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Study of colour and acrylamide formation in coffee, wheat flour and potato chips during heating

Vural Gökmen [a,*], Hamide Z. Şenyuva [b]

[a] Food Engineering Department, Hacettepe University, 06532 Beytepe, Ankara, Turkey
[b] Ankara Test and Analysis Laboratory, Scientific and Technical Research Council of Turkey, Ankara 06330, Turkey

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Abstract

The effects of heating on colour generation measured as CIE colour space parameters of $L^*a^*b^*$ and acrylamide formation were studied in various food matrices including green coffee, wheat flour and potato chips at different temperatures. Changes in both the acrylamide concentration and the redness parameter a^* during heating at relatively higher temperatures followed a typical kinetic pattern in which an initial increase to an apparent maximum followed by a subsequent decrease was observed. The similarities between the changes in acrylamide and redness parameter a^* during heating revealed that colour may be a reliable indicator of acrylamide levels in thermally processed foods. The overall results suggest that both acrylamide and redness parameter a^* form as intermediate products during Maillard reaction. Since an apparent decrease was observed in its level during prolonged heating at certain temperatures, prediction of acrylamide level in foods during processing should be based on realistic reaction mechanism, instead of simple linear regression model.

Keywords: Acrylamide; Colour; Heating; Green coffee; Wheat flour; Potato chips

1. Introduction

Acrylamide formation was found to occur during the browning process by Maillard reaction of reducing sugars with asparagine at temperatures above 120 °C (Friedman, 2003; Mottram, Wedzicha, & Dodson, 2002; Stadler et al., 2002; Yaylayan, Wnorowski, & Locas, 2003). Coloured products are also formed in foods during heating as a result of Maillard reaction (Márquez & Añón, 1986; Pedrechi, Moyano, Kaack, & Granby, 2005; Şenyuva & Gökmen, 2005). In the Maillard reaction, melanoidins are known as the main end product of the reaction. These brown polymers have significant effect on the quality of food, since colour is an important food attribute and a key factor in consumer acceptance. The mechanism of the formation of brown colour is not fully understood and the structure of melanoidins is largely unknown (Martins & van Boekel, 2003).

Since colour can easily be measured, it may be used as an indicator of other Maillard reaction products like acrylamide. Colour of foods has been measured usually in units $L^*a^*b^*$ which is an international standard for colour measurements, adopted by the Commission Internationale d'Eclairage (CIE) in 1976. L^* is the luminance or lightness component, which ranges from 0 to 100 (black to white), and parameters a^* (from green to red) and b^* (from blue to yellow) are the two chromatic components, which range from −60 to 60 (Papadakis, Abdul-Malek, Kamdem, & Yam, 2000).

This paper presents the changes in colour and acrylamide levels with time in green coffee, wheat flour and potato chips during heating at different temperatures. The relation between the kinetic patterns of CIE colour

* Corresponding author. Fax: +90 312 2992 123.
E-mail address: vgokmen@hacettepe.edu.tr (V. Gökmen).

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parameters of $L^*a^*b^*$ and acrylamide was investigated in detail.

2. Experimental

2.1. Chemicals and consumables

Acrylamide (99+%) was obtained from Sigma (Diesenhofen, Germany). Methanol, potassium hexacyanoferrate, zinc sulfate, formic acid (98%) and acetic acid (glacial) were of analytical grade and obtained from Merck (Darmstadt, Germany). LC grade water was used throughout the experiments (MilliQ system, Millipore, Bedford, MA, USA). Oasis HLB (1 ml, 30 mg) SPE cartridges were supplied by Waters (Milford, MA, USA). The analytical column (Inertsil ODS-3, 250 × 4.6 mm, 5 μm) was obtained from HiChrom (Berkshire, England).

Stock solution of acrylamide (1 mg/ml) was prepared by dissolving in distilled water. Working standards were prepared by diluting the stock solution of acrylamide to concentrations of 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.5 and 1.0 μg/ml with distilled water. Carrez I solution was prepared by dissolving 15 g of potassium hexacyanoferrate in 100 ml of water and Carrez II solution by dissolving 30 g of zinc sulfate in 100 ml of water.

2.2. Heat treatments

2.2.1. Coffee

Three grams of ground green coffee was put in a headspace vials and sealed. Samples were heated in a temperature controlled oven (Heraeus Instruments model T 60) set to 150, 200 and 225 °C for the determination of time-dependent changes in acrylamide and colour with sampling at 0, 5, 10, 15, 20 and 30 min. Immediately after heating for each selected time, the headspace vials allowed to cool to room temperature prior to colour and acrylamide analyses.

2.2.2. Wheat flour

Three grams of wheat flour was put in a headspace vials and sealed. Samples were heated in a temperature controlled oven (Heraeus Instruments model T 60) set to 150, 180 and 220 for the determination of time-dependent changes in acrylamide and colour with sampling at 0, 5, 10, 15, 20, 30, 45 and 60 min. Immediately after heating for each selected time, the headspace vials allowed to cool to room temperature prior to colour and acrylamide analyses.

2.2.3. Potato chips

Potatoes peeled, chipped (2 mm) and deep fried in 5 L of hot vegetable oil contained in an electrical fryer at 150, 170, 190 and 210 °C. For a time-dependent changes in acrylamide and colour, potato chips were fried up to 60 min with a sampling at 0, 1, 3, 5, 8, 10, 15, 30, 45 and 60 min. For each selected sampling time, the chips were drained after frying over a wire screen for 5 min and allowed to cool to room temperature prior to colour and acrylamide analyses.

2.3. Measurement of acrylamide

2.3.1. Sample preparation

A sample preparation procedure previously described by us elsewhere was used (Gökmen, Şenyuva, Acar, & Sarıoğlu, 2005). Finely ground sample (1 g) was weighed into a 10 ml glass centrifuge tube with cap. The sample was suspended in 5 ml of methanol and extracted for 2 min in a vortex mixer. The suspension was centrifuged at 5000 rpm for 10 min (Sigma model 2–16 K). The clear supernatant was transferred into a centrifuge tube and treated with Carrez I and II solutions (25 μl each) to precipitate the co-extractives. Following centrifugation at 5000 rpm for 5 min, 1.0 ml of clear supernatant (0.2 g sample) was quantitatively transferred into a conical bottom glass test tube placed in a water bath at 40 °C (Zymark TurboVap® LV Evaporator) and evaporated to dryness under nitrogen at 3 psig. The remaining residue was immediately redissolved in 1 ml of water by mixing in a vortex mixer for 1 min. For the SPE clean-up, Oasis HLB cartridge was preconditioned consequently with 1 ml of methanol and 1 ml of water at rate of two drops per second using a syringe. Then, 1 ml of the extract was passed through the cartridge at a rate of one drop per second using a syringe. The first 10 drops of the effluent were discarded to prevent any dilution of sample by replacing water hold in the sorbent void fraction with the sample effluent. The forthcoming drops were collected and filtered through a 0.45 μm syringe filter. Twenty microlitres of the final test solution was injected onto LC column for quantitation by LC–MS.

2.3.2. LC–MS analysis

LC–MS analyses were performed by an Agilent 1100 HPLC system (Waldbronn, Germany) consisting of a binary pump, an autosampler and a temperature controlled column oven, coupled to an Agilent 1100 MS detector equipped with atmospheric pressure chemical ionization (APCI) interface. The analytical separation was performed on a Inertsil ODS-3 column (250 × 4.6 mm, 5 μm) using the isocratic mixture of 0.01 mM acetic acid in 0.2% aqueous solution of formic acid at a flow rate of 0.6 ml/min at 25 °C. The LC eluent was directed to the MS system after a delay time of 6.5 min using MSD software. Data acquisition was performed in selected ion monitoring (SIM) mode using the interface parameters: drying gas (N_2, 100 psig) flow of 4 l/min, nebulizer pressure of 60 psig, drying gas temperatures 325 °C, vaporizer

temperature of 425 °C, capillary voltage of 4 kV, corona current of 4 μA, fragmentor voltage of 55 eV. Ions monitored were m/z 72 and 55 for the quantification of acrylamide in the samples.

2.4. Measurement of colour

Colour measurements (CIE $L^*a^*b^*$ colour space) were performed using a Minolta CM-3600d model spectrophotometer. Flour and coffee samples were transferred into a disposable cuvette to measure the reflectance at least twice from both front and rear sides. Potato chips were aligned to sample measurement hole manually to measure the reflectance at from both front and rear sides.

3. Results and discussion

The effects of heating on colour generation and acrylamide formation were studied in various food matrices including green coffee, wheat flour and potato chips at different temperatures. It should be noted that heating was intentionally prolonged to examine the relation between colour and acrylamide, and therefore, temperature and time range of thermal treatments applied here may not be identical to those commonly applied for roasting, baking or frying.

In green coffee, the amount of acrylamide measured increased rapidly at the onset of heating, reaching an apparent maximum, and then decreasing exponentially as the rate of degradation exceeds the rate of formation at 200 and 225 °C (Fig. 1). However, the amount of acrylamide continued to increase during heating at 150 °C. The acrylamide level was reduced by a factor of approximately 20 at the end of 30 min of heating at 200 and 225 °C, compared to the highest level recorded. Although CIE $L^*$and b^* decreased exponentially with time, CIE a^* increased rapidly at the onset of heating, reaching an apparent maximum, and then decreasing exponentially at 200 and 225 °C, but reached to a maximum with continuous increase at 150 °C. It was interesting to see that changes in acrylamide levels and CIE a^* followed almost the same trend during heating at 150, 200 and 225 °C. As noted by other researchers (Taeymans et al., 2004), the results obtained in this study also revealed that the darker coloured coffee may contain lower amounts of acrylamide than the light coloured coffee.

In wheat flour, a time lag of about 10 min was observed for acrylamide formation during heating at 150, 180 and 220 °C. After 10 min, the amount of acrylamide increased to an apparent maximum within 30 min and then decreasing exponentially at 180 and 220 °C. However, the amount of acrylamide continued to increase within 60 min of heating at 150 °C (Fig. 2). CIE L^* decreased exponentially with time at all temperatures

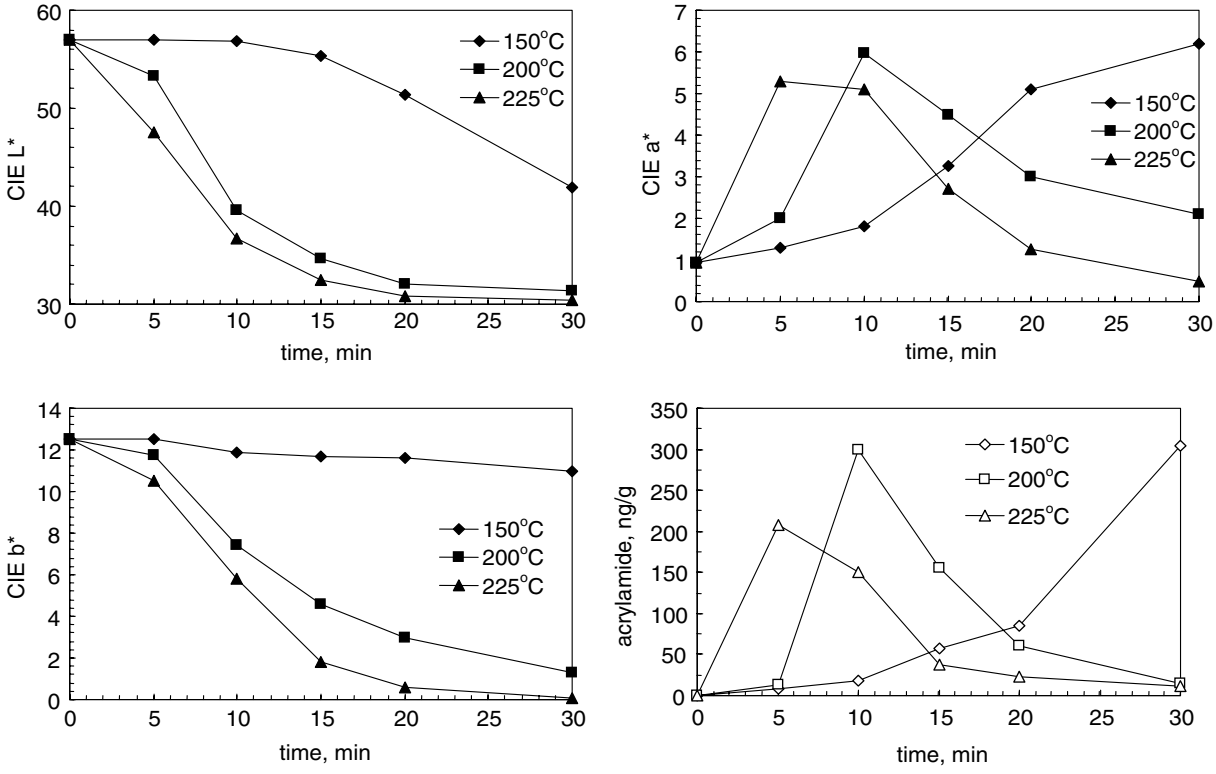

Fig. 1. Change of CIE L^*a^*b* and acrylamide in coffee during heating at 150, 200 and 225 °C.

studied. However, CIE a^* and b^* increased rapidly to an apparent maximum within 30 min, and then decreasing exponentially at 220 °C, while these values continued to increase within 60 min of heating at 150 and 180 °C. The changes in acrylamide levels and CIE a^* followed the similar trends at 150, 180 and 220 °C within 30 min, but the kinetic trends tended to change after 30 min during heating at 180 °C.

Amrein, Schönbächler, Escher, and Amado (2004) have reported a significant correlation between the L^* and the acrylamide content during baking at 180 °C. Assuming a linear correlation between acrylamide concentration and baking time, they have claimed that prolonged baking or excessive browning should be avoided in order to minimize the acrylamide content. However, our results confirmed that prolonged heating at 180 and 220 °C results in a decrease in the acrylamide concentration of wheat flour (Fig. 2). Since the thermal decomposition of acrylamide have been shown previously at temperatures above 120 °C, acrylamide concentration found in heated foods must be the result of concurrent formation and decomposition (Biedermann, Biedermann-Brem, Noti, & Grob, 2002). It is, therefore, thought that a prediction based on a simple linear correlation might not be reliable in the case of prolonged heating.

Surdyk, Rosén, Andersson, and Åman (2004) have also reported a highly significant correlation between colour and acrylamide content in bread crust during baking. However, they have shown that amino acids other than asparagine were also involved in the browning reactions. So, contribution of the products of Maillard reaction formed by these amino acids should also be taken into account on the development of colour during heating.

In potato chips, CIE L^* and b^* of potato chips decreased exponentially with time at all temperatures studied, while CIE a^* increased rapidly at the onset of heating, reaching an apparent maximum within 3–4 min and decreasing exponentially afterward during heating at 190 and 210 °C. CIE a* reached to a plateau within 10 min of heating at 170 °C (Fig. 3). The changes in the amounts of acrylamide followed a kinetic trend similar to that of CIE a^* at 190 and 210 °C. The acrylamide concentrations tended to decrease exponentially after reaching an apparent maximum within 15, 8, 5 and 10 min of heating at 150, 170, 190 and 210 °C, respectively. These results suggest that acrylamide forms as an intermediate product during Maillard reaction and its concentration begins to decrease as the rate of degradation exceeds the rate of formation during heating.

Pedrechi et al. (2005) have reported that L^* and b^* did not show considerable changes as those shown by a^* during frying of potato chips. A linear correlation have been found between the acrylamide concentration and the colour of potato chips represented by the redness component a^* at temperatures of 120, 150 and 180 °C for up to 5 min of frying. However, the effect of prolonged frying on acrylamide concentration and colour has not been mentioned by these researchers.

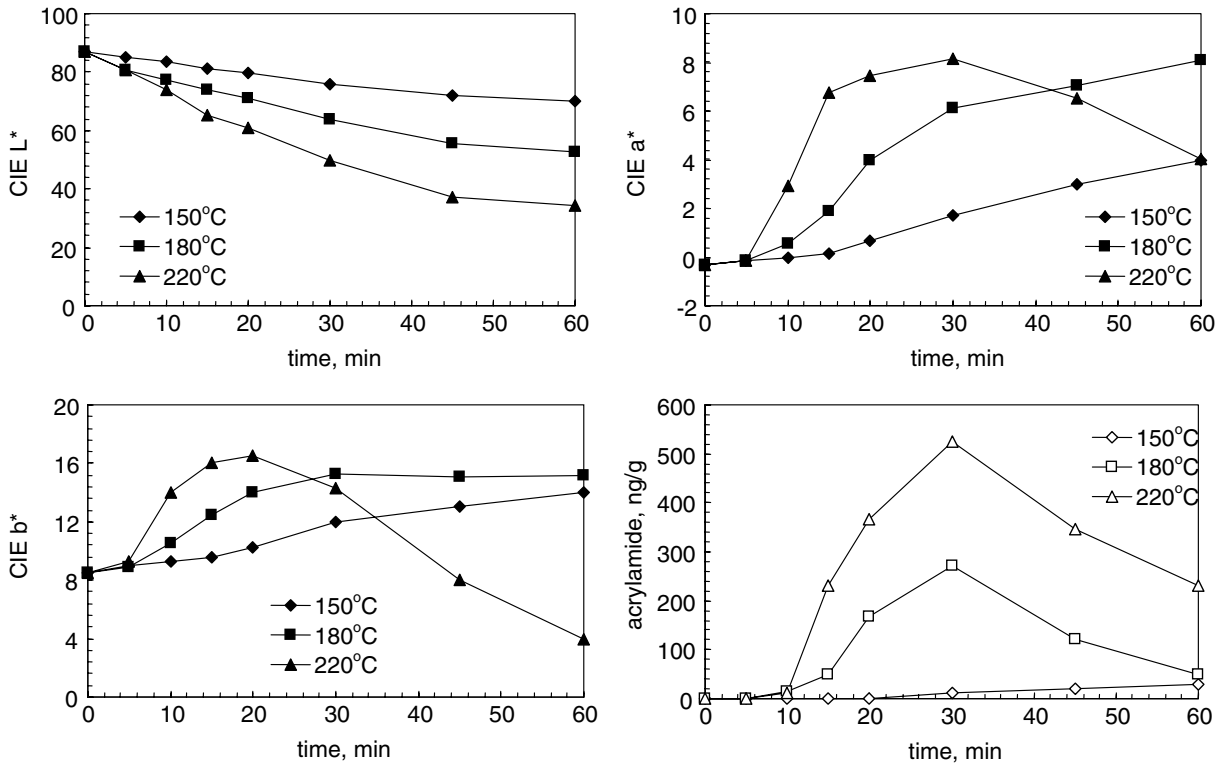

Fig. 2. Change of CIE $L^*a^*b^*$ and acrylamide in wheat flour during heating at 150, 180 and 220 °C.

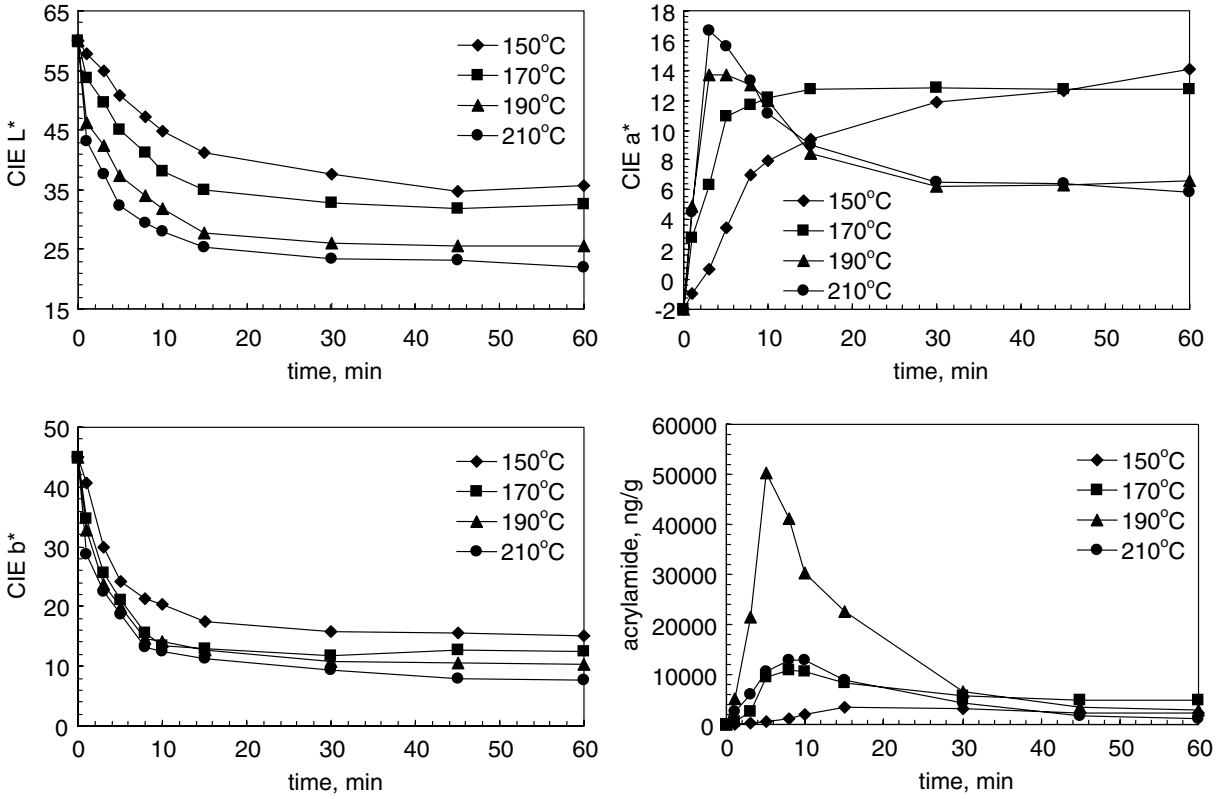

Fig. 3. Change of CIE $L^*a^*b^*$ and acrylamide in potato chips during heating at 150, 170, 190 and 210 °C.

Taubert, Harlfinger, Henkes, Berkels, and Schömig (2004) have investigated the relation between the level of surface browning and acrylamide concentration of French fries with linear regression. They have reported that a close correlation could be for small-surface material being fried. A somewhat less close correlation was observed for intermediate surface material, while for large-surface material no correlation was observed, preventing surface browning alone being a reliable predictor of acrylamide concentration.

Changes in both acrylamide levels and CIE a^* parameter of green coffee, wheat flour and potato chips during heating at relatively higher temperatures followed a typical kinetic pattern in which an initial increase to an apparent maximum followed by a subsequent decrease was observed. Despite the chemical pathways for the formation of acrylamide through Maillard reaction are rather complex, the reaction may be written in a simplified form taking acrylamide as an intermediate product,

$$\text{asparagine} + \text{sugar} \xrightarrow{k_1} \text{acrylamide}$$

$$+ \text{unknown intermediates} \xrightarrow{k_2} \text{unknown end products}$$

According to the simplified chemical reaction in series mentioned above, the rate of change of acrylamide may be written as follows:

$$+\frac{dC_{\text{Acrylamide}}}{dt} = k_1 C^{n}_{\text{Asparagine}} \cdot C^{m}_{\text{Sugar}} - k_2 \cdot C^{k}_{\text{Acrylamide}}$$

where k_1 and k_2 are apparent rate constants for acrylamide formation and deformation, respectively, and n, m, k are the rate orders with respect to asparagine, sugar and acrylamide.

Considering a chemical reaction mechanism in which acrylamide forms as an intermediate, the change of acrylamide level in foods with time during heating cannot be explained by means of simple linear regression models. Instead, the differential equation given above needs to be solved after rate orders (n, m, and k) determined experimentally. Nevertheless, the results obtained in this study demonstrated a relationship between colour generation represented by the redness component a^* and acrylamide level in foods during heating. Experiments are ongoing to clarify reaction mechanisms in more details for colour generation and acrylamide formation, and, to put forward and idea about the apparent kinetic parameters as a function of temperature.

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