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ACRYLAMIDE IN COMMERCIAL POTATO CHIPS FROM WARSAW MARKET

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Acrylamide contents of 32 samples of commercial potato chips, purchased from January 2004 till April 2005 on the local market were determined. The concentrations of acrylamide in chips ranged from 380 μg/kg to 861 μg/kg and fitted to the data reported in recent literature.

INTRODUCTION

In April 2002, scientists from the Swedish National Food Administration and Stockholm University announced, at a press conference, the finding of wide range (30–2300 μg/kg) of acrylamide contents in some foods. Shortly after that, the presence of acrylamide in similar foods was confirmed (some contents of acrylamide reached up to 12000 μg/kg) by researchers from Canada, USA and some West European countries [JIFSAN/NCFST, 2002; DHHS/FDA/CFSAN, 2002]. It became clear that the presence of acrylamide in foods was not caused by contamination, but that it is an inherent property of carbohydrate-rich food formed by frying, baking, grilling, roasting *etc*.

The public opinion and even some scientists were shocked. It was known for years that toxic acrylamide and its degradable polymers and copolymers were widely used in industrial applications (cement binder, paper and textiles production, flocculants in waste-water treatment, soil conditioners, cosmetics and toiletries, and laboratory gels) and can appear in tobacco smoke. In common opinion, the threat could come from inhalation, smoking or by skin but not from food. The information about the potential risk of food-borne acrylamide not only alerted regional health and food organisations but also inspired research activities. Starting since half of 2002 papers have been published on the determinations of acrylamide in foods and on new developments in analytical procedures [DHHS/FDA/CFSAN, 2002; JIFSAN/NCFST, 2002; Tareke *et al*., 2002]. Later on, more basic investigations on the mechanisms and conditions of acrylamide formation in foods [Bęcalski *et al*., 2003; Friedman, 2003; Yaylayan *et al*., 2003; Zyzak *et al*., 2003, Matthaus *et al*., 2004] were performed. Then papers on reduction of acrylamide content in food by agricultural, dietary and technological procedures were published as well [Amrein *et al*., 2003, 2004; Brathen *et al*., 2005; Fiselier & Grob, 2005; Grob *et al*., 2003; Kita *et al*., 2004; Pedreschi *et al*., 2004; Taubert *et al*., 2004]. A new light was also cast on the toxicological studies into the acrylamide in bulk and in food [Report FAO/WHO Consultation, 2002; Rosen, 2002]. It has been shown in numerous reports [DHHS/FDA/CFSAN, 2002; EUC/SFC, 2002] that fried potato products (French fries, chips/crisps, baked potatoes) contain the highest, among foods, quantities of acrylamide.

Literature reviews have shown that among the papers published there were no reports on analyses and acrylamide contents in foods produced and sold in Poland. It was the purpose of this work to perform a long-term study (January 2004 – April 2005) based on screening acrylamide content in potato chips from the local market.

MATERIALS AND METHODS

Chips sampling. Every month, since January 2004 till April 2005, several bags of potato chips produced by two big producers, one coded CCCh and second FLCh, were purchased at a local supermarket. Directly after the purchase, the mean samples of each kind of chips were prepared by roughly crushing (flakes about 5 × 5 mm). Next day the "wet procedures" were performed to prepare extracts for acrylamide determinations. Samples of extracts, ready for acrylamide determinations, were placed in glass ampoules that were sealed and covered with black paint. Each sample was coded using the following system: batch/producer code/ Roman number/year of analysis (2004 or 2005). There were four batches A, B and C, D for chips produced from 2003 and 2004 potato crops, respectively. Roman numerals (I–XII)

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denote calendar months of the year. The ampoules with solutions were stored in a refrigerator until 8 working samples (4 of each kind of chips) were collected. Then they were transferred to a GC-MS laboratory where acrylamide contents were determined.

Chemicals. Acrylamide (2-propene amide) for calibration of >99.5% purity was obtained from Sigma-Aldrich. As the internal standard, and for recovery measurements the 2,3,3-d3 acrylamide (98 % pure), obtained from Cambridge Isotope Laboratories was used. The Carrez–I and Carrez–II solutions for clarifications were prepared by solving 37.5 g $K_4[Fe(CN)_6]$ or 75 g of $ZnSO_4$ in 250 mL of water, respectively. Water was double distilled from a glass laboratory unit. Organic solvents used (ethyl acetate, hexane, heptane) were of analytical grade.

Acrylamide determination. About 10 g of crushed chips was milled in a laboratory mill. To the weighed sample (4.00 g) of chips powder 50 μL of internal standard (150 μg/mL) was added. Then the sample was extracted with water at 60°C for 3 h using an ultrasonic bath. Extract was centrifuged for 15 min at 2500 × g. The supernatant solution was defatted by hexane + heptane equal weights mixture and clarified by Carrez I and II solutions (5 mL of each). The precipitate was separated by centrifugation, acrylamide was salted with NaCl and extracted from aqueous phase by 4-fold extraction with 25 mL of ethyl acetate. Organic phases were filtered, collected and then evaporated under vacuum. Total volume of solution was adjusted to 1 mL with ethyl acetate and transferred into a glass ampoule. Each analytical batch included extra 1–2 spiked with deutered acrylamide samples for acrylamide recovery measurements.

The GC-MS analyses were carried out using the electrospray ionisation mode (EI, 70 eV). The Hewlett Packard GC 5890 Series II equipped with DB capillary column (30 mm × 0.25 mm i.d., 0.25 μm film thickness) and the Hewlett Packard MS 5989A were used. The carrier gas was helium at a flow rate of 1.0 mL/min. The temperature programme was: initial 80°C for 2 min, then 80°C → 220°C with 10°C/min increase, final temperature was held for 1 min. Injector and ion source temperatures were 240°C and 200°C, respectively. For the determination of acrylamide and deuterated acrylamide the selected ion monitoring technique (m/z, 71→55, 74→58) was used.

The significance of differences for the results obtained was estimated with an analysis of variance (at 0.05 significance level). The least significant differences (NIR) were calculated in accordance with the Tukey's test [Oktaba, 1986]. The results were also correlated with running months using the Microsoft Excel Programme.

RESULTS AND DISCUSSION

The results of acrylamide determinations in commercial potato chips sampled from January 2004 till April 2005 are listed in Table 1. Laboratory experiments with deuterated acrylamide showed that its recovery was at the level of 97±5%. The repeatability of acrylamide determinations in this study was ±25 μg/kg. The detection limit was about 50 μg/kg. The quantification above 200 μg/kg content is precise and can be used for screening purposes. As it can be seen from Table 1, the acrylamide contents of chips originating from both producers are alike. These contents (from 380 μg/kg to 861 μg/kg) fall into the range reported in literature and being rather on its lower edge. Acrylamide contents have also been reported in a selected group of food products purchased on the USA market [DHHS/FDA/CFSAN, 2002]. The contents of acrylamide in 40 samples of potato chips ranged from 117 μg/kg to 2763 μg/kg with an average content of 461 μg/kg. Tareke *et al*. [2002] reported the contents of acrylamide (1300 μg/kg to 3897 μg/kg; average 1739 μg/kg) in restaurant prepared and in purchased chips. Friedman [2003] lists the contents of acrylamide in various food products, for chips these contents are in the range of 170 μg/kg – 3700 μg/kg. Table 2 reports on the average con-

TABLE 1. Acrylamide content (μg/kg) in samples of commercial potato chips.

Batch and sample code	Acrylamide content (μg/kg)	Batch and sample code	Acrylamide content (μg/kg)
A/ CCCh/ I/ 2004	740	C/ CCCh/ IX/ 2004	380
A/ FLCh/ I/ 2004	528	C/ FLCh/ IX/ 2004	393
A/ CCCh/ II/ 2004	686	C/ CCCh/ X/ 2004	414
A/ FLCh/ II/ 2004	714	C/ FLCh/ X/ 2004	440
A/ CCCh/ III/ 2004	686	C/ CCCh/ XI/ 2004	425
A/ FLCh/ III/ 2004	664	C/ FLCh/ XI/ 2004	477
A/ CCCh/ IV/ 2004	706	C/ CCCh/ XII/ 2004	462
A/ FLCh/ IV/ 2004	734	C/ FLCh/ XII/ 2004	488
B/ CCCh/ V/ 2004	758	D/ CCCh/ I/ 2005	612
B/ FLCh/ V/ 2004	763	D/ FLCh/ I/ 2005	635
B/ CCCh/ VI/ 2004	808	D/ CCCh/ II/ 2005	586
B/ FLCh/ VI/ 2004	822	D/ FLCh/ II/ 2005	560
B/ CCCh/ VII/ 2004	846	D/ CCCh/ III/ 2005	622
B/ FLCh/ VII/ 2004	828	D/ FLCh/ III/ 2005	608
B/ CCCh/ VIII/ 2004	861	D/ CCCh/ IV/ 2005	716
B/ FLCh/ VIII/ 2004	847	D/ FLCh/ IV/ 2005	755

A, B, C, D – batches; 2004 and 2005 – years of analysis; I–XII calendar months

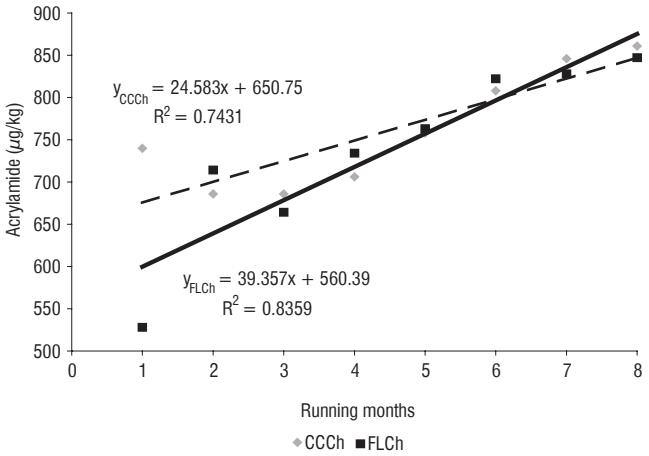

FIGURE 1. Acrylamide content (μg/kg) in chips produced in subsequent months of 2004 (potato crops 2003).

tents of acrylamide in chips produced from potato crops of 2003 and 2004. As indicated by NIR values, the differences in acrylamide contents in production series (2003 and 2004 potato crops) are negligible. It suggests that the production and quality of chips are stable. In spite of this, there are linear correlations, with high determination coefficients (R^2), between acrylamide contents and running months of production for both series (Figures 1 and 2). The calculated correlation coefficients between acrylamide contents in CCCh and FLCh chips produced in 2003 and 2004 accounted for 0.67 and 0.98, respectively. Amrein *et al*. [2004] reported data on

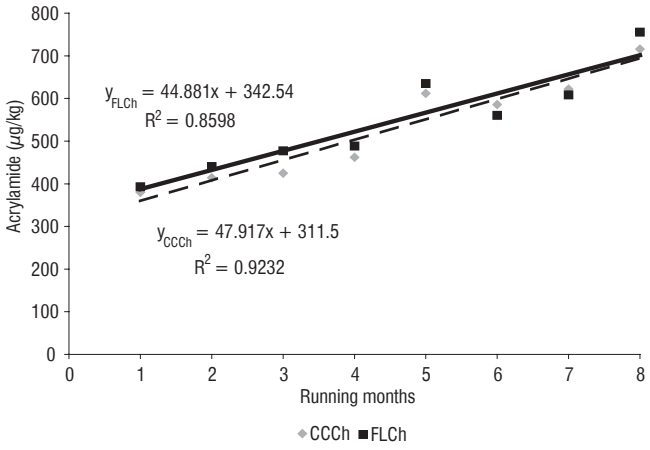

FIGURE 2. Acrylamide content (μg/kg) in chips produced in subsequent months of 2004/2005 (potato crops 2004).

reducing sugars (glucose + fructose), asparagine, glutamine, glutamic acid, aspartic acid and total free amino acids contents in more than 50 potato samples of 15 cultivars from the 2003 harvest. The potential for acrylamide formation (194 μg/kg – 3823 μg/kg) in those samples was also determined. It has appeared that reducing sugar content strongly correlated with acrylamide, whereas no correlation was found between acrylamide and free asparagine or the pool of free amino acids. Reducing sugar content of potatoes depends on the temperature of their storage and influences acrylamide formation during potatoes frying. Unfortunately detailed studies on storage temperature and acrylamide formation relationships are rather scarce [Fiselier *et al*., 2005]. As there was no information about the history of commercial chips production (time and temperature of frying) and potatoes used (asparagine and reducing sugars contents and storage regimes) no detailed discussion is possible. It is advisable to perform additional studies on acrylamide contents in fried potato products but they should be done in co-operation with food technologists and local producers.

CONCLUSIONS

Chips investigated in this work contained no excessive amounts (<861 μg/kg) of acrylamide. From this point of view chips were of high quality. When they are eaten occasionally there is no threat for consumers posed by food-borne acrylamide.

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TABLE 2. Mean acrylamide contents (μg/kg) in CCCh and FLCh chips produced from 2003 and 2004 potato crops.

Symbol	2003			2004		
	A	B	A & B	C	D	C & D
CCCh	704.5	818.3	761.4	420.3	634.0	527.1
FLCh	660.0	815.0	737.5	449.5	639.5	544.5
$NIR_{(\alpha=0.05)}$	117.7	71.6	95.9	66.8	123.0	129.1

A, B, C, D letters denote analytical batches as in Table 1; NIR = the least significant difference (calculated at α=0.05)

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AKRYLOAMID W HANDLOWYCH CHIPSACH ZIEMNIACZANYCH Z RYNKU WARSZAWSKIEGO

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Oznaczano zawartości akryloamidu w 32 próbkach chipsów ziemniaczanych produkowanych przez dwóch dużych krajowych producentów i sprzedawanych na rynku warszawskim. Chipsy do badań kupowano każdego miesiąca w okresie od stycznia 2004 do kwietnia 2005. Procedury analityczne wdrażano bezpośrednio po zakupie. Do oznaczeń wyekstrahowanego wodą akryloamidu z chipsów (odzysk 97±5%) zastosowano metodę GLC/MS w systemie EI, 70 eV. W oznaczeniach ilościowych akryloamidu i deuterowanego akryloamidu monitorowano jony: m/z = 71→55 i 74→58. Zawartość akryloamidu w chipsach obu producentów była podobna (od 380 μg/kg do 861 μg/kg, tab. 1.) i mieściła się w dolnej strefie danych literaturowych podawanych dla tego typu produktów. Powtarzalność oznaczeń sięgała ±25 μg/kg, a dolna granica detekcji około 50 μg/kg. Powyżej 200 μg/kg zawartości akryloamidu oznaczenia były ilościowe. Przeprowadzono analizę statystyczną uzyskanych wyników.