Changes of Acrylamide Levels in Food Products during Technological Processing

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Abstract: Acrylamide represents toxic compound presence of which in heat processed foodstuffs has been proven only recently. This chemical is of a great health concern since it is classified as a human carcinogen by the International Agency for Research on Cancer (IARC). Relatively high amounts of acrylamide have been found mainly in starch rich foods such as potato chips, French fries, roast potatoes, breakfast cereals and crisp bread. Concentrations of this hazardous substance in certain food products may reach up to several mg/kg, depending on the type of raw commodity and the way of its processing. Changes of acrylamide levels in potato chips during frying process were monitored in our study. New analytical procedure employing gas chromatography coupled with high resolution time of flight mass spectrometry (GC/HRTOF-MS) was developed for this purpose. The major factors that affect acrylamide levels in chips such as asparagine and reducing sugars (the main precursors of acrylamide) content in raw potatoes as well as the processing conditions setting (time and temperature) were monitored. Under experimental conditions we used, rapid formation of acrylamide occurred after 150 s, temperature of oil bath was approx. 140°C at that time. In overfried chips the levels of acrylamide exceeded 10 mg/kg.

Keywords: acrylamide; potato chips; high-resolution time-of-flight mass spectrometer; GC/MS; TOF

INTRODUCTION

Potato products (such as French fries and chips) are among dietary items containing the highest amounts of acrylamide that has been recently identified as food carcinogen. Maillard reaction is the main route of acrylamide formation [1]. Free amino acids, mainly asparagine, and reducing sugars have been shown as its important precursors in sugar-rich heat processed food. Processing conditions, such as time, temperature, water activity as well as matrix composition largely influence the kinetics of acrylamide formation and degradation [2]. It should be noted that also other reaction pathways are foreseen to be responsible for acrylamide formation. Intensive research is ongoing in this area [3].

As regards potato fries and chips, frying time and temperature are the most important technological parameters affecting acrylamide content in final product. Their influence was studied both in real samples [4] and model systems (equimolar mixture of asparagine and glucose) [5]. Both sets of experiments indicated that the temperature needed for formation of acrylamide is above 100°C. Under experimental conditions (temperature of oil bath 200°C) acrylamide content exponentially increased in the first phase of frying and then successive decrease of its amount was observed, probably because its degradation becomes predominant [4].

Acrylamide levels in potato products are also considerably affected by asparagine and reducing sugars content in raw material. Asparagine represents typically 40% of the total amino-acid content and its levels are about 10^3 mg/kg. Compared to this amino acid, concentrations of glucose and fructose vary largely ranging between 10^1 to 10^3 mg/kg.

The concentrations of reducing sugars are substantially influenced by storage temperature. Cold accumulation of sugars is a gradual process occurring at temperatures of less than 10°C. Along with temperature, cultivar is one of the most important factor in regulating the amount of reducing sugars in potatoes [6].

In the presented study, the dynamics of acrylamide formation in potato chips during technological processing was investigated.

EXPERIMENTAL

Materials. Acrylamide (99.8%) and acrylamide (2,3,3-D_3) (98%) were purchased from Sigma-Aldrich (Germany) and Cambridge Isotope Laboratories (USA), respectively.

Methods. Samples were homogenised using laboratory blender. 3 g of representative sample were weighed into a 45 ml centrifuge flask with a screw cap. After addition of 30 µl (50 µg/ml) of D_3-acrylamide (internal standard) and 4.5 ml of demineralised water sample was allowed to swell 30 min in ultrasonic bath held at 70°C. Homogenate was mixed 5 minutes with 24 ml of *n*-propanol by Ultra Turrax. Centrifugation (10 min at 6000 rpm) followed. 10 ml of supernatant were transferred into a 50 ml flask. 5 drops (about 60 mg) of a vegetable oil were added and the water/propanol azeotropic mixture was removed by rotary evaporator. The residue left on the wall of flask was re-extracted with 2 ml of acetonitrile and defatted by shaking with hexane (10 ml and 5 ml). 1 ml of the acetonitrile (bottom) phase was transferred into an autosampler vial for GC-MS analysis.

Identification and quantification. Analyses were performed by a gas chromatograph GC System 6890 Series (Agilent Technologies, Palo Alto, CA, USA) coupled to a GCT high-resolution time-of-flight mass spectrometer (Micromass, Manchester, UK). The GC system was equipped with an electronic pressure control (EPC), a split/splitless injector and a PAL Combi autosampler (CTC Analytics, Zwingen, Switzerland). An Innowax (30 m × 0.25 mm × 0.25 µm) capillary column used for separation was operated under following conditions: oven temperature program: 70°C for 1.0 min, 20°C/min to 200°C (8.50 min); helium flow rate: 1.0 ml/min; injection mode: pulsed splitless 1.0 min, 4 ml/min; injection temperature: 250°C; injection volume: 1 µl. Acquisition rate: 2 Hz; pusher interval: 33 µs (30.303 raw spectra/second); inhibit push value: 14; time-to-digital converter: 3.6 GHz; mass range: *m*/*z* 45–500; ion source temperature: 220°C; transfer line temperature: 200°C; detector voltage: 2200 V. The limit of quantification was 25 µg/kg of potato chips and the repeatability of measurements expressed as a relative standard deviation (RSD) was 8.0%.

Frying experiments. The potato chips were made from potato cultivar Saturna. The amount of glucose was 90 mg/kg, fructose 160 mg/kg and asparagine 1800 mg/kg. The oil used for frying was high temperature refined rape oil and its temperature before frying was 162°C. The technological processing starts with peeling of potatoes. After that potatoes are cut into slices (1–1.5 mm) thick and washed in cold water. Excessive water is removed by centrifugation. These slices are fried in the 110 l deep fryer.

Two sets of experiments were carried out. In the first one (Table 1) fresh oil was used for frying, samples were taken in 30 s intervals until 180 s when typical organoleptic properties (texture, colour, flavour) were achieved. Second set (Table 2) was quite similar (oil from previous use) with extended sampling period up to 360 s to enable documentation of the acrylamide levels in overfried samples.

Table 1. SET A – samples obtained from frying in the fresh oil

Samples	Frying time (s)	Oil temperature (°C)
1A	30	123
2A	60	126
3A	90	130
4A	120	135
5A	150	140
6A	180*	148

*this sample represents potato chips with required organoleptic properties

Table 2. SET B – samples purchased from frying in the same oil after 30 min

Samples	Frying time (s)
1B	60
2B	120
3B	150
4B	180
5B	210*
6B	240*
7B	360*

*these samples represent overfried chips

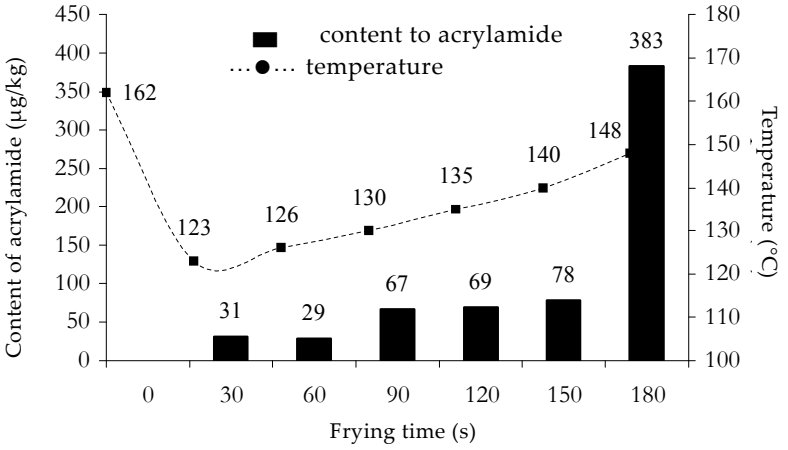

Figure 1a. Acrylamide formation during frying (SET A)

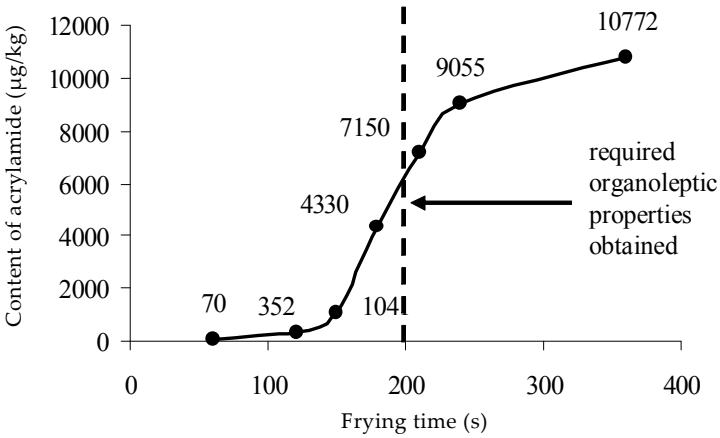

Figure 1b. Acrylamide formation during frying in the second set of samples (SET B)

RESULTS AND DISCUSSION

As shown in Figure 1a in experiment A the acrylamide content in final sample reached 383 µg/kg. Its rapid increase occurred at about 150 s. At that point the moisture in potato slices probably dropped below the critical value and the rate of Maillard reaction rapidly increased.

From quantitative point of view, the dynamics of acrylamide formation was rather different in experiment B (Figure 1b). At 180 s (time needed to finalize production of chips) the content of acrylamide was roughly ten times higher as compared to previous experimental set. The levels of toxicant in deeply browned chips (frying time 360 s) were as high as 10 772 µg/kg. In spite of higher extent of acrylamide formation during normal frying time, the starting point of its intensive formation was quite similar – 150 s. At the moment we are unable to explain such significant differences in determined levels of acrylamide in chips prepared from the same raw material; the changed heat properties of oil bath (fresh oil was used only in experiment A), or other uncontrolled technological conditions may be responsible for this phenomenon.

CONCLUSIONS

The dynamics acrylamide formation during frying has several phases, at the beginning this hazardous compound increases only slowly, however, when the moisture content falls below the critical value (under our experimental conditions this occurred after 150 s) steep increase of acrylamide levels occurs. When frying was prolonged beyond the time needed to obtain optimum organoleptic properties of chips, the increase of acrylamide was already slowned down probably due to low content of its precursor, at the same time the degradation of this compound may also occur.

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