Coffee represents an interesting foodstuff for secondary shelf life modelling, since it is known that almost immediately after its exposure to environmental influences, aroma and colour degradation reactions occur. These reactions can be prevented or retarded by a packaging material, adapted to the given type of food. The aim of this paper was to estimate parameters of zero and first order kinetics for colour changes during secondary shelf life at simulated household storage conditions for roasted ground coffee in two different types of packaging materials: tin cans and triplex bags. Probability values for both estimated kinetic models were lower than 0.05 and all model parameters were considered statistically significant. When comparing kinetic parameters for two packaging materials, colour component change rate constants in most cases were lower for tin can packaging, which meant that tin can served as a better colour protector and a better light barrier.

**Key words:** roasted ground coffee, colour change, kinetic modelling, secondary shelf-life.

**INTRODUCTION**

The total appearance of food depends on many important interdependent factors such as visual identification, safety, texture, flavour or colour (Hutchings, 2002). Because colour is closely related to other food quality factors, it is considered an important grading factor of food products such as meat, fruit, vegetables, corn, rice and many other (McCraig, 2002). Changes in colour of food products can occur due to numerous biochemical reactions, especially in foods of plant or animal origin, or due to exposure to ambient conditions (e.g. air, humidity, temperature, light) during storage. These changes can be prevented or retarded by an appropriate packaging material, adapted to the given type of food. Determination of colour changes during storage represents a significant method in food quality determination and shelf life prediction of food products (Bicho et al., 2012). In most cases, colour parameters are used for monitoring the progress of different food preservation operations such as roasting, drying or freezing (Maskan, 2001). Although kinetic models have been extensively used for prediction of colour changes during food processing (Anderson et al., 2003, Corzoand Alvarez, 2012), there were only few cases of reliable kinetic models describing changes in food properties during secondary shelf life (Ochoa et al., 2001, Zhang et al., 2011). Coffee represents an interesting foodstuff for secondary shelf life modelling, since it is known that almost immediately after package opening, aroma and colour degradation reactions occur. These reactions usually proceed with a higher rate after package opening due to the changed storage conditions and exposure of coffee powder to air, humidity and light (Anese, 2006). One of the most widely spread forms of coffee, roasted and ground coffee, is comprised solely of ground particles originating from the roasted coffee bean, and is subjected mostly to chemical and physical changes during storage due to changes in volatile organic compounds composition (Clarke, 2003). Subsequently, these changes result in modification of aroma, but also affect colour of coffee powder. The aim of this paper was to estimate parameters of zero and first order kinetics for colour changes during secondary shelf life at simulated household storage conditions for roasted ground coffee. The paper also aimed to compare colour change kinetics for two different types of packaging materials: tin cans and triplex bags.

**MATERIAL AND METHOD**

**Material**

Roasted ground coffee powders were supplied by Franck d.o.o. (Zagreb, Croatia). Samples (150 grams of each) were packed in two types of packaging: tin cans and triplex (PE/Al/PET) bags of a total volume of 0.8 dm$^3$, and stored for 6 months in a dark cupboard, at 50-60 % relative humidity and a temperature of 17-22 °C, with an aim to simulate household storage conditions. Packaging materials were opened consecutively each month of storage and colour measurements were performed.

**Methods**

Colour measurements were performed using a CM-700d spectrophotometer (Konica Minolta Sensing INC., Japan). Prior to analysis, spectrophotometer was calibrated on a white standard tile. Colour was recorded based on the $L^*,a^*,b^*$ scale ($L^*$: brightness, $a^*$: redness, $b^*$: yellowness). (Benković and Bauman, 2011, Benković and Bauman, 2013, Radojčin et al., 2011). Using $L^*$, $a^*$ and $b^*$ values, total colour difference (AE), Chroma and Hue angle were also calculated according to following equations:
While calculating total colour difference, samples in the initial day of storage were taken as reference samples. Measurements were performed in triplicate, consecutively, each month of storage.

**Colour change kinetic modelling**

Experimentally determined colour component values (all 3 parallel measurements for each colour component, without the calculation of the mean value) were used to model colour changes during storage.

Two kinetic models were proposed: zero order kinetics (eq. 4) and first order kinetics (eq. 5):

\[
\Delta E = \sqrt{(L^* - L_0)^2 + (a^* - a_0)^2 + (b^* - b_0)^2}
\]

\[
\text{Chroma} = \sqrt{(a^2 + b^2)}
\]

\[
\text{Hue angle} = \tan^{-1}(b/a)
\]

\[
C = C_0 \pm kt
\]

\[
C = C_0 \cdot e^{kt}
\]

where \(C\) represents the value of the tested colour parameter at time \(t\); \(C_0\) represents the initial value of the colour parameter (at \(t=0\)) and \(k\) represents the colour change constant. Experimental data were fitted directly to kinetic models, without prior linearization, in order to minimize errors. Kinetic model parameters were estimated using Wolfram Research Mathematica version 9.0 (Wolfram, UK). The appropriate kinetic model was chosen as the kinetic order corresponding to the maximum correlation coefficient between the observed and the predicted values.

**RESULTS AND DISCUSSION**

Colour change kinetics during 6 months of storage of ground roasted coffee packed in two different packaging materials was described with zero- (Eq. 4) and first- (Eq. 5) order kinetic models. Colour components change for roasted ground coffee sample packed in tin can is shown in Figure 1.

![Fig. 1. Kinetics of change of colour components as a function of storage time for sample of ground roasted coffee packed in tin can (a) \(L^*\), (b) \(a^*\), (c) \(b^*\), (d) \(\Delta E\), (e) Chroma, (f) Hue angle. For the sake of clearer data presentation, some data points were omitted from the figure](image-url)
According to the results shown in Figure 1, all colour components exhibited changing values as a function of time. $L^*$ values ranged from 23.81 to 28.23 as seen in Fig.1a, and decreased with storage time. These values show that the ground roasted coffee used in this study can be classified as medium to dark roasted (Sacchetti et al., 2009). $a^*$ colour component ranged from 11.25 to 12.46, (Fig. 1b) and the $b^*$ component from 17.55 to 19.29 (Fig.1c). An increase of the red colour component and a decrease of the $b^*$ component with storage time was also detected, as seen in Figs. 1b and 1c. Total colour difference of the sample was calculated using all three colour components, and the result is shown in Fig. 1d. Total colour difference values ranged from 3.50 to 5.02.

A slight increase in $\Delta E$ value was visible with storage time, which meant that the colour change becomes higher with prolonged storage time. As a consequence of changes in $a^*$ and $b^*$ values, Chroma value, which is considered as a colour saturation indicator (Maskan, 2001), decreased with storage time (Fig. 1e). Hue angle values exhibited the same trend (Fig. 1f).

Based on literature review, ground roasted coffee colour changes begin immediately after package opening. Exposure of the package contents to air, moisture and sunlight accelerates chemical and physical changes occurring in ground roasted coffee (Kreuml et al., 2014). For example, colour changes during storage usually include deterioration of colour known as fading, which was detected in this case as a decrease in Chroma values.

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**Fig. 2.** Kinetics of change of colour components as a function of storage time for sample of ground roasted coffee packed in triplex bag (a) $L^*$, (b) $a^*$, (c) $b^*$, (d) $\Delta E$, (e) Chroma, (f) Hue angle. For the sake of clearer data presentation, some data points were omitted from the figure.
Some colour changes detected for the ground roasted coffee packed in triplex bags exhibited an opposite trend in comparison with ground roasted coffee packed in tin can. As seen in Fig. 2a, $L^*$ values showed a slight increase with prolonged storage time. These results are in accordance with Rendon et al. (2014), who also detected a decrease in $L^*$ values of ripe coffee beans with an increase in storage time. An increase in brightness and a simultaneous increase in redness and yellowness indicated colour fading during storage. Although only $L^*$ values increased in this case (from 24.74 to 26.13), while $a^*$ and $b^*$ values decreased, form 12.48 to 11.00 for $L^*$ with ground roasted coffee packed in tin can. As seen in Fig. 2b, packed in triplex bags exhibited an opposite trend in comparison with ground roasted coffee packed in tin can. As seen in Fig. 2c, total colour difference (Fig. 1d) and Chroma results (Fig. 1e) confirm that this ground roasted coffee sample also underwent changes in colour intensity, which faded during storage. Hue angle value also decreased from 0.994 to 0.970 (Fig. 1f). Although Hue changes were detected, during all 6 months of storage values remained in the 55 - 60° range, which corresponds to red Hue.

In direct comparison of two samples packed in different packaging materials, different behaviour was detected for parameters $L^*$ and $a^*$, which can be attributed to the packaging material. All other parameters exhibited the same trend: a drop in $b^*$ values, with diminishing yellow components, a rise in the total colour change and drop in Chroma and Hue. All of the above listed changes were more pronounced for the ground coffee sample packed in triplex bag.

Kinetic parameters for the zero- and first-order kinetic models are presented in Table 1.

Table 1 defines initial values of $L^*$, $a^*$, $b^*$, $\Delta E$, Chroma and Hue angle for zero and first order colour component change rate for sample packed in tin can. As seen from Table 1, initial (C0) values for each colour parameter for the first and second order kinetics are very similar, e.g. $C_0$ value for the $L^*$ parameter equals 27.593 for the zero-order kinetics and 27.688 for the first-order kinetics. Probability values for both kinetic models are lower than 0.05 and all model parameters were considered statistically significant. However, $R^2$ goodness of fit varies significantly for different colour components. The best fit was obtained for $L^*$ values for both kinetic orders and the lowest fit were calculated for $\Delta E$ and Chroma values, also for both kinetic orders. The – auspice presented a decrease in colour component values for $L^*$, $a^*$, Chroma and Hue in both cases. Furthermore, based on the $k_v$ values, the fastest change was detected in brightness of the sample, while Hue angle changed the slowest during 6 months of storage. $R^2$ goodness of fit were the highest in the case of $L^*$ component, followed by $a^*$ component, and relatively low for all the other colour components. This indicates that zero- and first-order kinetic modelling is suitable for the prediction of the behaviour of $L^*$ and $a^*$ components during prolonged storage time. However, since zero order kinetics represented a linear approximation, it is recommended as more appropriate and easier to use for describing colour changes.

As shown in Table 2, initial values of the colour components calculated for zero- and first-order kinetics do not differ considerably. The same could be observed for $R^2$ goodness of fit. The best $R^2$ value was obtained for Chroma values for both kinetic models. It is important to emphasize that $L^*$ values showed very poor $R^2$ values in both cases, and both estimated colour component change rates were considered statistically insignificant ($p>0.05$). $C_0$ kinetic parameter for first order kinetic model describing $\Delta E$ change was also considered statistically insignificant. By direct comparison of reaction rate constants, decreasing trend was visible for $a^*$, $b^*$, Chroma and Hue angle values.

When comparing kinetic parameters for two packaging materials, colour component change rate constants in most cases were lower for tin can packaging, meaning tin can served as a better colour protector and a better light barrier. Furthermore, goodness of fit for $\Delta E$ values was higher for first order kinetics for both packaging types. Overall, zero and first kinetic models for colour component change exhibited better fit for sample packed in triplex bag. Also, a significant difference was detected in initial $\Delta E$ values for two types of packaging used, which indicated that, although $\Delta E$ reaction rate was slower for tin can samples, initial change according to the reference sample was bigger for tin can sample.

### Table 1. Parameters of zero- and first-order kinetics of colour components change for ground roasted coffee sample packed in tin can

<table>
<thead>
<tr>
<th>Param.</th>
<th>$C_0$±st.err.</th>
<th>p-value</th>
<th>t-value</th>
<th>$k_v$/day±st.err.</th>
<th>p-value</th>
<th>t-value</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L^*$</td>
<td>27.593±0.372</td>
<td>&lt;0.0001</td>
<td>74.255</td>
<td>-0.029±0.004</td>
<td>&lt;0.0001</td>
<td>-7.711</td>
<td>0.821</td>
</tr>
<tr>
<td>$a^*$</td>
<td>11.584±0.110</td>
<td>&lt;0.0001</td>
<td>105.524</td>
<td>0.006±0.001</td>
<td>0.0003</td>
<td>4.581</td>
<td>0.567</td>
</tr>
<tr>
<td>$b^*$</td>
<td>18.691±0.571</td>
<td>&lt;0.0001</td>
<td>81.671</td>
<td>-0.008±0.003</td>
<td>0.0124</td>
<td>-2.940</td>
<td>0.419</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>3.526±0.327</td>
<td>&lt;0.0001</td>
<td>10.796</td>
<td>0.007±0.003</td>
<td>0.0373</td>
<td>2.341</td>
<td>0.314</td>
</tr>
<tr>
<td>Chroma</td>
<td>22.008±0.150</td>
<td>&lt;0.0001</td>
<td>146.530</td>
<td>-0.004±0.002</td>
<td>0.0369</td>
<td>-2.348</td>
<td>0.315</td>
</tr>
<tr>
<td>Huean.</td>
<td>1.014±0.009</td>
<td>&lt;0.0001</td>
<td>112.125</td>
<td>-3.231±0.003</td>
<td>0.0046</td>
<td>-3.328</td>
<td>0.425</td>
</tr>
</tbody>
</table>

### Table 2. Parameters of zero- and first-order kinetics of colour components change for ground roasted coffee sample packed in triplex bag

<table>
<thead>
<tr>
<th>Param.</th>
<th>$C_0$±st.err.</th>
<th>p-value</th>
<th>t-value</th>
<th>$k_v$/day±st.err.</th>
<th>p-value</th>
<th>t-value</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L^*$</td>
<td>27.688±0.362</td>
<td>&lt;0.0001</td>
<td>76.412</td>
<td>-0.001±1.395·10^-4</td>
<td>&lt;0.0001</td>
<td>-8.355</td>
<td>0.838</td>
</tr>
<tr>
<td>$a^*$</td>
<td>11.594±0.109</td>
<td>&lt;0.0001</td>
<td>105.901</td>
<td>4.544±10^-4</td>
<td>0.0004</td>
<td>4.465</td>
<td>0.559</td>
</tr>
<tr>
<td>$b^*$</td>
<td>18.704±0.230</td>
<td>&lt;0.0001</td>
<td>81.218</td>
<td>-4.370±10^-4</td>
<td>0.0113</td>
<td>-2.990</td>
<td>0.425</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>3.556±0.290</td>
<td>&lt;0.0001</td>
<td>12.252</td>
<td>0.002±7.562·10^-4</td>
<td>0.0342</td>
<td>2.389</td>
<td>0.321</td>
</tr>
<tr>
<td>Chroma</td>
<td>22.011±0.151</td>
<td>&lt;0.0001</td>
<td>145.979</td>
<td>-1.892±8.018·10^-4</td>
<td>0.0361</td>
<td>-2.360</td>
<td>0.316</td>
</tr>
<tr>
<td>Huean.</td>
<td>1.015±0.009</td>
<td>&lt;0.0001</td>
<td>111.724</td>
<td>-3.303±9.754·10^-5</td>
<td>0.0041</td>
<td>-3.386</td>
<td>0.430</td>
</tr>
</tbody>
</table>
CONCLUSION

Zero- and first-order kinetic models used in this study, exhibited similar fit for all tested colour components. Due to linear approximation and simpler analysis, zero-order kinetic models are proposed as more appropriate for ground roasted coffee colour change modelling. A significant difference was detected in parameter fitting for different packaging materials. Better goodness of fit was accomplished for triplex packaging.

REFERENCES


