ÚSTAV ZEMĚDĚLSKÝCH A POTRAVINÁŘSKÝCH INFORMACÍ

POTRAVINÁŘSKÉ VĚDY

FOOD SCIENCES

2

ROČNÍK 13
PRAHA 1995
CS ISSN 0862-8653

ČESKÁ AKADEMIE ZEMĚDĚLSKÝCH VĚD

POTRAVINÁŘSKÉ VĚDY
FOOD SCIENCES

An international journal published by the Czech Academy of Agricultural Sciences and with the promotion of the Ministry of Agriculture of The Czech Republic

Abstracts from the journal is comprised in Agrindex of FAO (AGRIS database), Food Science and Technology Abstracts, Dairy Science Abstracts, Chemical Abstracts, WLAS, TOXILINE PLUS and Czech Agricultural Bibliography.

Aim and scope: The journal publishes original scientific papers, short communications, and selectively reviews, that means papers based on the study of technical literature and reviewing knowledge in the given field. Published papers are in Czech, Slovak or English.

Subscription information: Subscription orders can be entered only by calendar year and should be sent to the contact address.
Subscription prise for 1995 is 210 Kc, 48 USD (Europe) and 56 USD (overseas)

Periodicity: The journal is published six time a year.

Contact address: Slezská 7, 120 56 Prague 2, Czech Republic,
tel. 02/251 098; fax 02/257 090

Potrav. Vědy, *13*, 1995 (2) : 85–91

KINETICS OF 2-CHLORO-1,3-PROPANEDIOL DEGRADATION IN MODEL SYSTEMS AND IN PROTEIN HYDROLYSATES*

Marek DOLEŽAL, Jan VELÍŠEK

Institute of Chemical Technology – Department of Food Chemistry and Analysis, Prague, Czech Republic

Abstract: Glycerol monochlorohydrins, namely 3-chloro-1,2-propanediol and 2-chloro-1,3-propanediol, which arise as the major contaminants in hydrolyzed vegetable proteins, decompose relatively readily in alkaline solutions. This reaction can be employed to lower the levels of both these contaminants in hydrolyzed vegetable proteins. Degradation of 2-chloro-1,3-propanediol was studied in model solutions (at pH values ranging from 8 to 9) at temperatures of 65 °C and 85 °C. The used HPLC method separated well 2-chloro-1,3-propanediol from its reaction products. Rate constants of 2-chloro-1,3-propanediol degradation were calculated and compared to those of 3-chloro-1,2-propanediol degradation. It was found that the former isomer is about ten times more stable than the latter isomer. The consequences of greater stability of 2-chloro-1,3-propanediol were discussed with respect to its occurrence in hydrolyzed vegetable proteins.

2-chloro-1,3-propanediol; 3-chloro-1,2-propanediol; monochloropropanediols; hydrolyzed vegetable proteins; degradation of HPLC

Hydrolyzed vegetable proteins (HVPs) are used throughout the world as savoury ingredients, seasonings and flavour enhancers in soups, sauces and ready-to-eat meals. HVPs are commonly produced by hydrochloric acid hydrolysis of proteinaceous vegetable materials. It has been established (Velíšek et al., 1978), that hydrochloric acid and the residual lipids occurring in the raw materials used (in oil seed meals) are the major precursors to the four known chlorohydrins of glycerol: 3-chloro-1,2-propanediol (3-MCPD), 2-chloro-1,3-propanediol (2-MCPD), 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol. It has been proved that the main contaminant of HVPs showing mutagenic (Šilhánková et al., 1982) and potentially carcino-

* This work was supported in part by research grant no. 509/93/0419 from the Grant Agency of Czech Republic.

genic activities is 3-MCPD. This compound is found in HVPs at the level of several hundreds of mg per kg. Its isomer 2-MCPD occurrs in about ten times lower amount (Velíšek et al., 1991; Bergen et al., 1992).

Both chloropropanediols are relatively unstable in aqueous alkaline media and this unstability is used to lower the levels of chloropropanediols in commercial HVPs. The stability of 3- MCPD in alkaline solutions was studied by Velíšek and Davídek (1989), that of 2-MCPD is not known.

This work was focused on the study of 2-MCPD behaviour in model solutions. The aim of the research was to obtain data which would enable (knowing its original level and its rate of decomposition) the prediction of the levels of 2-MCPD in HVPs during the decontamination process and in the decontaminated hydrolysates.

MATERIAL AND METHODS

Material, Chemicals, Reagents and Solutions

HVP sample was obtained from Vitana a.s., Byšice, CZ. Monochloropropanediols were synthesized (Conant, Quayle, 1946) and 2-MCPD was isolated from its mixture with 3-MCPD by a preparative gas chromatography. Phenylboronic acid was purchased from Aldrich, Milwaukee, Wisconsin, U.S.A. All other chemicals were obtained from Lachema, Brno, CZ.

Procedures and Methods

Degradation of 2-MCPD in model systems: 100 μg of 2-MCPD was dissolved in 400 μl of a phosphate buffer (pH 8 or 9) and the solutions were stored in a thermostat at 65 or 85 °C. Aliquots were taken, cooled and analyzed by HPLC.

Degradation of 3-MCPD and 2-MCPD in HVPs: A sample of a soybean hydrolysate (200 g) was made alkaline (it was adjusted to pH 8 or 9) using 40% sodium hydroxide and heated to 65 or 85 °C. Aliquots of about 1 ml were taken, cooled and after derivatization with a phenylboronic acid reagent analyzed using the GLC method described by Plantinga et al. (1991).

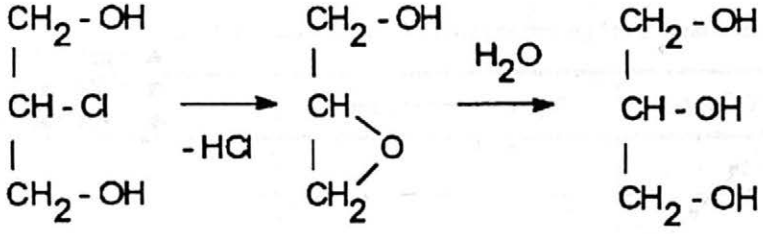
Instrumentation: The HPLC system was a Spectra Physics, San Jose, California, U.S.A., consisting of the pump SP 8810 and the differential re-

fractive index detector Shodex RI SE 61. The chromatographic column was a 250 x 4 mm stainless steel column filled with Separon SGX C18, 5 μm, Tessek, Prague, CZ. The column was joined to a Tessek guard precolumn filled with the same stationary phase. A water-methanol (99 : 1, v/v) mixture was used as a mobile phase at a flow rate of 0.5 ml/min. The injection loop had a volume of 20 μl.

The GLC measurements were performed using a Hewlett-Packard 5890 Series II instrument equipped with a flame-ionization detector and an SPB-1 fused silica capillary column (30 m x 0.20 mm ID, film thickness of 0.80 μm), Supelco, Bellefonte, Pennsylvania, U.S.A. The GLC operating conditions were as follows: carrier gas (nitrogen) flow rate of 1 ml/min (split ratio of 10 : 1). The initial oven temperature was 60 °C for 1 min. It was programmed from 60 to 200 °C (at a rate of 6 °C/min) and then from 200 to 250 °C (at a rate of 30 °C/min). The injector and detector temperatures were set at 200 and 280 °C, respectively.

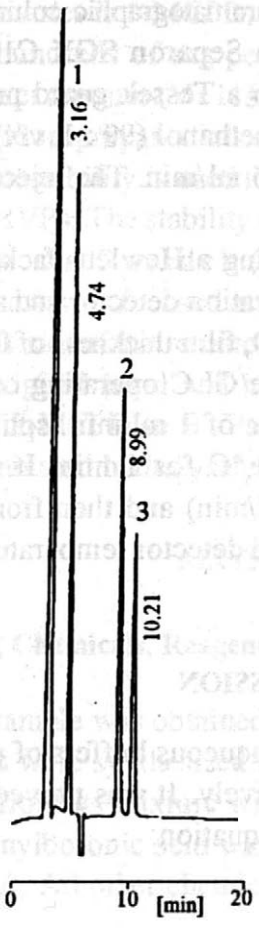
RESULTS AND DISCUSSION

The degradation of 2-MCPD was studied in aqueous buffers of pH 8 and 9 and at temperatures of 65 and 85 °C, respectively. It was proved that the reaction proceeded according to the following equation:



2-MCPD glycidol glycerol

Glycerol reacted to a small extent with the intermediate glycidol giving rise to trace amounts of diglycerol isomers and higher oligoglycerols. An example of 2-MCPD reaction mixture analyzed by HPLC is given in Fig. 1.



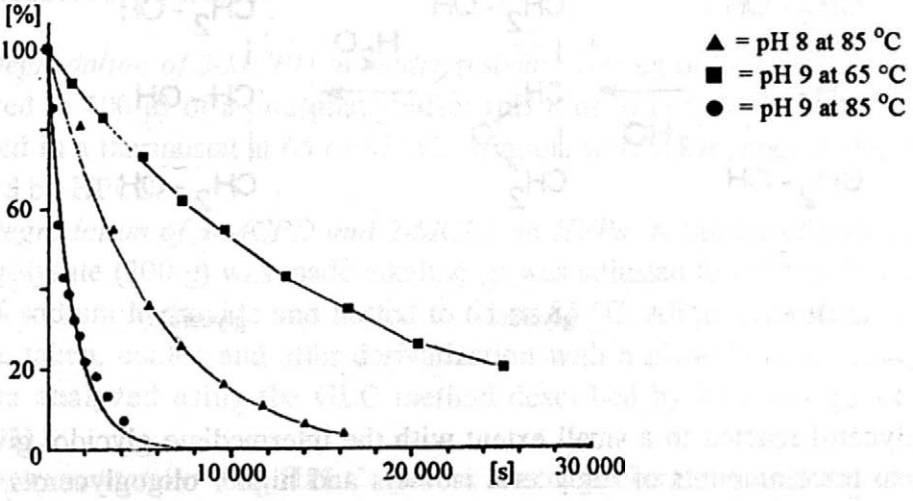
1. Separation of 2-MCPD degradation products

1 = glycerol
2 = glycidol
3 = 2-MCPD

Fig. 2 shows the changes of 2-MCPD concentration in the analyzed solutions.

The rate constants of 2-MCPD degradation were calculated from the data presented in Fig. 2 employing the first order reaction kinetics. The obtained rate constants are summarized in Table I. These values are approximately 7 times (pH 8 at 85 °C), 13 times (pH 9 at 85 °C) and 18 times (pH 9 at 65 °C) lower than the values of the rate constants calculated for 3-MCPD (Doležal, Velíšek, 1992). It is evident that 2-MCPD is more stable than its isomer 3-MCPD.

The difference in these two chloropropanediols stability has a serious practical consequences. The ratio of 2-MCPD to 3-MCPD concentrations found in un-



2. Comparison of 2-MCPD degradation under various conditions

I. Calculated rate constants of 2-MCPD degradation

pH	t [°C]	$k \cdot 10^4$ [s^{-1}]
8	85	1.83
9	65	0.637
9	85	7.60

treated commercial HVPs normally ranges from 0.14 to 0.25 as 3-MCPD is the major HVPs contaminant and 2-MCPD occur in about ten times lower quantities. 3-MCPD is degraded faster than 2-MCPD during the alkaline treatment of HVPs and 2-MCPD then accumulates in the treated hydrolysate. The ratio of concentrations of these two compounds increases and if 3-MCPD is totally destroyed, more toxic 2-MCPD becomes the only chlorine-containing compound found in the treated HVPs.

This phenomenon is documented in Table II. The data were obtained analyzing commercial soybean meal hydrolysates not treated with sodium hydroxide and a hydrolysate which was heated in pH 9 at 85 °C. It is clear that the conditions (pH, temperature and time of the treatment) used for decontamination of HVPs have to be calculated for the more stable HVPs constituent, 2-MCPD.

II. Calculated ratio 2-MCPD/3-MCPD and its changes during HVP treatment

Product	Time of treatment *t* [h]	2-MCPD/3-MCPD ratio
Untreated HVP	–	0.14–0.25
HVPs during treatment	0	0.14
	0.13	1.38
	0.27	4.50
	0.50	17.14
	0.75	66.00
	1.10	260

References

CONANT, J. B. – QUAYLE, O. R.: Org. Synth., Coll. Vol. I, 1946: 294–296.
BERGEN, C. A., van – COLLIER, P. D. – CROMIE, D. D. O. – LUCAS, R. A. – PRESTON, H. D. – SISSONS, D. J.: Determination of chloropropanols in protein hydrolysates. J. Chromatogr., *589*, 1992 :109–119.
DOLEŽAL, M. – VELÍŠEK, J.: Kinetics of degradation of 3-chloro-1,2-propanediol in model systems. In: Proc. Chemical Reactions in Foods II. Prague, VÚPP-STI 1992: 297–302.
PLANTINGA, W. J. – TOORN, W. G., van – STEGEN, G. H. D., van der: Determination of 3-chloropropane-1,2-diol in liquid hydrolysed vegetable proteins by capillary gas chromatography with flame ionization detection. J. Chromatogr., *555*, 1991: 311–314.
ŠILHÁNKOVÁ, L. – ŠMÍD, F. – ČERNÁ, M. – DAVÍDEK, J. – VELÍŠEK, J.: Mutagenicity of glycerol chlorohydrins and of their esters with fatty acids present in protein hydrolysates. Mutation Res., *103*, 1982: 77–81.
VELÍŠEK, J. – DAVÍDEK, J. – HAJŠLOVÁ, J. – KUBELKA, V. – JANÍČEK, G. – MÁNKOVÁ, B.: Chlorohydrins in protein hydrolysates. Z. Lebensm. Unters. Forsch., *167*, 1978 : 241–244.
VELÍŠEK, J. – DAVÍDEK, J.: Stabilita chlorhydrinů glycerolu ve vodných roztocích. Potrav. Vědy, *7*, 1989 : 1–5.
VELÍŠEK, J. – DAVÍDEK, J. – DAVÍDEK, T – LEDAHUDCOVÁ, K. – DOLEŽAL, M.: 3-Chloro-1,2-propanediol derived amino compounds in protein hydrolysates. In: Proc. Euro Food Chem. VI. Hamburg, B. Behrs Verlag 1991: 596–601.

Received December 29, 1994

Kinetika degradace 2-chlor-1,3-propandiolu v modelových systémech a v bílkovinných hydrolyzátech

Byla vypracována HPLC metoda vhodná pro analýzu modelových roztoků monochlorpropandiolů vyskytujících se jako endogenní toxické látky v potravinářských kyselých hydrolyzátech bílkovin. Danou metodou byla sledována rychlost rozkladu 2-chlor-1,3-propandiolu (2-MCPD) v prostředí o pH 8 a 9, při teplotě 65 nebo 85 °C. Tyto podmínky byly zvoleny jako simulace technologických postupů užívaných k odstranění uvedených chlorovaných kontaminantů z hydrolyzátů bílkovin. Ze získaných experimentálních dat byly vypočteny rychlostní konstanty degradace 2-MCPD, které byly zhruba desetkrát nižší než rychlostní konstanty rozkladu jeho isomeru, 3-chlor-1,2-propandiolu (3-MCPD). Z těchto výsledků bylo zřejmé, že v průběhu

ověřeny na sójovém hydrolyzátu zahřívaném po zalkalizování na pH 9 při teplotě 85 °C. Podmínky dekontaminace potravinářských kyselých hydrolyzátů bílkovin je tedy nutné volit s ohledem na stabilitu 2-MCPD.

2-chlor-1,3-propandiol; 3-chlor-1,2-propandiol; monochlorpropandioly; potravinářské hydrolyzáty bílkovin; HPLC

Contact address:

Ing. Marek Doležal, Vysoká škola chemicko-technologická,
Ústav chemie a analýzy potravin, Technická 5, 166 28 Praha 6, Česká republika,
tel.: 02/2435 3178, fax: 02/311 99 90

INFORMACE

Jak jsme již v našem časopise informovali, uskuteční se ve dnech 18. až 20. září 1995 ve Vídni konference **EURO FOOD CHEM VIII**, věnovaná analýze potravin.

Pro další zájemce o účast na této konferenci uvádíme program referátů.

Sekce 1: Vzorkování a příprava vzorků

R. Stephany (NL): Clean-up Procedures; W. de Koe: Sampling and Sampling Plans; M. Barroso, L. J. R. Barron (E): Optimization of the Analytical Conditions Dealing with the Volatile Fraction of Cheese During Dynamic Headspace and Trap Desorption by Microwave Energy; H. F. de Brabander, P. Batjoens, F. Smets, G. Pottie (B): Methods for Residue Analysis: Improvement of Sample Throughput; H. Kallio (FIN): Dense Gas Extraction as a Preparation Method; M. Murkovic, H. Löw, G. Santag, W. Pfannhauser (A): Heterocyclic Aromatic Amines in Commercial Bouillons; S. Tömösközi, I. Berecz, R. Mendi, T. Kovac, F. Örsi (H): Determination of Cholesterol Content in Foods by Flow Injection Analysis.

Sekce 2: Chormatografie a příbuzné techniky

P. Schreier (D): Chiral Chromatographic Methods; A. Mangia (I): Application of Multidimensional Detection Methods; Th. Henle (D): The Amino Acid Analyzer – Still Powerful in Food Analysis and Research; C. De Luca, S. Passi, E. Quattrucci (I): A GC-MS Method for the Analysis of Tocopherol and Low –Molecular Weight Phenol Contents in Foods of Vegetable Origin; A. Mosandl (D): Authenticity Assessment of Flavours and Fragrances; H. Steinhart (D): Application of Capillary Electrophoresis; M. L. Palop, A. Garcia, L. Cabezas, A. L. y Briones (E): Use of Pulsed Fied

Gel Electrophoresis for Strain Identification of *Lactococcus* sp.; T. M. Sauri (FIN): Determination of Chloropropanol in Preparations with Protein Hydrolysates; G. van Vyncht, P. Gaspar, S. Preece, E. DePauw, G. Maghuin-Rogister (B): Development of GC and LC-MS/MS Methods for the Multiresidue Detection of β-Agonists in Urine and Liver; S. Schlemitz, W. Pfannhauser (A): Determination of Nitropolycyclic Aromatic Hydrocarbons in Foods; J. Mäkinen, P. Laakso, P. Manninen, H. Kallio (FIN): Analysis of Post-parturition Changes in the Colostrum Triacylglycerols by Chromatographic and Mass Spectrometric Methods; L. Cossignani, F. Santinelli, M. S. Sinonetti, P. Damiani (I): Exploratory Linear Discriminant Analysis for Climatic Differentiation of Umbrian Extra-Virgine Olive Oils by Means of Stereospecific Analysis of Triacylglycerol Fractions.

Sekce 3: Senzorické techniky

O. Wolfbeis (A): Senzor Techniques and Their Application in Food Analysis; Th. Talou (F): New Trends in Application of Multigas Sensors; L. Campanella, G. Favro, M. P. Sammartino, M. Tomasetti (I): Total Phenol Analysis in Olive Oil and Derivatives Using a Biosensor Working in Organic Solvents; L. Labadini, R. Marchelli, A. Dossena, G. Palla, G. Mori, C. Bocchi, M. Pilone, S. Butto (I): Chiral Analysis as a Quality Control Tool in Food Industry: From GC an HPLC to Biosensors; C. Di Natale, F. Davide, A. D'Amigo, G. Sberveglieri, P. Nelli, G. Faglia (I): Metal Oxide Semiconductor Gas Sensors Array as a Tool for the Analysis of Wine.

Sekce 4: Spektroskopické metody

T. Naes (N): NIR Applications and Statistical Evaluation; A. C. Tas (NL): Spectroscopy and Direct Mixture Analysis; L. Munck (DK): On-line Fluorescence Screening Methods Including Image Analyis; K.-W. Bögl (D): Identification of Food Irradiation; D. N. Rutledge, M. C. Vachier (F): Nuclear Magnetic Resonance Relaxation Time Measurements of Water in Gelatine: A Preliminary Study; P. S. Belton, E. K. Kemsley, J. Potter, R. H. Wilson (UK): Infrared Emission Spectroscopy for the Analysis of Heated Materials; C. Biberauer, P. Garry, J.-L. Venduevre, F. Bauer (A/F): Analytical Methods for the Characterisation of Sanitation Product Residues on Working Surfaces.

Sekce 5: Bioafinitní metody

G. Van Peteghem (B): Real Time Methods in Veterinary Drug Residue Analysis; M. Morgan (UK): Immunological Clean-up Procedures; U. Candrian (CH): Application of Nucleic Acid Amplification Methods; G. Schreiber, G. Schulzki, K.-W. Bögl (D): Detection of Food Modified by the Use of Genetic Engeneering; H. Lieve (B): Specific and Rapid Detection of Foodborne Bacteria with Genetic Technology; A. Sass-Kiss (H): Immuno-analytical Method for the Determination of Juice Content of Citrus Juice Products.

Mimo tato sdělení bude prezentováno přes 160 posterů.

Další informace o konání této konference můžete získat na adrese:

Prof. Jiří Davídek, Vysoká škola chemicko-technologická, Technická 1905, 166 28 Praha 6,tel.: 02/2435 3179, fax: 311 99 90

Potrav. Vědy, *13*, 1995 (2) : 93–102

GLUCOSINOLATES IN COOKED CABBAGE (*BRASSICA OLERACEA* L. VAR *CAPITATA*) *

Bahru W. KASSAHUN, Jan VELÍŠEK, Jiří DAVÍDEK

Institute of Chemical Technology – Department of Food Chemistry and Analysis, Prague, Czech Republic

Abstract: The effect of cooking on cabbage (*Brassica oleracea* L. var. *capitata*) glucosinolates was investigated by cooking the cabbage sample (Aneto F1, summer early variety) for 5, 10, 15, 30, 45 and 60 min. This process resulted in a decrease of glucosinolate content by more than 50% in 5 min and 10 min cooked cabbage. Cooking for more than 30 min caused substantial loss of glucosinolates: in 60 min cooked cabbage a small amount of sinigrin (2-propenyl glucosinolate) was found and other glucosinolates were lost almost completely. The cause for the loss of glucosinolates in the 45 and 60 min cabbage can be that glucosinolates are susceptible to prolonged exposition of heat. On the other hand loss of glucosinolates during cooking for 5 to 30 min may be the outcome of the combined effect of the enzymatic degradation (caused by the endogenous thioglucosidase) and the heat applied to cook the sample.

glucosinolate composition; cooked cabbage; decrese in content

Glucosinolates, a well-defined secondary plant metabolites, are present in the order *Caparales*, to which the *Brassica* genus belongs. They co-exist with (but apart from each other) thioglucosidase enzyme, myrosinase (thioglucoside glucohydrolase EC 3.2.3.1) (McGregor et al., 1983). The damage of the plant tissue in the presence of water allows the contact of the substrates with the enzyme and as a result glucosinolates can be hydrolysed to a number of compounds. The thioglucosidase splits the glucose moiety at the β-thioglucosidic bond. Other products are formed by Lossen-type rearrangement of the liberated aglucone (Ettlinger, Lundeen, 1956). In regard to the influence which the reaction medium exerts (pH, the presence of cations, Fe^{3+}/Fe^{2+}, etc.) (Uda et al., 1986), except equimolar amount of glucose and bisulphate, the main products are isothiocyanates, nitriles, oxa-

* This work supported in part by research grant no. 509/93/2483 from the Grant Agency of Czech Republic.

zolidine-2-thiones and other compounds. The character of the side chain also contributes to this process. Glucosinolates are sensitive to extreme reaction media: in strong acidic conditions they can be oxidised to carboxylic acids and in alkaline solutions may be transformed to corresponding amino acids (Olsen, Soerensen, 1980).

Glucosinolates are intensively studied plant constituents for many years. This fact is impinged by the physiological activity of their enzymatic degradation products (Fenwick et al., 1983b).

Glucosinolate breakdown products participate in the formation of the flavour of meals from *Brassica* vegetables: isothiocyanates are pungent (McGregor et al., 1983), goitrin (a degradation product of progoitrin) is known to be intensively bitter (Sones et al., 1984), 2-propenyl glucosinolate also contributes to bitterness (Fenwick et al., 1983a). Benzyl isothiocyanate from glucotropaeolin (benzyl glucosinolate) in land cress (*Coronopus didymus* L.) has been alleged to be a major intermediate of benzyl methyl sulfide and benzyl mercaptan, which cause off-flavour in heat treated milk (Walker, Gray, 1970). These hydrolysis products also interfere in certain physiological processes exhibiting either harmful or beneficial effects. Beyond the well-known effect of goitrogenicity of 5-vinyloxazolidine-2-thione, the volatile isothiocyanates possess antifungal, antibacterial and other properties (Fenwick et al., 1983b). Phytotoxicity of higher homologues of methylsulfonyl isothiocyanates (octyl, nonyl and decyl) was also reported (Yamane et al., 1992). On the contrary, the hydrolysis products of indole glucosinolates, indole-3-methanol and ascorbigen (the reaction product of indole-3-methanol and ascorbic acid) are found to be engaged in decreasing the risk of chemical carcinogenesis (McDanell et al., 1988).

The effect of cooking on total and individual glucosinolate content was examined by different researchers (Vos et al., 1988; Rosa, Heaney, 1993; Kassahun et al., 1994). Depending on the processing conditions (cooking, fermenting, storage, freezing, etc.), the content of intact glucosinolates was reduced by different proportions. Cooking of cabbage for a short time (5 and 10 min) caused a decrease in glucosinolate content mainly by leaching into the cooking water and losses caused by glucosinolate degradation were found to be unaccountable. However, considerable losses occurred when the cabbage was cooked for 45 and 60 min. MacLeod and MacLeod (1968) analysed the volatile components of cooked cabbage using gas

chromatography and mass spectrometry and found dimethyl sulphide as a dominant product; dimethyl disulfide was also present as a minor compound. A compound from which dimethyl disulfide can be formed in *Brassica* vegetables has been described as S-methyl-L-cysteine sulfoxide. Allyl cyanide, allyl isothiocyanate, other isothiocyanates and nitriles were found. But there is no evidence if the degradation of some glucosinolates of cabbage such as glucoiberin (3-methylsulfinylpropyl glucosinolate), glucoraphanin (4-methylsulfinylbutyl glucosinolates), etc., could also lead to the formation of those or related alkyl sulfides (notably mono, di, tri and tetra sulfides). In boiled cabbage, kale and kohlrabi, Michajlovskij et al., (1969, 1970) measured the content of glucosinolates (via their hydrolysis products) and reported losses approximately half or less than half of the content of the glucosinolates. Sinigrin was found to have more resistance to the effect of cooking than progoitrin, glucoibervirin, etc.

Our present experiment was conducted to estimate the loss of glucosinolates by cooking the cabbage for varying period of time under conditions of common consumer practice. The composition and quantitation of glucosinolates were performed by analysing cooked cabbage using capillary gas-liquid chromatography.

MATERIALS AND METHODS

Material

Freshly harvested head cabbage (Aneto F1) early summer variety was supplied by Central Breeding Station, Dobřichovice, Czech Republic.

Chemicals, Reagents and Solutions

The chemicals and reagents used were previously reported (Kassahun et al., 1994, 1995).

Sample Preparation

Preparation of sample for gas chromatographic analysis of glucosinolates was performed according to the previously described method (Kassahun et al., 1994). The general view of the method is as follows: freshly sliced cabbage (75 g, about 15 mm slice diameter) was mixed with 75 ml cold water in a 250ml round bottom flask and cooked under reflux for 5, 10, 15, 30,

45 and 60 min. After cooking the sample was allowed to cool and glucosinolates were extracted from the cooked cabbage with absolute and aqueous methanol as described by Heaney, Fenwick (1980). The cooking water was evaporated to a minimum volume (about 25 ml); the proteins and other components were precipitated by adding equimolar solution of lead and barium acetate (0.5 M). Following centrifugation (6 x 1000 g, 10 min) the supernatant was adjusted to a volume of 50 ml and 5 ml of this extract was applied to a DEAE Sephadex A-25 anion exchange column (acetate form). Interfering compounds were eluted with 0.02 M pyridine acetate and glucosinolates subsequently desulfated (12 hrs) by adding aryl sulfatase type H-1 (EC 3.1.6.1). Following the elution of desulfoglucosinolates with water (4 ml), the eluent was thoroughly evaporated and the residue dried under a stream of nitrogen. This sample was silylated (pyridine : BSTFA : TMCS = = 100 : 100 : 10, v/v/v) within 20 min at 120 °C and analysed by gas-liquid chromatography.

Apparatus

Gas liquid chromatographic analysis of the pertrimethylsilyl derivatives of desulphoglucosinolates was carried out on the instrument Hewlett Packard model 5890A equipped with a flame ionisation detector (FID) and a fused silica capillary column (25 m x 0.25 mm) with stationary phase SE-54, film thickness 0.25 μm. The temperature was linearly programmed from 200 to 285 °C with an increase of 4 °C/min. Injector and detector temperature were 285 and 300 °C, respectively.

RESULTS AND DISCUSSION

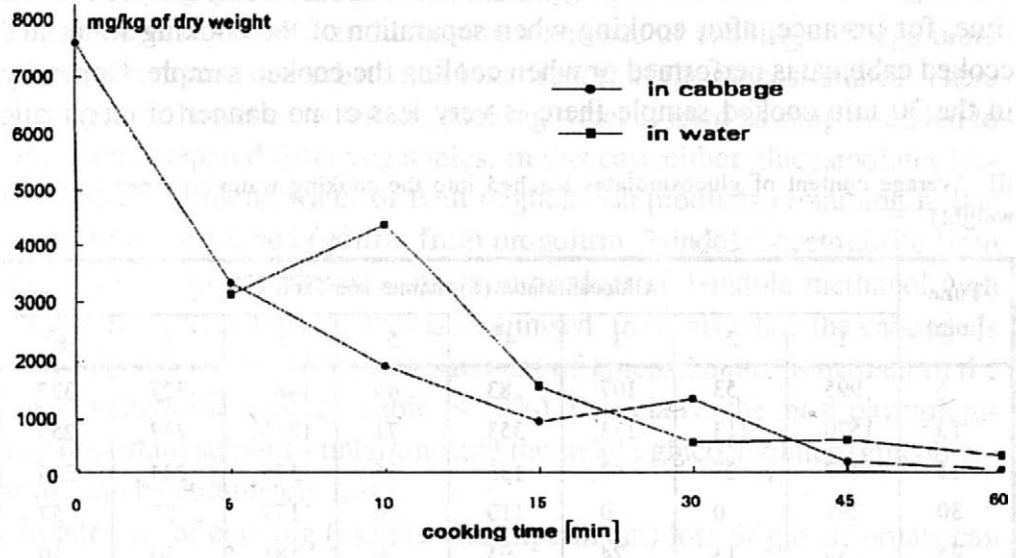
The glucosinolates found in the analysed cabbage samples are listed in Table I in their gas chromatographic elution order. The results are in agreement with the work of Fenwick et al. (1983b).

Values of individual glucosinolate content quantified in the cooked cabbage as well as in the cooking water are given in Tables II and III. Glucobrassicanapin (4-pentenyl glucosinolate) and gluconapoleiferin (2-hydroxy--4-pentenyl glucosinolate) were present in traces, less than 1 mg per kg of dry weight, either in the cooked cabbage or in the cooking water. Therefore, they are excluded from the results summarised in the tables. The value of minor indole glucosinolates, neoglucobrassicin (N-methoxy-3-indolylme-

I. List of glucosinolates (GLs) quantified in cooked cabbage

No.	Semisystematic name	Trivial name
1	2-propenyl GLs	sinigrin
2	3-butenyl GLs	gluconapin
3	2(R)-hydroxy-3-butenyl GLs	progoitrins
4	methylthio-3-propyl GLs	glucoibervirin
5	methylthio-4-butyl GLs	glucoerucin
6	2-phenethyl GLs	gluconasturtiin
7	3-indolyl methyl GLs	glucobrassicin
8	N-methoxy-3-indolyl methyl GLs	neoglucobrassicin
9	4-hydroxy-3-indolyl methyl GLs	
10	4-methoxy-3-indolyl methyl GLs	

thyl glucosinolate), 4-hydroxyglucobrassicin and 4-methoxyglucobrassicin is given as a sum of their individual contents (Table II and III). The same was done with the sulphur containing glucosinolates, glucoibervirin (methylthio-3-propyl glucosinolate), glucoerucin (methylthio-4-butyl glucosinolate). For comparison, the values of total glucosinolates from Tables II and III are used to construct Fig. 1.



1. Change of total glucosinolate content in cooked cabbage and cooking water

II. Average content of glucosinolates in cooked cabbage (mg per kg of dry weight)

Time [min]	Glucosinolates (for names see Table I)							
	1	2	3	4[a]	5	6	7	8[b]
0	2 528	277	239	638	94	3 367	443	443
5	965	56	187	376	48	1 468	207	207
10	804	37	126	287	45	452	120	120
15	305	10	34	99	0	382	88	88
30	487	40	58	49	18	563	79	79
45	56	13	28	26	0	51	0	0
60	18	0	0	0	0	0	0	0

[a] the sum of the content of glucoibervirin and glucoerucin

[b] the sum of the content of neoglucobrassicin, 4-hydroxyglucobrassicin and 4-methoxyglucobrassicin

The total content of glucosinolates in 5, 10, and 15 min cooked material was decreasing as the cooking time prolonged. But the content found in 30 min cooked cabbage is greater than that found in the 15 min cooked one. The reason might be that glucosinolates can be hydrolysed by the combined action of heat and the endogeneous enzyme thioglucosidase during the 15 min cooking, whereas thioglucosidase activity can be destroyed by a continous cooking 15 to 30 min and thus glucosinolates cannot be hydrolysed in the time, for instance, after cooking when separation of the cooking water and ccoked cabbage is performed or when cooling the cooked sample. Generally in the 30 min cooked sample there is very less or no danger of enzymatic

III. Average content of glucosinolates leached into the cooking water (mg per kg of dry weight)

Time [min]	Glucosinolates (for names see Table I)							
	1	2	3	4[a]	5	6	7	8[b]
5	995	53	107	83	49	1489	327	327
10	1570	113	153	353	71	1815	257	257
15	487	23	42	133	35	575	234	234
30	299	0	0	110	0	174	57	57
45	236	13	24	95	0	181	10	10
60	109	0	25	41	16	52	12	12

degradation. The quantity of glucosinolates in the 5 and 10 min cooked cabbage remained greater than that of either 15 or 30 min cooked sample, however.

The major glucosinolates found in cooked cabbage were sinigrin and glucobrassicin. Of the initial content of sinigrin found in the fresh material, 38 and 32% (5 min cooked) and 40 and 62% (10 min cooked) was found in the cooked cabbage and cooking water, respectively. In the case of glucobrassicin the portion found in the cooked cabbage and cooking water was 43.5 and 44% (5 min cooked) and 13 and 53% (10 min cooked), respectively. In the 60 min cooked cabbage the amount of sinigrin found was very low and other glucosinolates were completely lost.

The contents of glucobrassicin and the sulphur-containing glucosinolates, glucoibervirin and glucoerucin were decreased more drastically than sinigrin as the cooking time exceeds 15 min; i.e. in 30 and 45 min cooked cabbage. Comparing to sinigrin and glucobrassicin, progoitrin is one of the minor (but occurs in significant amount) glucosinolates in cabbage. From the obtained results it can be seen that this glucosinolate seems to have relative resistance to the effect of cooking. The reduction in its content was slower (Tables II and III) than that of any other glucosinolate in the cabbage. Generally, cooking for more than 30 minutes significantly reduced the content of all glucosinolates in the analysed samples with higher losses in the content of sulphur-containing and indole glucosinolates.

It can be easily seen that the common practice of cooking cabbage more than 30 min results in a substantial loss of most of the glucosinolates. There are occations, however, when the cooking water is used as soup or added to some soups prepared from vegetables. In this case either glucosinolates leached into the cooking water or their degradation products remaining in this water can be consumed (goitrin from progoitrin, 3-indolyl acetonitrile from glucobrassicin or ascorbigen – reaction product of 3-indole methanol with ascorbic acid, etc.); thus the loss is minimised. In meals when the cabbage is cooked for more than 45 min, the amount of glucosinolates remained in the cooked material is unaccountable (< 10%). Especially, the most physiologically important sulphur-containing and the indole glucosinolates (glucobrassicins) can be completely lost.

In our way of cooking (used in this experiment) loss of glucosinolate can proceed at the beginning of cooking by enzymatic hydrolysis until the sam-

ple starts to boil, and later (esp. during cooking to 30 min) this loss may apparently emerge as the outcome of the combined action of the thioglucosidase (myrosinase) and heat applied to cook the sample. The major part of the glucosinolate loss during cooking, for more than 30 min, can be caused by heat.

The volatile breakdown products of glucosinolates formed during cooking were found to be nitriles, isothiocyanates, etc.; the major product being 2--propenyl isothiocyanate and methylthio-3-propyl nitrile. Non-volatile degradation products of indole glucosinolates (the major being indole-3-acetonitrile) remained in the cooking water. Determination and characterisation of these products, the chemical aspects of these reactions in cooked cabbage will be the target of our further study.

References

ETTLINGER, M. G. – LUNDEEN, A. J.: J. Amer. Chem. Soc., *78*, 1956: 4172 to 4177.

FENWICK, G. R. – GRIFFITHS, N. M. – HEANEY, R. K.: The role of glucosinolates and their breakdown products: bitterness in Brussels sprouts (*Brassica oleracea* L. var. *gemmifera*). J. Sci. Food Agric., *34*, 1983a: 73–80.

FENWICK, G. R. – HEANEY, R. K – MULLIN, W. J.: Glucosinolates and their breakdown products in food and food plants. CRC. Crit. Rev. Food Sci. Nutr., *18*, 1983b: 123–201.

HEANEY, R. K. – FENWICK, G. R.: The analysis of glucosinolates in *Brassica* species using gas chromatography. Direct determination of the thiocyanate ion precursors, glucobrassicin and neoglucobrassicin. J. Sci. Food Agric., *31*, 1980: 593–599.

KASSAHUN, B. W. – VELÍŠEK, J. – DAVÍDEK, J. – HAJŠLOVÁ, J.: The change of cabbage (*Brassica oleracea* L. var. *capitata*) glucosinolate content during storage. Potrav. Vědy, *3*, 1995: 13–24.

KASSAHUN, B. W. – VELÍŠEK, J. – DAVÍDEK, J.: Changes of glucosinolate content in cabbage (*Brassica olercea* L. var. *capitata*) during processing. In: Proc. Int. Euro Food Tox. IV Conf.: Bioactive Substances in Food of Plant Origin, Vol. 1, Olsztyn, Poland 1994: 32–35.

McDANELL, R. – McLEAN, A. E. M. – HANLEY, A. B. – HEANEY, R. K. – FENWICK, G. R.: Differential induction of mixed function oxidase (MFO) activity in rat liver and intestine by diets containing processed cabbage: Correlation with cabbage levels of glucosinolates and glucosinolate hydrolysis products. Food. Chem. Toxicol., *25*, 1987: 363–368.

McGREGOR, D. I. – MULLIN, W. J. – FENWICK, G. R.: Analytical methodology for determining glucosinolates composition and content. J. Assoc. Offic. Anal. Chem., *66*, 1983: 825–849.
MacLEOD, A. J. – MacLEOD, G.: Volatiles of cooked cabbage. J. Sci. Food. Agric., *19*, 1968: 273–277.
MICHALOVSKIJ, N. – SEDLÁK, J. – KOŠTEKOVÁ, O.: Effect of thermal treatment on the content of goitrogenic substances in plant foods. Rev. Czech Med., *15*, 1969: 132–144.
MICHAJLOVSKIJ, N. – SEDLÁK, J. – KOŠTEKOVÁ, O.: Content of naturally occurring goitrogens in boiled plants of *Brassica* family. Endocrinol. Exper., *4*, 1970: 51–62.
OLSEN, O. – SOERENSEN, H.: Sinalbin and other glucosinolates in seeds of double low rape species and *Brassica napus* cv. *bronowski*. J. Agric. Food Chem., *28*, 1980: 43–48.
ROSA, E. A. S. – HEANEY, R. K.: The effect of cooking and processing on the glucosinolate content: Studies on four varieties of Portuguese cabbage and hybrid white cabbage. J. Sci. Food Agric., *62*, 1993: 259–265.
SONES, K. – HEANEY, R. K. – FENWICK, G. R.: An estimate of the mean daily intake of glucosinolates from cruciferous vegetables in UK. J. Sci. Food Agric. *35*, 1984: 712–720.
UDA, Y. – KURATA – ARAKAWA, N.: Effects of the ferrous ion on the degradation of glucosinolates by myrosinase. Agric. Biol. Chem., *50*, 1986: 2735–2740.
VOS, R. H., de – BLIJLEVEN, W. G. H.: The effect of processing conditions on glucosinolates in cruciferous vegetables. Z. Lebensm. Unters. Forsch., *187*, 1988: 525–529.
WALKER, N. J. – GRAY, I. K.: The glucosinolate of land cress (*Coronopus didymus* L.) and its enzymic degradation products as precursors of off-flavor in milk. A review. J. Agric. Food Chem., *18*, 1970: 346–352.
YAMANE, A. – FUJIKURA, J. – OGAWA, H. – MITUZANI, J.: Isothiocyanates as alleophatic compounds from Roripa indica Hiern (Cruciferae) roots. J. Chem. Ecol., *18*, 1992: 1941–1953.

Received February 21, 1995

Glukosinoláty ve vařeném zelí
(Brassica oleracea L. var. *capitata)*

Vliv vaření na glukosinoláty přítomné v zelí (*Brassica oleracea* L. var. *capitata*) byl zkoumán vařením vzorků hlávkového zelí (Aneto F1, raná letní odrůda) po dobu 5, 10, 15, 30, 45 a 60 min. Výsledkem bylo snížení obsahu glukosinolátů o více než

50 % původního obsahu u zelí vařeného 5 a 10 min. Vaření po dobu delší než 30 minut způsobilo značnou ztrátu glukosinolátů: v zelí vařeném 60 min bylo zjištěno malé množství sinigrinu (2-propenyl glukosinolátu) a došlo k teměř úplné ztrátě ostatních glukosinolátů. Příčinou ztráty glukosinolátů v zelí vařeném 45 a 60 min může být degradace glukosinolátů. Na druhé straně ztráta glukosinolátů během vaření po dobu 5 až 30 min je hlavně výsledkem kombinovaného účinku enzymové degradace (zapříčiněné endogenní thioglukosidasou) a tepla.

složení glukosinolátů; vařené zelí; snížení obsahu glukosinolátů

Contact Address:

Prof. ing. Jan Velíšek, DrSc., Vysoká škola chemickotechnologická,
Ústav chemie a analýzy potravin, Technická 5, 166 28 Praha 6, Česká republika,
tel.: 02/2435 5217, fax: 02/311 99 90

Potrav. Vědy, *13*, 1995 (2) : 103–109

THE EFFECT OF FOOD HEATING PRODUCTS ON CORROSION OF CANS

Jaroslav DOBIÁŠ, Michal VOLDŘICH, Dušan ČURDA, Petros PELAVAS

Institute of Chemical Technology – Department of Food Preservation and Meat Technology, Prague, Czech Republic

Abstract: The influence of heat treatment of 14 liquid foods and/or food simulating solutions on their aggressivity against the lacquered tinned cans was studied. The corrosion effect of canned testing solutions during sterilisation and 10 month storage at 20 °C was compared with that of the same samples which had been refluxed for 16 hours before filling into packaging, sterilisation and storage. No acceleration of corrosion rate was found for preheated samples but ten of those simulants provided the retarded rate of iron dissolving and five of them showed the lower rate of tin corrosion. For the rest of the tested samples no significant differences were found.

corrosion; cans; canned food; heating

By the Arrhenius equation the rate of chemical reactions increases exponentially with the linear increase of temperature and the rate of diffusion processes follows the similar relation. The acceleration by increased temperature is used in many common tests of the possible effect of packaged food on corrosion of metal packagings during storage. For example conclusions for one year stability of cans at 20 °C are often done using results of three month storage tests at 40 °C, i.e. the value Q_{10}= 2 for corrosion processes is supposed. But in fact there are numerous exceptions. The regular course of corrosion rate changes with increased temperature is typical for reactions providing soluble corrosion products considering only one control process within the whole range of temperature. In such complex systems like heated foods this assumption is not often valid with a consequent irregularity in corrosion rate changes.

Only little has been published on the effect of temperature on the course of cans corrosion. Maercks and Maercks (1971) measured the effect of temperature on changes in the corrosion current in some liquid foods and/or food simulants and found irregular behaviour for all of them. As mentioned

above the corrosion rate is often supposed to increase twice with temperature elevation of 10 °C. But the authors found this acceleration after temperature change of 15 °C for 1.5% water solution of NaCl + 1% acetic acid, 23 °C for tomato soup and 75 °C for tomato purée. The very low dependence of corrosion current on temperature changes in the range 20–80 °C was determined for 0.5% solutions of oxalic acid and 3% acetic acid showed even the negative temperature coefficient, i.e. corrosion was retarded by increased temperature.

The same authors (Maercks, Maercks, 1971) described complex conditions during thermal sterilisation of food. For example while at 20 °C canned carrot dissolved slightly iron, in the temperature range 40–60 °C the corrosion rate of iron was three times higher and between 70–80 °C it decreased rapidly and corrosion of tin started. The described changes could be caused by expelled tissue gas, especially oxygen, during heating.

McHardy (1966) tested corrosion of aluminium cans and he found 10–15 times higher corrosion current during sterilisation compared with conditions at 20 °C. Hottenroth (1968) described less corrosion of fish meat cans at 40 °C compared with that at 20 °C although generally lower temperature extends shelflife of canned food (Cecil, Woodroof, 1963). Seow and Shanmugam (1992) found difference in the activation energy of iron and tin dissolving during internal corrosion of cans with jackfruit juice during storage at 30–50 °C. On the other hand Passy and Manheim found regular changes of corrosion rate of cans for canned melon (Mannheim, Passy, 1982), lemon juice and tomato purée (Passy, Mannheim, 1984) at temperatures 15–45 °C. Kolomiec (1976) tried to formulate mathematic relations for changes of some quality characteristics of cans during different time-temperature conditions of storage and he demonstrated their use for some canned meat products.

The aim of the present work was to follow the effect of products formed during heat treatment of 14 foodstuffs and/or food simulants on the corrosion of lacquered tinned cans.

MATERIAL AND METHODS

In Table I the list of used 11 food simulants and 3 liquid foodstuffs is given. The samples of those foods were filled into cans (volume 190 ml)

made of electrolytically tinned steel (amount of tin 10 g/m^2), with inner surface covered by lacquer BASF 23960 containing aluminium pigment (5.2 ± ± 0.4 g/m^2), porosity of which was 1.04 ± 0.34 mg Sn per 180 ml 0.1M HCl [according to Czech standards (ČSN 16 0201) as amount of tin dissolved in 0.1M HCl under standard conditions of test].

I. List of used food and/or food simulants

Sample number	Food or food simulant (water solutions)	pH
1	1% acetic acid	2.85
2	1% acetic acid + 1.5% NaCl	2.87
3	1% acetic acid + 5% saccharose	2.85
4	1% acetic acid + 1.5% NaCl + 5% saccharose	2.90
5	20% saccharose	5.50
6	1% citric acid	2.50
7	1% citric acid + 20% saccharose	2.35
8	1% malic acid + 20% saccharose	2.40
9	1% gelatine + 1% saccharose	6.10
10	1% gelatine + 1% saccharose + 0.1% cystein HCl	3.70
11	1% gelatine + 1% NaCl + 0.1% cystein HCl	3.90
12	strawberry juice	3.50
13	apple juice	2.80
14	brine of sauerkraut (diluted by water at ratio 3 : 2)	3.70

Filled and closed cans were heated at 90 °C for 10 min, for low acid samples, i.e. number 5, 9, 10, 11 in Table I, the treatment at 120 °C for 60 min were used. The same solutions were refluxed for 16 hours to simulate six month storage at 20 °C considering Q_{10} coefficient of food constituent 2, then they were cooled and filled into cans and sterilised as mentioned above. After sterilisation all samples were storaged at 20 °C for ten months. Then the amount of tin and iron in samples was determined colorimetrically, the former after reaction with quercetine and the latter with 2,2′-dipyridyl (ČSN 16 0201). Seven parallel samples were always analysed. From the difference

in metal content the inhibition effect of constituents formed in preheated foods and/or food simulants (*I*) was expressed:

$$I = (C_m - C_{mh}) \cdot 100/C_m \qquad [\%]$$

where: C_m – the metal concentration in tested sample

C_{mh} – the metal content in preheated food and/or food simulant

RESULTS AND DISCUSSION

The results obtained for determination of iron and tin content in all tested samples after ten month storage at 20 °C are given in Tables II and III. On

II. Changes of iron content (mg/kg) in canned foods and/or food simulants during sterilisation and 10-month storage at 20 °C. The comparison of corrosion effect of samples without and with preheating treatment, i.e. 16 hours refluxing before filling and sterilisation

Sample number	Fe content in samples		Difference [mg.kg^{-1}]	Inhibition effect of heating products [%]
	without preheating	with preheating		
	[mg.kg^{-1}]			
1	84.0	76.0	8.0	9.5
2	130.0	98.0	32.0	24.5
3	31.0	15.0	16.0	51.5
4	66.0	26.0	40.0	60.5
5	16.0	12.0	4.0	25.0
6	152.0	104.0	48.0	31.5
7	18.5	19.0	–0.5	–2.7
8	24.5	24.0	0.5	2.0
9	14.5	14.5	0	0
10	30.0	25.5	4.5	15.0
11	84.0	64.0	20.0	24.0
12	82.5	62.5	20.0	24.0
13	23.5	14.0	9.5	40.5
14	24.0	25.0	–1.0	–4.1

their basis the influence of compounds arising in tested foods and their simulants during heating on can corrosion was possible to estimate. The given results are means of seven parallel determinations with standard deviations for all samples in the range 25–40%. It was a consequence of high variability of lacquer porosity determination (standard deviation 34% – see above).

III. Changes of tin content (mg/kg) in canned foods and/or food simulants during sterilisation and 10-month storage at 20 °C. The comparison of corrosion effect of samples without and with preheating treatment, i.e. 16 hours refluxing before filling and sterilisation

Sample number	Sn content in samples		Difference [mg.kg^{-1}]	Inhibition effect of heating products [%]
	without preheating	with preheating		
	[mg.kg^{-1}]			
1	10.5	4.0	6.5	62.0
2	13.0	6.0	7.0	54.0
3	3.5	3.5	0	0
4	4.0	4.0	0	0
5	1.5	1.5	0	0
6	107.0	105.5	1.5	1.4
7	37.5	33.5	4.0	10.5
8	34.5	32.0	2.5	7.0
9	1.5	1.5	0	0
10	2.5	2.5	0	0
11	5.5	5.5	0	0
12	69.5	56.0	13.5	19.5
13	22.5	11.5	11.0	49.0
14	4.0	4.0	0	0

The data indicate that no acceleration of can corrosion during processing and storage of samples preheated before filling into cans was found comparing with corrosion conditions for materials heated only during sterilisation in packing. There was either no significant difference in corrosion effect between both types of samples or the releasing of metals into tested sample was retarded in the case of preheated foods and/or food simulants. Iron corrosion

was slowed down in 10 cases and that of tin in 5 samples out of 14 tested food materials. The most important inhibition effect on iron corrosion was found for food simulant number 4 (i.e. 1% acetic acid + 1.5% NaCl + 5% saccharose) I = 60.5%, simulant 3 (1% acetic acid + 5% saccharose) I = = 51.5%, apple juice I = 40.5%, simulant 6 (1% citric acid) I = 31.5 %. The inhibition effect about I = 25% was found for simulants 2, 5, 11 and strawberry juice, I = 15% for simulant 10 and I = 9.5% for simulant 1.

Considering tin corrosion the most significant inhibition effect was found for simulant 1 (1% acetic acid) I = 62%, simulant 2 (1% acetic acid + 1.5% NaCl) I = 54% and apple juice I = 49%, while for strawberry juice and simulants 7 and 8 the I values ranged from 7% to 19.5%.

The given results confirm that the aggressivity of many foods against metal packaging materials changes during heat treatment. It is very probable that the inhibition factors retarding can corrosion in described experiments also participate in irregular changes of corrosion rate under elevated temperature. Unfortunately at present there is little data enabling more precise explanation of that problem.

References

CECIL, S. R. – WOODROOF, J. G.: The stability of canned foods in long-term storage. Food Technol., *17*, 1963: 639–646.

HOTTENROTH, B. – MOHR, W.: Vergleichende Langzeit – Lagerversuche mit Weissblech- und Aluminiumdosen. Verpackungs Rundschau, *19*(12), 1968: Tech.-wiss. Biel. 83–87.

KOLOMIEC, M.: K voprosam prognozirovanija srokov chranenija delikatesnych mjasnych konservov. Mjasnaja industrija SSSR, *12*, 1976: 33.

MAERCKS, O. – MAERCKS, I.: Weitere Untersuchungen über der Einfluss der Füllgut-Aggressivität auf die Korrosion lackierter Weissblechdosen. Verpackungs Rundschau, *22*(4), 1971: Tech.-wiss. Biel. 29–31.

MANNHEIM, C. H. – PASSY, N.: Internal corrosion and shelf-life of food cans and methods of evaluation. CRC Crit. Rev. Food Sci. Nutrit., *17*(4), 1982: 371–407.

McHARDY, J.: Corrosion of aluminium cans. Modern Packing, *39*, 1966: 161–163.

PASSY, N. – MANNHEIM, C. H.: Interaction of lacquer coated cans with various food products – evaluation by polarization studies. In: Proc. Euro Food Pack, Wien, 1984: 58–62.

SEOW, C. C. – SHANMUGAM, G.: Storage stability of canned jackfruit (*Artocarpus heterophyllus*) juice at tropical temperaure. J. Food Sci. Technol. – India, *29*(6): 1992: 371–374.
ČSN 16 0201. Zkoušení konzervových plechovek.

Received July 20, 1994

Vliv produktů záhřevu na korozi konzerv

Byl sledován vliv produktů záhřevu u 14 různých modelových i přírodních náplní na korozi lakovaných konzervových plechovek. Byly porovnány účinky náplní předběžně nezahřívaných (pouze sterilovaných) s účinky stejných náplní předem podrobených záhřevu při 100 °C po dobu 16 hodin ve skleněných obalech a potom uzavřených do plechovek a sterilovaných jako předchozí předem nezahřívané náplně. Po desetiměsíčním skladování při 20 °C nedošlo u předem zahřívaných vzorků ani v jediném případě k urychlení koroze, nýbž buď k jejímu zpomalení nebo mezi předem zahřívanými a nezahřívanými vzorky nebyl prokázán významný rozdíl. Pokud jde o korozi železa, deset ze čtrnácti zkoušených náplní vykazovalo inhibiční účinek po předběžném zahřívání. V případě cínu byl tento jev nalezen u pěti vzorků.

koroze; konzervové plechovky; konzervované potraviny; tepelná sterilace

---

Contact address:

Ing. Jaroslav Dobiáš, CSc., Vysoká škola chemicko-technologická, Ústav konzervace potravin a technologie masa, Technická 5, 166 28 Praha 6, Česká republika, tel.: 02/2435 3083, fax.: 02/311 99 90

INSTITUTE OF AGRICULTURAL AND FOOD INFORMATION
Slezská 7, 12056 Praha 2, Czech Republic
Fax: (0042 4) 257 090

In this institute scientific journals dealing with the problems of agriculture and related sciences are published on behalf of the Czech Academy of Agricultural Sciences and Slovak Academy of Agricultural Sciences. The periodicals are published in the Czech or Slovak languages with summaries in English or in English with summaries in Czech or Slovak.

Subscription to these journals be sent to the above-mentioned address

Journal	Number of issues per year	Yearly subscription in USD Europe	overseas
Rostlinná výroba (Plant Production)	12	118,-	123,-
Živočišná výroba (Animal Production)	12	118,-	123,-
Zemědělská ekonomika (Agricultural Economics)	12	118,-	123,-
Lesnictví – Forestry	12	118,-	123,-
Veterinární medicína (Veterinary Medicine - Czech)	12	92,-	96,-
Potravinářské vědy (Food Sciences)	6	48,-	56,-
Zemědělská technika (Agricultural Engineering)	4	35,-	37,-
Ochrana rostlin (Plant Protection)	4	35,-	37,-
Genetika a šlechtění (Genetics and Plant Breeding)	4	35,-	37,-
Zahradnictví (Horticultural Science)	4	35,-	37,-

Potrav. Vědy, *13*, 1995 (2) : 111–129

MICROWAVE HEATING OF HETEROGENEOUS FOOD PRODUCTS – HEATING RATE AND TEMPERATURE UNIFORMITY

Jiřina HOUŠOVÁ, Karel HOKE

Food Research Institute Prague, Czech Republic

Abstract: Heating kinetics and heating uniformity were followed in an experimental study of microwave heating of multicomponent ready meals. More than 100 samples of 16 kinds of sterilized and frozen meals from actual Czech production were heated in domestic microwave oven MOULINEX FM 2915 (850 W). Three types of one-portion trays were used for tested meals packing and a fibre-optic system LUXTRON for monitoring of local temperatures in heated meal samples. Heating was provided from frozen or chilled temperature of meals to reaching the temperature of 80 °C in the slowest heated place of sample. Uneven heating of the most of tested meals was observed particularly by the heating of complete meals from frozen state. Overheating of outer parts of meals, particularly near the corner of trays, fast heating of a liquid component of meal (gravy, sauce), fast heating of cereal garnish (dumplings, pasta, rice), slower heating of meat pieces, intensive boiling of liquid parts of meals from the first minute of heating, followed by a worsening of their consistency, drying, local browning and crisping of parts of meat over the sauce layer or dumplings in a separate compartment of tray were observed in most experiments, particularly with complete meals samples. Big shortcomings in the design of tested meals and reheating instruction for microwave heating were found out.

microwave heating; ready meals; temperature distribution; heating rate; heating uniformity

The most frequent use of microwave heating in the food sector is still the reheating of ready meals stored for a certain period in chilled or frozen state, or sterilized food in an adequate package. This reheating carried out before eating of such food should ensure both restoring of all original properties of a fresh made meal and recovering its hygienic safety.

A number of recent foreign studies point out certain hygienic risks of this application – in particular those of reheating chilled food (Insulli, Denton, 1992; Dealler, Rotowa, 1992). Observed and confirmed was also a possibility of surviving of pathogenous microorganisms (*Salmonella*, *Lys-*

teria) during thermal processing of minced meat products in microwave devices (Hollywood et al., 1991; Steinhauser et al., 1993).

Non-uniformity of heating which consequently causes an insufficient heating effect in some parts of the food has been considered one of the reasons why eventually pathogenous organisms survive during the thermal processing of food by microwave (Ohlsson, 1990; Steihauser et al., 1993; Hollywood et al., 1991).

The non-uniformity of heating is related to the principle of microwave heating together with its technical realization – with the design and parameters of microwave oven as well as to the composition, dielectrical and physical properties, shape and volume of reheated food.

Certain non-uniformity of heating takes place even in microwave heating of homogeneous materials, which is shown in the first part of our study (Houšová et al., 1994) as well as in publications of other authors (Burfoot, Foster, 1991; Datta et al., 1992; Jakobsen, Mikkelsen, 1993 and others).

The reason in this case is the combination of dielectrical, thermal and physical properties, shape and dimensions of heated material as well as distribution of energy in the cavity of the microwave oven and other process parameters (Chen et al., 1993).

Let us assume that the heterogeneity of the heated material only worsens expressively the unevenness of distribution of temperatures. According to Simovjan et al. (1985) by the microwave heating of ready meals, which are an example of expressive heterogeneous material, problems with heating uniformity can be expected in all cases when dielectric properties of the individual components differ more than twice.

Results of the second part of our experimental study, focused on development and distribution of local temperatures during the microwave heating of two- or multicomponent type of food products and presented in this article, prove this fact.

MATERIAL AND METHODS

Experimental equipment

Domestic microwave oven MOULINEX FM 2915 Q, declared output 850 W, frequency 2450 MHz, cavity's volume 24 liters, without turntable

(removable glass shelf on the bottom of the oven), five basic output degrees, four intersteps.

Material

The experimental study was carried out with samples of common types of ready meals from actual Czech production. Microwave heating can be used for tested meals as one of the methods of their reheating before eating. Different kinds of common Czech two- or multicomponent meals were selected differing in chemical composition, physical properties, quantity and shapes of individual components. In all cases the meal of one portion packaging was used with a prolonged shelflife by sterilization or by freezing. Tested meals, supplied directly by manufacturers, were packaged in three different one portion trays (Fig. 1):

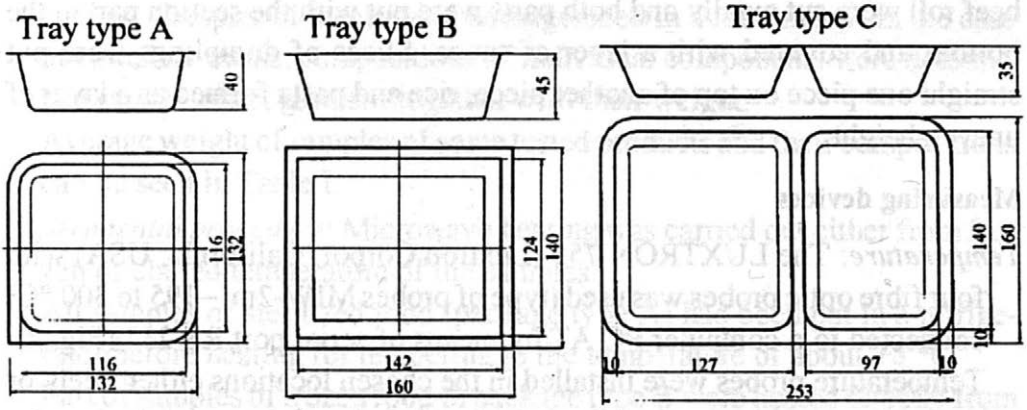
A – one compartment tray from polypropylene,

B – one compartment tray from carton, laminated by polypropylene,

C – two compartment tray from polypropylene.

More than 100 samples of 16 kinds of meals, packaged in trays of A, B or C type was used in this study.

From the actual production of sterilized meals in plastic trays (A) six types of meals were tested (lentils and smoked pork, smoked side of pork, white beans and tomato sauce, sausage, beans and tomato sauce, minced meat and cream sauce, minced meat and tomato sauce) and out of the other sterilized products green peas in salty water were also tested. Although the



1. Trays used during microwave heating experiments

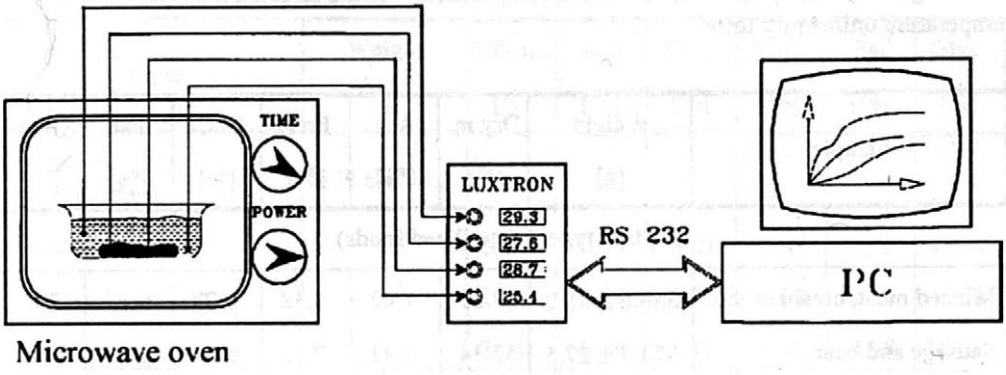
declared weight for all products was 380 g, the tested samples differed a lot: from 330 g (average value for minced meat in tomato sauce samples) to 407 g (average value for smoked side of pork and beans samples). The weight of individual meal samples also differed a lot – the deviation oscillated between 30–50 g according to the sort of meal.

From the production of frozen meals packaged in carton trays (B type), three meals containing meat with or without sauce were chosen for the test; slice of beef with sour cream sauce, fried minced meat patty (without any gravy) and pork goulash (small pieces of meat in sauce). The same type of package was used for heating tests of two cereal meals, packaged by the manufacturer in polyethylene bags – potato dumplings filled with chopped smoked meat (4 pieces, cylindrical form) and dumplings filled with plum jam (4 pieces, spheric form). Average weight of these products was from 197 g (average value for minced patty) to 346 g (potato dumplings with filling) with the deviation of 6–18 g.

From complete frozen meals packaged in two compartment plastic trays of C type six meals were chosen for the microwave heating tests: stuffed green paprika, tomato sauce and rice, roast pork (sliced) with sauerkraut and dumplings (4 slices), lentils and scrambled egg, dill cream sauce, boiled egg and dumplings (4 slices), pork stew (small pieces in sauce) with pasta, stuffed beef roll with rice. Average weight of this kind of samples was 337 g (lentils and scrambled egg) till 533 g (pork stew and pasta), the deviation being 30–40 g. In this kind of meal the garnish (rice, pasta, dumplings) and also scrambled eggs were put in the smaller part of trays and meat, sauce, sauerkraut or lentils were put in the larger one. Stuffed paprika, boiled egg, beef roll were cut axially and both parts were put with the section part to the bottom and covered with a layer of sauce. Slices of dumplings were put straight one piece on top of another piece, rice and pasta formed as a layer of uneven height.

Measuring devices

Temperature: The LUXTRON 755 (Luxtron Corpor. California, USA) with four fibre optic probes was used (type of probes MIW-2m, –195 to 300 °C) connected to a computer PC AT by means of serial port RS 232 (Fig. 2). Temperature probes were installed in the chosen locations either freely or to fix their position a plexiglass plate with holes and special devices for fixation of probes were used. In this case a plexiglass plate replaced the



2. Temperature measurement set-up with fibre optic system LUXTRON 755

cover of the tray. To install measure probes in the frozen meal, small holes were drilled in required locations.

Weight: OWA balance with upper scale with capacity upto 5 kg (OWA Labor, Germany).

Time: Digital stop-watch DS30 (Pragotron, Czechoslovakia).

Energy: Special modified watt-meter (Křižík, Dukla Prešov, Czechoslovakia).

Chemical analysis: Dry matter (drying of each sample by sea sand at the temperature of 103 °C to reach constant weight), fat content (extraction according to Soxhlet), proteins (Kjeldahl's method), content of chlorides (reacting with $AgNO_3$ indicator K_2CrO_4), content of ash (burning in electric muffle furnace at the temperature of 600 °C). Content of glycides calculated. Samples of meals were homogenized in a food mixer. In the case of complete meals, compositions of individual components were determined (meat, sauce, garnish) together with their weight.

Average weight of samples of some tested products and their compositions can be seen in Table I.

Experimental procedure: Microwave heating was carried out either from frozen or chilled temperature of the samples.

All samples of sterilized food (package type A) had been put in a refrigerator before heating for tempering to the temperature of about +5 °C.

Part of samples of frozen food in package type B were heated directly from the frozen state (temperature of samples before heating about –15 °C), part of samples had been tempered before heating for one hour at the room

I. Average values of weight[+] and chemical composition[++] of the selected meal samples used for temperature uniformity tests

Sample	Weight [g]	Dry m. [%]	Ash [%]	Prot. [%]	NaCl [%]	Fat [%]	Glyc. [%]
a) tray type A (sterilized foods)							
Minced meat, cream sauce	380.0 ± 35.0	25.29	1.42	6.38	1.77	9.85	7.67
Sausage and bean	373.7 ± 27.5	57.34	1.43	7.29	0.54	2.53	46.09
Smoked pork and bean	406.7 ± 49.4	47.00	1.28	7.36	0.71	6.64	31.72
Lentils and smoked pork	401.3 ± 28.6	45.45	1.17	7.63	0.68	7.08	29.57
b) tray type B (frozen meals)							
Minced meat patty fried	197.3 ± 14.3	21.69	1.27	4.89	1.37	7.73	6.43
Beef in cream sauce	238.5 ± 9.4						
meat		31.95	1.25	26.96	0.96	3.05	0.67
sauce		15.40	0.99	2.41	0.80	3.60	8.40
c) tray type C (frozen meals)							
Pork stew, pasta	533.4 ± 32.4						
meat		36.20	1.25	14.69	1.08	19.35	0.90
gravy		13.85	1.32	1.79	1.14	4.18	6.57
pasta		23.55	0.61	2.77	0.51	2.52	17.65
Roast pork, cabbage, dumpllings	399.3 ± 38.0						
meat		38.35	0.92	16.55	0.45	19.37	1.52
dumpling		55.40	1.45	6.64	1.03	0.70	46.62
cabbage		13.30	1.10	1.17	0.91	1.15	9.89
Stuffed paprika, tomato sauce and rice	459.2 ± 38.0						
paprika		24.60	1.19	8.85	0.77	6.53	8.04
sauce		22.75	0.85	1.33	0.68	11.41	9.12
rice		48.40	1.06	2.58	0.76	4.97	39.80

Table I continue

Sample	Weight [g]	Dry m. [%]	Ash [%]	Prot. [%]	NaCl [%]	Fat [%]	Glyc. [%]
Dill gravy egg, dumplings	474.6 ± 34.2						
dumplings		50.30	0.99	5.41	0.88	0.52	43.36
egg		29.10	1.08	11.36	0.07	10.10	6.58
gravy		22.85	0.49	1.10	0.41	4.98	16.29
Filled beef roll dumplings	463.2 ± 42.1						
meat		31.45	1.46	15.39	0.93	11.67	3.46
dumplings		49.50	1.22	6.00	0.90	0.49	41.79

[+] average values from all tested samples
[++] average values from two samples

temperature (temperature of samples before heating being approx. –3 °C), other samples had been tempered in refrigerator to the temperature of about +5 °C.

Before heating the weight of samples was established, samples were situated in the middle of a glass shelf at the bottom of the microwave oven, probes of Luxtron were inserted into the specific locations of the samples and parameters of the microwave heating and interval of temperature collection were fixed.

Locations of Luxtron probes were selected by preliminary tests in which the thermocouple probe was used. Probes of Luxtron were afterwards installed in such locations of the samples where different rate of heating was expected (edge and central location, individual components, large and small pieces, etc.) One of the probes was always installed at a place with expected slowest heating to control the limit values of temperature and heating time. Actual probe locations were marked on each record from temperature measurement.

Regime of microwave heating: Full power (level III - majority of tests), lower levels of heating (II, I – part of tests), combination of lower and full power (some tests when heating began from freezing temperatures).

Time of microwave heating: Till reaching 80 °C temperature at the place of slowest heating (and/or in some tests alternatively till 70 °C and 60 °C). The 80 °C temperature was derived from the Hygienic Standard of the Czech Ministry of Health No. 54/1980 (ČSR) referring to production, distribution and re-heating of frozen and chilled meals.

In most tests local temperatures of samples were monitored during 10 minutes after the end of microwave heating (post-process delay) without taking out the samples from the oven.

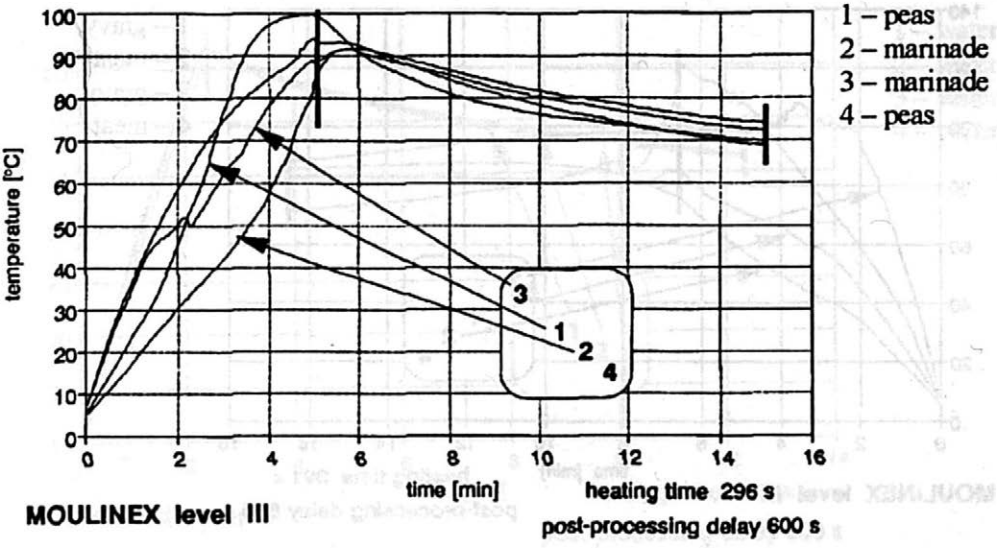
After microwave heating (or post-process delay), final weight of the samples was found out, and its sensoric values were judged.

Each microwave heating regime was repeated three times at least, in the case of significant differences between the samples of certain meals (in total weight, in the weight of components, etc.) the number of repetitions was higher.

RESULTS AND DISCUSSION

Distribution and time development of local temperatures during microwave heating of different kinds of multi-component meals, packaged in one portion trays with one or two compartments and heated up either from chilled or frozen state are shown in the following six figures. Time-temperature history is shown both for the phase of microwave heating and for post--processing phase. Some time delay after heating is recommended to balance local temperatures of food after heating, eventually to warm up the part of product insufficiently heated.

Fig. 3 demonstrates the course of four local temperatures during microwave heating of two-component product with solid (green peas) and liquid part (salty marinade). In this case (sample 380 g) weight of peas was 250 g and marinade 130 g. The graph shows the high rate of heating of liquid in the corners of the tray and evidently a slow rate of heating in the centre of the package. This phenomenon was observed in all other experiments, independently of the kind of food and kind of package and was also observed during our former microwave heating tests of similarly packed wholly homogeneous materials (Houšová et al., 1994). Overheating of material in the corners of trays can be correlated with geometrical form and dimensions of

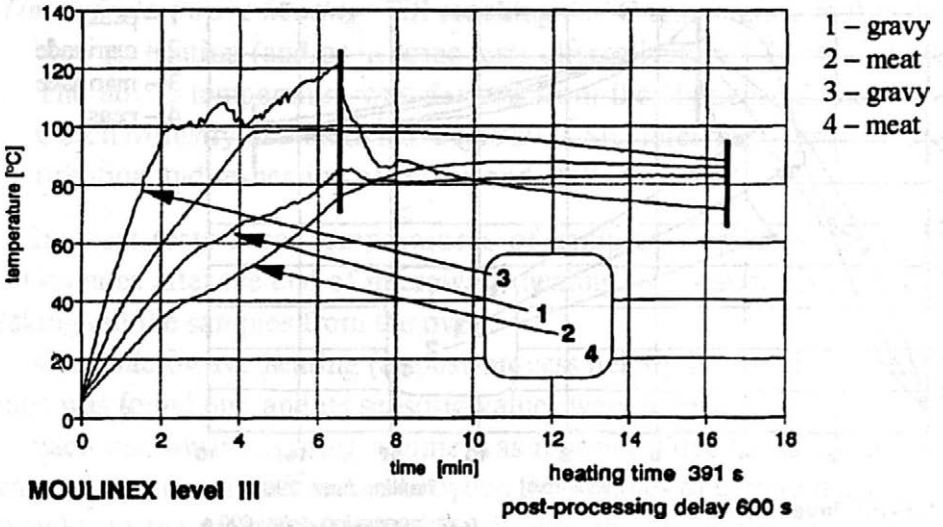


3. Development of local temperatures of heterogeneous material during microwave heating and post-processing delay — green peas in salty marinade, 380 g, package A

packages and microwave power absorption and other physical properties of heated material.

During the microwave heating of this product the difference in the temperature in the middle of the tray and temperature near the corners was from 15 to 50 °C (depending upon exact location of the probe installed, weight and composition of the sample and time of heating). After post-process delay the difference between maximal and minimal temperatures was lowered to 5–10 °C. In this product during post-process delay the central parts of samples were further heated by additional 10 °C.

Fig. 4 demonstrates time development of four local temperatures in the sample of meal with lentils and meat equally packed and heated. This meal consists of lentils, sauce of high viscosity and small pieces of meat. The graph shows again slow heating of the central part of the food and the faster heating of food near the corners of the tray. The temperature of meal near the corner quickly reached the boiling-point and regarding its composition (high content of fat and salt) and its high viscosity increased about 100–120 °C. In the graph maximum temperature oscillation after reaching the boiling-point can be seen related with the observed explosive releasing of bubbles of steam ("vulcano effect" – Ohlsson, 1983; Cable, Saaski, 1990 –

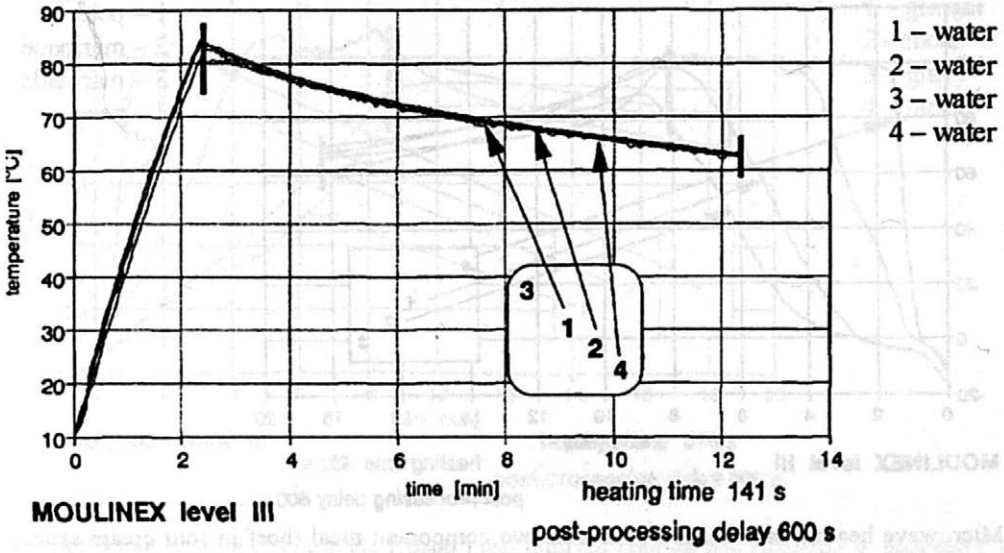


4. Development of local temperatures of heterogeneous material during microwave heating and subsequent post-processing delay — lentils and smoked meat, 407 g, package A, heating begins from a chilled state

overheating of steam and after the explosion of bubbles a decline of pressure and with it also reduction in temperature).

Fig. 5 is included for comparison and represents development of local temperatures during microwave heating of an equally packed sample of water. Very good temperature uniformity in this case (range of temperatures during this process 3 °C) is related to the values of penetration depth for water and the dimensions of package and low viscosity value, which makes possible natural convection of water in package. All these factors act together to equal the local temperatures.

Problems connected with microwave heating of frozen material and frozen multi-component food especially are documented in Fig. 6. This figure represents the time-local temperatures history of microwave heating of two-component food, consisting of meat slices (weight 35 g) covered with a layer of thick sauce (196 g) warmed up in a package of B type tray directly from frozen state. Although the weight of the sample was low (231 g), the heating process till reaching the final minimum temperature of 80 °C lasted more than 8 minutes, from which more than 3 minutes fell to the defrosting of meat in the middle of the tray. Fast defrosting and subsequent fast increase in sauce temperature in the corners of the tray and in the marginal parts of the sample and very slow defrosting and warming up of the middle

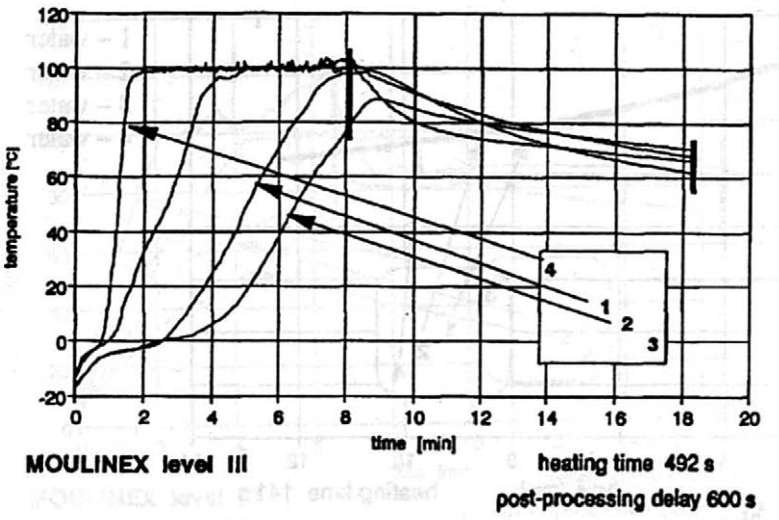


5. Microwave heating of potable water sample (318 g) in a tray of A type – development of local temperatures

part of the food was observed. The range of temperatures during considerable part of heating was 100 °C. At the moment of visible boiling of sauce near the wall of the tray the central part of meal was still frozen. The boiling of the sauce for a few minutes caused significant evaporation losses (total weight loss up to 30%) and consequently a negative consistency change and deterioration of sensoric properties of the meal.

The course of microwave heating of complete multi-component meal in two-compartment package of the C type is shown in Figs. 7 and 8.

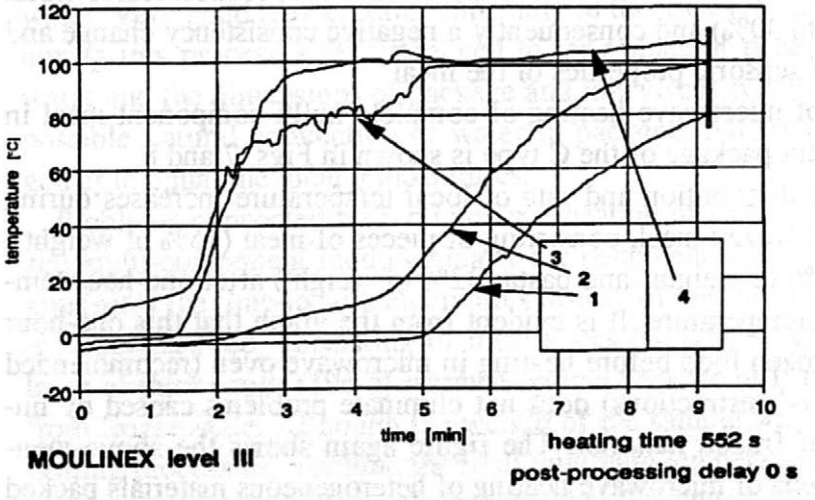
Fig. 7 shows distribution and rate of local temperature increases during the heating of a frozen meal, consisting of pieces of meat (15% of weight), meat sauce (53% of weight) and pasta (32% of weight) after one-hour tempering at room temperature. It is evident from the graph that this one-hour tempering of frozen food before heating in microwave oven (recommended in manufacturers' instructions) does not eliminate problems caused by uneven heating of frozen material. The figure again shows the above-mentioned phenomena of microwave heating of heterogeneous materials packed and heated in flat rectangular trays – a slow heating of middle parts of the food in comparison with the marginal parts, fast increase in garnish temperature (due to its porosity, small density, specific heat and penetration depth),



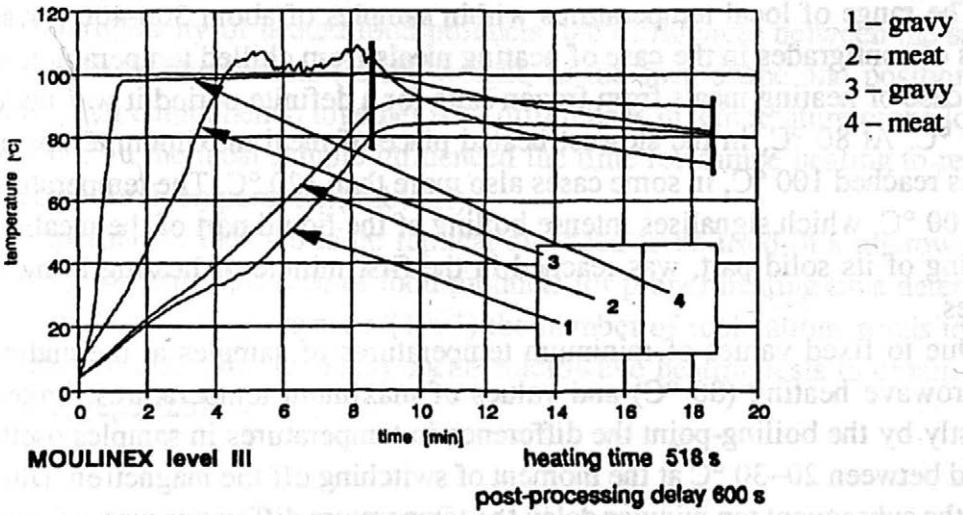
6. Microwave heating of a portion of frozen two component meal (beef in sour cream sauce, 231 g, package B) – development of local temperatures

a slower heating up of meat pieces in comparison with the thin layers of liquid part with higher content of salt and fat.

Fig. 8 shows the course of microwave heating of a complete meal after its preliminary defrosting and tempering in refrigerator. This meal (average weight of sample 477 g) consisted of 23% rice (in a small compartment of



7. Microwave heating of a portion of complete frozen meal (pork stew, pasta, 484 g) after one hour tempering at the room temperature – development of local temperatures during heating and post-processing delay



8. Microwave heating of complete frozen meal (stuffed paprika and rice, 463 g, package C) – after tempering in refrigerator

tray), stuffed green paprika filled with minced meat (30% of weight) and tomato sauce (40% of weight). Preliminary tempering of the frozen food at chilling temperature shortened the microwave heating process in comparison with the heating of the same food after one-hour tempering at room temperature in average by 30%. The period with high temperature differences and extreme local temperatures within the meal influencing negatively its quality after heating was also shortened. Negative influence of the heterogeneity of heated material with expressively different composition, dielectric and other physical properties, volume and shape of individual parts on the evenness of heating has persisted. The difference in temperatures in various parts of meal reached tens of centigrades during heating, in post-process delay it was reduced to 10–20 °C.

CONCLUSION

The exact information on heating kinetics and heating uniformity of multi--component food products with components of different composition, physical properties, weight, geometric form and dimensions in packages of definite geometry was obtained from experimental study of microwave heating of ready meals.

The range of local temperatures within samples of about 300-400 g was tens of centigrades in the case of heating meals from chilled temperature, in the case of heating meals from frozen state for a definite period it was up to 100 °C. At 80 °C, in the slowest heated place of meal maximum temperatures reached 100 °C, in some cases also more than 120 °C. The temperature of 100 °C, which signalises intense boiling of the liquid part of the meal, or drying of its solid part, was reached in the first minute of heating in most cases.

Due to fixed values of minimum temperatures of samples at the end of microwave heating (80 °C) and values of maximum temperatures limited mostly by the boiling-point the difference in temperatures in samples oscillated between 20–30 °C at the moment of switching off the magnetron. During the subsequent ten minutes delay the temperature difference was reduced to 5–20 °C according to the kind of meal and further heating in the coolest part of the meal was observed in many experiments.

Uneven distribution of local temperatures in samples of multi-component meals during microwave heating, as a result of different rates of temperature increase in their different parts, is due to a complex of influences: geometrical form of package (overheating of material in the corners of rectangular package), the mechanism of microwave absorption in the material (the quantity of absorbed energy decreases from the surface inside by exponential progression), different depth of penetration of individual components, different thermal and other physical properties and quantity, and volume of components. Distribution of microwave energy inside the heating cavity has also some influence. In the case of the microwave oven used for experiments certain unevenness of the microwave field was confirmed, but the influence of heated meals seems to be more important.

Uneven heating was expressive in particular during microwave heating of frozen complete meals with extremely different dielectric and other physical properties of garnish (dumplings, rice, pasta), gravy or sauce and meat part of the meal, which mostly have also different weight, shape and volume and by heating of frozen meals (so called "run away heating" was observed – Ohlsson, 1983). In these cases the high temperature differences and locally high temperatures during heating cause a significant decrease in sensoric quality of food after heating, eventually full destruction of some of its parts.

Heterogeneity of heated food products, the differences between the samples of individual meals (in the weight, in the size, shape and position of individual components) together with differences in temperature probe location within the meal sample influenced the time for sampe heating to reach the safe final temperature (Table II).

Experiments indicate more replications need to be used in a microwawe heating test with this type of food products for proper heating time determination. According to James (1993) the number of replications needs to be at least 10 and more for ready meals microwave heating tests to obtain the idea of repeatability.

II. Heating test parameters

Sample	Weight [g]	Initial temperature [°C]	MV power [W]	MW heating time [s]	Energy used [kJ]	Note
a) tray type A						
Minced meat in cream sauce	380.0 ± 35.0	4.7	850	479 ± 67	685.4	-
Sausage and bean	373.7 ± 27.5	3.0	850	393 ± 41	562.4	-
Smoked pork and bean	462.0	5.2	850	530	758.4	1
	391.0	6.6	850	294	420.7	1
	367.0	4.0	850	279	399.2	1
Lentils and smoked pork	385.5 22.7	4.9	850	333 ± 45	476.5	-
	404.7 ± 28.6	5.8	850	372 ± 35	532.3	-
	454.0	6.6	567	750	715.5	1
b) tray type B						
Minced meat patty	197.3 ± 14.3	–11.6	212 + 850	741 ± 251	603.6	2
Filled potato dumplings	346.2 ± 18.1	–13.9	212+ 850	636	362.9	3
Beef, cream sauce	238.3 ± 9.9	–12.1	212 + 850	1101 ± 157	727.4	4
	242.0 ± 15.6	–12.2	850	481 ± 15	667.1	-
	237.2 ± 9.0	4.3	850	298 ± 23	425.2	-

Table II continue

Sample	Weight [g]	Initial temperature [°C]	MV power [W]	MW heating time [s]	Energy used [kJ]	Note
c) tray type C						
Pork stew	527.0 ± 61.5	–2.6	850	532 ± 28	726.5	5
pasta	547.0 ± 17.5	–3.9	850	711 ± 152	967.9	5
Roasted pork	431.0 ± 26.9	–3.2	850	572 ± 16	784.8	5
cabbage, dumplings	380.5 ± 40.8	4.2	850	372 ± 61	526.7	7
Lentils	354.7 ± 31.3	–3.9	850	667133	894.2	5
scrambled eggs	364.3 ± 11.5	4.1	850	425 73	594.5	7
Stuffed paprika and rice	476.3 ± 55.4	–5.5	850	733 ± 161	1002.2	5
	477.7 ± 8.5	–1.2	850	673 ± 69	923.5	6
Dill gravy	472.8 ± 32.3	–4.2	850	715 ± 188	963.9	5
egg, dumplings	496.0 ± 25.2	5.5	850	467 ± 179	663.7	6
Filled beef roll	467.7 ± 57.0	–4.3	850	791 ± 164	1058.6	5
dumplings	446.7 ± 28.0	2.1	850	423 ± 48	587.2	6

1 - orientation test only
2 - two power levels were used - 212 W, 435 s (level *) and 850 W (level III)
3 - two power levels were used - 212 W, 540 s (level *) and 850 W (level III)
4 - two power levels were used - 212 W, 831 s (level *) and 850 W (level III)
5 - tempering of frozen sample 1 hour at room temperature
6 - tempering of frozen sample 1 day in refrigerator
7 - tempering of frozen sample 2 days in refrigerator
Declared values of power are used in all cases

Results of this study confirm difficulties by design of multi-component food products for microwave heating. The optimal design requires careful balancing of sort, quantity and form as well as location of different components of the product in a package and careful choice of optimal package. Formulation of optimal reheating instructions for microwave heating, taking into consideration kinetics of heating of each individual food product, is necessary. Many shortcomings in the actual Czech microwaveable food pro-

ducts following from ignorance of microwave heating characteristics were found out by this study.

Acknowledgement

The authors gratefully acknowledge the funding of this work by the Czech Ministry of Agriculture. Appreciation is also extended to Mr. Petr Topinka for useful technical assistence with this work and to Mrs. Jana Mňuková for help with chemical analyses.

References

BURFOOT, D. – FOSTER, A. M.: Microwave reheating of ready meals. MAFF, Food Safety Directorate, 1992, London, UK.

CABLE, D. W. – SAASKI, E.: Fibreoptic pressure measurement of spontaneous bumping/splattering of foods during microwaving. Food Techn., *44*, 1990: 120.

CHEN, D. – SINGH, R. K. – HAGHIGHI, K. – NELSON, P. E.: Finite element analysis of temperature distribution in microwaved cylindrical potatoe tissue. J. Food Engn, *18*, 1993: 351–368.

DATTA, A. – PROSETYA, H. – HU, V.: Mathematical modelling of batch heating of liquids in microwave cavity. J. Microwave Power and Electromagnetic Energy, *27*, 1992: 38–48.

DEALLER. S. F. – ROTOWA, N. A. – LACEY, R. W.: Ionixed molecules reduce penetration of microwaves into food. Int. J. Food Sci. Technol., *27*, 1992: 153–157.

HOLLYWOOD, N. W. – VARABIOFF, Y. – MITCHELL, G. E.: The effect of microwave and conventional cooking on the temperature profiles and microbial flora of minced beef. Int. J. Food Microbiol., *14*, 1991: 67–76.

HOUŠOVÁ, J. – HOKE, K. – TOPINKA, P.: Distribution and profiles of local temperatures in homogeneous materials during microwave heating. Potrav. Vědy, *12*, 1994: 393–406.

INSULLI, P. – DENTON, D.: Soutwork microwave temperature surwey. Brit. Food J., 1992(6): 18–21.

JAKOBSEN, I. – MIKKELSEN, B. E.: Temperature profiles of instant formula heated in microwave oven. Proc. Int. Conf. Microwaves and High Frequencies. Göteborg, 1993.

JAMES, S. J.: Factors affecting the microwave heating of chilled foods. Food Science and Techn. Today, *7*, 1993: 28–36.

OHLSSON, T.: Fundamentals of microwave cooking. Microwave World, 1983(March-April): 4–9.

OHLSSON, T.: Controlling heating uniformity – the key to successful microwave products. SIK-Publ. 520, 1990, Sweden.

Potrav. Vědy, *13*, 1995 (2): 111–129

SIMOVJAN, S. V. – BLAGORAZUMOVA, D. V. – SUMAROKOV, N. V.: Stepeň rovnoměrnosti nagreva produktov v SVČ – pečach s pověrchnostnoj volnoj. Izvestija Vuzov., Pišč. Technol., 1983(6): 86–88.
STEINHAUSER, L. – STEINHAUSEROVÁ, I. – LUKÁŠOVÁ, J. – BUDIG, J.: Effect of microwave heating on survival of microorganisms in hamburgers. In: Review papers and abstracts of the 39th Int. Congr. Meat Sci. Technol., Calgary, Canada, 1993: 289.

Received December 14, 1994

Mikrovlnný ohřev heterogenních potravin – rychlost a rovnoměrnost ohřevu

Kinetika ohřevu a rozložení teplot v ohřívaném materiálu byly předmětem experimentální studie mikrovlnného ohřevu hotových jednoporcově balených pokrmů. Více než 100 vzorků 16 druhů běžných typů pokrmů balených do tří druhů plochých jedno- či dvoudílných misek ze současné tuzemské nabídky bylo ohříváno v mikrovlnné troubě pro domácnost MOULINEX FM 2915 (850 W štítkový výkon, bez otočného talíře) při monitorování průběhu teplot v několika místech pokrmu a při hodnocení kvality pokrmů po ohřevu. Fluoroptický měřicí systém LUXTRON 755 se čtyřmi sondami z optických vláken typu MIW byl použit pro měření teplot pokrmů během ohřevu i během následující desetiminutové vyrovnávací prodlevy. Pokrmy byly před ohřevem temperovány na chladírenskou teplotu, případně alternativně ohřívány přímo ze skladovací mrazírenské teploty, resp. po jednohodinové temperaci při teplotě místnosti (instrukce jednoho z výrobců). Průběh ohřevu byl sledován do dosažení teploty 80 °C v nejpomaleji ohřívaném místě pokrmu podle stávající Hygienické směrnice MZd ČSR č. 54/1980. Alternativně byly ověřovány i případné instrukce výrobců pokrmů. Nerovnoměrný ohřev s rozdíly teplot v desítkách stupňů během ohřevu a s rozpětím teplot 20 až 30 °C v okamžiku vypnutí magnetronu byl pozorován při ohřevu všech typů pokrmů, v řadě případů s negativním dopadem na jejich finální kvalitu. Společným rysem průběhu MV ohřevu testovaných pokrmů byl rychlý vzestup teploty pokrmu v blízkosti rohů obalu a u jeho stěn při výrazně pomalejším prohřívání středové části, rozdílná rychlost vzestupu teploty jednotlivých složek pokrmu (omáčky či šťávy, kousků masa, cereální přílohy), dramaticky rozdílná zejména při ohřevu kompletních pokrmů s knedlíky jako přílohou, var tekuté části pokrmu již během prvé minuty ohřevu, její postupné zahušťování a tvorba povrchového škraloupu, pomalý ohřev kousků masa, vysoušení, hnědnutí a ztvrdnutí částí masa vyčnívajících nad vrstvu tekutiny, rychlý ohřev, vysoušení až příp. spálení přílohových knedlíků, velmi porézních a s nízkou vlhkostí. Nerovnoměrnost ohřevu

související s geometrickým tvarem a rozměry obalů i s odlišným složením, dielekrickými, tepelnými a dalšími fyzikálními vlastnostmi jednotlivých složek pokrmů i s jejich objemem, tvarem a umístěním v obalu výrazně zesílila při ohřevu zmrazených pokrmů přímo ze zmrazeného stavu (výrazné rozdíly dielekrických vlastností rozmrazené a nerozmrazené časti pokrmu, vedoucí k prioritnímu ohřevu již rozmrazené části). Výsledky studie potvrzují obtížnost vývoje potravinářských výrobků pro mikrovlnný ohřev. Ten vyžaduje pečlivé vyvážení druhu, množství, tvaru a umístění jednotlivých složek výrobku v obalu s ohledem na jejich dielektrické, tepelné a další fyzikální vlastnosti, volbu optimálního tvaru a rozměru obalu i pečlivou tvorbu instrukcí pro finální ohřev, vycházejících z kinetiky ohřevu každého druhu výrobku a jeho složek. Výsledky studie prokazují, že v případě testovaných pokrmů nebyl tento přístup respektován.

mikrovlnný ohřev; hotové pokrmy; rozložení teploty; teplotní stupnice

---

Contact address:

Ing. Jiřina Houšová, CSc., Výzkumný ústav potravinářský Praha,
Radiová 7. 102 31 Praha 10-Hostivař, Česká republika,
tel.: 02/705 907, fax:02/701 983

Ústav zemědělských a potravinářských informací

vydává

POTRAVINÁŘSKÉ AKTUALITY (PA)

Časopis s dlouholetou tradicí se zabývá nejnovějšími poznatky ve světové potravinářské vědě, technologii, technice i ekonomice. Vychází v 8 samostatných řadách – jako 8 časopisů:

EKONOMIKA, TECHNOLOGIE A TECHNIKA
Vychází 10krát ročně, 65 stran, roční předplatné 610 Kč

VÝŽIVA, LEGISLATIVA
Vychází 5krát ročně, 36 stran, roční předplatné 360 Kč

NÁPOJOVÝ PRŮMYSL
Vychází 10krát ročně, 36 stran, roční předplatné 560 Kč

MLÉKÁRENSKÝ PRŮMYSL
Vychází 5krát ročně, 36 stran, roční předplatné 360 Kč

MLÝNSKÝ, PEKÁRENSKÝ A CUKRÁRENSKÝ PRŮMYSL
(včetně škrobárenství)
Vychází 5krát ročně, 40 stran, roční předplatné 360 Kč

MASNÝ PRŮMYSL
Vychází 5krát ročně, 36 stran, roční předplatné 360 Kč

LIHOVARSKO-KONZERVÁRENSKÝ PRŮMYSL
Vychází 5krát ročně, 36 stran, roční předplatné 360 Kč

DRŮBEŽÁŘSKÝ PRŮMYSL
Vychází 2krát ročně, 50 stran, roční předplatné 240 Kč

Uvedené publikace můžete objednat na adrese:

Ústav zemědělských a potravinářských informací
Londýnská 55, 120 21 Praha 2,
tel.: 02/250 051-4, fax: 02/207 411

Potrav. Vědy, *13*, 1995 (2): 131–137

POROVNANIE CITLIVOSTI DISKOVEJ DIFÚZNEJ METÓDY, INTESTU A DELVOTESTU P PRI STANOVENÍ REZÍDUÍ ANTIBIOTÍK V MLIEKU

Comparison of Sensitivity of Disk Diffusion Method, INTEST and Delvotest P at Determination of Antibiotic Residues in Milk

Bernadetta HOZOVÁ, Mária GREIFOVÁ, Fridrich GÖRNER, Jaroslav ZEMANOVIČ

Faculty of Chemical Technology of the Slovak Technical University, Bratislava, Slovak Republic

Abstract: The objective of the paper was to investigate and compare sensitivity of disk diffusion method, INTEST and Delvotest P at determination of residues of antibiotics the most frequently used in clinical practice (penicillin, ampicillin, chloramphenicol, tetracycline, streptomycin) and to check detection limits declared in literature. Disk diffusion method was found to be most sensitive for penicillin and ampicillin, while for chloramphenicol detection limits of all tests were almost identical, INTEST was the most suitable method for tetracycline and there were differences in detection limits for streptomycin determined by the particular methods: Delvotest P (5–10 times) showed the highest sensitivity. The determined detection limits were within the interval of values declared in firm literature, hence they can be recommended for routine assays in dairy factories.

antibiotic residues; detection limits; disk diffusion method; INTEST; Delvotest P; milk

Abstrakt: Cieľom práce bolo skúmanie a porovnanie citlivosti diskovej difúznej metódy, INTESTU a Delvotestu P pri stanovení rezíduí antibiotík najčastejšie používaných v klinickej veterinárnej praxi (penicilín, ampicilín, chloramfenikol, tetracyklín, streptomycín) a overenie detekčných limitov deklarovaných literatúrou. Pre penicilín a ampicilín sa potvrdila ako najcitlivejšia disková difúzna metóda, pre chloramfenikol boli detekčné limity všetkých testov takmer v zhode, pre tetracyklín bol najvhodnejší INTEST a pre streptomycín sa detekčné limity zistené jednotlivými technikami výrazne líšili, pričom najcitlivejší bol Delvotest P (5–10 raz). Zistené detekčné limity zapadali do intervalu hodnôt dek-

larovaných firemnou literatúrou a možno ich odporučiť pre rutinné stanovenia v mliekárenských závodoch.

rezíduá antibiotík; detekčné limity; disková difúzna metóda; INTEST; Delvotest P; mlieko

Smernica Európskeho spoločenstva (EEC Council Directive 85/397, 1992) vymedzila štyri základné akostné znaky surového mlieka a jedným z nich sú rezíduá antibiotík. Aj naša norma STN 57 0529 (1993) na surové kravské mlieko v článku 2.3.6 a 4.1 písmeno c zahrňuje požiadavku pravidelného (dva razy mesačne) a povinného sledovania inhibičných látok v nakupovanom surovom mlieku. Stanovenie rezíduí látok inhibujúcich rast mliekárenských kultúr musí byť negatívne. Pozitívny výsledok – nezávisle od druhu existujúcich inhibičných látok vedie vždy nielen ku zrážkam z ceny, ale takéto mlieko musí byť vylúčené z dodávok na mliekárenské ošetrenie a spracovanie (syry, jogurty).

Revidovaná norma STN 57 0531 (1994) určuje podmienky metód stanovenia rezíduí antibiotík a látok inhibujúcich rast mliekárenských kultúr v mlieku (surové, pasterizované, sušené mlieko po obnovení, chemicky konzervované mlieko) a mliekárenských výrobkoch nasledovne:

Metóda A – Difúzna disková metóda stanovenia penicilínu (citlivosť 0,0025 m.j./ml),

Metóda B – Difúzna disková metóda stanovenia penicilínu (citlivosť 0,008 m.j./ml),

Metóda C – Difúzna metóda v liekovkách,

Metóda D – INTEST a INTEST AS,

Metóda E – BRT-test,

Metóda F – Delvotest P a Delvotest SP.

Z toho vyplynula nutnosť – okrem štandardizovanej klasickej difúznej metódy – posúdiť použiteľnosť komerčne vyrábaných mikrotitračných testov, a to INTESTU a Delvotestu P. Rozhodujúcim kritériom tohto porovnania boli detekčné limity pre jednotlivé antibiotiká v mlieku udané v literatúre a deklarované aj jednotlivými výrobcami testov.

MATERIÁL A METÓDY

Na testovanie boli použité delené mikrodoštičky INTEST 0-96/6x16 (Mlékárenský průmysl, závod 01, Klatovy, Česká republika) a Delvotest P (Royal Gist Brocades, Food Ingredients Division, Holandsko). Pri klasickej diskovej metóde bol použitý GTK agar (Imuna, Šarišské Michaľany, Slovenská republika) a kmeň *Bacillus stearothermophilus* var. *calidolactis* C 953 zo zbierky mikroorganizmov VÚV v Bratislave. Boli použité nasledovné antibiotiká: procain penicilín G, ampicilín, streptomycín (sodná soľ), D-chloramfenikol, chlórtetracyklín hydrochlorid (Biotika, a.s., Slovenská Ľupča, Slovenská republika) a sušené mlieko (MEDMILK, a.s., Veľký Meder, Slovenská republika).

Použité metódy (STN 57 0531, 1994)

Difúzna disková metóda

Papierový disk nasiaknutý skúmanou vzorkou sa položí na povrch agarovej živnej pôdy s *B. stearothermophilus*. Inkubácia (64 ± 1 °C/4–5 h), pri ktorej dochádza k rastu testovacieho kmeňa, spôsobuje zakalenie agarovej pôdy. Ak sú vo vyšetrovanej vzorke prítomné látky inhibujúce rast testovacieho kmeňa, vznikajú okolo disku číre zóny. Ich veľkosť závisí od koncentrácie a typu antimikrobiálnej látky a porovnávajú sa s veľkosťou zón vytvorených kontrolnými roztokmi penicilínu so známymi koncentráciami.

INTEST a Delvotest P

Uvedené metódy kombinujú princíp agarových difúznych testov so zmenou farby indikátora v dôsledku aktívneho metabolizmu testovacieho mikroorganizmu v neprítomnosti inhibítora. Skúmaná vzorka je dávkovaná do mikrotitračných doštičiek s jamkami vyplnenými agarovou živnou pôdou obsahujúcou *B. stearothermophilus* var. *calidolactis*. Inkubácia (64 ± ± 1 °C/2,5–5 h), pri ktorej dochádza k rastu testovacieho kmeňa, spôsobuje, že farba indikátora (brómkrezolová červená) sa mení z modrofialovej na žltú. Ak sú vo vyšetrovanej vzorke prítomné látky inhibujúce rast testovacieho kmeňa, farba indikátora zostáva modrofialová.

Výber antibiotík bol daný frekvenciou používania v klinickej veterinárnej praxi a použité koncentračné rozmedzia (m.j./ml alebo μg/ml) dokumentuje

tab. II. V zmysle odporúčania IDF (1991) a firmy Mlékárenský průmysl, Klatovy, bola dodržaná hodnota pH obnoveného sušeného mlieka nad 6; vykonaná bola aj tepelná inaktivácia prirodzených inhibítorov 5 min pri 85 °C. Výsledky dosiahnuté diskovou metódou (pozit. – priemer zón nad 1 mm) boli konfrontované s detekčnými limitami udávanými v literatúre pre všetky tri testy.

VÝSLEDKY A DISKUSIA

V tab. I sú prezentované hodnoty citlivosti diskovej difúznej metódy, INTESTU a Delvotestu P podľa dostupnej literatúry. Kedže sa uvádza, že Delvotest P je citlivý zvlášť na penicilíny (STN 57 0351, 1994), pravdepodobne z tohto dôvodu sme sa stretli v novšej literatúre iba s testovaním penicilínu. Tab. II súhrnne uvádza experimentálne použité koncentračné rozmedzia vybraných antibiotík (penicilín G, ampicilín, streptomycín, chroramfenikol a tetracyklín) na detekciu citlivosti jednotlivých uvedených testov. Tab. III dokumentuje experimentálne zistené detekčné limity zvolených antibiotík v mlieku pomocou troch testov vedľa seba: klasickou diskovou metódou,

I. Porovnanie citlivosti testov na niektoré antibiotiká (podľa literárnych údajov) – Comparison of sensitivity of assays of some antibiotics (according to literature data)

Antibiotikum[1]	Disková difúzna metóda[2]	INTEST	Delvotest P
Penicilín[x]	0,0025[a] 0,004–0,005[b]	0,005[a]	0,004[a, c, d]
Ampicilín		0,008[a]	
Chloramfenikol	10,000–20,000[b]	4,000[a]	
Tetracyklín		0,300[a]	
Streptomycín	8,000–10,000[b]	10,000[a]	

x - vyjadrené v m.j./ml, ostatné antibiotiká v µg/ml – given in i.u./ml, other antibiotics are in µg/ml

[a] firemná literatúra – firm literature: INTEST, Mlékárenský průmysl, s.p. Klatovy, ČR; Delvotest P, Royal Gist Brocades, Holandsko

[b] Ryšánek, Schlegelová (1993)

[c] Mc Grane et al. (1994)

[d] STN 57 0531 (1994)

[1] antibiotics; [2] disk diffusion method

II. Koncentračné rozmedzia vybraných antibiotík – Concentration ranges of some antibiotics

Penicilín[x]	0,002	0,003	0,005	0,010	0,020	0,100	1,000
Ampicilín	0,005	0,007	0,010	0,030	0,050	0,100	1,000
Chloramfenikol	5,000	7,000	8,000	9,000	10,000	15,000	20,000
Tetracyklín	0,100	0,200	0,300	0,400	0,500	0,600	0,700
Streptomycín	1,000	3,000	5,000	7,500	10,000	12,000	20,000

x – vyjadrené v m.j./ml, ostatné antibiotiká v μg/ml – given in i.u./ml, other antibiotics in μg/ml

INTESTOM a Delvotestom P (získané výsledky sú priemerom najmenej piatich stanovení).

Ako vidieť, detekčný limit pre penicilín (0,0025 m.j/ml) korešponduje s detekčnými limitmi zistenými inými autormi (tab. I) alebo deklarovanými firemnou literatúrou (0,004–0,005 m.j./ml). Taktiež zapadá do rozmedzia maximálnych prípustných množstiev rezíduí inhibičných látok v mlieku, ktoré udáva IDF (1991) a EEC (1992) – 0,004 μg/ml/g. Ako príklad stanove-

III. Detekčné limity vybraných antibiotík v mlieku zistené tromi testami – Detection limits of some antibiotics in milk determined by three assays

Testy[1]	Antibiotiká[n 3]				
	Penicilín[x]	Ampicilín	Chloramfenikol	Tetracyklín	Streptomycín
Disková difúzna metóda[2]	0,0025	0,010	9,000–10,000	**	4,000–5,000
INTEST 0–96/6x16	0,005	*	9,000–10,000	0,300–0,400	7,000–10,000
Delvotest P	0,003–0,004	*	7,000–10,000	**	1,000

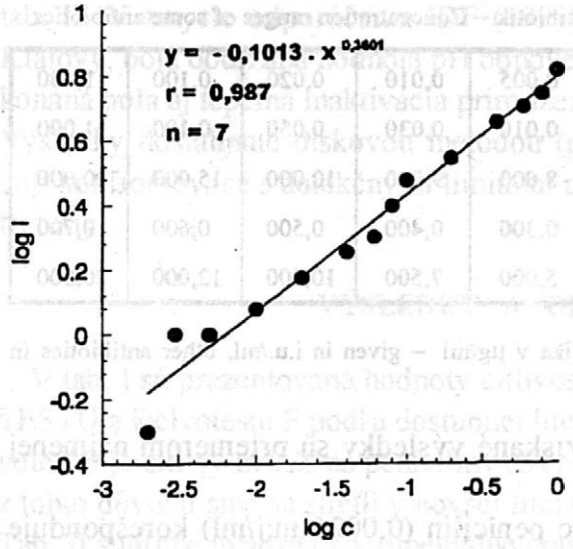
x – vyjadrené v m.j./ml, ostatné antibiotiká v μg/ml – given in i.u./ml, other antibiotics are in μg/ml

n – získané údaje sú priemerom minimálne piatich stanovení – acquired data are average values of minimally five assays

* neanalyzované – non-analyzed

** diskovou difúznou metódou a Delvotestom P detekčný limit vo zvolenem koncentračnom rozmedzí antibiotika nebol zistený – detection limit was not determined by disk diffusion method and Delvotest P in concentration ranges

[1]assays; [2]disk diffusion method; [3]antibiotics



1. Analytická čiara pre penicilín – Analytic curve for penicillin

I = veľkosť zóny – zone size [mm]
c = koncentrácia penicilínu [m.j./ml] – penicillin concentration [i.u./ml]
n = počet stanovení – number of assays

nia rezíduí antibiotík diskovou metódou uvádzame na obr. 1 analytickú čiaru pre penicilín.

Pri hodnotení detekčného limitu pre ampicilín, ktorý bol z technických príčin stanovený len klasickou diskovou metódou možno konštatovať, že je o niečo vyšší (0,01 μg/ml), než uvádza firemná literatúra (tab. I).

Čo sa týka detekčných limitov pre chloramfenikol, IDF (1991) uvádza 15,0 μg/ml, hodnoty v literatúre sa pohybujú v rozmedzí 4,0–20,0 μg/ml; nami získané hodnoty pri všetkých testoch boli 7,0–10,0 μg na 1 ml mlieka.

Citlivosť INTESTU pre tetracyklín (0,3–0,4 μg/ml) koreluje s údajmi v propagačnom materiáli. Nižšie detekčné limity 0,1–0,2 μg/g popisuje Suhrenová (1993) pri použití titračného testu s *Bacillus cereus* var. *mycoides* ATCC 9634 s TTC ako indikátorom. Pri aplikácii klasickej difúznej metódy ako aj Delvotestu P sa nám nepodarilo detekovať ani vyššie zvolené koncentračné hladiny tohto antibiotika (0,7 μg/ml), čo v tomto prípade poukazuje na nevhodnosť aplikácie týchto dvoch testov.

Z našich experimentálnych výsledkov vyplynulo, že streptomycín bol detekovaný s citlivosťou omnoho vyššou, než zodpovedá hodnotám v tab. I. Detekčný limit 4,0–5,0 μg/ml dosiahnutý štandardizovanou diskovou metódou bol približne dvojnásobne nižší, a Delvotestom P získaný limit (1,0 μg na 1 ml) bol až desaťnásobne nižší, než ako vyplýva z literárnych prameňov v tab. I (IDF udáva detekčný limit až 13,0 μg na 1 ml mlieka).

Z uvedeného je zrejmé, že porovnaním troch metód stanovenia rezíduí antibiotík sa dosiahla dobrá zhoda výsledkov. Detekčné limity vybraných anti-

biotík korešpondovali, ba v niektorých prípadoch (streptomycín) boli nižšie ako deklaruje firemná a citovaná odborná literatúra. Ukázalo sa, že použité metódy sa vyznačujú dostatočnou citlivosťou na zachytenie maximálnych prípustných množstiev rezíduí antibiotík v mlieku podľa požiadaviek IDF (1991) a EEC (1992).

Literatúra

Mc GRANE, P. – EARLY, J. – ROWE, M. T.: Modified Delvotest P for the quantitative estimation of penicillin in raw milk. Milchwissenschaft, *49*, 1994: 507–510.

RYŠÁNEK, D. – SCHLEGELOVÁ, J.: Účinnosť BR-testu a INTESTU při stanovení reziduí chemoterapeutik v syrovém a prezervovaném mléce. Vet. Med.–Czech, *38*, 1993: 215–222.

SUHREN, G.: Experiences with an IDF – experimental study for the detection of penicillin and tetracycline applying routinely used methods. Bull. Int. Dairy Fed., *283*, 1993: 15–19.

EEC: Community procedure for the establishment of maximum residue limits of veterinary medicinal products in foodstuffs of animal origin. O. J. Europ. Com., L 73, 1992: 8–14.

IDF: Detection and confirmation of inhibitors in milk and milk products. Doc. IDF, *258*, 1991: 99.

STN 57 0529: Surové kravské mlieko na mliekárenské ošetrenie a spracovanie. SÚTN, Bratislava 1993: 8.

STN 57 0531: Stanovenie rezíduí antibiotík a látok inhibujúcich rast mliekárenských kultúr v mlieku a mliečnych výrobkoch. Bratislava, ÚNMS 1994: 1–66.

Došlo 16. 2. 1995

Kontaktní adresa:

RNDr. Bernadetta Hozová, CSc., Slovenská technická univerzita, Chemickotechnologická fakulta, Radlinského 9, 812 37 Bratislava, Slovenská republika, tel.: 07/326 021, fax: 07/493 198

Ústav zemědělských a potravinářských informací

vydává v roce 1995 následující

POTRAVINÁŘSKÉ PUBLIKACE NEPERIODICKÉ

Patogenní mikroorganismy v mléce a mlékárenských výrobcích
(*E. Jičínská – J. Havlová*)
Asi 100 stran, předběžná cena 140 Kč.

Metody detekce a prevence patogenních mikroorganismů v potravinách a v prostředí potravinářských závodů
(*E. Jičínská – J. Havlová*)
Asi 80 stran, předběžná cena 120 Kč

Slovník mlýnských, pekárenských, těstárenských, cukrářských a extruzních výrazů (*J. Skládalová – O. Kopáčová*)
Asi 100 stran, předběžná cena 150 Kč.

Potravinářství 94 (*L. Benešová a kol.*)
Asi 100 stran, předběžná cena 150 Kč.
Připravovaný sborník volně navazuje svým obsahem na předchozí dva svazky.

Výživa ve stáří (*J. Dostálová – B. Turek*)
Asi 60 stran, předběžná cena 85 Kč.

Uvedené publikace můžete objednat na adrese:

Ústav zemědělských a potravinářských informací
Londýnská 55, 120 21 Praha 2,
tel.: 02/250 051-4, fax: 02/207 411

Potrav. Vědy, *13*, 1995 (2): 139–154

VAKUOVÉ CHLAZENÍ KUSOVITÝCH POTRAVIN*

Vacuum Cooling of Foods in Pieces

Rudolf GRÉE, Martin DOSTÁL, Milan HOUŠKA

Food Research Institute Prague, Czech Republic

Abstract: Besides heating, subsequent fast cooling is a part of the hygienically correct manufacture of safe foods. The modern method of vacuum cooling has been used for liquid foods on a larger scale. The objective of the present paper is to investigate the use of this method also for foods in pieces. The physical principle of vacuum cooling is controlled water evaporation from an open water surface (in liquid foods) or from the surface and pores (in foods in pieces) as a result of the effect of heat taken away from the batch heat as depending upon pressure. The method has several positive features enabling to be used in the food industry. These include particularly the speed of cooling, which eliminates the time interval of higher temperatures acting on thermolabile food components. A risk of multiplication of undesirable microorganisms is reduced that is large at uncontrolled cooling of foods in pieces. The economic aspects of this method involving savings in secondary media (cooling water, electrical power) are also favorable. A laboratory apparatus was employed for experimental vacuum cooling (Fig. 1). An oil vacuum pump was used to induce the required vacuum. A mercury vacuometer and a mercury U-manometer registered pressure data. Sample temperatures were registered continually and data were entered in time sequence into a computer file. These foods were examined: potatoes (BR), carrot (MR), horse sausage (KS), smoked pork (UM). The samples were in shape of cylinders (diameter D, height H) and prisms (dimensions H_1, H_2, H_3). Weighing determined mass of sample before heating (m_1), after heating (m_2), after vacuum cooling (m_3). Heating consisted in these methods: traditional cooking of samples in water (10 minutes), cooking of samples in water in microwave oven having the power of 650 W (10; 7; 5; 2 minutes). Temperatures T_2 (beginning of cooling), T_3 (end of cooling) were determined from time course of temperatures. Applying certain simplified conditions, mass transfer coefficient k_m was calculated, which shows the rate of mass transport from unit area at unit temperature gradient. The authors believe that this parameter is typical of the material in question under vacuum cooling. The materials with higher water content have the higher value of this

* Práce byla provedena v rámci výzkumného úkolu č. 510/93/0805 financovaného GA ČR.

coefficient than the materials with lower water content and higher fat content. The quality of foods with high water content is not mostly changed by vacuum cooling. Meat products showed the drying out of surface layers, but the quality was maintained in the other parts. These foods should be cooled simultaneously with water cooling.

vacuum cooling; foods in pieces; mass transfer; mass transfer coefficient

Abstrakt: Na modelovém eperimentálním zařízení byl studován způsob vakuového chlazení vybraných kusovitých potravin rostlinného i živočišného původu. Za zjednodušujících předpokladů vzhledem ke složitosti energetických i materiálových transportních dějů provázejících fenomén vakuového chlazení byl sledován součinitel přenosu hmoty, který udává rychlost transportu hmoty v jednotkovém režimu. Tento součinitel je autory pokládán za významné kritérium vakuového chlazení. Z praktického hlediska byl sledován a hodnocen hmotnostní úbytek vakuově chlazených vzorků a stanovena střední hodnota relativních hmotnostních úbytků. Současně byly orientačně hodnoceny i senzorické a texturní vlastnosti zchlazených vzorků kusovitých potravin.

vakuové chlazení; kusovité potraviny; přenos hmoty; součinitel přenosu hmoty

Součástí hygienicky správné výroby bezpečných potravin je kromě ohřevu i následné dostatečně rychlé chlazení. Této operaci, na rozdíl od ohřevu, byla v minulosti věnována poněkud menší pozornost. Naproti tomu v zahraničí jsou například maximální doby chlazení velkých kusů masa stanoveny v hygienických předpisech (Nolan, 1987; Burfoot et al., 1990). V souvislosti s výrobou chlazených a zmrazených pokrmů určených pro společné stravování se připravují obdobné předpisy i u nás. Jedním z velmi efektivních způsobů chlazení kusovitých potravin je chlazení vakuové.

Fyzikální podstata vakuového chlazení se vyznačuje několika aspekty, jejichž využití v oblasti zpracování potravin je více než zajímavé. Je to především rychlost chlazení, s níž lze úspěšně eliminovat delší působení vyšších teplot na citlivé termolabilní složky potravin (např. degradace řetězce pektinových složek, snížení obsahu vitaminů nebo změna barvy). Z hlediska bezpečnosti potravin je rychlost chlazení rovněž důležitá. Čím je rychlost chlazení vyšší, tím více se snižuje riziko pomnožení nežádoucích mikroorganismů. Dlouhodobé setrvání potravin na teplotách v rozsahu 30–40 °C je z hlediska růstu těchto mikroorganismů přímo ideální.

Při vakuovém chlazení tekutých a kašovitých látek je intenzita chlazení řízena odparem vody z volné hladiny za postupného snižování tlaku. Teplo potřebné k odpaření vody se čerpá z tepelného obsahu vsádky, což tvoří základní princip vakuového chlazení. Přitom lze očekávat, že při difuzních dějích, které provázejí tuto chladící metodu, může dojít ke snížení obsahu složek, jež tvoří charakteristickou senzoriku chlazeného produktu (vonné látky). Proces lze využít cíleně i k finálnímu zahuštění vsádky.

U kusovitých potravin je nutné experimentálně ověřit možnost použití vakuového chlazení a určit technologickou únosnost této operace v návaznosti na její nepopiratelnou ekonomičnost. Z principu vakuového chlazení a díky jeho rychlosti vznikají totiž značné úspory sekundárních médií (chladící voda, elektrická energie) ve srovnání s jinými typy chlazení.

Praktická rychlost chlazení kusových potravin je dána působením řady faktorů. Jde především o rychlost přenosu hmoty, a to i z pórů potravin, měrnou tepelnou kapacitu produktu a tím jeho složení, tepelnou vodivost, porozitu, tvar atd. Při jinak stejných podmínkách (rozměry vzorku, hodnota vakua, rozměry zařízení) je rychlost chlazení pro daný materiál charakteristická.

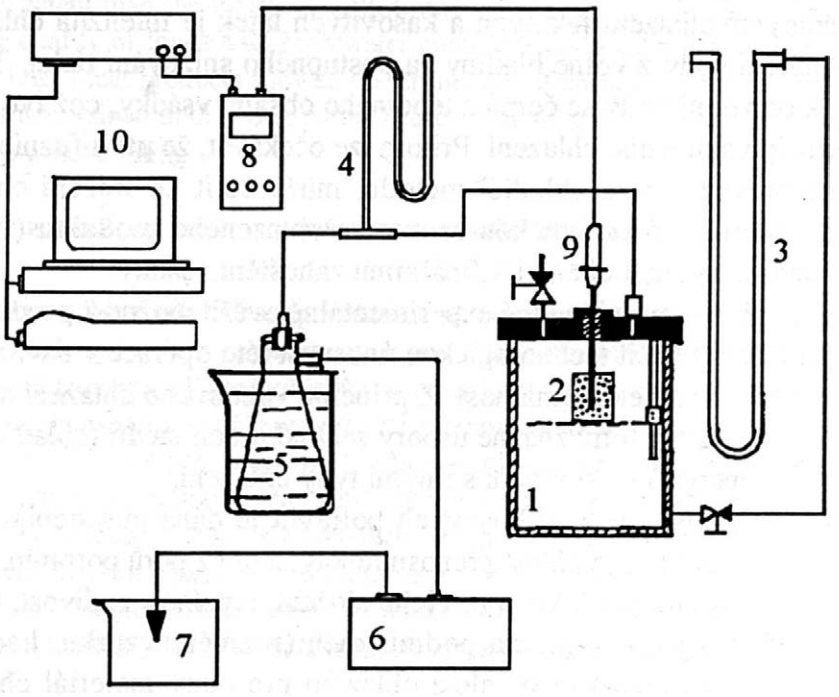
Vakuové chlazení se často používá u kapalných a kašovitých potravin. Cílem této práce je zmapovat možnost jeho použití i pro oblast kusovitých potravin.

MATERIÁL A METODY

Aparatura

Experimentální vakuové chlazení bylo provedeno na laboratorní aparatuře, jejíchž schéma je uvedeno na obr. 1. Základním prvkem aparatury je nerezová tlaková nádoba 1 opatřená masivním utěsněným víkem, která nese stavitelnou podložku 2 k uložení vzorku zkoumané potraviny. Víko je dále opatřeno zavzdušňovacím ventilem, těsněnou průchodkou pro čidlo teploty a vývodkou pro měření vakua. Obdobná vývodka s ventilem je na spodní straně nádoby.

Potřebný podtlak je vyvozován olejovou vývěvou 6, v jejímž sání je zapojen kondenzátorový člen 5, rtuťový vakuometr 4 s napojením na vývodku vakua nádoby 1. Paralelně je k nádobě připojen rtuťový U-manometr 3.



1 = nádoba – vessel; 2 = vzorek – sample; 3 = U-manometr; 4 = vakuometer –vacuometer; 5 = kondenzor – condenser; 6 = vývěva – vacuum pump; 7 = sběrač –vessel; 8 = termometr – digital thermometer; 9 = teplotní čidlo – temperature sensor; 10 = počítač – computer

1. Schéma experimentální aparatury – Scheme of experimental apparatus

Teplota vzorku je kontinuálně snímána teplotním čidlem 9 (platinový odporový teploměr) a vyhodnocována v zařízení 8 (Therm Ahlborn, SRN), kde dochází k jejímu převodu na stejnosměrné napětí. To je pak měřeno v pevných časových intervalech přesným programovatelným multimetrem M1T380 (Metra Blansko), který je spojen pomocí rozhraní HP-IB s počítačem IBM-PC AT. Ten zajišťuje sběr dat z voltmetru (tj. sběr teplot a času) a naměřené údaje ukládá do datového souboru pro další zpracování.

Metodika měření

Pro experimenty byly vybrány následující potraviny: brambory (dále BR), mrkev (MR), měkký salám koňský (KS), uzené maso (UM). Z uvedených materiálů byly vytvořeny válcové vzorky o průměru D (50; 40; 20 mm) a výšce H (40 nebo 20 mm). Pouze vzorky z uzeného masa byly vytvořeny i ve formě hranolů o rozměrech H_1, H_2, H_3. Tvary a rozměry vzorků byly

voleny proto, aby u geometricky shodných vzorků, avšak různé struktury a složení bylo možné výsledky chlazení přímo porovnat.

Jednotlivé vzorky byly nejdříve zváženy (hmotnost m_1) a pak tepelně opracovány. K ohřevu byly použity dva způsoby: klasický var ve vodní lázni po dobu 10 minut a var ve vodní lázni po dobu 10, 7, 5, 2 minut při použití mikrovlnné trouby o výkonu 650 W (štítková hodnota) a frekvenci 2 450 MHz (trouba Samsung s otočným stolkem). Po ukončení ohřevu byly vzorky opět váženy (hmotnost m_2) a následně umístěny na podložku nádoby 1měřící aparatury se zavedeným teplotním čidlem 9 do středu měřeného vzorku.

Po dokonalém utěsnění nádoby 1 byla zapnuta vývěva. Časový průběh evakuace nádoby byl v intervalech 5 sekund sledován na rtuťovém U-manometru a zaznamenáván až do stavu konstantního vakua (přibližně po dobu 30–35 sekund). Hodnota absolutního tlaku byla stanovena z údaje U-manometru a barometrického tlaku v době měření. Ustálená hodnota vakua byla kontrolována na rtuťovém vakuometru 4. Údaje z teplotního čidla 9, snímané ve zvoleném časovém režimu, byly zpracovány v počítačové aparatuře 10 ve tvaru numerických či grafických výstupů ve funkční závislosti $T = T(t)$.Po skončení měření průběhu teplot byla stanovena finální hmotnost vzorku m_3.

Způsob vyhodnocení naměřených výsledků

Při experimentálním sledování vakuového chlazení kusovitých potravin byly pro jednotlivé vzorky stanoveny tyto údaje: rozměr vzorků před ohřevem D, H, resp. H_1, H_2, H_3, hmotnosti vzorků před ohřevem, po ohřevu a po vakuovém chlazení m_1, m_2, m_3 a dále časový průběh teploty T v geometrickém středu vzorku v závislosti na čase t měřeném od počátku spuštění vývěvy. Z naměřeného průběhu teplot lze vybrat teplotu vzorku na počátku vakuového chlazení T_2 a na konci vakuového chlazení T_3. Všechny tyto veličiny jsou uvedeny v tab. I až IV.

Nejprve se zaměřme na integrální tepelnou bilanci vzorku. Předpokládejme, že během vakuového chlazení odebíráme vzorku teplo tím, že odpařujeme vodu ze vzorku a odebíráme teplo odpovídající množství odpařené vody. Pak můžeme napsat

$$(m_2 - m_3) \,.\, r_m = c_m \,.\, (T_2 - T_3) \,.\, m_m \qquad [1]$$

I. Experimentální výsledky vakuového chlazení brambor – Experimental results of vacuum cooling of potatoes

Vzorek[1]	Rozměr[2] Ø [mm]	Hmotnost vzorku[3]			Tlak na konci vakuového chlazení[7] [Pa]	Teplota vzorku[8]		Celková doba vakuového chlazení[11] [s]
		před ohřevem[4] m_1[g]	po ohřevu[5] m_2[g]	po vakuovém chlazení[6] m_3[g]		před vakuovým chlazením[9] T_2[°C]	po vakuovém chlazení[10] T_3[°C]	
BR-11	39,0-39,0	49,30	49,60	45,50	4 906	89,7	31,0	183,0
BR-12	38,5-38,0	48,00	48,60	44,30	4 906	91,3	33,2	240,3
BR-21	40,0-40,5	54,40	54,00	50,20	6 100	89,0	38,4	301,5
BR-22	22,4-40,2	16,80	16,90	15,40	6 100	90,2	30,8	182,9
BR-31	49,5-22,2	44,50	45,20	41,10	5 437	81,1	30,2	179,1
BR-32	49,5-20,2	39,55	40,10	35,90	5 437	74,4	26,1	239,2
BR-33	39,3-19,9	24,75	25,40	22,75	5 340	77,4	22,0	238,8
BR-34	39,6-19,3	24,55	25,70	22,75	5 304	77,4	22,0	238,8
BR-35	22,0-20,0	8,05	8,50	7,35	2 652	76,7	7,3	492,3
BR-41	49,1-20,6	42,80	43,80	39,70	5 967	80,1	29,7	239,7
BR-42	49,3-19,6	38,10	39,10	35,40	5 967	76,1	28,1	241,7
BR-43	48,4-20,1	39,60	40,30	36,95	19 492	80,9	34,7	261,7

střední hmotnostní úbytek - mean mass loss: 9,6 %

Vařeno ve vodní lázni po dobu 15 minut s použitím výhřevné plochy - cooling of samples in water for 15 minutes, classical heating in cooking pot

[1]sample; [2]dimension; [3]mass of sample; [4]before heating; [5]after heating; [6]after vacuum cooling; [7]final pressure in vacuum cooling; [8]initial temperature of samples; [9]before vacuum cooling; [10]after vacuum cooling; [11]total cooling time

II. Experimentální výsledky vakuového chlazení mrkve - Experimental results of vacuum cooling of carrot

Vzorek[1]	Rozměr[2] Ø [mm]	Hmotnost vzorku[3]			Tlak na konci vakuového chlazení[7] [Pa]	Teplota vzorku[8]		Celková doba vakuového chlazení[11] [s]
		před ohřevem[4] m_1[g]	po ohřevu[5] m_2[g]	po vakuovém chlazení[6] m_3[g]		před vakuovým chlazením[9] T_2[°C]	po vakuovém chlazení[10] T_3[°C]	
MR-11	22,4-38,2	15,60	13,90	12,40	5 569	86,4	23,1	361,6
MR-12	40,3-40,2	49,30	45,80	41,20	5 304	91,9	29,5	361,5
MR-13	40,0-21,0	26,00	24,30	22,20	6 630	88,6	38,7	177,7
MR-14	40,0-21,5	27,30	24,95	22,65	6 630	85,3	33,5	298,7
MR-21	39,6-40,4	50,30	48,70	44,50	4 508	90,2	33,3	132,3
MR-22	22,6-19,6	7,85	7,35	6,65	3 713	70,9	21,1	122,0
MR-23	49,5-21,6	39,75	38,00	34,30	4 774	78,7	28,0	175,8
MR-24	40,0-21,7	27,80	26,25	23,70	4 906	78,6	26,6	188,9

střední hmotnostní úbytek - mean mass loss: 9,5 %

Vařeno ve vodní lázni po dobu 15 minut s použitím výhřevné plochy - cooling of samples in water for 15 minutes, classical heating in cooking pot

[1]sample; [2]dimension; [3]mass of sample; [4]before heating; [5]after heating; [6]after vacuum cooling; [7]final pressure in vacuum cooling; [8]initial temperature of samples; [9]before vacuum cooling; [10]after vacuum cooling; [11]total cooling time

III. Experimentální výsledky vakuového chlazení koňského salámu - Experimental results of vacuum cooling of horse sausage

Vzorek[1]	Rozměr[2] Ø [mm]	Hmotnost vzorku[3]			Tlak na konci vakuového chlazení[7] [Pa]	Teplota vzorku[8]		Celková doba vakuového chlazení[11] [s]
		před ohřevem[4] m_1[g]	po ohřevu[5] m_2[g]	po vakuovém chlazení[6] m_3[g]		před vakuovým chlazením[9] T_2[°C]	po vakuovém chlazení[10] T_3[°C]	
KS-11*	39,7-18,9	22,50	20,50	18,90	3 713	59,3	20,8	301,7
KS-12$	40,0-18,8	20,80	16,90	15,40	3 713	63,5	22,9	357,1
KS-13@	50,0-21,0	38,00	28,10	25,80	4 243	86,6	25,9	419,2
KS-14@	21,0-20,0	6,20	2,60	2,40	3 580		20,1	360,0
KS-15#	20,8-19,5	6,50	3,20	2,95	3 713		21,7	480,0
KS-16#	21,0-21,0	7,60	4,30	4,00	3 978	71,3	22,5	241,5
KS-17#	48,0-39,0	60,80	36,80	33,80	4 243		24,0	600,0
KS-18@	20,0-41,0	13,80	8,30	7,50	3 978	88,8	22,0	489,1
KS-19#	38,0-41,0	44,70	29,10	26,60	5 437	91,7	27,6	301,1
KS-110#	49,0-40,0	73,20	42,30	38,90	4 243	94,4	24,1	653,6

střední hmotnostní úbytek - mean mass loss: 8,2 %

* Vařeno ve vodní lázni po dobu 10 minut s použitím výhřevné plochy – cooking of samples in water for 10 minutes, classical heating in cooking pot

$ Vařeno ve vodní lázni po dobu 2 minut s použitím mikrovlnné trouby o výkonu 650 W zapnuté na 4. stupeň – cooking of samples in water for 2 minutes in microwave oven having power 650 W, switched to 4-th level of power

@ Vařeno ve vodní lázni po dobu 5 minut s použitím mikrovlnné troby o výkonu 650 W zapnuté na 4. stupeň – cooking of samples in water for 5 minutes in microwave oven having power 650 W, switched to 4-th level of power

Vařeno ve vodní lázni po dobu 7 minut s použitím mikrovlnné trouby o výkonu 650 W zapnuté na 4. stupeň – cooking of samples in water for 7 minutes in microwave oven having power 650 W, switched to 4-th level of power

[1]sample; [2]dimension; [3]mass of sample; [4]before heating; [5]after heating; [6]after vacuum cooling; [7]final pressure in vacuum cooling; [8]initial temperature of samples; [9]before vacuum cooling; [10]after vacuum cooling; [11]total cooling time

IV. Experimentální výsledky vakuového chlazení uzeného masa - Experimental results of vacuum cooling of smoked pork

Vzorek[1]	Rozměr[2] Ø [mm]	Hmotnost vzorku[3]			Tlak na konci vakuového chlazení[7] [Pa]	Teplota vzorku[8]		Celková doba vakuového chlazení[11] [s]
		před ohřevem[4] m_1[g]	po ohřevu[5] m_2[g]	po vakuovém chlazení[6] m_3[g]		před vakuovým chlazením[9] T_2[°C]	po vakuovém chlazení[10] T_3[°C]	
UM-11	40,0-25,0	31,10	17,60	15,90	3 978	84,6	22,9	480,5
UM-12	37,0-27,0	33,20	23,30	21,10	4 243	87,3	20,0	480,2
UM-13	38,0-26,0	27,60	11,30	10,50	4 243	66,8	23,3	482,1
UM-14	37,0-22,5	25,20	11,60	10,70	3 845	80,6	18,6	487,0
UM-15	21,0-28,0	9,30	3,80	3,40	3 713	62,8	18,2	481,5
UM-16	20,0-31,0	11,30	7,00	6,20	3 978	85,4	7,0	731,4
UM-17	30x28x28	23,20	14,00	12,60	3 978	89,4	20,7	483,0
UM-18	27x20x28	14,20	9,30	8,40	3 978	85,2	15,2	542,2

střední hmotnostní úbytek - mean mass loss: 9,5 %

Vařeno ve vodní lázni po dobu 10 minut s použitím mikrovlnné trouby - cooling of samples in water for 10 minutesin mi crowave oven having power 650 W switched to 4-th level of power

[1]sample; [2]dimension; [3]mass of sample; [4]before heating; [5]after heating; [6]after vacuum cooling; [7]final pressure in vacuum cooling; [8]initial temperature of samples; [9]before vacuum cooling; [10]after vacuum cooling; [11]total cooling time

kde jsme použili střední hodnoty všech veličin. Střední hodnotu výparného tepla vody r_m uvažujeme při střední teplotě $T_m = (T_2 + T_3)/2$. Hodnotu r_m jsme stanovili ze vztahu (Šesták et al., 1980):

$$r_m = 2{,}255 \,.\, 10^6 \left[\frac{374.15 - T_m}{274{,}15}\right]^{0.38} \qquad [2]$$

Střední hmotnost vzorku při vakuovém chlazení je $m_m = (m_2 + m_3)/2$.

Z tepelné bilance [1] lze vyjádřit střední hodnotu měrné tepelné kapacity vzorku:

$$c_m = \frac{r_m \,.\, (m_2 - m_3)}{m_m \,.\, (T_2 - T_3)} \qquad [3]$$

Během procesu vakuového chlazení dochází k hmotnostnímu úbytku chlazeného vzorku, tj. dochází k poklesu hmotnosti vzorku a ke snižování jeho teploty při snižování tlaku nasycených par v okolí vzorku. Dochází k transportu hmoty ze vzorku. Předpokládejme, že hnací silou tohoto transportu hmoty je právě rozdíl koncentrací vlhkosti prostředí a vzorku, vyjádřený (na základě předpokladu existence volné vody na povrchu vzorku) rozdílem tlaku sytých par při teplotě vzorku a parciálním tlakem vodních par v prostředí (vyjádřeném přibližně jako celkový tlak v systému). Transport hmoty je ovlivňován i velikostí povrchu vzorku S.

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \dot{m} = k_m S[P(T(t)) - p(t)] \qquad [4]$$

Ve vztahu [4] vystupuje veličina k_m jakožto součinitel přestupu hmoty. Čím je tento součinitel větší, tím dochází k intenzivnějšímu transportu hmoty. K tomu, abychom součinitel k_m, který bude zřejmě pro danou konfiguraci charakteristický, vyhodnotili, budeme muset znát nejen časový průběh tlaku v měřeném prostoru, ale i časový průběh hmotnosti vzorku. Protože jsme však z technických důvodů časový průběh hmotnosti vzorku neměřili, nemůžeme určit veličinu $\mathrm{d}m/\mathrm{d}t$ a musíme se pokusit tento průběh zrekonstruovat. Opět z tepelné bilance, tentokráte mezi stavy t a $t - \mathrm{d}t$ můžeme napsat:

$$[m(t - \mathrm{d}t) - m(t)]\, r_m = c_m \,.\, [T(t - \mathrm{d}t) - T(t)] m_m \qquad [5]$$

a tudíž

$$dm / dt = \frac{m(t-dt) - m(t)}{dt} = \frac{c_m . [T(t-dt) - T(t)]}{r_m . dt} \quad [6]$$

kde m_m, c_m, r_m jsou tytéž veličiny jako v rovnici (1) a dt je časový krok. Ze vztahu [6] můžeme pro malý časový krok dt určit průběh dm/dt v závislosti na čase. Začátek výpočtu je v čase $t = 0$, tj. pro počátek vakuového chlazení, kdy má vzorek teplotu T_2. Za časový krok vyhodnocení bereme z důvodu následného vyhodnocení časový krok, s nímž byl měřen průběh tlaku (5s). Přepíšeme-li vztah [4] do tvaru

$$\frac{dm / dt}{S_R} = k_m . [P((Tt)) - p(t)] \quad [7]$$

kde S_R je redukovaná plocha vzorku, pak můžeme pomocí lineární regrese mezi levou a pravou stranou vztahu (7) určit hodnoty součinitele přestupu hmoty k_m. V tomto vztahu jsme místo plochy vzorku vzali hodnotu S_R, tj. hodnotu redukovanou na konec varu a počátek vakuového chlazení.

Původní počáteční plocha povrchu válcového vzorku je

$$S = \pi DH + \pi D^2/2 \quad [8a]$$

a vzorku tvaru kvádru je

$$S = 2 . (H_1H_2 + H_2H_3 + H_1H_3) \quad [8b]$$

Vzhledem k tomu, že v procesu vaření vzorku došlo ke změně jeho tvaru, který navíc nebyl přesně definovatelný, budeme hodnotu S_R určovat pouze přibližně na základě předpokladu konstantní hustoty a lineární změny všech délkových rozměrů před varem a po varu. Pak lze určit:

$$S_R = [\frac{m_2}{m_1}]^{2/3} . S \quad [9]$$

Tlak sytých par ve vztazích [4] a [7] určíme podle práce Šesták et al. (1980):

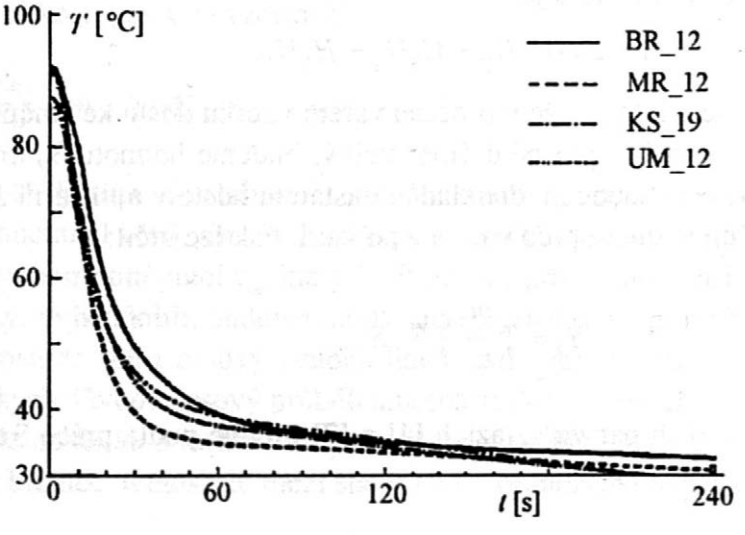
$$\ln P = 23.1964 - \frac{3816,44}{T+227,02}$$

VÝSLEDKY A DISKUSE

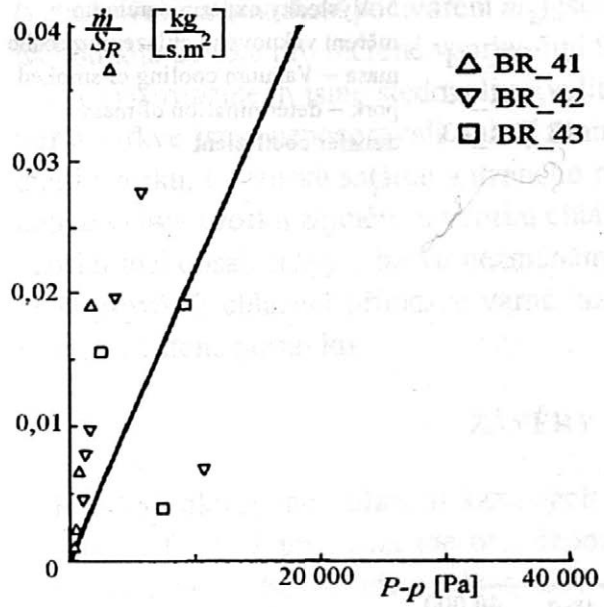
Základní experimentální data jsou souborně uvedena v tab. I až IV. Typické průběhy časové závislosti vnitřní teploty T vybraných vzorků při vakuovém chlazení jsou uvedeny v obr. 2. Průběh teplot je pro všechny vzorky analogický. Je charakterizován rychlým poklesem teploty ve fázi prvé (odpar volné teploty vody z povrchu) a pomalejším poklesem teploty ve fázi druhé (odpar vody z pórů). Uvedené vyhodnocení součinitele přestupu hmoty mohlo být provedeno podle vztahu (4) pouze pro prvou fázi chlazení, při níž je teplota vzorku vyšší než teplota syté páry v jeho okolí.

Zpracované výsledky experimentálního chlazení brambor, koňského salámu a uzeného masa jsou v závislosti na druhu vzorku uvedeny na obr. 3 až 5. (Při chlazení mrkve nebyly měřeny průběhy tlaku.) V uvedených obrázcích jsou zakresleny vztahy stanovené lineární regresí naměřených experimentálních dat.

Mechanismus vakuového chlazení kusovitých potravin je značně složitý a stupeň znalosti rozhodujících přenosových jevů (přenos energie a hmoty), skladby materiálu vzorků a jeho vlastností zatím dovoluje řešit a vysvětlovat jeho podstatu pouze za zjednodušujících předpokladů. Teplotu vzorku měřenou v jeho geometrickém středu považujeme za střední kalorimetrickou, materiálové vlastnosti vzorku jsme považovali v daném oboru teplot za



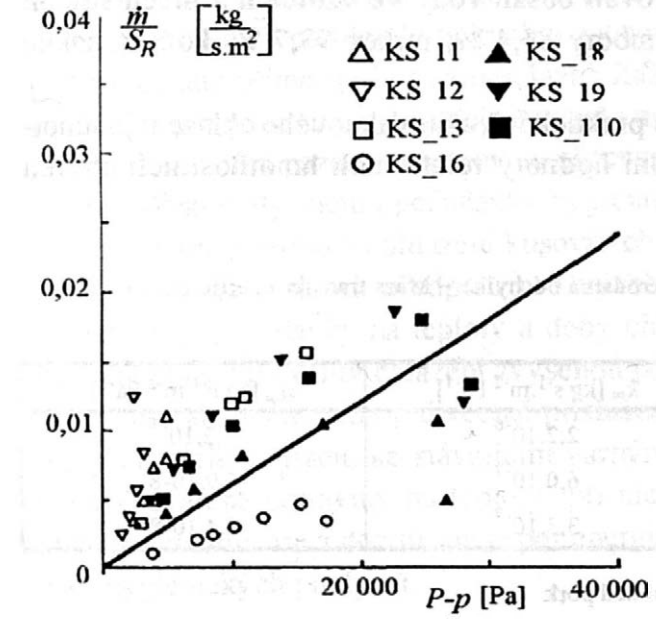
2. Časový průběh teplot uvnitř vybraných vzorků při vakuovém chlazení – Time-temperature dependences of selected samples in vacuum cooling



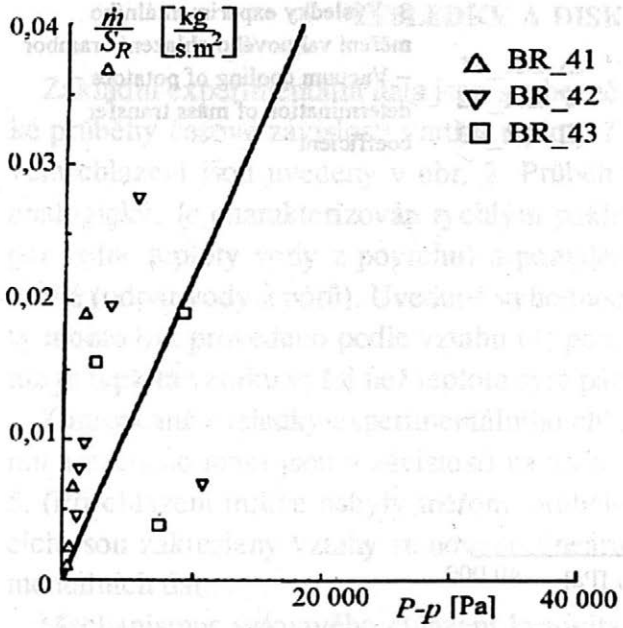
3. Výsledky experimentálního měření vakuového chlazení brambor – Vacuum cooling of potatoes – determination of mass transfer coefficient

konstantní, povrch vzorku nebyl stanoven experimentálně, ale přibližným výpočtem, vzorky byly považovány za homogenní.

Na základě uvedeného postupu vyhodnocení i všech zjednodušujících předpokladů byly stanoveny hodnoty součinitele přenosu hmoty k_m, které udávají rychlost transportu hmoty z jednotkové plochy při jednotkovém teplotním spádu. Tento součinitel byl vyhodnocen pro každý materiál (kromě



4. Výsledky experimentálního měření vakuového chlazení koňského salámu – Vacuum cooling of horse sausage – determination of mass transfer coefficient



5. Výsledky experimentálního měření vakuového chlazení uzeného masa – Vacuum cooling of smoked pork – determination of mass transfer coefficient

mrkve) zvlášť a může být pokládán za parametr charakterizující daný vakuově chlazený materiál za daných podmínek. Získané hodnoty součinitelů přestupu hmoty k_m včetně jejich směrodatných odchylek jsou uvedeny v tab. V. Z obr. 3–5 a z tab. V se zdá, že materiály s vyšším obsahem volné vody (brambory) mají řádově vyšší součinitel přestupu hmoty než materiály s nižším obsahem vody a s určitým obsahem tuku (uzené maso, salám). Před vakuovým chlazením byl zjišťován obsah vody ve vzorcích a určen střední hodnotou ze tří měření: brambory 81,4 %; mrkev 93,7 %; koňský salám 67,3 %; uzené maso 67,5 %.

Důležitým parametrem pro praktické využití vakuového chlazení je hmotnostní úbytek vzorků. Střední hodnoty relativních hmotnostních úbytků

V. Součinitel přestupu k_m a jeho směrodatná odchylka – Mass transfer coefficient and its standard deviation

Materiál[1]	k_m [kg.s^{-1}.m^{-2}.Pa^{-1}]	s_{k_m} [kg.s^{-1}.m^{-2}.Pa^{-1}]
Brambory[2]	$2{,}2.10^{-6}$	$7{,}2.10^{-7}$
Koňský salám[3]	$6{,}0.10^{-7}$	5,9.10-8
Uzené maso[4]	$3{,}3.10^{-7}$	3,4.10-8

[1]food; [2]potatoes; [3]horse sausage; [4]smoked pork

(vztažených na hmotnost po uvaření m_2) jsou uvedeny v tab. I až IV. Průměrná hodnota úbytku pro měřené vzorky činí 9,2 %.

Při experimentech jsme sledovali i kvalitu chlazených potravin. U brambor a mrkve jsme nepozorovali ani významné snížení kvality vzhledu, ani chuti vzorků. U vzorků salámu a uzeného masa docházelo k oschnutí povrchové vrstvy vzorků zejména u vzorků chlazených na nejnižší teploty. Střed vzorků měl obsah šťávy a barvu nezměněny. Pro tyto materiály bude vhodnější provádět chlazení přímo ve varné lázni, aby nedocházelo k osychání povrchu vařené potraviny.

ZÁVĚRY

Křivka vakuového chlazení kusových potravin vykazuje dvě charakteristické fáze. V prvé fázi jde pravděpodobně o odpařování volné vody z povrchu, ve druhé fázi jde o odpar vody z pórů. Pro prvou fázi byl vytvořen matematický model procesu a stanoveny hodnoty součinitele přestupu hmoty pro chlazení brambor, koňského salámu a uzeného masa. O mrkvi lze předpokládat, že její vakuové chlazení probíhá podobně jako u brambor. Hodnoty součinitele přestupu hmoty jsou u brambor řádově vyšší než u masných výrobků. Hmotnostní úbytek je v průměru roven 9,2 % z hmotnosti vařených potravin.

Kvalita potravin s vysokým obsahem vody se vakuovým chlazením podstatně nemění. U masných výrobků bylo pozorováno osychání povrchových vrstev, v ostatních partiích byla kvalita zachována. Tyto potraviny by bylo vhodné chladit přímo spolu s varnou lázní. Zdá se tedy, že vakuové chlazení je vhodné pro potraviny s dostatečně vysokým obsahem volné vody.

Dosud se velká pozornost věnovala ohřevu potravin (mikrovlnný ohřev). V souvislosti s rostoucími požadavky hygieniků se jeví nutnost věnovat neméně stejnou pozornost i chlazení kusovitých potravin. Vzhledem k připravované změně českých předpisů pro výrobu hotových pokrmů (budou deklarovány požadavky na teploty a doby chlazení) budou výrobci nuceni věnovat otázkám kvality chlazení zvýšenou pozornost.

Proces vakuového chlazení včetně příslušného zařízení (například ve formě přídavného zařízení ke stávajícím varným kotlům) umožní předchladit čerstvě uvařené potraviny na teploty, při nichž se mohou vložit přímo do chlazeného prostoru a docílit tím úspor energie, času a lidské práce při dodržení hygienických předpisů.

Seznam symbolů

c_m	střední měrná tepelná kapacita (J. kg^{-1}.K^{-1})
T	teplota vzorku (°C)
T'	teplota sytých par (°C)
T_2, T_3	teplota vzorku po uvaření a po zchlazení (°C)
T_m	střední teplota vzorku (°C)
t	čas (s)
r_m	výparné teplo (J. kg^{-1})
D	průměr válcového vzorku (m)
H	výška válcového vzorku (m)
H_1, H_2, H_3	rozměry vzorku ve tvaru kvádru (m)
m_1, m_2, m_3	hmotnosti vzorku před a po ohřevu, a po chlazení (kg)
m_m	střední hmotnost (kg)
S	plocha vzorku (m^2)
S_R	plocha vzorku redukovaná (m^2)
P	absolutní tlak ve vakuovém prostoru (Pa)
P	tlak sytých par při teplotě vzorku (Pa)
m	hmotnostní tok (kg.s^{-1})
k_m	součinitel přestupu hmoty (kg.s^{-1}.m^{-2}.Pa^{-1})

Literatura

BURFOOT, D. – SELF, K. P. – HUDSON, W. R. – WILKINS T. J. – JAMES, S. J.: Effect of cooking and cooling method on the processing times, mass losses and bacterial condition of large meat joints. Int. Food Sci. Technol., *25*, 1990: 657–667.

NOLAN, E. J.: Calculation of an approximate cooling curve for cooked roast beef. Food Process Engineer. *9*, 1987: 247–263.

ŠESTÁK, J., et al: Transportní a termodynamická data pro výpočet aparátů a strojního zařízení. [Skripta ČVUT] Praha, 1980.

Došlo dne 9. 2. 1995

Kontaktní adresa:

Ing. Rudolf Grée, Výzkumný ústav potravinářský Praha, Radiová 7, 102 31 Praha 10-Hostivař, Česká republika, tel.: 02/702 330, fax: 02/701 983

Potrav. Vědy, *13*, 1995 (2) : 155–168

REVIEWS

SINAPINES AND OTHER PHENOLICS OF *BRASSICACEAE* SEEDS*

Jan POKORNÝ, Zuzana RÉBLOVÁ

Prague Institute of Chemical Technology – Department of Food Chemistry and Analysis, Prague, Czech Republic

Some antinutritional or even toxic substances are found in many plant products used for food, such as phytates or tannins. Other substances occur, however, only in species of a single plant family or a single subfamily or in some cases even of a single genus, such as glucosinolates, which are typical components of *Brassicaceae*. Another group of compounds, characteristic for the same family, are sinapines. They were detected, however, also in other edible plants, e.g. in persimmons (Sattar et al., 1992).

Structure of Sinapines and their Properties

Sinapines are choline esters of phenolic acids, derived either from cinnamic acid (both stereoisomers may be present in varying proportions) or from benzoic acid. The name of the group is derived from the choline ester of (*E*)-sinapic acid, which is the most widely occurring representative. In this review, sinapine is the choline ester of sinapic acid, choline esters of this and other phenolic acids accompanying sinapic acid are called sinapines. As sinapines contain phenolic groups, which have weakly acidic character on one hand, and quartenary amine groups, which have strongly basic character on the other hand, they may form several ionic forms which are in equilibrium, depending on the pH-value (Smyk, Drabent, 1989).

Sinapines are formed from sinapic acid (or another phenolic acid, respectively) and choline by catalytic action of aromatic choline esterase, which was isolated from *Sinapis alba* seeds (Clausen et al., 1985a, b). They may be hydrolyzed by the same enzyme during the storage of seeds. The liberated phenolic acids may form esters with sugars, such as glucose or sophorose.

Sinapines have moderate antioxidant activity, derived from the bound phenolic acid, but the activity is generally lower than that of the respective acid (Nowak et al., 1992). Contrary to phenolic acids, sinapines have no antimicrobial activity.

* Supported by Czech Grant Agency, No. 509/93/2483 from the Grant Agency of Czech Republic.

Sinapines were found the cause of bitter taste of rapeseed meal (Clandinin, 1961). The taste of sinapines is both bitter and astringent (Ismail et al., 1981). The bitterness of sinapine is more intensive than that of either sinapic acid or choline hydrochloride, being approximately equivalent to the bitterness of caffeine. Because of the sinapine content in rapeseed and mustard extracted meals, these materials may be objectionable not only for human consumption, but even for animals (Sosulski, 1979; Zadernowski et al., 1981). Their effect was reviewed from various aspects (Shahidi, Naczk, 1992).

Occurrence of Sinapines

Sinapines were detected in many seeds of the *Brassicaceae* family, such as in the following genera (alphabetically): *Arabis, Brassica, Cakile, Diplotaxis, Eruca, Hesperis, Matthiola, Raphanobrassica, Raphanus* and *Sinapis*. The composition of phenolic acids bound in the sinapines is genetically conditioned. The content of various representatives of sinapines is highly variable, both between and within species, but depends not only on the species, but also on environmental conditions (Bouchereau et al., 1991).

Mustard seeds are used for the production of mustard, therefore sinapines are present in all brands of mustards, irrespective whether they were produced from seeds of the genus *Sinapis* or *Brassica* (Kerber, Buchloh, 1980). Comparable amounts of sinapines were found in seeds of both white mustard and black mustard (Karig, 1975). Bound p-hydroxybenzoic acid prevails in white mustard seeds while bound sinapic acid is characteristic of seeds of turnip rape (*Brassica campestris* L.) (Durkee, Thivierge, 1975). Dijon mustard is prepared from seeds of *Brassica juncea* which contain about 1 % sinapine, where bound sinapic acid is accompanied by minor related phenolic acids (Vangheesdaele, Fournier, 1980). The content of tannins is only small. In spite of their bitter and astringent taste, sinapines do not affect the flavour of mustard in any substantial degree.

Detailed information on the sinapine content is available for oilseeds because extracted meals produced by their processing are depreciated by sinapines as animal feed. Appelqvist (1971) reviewed the older results on turnip rape (sarson) and rape seeds. The disadvantages of *Crambe abyssinica* as an oilseed are the high content of glucosinolates, dietary fibre, and of sinapines as well (Cornelius, Simmons, 1969). Therefore, low sinapine content is listed (Thomas, Bruck, 1985) among the requirements for new rape cultivars. Brazil cultivars (Lajolo et al., 1991) possess particularly high content (3.4%) of sinapines. High variability in the sinapine content (0.15–0.55%) and of total phenolics (Maqbool et al., 1993) indicates the possibility of selecting low-polyphenol plants, or even seeds, for a further breeding programme.

Sinapine Content in Rapeseed

Compared to other oilseeds, rapeseed or mustard seed are particularly rich in phenolics, most of them being esterified with choline – this group is called sinapines, as mentioned, above the ratio of esterified phenolic acids in total phenolic acids is significantly lower in other oilseeds (Kozlowska et al., 1983). The data show that the content of esterified phenolic acids is more than ten times higher in seeds of rape and mustard. On the contrary, the contents of free phenolic acids and phenolic acids bound in water-insoluble derivatives were not very different from those in non-*Brassicaceae* oilseeds.

Results reported by Voškeruša and Kolovrat (1989) show that rapeseed possesses sinapine contents (determined spectrophotometrically at 330 nm) close to those of other seeds of the same subfamily. The following amounts were reported (expressed in mmol/kg): winter rape (*Brassica napus* L. f. *biennis*): high-erucic: 53.40–59.25 (mean: 55.92), zero-erucic: 56.41–71.26 (mean: 66.01), double-low: 50.12–80.15 (mean: 66.70), and in summer rape (*Brassica napus* L. f. *annua*): 52.95–74.25 (mean: 61.37) and double-low: 50.73–76.10 (mean: 66.30) mustard (*Sinapis alba* L.): 25.80–57.00 (mean: 46.00), *Brassica juncea* Czern. et Coss.: 47.10, *Brassica carinata*: 49.25, *Brassica campestris* L. f. *biennis*: 42.70, *Brassica campestris* L. f. *annua*: 43.60–49.42, *Raphanus sativus* L.: 60.35–74.40, *Brassica napus* L. var. *napobrassica*: 51.15–61.78. In a single cultivar of double-low rapeseed (66 samples), the content of sinapines varied between 44.05 and 90.85 mmol in 1 kg of defatted meal, which is rather high variability. Differences

I. Comparison of sinapine contents in individual plants of different rapeseed cultivars [%], adapted after Clausen et al., 1985

Rapeseed species investigated	Cultivar investigated	Concentration range [%]	Mean value [%]
B. campestris	Candle	0.39–0.76	0.62
	Tobin	0.57–0.69	0.65
B. napus	Gulliver	0.72–0,94	0.80
	Altex	0,62—0.77	0.70
	Erglu	0.74—0.90	0.81
	Line	0.79—1.06	0.86
	Karat	0.81—0.98	0.88
	Mary	0.69—0,83	0.77
	Regent	0.74—0.84	0.79
	Tower	0.72—0.79	0.75

between particular cultivars and between different plants of the same cultivar (Clausen et al., 1985a, b) are shown in Table I.

While the content of sinapines only moderately differs (if average contents of larger series of samples are compared) in different types of rapeseed cultivars (high-erucic, zero-erucic, double-zero), it is substantially lower in yellow-hull cultivars compared to dark-hull cultivars (Zadernowski, 1987), as shown in Table II. Influences of the cultivar and of the locality were reported by Mueller et al. (1978). Shahidi and Naczk (1992) reviewed the literature on the sinapine content. High content given by some authors, e.g. between 2–3% (Blair, Reichert, 1984) or even more may be caused by the analytical method used.

II. Comparison of phenolics content in different types of rapeseed flours (mmol/kg), adapted after Zadernowski (1987)

Type of rapeseed analyzed	Rapeseed cultivar analyzed	Free phenolic acids	Esterified phenolic acids	Glycosidic phenolic acids	Insoluble bound phenolic acids	Total phenolic acids
High erucic	Gorczaski	10.90	62.75	0.49	0.56	74.70
	Skrzeszowicki	9.82	64.18	0.56	0.72	75.28
Low erucic	Bronowski	10.70	58.10	0.57	0.70	70.07
Zero erucic	Beryl	10.59	63.12	0.50	0.67	74.88
	Brink	10.85	58.12	0.55	0.68	70.20
	Jet neuf	11.85	61.47	0.45	0.71	74.48
Double zero	Start	12.93	54.15	0.65	0.75	68.48
	Jantar	12.12	56.30	0.51	0.79	69.72
	BKH-180	8.70	62.98	0.57	0.71	72.96
Yellow hulls	Candle	15.33	47.20	0.56	0.68	63.78
	Yellow sarson	0.73	38.86	0.16	0.46	40.21

The content of sinapines is only low in green seeds, but the absolute content of both phenolics and of the choline-esterified fraction increases during the ripening (Table III) as reported for two rapeseed cultivars (Rotkiewicz et al., 1987). More than 90% total phenolics turn into their choline esters in ripe seeds (Rotkiewicz et al., 1987).

III. Changes of phenolics during the ripening of rapeseed (variety Start, expressed in mg/g, adapted after Rotkiewicz et al., 1987)

Date of harvesting	Soluble in diethyl ether	Water soluble, total	Sinapine (ester-bound)	Total phenolics
20. 06.	0.41	2.50	0.60	2.91
23. 06.	0.49	2.90	0.72	3.39
26. 06.	0.56	3.10	1.10	3.63
29. 06.	0.70	3.50	1.30	4.20
02. 07.	0.98	4.30	2.53	5.28
05. 07.	2.68	8.60	5.50	11.28
08. 07.	3.24	9.20	6.80	12.44
11. 07.	3.19	13.80	10.53	16.99
14. 07.	2.58	17.40	11.35	19.98
17. 07.	2.56	17.30	12.02	19.86
20. 07.	2.60	18.20	14.10	20.80
23. 07.	2.73	18.10	13.85	20.83
26. 07.	2.84	18.10	13.90	20.94
29. 07.	2.82	18.20	14.10	21.02

Phenolic Acids Bound in Sinapines

The composition of phenolic acids bound in sinapines isolated from rapeseed flour is shown in Table IV (Kozlowska et al., 1983). They confirmed older results from the same laboratory (Krygier et al., 1982). The ester fraction consists mainly of ester of (*E*)-sinapic acid, followed by (*Z*)-sinapic acid. The content of these two esters exceeds 80% total phenolic acids esterified with choline. The content was in agreement with older results on different Polish cultivars (Rotkiewicz et al., 1976). The compositions of free phenolic acids and of insoluble compounds were distinctly different. Cinnamic and caffeic acids were not bound to choline.

On the contrary, sinapines isolated from mustard seed and extracted mustard meal consisted mainly of esterified p-hydroxybenzoic acid (Kozlowska et al., 1983).

IV. Phenolic acids in rapeseed flour (adapted after Kozlowska et al., 1983)

Phenolic acid	Free phenolic acids (mg/kg)	Esterified phenolic acids (mg/kg)	Insolubly bound phenolic acids (mg/kg)
Salicylic	1–31	7–10	1–3
Cinnamic	trace–10	–	–
p-Hydroxybenzoic	0–22	trace–27	0–trace
Vanillic	trace–9	trace–12	0–1
Gentisic	trace–8	trace–9	–
o-Coumaric	3–11	–	3–4
Protocatechuic	4–14	trace–18	–
Syringic	1–24	trace–23	1–2
p-Coumaric	trace–30	trace–8	7–8
cis-Caffeic	–	trace–21	–
cis-Sinapic	32–101	445–989	6–7
trans-Ferulic	9–47	8–79	5–9
trans-Caffeic	trace–18	0–trace	–
trans-Sinapic	35–516	1713–5971	7–20
Total	119–718	2224–7000	31–50

Zadernowski (1987) identified 13 phenolic acids from the benzoic and cinnamic acid series, 85% bound in sinapines, while the rest was free or bound in glycosides. The fraction of total phenolic acids consisted from 55% of sinapic acid.

The composition of phenolic acids in sinapines should be studied in more detail as the antioxidant activity of sinapines depends mainly on the phenolic acid bound in the ester. In such oxylabile substrates as rapeseed oil, it would be useful to consider the possibility of stabilization of residual lipids in extracted meals by phenolics present.

Tannins and Other Non-sinapine Phenolics in Rapeseed

The tannin content was found only rather low (between 0.1–0.2%) in Canadian rapeseed (Mitaru et al., 1982) and in Czech rapeseed (Pokorný et al., 1994), while 0.45–0.62% tannins were found in turnip rapeseed (*Brassica campestris* L.)

collected in Nepal (Deitz, King, 1987). Higher amounts of phenolics were found in tropical rapeseed samples (Bibi et al., 1991), and various procyanidines, proanthocyanidines and flavan-4-ols were reported. The content of non-sinapine phenolics was rather high in our latest experiments with Polish rapeseed and rapeseed extracted meal (Réblová et al., 1994).

The level of tannins obviously depends very much on the analytical method used, and more results should be collected in future, with use of HPLC. The content of tannins was discussed in the case of Canola and Canadian rapeseed (Shahidi, Nack, 1992).

Distribution of Sinapines in the Seed

Phenolics are not evenly distributed in seed. We demonstrated (Pokorný et al., 1994) that sinapines were mainly concentrated in kernels, while their content in hulls was much lower. Tannins were present at higher amounts in hulls, in conformity with the literature (Leung et al., 1971). They are bound (in turnip rapeseed hulls) to various carbohydrates, at least partially (Theander et al., 1977). Tannins isolated from Canola hulls (Mitaru et al., 1983) had no deleterious effect on the nutritive value of the hulls in broiler chickens, which is rather surprising, and should be confirmed by other experiments. In tropical rapeseeds, hulls were lower in sinapine, tannic acid and total phenolics, but contained higher levels of some classes of condensed tannins (Bibi et al., 1991).

Yellow seeds contain less phenolics generally, therefore their hulls are obviously preferable as low-phenolic material as well. For human nutrition, yellow-hull seeds are considered as the only suitable material.

The progress of dry classification of ground seeds allows to consider the dehulling as a commercially feasible process. Therefore much more attention should be paid to the distribution of phenolics in rape and other *Brassicaceae* oilseeds. The rapeseed proteins are a very valuable source of nutrients, and if the fractionation improved the composition of extracted rapeseed meal, it would be possible to use rapeseed as the equivalent of soybeans for human nutrition.

Effect of Tannins and Other Phenolics on the Nutritive Value

Rapeseed tannins consist of flavonol glycosides and various other related substances. Glycosides of sinapoylkaempferol were identified in both *Brassica* and *Sinapis* species (Durkee, Harborne, 1973). Glucose and sophorose were bound in these glycosides (Tantawy et al., 1983).

Tannins and phenolic acids present in extracted rapeseed meal react with proteins, decreasing the nutritive value for chickens (Yapar, Clandinin, 1972; Clandinin, Heard, 1968).

The effect of sinapines was tested in experiments with rats (Larsen et al., 1983). Choline esters were decomposed in the digestive system of rats, without substantially affecting the nutritive value. The low content of tannins in rapeseed was not found to decrease the nutritive value, particularly the nutritive value of proteins in poultry (Blair, Reichert, 1984).

Effect of Sinapines Fed to Laying Hens on the Taint of Egg Yolk

The chief interest of food technologists concerning sinapines is based on their contribution to the fishy off-flavour of egg-yolk of brown-shelled eggs of laying hens fed rapeseed extracted meal. It is found only in brown eggs, and in cases when larger amounts of rapeseed meal were fed to laying hens. It was first recorded in 1928 (Curtis et al., 1978). If the content of sinapines exceeds 1 g/kg of the ration, fishy odour in eggs appeared (Goh et al., 1979a). Fishy or crabby off-flavour was detected in about 10% eggs (Curtis et al., 1979). The fishy taint was perceived when the trimethylamine content was high in egg yolk (Goh et al., 1985), for instance, if it exceeded 1 mg/kg (Fenwick et al., 1980), and was obviously connected with the consumption of rapeseed meal containing sinapine (Hobson-Frohock et al., 1977; Pearson et al., 1980). Feeding sinapine bisulphate caused 57% fishy eggs, but feeding choline bisulphate had no effect on the production of fishy taint (Goh et al., 1979b). Under normal conditions, trimethylamine liberated from choline is oxidized by hepatic trimethylamine oxidase into trimethylamine oxide (Pearson et al., 1979). Sinapine seems to inhibit trimethylamine oxidase (Curtis et al., 1979), but other substances present in rapeseed have similar effect, e.g. vinyloxazolidine thione (Fenwick et al., 1980; Goh et al., 1983), which is the major degradation product of rapeseed glucosinolates. Hens containing high trimethylamine oxidase activities are particularly affected (Fenwick et al., 1980).

For this reason, several attempts were made to reduce the tainting potential of rapeseed extracted meal (Fenwick et al., 1979).

Processes to Reduce the Sinapine Content of Extracted Rapeseed Meal

It was found difficult to improve the nutritive value of extracted rapeseed meal by modifying the rapeseed processing. Two methods have been proposed, namely, the dehulling and the toasting (Bille et al., 1983), and it was recommended to improve the rapeseed composition rather by breeding.

The ethanol extraction combined with hydrothermical treatment could reduce the concentration of phenolics (Kozlowska et al., 1991). We have found (Réblová et al., 1994) that the extrusion cooking reduced the content of sinapines only insignificantly. The microbial degradation of phenolic compounds improved the

digestibility of canola flour (Lacroix et al., 1989). Several microorganisms of *Pseudomonas* and *Rhodotorula* species were found effective. The partial acetylation of extracted canola meal with acetanhydride reduced the level of free phenolic acids and the production of free phenolic acids by hydrolysis of choline esters (Ponnampalam et al., 1987), but it has found no commercial application yet.

The treatment of rapeseed meal with calcium hydroxide decreased the content of sinapines (Fenwick et al., 1979, 1984), tannins and progoitrin, but could not entirely prevent the tainting of eggs. A suitable extraction process with slightly acidic aqueous solvents resulted in the production of non-toxic and tasteless protein isolate (Owen et al., 1971). Most phenolic acids were detected in the aqueous extract (Lo, Hill, 1972). Most glucosinolates and large part of phenolics were removed by extraction of canola meals with a mixture of ammonia with methanol and hexane (Diosady et al., 1985). Another procedure using ammonium carbonate reduced the sinapine content as well (Schwenke et al., 1990). Another process of double-phase extraction of rapeseed with 10 % ammonium hydroxide and hexane produced rapeseed meal with reduced contents of both glucosinolates and phenolics (Naczk et al., 1988).

Future Trends

Sinapines belong to undesirable antinutritional compounds in *Brassicaceae* seeds, particularly in rapeseed. They decrease the acceptability of extracted oilseed meals, their nutritive value, and may impart fish taint to eggs of brown-egg laying hens. It is expensive and difficult to remove sinapines when once present. The optimum solution would be to reduce the sinapine content by breeding.

References

APPELQVIST, L. A.: Composition of seeds of cruciferous oil crops. J. Am. Oil Chem. Soc., *48*, 1971: 851–859.

BIBI, N. – SATTAR, A. – CHAUDRY, M. A.: Phenolic constituents in major fractions of typical rapeseed. Nahrung, *35*, 1991: 1053–1059.

BILLE, N. – EGGUM, B. O. – JACOBSEN, I. – OLSEN, O. – SOERENSEN, H.: The effects of processing on antinutritional constituents and nutritive value of double low rapeseed meal. Z. Tierphysiol. Tierernaehr. Futtermittelkunde, *49*, 1983: 148–163.

BLAIR, R. – REICHERT, R. D.: Carbohydrate and phenolic constituents in a comprehensive range of rapeseed and canola fractions: Nutritional significance for animals. J. Sci. Food Agr., *35*, 1984: 29–35.

BOUCHEREAU, A. – HAMELIN, J. – LAMOUR, I. – RENARD, M. – LARHER, F.: Distribution of sinapine and related compounds in seeds of *Brassica* and allied genera. Phytochem., *30*, 1991: 1873–1881.
CLANDININ, D. R.: Effect of sinapine, the bitter substance in rapeseed or meal, on the growth of chickens. Poultry Sci., *40*, 1961: 384–387.
CLANDININ, D. R. – HEARD, J.: Tannins in prepress–solvent and solvent–processed rapeseed meal. Poultry Sci., *47*, 1968: 688–691.
CLAUSEN, S. – LARSEN, L. M. – PLOEGER, A. – SOERENSEN, H.: Aromatic choline esters in rapeseed. World Crops, *11*, 1985a: 61–72.
CLAUSEN, S. – LARSEN, L. M. – PLOEGER, A. – SOERENSEN, H.: Aromatic choline esterase and catabolism of aromatic choline esters. Proc. Semin. CEC Progr. Res. Plant Prot. Improv., Copenhagen, 1984 Adv. Prod. Util. Cruciferous Crops, 1985b: 138–147.
CORNELIUS, J. A. – SIMMONS, E. A.: *Crambe abyssinica* – a new commercial oilseed. Trop. Sci., *11*, 1969: 17–22.
CURTIS, R. F. – FENWICK, G. R. – HOBSON–FROHOCK, A. – HEANEY, R. – LAND, D. G.: Fishy taints in eggs. Int. Congr. Food Sci. Technol., Abstr., 1978: 291.
CURTIS, F. – FENWICK, R. – HEANEY, R. – HOBSON–FROHOCK, A. – LAND, D.: Rapeseed meal and egg taint. Proc. Fifth Int. Rapeseed Conf., *2*, 1979: 300–302.
DEITZ, H. M. – KING, R. D.: Characterization of rapeseed (*Brassica campestris*) from Nepal and evaluation of processing methods. Trop. Sci., *27*, 1987: 147–153.
DIOSADY, L. L. – NACZK, M. – RUBIN, L. J.: The effect of ammonia concentration on the properties of Canola meals produced by the ammonia-methanol/hexane extraction system. Food Chem., *18*, 1985: 121–130.
DURKEE, A. B. – HARBORNE, J. B.: Flavonol glycosides in *Brassica* and *Sinapis*. Phytochem., *12*, 1973: 1085–1089.
DURKEE, A. B. – THIVIERGE, P. A.: Bound phenolic acids in *Brassica* and *Sinapis* oilseeds. J. Food Sci., *40*, 1975: 820–822.
FENWICK, G. R. – BUTLER, E. J. – PEARSON, A. W.: Rapeseed meal and egg taint – the current situation. Poultry Sci., *19*, 1980: 128.
FENWICK, G. R. – CURL, C. L. – PEARSON, A. W. – BUTLER, E. J.: The treatment of rapeseed meal and its effect on chemical composition and egg tainting potential. J. Sci. Food Agr., *35*, 1984: 757–761.
FENWICK, G. R. – HOBSON–FROHOCK, A. – LAND, D. G. – CURTIS, R. F.: Rapeseed meal and egg taint: treatment of rapeseed meal to reduce tainting potential. Brit. Poultry Sci., *20*, 1979: 323–329.
GOH, Y. K. – CLANDININ, D. R. – ROBBLEE, A. R. – DARLINGTON, K.: The effect of level of sinapine in a laying ration on the incidence of fishy odor in eggs from brown-shelled egg layers. Canad. J. anim. Sci., *59*, 1979a: 313–316.
GOH, Y. K. – MUELLER, M. M. – CLANDININ, D. R. – ROBBLEE, A. R.: The effects of choline and sinapine bisulfate in a laying ration on the incidence of fishy

odor in eggs from brown-shelled egg layers. Canad. J. anim. Sci., *59*, 1979b: 545–549.

GOH, Y. K. – ROBBLEE, A. R. – CLANDININ, D. R.: Influence of glucosinolates and free oxazolidinethione in a laying diet containing a constant amount of sinapine on the trimethylamine content and fishy odor of eggs from brown-shelled egg layers. Canad. J. anim. Sci., *63*, 1983: 671–676.

GOH, Y. K. – ROBBLEE, A. R. – CLANDININ, D. R.: Influence of glucosinolates and free oxazolidinethione in a laying diet containing a constant amount of sinapine on the thyroid size and hepatic trimethylamine oxidase activity of brown-egg layers. Canad. J. anim. Sci., *65*, 1985: 921–927.

HOBSON–FROHOCK, A. – FENWICK, G. R. – HEANLEY, R. K. – LAND, D. G. – CURTIS, R. F.: Rapeseed meal and egg taint: association with sinapine. Brit. Poultry Sci., *18*, 1977: 539–541.

ISMAIL, F. – VAISEY-GENSER, M. – FYFE, B.: Bitterness and astringency of sinapine and its components. J. Food Sci., *46*, 1981: 1241–1244.

KARIG, F.: TAS-Verfahren zur Analyse der Inhaltsstoffe von Senfsamen. J. Chromatogr., *106*, 1975: 477–480.

KERBER, E. – BUCHLOH, G.: Sinapingehalte in Speisesenf. Z. Lebensm.–Unters.-Forsch., *171*, 1980: 355–356.

KOZLOWSKA, H. – ROTKIEWICZ, D. A. – ZADERNOWSKI, R. – SOSULSKI, F. W.: Phenolic acids in rapeseed and mustard. J. Am. Oil Chem. Soc., *60*, 1983: 1119–1123.

KOZLOWSKA, H. – ZADERNOWSKI, R. – NOWAK, H. – PISULA, M.: The influence of selected technological processes on the improvement of rapeseed meal and feed quality. I. The influence of hydrothermal treatment and ethanol extraction on chemical composition of rapeseed products. Nahrung, *35*, 1991: 485–489.

KRYGIER, K. – SOSULSKI, F. – HOGGE, L.: Composition of phenolic acids in rapeseed flour and hulls. J. agr. Food Chem., *30*, 1982: 334–336.

LACROIX, M. – AMIOT, J. – NOUE, J., de la – BRISSON, G. J. – LACHANCE, O.: Microbial degradation of phenolic compounds extracted from canola flour. Microbiol., Alim., Nutr., *7*, 1989: 239–249.

LAJOLO, F. M. – LANFER-MARQUEZ, U. M. – FILISETTI-COZZI, T. M. C. C. – McGREGOR, D. I.: Chemical composition and toxic compounds in rapeseed (*Brassica napus* L.). J. agr. Food Chem., *39*, 1991: 1933–1937.

LARSEN, L. M. – OLSEN, O. – PLOEGER, A. – SOERENSEN, H.: Phenolic choline esters in rapeseed: Possible factors affecting nutritive value and quality of rapeseed meal. Proc. Sixth Int. Rapeseed Conf., Paris, *1*, 1983: 1577–1582.

LEUNG, J. – FENTON, T. W. – MUELLER, M. M. – CLANDININ, D. R.: Condensed tannins of rapeseed meal. J. Food Sci., *44*, 1979: 1313–1316.

LO, M. T. – HILL, D. C.: Composition of the aqueous extracts of rapeseed meals. J. Sci. Food Agric., *23*, 1972: 823–830.

MAQBOOL, A. – BADSHAH, A. – CHAUDHRY, M. A.: Phytic acid, polyphenols and potential nutrients in *Brassica* seeds. Pakistan J. sci. ind. Res., *36*, 1993: 23–26.
MITARU, B. N. – BLAIR, R. – BELL, J. M. – REICHERT, R. D.: Tannin and fiber contents of rapeseed and canola hulls. Canad. J. anim. Sci., *62*, 1982: 661–663.
MITARU, B. N. – BLAIR, R. – REICHERT, R.: Effect of canola hulls on growth, feed, efficiency, and protein and energy utilization in broiler chickens. Canad. J. anim. Sci., *63*, 1983: 655–662.
MUELLER, M. M. – RYL, E. B. – FENTON, T. – CLANDININ, D. R.: Cultivar and growing location differences in the sinapine content of rapeseed. Canad. J. anim. Sci., *58*, 1978: 579–583.
NACZK, M. – SHAHIDI, F. – RUBIN, L.: A new extraction process for rapeseed: a review. Rev. fr. Corps gras, *35*, 1988: 3–6.
NOWAK, H. – KUJAWA, K. – ZADERNOWSKI, R. – ROCZNIAK, B. – KOZLOWSKA, H.: Antioxidative and bactericidal properties of phenolic compounds in rapeseeds. Fett-Wiss.-Technol., *94*, 1992: 149–152.
OWEN, D. F. – CHICHESTER, C. O. – GRANADINO, C. J. – MOENCKEBERG, B. F.: A process for producing nontoxic rapeseed protein isolate and an acceptable feed byproduct. Cereal Chem., *48*, 1971: 91–96.
PEARSON, A. W. – BUTLER, E. J. – CURTIS, F. – FENWICK, G. R. – HOBSON-FROHOCK, A. – LAND, D. G.: Effect of rapeseed meal on hepatic trimethylamine oxidase activity in the domestic fowl in relation to egg taint. J. Sci. Food Agr., *30*, 1979: 291–298.
PEARSON, A. W. – BUTLER, E. J. – FENWICK, G. R.: Rapeseed meal and egg taint: the role of sinapine. J. Sci. Food Agr., *31*, 1980: 898–904.
POKORNÝ, J. – SVOBODA, Z. – KÁŇOVÁ, J. – RÉBLOVÁ, Z. – FARNÍKOVÁ, L.: Phenolic and other antinutritional substances in rapeseed and their changes during dehulling. EUROFOOD TOX IV Conf., Olsztyn, 1994.
PONNAMPALAM, R. – VIJAYALAKSHMI, M. A. – LEMIEUX, L. – AMIOT, J.: Effect of acetylation on composition of phenolic acids and proteolysis of rapeseed flour. J. Food Sci., *52*, 1987: 1552–1556.
RÉBLOVÁ, Z. – FARNÍKOVÁ, L. – PISKAČOVÁ, J. – POKORNÝ, J.: Changes of glucosinolates and other antinutritional substances in rapeseed-legume mixtures during heat treatment. COSEMI 93/4 Conf., Wageningen, 1994.
ROTKIEWICZ, D. – KOZLOWSKA, H. – WIATEK, L.: Zwiazki fenolowe w niektórych odmianach rzepaków (*B. napus*) uprawianych w Polsce. Hodowla Roślin Aklim. Nasien., *20*, 1976: 447–454.
ROTKIEWICZ, D. – KOZLOWSKA, H. – ZADERNOWSKI, R. – BUDZYSŃKI, W. – HORODYSKI, A.: Zmiany zawartości zwiazków fenolowych i fityn podczas rozwoju i dojrzewania nasion rzepaku. Acta Acad. agr. Techn. olsten., Technol. Alim., *21*, 1987: 153–163.

SATTAR, A. – BIBI, N. – CHAUDRY, M. A.: Phenolic compounds in persimmon during maturation and on–tree ripening. Nahrung, *36*, 1992: 466–472.
SCHWENKE, K. D. – KROLL, J. – LANGE, R. – KUJAWA, M. – SCHNAAK, W. – STEINERT, A.: Preparation of detoxified high functional rapeseed flours. J. Sci. Food Agr., *51*, 1990: 391–405.
SHAHIDI, F. – NACZK, M.: An overview of the phenolics of canola and rapeseed: Chemical, sensory and nutritional significance. J. Am. Oil Chem. Soc., *69*, 1992: 917–924.
SMYK, B. – DRABENT, R.: Spectroscopic investigation of the equilibria of the ionic forms of sinapic acid. Analyst, *114*, 1989: 723–726.
SOSULSKI, F.: Organoleptic and nutritional effects of phenolic compounds on oilseed protein products: a review. J. Am. Oil Chem. Soc., *56*, 1979: 711–715.
TANTAWY, B. – ROBIN, J. P. – TOLLTER, M. T.: Caractérisation de deux glycosides acylés du kaempférol dans les extraits éthanoliques des tourteaux de colza "0-thio". Proc. Sixth Int. Rapeseed Conf., Paris, *1*, 1983: 1313–1320.
THEANDER, O. – AMAN, P. – MIKSCHE, G. E. – YASUDA, S.: Carbohydrates, polyphenols, and lignin in seed hulls of different colors from turnip rapeseed. J. Agr. Food Chem, *25*, 1977: 270–273.
THOMAS, A. – BRUCK, C. G., vom: Forderungen der Lebensmitelindustrie an neue Rapssorten. Fette, Seifen, Anstrichmittel, *87*, 1985: 460–463.
VANGHEESDAELE, G. – FOURNIER, N.: Chemical composition of *Brassica juncea* used for making Dijon mustard. Rev. fr. Corps gras, *27*, 1980: 15–22.
VOŠKERUŠA, J. – KOLOVRAT, O.: Obsah sinapinu v semeni brukvovitých olejnin. Rostl. Výr., *35*, 1989: 1087–1093.
YAPAR, Z. – CLANDININ, D. R.: Effect of tannins in rapeseed meal on its nutritional value for chicks. Poultry Sci., *51*, 1972: 222–228.
ZADERNOWSKI, R.: Studia nad zwiazkami fenolowymi mak rzepakowych i rzepikowych. Acta Acad. Agr. Techn. Olsten., *21F*, 1987: 3–55.
ZADERNOWSKI, R. – KOZLOWSKA, H. – SOSULSKI, F. W.: Determination of sinapine as a compound responsible for a taste of rapeseed flour. Int. Symp. Flavour Res. Concepts Meth., Rydzyna, 1981.

Sinapiny a jiné fenolické látky v semenech čeledi *Brassicaceae*

V semenech rostlin čeledi brukvovitých jsou přítomny estery kyseliny sinapové a příbuzných fenolických kyselin s cholinem, které se nazývají sinapiny. Jsou příčinou vysokého obsahu fenolických látek v olejninách z čeledi brukvovitých (hlavně řepky olejné), způsobují hořkost těchto semen i extrahovaných škrobů a vedou i k nestabilitě barvy. Jejich obsah velice kolísá v závislosti na druhu, ale i na odrůdě a kul-

tivačních podmínkách. Asi 80 % vázaných kyselin tvoří kyseliny sinapové (oba stereoizomery), dále jsou přítomny další kyseliny řady skořicové i benzoové. Kromě sinapinů je v těchto semenech přítomno i menší množství taninů, volných kyselin a dalších fenolických derivátů. Zatímco sinapiny jsou hlavně obsaženy v jádrech, třísloviny jsou spíše koncentrovány ve slupkách. Fenolické látky snižují nutriční hodnotu bílkovinného podílu a u nosnic snášejících hnědá vejce mohou způsobovat rybí pach. Proto se vyskytlo několin návrhů na snížení obsahu sinapinů, hlavně extrakcí alkalickými roztoky nebo alkoholy, nejvhodnější je však vyšlechtit nové odrůdy se sníženým obsahem sinapinů.

Contact address:

Prof. ing. Jan Pokorný, DrSc., Vysoká škola chemicko-technologická,
Ústav chemie a analýzy potravin, Technická 5, 166 28 Praha 6, Česká republika,
tel.: 02/2435 3264, fax: 02/311 99 90

Instructions for authors

Manuscripts in duplicate should be addressed to: RNDr. Marcela Braunová, Ústav zemědělských a potravinářských informací, Slezská 7, 120 56 Praha 2, Czech Republic.

Authors have full responsibility for the contents of their papers, including any correction made by the editors. The board of editors of this journal will decide on paper publication, with respect to expert opinions, scientific importance, contribution and quality of the paper.

Original papers should not consist of more than 12 typewritten pages (2-linespacing), short communications may not exceed 3 typewritten pages. Tables, figures and photos shall be enclosed separately. The text must contain references to all these annexes.

Abstract is an information selection of the contents and conclusions of the paper, it is not a mere description of the paper. It must present all substantial information contained in the paper. It shall not exceed 170 words. It shall be written in full sentences, not in form of keynotes. It is published in the language the paper is written in, it should comprise base numerical data including statistical data. Each manuscript must contain a short or a longer summary.

Introduction has to present the main reasons why the study was conducted, and the circumstances of the studied problems should be described in a very brief form.

Material and Methods: Only original method shall be described, in other cases it is sufficient enough to cite the author of the used method and to mention modifications of this method. This section shall also contain a description of experimental material.

In the section **Results** figures and graphs should be used rather than tables for presentation of quantitative values. The same data should not be presented in both tables and figures. A statistical analysis of recorded values should be summarized in tables. This section should not contain either theoretical conclusions or deductions, but only factual data should be presented here.

Discussion contains an evaluation of the study, potential shortcomings are discussed, and the results of the study are confronted with previously published results (only those authors whose studies are in closer relation with the published paper should be cited).

The **citations** shall be presented pursuant to the standard. They are arranged alphabetically according to the surname of the first author. References in the text to these citations comprise the author's name and year of publication. Only the papers cited in the text of the study shall be included in the list of references. All citations shall be referred to in the text of the paper.

If any abbreviation is used in the paper, it is necessary to mention its full form at least once to avoid misunderstanding. The abbreviations should not be used in the title of the paper nor in the summary.

The author shall give his full name (and the names of other collaborators), academic, scientific and pedagogic titles, full address of his workplace and postal code, telephone and fax number.

OBSAH – CONTENTS

PŘEHLEDY – REVIEWS

Vědecký časopis POTRAVINÁŘSKÉ VĚDY ◆ Vydává Česká akademie zemědělských věd – Ústav zemědělských a potravinářských informací, Praha ◆ Redakce: Slezská 7, 120 56 Praha 2, tel.: 02/251 098, fax: 02/257 090 ◆ Sazba a tisk: ÚZPI Praha ◆

Rozšiřuje Ústav zemědělských a potravinářských informací, referát odbytu, Slezská 7, 120 56 Praha 2