration, but also the size and dispersion of air bubbles (Sofjan & Hartel 2004).

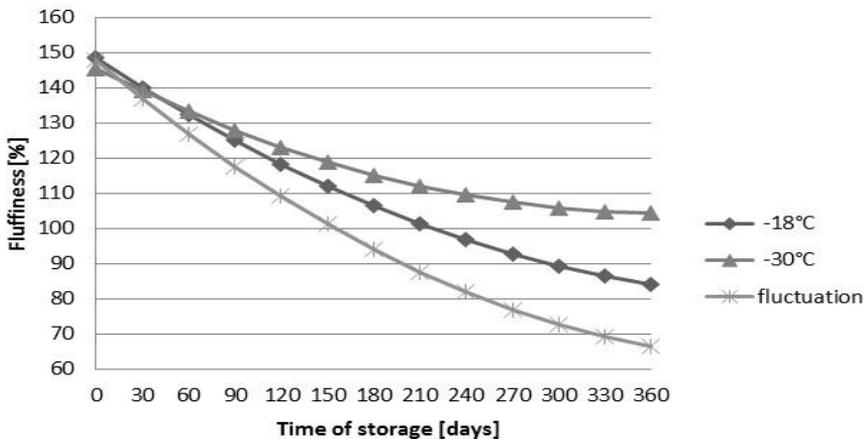


Figure 1. Changes of overrun of vanilla ice cream at a temperature of -18°C, at a constant temperature -30°C and under conditions of temperature fluctuations -14 ÷ -22°C during 360 days storage

Source: own research.

Aeration of in a mixture results air bubbles dispersed phase, the freezing causes the formation of a dispersed second phase - the phase of the ice crystals. Bubbles and crystals are usually the size of 20 to 50 microns (Goff 2001).

Aeration has a significant influence on the ice crystal size variation, and therefore also on the microstructure of frozen desserts. Higher air content causes in fact the formation of a of non-frozen, dispersed around the air bubbles thin layer. This results in smaller ice crystal size (Flores & Goff 1999a).

The air content in ice cream at 70% is quite sufficient to disperse the ice crystals well (Flores & Goff 1999a). Smaller overrun results in larger ice crystals and also leads to a reduction in hardness (Abd El-Rahman et al. 1997, Prindiville et al. 1999). Increasing overrun in ice cream (from 80% to 100% or 120%) leads to the formation of slightly smaller air bubbles and ice crystals. Increasing the overrun makes the ice cream softer and more resistant to melting (Sofjan & Hartel 2004).

The size of air bubbles in the ice is influenced by many factors. Stirring during the freezing causes the larger bubbles are divided into smaller ones. The surfaces of air bubbles are covered with large amount of fatty globules. Fat creates a network on the surface of the bubble, which protects him from connecting with other bubbles (Chang & Hartel 2002a, Chang & Hartel 2002b, Marshall & Arbuckle 2000, Sofjan & Hartel 2004, Walstra 1989, Wildmoser H. et al. 2004).

During storage of ice cream in the air cells changes occur as a result of three basic mechanisms: disintegration, merger and loss of water. The rate of change of air cells is dependent on the technological process, the storage temperature, as well as the composition of the ice-cream mixture. Slowdown of deterioration of the dispersion of air bubbles in the ice cream can be achieved by the use of emulsifiers, stabilizers and a decrease in the storage temperature. Ice storage for 4 months at -15°C causes the formation of connections and channels between the air bubbles, resulting in a short time to the formation of air bubbles of irregular shape, and even air holes inside the ice cream (Chang & Hartel 2002a).

Connecting of single cells leads to the formation of gas channels and removing air from the deeper layers of the ice cream to the outside. This leads to the collapse of the surface of the ice, particularly at elevated storage temperatures. Air bubbles connecting is an important mechanism for destabilizing the structure of ice cream and occurs when the coating cracks and bubbles join. Air bubbles combining leads to shrinkage of the ice cream, irreversible changes in the volume of the product. This process can be minimized using the appropriate storage temperature (Barfod 2001, Turan et al. 1999).

During storage of the ice cream in a variable temperature emulsifiers increase thermal shock resistance and melting by reducing growth of ice crystals and bubbles. Emulsifiers improve the stability of the air bubbles and give better their distribution. The use of higher aeration gives more air bubbles. High air content protects ice cream against build up of ice crystals in the presence of emulsifiers during thermal shocks (Barfod 2001).

The most preferred method of long term storage of ice cream with a high fat content is to store them at temperature as low as possible. The benefits of such a method of storage must be proportionate to the cost of storage. The indicated temperature during long-term storage in order to maintain the high quality of the products is the temperature of -30°C or lower (Gormley et al. 2002).

The purpose of a neutral substance is to provide ice cream delicate, smear and smooth texture. Thanks to them ice cream obtain the correct consistency, which is reflected during consumption. During storage of ice cream they are exposed to temperature changes every time you open and close the lid of the freezer or the automatic defrost. The stabilizers extend and impede the process of melting of the ice crystals during temperature variations, which results in fewer large ice crystals. The presence of neutral substance also reduces the sensation of cold when the ice cream melting in the mouth, and especially promotes aeration device, in fact ice-cream mix to become more dense, has the capacity to absorb a greater amount of air.

Resistance to change in the quality of the product taking place under the influence of temperature fluctuations during transport and storage is its distinct feature. Ice exposed to a fairly short period of time at a temperature above the melting point will deform, change not accepted by the consumer (Palich & Świtka 1987).

Well-known characteristic ice cream feature - melting or melt-in - is dependent inter alia on the stabilizers and emulsifiers. The desired product melts at a moderate speed, the resulting liquid form has the appearance of the original mixture. Commonly known disadvantages are excessive foaming, shear and too slow melting.

The temperature at which ice cream begin to melt is closely related to the temperature of the freezing mixture of ice-cream. Their melting behavior of ice cream is very important feature and depends on the composition of the ice-cream mixture, and additives, as well as the size of the fat globules (Koxholt et al. 2001). The network formed by agglomerates of fat prevents the loss of the shape of the ice cream. Storage conditions of ice cream and related recrystallization, are also very important in the case of melting. The rate of melting and the shape of ice cream are also influenced by the type and the added amount of emulsifier (Bolliger et al. 2000, Granger C. et al. 2005).

Changes of melting of ice cream studied are shown in Figure 2 Determination of melting of ice cream was made by the method developed by the Central Laboratory of Refrigeration. According to this method, leakage after 60 minutes less than 3 ml indicates a high resistance to melting of ice cream.

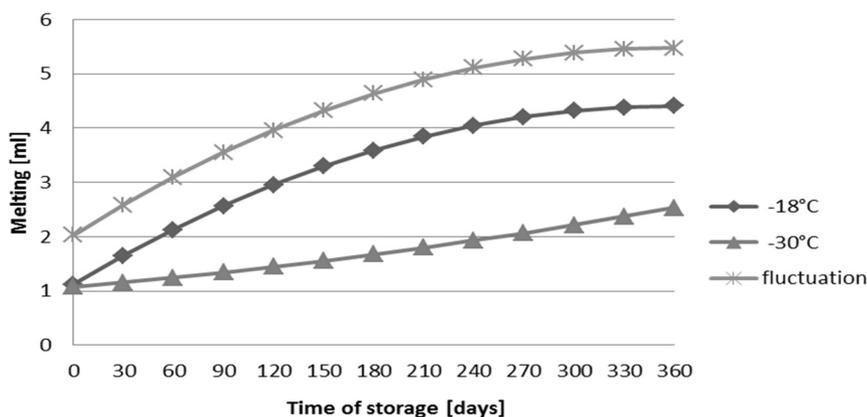


Figure 2. Changes of melting of vanilla ice cream at a temperature of -18°C, at a constant temperature -30°C and under conditions of temperature fluctuations -14 ÷ -22°C during 360 days storage

Source: own research.

This feature deteriorated in proportion to the passage of time of storage. Dynamics of melting changes depended on the temperature of ice cream storage and increased with increasing storage temperature.

The initial value of melting of ice cream was 1.0 ml. Melting behavior of ice cream throughout the storage period showed a rising tendency. Dynamics of changes depended on the storage temperature. The greatest growth of melting was found in ice cream stored in the variable temperature. Differences were found in the values of final melting of ice cream stored in different conditions. Melting behavior of ice cream exceeded the critical value of 3 ml after 60 days of storage at a variable temperature, and ice cream stored at -18°C after 150 days of storage. The ice stored at -30°C there didn't exceed 3 ml at all.

Melting behavior of ice cream, the ability to liquefaction in the mouth and at room temperature is important for the consumer characteristic. Melting behavior depends on the fat content in ice cream. Ice cream melts faster if they contain little fat. With the increase of the fat content the melting time is increased. The fat content has an impact on many characteristics of ice cream, including hardness. Ice cream with a fat content of 10% longer to melt and are softer than ice cream with a fat content of 7%. With the increase in fat content the organoleptic assessment, the creaminess and softness of the ice cream are also increasing. The optimal formation of the fat in the ice cream structure is responsible for many desirable features, including the ability to retain a shape, and the slow pace of melting and smooth texture during melting (Frost et al. 2005, Goff 1997, Roland et al. 1999).

Fat plays an important role in stabilizing the structure of the ice cream. Partially agglomerated fat globules are mainly responsible for the stabilization of air bubbles and foam structure. The destabilization of fat globules and resistance to melting of ice cream depends on the ice-cream mixture homogenizing, the agglomerates of fat are formed then. Depending on mechanical failure of the fat globules the air bubble surface is more or less covered by the partially destabilized fat agglomerates. However, there are areas stabilized by the intact of fat globules in milk and protein. With this structure of the air bubble surface which protects it from collapsing there can be obtained ice cream with a stable structure, with a high resistance to melting. An important element is the size of the agglomerates of fat and air bubbles (Koxholt et al. 2001).

The melting behavior of ice cream is influenced by the dry matter content, fat, sugars, and the use of stabilizers. In order to improve the quality of ice cream and reduce the calorific value, fat contained in ice cream can be replaced completely with use of inulin, while maintaining a creamy, soft, proper fats taste. Moreover, inulin, acting to stabilize prevents the formation of a rough, "cold" texture when the temperature changes during storage of ice cream (Wouters, 1998).

Conclusions

During storage of ice cream changes resulting in deterioration in the quality of ice cream occurred. Long-term storage of ice cream had a negative impact on their quality. Storage temperature fluctuation has a significant impact on increasing the dynamics of changes in the quality of family traits of ice cream, reducing their storage stability. Ice kept the desired (greater than 100%) degree of aeration during the 150 days of storage at a variable temperature, and during 210 days at -18°C . Only those stored at -30°C had appropriate overrun throughout storage. Ice cream stored in the variable temperature kept high resistance to melting for 60 days, while those stored at -18°C remained the same during 120 days. Ice stored at the lowest temperature of -30°C kept corresponding melting resistance throughout the whole storage. Based on the survey, it was found that the family ice cream stored at the recommended temperature of -18°C retain good quality for about three months. The best of family of ice cream storage temperature is the temperature -30°C instead of two years recommended by producer.

References

- Abd El-Rahman, Madkor A. M., Ibrahim F. S., Kilara A., 1997, Physical characteristics of frozen desserts made with cream, anhydrous milk fat, of milk fat fractions, *Journal of Dairy Science* 80, 1926-1935.
- Barfod N. M., 2001. The emulsifier effect, *Dairy Industries International* 1, 32-33.
- Bergman-Szczepanik D., Kałuziak H., 1988, Metody oceny stabilizatorów do lodów, *Chłodnictwo* 2, 18-21.
- Bolliger S., Goff H.D., Tharp B.W., 2000, Correlation between colloidal properties of ice cream mix and ice cream, *International Dairy Journal* 10, 303-309.
- Campbell J., Marshall R., 1982, *Podstawy produkcji mleka spożywczego i tego przetworów*, PWN, Warszawa.
- Chang, Y., Hartel R. W., 2002a, Stability of air cells in ice cream during hardening and storage, *Journal of Food Engineering* 55, 59-70.
- Chang, Y., Hartel R. W., 2002b, Development of air cells in a batch ice cream freezer, *Journal of Food Engineering* 55, 71-78.
- Czerwińska D., 2006, Przełamać lody, *Przegląd Gastronomiczny* 7-8, 11-12.
- Dzwolak W., Ziajka S., 1998, *Produkcja mlecznych deserów mrożonych*, OWH Warszawa.
- Flores A. A., Goff H. D., 1999, Ice Crystal Size Distributions in Dynamically Frozen Model Solutions and Ice Cream as Affected by Stabilizers, *Journal of Dairy Science* 82, 1399-1407.

- Frøst, M.B., Heymann H., Bredie W.L.P., Dijksterhuis G.B., Martens M., 2005, Sensory measurement of dynamic flavour intensity in ice cream with different fat levels and flavourings, *Food Quality and Preference* 16, 305-314.,
- Goff, H. D., 1997, Colloidal aspects of ice cream – a review, *International Dairy Journal* 7, 363-373.
- Goff H. D., 2001, Ice cream under control. *Dairy Industries International* 1, 26-27, 29-30.
- Gormley, R., Walshe T., Hussey K., Butler F., 2002, The Effect of Fluctuating vs. Constant Frozen Storage Temperature Regimes on Some Quality Parameters of Selected Food Products. *Lebensmitt Wissenschaft und Technologie* 35, 190-200.
- Granger C., Leger A., Bary P., Langendorff V., Cansell M., 2005, *Influence of formulation on the structural networks in ice cream*, *International Dairy Journal* 15, 255–262
- Grzebińska W., 2004, Lody. Zmrożona słodycz, *Przegląd Gastronomiczny* 4, 10-11.
- Hartel R.W, 1996, Ice crystallization during the manufacture of ice cream, *Trends in Food Science and Technology* 10, 315-321.
- Koxholt M. M. R., Eisenmann B., Hinrichs J., 2001, Effect of the fat globule sizes on the meltdown of ice cream, *Journal of Dairy Science* 84, 31-37.
- Marshall R. T., Arbuckle W. S., 2000, *Ice cream*, 5th ed. Aspen Publishers, Gaithersburg.
- Oziemkowski P., 1997. Wykorzystanie stabilizatorów firmy Meyhall na bazie naturalnych hydrokolidów w technologii produkcji lodów. *Materiały VI Sesji Naukowej: Postęp w Technologii, Technice i Organizacji Mleczarstwa*. Olsztyn, 20-21 luty, str. 246-250.
- Palich P., J. Świtka, 1987, Wskaźniki czasowo – temperaturowe i ich zastosowanie, *Chłodnictwo* 12, 12–14.
- PN 67/A-86430.
- Polak E., H. Kałuziak, 2000a, Rola białka w lodach i metody jego oznaczania. *Przegląd Piekarski i Cukierniczy* 8, 54-55.
- Polak E., H. Kałuziak, 2000b, Lody – wybrane zagadnienia, *Przemysł Spożywczy* 4, 33–35.
- Polak E., 2005, Od czego zależy jakość lodów, *Przegląd Piekarski i Cukierniczy* 8, 78-81.
- Prindiville, E. A., Marshall R. T., Heyman H., 1999, Effect of milk fat on the sensory properties of chocolate ice cream, *Journal of Dairy Science* 82, 1425-1432.
- Rakowska D., 1985, Jakość lodów i mrożonych deserów, *Chłodnictwo* 2, 12-13.

- Roland A. M, Phillips L. G., Boor K. J., 1999, Effects of fat content on the sensory properties, melting, color, and hardness of ice cream. *Journal of Dairy Research* 82, 32-38.
- Soukoulis Ch., Lyroni E., Tzia C., 2010, *Sensory profiling and hedonic judgement of probiotic ice cream as a function of hydrocolloids, yogurt and milk fat content*, *LWT - Food Science and Technology* 43, 1351-1358.
- Sofjan R. P., Hartel R. W., 2004, Effects of overrun on structural and physical characteristics of ice cream, *International Dairy Journal* 14, 255-262.
- Turan S., Kirkland M., Trusty P. A., Campbell I., 1999, Ingredient interaction, *Dairy Industries International* 1, 27, 29-31.
- Walstra, P., 1989, Principles of foam formation and stability, in Wilson, A. J. (ed) *Foams: Physics, Chemistry and Structure*, Springer, Berlin (pp. 1–15).
- Wildmoser H., Scheiwiller J., Windhab E.J., 2004, *Impact of disperse microstructure on rheology and quality aspects of ice cream*, *Lebensm.-Wiss. u.-Technol.* 37, 881–891.
- Wouters R., 1998, Nice – but not naughty, *Dairy Industries International* 6, 25, 27.

MINERAL CONTENT IN TRADITIONAL AND CONVECTIONAL PORK MEAT AND PRODUCTS

**Monika Radzymińska¹, Bożena Garbowska¹,
Dominika Jakubowska¹, Ewa Siemianowska²**

*¹Chair of Commodity Science and Food Research,
University of Warmia and Mazury in Olsztyn*

*²Chair of Foundations of Safety,
University of Warmia and Mazury in Olsztyn
ewa.siemianowska@uwm.edu.pl*

Introduction

The European Union, seeking the preservation of cultural identity, including culinary heritage, has introduced a system of regional and traditional products. This system is based on three categories: Protected Designation of Origin, which refers to products very closely related to the area which name they bear; Protected Geographical Indication, which, in a specified Geographic Area, will concern production or processing or reparation and Traditional Speciality Guaranteed, a necessary condition of which is to describe the traditional character of the product (Borowski 2010, Sztejn & Wiszniewska-Laszczych 2010, Tyrán 2007). We are witnessing a reassertion of foods with local and regional identities. Guerrero et al. (2010) studies showed that southern European regions tended to associate the concept of "Traditional" more frequently with broad concepts dry as heritage, culture or history, and Central and Nordic European regions tended to focus on practical issues, mainly dry as convenience, health or appropriateness. In the EU Member states we may observe a strong trend to stress their own regional affiliation. Local and regional food are valuable assets in our bid to develop the kind of tourism and recreation that are associated with nature and culture (Ilbery et al. 2000, Makała et al. 2006, Parrott et al. 2002, Siemieniako et al. 2011).

National tastes and preferences play a important role in the interest in authentic local produce. More leading manufacturers will need to retain strong local food production activities to give that preferred local flavour to their ranges (Lehtinen 2012). The system of protection and promotion of regional and traditional products is one of the most important factors influencing sustainable development of rural areas. Producers of food can protect their

articles on the European level (Council Regulations No 2081/92, No 2082/92) or they can label their products with the promotion sign which guarantee the traditional character of the production such as “Quality Tradition”, ”Culinary Heritage Warmia Mazury Powiśle”.

In many scientific studies, both in the field of food and medicine research, special attention is paid to the role of minerals content in the human diet. Calcium presents a number of different functions in the metabolic processes. It is an activator or an inhibitor of several enzymes, but above all it is the main component of bone tissues (Bréchar d et al. 2013; Numaga - Tomita and Punchline 2013; Parnis et al. 2013). Calcium is necessary to maintain the proper water-electrolyte and acid-base balance but also the muscle- nerve excitability (Berchtold et al. 2000; Urena et al. 2013). The adequate amount of calcium in the human body decreases the risk of ischemic heart diseases and the formation of kidney stones (Hamdani et al. 2013). Phosphorus, like calcium, plays a number of important functions in the organism (Fazlini et al. 2013). It is found in all cells of the body and affects the metabolism of proteins, fats, and carbohydrates. Additionally, it provides the balance of acid-base system [Finlay et al. 2013; Geddes et al. 2013; Oliveira and Machado 2013]. Magnesium, like calcium and phosphorous, is involved in the proper formation of the bone tissues structure (Louvet et al. 2013, Wu et al. 2013). It is also essential for the normal functioning of the cardiovascular system (Shechter and Shechter 2013) and many enzymes (e.g. kinases), which are involved in numbers of metabolic pathways in the body (Eshkoli et al. 2013, Song et al. 2013; Vadivel et al. 2013). Potassium, present in all body fluids, is responsible for the proper functioning of nerves and muscles, and formation of Na^+/K^+ and ATP. Potassium, like calcium and magnesium, is involved in the transmission of nerve impulses (Brunt et al. 2013; Nagaraj et al. 2013; Urrego et al. 2014). Iron is a component of hemoglobin, myoglobin, respiratory enzymes and many coenzymes. It participates in important organism activities, such as ATP formation (Ekiza et al. 2013; Sterling & Lill 2013; Vashchenko & MacGillivray 2013, Ye et al. 2013).

The aim of the study was to determine the differences in the content of iron, magnesium, calcium, potassium, and phosphorus in processed pork products from small local manufacturers and large producers.

Experimental procedures

The study was carried out on raw pork, pork ham and sausage produced by: a) small-scale producers (meat processing plants) that labelled their products with the sign “Culinary Heritage Warmia Mazury Powiśle” (CHWMP); b) small-scale producers that declared the use of local raw materials and methods for producing traditional products (L); c) large plants

that manufactured products with names related to the following terms: “rural”, “peasant”, “traditional”, and “for generations” (C). The research material (CHWMP and L) was selected on the basis of previously conducted studies (Radzymińska et al. 2009; Staniewska et al. 2009) that focused on the identification of meat products which, in the opinion of the producers, demonstrated exceptional quality, resulting mainly from the traditional method of production and from raw materials (of local origin).

Each sample of raw meat, ham and sausage (from different producers - about 1500 g) were homogenized to study. To analyze were taken three replicate of every meat and meat products samples.

Meat were mineralized in a mixture of nitric and perchloric acids (3:1) in an electric aluminium heating block with temperature programming (VELP DK 20, manufactured by VELP Scientifica, Italy), within 4-6 hours, gradually increasing the temperature from 120 to 200°C. Residue was transferred to 50 cm³ measuring flasks and filled up with deionised water. Ca, Mg, K and Fe contents were determined using flame atomic absorption spectroscopy (acetylene-air flame) using atomic absorption spectrometer Unicam 939 Solar (Great Britain), equipped with an Optimus data station, background correction (deuterium discharge lamp) and an appropriate cathode lamp. A 10% aqueous lanthanum chloride solution, in amounts ensuring a final concentration of La³⁺ at 1%, was added to all measured solutions for determining Ca. 1 mg/cm³ concentration standards of calcium and magnesium, diluted with 0.1M solution of HNO₃, were prepared on the basis of the BDH standards (Germany).

The concentration of phosphorus in the mineralizates was determined with colorimetric method with ammonium molybdate (VI), sodium sulphate (IV) and hydroquinone (transformation of phosphates in sulphuric acid with ammonium molybdate (VI) into phosphomolybdates which following reduction with sodium sulphate (IV) and hydroquinone to phosphomolybdic blue). Absorbance was measured at the wave length $\lambda = 610$ nm with the use of a spectrophotometer VIS 6000, KRÜSS OPTRONIC, Germany.

The differences in the tested elements between the examined categories of meat products (CHWMP, L, C) were determined with a one-way analysis of variance (ANOVA). The significance of differences was tested at the 0.05 significance level.

Results

An analysis of iron concentration in the tested products (Table 1) revealed the statistically significant content of this element in sausage. This product, labelled with the sign “Culinary Heritage Warmia Mazury Powiśle”,

had a significantly higher concentration of iron ($2.060 \text{ mg/g} \pm 0.950 \text{ mg/100 g}$) in comparison with sausage produced by other local manufacturers ($1.541 \pm 0.072 \text{ mg/100 g}$) and large-scale producers ($1.450 \pm 0.433 \text{ mg/100 g}$).

Table 1. Iron and phosphorus content in the meat and meat products, depending on its origin (mg/100g)

products	origin	P			Fe		
		\bar{x}	SD	ANOVA	\bar{x}	SD	ANOVA
Raw pork	L (n=9)	212	8	F=1.17; p=0.33	0.871	0.405	F=0.16; p=0.85
	CHWMP (n=5)	209	19		0.967	0.196	
	C (n=9)	205	6		0.823	0.201	
Ham	L (n=9)	255	96	F=0.39; p=0.68	1.080	0.218	F=0.36; p=0.70
	CHWMP (n=7)	242	60		1.031	0.263	
	C (n=13)	266	34		0.984	0.268	
Sausage	L (n=9)	209	37	F=0.86; p=0.46	1.541	0.072	F=5.87; p=0.04
	CHWMP (n=5)	244	26		2,060	0,950	
	C (n=9)	226	34		1,450	0,433	

n- samples; \bar{x} -mean; SD – standard deviation

L – traditional products; CHWMP – Culinary Heritage Warmia Mazury Powiśle

C - large plants that manufactured products with names related to the following terms: “rural”, “peasant”, “traditional”, and “for generations”

Source: own research

The average phosphorus content (Table 1) was similar in meat, ham and sausage and ranged from $205 \pm 6 \text{ mg/100 g}$ (in conventionally produced meat) to $266 \pm 34 \text{ mg/100 g}$ (in conventionally produced ham). The differences between particular categories of products were statistically insignificant ($p > 0.05$).

An analysis of product origin and type showed that the content of magnesium was similar (Table 2) and ranged from $20.9 \pm 3.2 \text{ mg/100 g}$ in the conventional ham to $25.2 \pm 1.3 \text{ mg/100 g}$ in CHWMP-labelled sausage. The concentration of calcium did not differ statistically ($p > 0.05$) as far as the origin of raw material was concerned. The sausages had a higher content of calcium (on average 14.008 mg/100 g) in comparison with meat (on average 2.960 mg/100 g) and ham (on average 9.086 mg/100 g).

Table 2. Magnesium, calcium, potassium, content in the meat and meat products, depending on its origin (mg/100g)

products	origin	Mg			Ca			K		
		\bar{x}	SD	ANOVA	\bar{x}	SD	ANOVA	\bar{x}	SD	ANOVA
Raw pork	L (n=9)	23.8	1.1	F=0.96 p=0.40	2.630	1.739	F=0.30 p=0.75	323	31	F=1.44 p=0.27
	CHWMP (n=5)	23.7	1.1		2.942	1.551		295	23	
	M (n=9)	22.9	1.2		3.308	1.933		328	19	
Ham	L (n=9)	22.6	4.4	F=1.38 p=0.27	9.941	4.070	F=0.39 p=0.68	342	63	F=0.04 p=0.96
	CHWMP (n=7)	23.9	4.5		8.427	5.590		339	74	
	M (n=13)	20.9	3.2		8.891	5.002		335	27	
Sausage	L (n=9)	22.5	5.3	F=0.45 P=0.65	14.853	1.506	F=0.32 p=0.73	376	8	F=1.26 p=0.34
	CHWMP (n=5)	25,2	1,3		13,876	2,129		310	80	
	M (n=9)	24,6	2,7		13,297	3,904		347	26	

n- samples; \bar{x} -mean; SD – standard deviation

L – traditional products; CHWMP – Culinary Heritage Warmia Mazury Powiśle

C - large plants that manufactured products with names related to the following terms: “rural”, “peasant”, “traditional”, and “for generations”

Source: own research

The origin of meat products ($p>0.05$) did not influence the content of potassium in the tested samples. The average concentrations of this element were similar in different types of products and ranged between 295 ± 23 mg/100 g in meat from the producers united in the culinary heritage network and 376 ± 8 mg/100 g in sausages produced by small local manufacturers.

Discussion

Meat is a rich source of minerals in the human diet. Iron deficiency causes anaemia, which is one of the major health problems. The studies carried out by Jimenez-Colmenero et al. (2010b) showed that the average concentration of this element amounted to 0.79 mg/100 g in raw pork sausage and 0.54 mg/100 g in cured smoked sausage. Chen et al. (1997) determined the content of iron in smoked ham at 1.0 mg/100 g.

During adulthood, iron stores gradually increase in men; in women, stores start to increase after menopause. Total body iron averages about 3.8 g in men and 2.3 g in women (Yip 2001). The extraordinary capacity of the human body to retain iron (15–40 g) is exhibited in individuals with hemochromatosis (Bothwell and MacPhail 1998). About one third of the total

body iron is bound to storage proteins, primarily ferritin or hemosiderin in the liver, spleen, and bone marrow. About two thirds of the total body iron serves metabolic or enzymatic functions. For example, the body requires iron for the synthesis of the oxygen transport protein hemoglobin and the oxygen storage protein myoglobin. Iron is required for the formation of iron-containing enzymes, which participate in electron transfer and oxidation–reduction reactions. Ironically, the toxic potential of iron derives from its primary biologic property, the ability to exist in two oxidation states. Some redox reactions, when not properly modulated by iron-binding proteins or antioxidants, can damage cellular components, including lipids, proteins, and nucleic acids (Brody 1994). Although iron is known to be an essential nutrient, it is not widely appreciated that iron deficiency anemia is the most common nutritional deficiency. Continued depletion of iron stores leads to iron deficiency anemia and serious biologic impairment. Iron deficiency anemia is related to delayed cognitive development and intellectual impairment (Grantham-McGregor and Ani 2001). Given the critical role of iron in oxygen transport and storage in muscle, it is not surprising that iron deficiency anemia also leads to reduced work capacity (Haas and Brownlie 2001). Since 1943, the Food and Nutrition Board of the Institute of Medicine has established guidelines for recommended dietary allowances (intakes) of iron (Swanson 2003). In general, individuals at greatest risk of iron deficiency anemia are those with increased iron needs.

Meat and meat products are one of the main sources of potassium in the human diet. This element plays an important role in energy conversion and membrane transport in the body. The studies conducted by (Jimenez-Colmenero et al. 2010a) found the average concentration of potassium in raw pork sausage to be 278.35 mg/100 g and 487 mg/100 g in cured smoked sausage. Based on the studies by Chen et al. (1997) it is assumed that the content of this element in smoked ham averages 120mg/100 g.

Traditional meat products may differ in composition depending on the origin and processing method (Borowski 2007, Gandemer 2009, Jiménez-Colmenero et al. 2001). Jiménez-Colmenero et al. (2010a) presented the components of dry-cured ham. According to these authors, dry-cured ham is a good source of iron (between 1.8 and 3.3 mg/100 g) and has considerable concentrations of phosphorus (157-180 mg/100 g), potassium (153-160 mg/100 g) and magnesium (17 and 24 mg/100 g). Chen et al. (1997) studies show that the average concentration of magnesium in raw sausage is 17mg/100 g and in cured smoked sausage it is 18.97mg/100 g. The content of calcium reaches 6.80mg/100 g, in cured smoked sausage it reaches 10.95mg/100 g (Jimenez-Colmenero et al. 2010b) and in smoked ham it averages 3.7mg/100 g (Chen et al. 1997). The content of selected elements in meat and meat products changes with the region where the pigs have been reared and depends on feeding and animal age as well as on additives used in

the processing of pork (Hansen et al. 2006). Thus, the concentration of microelements and essential elements may vary significantly.

Consumers consider meat to be a healthy and important component of the diet. According to Fernández-Ginés et al.(2005) future trends in the traditional meat industry direct it more and more to the design and production of functional foods. Consumers support the development of technologies that can improve the health attributes of meat products and guarantee eating quality (Resurreccion 2004, Verbeke et al. 2010). According to Andersen et al. (2005) a better understanding of consumer expectations in relation to perceived meat quality and their relation to existing and new objective quality control tools are areas that deserve further attention if the production of meat shall fulfil the demands of tomorrow.

Conclusions

It was found that the quality of meat and meat products manufactured both in small local companies and large-scale integrated plants did not differ in the concentration of phosphorus, magnesium, calcium and potassium. Anyway, the sausages labelled with the sign “Culinary Heritage Warmia Mazury Powiśle” had a significantly higher content of iron in comparison with products from other manufacturers.

Acknowledgements

This study was financially supported by the Polish Ministry of Science and Higher Education from sources for science in the years 2008-2011 under Research Project No. N N312 261035.

References

- Andersen H.J., Oksbjerg N., Therkildsen M.: 2005, *Potential quality control tools in the production of fresh pork, beef and lamb demanded by the European society*. Livestock Production Science, 94(1), 105-124.
- Berchtold, M. W., Brinkmeier, H., & Müntener, M. 2000. *Calcium ion in skeletal muscle: its crucial role for muscle function, plasticity, and disease*. *Physiological reviews*, 80(3), 1215-1265.
- Bréchar, S., Plançon, S., & Tschirhart, E. J. 2013. *New insights into the regulation of neutrophil NADPH oxidase activity in the phagosome: a focus on the role of lipid and Ca²⁺ signaling*. *Antioxidants & redox signaling*, 18(6), 661-676.
- Borowski J.: 2007, *Meat in human nutrition*. EJPAU, 10(4),02.
- Borowski J.: 2010, *Traditional food – its past and present*. EJPAU 13(2),12.

- Bothwell T.H., MacPhail A.P.: 1998, *Hereditary hemochromatosis: etiologic, pathologic, and clinical aspects*. Seminary Hematology, 35, 55–71.
- Brody T.: 1994. *Inorganic nutrients*. In T. Brody, Nutritional Biochemistry. San Diego, CA: Academic Press: 527–544.
- Brunt, V. E., Fujii, N., & Minson, C. T. 2013. *No independent, but an interactive, role of calcium-activated potassium channels in human cutaneous active vasodilation*. *Journal of Applied Physiology*, 115(9), 1290-1296.
- Chen H-Y., Pilkington D.H., Tharrington J.B., Allen J.C. 1997. *Developing a dry-cured ham nutritional database*. *Journal of Food Composition and Analysis*, 10, 190–204.
- Council Regulation (EEC) No 2081/92 of 14 July 1992 on the protection of geographical indications and designations of origin for agricultural products and foodstuffs.
- Council Regulation (EEC) No 2082/92 of 14 July 1992 on certificates of specific character for agricultural products and foodstuffs.
- Ekiz, C., Agaoglu, L., Karakas, Z., & Gurel, N. 2013. *The effect of iron deficiency anemia on the function of the immune system*. *The Hematology Journal*, 6(1), 579-583.
- Eshkoli, T., Feinshtein, V., Amash, A., Sheiner, E., Huleihel, M., & Holberg, G. 2013. *Magnesium Role in Cytokine Regulation of Hypoxic Placentas Related to Certain Placental Pathology*. In *Magnesium in Human Health and Disease* (pp. 51-63). Humana Press.
- Fazlini, M. F., Suriah, A. R., Zaitun, Y., Kandiah, M., Chee, W. S. S., Chan, Y. M., & Chan, S. P. 2013. *Calcium supplementation amongst postmenopausal women: Effect on serum calcium, phosphorus and magnesium level*. *International Food Research Journal*, 20(1).
- Fernández-Ginés J.M., Fernández-López J., Sayas-Barberá E., Pérez-Alvarez J.: 2005. *Meat products as functional foods: A review*. *Journal of Food Science*, 70(2), R37-R43.
- Finlay, J. C., Small, G. E., & Sterner, R. W. 2013. *Human influences on nitrogen removal in lakes*. *Science*, 342(6155), 247-250.
- Gandemer G.: 2009, *Dry cured ham quality as related to lipid quality of raw material and lipid changes during processing: A review*. *Grasasy Aceites*, 60, 297–307.
- Geddes, R. F., Finch, N. C., Syme, H. M., & Elliott, J. 2013. *The role of phosphorus in the pathophysiology of chronic kidney disease*. *Journal of Veterinary Emergency and Critical Care*, 23(2), 122-133.
- Grantham-McGregor S., Ani C.: 2001, *A review of studies on the effect of iron deficiency on cognitive development in children*. *Journal of Nutrition*, 131, 649S–666S.

- Guerrero L., Claret A., Verbeke W., Enderli G., Zakowska-Biemans S., Vanhonacker F., ... & Hersleth M.: 2010, *Perception of traditional food products in six European regions using free word association*. Food Quality and Preference, 21(2), 225-233.
- Haa, J.D., Brownlie T.: 2001, *Iron deficiency and reduced work capacity: a critical review of the research to determine a causal relationship*. Journal of Nutrition, 131, 676S–688S.
- Hamdani, N., Krysiak, J., Kreusser, M. M., Neef, S., dos Remedios, C. G., Maier, L. S., ... & Linke, W. A. 2013. *Crucial role for Ca²⁺/calmodulin-dependent protein kinase-II in regulating diastolic stress of normal and failing hearts via titin phosphorylation*. Circulation research, 112(4), 664-674.
- Hansen L.L., Claudi-Magnussen C., Jensen S.K., Andersen H.J. 2006, *Effect of organic pig production systems on performance and meat quality*. Meat Science, 74(4), 605-615.
- Ilbery B., Kneafsey M., Bamford M.: 2000, *Protecting and promoting regional speciality food and drink products in the European Union*. Outlook on Agriculture, 29(1), 31-31.
- Jiménez-Colmenero F., Carballo J., Cofrades S.: 2001, *Healthier meat and meat products: their role as functional foods*. Meat Science, 59(1), 5-13.
- Jimenez-Colmenero F., Pintado T., Cofrades S., Ruiz-Capillas C., Bastida S. 2010b. *Production variations of nutritional composition of commercial meat products*. Food Research International, 43, 2378-2384
- Jiménez-Colmenero F., Ventanas J., Toldrá F. 2010a. *Nutritional composition of dry-cured ham and its role in a healthy diet*. Meat Science, 84, 585–593.
- Lehtinen U.E.E.: 2012, *Sustainability and local food procurement a case study of finnish public catering*. British Food Journal, 114(8): 1053-1071.
- Louvet, L., Büchel, J., Steppan, S., Passlick-Deetjen, J., & Massy, Z. A. 2013. *Magnesium prevents phosphate-induced calcification in human aortic vascular smooth muscle cells*. Nephrology Dialysis Transplantation, 28(4), 869-878.
- Makafa H., Olkiewicz M., Moch P.: 2006, *Characteristics of sensory quality of bologna-type sausage from Polish and Italian markets*. ACTA Technologia Alimentaria, 5, 107-116.
- Nagaraj, C., Tang, B., Bálint, Z., Wygrecka, M., Hrzencak, A., Kwapiszewska, G., ... & Olschewski, A. 2013. *Src tyrosine kinase is crucial for potassium channel function in human pulmonary arteries*. European Respiratory Journal, 41(1), 85-95.
- Numaga-Tomita, T., & Putney, J. W. 2013. *Role of STIM1-and Orai1-mediated Ca²⁺ entry in Ca²⁺-induced epidermal keratinocyte differentiation*. Journal of cell science, 126(2), 605-612.
- Oliveira, M., & Machado, A. V. 2013. *The role of phosphorus on eutrophication: a historical review and future perspectives*. Environmental Technology Reviews, 2(1), 117-127.

- Parnis, J., Montana, V., Delgado-Martinez, I., Matyash, V., Parpura, V., Kettenmann, H., ... & Nolte, C. 2013. *Mitochondrial exchanger NCLX plays a major role in the intracellular Ca²⁺ signaling, gliotransmission, and proliferation of astrocytes*. *The Journal of Neuroscience*, 33(17), 7206-7219.
- Parrott N., Wilson N., Murdoch J.: 2002, *Spatializing quality: regional protection and the alternative geography of food*. *European Urban and Regional Studies*, 9(3), 241-261.
- Radzyńska M., Smoczyński S.S., Staniewska K., Garbowska B., Gątorska A., Jakubowska D. 2009, *The market of regional products manufactured by agrotourist farms – the present state and outlook for the future*. *Biuletyn Naukowy*, 30, 57-63.
- Resurreccion A.V.A. 2004, *Sensory aspects of consumer choices for meat and meat products*. *Meat Science*, 66(1), 11-20.
- Siemieniako D., Kubacki K., Głinska E., Krot K.: 2011, *National and regional ethnocentrism: a case study of beer consumers in Poland*. *British Food Journal*, 113(3), 404-418.
- Shechter, M., & Shechter, A. 2013. *The Role of Magnesium in the Cardiovascular System*. In *Magnesium in Human Health and Disease* (pp. 191-204). Humana Press.
- Song, Y., Zhang, C., Wang, L., Dai, Q., & Liu, S. 2013. *Magnesium Intake, Genetic Variants, and Diabetes Risk*. In *Magnesium in Human Health and Disease* (pp. 103-118). Humana Press.
- Staniewska K., Radzyńska M., Smoczyński S.S. 2009. *The potential of the regional delicacies of the meat trade in the region of Warmia and Mazury*. *Biuletyn Naukowy*, 30, 69-74.
- Stehling, O., & Lill, R. 2013. *The Role of Mitochondria in Cellular Iron–Sulfur Protein Biogenesis: Mechanisms, Connected Processes, and Diseases*. *Cold Spring Harbor perspectives in biology*, 5(8), a011312.
- Swanson C.A.: 2003, *Iron intake and regulation: implications for iron deficiency and iron overload*. *Alcohol*, 30, 99-102.
- Szteyn J., Wiszniewska-Laszczych A.: 2010, *Uregulowania prawne UE i krajowe dotyczące żywności tradycyjnej i regionalnej* (European and Polish regulations on traditional and regional food). *Medycyna Weterynaryjna*, 66(02), 79-82. (In Polish)
- Tyran E.: 2007, *Regional and traditional products as an important part of rural tourism offer*. *Oeconomia*, 6(3), 121-128.
- Urena, J., Fernandez-Tenorio, M., Porrás-Gonzalez, C., Gonzalez-Rodriguez, P., Castellano, A., & Lopez-Barneo, J. 2013. *A New Metabotropic Role for L-type Ca²⁺ Channels in Vascular Smooth Muscle Contraction*. *Current vascular pharmacology*, 11(4), 490-496.
- Urrego, D., Tomczak, A. P., Zahed, F., Stühmer, W., & Pardo, L. A. 2014. *Potassium channels in cell cycle and cell proliferation*. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 369(1638), 20130094.

Vadivel, K., Agah, S., Messer, A. S., Cascio, D., Bajaj, M. S., Krishnaswamy, S., ... & Bajaj, S. P. 2013. *Structural and Functional Studies of γ -Carboxyglutamic Acid Domains of Factor VIIa and Activated Protein C: Role of Magnesium at Physiological Calcium*. *Journal of molecular biology*, 425(11), 1961-1981.

Vashchenko, G., & MacGillivray, R. T. 2013. *Multi-copper oxidases and human iron metabolism*. *Nutrients*, 5(7), 2289-2313.

Verbeke W., Pérez-Cueto F.J., Barcellos M.D.D., Krystallis A., Grunert K.G. : 2010. *European citizen and consumer attitudes and preferences regarding beef and pork*. *Meat Science*, 84(2), 284-292.

Wu, L., Luthringer, B. J., Feyerabend, F., Schilling, A. F., & Willumeit, R. 2014. *Effects of extracellular magnesium on the differentiation and function of human osteoclasts*. *Acta Biomaterialia*.

Ye, P., Cheah, I. K., & Halliwell, B. 2013. *A high-fat and cholesterol diet causes fatty liver in guinea pigs. The role of iron and oxidative damage*. *Free radical research*, 47(8), 602-613. Yip R.: 2001, Iron. In B. A. Bowman, R. M. Russell (Eds.), *Present Knowledge in Nutrition* Washington, DC: ILSI Press: 311–328.

PERCEPTION OF PORK QUALITY BY STUDENTS

Anna Sylwia Tarczyńska

*Chair of Dairy Science and Quality Development, Faculty of Food Science,
University of Warmia and Mazury in Olsztyn,
sylviaol@uwm.edu.pl*

Introduction

The contemporary understanding of the concept of quality includes two aspects: quality as a feature (conformity with requirements) and quality as a relation (customer satisfaction). An analysis of the definition of quality reveals the three most common aspects (Zieliński G. 2010): characteristic features of a product (P.B. Crosby, J. Lock), satisfying the customer's needs (A.V. Feigenbaum, J. Juran, K. Ishikawa, ISO 9000), as well as improving a product in order to satisfy the future needs of a customer (W.E. Deming, J. Oakland). This is reflected in the practical operation of business entities which deal with food production. When the needs, expectations and behaviours of customers towards a product are known, as are its individual features, its most attractive parameters can be constantly improved and emphasised (Li Y. et al., 2012). However, food consumers and producers pay attention to different qualities. Consumers expect the food they buy to meet their needs – product quality is associated with its consumption-related value. On the other hand, although a manufacturer makes efforts to meet the customers' needs, he perceives quality as a vehicle which brings profits to his production company (Hamrol A. 2007). The quality of raw material is determined by its usability for production. Efforts made by food producing companies in order to gain profits are associated with outlays for research and development, including the development and launch of new products as well as perfecting the existing ones. Marketing activities, which include market research, advertising and promotion of product consumption, are an inseparable element (Prussak W. 200, Urbaniak M. 2007, Karaszewski 2006).

The main factors which determine the customer's choice of meat include organoleptic qualities, such as colour, smell, texture and fattiness. It is also important where the meat was bought – its cleanness and exposition of products, as well as the price (Połom, Baryłko-Piekielna 2004, Radzymińska, Smoczyński 2008, Pospiech, et al. 2014). Studies conducted by Ozimek (Ozimek I. 2006) have shown that consumers understand quality as

organoleptic attractiveness (freshness – 36.9%, tastiness – 33%, general appearance – 9.7%). Furthermore, these included health qualities, associated with food and nutrition safety, of which the most important were: nutritional value – 21.5%, health aspects – 18.2% and shelf life – 16.5%.

The food crises which have occurred in recent years have directed consumers' attention towards food safety. Consumers now require greater transparency in the food chain and require more information about the quality characteristics of food, such as its nutritional value, origin and methods of production (Mora C. et al. 2006).

Meat from different animals is not perceived by consumers in the same manner. Schroeder has shown that over 80% of consumers in Canada and the USA regard pork, beef and poultry as safe. The Japanese were the most sceptical when it came to the evaluation of meat safety (Schroeder et al. 2006). In further studies, Schroeder showed that the perception of meat safety by a consumer depends not only on the meat type, but also on a specific product. Unlike respondents from Spain and Ireland, Swedish, English and French consumers have concerns about the environmental hazards. According to respondents, serious hazards include those which originate during the production process. Consumers in France, Belgium and Greece were the most concerned about the hazards caused by the use of hormones and antibiotics in animal breeding (Berg 2004, Ozimek et al. 2004). Microbiological hazards were also regarded as important in food safety assessments. Consumers are aware of the importance of microbiological contamination of food, but they do not fully realise the hazard that such contaminations pose. Respondents frequently express concerns about GMO, which are often associated with adverse effects on health. The lowest concerns in regard to food containing GMO were expressed by the Spanish, the Dutch and the Finns, whereas the lowest trust concerning GMO food was expressed by the Austrians, the Danish, the Greeks and the French (Jakubowska et al. 2010).

The perceived safety of meat products depends on a number of factors. A study conducted by Jakubowska et al. (2010) showed it to be significantly affected by demographic characteristics. The respondent age was the strongest differentiating factor. Rudy et al. (2011) showed the effect of consumer age on their purchase preferences regarding different kinds of meat. Respondents aged 55 and more choose pork more frequently than the others, whereas the younger generation chooses poultry more frequently.

One of the important factors in ensuring food safety is the supervision over all the stages of the food chain; in the case of products of animal origin – from rearing to distribution. Responsibility for meat quality is borne by the breeder, the producer, the distributor and the consumer. By implementing and observing the rules of GHP and GMP as well as the HACCP system, and the requirements of voluntary systems of quality management, a company

confirms that it cares about the safety and quality of its products. Some manufacturers of meat products also implement systems which are specific to their branch of industry: QAFP (*Quality Assurance for Food Products*) or PQS (*Pork Quality System*). The aim of the QAFP is to obtain meat which is characterised by high, guaranteed quality which meets the requirements laid down in the standard. It includes control from the moment when the animals' welfare has to be assured so that the meat is safe and of good quality (Obiedziński et al. 2009). Unlike QAFP, PQS focuses on pork only. The aim of the system is to obtain pork of above-standard quality, for example, by guaranteeing a lower content of intramuscular fat (approx. 2.5%). Like QAFP, PQS also covers all the stages of the production process. Fulfilling the conditions of the PQS system guarantees that pork obtained in the process is of better quality, from the point of view of both consumers and producers (Hammermeister 2011, Mocarski 2011).

These considerations lead one to the conclusion that developing modern perception of food quality is dominated by two aspects: improvement of sensory qualities and a guarantee of the safety of the finished product. Companies can analyse the effectiveness of the quality management system based on customer satisfaction (Pawłowska, Strychalska - Rudzewicz 2007).

The aim of this study was to determine consumer satisfaction in regard to pork offered for sale, to determine the decisive factors in the purchase and consumption of pork and the respondents' perception of the role of systems of food safety management (HACCP, ISO 22000, QAFP, PQS) and quality marks ("Poznaj Dobrą Żywność", "Jakość i tradycja", mark of compliance with the Polish Standard), as well as their concerns about hazards to food safety, which may be present in pork products.

Material and methods

The research method applied in the study was a two-part questionnaire. The first part included multiple choice questions regarding: consumption of pork, factors which affect the consumer's decision to buy pork, the place where the consumer buys meat, the perception of systems of food safety and quality marks and knowledge and concerns regarding hazards to food safety. The other part contained sociodemographic questions.

The study was conducted in the first half of 2013 on a group of 165 consumers. The subject of the study were students of Polish universities, in various years of regular and extramural studies. The method of non-random sample choice ("convenience sample") was applied. There were 86% female and 14% male participants. 60% of them were regular students. According to their statements, the study major of 33% of them was associated with food production or safety. Residents of rural areas accounted for 28% of the

respondents, 36% lived in cities with the populations exceeding 100,000 and the remaining 36% lived in smaller towns. The respondents represented all the provinces of Poland.

The results were encoded in the Statistica 10 programme. The questions to which they could give one answer were encoded by the arithmetic method, whereas those to which several answers could be given were encoded by the binary method. The relationship between the variables and the attributes of a group was determined by conducting a χ^2 test at the level of significance $\alpha=0.05$.

Results and discussion

The highest percentage of the respondents eat pork once a week (59.5%). Pork is eaten once a month by 22.2% of the respondents and every day by 16.3%. The other respondents consume pork less than once a month. In order to investigate the factors which affect students' decisions to buy pork, respondents were asked to choose 4 out of 8 variants of an answer: texture, previous experience, brand, colour, appearance of a package, date of expiry, price, quality mark (ISO, QAFP, etc.). The majority of respondents (over 82.3%) chose expiry date, colour of pork (70.6%), price (about 64%), previous experience (42.5%) and texture (31.4%). The other options, such as brand (21.6%), package appearance (9.8%), or quality marks (10.5%) were less important to the respondents.

The respondents' opinions were significantly varied for the "previous experience" option, where they were differentiated by the study major ($\chi^2 = 5.02$ and $p=0.03$). Students of non-food-related subjects chose it more frequently (49%) than those who studied subjects related to food (about 30%). The type of studies differentiated the students' opinions with respect to the "package appearance" option ($\chi^2=4.47$; $p=0.03$). The respondents in regular studies pay attention to the package appearance less frequently (86%) than those in extramural studies (97%). The place of residence was a differentiating factor with respect to the opinion on the importance of quality marks in buying pork ($\chi^2=11.43$; $p=0.009$). The respondents – residents of villages and towns with a population below 50,000) declared that they paid attention to quality marks more frequently than the inhabitants of bigger cities. The students' opinions that the price is the most important factor in buying pork was differentiated by the average per capita income in a household – the higher the income, the lower the percentage of respondents who claim that price is important to them when they buy meat ($\chi^2=12.5$; $p=0.006$).

Assuming that a customer sees a difference in the quality of products depending on the place where they buy them, respondents were asked where – in their opinion – one can buy high quality pork. The responses are shown in Fig. 1.

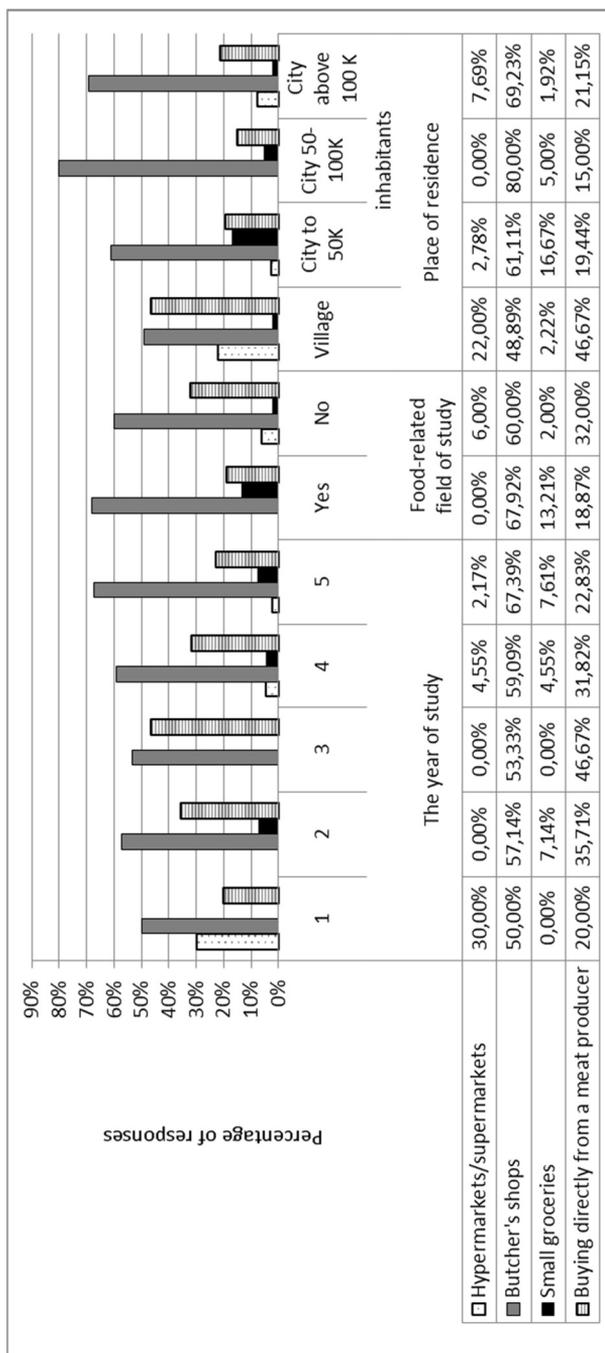


Figure 1. The factors significantly differentiating opinions regarding places for buying pork.

Source: own research.

The respondents' opinions were differentiated statistically by:

- the year of study ($\chi^2=25.6$; $p=0.012$) – as many as 30% of first-year students responded that good quality meat can be bought at supermarkets,
- studying at a food-related major ($\chi^2=13.099$; $p=0.004$) – none of the respondents – students of food-related majors – were of the opinion that good quality meat can be bought at a supermarket; moreover, the responses given by these students indicated "butcher's shops" more frequently than any other places. Furthermore, students of non-food-related majors also chose butcher's shops, but a high percentage of them chose buying meat directly from a meat producer (Fig. 18).
- place of residence ($\chi^2=24.14$; $p=0.004$) – students who live in the country have a similar opinion about butcher's shops and buying pork directly from meat producers as a source of best quality pork; on the other hand, city dwellers mostly chose butcher's shops as places to buy the best quality pork.

Respondents were asked why they ate pork. They were allowed to choose 2 possible responses out of 5: eating pork as a habit, because of its taste, because it can be cooked in many ways, because of its price, because of its availability. The respondents chose mainly the multitude of cooking options (69%), taste value (40%) and high availability of pork (28%). The frequency of choosing the "eating pork as a habit" option was differentiated significantly by the study major ($\chi^2=6.27$; $p=0.012$). Only 7.5% of the respondents – students of food-related majors – chose a habit as the cause of eating pork, whereas the other group of students chose this response twice more frequently.

In order to investigate the knowledge and perception of specific quality systems and marks, which have food safety as their main objective, students were asked about their knowledge of the HACCP, ISO 22000, QAFP, PQS systems, the "Poznaj Dobrą Żywność" ("Experience Good Food"), „Jakość i tradycja” ("Quality and Tradition") quality marks and the compliance with the Polish Standard. The respondents chose "I know" or "I don't know". If they chose "I know", then they had one of three options to choose: "it guarantees food safety", "it doesn't guarantee food safety", "I've heard about it, but I don't know if it's effective".

When asked about systems which guarantee meat safety and high quality, the respondents declared the highest knowledge of the HACCP system and the ISO 22000 food safety assurance system. 62% of the respondents claimed to know the HACCP system, but only 37% thought it was effective. Similar results were obtained in regard to the ISO 22000 food safety assurance system. The QAFP and PQS systems were the least well-known of those mentioned. 60% of the respondents claimed that they did not know them, but no "it is not effective" responses were given.

These systems were significantly differentiated by (Tab. 1):

- the study major – students of food-related majors in their majority (70%) think that the HACCP system and a ISO 22000 certificate guarantee food safety, whereas for the QAFP and PQS systems, over 30 % of such responses were given. On the other hand, respondents studying non-food-related majors usually declared ignorance of those systems;
- type of studies – students of regular studies were of the opinion that the systems are effective more frequently – this applied especially to HACCP and the ISO 22000 certificate, for which this opinion was expressed by 40% of the respondents. On the other hand, extramural students chose the "I don't know" option for each of them.

The findings regarding the quality marks are very similar. In each case, the majority of the respondents (over 40%) claimed not to know the quality marks. A high percentage of the respondents declared that they knew a quality mark, but that they could not say whether it was effective. Only 20% of the respondents claimed that the "Poznaj Dobrą Żywność" and "Jakość i Tradycja" marks were a guarantee of food safety.

Table 1. Results of the χ^2 test and probability at the level of significance of $\alpha=0.05$ in regard to the knowledge of safety systems in meat product manufacture

Criteria		Systems				Marks		
		HACCP	ISO 22000	QAFP	PQS	Poznaj Dobrą Żywność	Jakość i tradycja	Compliance with PS
Sex	χ^2	0.96	2.39	3.31	3.05	2.23	1.40	0.65
	p	0.81	0.49	0.19	0.22	0.52	0.70	0.88
Year of study	χ^2	61.59	44.38	22.36	23.09	15.69	12.71	24.43
	p	0.000	0.000	0.004	0.003	0.21	0.39	0.02
Food-related major	χ^2	68.58	56.49	17.67	34.23	8.31	7.74	45.41
	p	0.000	0.000	0.000	0.000	0.04	0.05	0.000
Type of studies	χ^2	13.28	12.36	9.88	8.33	1.28	3.79	7.54
	p	0.004	0.006	0.007	0.015	0.73	0.29	0.06
Place of residence	χ^2	28.02	12.89	4.46	5.77	8.32	7.16	17.04
	p	0.001	0.17	0.61	0.45	0.50	0.62	0.048

Source: own research.

Respondents' opinions were differentiated statistically only by having a study major related to food. The majority of respondents – students of non-food-related majors – responded that they did not know any quality marks. For the "Poznaj Dobrą Żywność" mark it was over 55% responses, for "Jakość i Tradycja"- over 46%, and for compliance with the Polish Standard – over 63% of the responses. The respondents – students of food-related majors – declared a slightly higher level of knowledge of the quality marks. Moreover,

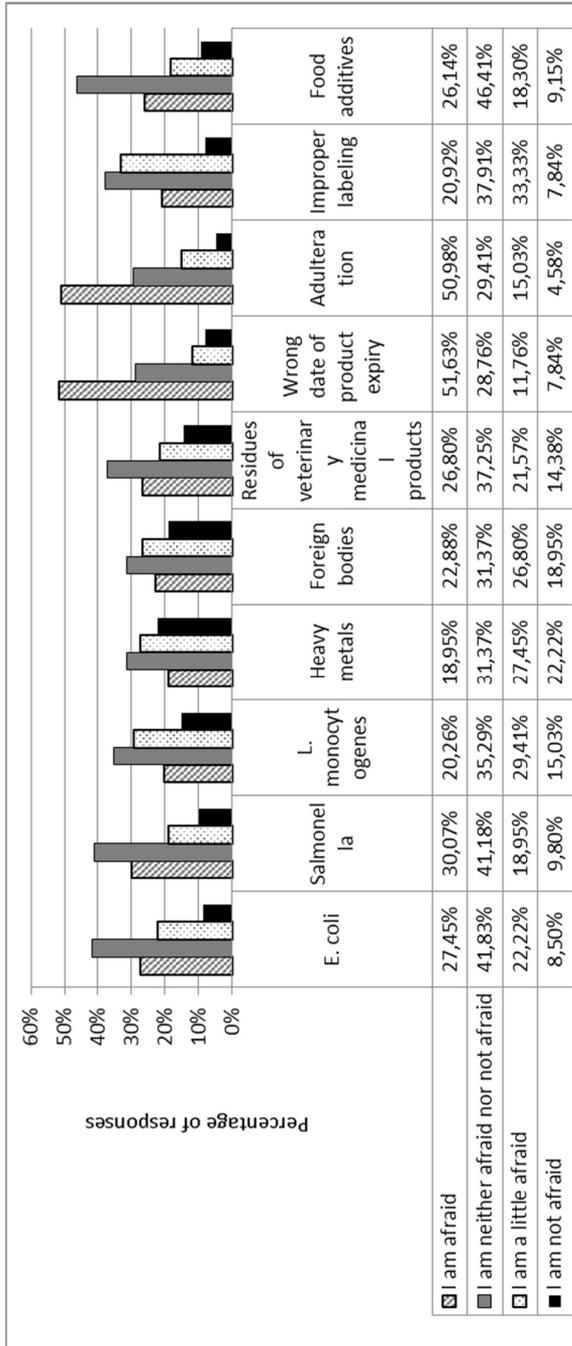


Fig. 2 Opinions regarding perceptions of food safety hazards in pork products.

Source: Own research.

a higher percentage of them think that the marks are a guarantee of food safety: "Poznaj Dobrą Żywność" (26%), "Jakość i Tradycja" (34%), the mark of compliance with the Polish Standard (28%).

One of the objectives of implementation of food quality and safety systems is to meet the customers' needs and to increase their satisfaction. Quality marks are placed on food products to inform a customer that the manufacturer guarantees the high quality of its products. Therefore, the students' attitudes to quality marks placed on pork products were investigated. Opinions on the link between high quality and a quality mark placed on a product were divided. Nearly 44% of the respondents were of the opinion that a quality mark is a guarantee of high quality. About 25% of the respondents did not think that the products bearing such marks were of higher quality, and it did not matter to over 32%. Statistically, the respondents' opinions were differentiated by a link of their study major with food ($\chi^2=22,66$; $p=0.000$). Nearly 70% of students of food-related majors declared having a favourable attitude towards quality marks placed on pork products. On the other hand, opinions were divided among students of non-food-related majors – the presence of such marks did not matter to 42% of them.

Furthermore, the respondents were asked to express their opinions about selected hazards to meat product safety with 4 possible responses to choose from: I am afraid, I am neither afraid nor not afraid, I am a little afraid, I am not afraid. The results are presented in Fig. 2. Each of the hazards is a source of concern for the respondents. The greatest reason for concern is the hazard which arises from providing a wrong date of product expiry on the product package and from an improper package of a meat product (in each of these cases, over 50% of the respondents chose "I am afraid very much"). The source of the smallest concern was the potential presence of heavy metals or foreign bodies in meat (about 20% of the responses). Statistically, the respondents' opinions were differentiated by a link between their study majors and food in regard to such hazards as: *Salmonella sp.* ($\chi^2=9.82$; $p=0.02$), residues of veterinary medicinal products ($\chi^2=29.96$; $p=0.000$) and food additives ($\chi^2=15.46$; $p=0.001$).

Conclusions

This survey has led the author to the following conclusions:

1. Students readily eat pork and its products. The majority of the respondents (over 59%) eat pork once a week. The factors indicated as decisive in the choice of pork suggest satisfaction in regard to the pork products offered on the market.
2. The main criteria in buying decisions were the price and expiry date of products.

3. Respondents thought that the quality of pork varies depending on the place of sale. Trusted sources of pork include butcher's shops and meat producers, as opposed to supermarkets and small round-the-corner shops.
4. The students did not demonstrate a knowledge of quality marks or systems. Moreover, they did not think that such quality marks are a guarantee of high product quality. This results from ignorance and low awareness of the actions taken in order to ensure food safety. The level of recognition is the highest for HACCP and the lowest for PQS. When it comes to quality signs, "Jakość i Tradycja" is the most frequently recognised sign and the mark of compliance with the Polish Standard is the least frequently recognised sign.
5. Students expressed the greatest concern in regard to meat safety hazards associated with providing a wrong expiry date and those arising from giving false information about ingredients. Among microbiological hazards, the respondents expressed their concern regarding *Escherichia coli* and *Salmonella* more frequently than regarding *Listeria monocytogenes*.
6. Statistically, the respondents' opinions were the most differentiated by their study major. The knowledge and awareness of students of food-related majors regarding the issues under study is higher.

Acknowledgments

Thanks to Miss Jolanta Tomaszewska for co-operation in the implementation of the survey.

References

- Berg L., 2004, *Trust in food in the age of mad cow disease: a comparative study of consumers' evaluation of food safety in Belgium, Britain and Norway*, *Appetite*, 42, 21-32.
- Hammermeister A., 2009, *System jakości wieprzowiny*, *Trzoda Chlewna*, 10, 22-25.
- Hamrol A., 2007, *Zarządzanie jakością z przykładami*, PWN, Warszawa.
- Jakubowska D., Radzymińska M, Smoczyński S. S., 2010, *Określenie determinant wpływających na percepcję ryzyka w zakresie bezpieczeństwa mięsa i produktów mięsnych*. *Żywność. Nauka. Technologia. Jakość*, 1(68), 123 – 129.
- Karaszewski R., 2006, *Nowoczesne koncepcje zarządzania jakością*, Dom Organizatora, Toruń.

- Li Y., Zhao H., Yang Y., 2012, *The study on the Preferences of Customer Personal Values with Chinese Culture Background in Services*, Physics Procedia, 33, 505 – 510.
- Mocarski T., 2011, *Nowa jakość wieprzowiny. Najnowsze wyniki badań mięsa PQS*, Bezpieczeństwo i Higiena Żywności, 12, 42-43.
- Mora C., Menozzi D., Faioli G., Carlos P., Briz J., Felipe I., 2006, *Traceability perception of beef: a comparison between Spanish and Italian consumers*
<http://ageconsearch.umn.edu/bitstream/10093/1/sp06mo04.pdf> accessed 15 March 2013.
- Obiedziński M. W., Pisula A., Płonka S., Różycki M., Węglarzy K., Czubała A., Florowski T., Obiedziński M. M., 2009, *System gwarantowanej jakości żywności QAFP*, Gospodarka Mięsna, 11, 16-18.
- Ozimek I., 2006, *Bezpieczeństwo żywności w aspekcie ochrony konsumenta w Polsce*, Wyd. SGGW, Warszawa.
- Ozimek I., Gutkowska K., Żakowska – Biemans S., 2004, *Postrzeganie przez konsumentów zagrożeń związanych z żywnością*. Żywność. Nauka. Technologia. Jakość, 4(41) Supl., 100-111.
- Pawłowska B., Strychalska-Rudziewicz A., 2007, *Satysfakcja klienta w przedsiębiorstwach przemysłu spożywczego*, Przemysł Spożywczy, 10, 54-57.
- Połom A., Baryłko-Piekielna N., 2004, *Analiza czynników decydujących o preferencjach polskich konsumentów mięsa wieprzowego*. Żywność. Nauka. Technologia. Jakość, 3(40), 7-23.
- Pospiech E., Łyczyński A., Borzuta K., *Problemy jakości mięsa wieprzowego*. Instytut Biotechnologii Przemysłu Rolno-Spożywczego.
<http://www.ipmt.waw.pl/content/File/Pospiech.pdf> accessed 7 May 2014.
- Prussak W. 2006. *Zarządzanie jakością. Wybrane elementy*. Wyd. Politechniki Poznańskiej, Poznań.
- Radzyńska M., Smoczyński S., 2008, *Analiza czynników wyboru przetworów mięsnych wśród studentów*. Żywnienie człowieka i metabolizm, 5/6, 405-411.
- Rudy M., Stanisławczyk R., Głodek E., 2011, *Wpływ wieku konsumentów z województwa podkarpackiego na ich preferencje w stosunku do produktów mięsnych*, Postępy Techniki Przetwórstwa Spożywczego, 1, 76-81
- Schroeder T., Tonsor G., Mintert J., Pennings J.M.E., 2006, *Consumer Risk Perceptions and Attitudes about Beef Food Safety: Implications for Improving Supply Chain Management*, Kansas State University Agricultural Experiment Station and Cooperative Extension Service.
<http://www.naiber.org/publications/naiber/consumer.perceptions.final.pdf> accessed 12 January 2014.
- Urban S., 2005, *Jakość mięsa i przetworów mięsnych*, Gospodarka Mięsna, 3, 14-17

Urbaniak M. 2007. *Zarządzanie jakością, środowiskiem oraz bezpieczeństwem w praktyce gospodarczej*. Difin, Warszawa.

Zieliński G., 2010, *Żywność wysokiej jakości – perspektywa klienta*, in: *Jakość i bezpieczeństwo produktu oraz ochrona środowiska w sektorze rolno-spożywczym*, Prace i Materiały Wydziału Zarządzania Uniwersytetu Gdańskiego, 2/1: 11-18.

INVESTIGATION OF ACIDIC SOLUTIONS BY POTENTIOMETRIC TASTE SENSOR WITH ALL SOLID STATE ELECTRODES

Elwira Tymoszuik, Maria Szpakowska

*Department of Quality Management and Commodity Science,
Faculty of Management and Economics, Gdansk University of Technology,
Elwira.Tymoszuik@zie.pg.gda.pl,*

Introduction

Sensors belong to fast methods of instrumental analysis. Due to the mode of operation they can be divided into two groups: on-line and at-line. The first ones may be used in some technological processes for direct measurements. The advantage of such sensors is the possibility of obtaining quality data in short time, which allows improving the process parameters immediately. The at-line sensors have longer time responses and they are used mainly in laboratory scale for research purposes.

Taking into account the mechanism of action on-line and at-line sensors they may be classified into the following groups according to European Concerted Action (ASTEQ) (Holm 2005):

- biosensors – sensors which contain some biological material (e.g. enzymes, antibodies);
- potentiometric chemical sensors, - sensors using an electric signal as a detection, e.g. metal oxide semiconductors, field effect transistors, conducting polymer sensors, lipid/polymer membrane sensors;
- NIR, NIT, FTIR, thermography, nuclear or electron magnetic resonance – sensors using interaction with electromagnetic waves;
- sensors using interaction with ultrasonic waves (100 kHz-1MHz);
- sensors using changes in frequency, e.g. quartz crystal microbalance, surface acoustic wave.

Potentiometric sensors belonging to the on-line sensor group, have found application in the evaluation of the quality different food products (Toko 1998; Szpakowska, Magnuszewska & Szwacki 2006; Lvova et al. 2002; Ciosek, Augustyniak & Wróblewski 2004). The reason for using such devices in food industry was to make quality foodstuffs estimation more objective than

by organoleptic methods (Szpakowska, Marjańska & Tymoszuk 2013). There are two approaches: organoleptic testing and sensory analysis (PN-ISO 4121: 1998). The first one is fully subjective method and may be used by each consumer. Sensory analysis is done by experts in standard conditions and is a more objective method of food quality estimation. However, both methods are based on human taste reception, which depends on many conditions (e.g. nature of a human being, health of experts, intensity of taste, condition of testing).

The mechanism of taste perception in human beings is a complicated process. Vivid organisms have the capacity of distinguishing the properties of chemical substances, which are present in food products. During chewing they are dissolved in the saliva. Then taste molecules are caught by taste buds, situated in gustatory cells on the surface of tongue. There are about 2000 taste buds on the tongue (Villem 1990). Each of taste buds contains about 50 taste cells. Taste substance reaching the internal surface of taste buds through ionic channels or directly, leads to the excitation of taste receptor present in the biological membrane (Baryłko – Pikielna 1975). These substances get associated with receptor proteins and they provoke the emission of signals to the cell interior where electric impulse is generated. After that this information is transmitted by the nerve fibers to the brain where in the vicinity of cortex the perception and association reactions take place. Next step is identification of these substances and determination of taste impression. It should be added that taste recognition by potentiometric sensors in which the membranes of the electrodes contain artificial lipid compounds is directly correlated with human taste reception. Such sensor can detect tastes in a similar manner to the human sense of taste. The electrodes play role of transducer transforming taste information generated by chemical substances into electric signals, which are analyzed by a computer.

The substances responsible for taste may be divided into six groups. There are six kinds of basic qualities of taste: sweetness, saltiness, sourness, bitterness, umami and, recently described, fatness.

Sweet taste is produced by different types of sugars (e.g. sucrose, fructose, maltose, lactose) or artificial sweet substances (e.g. aspartame, cyclamate, acesulfame K). Some ketones, esters, alcohols, amino acids, glycols are also sweet (Skolik 2011). However, they are not used in food technology for larger scale.

Salty taste is caused by cations of inorganic salts such as sodium chloride, potassium chloride or ammonium chloride. In food industry mainly sodium chloride is used.

Sour taste is produced by organic or inorganic acids, e.g. hydrochloric, nitric, phosphoric, acetic, citric, lactic, tartaric acids. In general in food

products organic acids are used. Intensity of sour taste depends on the proton concentration.

Bitter taste is caused by some alkaloids (e.g. quinine, caffeine, strychnine), electrolytes (e.g. magnesium sulphate) or some amides, glycosides, ketones, aldehydes.

Umami taste resembles meat taste. It is produced mainly by monosodium glutamate. This compound is a component of the seasoning kitchen (vegeta, kucharek, magi), which improves a taste of meat or other foodstuff (Szapowska, Tymoszuć 2012).

Recently fat taste was described and added to the taste classes (Stewart et al. 2010). This taste is produced by fat acids present in some food (e.g. butter, margarine, lard).

There are such gustatory expressions as astringency. It may be caused by tannins present in red wines, tea or unripe fruits.

Global taste of a given food product is a composition of taste substances present in this product. Therefore, elaboration of potentiometric taste sensors with global selectivity has been a great challenge for scientists (Toko 1996). Taste sensors contain a set of lipid-polymer electrodes and reference electrode immersed in a given taste substance solution. Two types of lipid-polymer electrodes have been used: Ion Selective Electrode (ISE) and All Solid State Electrode (ASSE). The first one contains a polymer membrane layer composed of polyvinyl chloride, lipophilic compound and plasticizer. This electrode is filled with KCl solution of given concentration. ASSE consists of a layer of an electro active polymer covering glassy carbon disc and an outer layer made from polyvinyl chloride with lipophilic compound and plasticizer.

ISSEs or ASSEs with different lipophilic compounds have been used in the polymer membrane of sensors proposed by various scientific groups (Hayashi et al. 1990; Toko 1998; Szapowska, Magnuszewska & Szwacki 2006; Lvova et al. 2002; Ciosek, Augustyniak & Wróblewski 2004). The potentiometric taste sensors were applied for controlling food quality or product recognition from various branches such as beer (Kobayashi et al. 2010), green tea (Hayashi et al. 2008; Nobuyuki 2013), coffee (Fukunaga et al. 1996), milk (Ciosek, Wróblewski 2007), soya sauce (Iiyama, Yahiro & Toko 2000), tomato (Beullens et al. 2008), soft drinks (Szapowska, Magnuszewska & Szwacki 2006; Szapowska, Marjańska 2007). Some electronic tongue was applied also for evaluating the quality of low alcohol content drinks (Baldacci 1998).

The potentiometric taste sensor with five ISEs containing lipophilic compound-polymer membranes (Szapowska, Szwacki & Lisowska-Oleksiak 2004) were tested in sour solutions (hydrochloric, citric and acetic acids). It was found that the electrode responses containing positively charged

membranes (bezyłhexadecyldimetylammonium chloride monohydrate or hexadecylamine) decreases with increasing of acid concentration, meanwhile the effect is opposite in case of negatively charged or neutral membranes (elaidic acid, 1-dodecanol or cholesterol). In case of ASSEs it was found that electrodes with positively, negatively charged and neutral membranes behave similarly in contradiction to ISEs (Szpakowska, Marjańska & Lisowska-Oleksiak 2009). Moreover, straight line relationship of $E = f(C)$ for hydrochloric acid was found suggesting that such electrodes can be used for pH determination.

In this work a new potentiometric taste sensor containing six all solid-state electrodes with lipophilic compounds – polymer membranes has been proposed. The following lipophilic compounds were used in the polymeric membrane: hexadecyltrimethyloammonium bromide, hexadecyl amine, palmitic acid, lauric acid, decanoic acid and cholesterol. The behavior of this potentiometric sensor in acid solutions (hydrochloric and tartaric acid) of different concentration was examined.

Since such sensor has a concept of global selectivity, which implies the ability to classify chemical substances into few groups as found in real taste reception in biological systems, it is planned to apply this sensor for quality control of red wines produced in Poland. However, it should be taken into account that the evaluation of wine quality is a complicated problem due to the great variety of chemical compounds present in their composition. Wine is made up of water (60 - 90%), ethanol (9 - 18%) as well as of sugars, dyestuff, polyphenols, tannins, mineral salts, vitamins, azocompounds, organic acids and aromatic substances in form of esters, aldehyds and polyphenols (Gawlik, Nowak & Baran 2008). Also some organic acids (tartaric, lactic, malic, succinic and acetic acids) are present in a red wine (Pandell 1999; Tymoszuik, Marjańska 2013).

Material and methods

Materials

Poliy(vinylchloride) high molecular weight (PVC), hexadecyl amine were from Fluka. Dioctyl phenylphosphonate (DOPP) – 99,5%, hexadecyltrimethyloammoniumbromide, palmitic acid - 99%, lauric acid - 99,5%, decanoic acid 99+%, cholesterol, 3,4-ethylenedioxythiophene (EDOT) and poly(sodium 4-styrenesulfonate) (NaPSS) were from Aldrich. Potassium chloride, tetrahydrofuran were from POCH. All other chemicals were of analytical grade. The aqueous acids solutions were prepared with distilled water.

The PEDOT preparation

The PEDOT was obtained by electrochemical synthesis. The setup to synthesis consists of three electrodes: Ag/AgCl/Cl⁻ (10⁻¹M KCl) glass reference electrode, platinum mesh as auxiliary electrode and working electrode with glassy carbon (GC) disc (area = 0.071 cm²). Prior to polymerization GC working electrodes were polished on the moistened with 0.3 μm alumina. Then these electrodes were rinsed using distilled water and cleaned in ultrasonic bath. The PEDOT was obtained by dissolving 10⁻² M EDOT, 10⁻¹ M NaPSS in redistilled water. Then, solution of PEDOT was deposited on the glassy carbon disc working electrodes by galvanostic electrochemical polymerization as conducting electrolyte at constant electric potential (850 mV). Potential charges of 5.89 mC give 0.5 thickness layer of PEDOT.

ASSEs and aqueous solutions preparation

Each of working electrode consists of two layers. The inner layer was the conductive polymer PEDOT. The outer layer was lipophilic compound / polymer membrane containing wt. 61 % PVC, wt. 38.5 % plasticizer DOPP and wt. 0.5 % of appropriate lipid compound. All substances were dissolved in 5 ml THF. After drying, the electrodes were conditioned in solution of potassium chloride at concentration 10⁻³ M during 24 h.

The lipophilic compound /polymer membranes were prepared with the following reagents: poly (vinyl chloride) (PCV), plasticizer dioctyl phenylphosphonate (DOPP), tetrahydrofuran (dissolvent) and appropriate lipophilic compound. The following lipophilic compounds were used: hexadecyltrimethyloammonium bromide, hexadecyl amine, palmitic acid, lauric acid, decanoic acid and cholesterol. The acid solutions used in the experiments contain hydrochloric or tartaric acid in the concentration range of 10⁻⁵ – 10⁻² M.

The solution of 10⁻³ M chloride potassium was used for conditioning the electrodes.

Experimental setup

The experimental setup consists of six ASSEs, Ag/AgCl/Cl⁻ reference electrode and voltmeter Atlas (Sollich Company) connected with a computer (Fig. 1). The following ASSE were used: e1 - hexadecyltrimethyloammonium bromide, e2 – hexadecyl amine, e3 - palmitic acid, e4 – lauric acid, e5 – decanoic acid, e6 – cholesterol.

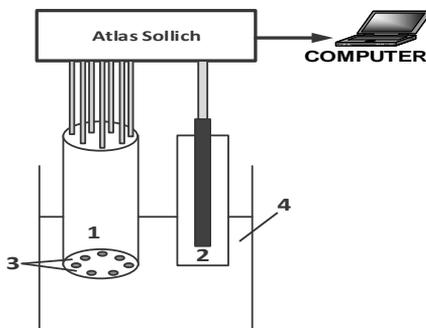


Figure 1. Experimental setup: 1 – six ASSEs, 2 - Ag/AgCl/Cl⁻ reference electrode, 3 – lipophilic compound / polymer membrane, 4 – aqueous solution of acid substance

Source: self elaboration.

The working ASSEs were conditioned in 10^{-3} M KCl during 24 h prior to and between measurements. After that these electrodes were immersed in appropriate aqueous solutions of sour substances at in the range of 10^{-5} M to 10^{-2} M concentrations. The electrodes' responses were measured using high - input – impedance voltmeter of Atlas Solich Company.

Results and discussion

Sensitivity of ASSE

The sensitivity of six ASSEs of three types: positively charged (hexadecyltrimethyloammonium bromide, hexadecyl amine), negatively charged (palmitic, lauric, decanoic acids) and neutral (cholesterol) ones of elaborated potentiometric taste sensor in the concentration range of 10^{-5} M to 10^{-2} M in hydrochloric and tartaric acids solutions was examined.

The results obtained in appropriate acid solutions for three electrodes: hexadecyltrimethyloammonium bromide, palmitic acid and cholesterol are presented in Fig. 1. In all cases the relationships $E = f(\log C)$ are linear. In case of electrodes containing polymeric membrane with palmitic acid or cholesterol immersed in hydrochloric acid solution (Fig. 1a) the determination coefficients are quite good (0.9869, 0.9945, respectively). This is not the case of electrode with hexadecyltrimethyloammonium bromide in the membrane where the value of determination coefficient is much lower.

In case of the solutions containing tartaric acid the determination coefficients for these three electrodes are again quite good: hexadecyltrimethyloammonium bromide – 0.9582, palmitic acid – 0.9693, cholesterol – 0.9978 (Fig. 2b).

Taking into account the results obtained for all six electrodes the large slope of $E = f(\log C)$ was obtained for negatively charged electrodes containing decanoic or palmitic or lauric acid in polymeric membrane (57.38 mV, 55.87 mV, 54.35 mV, respectively) immersed in hydrochloric acid (Fig. 1a). The same electrodes immersed in tartaric acid gave the following results (56.76 mV, 42.26 mV, 40.78 mV, respectively). Comparing this two series of results it can be established that when negatively charged electrodes are immersed in a less dissociated acid they are less sensitive than when they are immersed in fully dissociated acid solution.

Interesting enough is that much smaller slopes of the $E = f(\log C)$ were obtained for cationic membrane component (hexadecyltrimethyloammonium bromide, 1.66 mV, hexadecyl amine 5.13 mV) both in HCl solutions. In tartaric acid we have the following values: - 5.08 mV and 5.58 mV, respectively. This shows that electrodes with positively charged membranes are less sensitive to concentration variation.

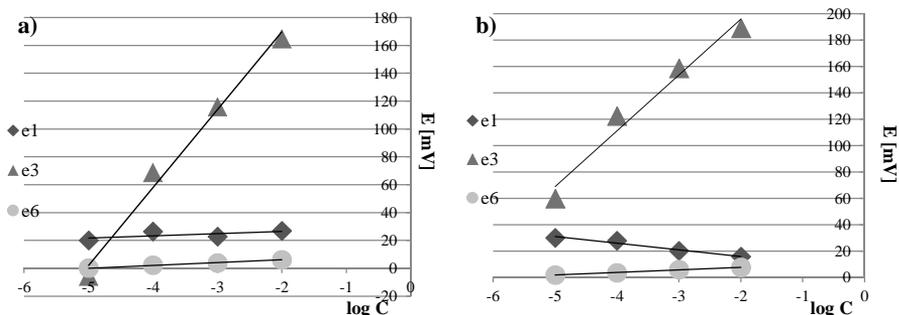


Figure 2. Electric potential (E) changes of ASSEs (e1 – hexadecyltrimethyloammonium bromide, e3 – palmitic acid, e6 – cholesterol) with electrolyte concentration, a) hydrochloric acid, b) tartaric acid.

Source: own research.

Polymeric membranes containing cholesterol are also less sensitive to the same solutions (1.99 mV in hydrochloric acid, 1.97 mV in tartaric acid) (Fig. 2).

The results obtained for all the six electrodes immersed in hydrochloric or tartaric acid solutions of 10^{-5} M to 10^{-2} M concentration range are presented in Fig. 3. As it can be seen the radar plot patterns are similar in both cases. However, the e1 to e4 electrode responses are slightly lower when immersed in hydrochloric acid then in tartaric acid. It is probably due to weaker dissociation of tartaric acid in comparison to HCl. It seems that there is a difference between electrode responses to strong or weak acids.

It should be noted that the cholesterol – polymer electrode responses are very small in comparison to other ASSE in both acid solutions (Fig. 3).

Considering the whole system of the six electrodes the following decreasing order of selectivity can be established:

decanoic acid > palmitic acid > lauric acid > hexadecyl amine > hexadecyltrimethyloammonium bromide > cholesterol.

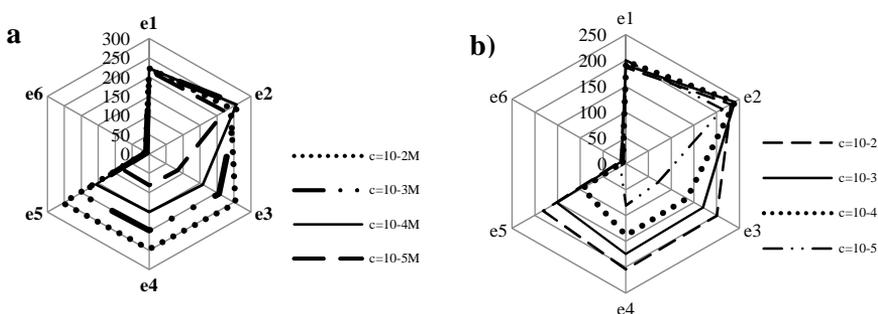


Figure 3. Potentiometric six-channel taste sensor responses to a) tartaric acid b) hydrochloric acid in given concentrations. ASSEs: 1e - hexadecyltrimethyloammonium bromide, 2e - hexadecyl amine, 3e - palmitic acid, 4e - lauric acid, 5e - decanoic acid and 6e - cholesterol.

Source: own research.

It should be noted that ASSEs with negatively charged membranes proposed in this taste sensor are much more sensitive to H^+ concentration than for other ASSEs in previously examined taste sensor (Szpakowska, Marjańska, & Lisowska-Oleksiak, 2009). Straight line relationship of $E = f(C)$ for HCl solution suggest that such electrode may be used for pH determination prior to calibration.

The preliminary studies reveal that proposed in this work potentiometric sensor with ASSEs containing lipophilic compounds in the membrane may be used for quality control of red wines.

Stability of ASSE

Stability of ASSEs was investigated in hydrochloric acid solution of concentration equal to 10^{-2} M during 7 days. The results obtained for three electrodes (e1, e3, e6) are presented in Fig. 4. The most stable was the electrode containing cholesterol in the polymeric membrane (e6). The other electrodes were reasonably stable only for three or four days. It means that in these cases stability should be improved.

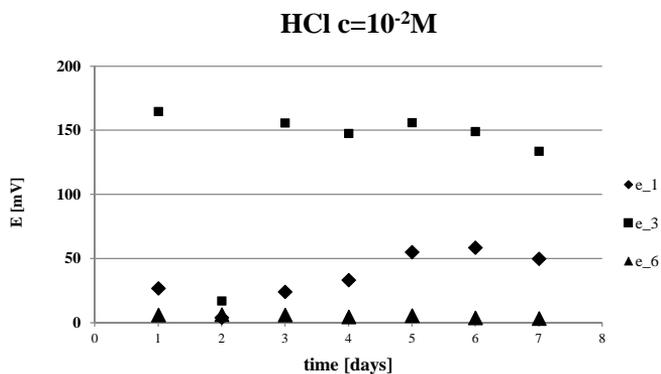


Figure 4. Stability of ASSE with: e1 – hexadecyltrimethyloammonium bromide, e3 - palmitic acid, e6 – cholesterol during 7 days.

Source: own research.

Conclusions

The results obtained in this work show clearly that electrodes containing negatively charged membrane (with anionic lipophilic compounds in the polymeric membrane) have higher sensitivity than the electrodes with neutral or positively charged membranes. Straight line relationship of $E = f(C)$ for HCl solution suggests that such electrode may be used for analytical application e.g. pH determination prior to calibration. It appears also that the electrode potential responses depend strongly on the structure of lipophilic compound present in the polymeric membrane. It was found also that the stability of lipophilic compound- membrane electrodes proposed in this six - channel taste sensor should be improved.

More research is necessary to confirm and generalize these conclusions.

References

- Baldacci S., Matsuno T., Toko K., Stella R., Rossi D.D., 1998, *Discrimination of wine using taste and smell sensors*, Sens. Mater., 10, no. 185 – 200.
- Baryłko – Piekielna N., 1975, *Zarys analizy sensorycznej*, Wydawnictwo Naukowo Techniczne, Warszawa.
- Beullens K., Meszaros P., Vermeir S., Kirsanov D., Legin A., Buysens S., Cap N., Nicolai B. M., Lammertyn J., 2008, *Analysis of tomato taste using two types of electronic tongues*, Sensors and Actuators B, 131, no. 10 – 17.
- Chen Q., Zhao J., Guo Z., Wang X., 2003, *Determination of caffeine content and main catechins contents in green tea (Camellia sinensis L.) using taste sensor*

technique and multivariate calibration, Journal of Food Composition and Analysis, 23, no. 353 - 358.

Ciosek P., Augustyniak E., Wróblewski W., 2004, *Polymeric membrane ion-selective and cross-sensitive electrode-based electronic tongue for qualitative analysis of beverages*, The Analyst, 129, no. 639 – 644.

Ciosek P., Wróblewski W., 2007, *Performance of selective and partially selective sensors in the recognition of beverages*, Talanta, 71, no. 738-746.

Fukunaga T., Toko K., Mori S., Nakabayashi Y., Kanda M., 1996, *Quantification of taste of coffee using sensor with global selectivity*, Sens. Mater, 8, no. 47 – 56.

Gawlik M. B., Nowak Ł., Baran M., 2008, *Analiza właściwości win produkcji polskiej*, Bromatologia i Chemia Toksykologiczna – XLI, 1, str. 15–20.

Hayashi N., Yamanaka M., Toko K., Yamafuji K., 1990, *Multichannel taste sensor using lipid membranes*, Sensors and Actuators B, 2, no. 205 – 213.

Hayashi N., Chen R., Ikezaki H., Ujihara T., 2008, *Evaluation of the umami taste intensity of green tea by a taste sensor*, J. Agric. Food Chem., 56, no. 7384 – 7387.

Holm F., *New and future at- and on-line sensors in food production: EU research results*, in: Amerongen A., Barug D., Lauwaars M. (ed.), 2005, *Rapid Methods for Biological and Chemical Contaminants in food and Feed*, The Netherlands, Wageningen Academic Publishers, no. 361-378.

Ikezaki H., Tanguchi A., Toko K., 1997, *Quantification of taste of green tea with taste sensor*, Trans IEE of Japan, 117-E, no. 465 - 470.

Iiyama S., Yahiro M., Toko K., 2000, *Measurements of soy sauce using taste sensor*, Sens Actuators B, 66, no.205

Kobayashi Y., Habara M., Ikezaki H., Chen R., Naito Y., Toko K., 2010, *Advanced taste sensors based on artificial lipids with global selectivity to basic taste qualities and high determination to sensory scores*, Sensors, 10, no. 3411 – 3443.

Legin A., Rudnitskaya L., Lvova L., Vlasov Yu., Di Natale C., D'Amico A., 2003, *Evaluation of Italian wine by the electronic tongue: recognition, quantitative analysis and determination with human sensory perception*, Analytica Chimica Acta, 484, no. 33 - 44.

Lvova L., Kim S. S., Legin A., Vlasov Y., Yang J. S., Cha G. S., Nam H., 2002, *All-solid-state electronic tongue and its application for beverage analysis*, Analytica Chimica Acta, 468, no. 303 - 314.

Nobuyuki H., 2013, *Objective evaluation of the taste intensity of tea by taste sensors*, in: Preedy V. R. (ed.), *Tea in health and disease prevention*, Elsevier, no. 103 - 114.

Pandell A. J., 1999: *The acidity of wine*. Wineperspective.
http://www.wineperspective.com/the_acidity_of_wine.html, accessed 08 April 2014.

PN-ISO 4121: 1998 *Sensory analysis - Methodology - Evaluation of food products by methods using scales*.

- Skolik A., 2011, *Smak w analizie sensorycznej*, Wydawnictwo Uniwersytetu Ekonomicznego w Poznaniu.
- Stewart J. E., Feinle – Bisset C., Golding M., Delahunty C., Clifton P.M., Keast R.S.J., 2010, Oral sensitivity to fatty acids, food consumption and BMI in human subjects, *British Journal of Nutrition*, vo. 104.
- Szpakowska M., Szwacki J., Lisowska-Oleksiak A., 2004, *Investigation of some taste substances using a set of electrodes with lipid – modified membranes*, *Desalination*, 163, no. 55 – 59.
- Szpakowska M., Magnuszewska A., Szwacki J., 2006, *On the possibility of using liquid or lipid, lipid like-polymer membrane systems as taste sensor*, *J. Membrane Sci.*, 273, no. 116 - 123.
- Szpakowska M., Marjańska E., 2007, *Sztuczny sensor smaku a zmysł smaku*, *Chemik*, 12, no. 576-579.
- Szpakowska M., Marjańska E., Lisowska-Oleksiak A., 2009, *Investigation of sour substances by a set of all – solid –state membrane electrodes*, *Desalination*, 241, no. 236 – 243.
- Szpakowska M., Tymoszek E., 2012, *Wybrane aspekty oceny jakości produktów żywnościowych*, in: Wiśniewska M. (ed.), *Journal of Management and Finance*, no. 104 – 113.
- Szpakowska M., Marjańska E., Tymoszek E., 2013, *Taste qualities estimation by taste sense and electrochemical sensors*, in: Śmigielska H. (ed.): *Current trends in Commodity Science: Analysis and consumer acceptance of food products*, Poznań University of Economics, no. 105-115.
- Toko K., 1998, *A taste sensor*, *Meas. Sci. Technol*, 9, no. 1919 – 1936.
- Tymoszek E., Marjańska E., 2013, *Selected aspects of the evaluation of the quality of grape wine*, in: Błaszczuk A. (ed.): *Current trends in Commodity Science: Innovations and product quality*, Poznań University of Economics, no. 109-120.
- Villee C. A., 1990, *Biologia*, Państwowe Wydawnictwo Rolnicze i Leśne, Warszawa.

INFLUENCE OF EXTREME HEATING ON COLOUR AND ANTIOXIDANT ACTIVITY OF DIFFERENT TYPES OF HONEY

Aleksandra Wilczyńska, Piotr Przybyłowski

*Department of Commodity Science and Quality Management,
Gdynia Maritime University,
a.wilczynska@wpit.am.gdynia.pl*

Introduction

Honey is a natural food produced by bees from nectars of blossom or from honeydew. There are numerous health benefits of honey which since ancient times has been known in many cultures. It has antimicrobial, antibacterial and antifungal properties, is a rich source of energy and bioactive substances. Honey is known also as a source of antioxidants such glucose oxidase, ascorbic acid, catalase, carotenoid derivatives, organic acids, Maillard reaction products, amino-acids and proteins, however the main components responsible for the antioxidant activity of honey are phenolics – flavonoids and phenolic acids. (Aljadi & Kamaruddin, 2004; Al-Mamary, Al-Meerri & Al-Habori, 2002; Gheldof & Engeseth, 2002; Gheldof et al., 2002; Weston, 2000; Küçük et al., 2007). Antioxidants play an important role among the components influencing the health properties of honey.

Numerous factors affect the quality of honey and thus its health properties, including the blending process, storage conditions, thermal treatment, etc. The most discussed topic relating to honey "quality" is heating. Thermal treatment is applied to the honey in order to slow down crystallization and fermentation processes and ensure stability during its commercial life. It may lead to drastic changes in honey's chemical composition and finally, heating to high temperatures may reduce the health benefits of honey. To minimise the effect of thermal treatment on the quality of honey, the lowest temperatures and shortest periods of heating are suggested. But when the heating is conducted incorrectly (too slow or too high temperature during pasteurisation or re-crystallisation), it can accelerate some chemical reactions. The heating affects colour - stimulates darkening because of non-enzymatic browning, including Maillard reaction and formation of HMF (Ibarz et al., 2000; Tosi et al., 2002). During heat treatment the activity of enzymes is

observed to decrease. The flavour and sugar compositions are changing as well (Escriche et al., 2009; Karabourniotti and Zervalaki, 2001; Tosi et al., 2008). Those changes are proportional to the temperature and heating time. The other effect of heating are changes in the antioxidant activity of honey. The antioxidant activity has been reported to be strongly affected by floral origin (honey type), especially by phenolics contents (Aljadi and Kamaruddin, 2004; Bertoncelej et al., 2007; Blasa et al., 2006; Küçük et al., 2007). But the studies did not preclude a potential contribution of other honey components to this activity. The level of the natural antioxidants is decreasing during heating, but the losses could be minimised or compensated for by the formation of the Maillard reaction products (Turkmen et al., 2005; Brudzynski and Miotto, 2011). However, there are very limited data indicating changes in colour and antioxidant activity during heating.

The aim of this study was, therefore, to assess the contribution of two factors, i.e.: botanical origin and heating, to the variability in colour and antioxidant activity in order to verify the thesis that thermal treatment affect these selected quality factors of honey.

Materials and methods

Samples

82 raw, unprocessed honey samples gathered in 2009 and 2010 flowering seasons were obtained directly from beekeepers. The floral origin of samples was specified by beekeepers regarding hive location and available floral sources and confirmed by melissopalynological analysis (Loveaux et al., 1978). Monofloral honeys were considered as such whenever the dominant pollen was found at over 45% of the total pollen (except the lime and acacia honeys, for these honeys the content of dominant pollen ought to be > 20% and >30%, respectively), and multifloral honeys were considered, when the content of dominant pollen was lower than 35%. Among studied were: 17 multifloral, 8 fir, 4 acacia, 3 goldenrods, 22 rape, 7 phacelia, 4 lime, 3 heather, 4 mixed nectar-honeydew and 10 buckwheat honeys. Each sample was divided into 5 100 g parts: one of them was analysed in its raw state (unheated) and four were analysed following heat treatment at 50, 60, 70 and 80° for 72 hours in a temperature-controlled oven. Immediately after heating, the honey samples were rapidly cooled down and kept in dark, at a room temperature (20°C) before analysis, maximum for 10 days.

Physicochemical analysis

Colour parameters (L^* , a^* , b^*) were established in the CIE system using a Minolta CR-400 Chroma-meter (Konica-Minolta, Japan). In order to

evaluate the colour differences among honey samples due to varietal factors (type, heating), $\Delta E^* = ((L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2)^{1/2}$, was calculated.

Antioxidant activity

The antioxidant activity was measured using two assays. The scavenging activity against 1,1-diphenyl-2-picrylhydrazyl hydrate (DPPH[•]) radical of honey was estimated according to the procedure described by Turkmen et al. (2005) with some modifications. The 2-g honey sample was dissolved in 10 mL of distilled water, centrifuged and filtered by a paper filter. Then 0.75 mL of the solution was mixed with 2.25 mL of 0.1mM methanol solution of DPPH[•] 1,1-diphenyl-2-picrylhydrazyl (Fluka, Germany). The control test was made with distilled water in place of the honey solution. The reaction mixtures were vortex-mixed well and left at a room temperature in the dark for incubation for 60 min. Absorbance was measured at $\lambda=517$ nm against methanol, using a UV-VIS spectrophotometer Unicam. The antioxidant activity was expressed as a percentage of inhibition of DPPH[•] radical and calculated from the equation:

$$AA[\%] = (Abs_{\text{contr}} - Abs_{\text{sample}}) / Abs_{\text{contr}} \cdot 100\%$$

The antioxidant activity of honey samples in the reaction with stable ABTS⁺ radical cation was determined according to Baltrušaitytė et al. (2007). ABTS⁺ was obtained in the reaction of a 2 mM stock solution of 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (Fluka, Germany in phosphate-buffered saline with potassium persulfate (POCH, Poland). The mixture was left to stand for 24 h. Prior to analysis, the ABTS⁺ solution was diluted with phosphate buffer saline (AppliChem, Germany) to produce a solution with absorbance of 0.80 ± 0.03 at $\lambda=734$ nm. The 2-g honey sample was dissolved in 10 mL of distilled water, centrifuged and filtered by a paper filter. Then 0.1 mL of the solution was mixed with 6 mL of ABTS⁺ solution, vortex-mixed well and after 15 min absorbance was measured at a wave length of 734 nm. The control test was made with distilled water in place of the honey solution. The antioxidant activity was expressed as percentage inhibition of ABTS⁺, calculated from the same equation as for DPPH[•].

To determine the total phenolic content of honeys, the method of Meda et al. (2005) was employed. Honey solutions with the concentration of 1g/10mL were centrifuged, filtered by a paper filter. Afterwards, 0.5 mL of the resultant solution was mixed with 2.5 mL of 0.2N solution of Folin-Ciocalteu reagent (Fluka, Germany). Then 2 mL of sodium carbonate solution (75g/L, POCH, Poland) was added. After incubation in dark and at room temperature for 2 h, absorbance of the reaction mixture was measured at $\lambda=760$ nm using a Unicam UV-VIS spectrophotometer. The standard curve

was produced for gallic acid within the concentration range from 0 to 200 mg/L. The total phenolics content (TP) was expressed as gallic acid equivalents in mg/100g of honey sample (mgGAE/100g).

Statistical analysis

One-way and two-ways analysis of variance (ANOVA) were used to examine the effects of botanical origin and heating on colour parameters, antioxidant activity and phenolics content of honey samples. The F-test was used to estimate the statistically significant differences (P-value <0.05). Correlation coefficients (r) were calculated additionally to determine the correlation between the particular parameters. The calculations were performed with statistical software package Statistica 6.0 (StatSoft Inc. Tulsa, USA).

Results and discussion

Table 1 shows the initial colour parameters of honey samples of different types (measured at 20°C) and their changes after thermal heating at 50-80°C for 72 hours. The colour depends on the biological origin of honey and is related to the content of phenolics, pollen, minerals and pigments. As it can be seen, the raw honeys with the greatest lightness were the acacia honeys ($L^*=40.4$). Buckwheat honeys exhibited the least lightness of the colour ($L^*=22.02$). In turn, a^* values (redness) were the highest in buckwheat honeys and the lowest (negative values – green direction) in acacia honeys. The highest b^* values were observed in the samples of multifloral and lime honeys. The buckwheat honeys had the lowest b^* values. These values are in agreement with those found by other researchers (Popek 2002).

It could be seen that heating had a considerable influence on the colour of the investigated honeys. L^* was found to decrease in all types of honey during thermal treatment. The higher the temperature was, the stronger the impact on lightness was.

Finally, in all types of honey heated at 80°C, the L^* fluctuated around 20. Values of a^* and b^* were also changing under heating, but those differences was rather negligible. Generally, it could be seen that a^* value raised in pale honeys, while in dark honeys (buckwheat, heather and fir) it decreased. In comparison with the initial value, in most honey types the b^* value was higher after heating at 50 and 60°C, and lower after heating at 70 and 80 °C. Table 2 presents the colour differences calculated between the raw and heated honeys at the range of four kinds of temperatures.

Table 1. Colour parameters of different types of honey and their changes during thermal heating

Honey type (n)	Temp.	L*				a*				b*			
		x	SD	min	max	x	SD	min	max	X	SD	min	Max
acacia (3)	-	40.40	2.57	37.28	43.56	-0.85	0.78	-1.48	0.29	21.21	3.68	16.14	24.88
	50	37.26	2.80	34.38	40.63	3.69	3.99	-0.86	8.48	23.40	3.69	18.67	27.47
	60	30.86	2.03	27.96	32.55	5.63	3.53	2.24	9.09	19.42	3.53	16.12	24.34
	70	26.43	4.52	20.33	31.26	8.47	4.98	1.05	11.73	12.30	7.53	2.17	20.38
	80	20.73	2.05	17.92	22.79	6.06	2.79	3.66	9.02	5.18	1.21	3.45	6.27
buckwheat (10)	-	22.02	1.79	20.06	25.86	4.51	2.68	1.56	9.01	4.89	2.09	2.69	8.63
	50	21.20	1.99	19.88	25.97	2.01	1.79	0.46	5.98	2.31	0.57	1.93	3.69
	60	20.63	0.34	20.35	21.27	1.51	0.97	0.52	3.33	2.22	0.28	1.73	2.54
	70	20.17	0.18	19.87	20.46	0.44	0.21	0.14	0.68	1.99	0.20	1.65	2.30
	80	19.77	0.66	18.18	20.22	0.42	0.23	0.18	0.84	1.91	0.29	1.56	2.26
phacelia (7)	-	29.40	7.97	21.02	42.52	2.12	2.88	-3.07	5.76	13.81	9.34	3.54	31.74
	50	32.29	8.46	20.47	42.68	2.37	2.92	-2.48	5.84	18.02	10.37	2.64	28.73
	60	30.44	7.12	20.63	39.71	4.77	3.72	-1.26	9.29	18.30	11.09	2.21	31.35
	70	25.65	4.27	20.03	31.64	6.49	4.37	0.43	11.93	11.03	6.79	1.77	20.04
	80	21.54	2.16	19.98	26.26	3.40	3.45	0.42	10.20	3.85	2.92	1.75	10.18
goldenrods (3)	-	28.59	1.11	27.65	29.82	0.98	0.94	0.20	2.02	11.34	0.57	10.87	11.98
	50	30.38	7.12	22.51	36.37	1.57	1.03	0.47	2.51	17.64	10.72	5.78	26.62
	60	32.31	7.31	24.05	37.95	3.07	2.46	1.45	5.90	20.50	12.40	6.60	30.44
	70	27.82	1.33	26.71	29.30	12.55	1.70	11.01	14.37	14.71	2.92	11.93	17.75
	80	22.61	0.17	22.43	22.76	7.73	0.69	7.32	8.53	5.72	0.85	4.83	6.52
heather (3)	-	23.81	1.45	22.91	25.48	4.84	1.70	2.93	6.20	6.93	2.95	5.15	10.34
	50	22.03	2.68	19.11	24.38	1.95	1.86	0.78	4.10	5.11	2.90	2.99	8.42
	60	22.80	2.74	20.98	25.96	3.56	4.30	0.82	8.52	5.63	4.50	2.85	10.82
	70	21.95	1.44	21.09	23.61	3.45	4.32	0.61	8.43	4.55	2.87	2.35	7.79
	80	20.86	0.57	20.51	21.52	2.05	1.68	0.65	3.91	3.14	0.69	2.41	3.79
honeydew (8)	-	23.24	2.89	20.88	29.67	2.60	2.23	0.44	7.17	6.11	3.92	3.04	14.21
	50	22.79	3.31	20.53	30.76	2.26	1.90	-0.20	5.26	5.65	5.77	2.06	19.47
	60	24.08	5.06	20.70	36.19	3.34	3.31	-0.29	8.33	6.89	8.04	1.90	25.76
	70	20.77	0.89	19.15	22.17	1.12	1.62	-0.12	4.35	2.94	1.03	1.79	4.96
	80	20.62	0.91	19.06	21.63	1.26	1.68	-0.33	3.10	3.11	0.58	2.51	3.84
lime (4)	-	32.18	3.45	28.62	36.89	0.52	0.75	-0.21	1.77	14.84	2.87	12.32	19.72
	50	34.64	4.39	27.34	39.15	4.09	4.93	-0.75	10.79	22.44	4.86	13.95	25.99
	60	32.37	7.98	21.17	40.50	4.63	2.49	1.89	7.63	21.85	10.23	8.23	30.51
	70	28.36	5.72	22.94	37.13	6.98	1.91	4.35	9.52	15.01	8.67	6.48	28.01
	80	22.71	1.43	20.94	24.50	6.47	2.91	1.81	8.78	5.87	2.15	3.42	9.04
mixed nectar-honeydew (4)	-	27.42	5.56	19.91	33.31	4.12	4.07	1.16	9.88	14.91	5.42	9.45	21.85
	50	27.67	2.92	23.30	29.35	7.51	0.54	6.73	7.93	14.57	4.89	7.28	17.60
	60	27.69	3.89	24.25	31.68	9.44	2.61	5.89	11.68	14.63	6.60	8.58	21.16
	70	22.18	1.32	20.30	23.11	6.04	3.85	0.47	9.16	5.48	2.25	2.40	7.16
	80	21.64	0.98	20.73	23.04	4.77	3.40	1.83	9.23	4.38	1.73	2.86	6.85
multifloral (17)	-	32.22	4.99	22.16	40.77	0.53	1.28	-1.87	2.25	14.71	4.66	4.81	22.27
	50	32.21	5.53	21.08	40.73	4.11	3.98	-1.74	10.57	18.37	7.20	2.64	32.06
	60	30.47	7.97	21.11	45.90	4.07	3.62	-1.44	11.17	15.88	10.58	1.97	30.31
	70	26.21	6.17	20.20	41.16	5.60	4.87	-0.12	12.13	11.79	9.63	1.96	34.29
	80	23.00	3.36	20.70	31.69	6.18	5.50	-0.02	17.79	6.67	6.02	2.35	21.70
rape (22)	-	32.65	4.66	25.47	43.09	0.52	1.09	-1.22	3.45	13.24	4.21	7.67	22.33
	50	33.34	3.65	25.80	39.89	3.25	3.39	-2.13	12.00	19.42	5.59	8.58	26.96
	60	31.59	6.15	20.23	41.52	4.63	3.23	-0.23	14.90	18.37	8.18	3.43	30.87
	70	27.65	5.12	20.00	36.83	8.04	3.73	0.01	12.94	14.09	8.37	1.93	28.70
	80	23.37	2.36	20.43	27.37	7.49	3.86	0.22	13.61	7.37	3.97	2.20	14.03

Source: own research.

Table 2. Colour differences (ΔE) between raw and heated honeys

Honey type	ΔE (CIE L*a*b*)			
	50°C	60°C	70°C	80°C
rape	6.79	6.66	9.07	13.00
lime	8.76	8.14	7.51	14.34
acacia	5.94	11.67	19.01	26.30
honeydew	0.72	1.37	4.28	4.20
buckwheat	3.69	4.25	5.33	5.54
multifloral	5.12	4.11	8.38	13.46
heather	3.84	2.08	3.32	5.54
mixed	3.41	5.33	10.96	12.03
phacelia	5.11	5.32	6.40	12.76
goldenrods	6.58	10.11	12.08	10.62

Source: own research.

These differences were more noticeable in the samples heated at 80°C than in those treated at 50 and 60°C, which indicates a great dependency of colour on temperature of heating. Greater colour differences occurred in the pale honeys, especially in acacia honeys.

Table 3. The impact of honey type and heating on selected parameters, $\alpha=0.05$

Parameter	Heating		Type	
	F(1,164)	p	F(1,164)	p
L*	9.12798	0.000000	15.51410	0.000000
a*	5.28501	0.000000	4.17240	0.000037
b*	7.55151	0.000000	15.83027	0.000000
AA _{DPPH}	4.02227	0.000000	3.39733	0.000499
AA _{ABTS}	12.30281	0.000000	14.33236	0.000000
TP	15.41343	0.000000	42.17375	0.000000

Source: own research.

As seen from the statistical analysis (ANOVA, F-Test values, table 3), the type of honey and temperature of heating as well had a significant effect on the colour parameters.

The ability of honey to scavenge free radicals was evaluated using the DPPH[•] and ABTS⁺ assays. The results obtained for the antioxidant activity are shown in table 4. In the raw honeys the average antioxidant activity in DPPH[•] reaction system varied from 47.2% in acacia to 83.4% in heather honeys. Generally, it could be said that this activity decreased in honey samples heated at 50 and 60° and increased in these treated at higher temperatures. There were some exceptions, e.g. in heather and fir honeys the radical scavenging activity in the samples heated at all temperatures was lower than in the same raw

honeys. Heather and fir honeys showed the highest starting value of antioxidant activity.

As well as antioxidant activity in DPPH[•] assay, in ABTS⁺ reaction system the highest average antioxidant activity was shown for the dark honeys – e.g. buckwheat honeys (50.17%). The antioxidant activity increased in almost all heated samples and reached the highest values in the honey heated at 80°C - in most honey types average value was around 70% (table 4). In multifloral, mixed (nectar-honeydew), lime and rape honeys heated at 50 and 60 °C the scavenging activity against ABTS⁺ free radicals decreased in comparison with the unheated honeys. However, at higher temperatures the average scavenging activity in those types of honey raised significantly.

The lowest average total phenolics content was observed in rape honey (47.5 mg/kg) and increased in the following order: lime (49.0 mg/kg), phacelia (51.3 mg/kg), acacia (53.1 mg/kg), nectar-fir (54.8 mg/kg), multifloral (62.5 mg/kg), goldenrods (80.7 mg/kg), honey dew (87.4 mg/kg), heather (155mg/kg) and buckwheat (177 mg/kg) (table 4). As it was expected, the dark honeys had the greater phenolics content. Similar results were obtained by Bertoneclj (Bertoneclj et al., 2007), Blasa (Blasa et al., 2006), Meda (Meda et al., 2005) and Lachman (Lachman et al., 2010).

It could be seen that in all honeys, except for the heather, the total phenolics content was increasing continuously during heat-treatment.

It is worth noting that the type of honey and thermal treatment influenced all parameters (table 3). Different trends in changes in the antioxidant activity and total phenolics content as affected by the heating process can result from differences in the formation of Maillard reaction products (MRP's). The increase of MRP's is the more noticeable in the higher temperatures (Turkmen et al, 2005).

According to previous studies (Brudzynski and Miotto, 2011; Wilczyńska 2010) the antioxidant activity measured using two assays was higher in the honeys with higher phenolics content and of darker colour. In this study, buckwheat honeys were the most active honeys against free radicals and contained the higher level of total phenolics.

The correlations between colour parameters, antioxidant activity and total phenolics content were studied as well (table 5).

Statistically significant ($p < 0.05$) linear correlations were found between L^* and b^* values ($r = 0.86$) and between antioxidant activity in ABTS⁺ reaction system and total phenolics content ($r = 0.83$). A strong negative correlation was found between L^* value and antioxidant activity in ABTS reaction system and total phenolic content ($r = -0.69$ for L^*/TP , $r = -0.71$ for L^*/AA_{ABTS} , $p = 0.05$). It means that changes in the total phenolics content and antioxidant activity are strongly connected with the formation of products of Maillard reactions. The latter play an essential role in honey darkening under heat treatment; the loss of natural antioxidants (polyphenols) is compensated for by the formation of the Maillard reaction products.

Table 4. Antioxidant activity (AA) determined by ABTS and DPPH assays and total phenolic content (TP) in different honey types. Changes during heat-treatment

Honey type (n)	Temp.	AA _{DPPH} [%]				AA _{ABTS} [%]				TP [GAE/100g]			
		x	SD	min	max	x	SD	min	max	x	SD	min	max
acacia (4)	-	31.33	5.78	25.58	36.70	6.00	6.01	2.29	12.93	35.71	5.40	29.74	40.55
	50	48.39	10.88	33.50	57.20	7.87	5.43	4.67	15.45	36.02	3.38	31.23	39.06
	60	25.93	11.75	14.62	36.95	13.21	8.64	8.98	20.09	37.91	4.78	34.23	44.87
	70	61.00	12.26	44.33	73.66	32.87	11.12	23.45	45.83	65.55	37.69	43.10	121.82
	80	62.28	15.22	39.90	73.53	67.54	14.56	49.23	89.13	73.38	7.59	64.24	80.91
buckwheat (10)	-	74.11	17.13	53.29	100.00	50.17	30.24	19.05	91.55	148.55	58.34	37.25	222.98
	50	58.82	20.89	17.28	81.37	64.97	12.64	47.44	81.31	189.21	68.57	76.36	258.09
	60	57.42	24.33	26.29	86.68	99.73	0.21	99.46	100.00	193.38	69.51	85.34	280.00
	70	64.79	29.25	12.95	100.0	99.89	0.24	99.46	100.00	248.80	47.67	167.03	300.15
	80	68.17	26.24	15.81	85.67	98.73	0.52	97.89	99.30	244.82	78.18	120.82	305.12
phacelia (7)	-	60.50	15.39	31.16	76.30	39.30	26.09	9.70	76.59	77.73	54.78	27.19	168.34
	50	60.50	15.39	31.16	76.30	42.28	29.58	4.55	74.64	83.12	73.73	25.61	210.57
	60	57.07	21.29	20.01	86.68	49.83	34.27	10.05	99.32	82.08	70.32	25.47	187.17
	70	70.58	10.10	52.53	85.12	58.69	30.12	20.03	100.00	117.25	86.91	48.84	269.16
	80	68.58	16.78	36.96	85.67	78.13	22.29	33.52	98.73	158.79	86.73	66.43	301.55
goldenrods (3)	-	53.37	3.11	50.19	56.40	40.90	33.31	21.19	79.36	80.67	78.76	32.56	171.56
	50	53.37	3.11	50.19	56.40	11.01	3.23	7.50	13.85	36.05	1.06	35.03	37.15
	60	55.97	3.52	52.86	59.79	20.74	3.05	17.39	23.37	38.02	0.45	37.72	38.53
	70	79.46	1.27	78.27	80.80	46.43	4.81	41.31	50.86	71.39	4.69	67.04	76.36
	80	73.59	3.44	70.63	77.36	49.58	3.43	47.32	53.52	92.32	4.86	88.40	97.76
heather (3)	-	95.16	8.39	85.47	100.0	32.76	17.95	21.42	53.46	123.65	60.06	71.91	189.52
	50	85.47	0.00	85.47	85.47	22.01	0.00	22.01	22.01	104.77	30.94	73.82	135.69
	60	43.14	0.00	43.14	43.14	65.91	0.00	65.91	65.91	108.63	21.64	83.79	123.37
	70	57.40	2.25	55.80	58.99	77.62	0.00	77.62	77.62	149.35	51.56	97.08	200.18
	80	53.54	2.18	51.10	55.30	78.45	0.00	78.45	78.45	177.86	36.49	136.99	207.17
honeydew (8)	-	67.74	15.99	37.93	83.51	31.08	17.61	9.60	54.43	60.83	9.40	45.44	72.95
	50	66.06	11.41	41.63	80.50	29.19	5.04	26.28	35.01	65.28	14.07	43.52	89.83
	60	44.35	27.58	8.12	75.37	54.28	2.93	51.22	57.07	70.76	13.12	46.14	87.20
	70	55.78	19.45	20.20	69.72	79.73	15.82	68.54	90.92	145.59	73.10	82.07	250.00
	80	53.49	20.22	11.82	72.06	81.76	0.90	81.13	82.39	129.10	19.10	95.87	151.03
lime (4)	-	62.69	9.84	51.97	77.10	23.47	6.31	17.80	30.33	44.98	4.63	38.06	50.56
	50	58.96	12.37	45.81	77.10	19.73	11.14	11.86	27.61	51.83	13.48	41.27	74.25
	60	54.04	14.07	41.21	72.96	30.71	10.18	23.51	37.91	50.87	16.29	39.41	79.68
	70	66.06	12.13	51.72	76.64	48.04	5.75	43.97	52.11	68.23	6.94	57.03	74.67
	80	62.70	13.35	44.33	77.79	85.77	5.58	81.83	89.72	108.7	27.56	82.92	148.45
mixed nectar-honeydew (8)	-	64.90	27.68	23.81	82.86	37.85	14.54	21.63	56.23	62.70	16.41	48.70	81.20
	50	67.53	22.47	34.36	82.86	26.69	10.12	20.02	38.33	69.81	13.37	59.06	89.35
	60	71.56	7.47	64.05	78.99	49.19	15.96	36.55	67.12	67.00	13.73	57.33	87.05
	70	65.50	12.18	51.82	81.48	84.89	7.48	76.53	90.92	145.9	70.17	97.88	250.00
	80	60.77	4.75	54.96	66.19	78.78	21.51	54.51	95.49	136.1	25.79	107.23	160.31
multifloral (17)	-	61.16	16.17	38.39	81.99	25.44	16.35	4.83	60.39	48.43	12.12	30.01	71.88
	50	57.73	15.21	38.39	81.99	16.27	10.09	4.46	30.65	52.17	13.26	30.70	82.25
	60	48.68	20.28	9.01	73.74	34.32	16.90	15.35	59.09	60.83	24.61	30.52	116.87
	70	68.25	10.56	43.10	82.11	51.40	13.48	33.96	68.86	102.9	51.78	46.36	250.00
	80	64.23	9.97	42.10	79.37	73.63	20.50	45.35	96.34	125.5	31.58	71.91	184.12
rape (22)	-	49.45	10.15	36.89	78.47	17.78	4.45	9.83	26.43	34.95	7.54	17.57	45.98
	50	51.36	11.02	19.65	66.87	6.97	3.69	1.32	12.43	38.09	7.90	29.20	70.45
	60	37.82	17.15	3.40	69.77	19.13	4.54	9.37	24.52	40.56	11.64	27.86	72.73
	70	66.71	9.45	46.73	81.99	33.91	16.15	2.45	56.18	62.61	26.83	36.23	132.32
	80	72.17	8.28	45.96	83.24	46.84	7.06	35.07	58.45	78.34	17.37	49.09	121.39

Source: own research.

Table 5. Correlation matrix

	L*	a*	b*	AA _{DPPH}	AA _{ABTS}	TP
L*	1.00	-	-	-0.30a	-0.59a	-0.63a
a*	-	1.00	-	0.21a	0.13a	-0.18a
b*	-	-	1.00	-0.19a	-0.52a	-0.62a
AA _{DPPH}	-0.30a	0.21a	-0.19a	1.00	0.51a	0.32a
AA _{ABTS}	-0.59a	0.13a	-0.52a	0.51a	1.00	0.66a
TP	-0.63a	-0.18a	-0.62a	0.32a	0.66a	1.00

Source: own research.

Conclusions

This study indicates that the dark honeys (buckwheat, fir, heather) showed the highest antioxidant activity and total phenolic content, while pale honeys (rape, acacia, lime) demonstrated the lowest respective values.

It was found that heating led to significant variations in levels of these quality parameters. Heat treatment leads also to an increase in the total phenolics content and antioxidant activity due to the formation of Maillard reactions products. It causes also the darkening (browning) of honey samples, which may contribute to the approval by the consumers.

Acknowledgments

This work was supported by the State Committee for Scientific Research (KBN) within the project 2065/B/P01/2009/36

References

- Aljadi A.M., Kamaruddin M.Y., 2004, *Evaluation of the phenolic contents and antioxidants capacity of two Malaysian floral honeys*, Food Chem., 85, 513-518.
- Al-Mamary, M., Al-Meerri, A., Al-Habori M., 2002, *Antioxidant activities and total phenolics of different types of honey*, Nutrition Res., 22, 1041-1047
- Baltrušaitytė, V., Venskutonis, P.R., Čeksterytė, V., 2007, *Radical scavenging activity of different floral origin honey and beebread phenolic extracts*, Food Chem., 101, 502-514.
- Bertoncelj J., Doberšek U., Jamnik M., Golob, T., 2007, *Evaluation of the phenolic content, antioxidant activity and colour of Slovenian honey*, Food Chem., 105, 822-828.
- Blasa M., Candiracci M., Accorsi A., Piacentini M. P., Albertini M.C., Piatti E., 2006, *Raw millefiori honey is packed full of antioxidants*, Food Chem., 97, 217-222.

- Brudzynski K., Miotto D., 2011, *The relationship between the Maillard reaction-like products and bioactivity of Canadian honeys*, Food Chem., 124, 869-874.
- Dustmann. J.H., 1979, *Antibacterial effect of honey*, Apiacta, 14, 7-11.
- Escriche J., Visquert M., Juan-Boras M., Fito. P., 2009, *Influence of simulated thermal treatments on the volatile fractions of different varieties of honey*, Food Chem., 112, 329-338.
- Gheldof, N., Wang, X.H., Engeseth, N.J., 2002, *Identification and quantification of antioxidant components of honeys from various floral sources*, J. Agric. Food Chem., 50 (21), 5870-5877.
- Gheldof, N., Engeseth, N.J., 2002, *Antioxidant capacity of honeys from various floral sources based on the determination of oxygen radical absorbance capacity and inhibition of in vitro lipoprotein oxidation in human serum samples*, J. Agric. Food Chem., 50, 3050-3055.
- Ibarz A., Pagan J., Giner. J.P.J., 2000, *Kinetic models of non-enzymatic browning in apple pure*, J. Sc.Food Agriculture, 80, 1162-1168.
- Karabournioti S., Zervalaki P., 2001, *The effect of heating on honey HMF and invertase*, Apiacta, 36 (4), 177-181.
- Küçük M., Kolayli S., Karaoğlu S., Ulusoy E., Baltacı C., Candan F., 2007, *Biological activities and chemical composition of three honeys of different types from Anatolia*, Food Chem., 100, 526-534.
- Lachman J., Orsák M., Hejtmánková A., Kovářová E., 2010, *Evaluation of antioxidant activity and total phenolics of selected Czech honeys*, LWT -Food Sc. Technol., 43, 52-58.
- Meda A., Lamien C.E., Romito M., Millogo J., Nacoulma O.G., 2005, *Determination of the total phenolic, flavonoid and proline contents in Burkina Fasa honeys as well as their radical scavenging activity*, Food Chem., 91, 571-577.
- Loveaux J., Maurizio A., Worwohl G., 1978, *Methods of melissopalynology by International Commission for Bee Botany of IUBS*, Bee World, 59, 139-157.
- Popek S., 2002, *A procedure to identify a honey type*, Food Chem., 79 (2), 401-406.
- Tosi E., Ciappini M., Re E., Lucero H., 2002, *Honey thermal treatment effects on hydroxymethylfurfural content*, Food Chem., 77, 71-74.
- Tosi E., Martinet M., Ortega H., Lucero H., Re E., 2008, *Honey diastase activity modified by heating*, Food Chem., 106, 883-887.
- Turhan I., Tetik N., Karhan M., Gurel F., Tavukcoglu H.R., 2008, *Quality of honeys influenced by thermal treatment*, LWT – Food Sc. Technol., 41, 1396-1399.
- Turkmen N., Sari F., Poyrazoglu E.S., Velioglu Y.S., 2005, *Effects of prolonged heating on antioxidant activity and colour of honey*, Food Chem., 95, 653-657.

Vaikousi H., Koutsoumanis K., Biliaderis C., 2009, *Kinetic modeling of non-enzymatic browning in honey and diluted honey systems subjected to isothermal and dynamic heating protocols*, J. Food Eng., 95, 541-550.

Weston, R.J., 2000, *The contribution of catalase and other natural products to the antibacterial activity of honey: a review*, Food Chem., 71, 235-239.

Wilczyńska A., 2010, *Phenolics content and antioxidant activity of Polish types of honey*, PJ.N.F.Sc., 60 (4), 309-313.

COMMODITY SCIENCE
IN RESEARCH AND PRACTICE

series consists of eight monographs:

**ACHIEVEMENTS AND CHALLENGES
OF COMMODITY SCIENCE IN THE AGE OF GLOBALIZATION**

Edited by Andrzej Chochół & Jerzy Szakiel

CONSUMER PROTECTION AND SATISFACTION

Edited by Andrzej Chochół

FOOD PRODUCTS' QUALITY

Edited by Małgorzata Miśniakiewicz & Stanisław Popek

FUTURE TRENDS AND CHALLENGES IN THE FOOD SECTOR

Edited by Małgorzata Miśniakiewicz & Stanisław Popek

INNOVATIONS IN PRODUCT DEVELOPMENT AND PACKAGING

Edited by Agnieszka Cholewa-Wójcik & Agnieszka Kawecka

NON-FOOD PRODUCTS' QUALITY & INNOVATIONS

Edited by Renata Salerno-Kochan

**TOWARDS QUALITY - MANAGEMENT SYSTEMS
AND SOLUTIONS**

Edited by Tadeusz Sikora & Joanna Dziadkowiec

TOWARDS SUSTAINABLE DEVELOPMENT

Edited by Waław Adamczyk

