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**ORIGINAL ARTICLE**

# The Use of Lipid Oxidation Indicators to Assess the Quality Deterioration of Potato Chips during Accelerated Shelf-Life Tests

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**Abstract**

Time-efficient determination of oxidation-caused changes in high-fat and long shelf-life snacks can be conducted with accelerated shelf-life tests (ASLTs). The purpose of this study was to assess the suitability of various oxidation indicators (fatty acid composition, volatile compounds and descriptive sensory analysis) for the development of ASLT methodology. For this, sunflower oil-based potato chips were stored at 20°C, 30°C, 40°C for 90 days. The results revealed that the rates of the degradation of fatty acids and the development of organoleptically perceived rancidity increased at higher storage temperatures throughout the experiment, following Arrhenius's behavior. However, as the changes in fatty acid composition does not provide information about organoleptical quality, it is not the best oxidation indicator for conducting ASLT. The analysis of volatile compounds showed that hexanal had the highest concentration throughout the experiment and was one of the key molecules based on GC-O analysis. However, the increase in hexanal concentration at higher storage temperature did not follow a linear trend due to the formation of methyl ketones. Therefore, it was concluded that sensorially assessed rancidity is the most suitable oxidation indicator to monitor the shelf-life of potato chips when conducting ASLTs due to its compliance with Arrhenius equation.

**Keywords:** Lipid oxidation, potato chips, accelerated shelf-life test, descriptive sensory analysis, fatty acid composition.



## 1. Introduction

The shelf-life of snacks with high fat content is mainly limited by the lipid oxidation process causing the development of rancidity (Chinnadurai & Sequeira, 2016). High-fat potato chips are considered shelf-stable, having a shelf-life of 2 months or more (Andress & Harrison, 2011). Therefore, the determination of shelf-life is time consuming and the alternative methods are of interest. To determine the "best before" date of these products time-efficiently, an accelerated shelf-life test (ASLT) could be used. With this method, the storage temperature is changed to influence the rate of oxidation and the results can be extrapolated to room temperature storage. However, to develop methodologies for ASLTs, suitable indicators and their reaction rates must be assessed during storage at different temperatures (Manzocco *et al*., (2016).

Potato chips are thinly sliced deep-fried snacks, with a moisture content of 1.5% (Kirkman, 2007). The nutritional composition of potato chips includes typically 6% of protein, 38% of fat and, 51% of carbohydrates (Saldivar, 2015). Sunflower oil, consisting mainly of linoleic and

oleic acid, is one of the main oils used to produce potato chips (Kita *et al*., 2007). The amount of oleic acid in sunflower oil can vary in ranges of 14%-39%, 42%-72%, or 75%-91%, and linoleic acid in ranges of 48%-74%, 19%-45%, or 2%-17%, depending on whether the oil is regular seed oil, mid-oleic or high-oleic oil (Codex Alimentarius, 1999).

One of the main indices of quality degradation of potato chips during shelf-life is the development of rancidity (Chinnadurai & Sequeira, 2016). The chemical process behind the development of rancidity is known as lipid oxidation which causes the formation of off-odors and off-tastes, loss of vitamins, alteration in color, degradation of proteins, and even the production of toxic substances (Kong & Singh, 2016). Lipid oxidation is typically catalyzed either by light, heat, enzymes, or metals, resulting in autoxidation, photooxidation, and enzymatic oxidation (Jacobsen, 2019). Autoxidation is the main mechanism that takes place as the result of reactions between free lipid radicals and oxygen. This process occurs in three stages: initiation, propagation, and termination. Unsaturated lipid molecules lose the hydrogen atom and produce free radicals in the initiation step. After this, the process moves into the propagation stage where the free lipid radicals react with atmospheric oxygen, generating peroxyl radicals. These react with new unsaturated fatty acids to form primary oxidation products, hydroperoxides, and new lipid radicals, continuing the chain reaction. Hydroperoxides, which are the first intermediates of lipid oxidation and have no odor or taste activity, break down into organoleptically perceived secondary oxidation products such as aldehydes, ketones, and alcohols. After this, the free radical chain reaction propagates until two free radicals join, forming a non-radical product and terminating the chain reaction (Jacobsen, 2019; Mozuraityte *et al*., 2016; Shahidi & Zhong, 2010).

The aim of ASLT is to accelerate the quality deterioration of food products by increasing the storage temperature without changing the order of processes taking place during storage in standard conditions (Corradini, 2018). These tests are mostly used to detect the physico-chemical quality changes in shelf-stable products which tolerate the conditions used for acceleration (Subramaniam, 2009). Developed ASLT methods must be based on quality-changing processes that take place in both accelerated and real-time storage (Man, 2016). As already described in many previous publications (Calligaris *et al*., 2019; Kong & Singh, 2016; Man, 2016; Mizrahi, 2004), the development of ASLT methods at higher storage temperatures is based on the Arrhenius equation (Equation 1) which shows the effect of temperature on the reaction rate:

$$k = k_0 * e^{-\frac{E_a}{RT}} \quad \textbf{(1),}$$

where $k$ is the reaction rate constant; $R$ is the molar gas constant; $T$ is the absolute temperature (K); $E_a$ is the activation energy of a reaction which shows the minimum amount of energy that must be provided for compounds to result in a chemical reaction; and $k_0$ is the pre-exponential factor that represents the frequency of collisions between reactant molecules (Conte *et al*., 2020; Frankel (2012b); Fu & Labuza, 1997; Toledo, 2007). The activation energy can be determined from an Arrhenius plot of ln k versus the reciprocal of absolute temperature (Fu & Labuza, 1997) or be calculated with the following (Equation 2) (Conte *et al*., 2020):

$$\ln k = \ln k_{ref} - \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \text{(2)},$$

where $k_{ref}$ is the apparent reaction rate at the average value of the storage temperatures and $T_{ref}$ is the central temperature in the study.

Frankel (2012b) stated that the activation energy of lipid oxidation in foods is in the range of 15-25 kcal/mol (62-104.6 kJ/mol). Calligaris *et al*. (2019) agreed that the activation energy of lipid oxidation ranges from 20-150 kJ/mol and added that the wide range is dependent on the characteristics, processing methods, and storage conditions of the product. Based on $E_a$ and $k_{ref}$, one can also calculate $k_0$ (Equation 3) (Conte *et al*., 2020):

$$k_0 = e^{\left(\ln k_{ref} + \frac{E_a}{RT_{ref}}\right)} \textbf{(3).}$$

The storage stability and lipid oxidation of potato chips have been previously investigated by several authors. For example, Lee & Pangloli (2013) studied the formation of volatile compounds during storage of potato chips fried in mid-oleic sunflower oil, stating that the concentrations of hexanal and 2-furaldehyde increased with storage time. Azarbad & Jeleń (2014) and Marasca *et al*. (2016) also stated that the formation of hexanal is the indicator to monitor the lipid oxidation process in fatty foods such as potato chips. Pangloli *et al*. (2002) stated based on the analysis of peroxide value that potato chips fried in sunflower oil are more prone to lipid oxidation than chips fried in palm oil and sunflower oil mixture due to the high concentration of polyunsaturated fatty acids in sunflower oil. Some parameters that Petukhov *et al*. (1999) monitored during the shelf-life of potato chips fried in canola oil were for example painty odor, peroxide value, and the amount of free fatty acids. In addition to these researches, ASLT models for fatty foods and potato chips based on lipid oxidation have been studied by Ragnarsson & Labuza (1977) and Labuza & Berquist (1983). However, there is no clear evidence on which indicators are the best to monitor lipid oxidation in potato chips when conducting accelerated shelf-life tests.

The present experiment aimed to monitor various lipid oxidation indicators of sunflower oil-based potato chips at different storage temperatures and assess their suitability for the development of ASLT methodologies.

## 2. Materials and Methods

### *2.1 Potato chips and packaging*

The potato chips fried in sunflower oil were purchased from a local supplier (Coop), produced by Pata S.p.A (Italy). The nutritional composition of 100 g of potato chips labeled on the package was 33 g of fat of which 3.7 g formed saturated fatty acids; 50 g of carbohydrates; 6.2 g of protein and 1 g of salt.

42 g of chips were repackaged in 20 cm x 20 cm plastic bags of 12 µm PET/40 µm LLDPE (AS Estiko-Plastar, Estonia). The oxygen transmission rate of the packaging material was 130 $cm^3/m^2$/24 h and the water vapor transmission rate was <3 g/ $m^2$/24h.

### *2.2 Reagents and standards*

Petroleum ether (Sigma-Aldrich, Germany), hexane (Honeywell, Germany), chloroform (Sigma-Aldrich, Germany), methanol (Sigma-Aldrich, Germany), hydrochloric acid (Honeywell, Austria), internal standard 4-methyl-2-pentanol (Sigma-Aldrich, Germany) were used.

### *2.3 Accelerated shelf-life test design*

Sealed bags of chips were stored in climate chambers at 20°C (Panasonic MLR-325H, Germany), 30°C (Venticell LSIS-B2V/VC 222, MMM Group, Germany), and 40°C (Memmert UN750, Germany) with 0% relative humidity. The test time in each storage condition was 90 days during which samples were taken at a 10-day interval. At each time point, 3 sample replicates from each storage condition were analyzed.

### *2.4. GC-MS analysis of Fatty Acid Methyl Esters (FAME)*

The fatty acid composition was determined for fresh samples (0 days) and for samples that were stored at each temperature for 70 and 90 days. The samples from each time point were collected and stored at -20°C until further analysis.

Extraction of fatty acids from the chips was carried out using a Velp Scientifica 158 series Soxhlet apparatus (VELP Scientifica Srl, Italy). Briefly, 3 g of chips were ground using mortar. Then the oil from the ground chips was extracted using petroleum ether. The process contained 20 min immersion, 8 min removing, 20 min washing, 10 min recovery, and 5 min cooling. After the process, petroleum ether was evaporated and oil was stored at -20°C.

Derivatization of oil was performed for the determination of fatty acid content. For this, 100 mg of oil was weighed and 1450 µl of hexane was added to prepare the stock liquor. Next, 200 µl of stock solution, 200 µl of chloroform:methanol (2:1), and 300 µL of 0.6M HCl:methanol were pipetted together. Then the vial was heated in the oven at 100°C for 60 minutes. After this, 200 µl of hexane was added and mixed for 5 minutes. Samples were stored overnight in a freezer (-20°C). Before chromatographic analysis, 5 µl from the upper layer of the sample was taken and 450 µl of hexane was added. Derivatization of each sample was performed in triplicate.

Chromatographic separations of methylated fatty acids were performed on an Agilent Technologies 7890A GC system (Agilent Technologies, United States) equipped with an ultra inert splitless liner (Agilent Technologies, type 5190-2293, United States). The gas chromatograph was coupled to an Agilent 5975C mass spectrometer (Agilent Technologies, United States) with an electron ionization source and a quadrupole mass analyzer. The separation of FAMEs was performed on a ZB-5MSi capillary column (30 m x ID 0.25 mm, film thickness 0.25 mm, Agilent Technologies, United States). Helium (6.0 purity) was used as a carrier gas at a constant flow rate of 1 mL/min. Sample injection (2.5µL) was performed in splitless mode at 275°C. The oven temperature programming was set as follows: initial temperature, 32°C, was held for 4 min, then increased to 225°C at a rate of 10°C/min, held for 6 min, and finally increased to 300°C at a rate of 10°C/min and held for 5 min. The total analysis time was 41 min. The mass spectrometer was operated with an electron impact ionization of 70 eV using scan mode in the mass range of 35–600 m/z. The transfer line from GC column to MS was set to 250°C, the source 230°C, and the quadrupole 150°C. Data was collected using the Agilent Mass Hunter Workstation Qualitative Analysis software. Matches for fatty acids were confirmed by comparing the RT of standard mixture as well as searching the NIST17 database. Qualitative analysis was carried out using five-point calibration curves.

### *2.5. SPME-GC-MS experimental procedure*

The solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS) was conducted from fresh samples (0 days) and from samples that were stored at each temperature for 10, 30, 50, 70, and 90 days. For this purpose, the samples from each time point were collected and stored at -20°C until further analysis.

For the extraction of volatiles, a handful of chips was homogenized using a mortar, and 0.5 g was weighed into a 10 mL sample vial. The vials were pre-incubated at 50°C for 5 minutes. SPME fiber (30/50µm DVB/Car/PDMS Stableflex, length 2 cm) was used to adsorb/absorb the volatile compounds from the headspace (HS) for 20 minutes. The absorbed/absorbed volatile compounds were subsequently desorbed into a GC injection port for 5 minutes.

Identification and quantification of volatile compounds were performed using a gas chromatograph system (2030; Shimadzu, Kyoto, Japan) equipped with a mass spectrometer (8050NX Triple Quadrupole; Shimadzu, Kyoto, Japan). A ZB5-MS column (30 m length × 0.25 mm i.d. × 1.0 µm film thickness; Phenomenex, Torrance, CA, USA) was used with helium as a carrier gas at a linear velocity of 35 cm sec-1. The oven was programmed to ramp up from 40°C at a rate of 7.5°C/min to a final temperature of 280°C with an additional holding time of 4 minutes (total run time 36 min). Mass spectra were obtained at ionization energy of 70 eV with a mass-to-charge ratio scan range of 35 to 250. For each sample, three analytical replicates were made.

Non-targeted identification of volatile compounds was carried out using GC-MS solution software (Shimadzu, Japan) and retention indices (RI). Experimental retention indices were calculated using the retention times of the eluting compounds normalized to the retention times of adjacent n-alkanes. The identification of the compounds was verified by comparing experimental retention indices to NIST17 and FFNSC libraries. Semi-quantitative approach against an internal standard (4-methyl-2-pentanol; 200 ppb) was used to quantify identified volatile compounds.

### *2.6 GC-Olfactometry experimental procedure*

The extraction of volatile compounds from chips stored for 90 days at 40°C was carried out using the headspace solid-phase microextraction followed by gas chromatography olfactometry (HS-SPME/GC-O). The suitable amount of ground chips (1.0 g) was added into a SPME glass vial and pre-incubated at 50°C for 5 min. Volatile compounds were extracted from the headspace with a DVB/Car/PDMS fiber (Stableflex, 2 cm, Supelco) for 20 minutes under stirring at 50°C.

GC-Olfactometry analysis was performed using a GC system (Agilent 7890A; Agilent Technologies Inc., Palo Alto, CA) equipped with a sniffing port (ODP; Gerstel Inc.). The column was a ZB5-MS 30 m × 0.25 mm × 1.0 µm. The temperature program was as follows: from 35°C at 45°C/min up to 85°C; from 85°C at 9°C/min up to 200°C; from 200°C at 45°C/min up to 280°C with an additional holding time of 1 minute (total run time 16.67 min). Four trained assessors carried out the GC-O study. Assessors were asked to describe volatile compounds eluting from the column and measure the overall intensity of each odor using a 1−5 scale. Each assessor evaluated the samples twice.

### *2.7 Sensory analysis*

Sensory analysis was conducted with trained assessors who have previous experience in similar shelf-life tests. During the whole experiment, a total of 8 different assessors (with an average age of 31 ± 7 years) took part in sensory evaluations. Quantitative Descriptive Analysis was conducted in a dedicated sensory room in accordance with ISO 8589:2007. Sensory data was collected with RedJade software (RedJade Sensory Solutions LLC, Martinez, CA, USA). The focus was on the oxidation processes evidenced in the odor, so the sensory analysis only assessed the intensity of the rancid odor. The intensity was scored on a 10-point scale with word anchors, i.e. 0 – "none", 1 – "very weak", 5 – "moderate", and 9 – "very strong".

At the beginning of the experiment, chips were first evaluated as a reference sample and then preserved at the temperature of 4°C. During each subsequent time point, chips stored at 20°C, 30°C, and 40°C were evaluated. Chips stored at each temperature were evaluated in three replicates (9 samples in total for one time point). However, the chips stored now at 4°C, were given to the assessors as the reference sample. This allowed panelists to evaluate whether (and to what extent) rancidity had occurred in the odor of samples stored at high temperatures. Each session lasted about 15 minutes.

### *2.8 Statistical analysis*

Statistically significant difference was assessed using R 4.2.0 (The R Foundation, Vienna, Austria) and R package "agricolae" 1.3-5 by applying ANOVA with Tukey-Kramer *post hoc* test or Kruskal-Wallis test followed by Fisher's least significant difference procedure ($\alpha = 0.05$).

## 3. Results and Discussion

### *3.1 Changes in the fatty acid composition*

The results of the FAME analysis confirmed that the amounts of methyl linoleate and methyl oleate form the biggest shares in sunflower oil extracted from the stored potato chips (Table 1). Therefore, their decrease during storage at different temperatures was studied in more detail (Fig. 1). At the beginning of the experiment, the amounts of linoleic and oleic acid methyl esters were quite similar with methyl linoleate being in a slightly bigger proportion. The former made up 49% and the latter 47% of all isolated FAMEs. During storage, the amount of methyl linoleate decreased faster at all temperatures compared to methyl oleate. In addition, the decrease of both FAMEs was faster at higher temperatures. The decrease of methyl linoleate at 20°C, 30°C, and 40°C during 90 days was 21%, 33%, and 50% respectively, while methyl oleate decreased 12% at 20°C, 23% at 30°C, and 32% at 40°C. This result is in agreement with literature data showing that polyunsaturated linoleic acid is more susceptible to oxidation than monounsaturated oleic acid since it has two double bonds, requiring less energy to remove the hydrogen atom (Amaral *et al*., 2018).

The concentration of fatty acids decreased steadily which was in accordance with Pignitter & Somoza (2012) who showed that the amount of polyunsaturated fatty acids decreases during both the induction period as well as when secondary oxidation products are produced. Therefore, the decrease in unsaturated fatty acids may be monitored to describe the rate of oxidation, although it is not suitable to be used as a shelf-life indicator since it does not describe the end of shelf-life determined by organoleptical quality.

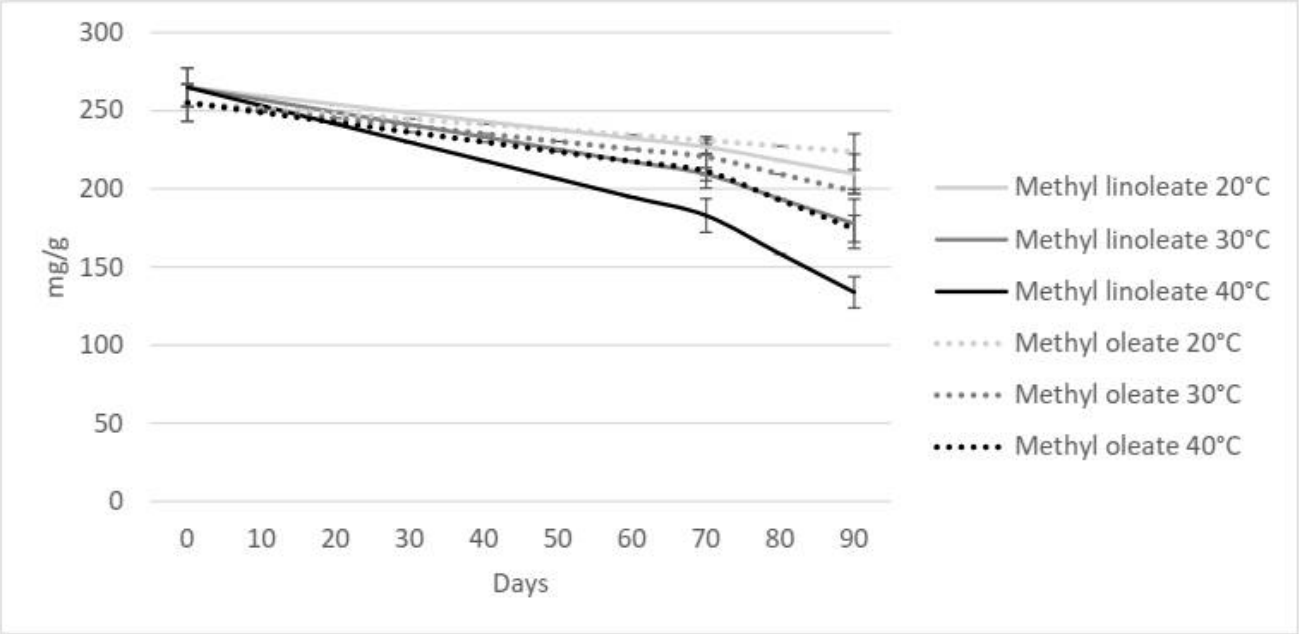


**Fig. 1.** Methyl linoleate and methyl oleate in sunflower oil extracted from potato chips during the shelf-life test in 20°C, 30°C, and 40°C storage

**Table 1.** Fatty acids extracted from potato chips stored at 20°C, 30°C, 40°C (mg/g)



| RT, min | Fatty acid | 0 days | 20°C | | 30°C | | 40°C | |
|---|---|---|---|---|---|---|---|---|
| | | | 70 days | 90 days | 70 days | 90 days | 70 days | 90 days |
| **22.03** | Methyl myristate | 0.08±0.00$^{ab}$ | 0.09±0.01$^{a}$ | 0.08±0.01$^{a}$ | 0.08±0.00$^{ab}$ | 0.08±0.01$^{ab}$ | 0.06±0.01$^{bc}$ | 0.04±0.1$^{c}$ |
| **23.973** | Methyl palmitoleate | 0.80±0.05$^{a}$ | 0.71±0.01$^{ab}$ | 0.68±0.02$^{cd}$ | 0.71±0.00$^{bc}$ | 0.69±0.02$^{bcd}$ | 0.66±0.02$^{de}$ | 0.47±0.06$^{e}$ |
| **24.192** | Methyl palmitate | 9.69±0.57$^{a}$ | 8.52±0.19$^{a}$ | 8.04±0.41$^{b}$ | 7.89±0.19$^{b}$ | 7.25±0.33$^{c}$ | 6.79±0.52$^{c}$ | 4.97±0.71$^{d}$ |
| **25.213** | cis-10-Heptadecanoic acid methyl ester | 0.12±0.02$^{a}$ | 0.10±0.02$^{ab}$ | 0.09±0.01$^{bc}$ | 0.08±0.01$^{abc}$ | 0.07±0.01$^{abc}$ | 0.08±0.00$^{abc}$ | 0.04±0.02$^{c}$ |
| **25.517** | Methyl heptadecanoate | 0.14±0.03$^{a}$ | 0.15±0.00$^{a}$ | 0.14±0.01$^{a}$ | 0.14±0.01$^{a}$ | 0.13±0.00$^{a}$ | 0.12±0.01$^{a}$ | 0.10±0.04$^{a}$ |
| **26.688** | Methyl linoleate | 264.94 ±12.50$^{a}$ | 226.83 ±4.25$^{ab}$ | 209.54 ±12.74$^{b}$ | 209.35 ±4.19$^{b}$ | 177.69 ±15.86$^{c}$ | 182.91 ±10.71$^{c}$ | 133.82 ±9.93$^{d}$ |
| **26.794** | cis-9-Oleic acid methyl ester | 255.09 ±11.84$^{a}$ | 231.00 ±2.39$^{b}$ | 223.70 ±11.56$^{bc}$ | 220.40 ±11.44$^{bc}$ | 198.44 ±1.47$^{de}$ | 211.20 ±10.68$^{cd}$ | 174.42 ±8.51$^{e}$ |
| **27.175** | Methyl stearate | 7.93±0.35$^{a}$ | 6.98±0.09$^{b}$ | 6.71±0.09$^{c}$ | 6.25±0.17$^{d}$ | 5.59±0.32$^{e}$ | 5.24±0.58$^{e}$ | 3.57±0.69$^{f}$ |
| **31.229** | Methyl arachidate | 1.11±0.11$^{a}$ | 1.08±0.03$^{ab}$ | 1.08±0.12$^{ab}$ | 1.07±0.05$^{ab}$ | 1.01±0.04$^{abc}$ | 0.91±0.07$^{bc}$ | 0.76±0.13$^{c}$ |
| **34.007** | Methyl behenate | 0.18±0.03$^{a}$ | 0.12±0.03$^{bc}$ | 0.09±0.03$^{cd}$ | 0.09±0.02$^{cd}$ | 0.06±0.02$^{d}$ | 0.10±0.05$^{ab}$ | 0.04±0.02$^{d}$ |
| **36.069** | Methyl lignocerate | 0.10±0.01$^{a}$ | 0.09±0.00$^{a}$ | 0.09±0.01$^{a}$ | 0.09±0.00$^{a}$ | 0.09±0.00$^{a}$ | 0.08±0.01$^{a}$ | 0.08±0.01$^{a}$ |

Data are presented as mean (± SD) (n=3) $^{a-f}$Means within each row for each compound with different superscripts are significantly ($p<0.05$) different.

### *3.2 Analysis of volatile compounds*

Some of the main volatiles identified in the stored samples as secondary oxidation products which according to the literature (Choe & Min, 2006; Frankel, 2012a; Xu *et al*., 2018) are responsible for off-odors in foods containing sunflower oil were hexanal, heptanal and pentanal from the linoleic acid cleavage of 13-hydroperoxide and decanal, nonanal and octanal from the oleic acid cleavage of 8-hydroperoxide,

10-hydroperoxide, and 11-hydroperoxide (Table 2).

**Table 2**. The main rancidity causing volatiles detected with GC-TQMS from potato chips during 90 days of storage at temperatures of 20°C, 30°C, and 40°C (ppb)

| RT, min | Compound | 0 days | 20°C | | | | 30°C | | | | 40°C | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 10 days | 30 days | 50 days | 70 days | 90 days | 10 days | 30 days | 50 days | 70 days | 90 days | 10 days | 30 days | 50 days | 70 days | 90 days |
| 5.19 | Pentanal | 22.04 ±2.22$^{g}$ | 23.12 ±2.64$^{fg}$ | 28.20 ±4.02$^{efg}$ | 34.74 ±2.22$^{cd}$ | 35.73 ±3.84$^{bcd}$ | 32.80 ±2.29$^{cde}$ | 25.61 ±5.82$^{efg}$ | 30.82 ±0.98$^{def}$ | 31.96 ±1.75$^{cde}$ | 34.92 ±3.99$^{bcd}$ | 38.18 ±3.11$^{bc}$ | 26.59 ±2.90$^{efg}$ | 29.00 ±2.14$^{efg}$ | 35.90 ±1.91$^{bcd}$ | 47.05 ±2.89$^{ab}$ | 2474.66 ±204.29$^{a}$ |
| 6.94 | 1-pentanol | 22.17 ±0.75$^{j}$ | 29.70 ±1.87$^{hi}$ | 38.37 ±0.53$^{fg}$ | 42.17 ±0.63$^{fg}$ | 48.28 ±2.51$^{d}$ | 48.91 ±2.44$^{de}$ | 30.90 ±1.70$^{hi}$ | 37.94 ±0.92$^{gh}$ | 41.86 ±0.49$^{fg}$ | 56.56 ±4.67$^{bc}$ | 56.59 ±0.54$^{abc}$ | 31.49 ±0.04$^{hi}$ | 43.24 ±4.32$^{ef}$ | 49.88 ±3.59$^{cd}$ | 70.07 ±4.51$^{ab}$ | 1644.14 ±46.06$^{a}$ |
| 7.43 | 2-Hexanone | 0.04 ±0.00$^{h}$ | 0.19 ±0.02$^{cdef}$ | 0.18 ±0.07$^{efgh}$ | 0.23 ±0.02$^{efgh}$ | 0.22 ±0.05$^{efgh}$ | 0.45 ±0.31$^{cdefg}$ | 0.16 ±0.01$^{gh}$ | 0.27 ±0.04$^{defg}$ | 0.38 ±0.02$^{bcde}$ | 0.72 ±0.23$^{abcd}$ | 1.04 ±0.27$^{ab}$ | 0.28 ±0.06$^{efg}$ | 0.80 ±0.04$^{abc}$ | 1.30 ±0.10$^{a}$ | 1.75 ±0.10$^{a}$ | 15.05 ±0.84$^{a}$ |
| 7.82 | Hexanal | 411.38 ±23.65$^{h}$ | 454.88 ±33.91$^{gh}$ | 542.43 ±51.38$^{defg}$ | 614.22 ±26.07$^{bcde}$ | 646.11 ±29.21$^{ab}$ | 653.15 ±159.36$^{abcde}$ | 478.19 ±56.12$^{efgh}$ | 501.77 ±118.11$^{cdefgh}$ | 564.03 ±31.09$^{bcdef}$ | 559.80 ±50.87$^{bcdef}$ | 621.90 ±44.75$^{abc}$ | 412.66 ±85.27$^{gh}$ | 432.40 ±66.93$^{fgh}$ | 462.67 ±30.21$^{fgh}$ | 509.13 ±29.11$^{cdefgh}$ | 15967.14 ±1386.70$^{a}$ |
| 9.83 | 2-Heptanone | 2.70 ±0.06$^{i}$ | 4.74 ±0.49$^{de}$ | 6.46 ±0.37$^{cd}$ | 7.58 ±0.36$^{de}$ | 7.67 ±0.45$^{cde}$ | 9.94 ±2.25$^{cd}$ | 5.81 ±0.56$^{ef}$ | 7.45 ±1.15$^{de}$ | 9.61 ±0.29$^{cd}$ | 12.47 ±1.54$^{bc}$ | 15.78 ±2.09$^{ab}$ | 7.68 ±0.09$^{de}$ | 11.77 ±1.36$^{bc}$ | 16.48 ±1.71$^{ab}$ | 20.93 ±1.23$^{a}$ | 468.37 ±0.88$^{a}$ |
| 10.15 | Heptanal | 7.78 ±0.28$^{h}$ | 16.75 ±2.16$^{gh}$ | 18.17 ±1.43$^{fgh}$ | 22.15 ±0.75$^{cdef}$ | 24.51 ±1.56$^{bc}$ | 18.63 ±0.48$^{fgh}$ | 18.66 ±1.44$^{efgh}$ | 18.55 ±4.33$^{defgh}$ | 20.75 ±7.77$^{cdef}$ | 22.89 ±1.06$^{cd}$ | 32.12 ±5.19$^{ab}$ | 21.94 ±0.60$^{cdefg}$ | 26.00 ±0.93$^{bcc}$ | 30.87 ±4.85$^{ab}$ | 32.24 ±1.45$^{ab}$ | 248.29 ±23.32$^{a}$ |
| 11.90 | 1-Octen-3-ol | 22.70 ±1.07$^{h}$ | 29.68 ±3.92$^{fgh}$ | 36.44 ±0.29$^{ef}$ | 36.56 ±4.41$^{def}$ | 35.17 ±3.27$^{efg}$ | 33.08 ±1.69$^{fgh}$ | 32.59 ±0.44$^{fgh}$ | 36.43 ±0.29$^{cdef}$ | 34.22 ±1.66$^{efgh}$ | 39.27 ±3.11$^{bcde}$ | 46.11 ±3.44$^{abc}$ | 28.03 ±0.47$^{gh}$ | 36.74 ±3.15$^{cdef}$ | 43.65 ±0.18$^{abcd}$ | 46.08 ±0.77$^{ab}$ | 1400.54 ±114.85$^{a}$ |
| 12.16 | 2-Octanone | 0.46 ±0.01$^{k}$ | 2.25 ±0.50$^{cd}$ | 2.84 ±0.19$^{de}$ | 3.41 ±0.39$^{cd}$ | 3.35 ±0.32$^{cd}$ | 4.51 ±0.68$^{bc}$ | 2.71 ±0.22$^{de}$ | 3.38 ±0.59$^{cd}$ | 3.58 ±1.18$^{cd}$ | 4.71 ±0.68$^{bc}$ | 7.24 ±0.93$^{ab}$ | 2.85 ±0.64$^{de}$ | 4.93 ±0.83$^{bc}$ | 6.68 ±0.91$^{ab}$ | 7.09 ±0.42$^{ab}$ | 46.63 ±3.92$^{a}$ |
| 12.49 | Octanal | 3.47 ±0.10$^{g}$ | 7.51 ±1.48$^{cd}$ | 7.67 ±0.21$^{cd}$ | 8.84 ±0.58$^{bc}$ | 9.63 ±1.23$^{bc}$ | 7.58 ±0.78$^{cd}$ | 8.28 ±0.73$^{cd}$ | 9.14 ±0.02$^{bc}$ | 10.55 ±1.03$^{ab}$ | 9.19 ±0.00$^{abc}$ | 11.30 ±0.50$^{ab}$ | 7.22 ±2.20$^{cd}$ | 10.53 ±0.98$^{ab}$ | 11.79 ±2.01$^{ab}$ | 12.59 ±0.29$^{a}$ | 198.00 ±10.55$^{a}$ |
| 13.28 | 3-Octen-2-one | 34.51± 0.12$^{h}$ | 52.07 ±3.06$^{cde}$ | 54.39 ±5.03$^{cde}$ | 45.81 ±0.38$^{fgh}$ | 45.29 ±1.56$^{fgh}$ | 42.90 ±1.05$^{fgh}$ | 49.69 ±2.81$^{bcd}$ | 48.46 ±1.75$^{cde}$ | 65.25 ±1.84$^{def}$ | 52.54 ±5.25$^{cde}$ | 65.25 ±2.82$^{ab}$ | 40.67 ±2.23$^{h}$ | 47.54 ±3.24$^{efg}$ | 61.31 ±2.64$^{abc}$ | 66.91 ±2.31$^{a}$ | 858.83 ±4.08$^{a}$ |
| 14.78 | Nonanal | 10.81 ±0.04$^{gh}$ | 12.30 ±2.18$^{defg}$ | 12.22 ±0.41$^{defg}$ | 13.20 ±1.05$^{cdefg}$ | 13.33 ±2.02$^{bcd}$ | 12.67 ±0.30$^{cde}$ | 13.00 ±0.34$^{cdef}$ | 12.79 ±1.35$^{bcd}$ | 12.49 ±0.81$^{bcd}$ | 11.35 ±0.84$^{cde}$ | 11.95 ±0.53$^{bcd}$ | 10.74 ±0.61$^{bc}$ | 10.44 ±0.01$^{bc}$ | 10.34 ±0.01$^{c}$ | 9.35 ±0.02$^{c}$ | 245.60 ±1.76$^{a}$ |
| 16.94 | Decanal | 0.32 ±0.01$^{i}$ | 1.05 ±0.60$^{efg}$ | 1.42 ±0.05$^{cdef}$ | 1.96 ±0.18$^{ab}$ | 1.96 ±0.30$^{abc}$ | 1.72 ±0.23$^{ab}$ | 1.12 ±0.12$^{ef}$ | 1.37 ±0.03$^{def}$ | 1.76 ±0.14$^{bcde}$ | 1.82 ±0.11$^{bcd}$ | 2.22 ±0.49$^{ab}$ | 1.17 ±0.12$^{ef}$ | 1.33 ±0.14$^{def}$ | 1.72 ±0.24$^{bcd}$ | 1.71 ±0.01$^{abcde}$ | 11.94 ±0.41$^{a}$ |
| 17.26 | 2,4-Nonadienal | 0.92 ±0.28$^{f}$ | 1.37 ±0.30$^{def}$ | 1.47 ±0.05$^{def}$ | 1.79 ±0.32$^{bcd}$ | 1.71 ±0.22$^{bcd}$ | 1.80± 0.28$^{bcd}$ | 1.44 ±0.13$^{def}$ | 1.40 ±0.36$^{def}$ | 1.65 ±0.17$^{cde}$ | 1.54 ±0.17$^{cde}$ | 2.81 ±0.61$^{ab}$ | 1.28 ±0.07$^{ef}$ | 1.40 ±0.14$^{def}$ | 1.70 ±0.16$^{cd}$ | 2.15 ±0.15$^{abc}$ | 152.10 ±29.54$^{a}$ |

Data are presented as mean (± SD) (n=3) $^{a-k}$Means within each row for each compound with different superscripts are significantly (p<0.05) different.

The full profile of aldehydes, ketones, and alcohols detected from analyzed samples is given in Tables 3, 4 and 5). From Table 2, it can be seen that in each storing temperature, the amount of isolated volatiles increased with time and hexanal was present in the largest amount among the components throughout the experiment. The significance of hexanal was also revealed from HS-SPME/GC-O analysis, which confirmed that it had one of the highest odor intensities (Table 6).

As hexanal has one of the lowest nasal odor threshold values among relevant aldehydes (320 ppm in oil) (Frankel, 2012a) and has been an important indicator of lipid oxidation in potato chips in previous studies as well (Marasca *et al*., 2016), it was also more specifically monitored in this experiment. Based on the information from the literature (Conte *et al*., 2020; Marasca *et al*., 2016), it was expected that the increase of hexanal is faster at higher temperatures. The results (Fig. 2) showed the opposite, where samples stored at 20°C had the highest and samples held at 40°C had the lowest amounts of hexanal until day 70. Similar findings were described by Manzocco *et al*. (2016), where the formation of hexanal at 25°C was slower than at 15°C. This may be explained by the mechanism of methyl ketone production from hexanal. For instance, Grebenteuch *et al*. (2021) indicated that hexanal may react further and produce alkan-2-ones such as 2-hexanone, 2-heptanone, and 2-octanone, and during these reactions, the hexanal content itself decreases. These alkan-2-ones were also identified in analyzed potato chips in this study and were found to increase faster at higher temperatures throughout the experiment (Table 2).

**Table 3.** Aldehydes, ketones, and alcohols isolated from potato chips stored at 20°C for 90 days (ppb)

| RT, min | Compound | 0 point | 10 days | 30 days | 50 days | 70 days | 90 days |
|---|---|---|---|---|---|---|---|
| 3.02 | Propanal, 2-methyl- | 1.67±0.37$^{g}$ | 1.83±0.18$^{fg}$ | 2.86±0.42$^{cd}$ | 5.07±0.24$^{a}$ | 5.15±1.21$^{a}$ | 7.70±2.38$^{a}$ |
| 3.44 | 2-Butanone | 3.79±0.89$^{gh}$ | 2.82±0.14$^{efgh}$ | 3.45±0.75$^{h}$ | 6.16±1.01$^{cdefg}$ | 5.51±1.52$^{defgh}$ | 7.03±2.28$^{bcde}$ |
| 3.56 | Butanal | 2.15±0.33$^{a}$ | 0.83±0.01$^{cdef}$ | 0.42±0.27$^{fgh}$ | 0.68±0.07$^{efg}$ | 0.74±0.29$^{def}$ | 0.91±0.42$^{bcde}$ |
| 4.42 | Butanal, 3-methyl- | 2.69±0.55$^{cd}$ | 1.97±0.06$^{d}$ | 2.97±0.27$^{bcd}$ | 4.23±0.05$^{abcd}$ | 4.62±1.28$^{ab}$ | 6.17±1.86$^{a}$ |
| 4.58 | Butanal, 2-methyl- | 5.60±0.64$^{cd}$ | 5.30±0.02$^{d}$ | 6.71±1.37$^{bcd}$ | 9.50±1.26$^{ab}$ | 10.48±3.59$^{ab}$ | 12.17±3.98$^{a}$ |
| 4.86 | 1-Penten-3-ol | 24.37±1.36$^{cd}$ | 24.89±0.23$^{cd}$ | 30.55±5.48$^{bc}$ | 33.95±4.07$^{ab}$ | 35.28±2.44$^{ab}$ | 42.39±15.69$^{ab}$ |
| 4.94 | 2-Pentanone | 0.95±0.32$^{f}$ | 1.06±0.09$^{def}$ | 1.58±0.50$^{def}$ | 1.84±0.30$^{bcde}$ | 1.69±0.57$^{cdef}$ | 2.39±0.99$^{abcd}$ |
| 5.09 | 2,3-Pentanedione | 2.23±0.17$^{a}$ | 2.18±0.10$^{a}$ | 1.46±0.18$^{b}$ | 0.69±0.14$^{c}$ | 0.47±0.09$^{cd}$ | 0.64±0.12$^{c}$ |
| 5.19 | Pentanal | 22.04±2.22$^{g}$ | 23.12±2.64$^{fg}$ | 28.20±4.02$^{efg}$ | 34.74±2.22$^{cd}$ | 35.73±3.84$^{bcd}$ | 32.80±2.28$^{cde}$ |
| 5.49 | Acetoin | 0.36±0.06$^{f}$ | 0.63±0.18$^{de}$ | 1.70±0.33$^{bc}$ | 2.57±0.30$^{ab}$ | 2.46±0.50$^{ab}$ | 6.38±1.21$^{a}$ |
| 6.42 | 2-Pentenal | 0.31±0.17$^{h}$ | 0.43±0.10$^{h}$ | 2.75±0.44$^{ef}$ | 4.42±0.38$^{cd}$ | 4.29±1.04$^{cde}$ | 6.24±1.99$^{bc}$ |
| 6.94 | 1-Pentanol | 22.17±0.75$^{i}$ | 29.70±1.87$^{hi}$ | 38.37±0.53$^{fg}$ | 42.17±0.62$^{fg}$ | 48.28±2.51$^{d}$ | 48.91±2.44$^{de}$ |
| 7.43 | 2-Hexanone | 0.04±0.00$^{h}$ | 0.19±0.02$^{cdef}$ | 0.18±0.07$^{fgh}$ | 0.23±0.02$^{efgh}$ | 0.22±0.05$^{efgh}$ | 0.45±0.31$^{cdefg}$ |
| 7.82 | Hexanal | 411.38 ±23.65$^{h}$ | 454.88 ±33.91$^{gh}$ | 542.43 ±51.38$^{bcdefg}$ | 614.22 ±26.07$^{abcd}$ | 646.11 ±29.21$^{ab}$ | 653.15 ±159.36$^{abcde}$ |
| 8.57 | Furfural | 0.42±0.04$^{g}$ | 0.97±0.18$^{de}$ | 2.58±0.18$^{abc}$ | 2.63±0.23$^{abc}$ | 2.43±0.40$^{bc}$ | 4.28±0.92$^{ab}$ |
| 9.83 | 2-Heptanone | 2.70±0.06$^{f}$ | 4.74±0.49$^{de}$ | 6.46±0.37$^{ef}$ | 7.58±0.36$^{de}$ | 7.67±0.45$^{de}$ | 9.95±2.25$^{cd}$ |
| 10.15 | Heptanal | 7.78±0.28$^{h}$ | 16.75±2.16$^{gh}$ | 18.17±1.42$^{fgh}$ | 22.15±0.75$^{cdef}$ | 24.51±1.56$^{bc}$ | 18.63±0.48$^{fgh}$ |
| 11.80 | Benzaldehyde | 5.94±0.16$^{h}$ | 6.73±0.79$^{h}$ | 11.72±0.82$^{def}$ | 17.39±2.58$^{bc}$ | 15.99±1.92$^{bc}$ | 21.74±3.16$^{ab}$ |
| 11.90 | 1-Octen-3-ol | 22.70±1.07$^{h}$ | 29.68±3.92$^{fgh}$ | 35.10±2.54$^{ef}$ | 36.56±4.40$^{def}$ | 35.17±3.27$^{efg}$ | 33.08±1.69$^{fgh}$ |
| 12.05 | 1-Heptanol | 7.48±0.00$^{d}$ | 10.03±1.94$^{abc}$ | 10.41±0.68$^{abc}$ | 10.52±0.20$^{abc}$ | 10.07±0.49$^{bcd}$ | 11.80±2.85$^{abc}$ |
| 12.16 | 2-Octanone | 0.46±0.01$^{e}$ | 2.25±0.50$^{cd}$ | 2.84±0.19$^{de}$ | 3.41±0.39$^{cd}$ | 3.35±0.32$^{cd}$ | 4.51±0.68$^{bc}$ |
| vi12.49 | Octanal | 3.47±0.10$^{d}$ | 7.51±1.48$^{cd}$ | 7.67±0.21$^{cd}$ | 8.84±0.58$^{bc}$ | 9.63±1.23$^{bc}$ | 7.58±0.78$^{cd}$ |
| 12.75 | 2,4-Heptadienal | 5.37±0.13$^{defg}$ | 5.63±1.21$^{def}$ | 9.49±0.91$^{a}$ | 8.74±0.88$^{ab}$ | 8.07±0.80$^{abc}$ | 8.92±1.72$^{ab}$ |
| 12.98 | 1-Hexanol, 2-ethyl- | 2.89±0.32$^{f}$ | 14.02±2.37$^{bcde}$ | 14.81±0.415$^{abcd}$ | 15.07±0.47$^{abc}$ | 15.03±0.82$^{abcd}$ | 12.67±0.30$^{def}$ |
| 13.28 | Oct-3-en-2-one | 34.51±0.12$^{h}$ | 52.10±3.06$^{cde}$ | 52.12±5.03$^{cde}$ | 54.39±2.65$^{bcd}$ | 45.81±0.38$^{fgh}$ | 45.29±1.05$^{fgh}$ |
| 13.78 | 2-Octenal | 6.65±0.16$^{fgh}$ | 9.23±1.59$^{abcd}$ | 9.98±0.66$^{ab}$ | 9.46±0.79$^{abc}$ | 8.33±0.96$^{bcdef}$ | 9.11±2.19$^{cdefg}$ |
| 14.15 | Acetophenone | 1.42±0.93$^{h}$ | 3.54±0.20$^{fgh}$ | 4.37±0.24$^{bcd}$ | 4.90±0.24$^{abc}$ | 4.43±0.06$^{bcd}$ | 5.69±0.80$^{a}$ |
| 14.78 | Nonanal | 10.81±0.04$^{bc}$ | 12.30±2.19$^{abc}$ | 12.22±0.41$^{abc}$ | 13.20±1.05$^{ab}$ | 13.33±2.02$^{abc}$ | 12.02±2.45$^{bc}$ |
| 16.03 | 1-Nonanol | 1.29±0.17$^{d}$ | 3.36±0.84$^{bcd}$ | 3.38±0.29$^{bcd}$ | 4.18±0.33$^{ab}$ | 3.96±0.47$^{ab}$ | 4.33±0.78$^{ab}$ |
| 16.36 | Benzaldehyde, 4-ethyl- | 0.19±0.16$^{f}$ | 0.51±0.19$^{ef}$ | 0.81±0.05$^{abc}$ | 0.81±0.13$^{bc}$ | 0.73±0.08$^{bcd}$ | 0.98±0.19$^{ab}$ |
| 16.94 | Decanal | 0.32±0.01$^{f}$ | 1.05±0.59$^{ef}$ | 1.42±0.05$^{cdef}$ | 1.91±0.18$^{ab}$ | 1.96±0.30$^{abc}$ | 1.96±0.38$^{ab}$ |
| 17.26 | 2,4-Nonadienal | 0.92±0.28$^{f}$ | 1.37±0.30$^{def}$ | 1.47±0.05$^{def}$ | 1.79±0.32$^{bcd}$ | 1.71±0.22$^{bcd}$ | 1.80±0.28$^{abcd}$ |
| 18.15 | 2-Decenal | 0.95±0.01$^{a}$ | 0.70±0.14$^{ab}$ | 0.50±0.08$^{bc}$ | 0.46±0.06$^{bc}$ | 0.39±0.09$^{cd}$ | 0.38±0.11$^{cd}$ |
| 18.36 | 1-Decanol | 1.53±0.00$^{abcd}$ | 0.96±0.17$^{d}$ | 1.11±0.07$^{d}$ | 1.72±0.26$^{abc}$ | 1.51±0.24$^{bcd}$ | 1.80±0.20$^{ab}$ |
| 21.81 | Dodecanol | 0.12±0.01$^{h}$ | 0.65±0.12$^{efgh}$ | 0.67±0.07$^{fgh}$ | 0.91±0.21$^{bcdef}$ | 0.82±0.04$^{cdefgh}$ | 0.94±0.16$^{bcd}$ |

Data are presented as mean (± SD) (n=3) $^{a-i}$Means within each row for each compound with different superscripts are significantly ($p<0.05$) different.



Hexanal was formed faster at lower temperatures until day 70, after which the amounts of hexanal and other key secondary oxidation products increased rapidly in potato chips stored at 40°C (Table 2). Similar results were found by Marasca *et al*. (2016) who at one point during the experimental study, detected a rapid increase of hexanal in sunflower oil-based potato chips in non-gas flushed packaging stored at 45°C. This phenomenon is explained by the mechanism of induction which is a time period during which the rate of oxidation is low but after which a rapid deterioration occurs (Calligaris *et al*., 2019; Gordon, 2004; Šimon *et al*., 2000).

**Table 4.** Aldehydes, ketones, and alcohols isolated from potato chips stored at 30°C for 90 days (ppb)

| RT, min | Compound | 0 point | 10 days | 30 days | 50 days | 70 days | 90 days |
|---|---|---|---|---|---|---|---|
| 3.02 | Propanal, 2-methyl- | 1.67±0.37$^{g}$ | 1.52±0.72$^{g}$ | 2.57±0.50$^{def}$ | 3.02±0.43$^{cd}$ | 3.29±0.77$^{bcd}$ | 3.99±0.22$^{ab}$ |
| 3.44 | 2-Butanone | 3.79±0.89$^{gh}$ | 3.80±1.07$^{fgh}$ | 4.70±0.25$^{efgh}$ | 6.39±1.03$^{cdef}$ | 6.69±1.39$^{cde}$ | 6.50±1.53$^{cdefg}$ |
| 3.56 | Butanal | 2.15±0.33$^{a}$ | 1.43±0.07$^{ab}$ | 1.22±0.38$^{abcd}$ | 1.01±0.09$^{bcd}$ | 0.53±0.02$^{efgh}$ | 0.21±0.01$^{gh}$ |
| 4.42 | Butanal, 3-methyl- | 2.69±0.55$^{cd}$ | 1.86±0.61$^{d}$ | 4.17±0.58$^{abcd}$ | 4.00±0.79$^{abcd}$ | 4.86±0.83$^{ab}$ | 4.89±0.40$^{a}$ |
| 4.58 | Butanal, 2-methyl- | 5.60±0.64$^{cd}$ | 2.58±1.13$^{d}$ | 8.43±1.40$^{abc}$ | 8.33±1.26$^{abc}$ | 10.69±1.68$^{a}$ | 9.62±0.68$^{a}$ |
| 4.86 | 1-Penten-3-ol | 24.37±1.36$^{cd}$ | 27.81±1.64$^{bcd}$ | 25.68±0.59$^{bcd}$ | 24.32±0.70$^{cd}$ | 35.76±4.85$^{ab}$ | 36.09 ±4.10$^{ab}$ |
| 4.94 | 2-Pentanone | 0.95±0.32$^{f}$ | 1.18±0.44$^{ef}$ | 1.46±0.23$^{def}$ | 1.55±0.15$^{def}$ | 2.17±0.60$^{abcd}$ | 2.52±0.51$^{abc}$ |
| 5.09 | 2,3-Pentanedione | 2.23±0.17$^{a}$ | 1.25±0.46$^{b}$ | 0.50±0.05$^{cd}$ | 0.21±0.04$^{de}$ | 0.05±0.02$^{gh}$ | 0.09±0.03$^{fg}$ |
| 5.19 | Pentanal | 22.04±2.22$^{g}$ | 25.60±5.81$^{efg}$ | 30.82±0.98$^{def}$ | 31.96±1.75$^{cde}$ | 34.92±3.99$^{bcd}$ | 38.18±3.11$^{abc}$ |
| 5.49 | Acetoin | 0.36±0.06$^{f}$ | 0.50±0.03$^{e}$ | 0.54±0.08$^{e}$ | 0.49±0.02$^{e}$ | 0.52±0.12$^{e}$ | 0.85±0.13$^{cd}$ |
| 6.42 | 2-Pentenal | 0.31±0.17$^{h}$ | 0.76±0.13$^{gh}$ | 2.39±0.57$^{fg}$ | 3.13±1.20$^{def}$ | 5.15±0.88$^{bc}$ | 7.85±1.40$^{ab}$ |
| 6.94 | 1-Pentanol | 22.17±0.75$^{i}$ | 30.90±1.70$^{hi}$ | 37.94±0.92$^{gh}$ | 41.86±0.50$^{fg}$ | 56.56±4.67$^{bc}$ | 56.59±0.54$^{abc}$ |
| 7.43 | 2-Hexanone | 0.04±0.00$^{h}$ | 0.16±0.01$^{gh}$ | 0.27±0.04$^{defg}$ | 0.38±0.02$^{bcde}$ | 0.72±0.23$^{abcd}$ | 1.04±0.27$^{ab}$ |
| 7.82 | Hexanal | 411.38 ±23.65$^{h}$ | 478.19 ±56.12$^{efgh}$ | 501.77 ±118.11$^{cdefgh}$ | 564.03 ±31.09$^{bcdef}$ | 559.80 ±50.87$^{abcdef}$ | 621.90 ±44.75$^{abc}$ |
| 8.57 | Furfural | 0.42±0.04$^{g}$ | 0.58±0.10$^{fg}$ | 0.77±0.07$^{e}$ | 0.74±0.15$^{ef}$ | 0.75±0.08$^{ef}$ | 1.88±0.13$^{cd}$ |
| 9.83 | 2-Heptanone | 2.70±0.06$^{f}$ | 5.81±0.56$^{ef}$ | 7.45±1.15$^{de}$ | 9.61±0.29$^{cd}$ | 12.47±1.54$^{bc}$ | 15.78±2.09$^{ab}$ |
| 10.15 | Heptanal | 7.78±0.28$^{h}$ | 18.66±1.43$^{efgh}$ | 18.55±4.33$^{defgh}$ | 20.75±7.77$^{cde}$ | 22.89±1.06$^{cd}$ | 32.12±5.19$^{ab}$ |
| 11.80 | Benzaldehyde | 5.94±0.16$^{h}$ | 6.99±0.25$^{h}$ | 9.53±0.54$^{fg}$ | 11.41±0.97$^{ef}$ | 13.07±1.13$^{de}$ | 20.89±2.54$^{ab}$ |
| 11.90 | 1-Octen-3-ol | 22.70±1.07$^{h}$ | 32.59±0.44$^{fgh}$ | 36.43±0.30$^{cdef}$ | 34.22±1.66$^{efgh}$ | 39.27±3.11$^{bcde}$ | 46.11± 3.44$^{abc}$ |
| 12.05 | 1-Heptanol | 7.48±0.00$^{d}$ | 9.72±0.87$^{bcd}$ | 9.82±1.23$^{bcd}$ | 10.66±0.03$^{abc}$ | 11.44±1.60$^{abc}$ | 13.37±2.18$^{ab}$ |
| 12.16 | 2-Octanone | 0.46±0.01$^{e}$ | 2.71±0.22$^{de}$ | 3.38±0.59$^{cd}$ | 3.58±1.18$^{cd}$ | 4.71±0.68$^{bc}$ | 7.24±0.93$^{ab}$ |
| 12.49 | Octanal | 3.47±0.10$^{d}$ | 8.28±0.73$^{cd}$ | 9.14±0.02$^{bc}$ | 10.55±1.03$^{ab}$ | 9.19±0.00$^{abc}$ | 11.30±0.50$^{ab}$ |
| 12.75 | 2,4-Heptadienal | 5.37±0.13$^{defg}$ | 5.78±0.31$^{cde}$ | 4.37±1.60$^{efg}$ | 3.72±1.57$^{gh}$ | 3.82±0.69$^{fgh}$ | 6.77±1.29$^{bcd}$ |
| 12.98 | 1-Hexanol, 2-ethyl- | 2.89±0.32$^{f}$ | 13.62±0.42$^{cdef}$ | 13.58±1.55$^{cdef}$ | 14.50±0.58$^{abcde}$ | 15.52±1.60$^{abc}$ | 19.04±0.91$^{ab}$ |
| 13.28 | Oct-3-en-2-one | 34.51±0.12$^{h}$ | 42.90±2.81$^{gh}$ | 49.69±1.75$^{de}$ | 48.46±1.84$^{def}$ | 52.54±5.25$^{cde}$ | 65.25±2.82$^{ab}$ |
| 13.78 | 2-Octenal | 6.65±0.16$^{fgh}$ | 8.83±1.05$^{abcde}$ | 8.86±0.06$^{abcde}$ | 7.22±0.67$^{cdefgh}$ | 6.91±0.81$^{efgh}$ | 9.29±1.57$^{abc}$ |
| 14.15 | Acetophenone | 1.42±0.93$^{h}$ | 3.20±0.18$^{fgh}$ | 3.57±0.33$^{ef}$ | 3.39±1.15$^{ef}$ | 4.30±0.15$^{cde}$ | 5.19±0.37$^{ab}$ |
| 14.78 | Nonanal | 10.81±0.04$^{bc}$ | 13.00±0.34$^{ab}$ | 12.79±1.35$^{abc}$ | 12.49±0.81$^{abc}$ | 11.35±0.84$^{bc}$ | 11.95±0.53$^{abc}$ |
| 16.03 | 1-Nonanol | 1.29±0.17$^{d}$ | 3.44±0.37$^{bcd}$ | 3.58±0.41$^{bcd}$ | 3.39±0.85$^{bcd}$ | 4.27±0.49$^{ab}$ | 5.91±1.35$^{a}$ |
| 16.36 | Benzaldehyde, 4-ethyl- | 0.19±0.16$^{f}$ | 0.49±0.05$^{ef}$ | 0.58±0.08$^{def}$ | 0.63±0.25$^{cde}$ | 0.75±0.03$^{bcd}$ | 1.08±0.32$^{ab}$ |
| 16.94 | Decanal | 0.32±0.01$^{f}$ | 1.12±0.12$^{ef}$ | 1.37±0.03$^{def}$ | 1.76±0.14$^{bcde}$ | 1.82±0.11$^{abcd}$ | 2.22±0.49$^{ab}$ |
| 17.26 | 2,4-Nonadienal | 0.92±0.28$^{f}$ | 1.44±0.13$^{def}$ | 1.40±0.36$^{def}$ | 1.65±0.17$^{cde}$ | 1.55±0.17$^{de}$ | 2.81±0.60$^{ab}$ |
| 18.15 | 2-Decenal | 0.95±0.01$^{a}$ | 0.71±0.02$^{ab}$ | 0.29±0.10$^{de}$ | 0.20±0.09$^{e}$ | 0.20±0.02$^{e}$ | 0.40±0.15$^{cd}$ |
| 18.36 | 1-Decanol | 1.53±0.00$^{abcd}$ | 1.16±0.24$^{d}$ | 1.27±0.17$^{cd}$ | 1.50±0.50$^{bcd}$ | 1.43±0.25$^{bcd}$ | 2.19±0.50$^{ab}$ |
| 21.81 | Dodecanol | 0.12±0.01$^{h}$ | 0.72±0.13$^{defgh}$ | 0.72±0.09$^{defgh}$ | 1.13±0.18$^{abc}$ | 0.83±0.12$^{cdefg}$ | 1.30±0.33$^{ab}$ |

Data are presented as mean (± SD) (n=3) $^{a-h}$Means within each row for each compound with different superscripts are significantly ($p<0.05$) different.

It is also known that the increase in temperature shortens the induction period (Velasco *et al.*, 2010). Therefore, it can be said that the induction period of lipid oxidation detected by volatile compound analysis ended on day 70 for the samples that were stored at 40°C.

Chips held at 20°C and 30°C did not reach the endpoint of the induction period and therefore did not show a rapid increase of volatiles throughout the experiment.

**Table 5.** Aldehydes, ketones, and alcohols isolated from potato chips stored at 40°C for 90 days (ppb)

| RT, min | Compound | 0 point | 10 days | 30 days | 50 days | 70 days | 90 days |
|---|---|---|---|---|---|---|---|
| **3.02** | Propanal, 2-methyl- | 1.67±0.37$^{g}$ | 2.08±0.50$^{efg}$ | 2.70±0.10$^{cde}$ | 3.10±0.21$^{bc}$ | 2.85±0.20$^{cd}$ | 8.91±0.30$^{a}$ |
| **3.44** | 2-Butanone | 3.79±0.89$^{gh}$ | 5.53±1.53$^{defgh}$ | 7.57±0.67$^{abcd}$ | 9.46±0.23$^{abc}$ | 9.96±0.13$^{ab}$ | 34.25±4.32$^{a}$ |
| **3.56** | Butanal | 2.15±0.33$^{a}$ | 1.34±0.00$^{abc}$ | 1.27±0.26$^{abc}$ | 0.90±0.14$^{bcdef}$ | 0.63±0.15$^{efgh}$ | 0.00±0.00$^{h}$ |
| **4.42** | Butanal, 3-methyl- | 2.69±0.55$^{cd}$ | 3.99±1.23$^{abcd}$ | 4.74±0.83$^{ab}$ | 4.57±0.30$^{abc}$ | 4.63±0.20$^{ab}$ | 3.77±3.23$^{abcd}$ |
| **4.58** | Butanal, 2-methyl- | 5.60±0.64$^{cd}$ | 9.40±0.61$^{ab}$ | 9.61±1.89$^{ab}$ | 8.55±0.84$^{ab}$ | 7.65±0.86$^{abcd}$ | 9.55±2.53$^{ab}$ |
| **4.86** | 1-Penten-3-ol | 24.37±1.36$^{cd}$ | 23.45±1.36$^{d}$ | 26.64±0.26$^{bcd}$ | 23.92±2.30$^{cd}$ | 26.50±1.36$^{bcd}$ | 69.25±19.90$^{a}$ |
| **4.94** | 2-Pentanone | 0.95±0.32$^{f}$ | 1.43±0.26$^{def}$ | 1.88±0.16$^{bcde}$ | 2.49±0.13$^{abc}$ | 2.77±0.25$^{ab}$ | 41.44±1.85$^{a}$ |
| **5.09** | 2,3-Pentanedione | 2.23±0.17$^{a}$ | 0.74±0.32$^{c}$ | 0.11±0.01$^{ef}$ | 0.02±0.00$^{h}$ | 0.02±0.01$^{h}$ | 0.07±0.01$^{fg}$ |
| **5.19** | Pentanal | 22.04±2.22$^{g}$ | 26.59±2.90$^{efg}$ | 29.00±2.14$^{efg}$ | 35.90±1.91$^{abcd}$ | 47.05±2.89$^{ab}$ | 2474.66±204.29$^{a}$ |
| **5.49** | Acetoin | 0.36±0.06$^{f}$ | 0.28±0.04$^{fg}$ | 0.19±0.03$^{gh}$ | 0.21±0.01$^{gh}$ | 0.13±0.00$^{gh}$ | 0.01±0.00$^{h}$ |
| **6.42** | 2-Pentenal | 0.31±0.17$^{h}$ | 1.69±0.45$^{fgh}$ | 4.05±0.90$^{cde}$ | 5.82±0.67$^{ab}$ | 5.43±0.61$^{bc}$ | 34.56±4.01$^{a}$ |
| **6.94** | 1-Pentanol | 22.17±0.75$^{i}$ | 31.50±0.04$^{hi}$ | 43.24±4.32$^{ef}$ | 49.88±3.59$^{cd}$ | 70.07±4.51$^{ab}$ | 1644.14±46.06$^{a}$ |
| **7.43** | 2-Hexanone | 0.04±0.00$^{h}$ | 0.28±0.06$^{efg}$ | 0.80±0.03$^{abc}$ | 1.30±0.10$^{a}$ | 1.75±0.10$^{a}$ | 15.05±0.84$^{a}$ |
| **7.82** | Hexanal | 411.38 ±23.65$^{h}$ | 412.66 ±85.27$^{gh}$ | 432.40 ±66.93$^{gh}$ | 462.67 ±30.21$^{fgh}$ | 509.13 ±29.11$^{defgh}$ | 15967.14 ±1386.70$^{a}$ |
| **8.57** | Furfural | 0.42±0.04$^{g}$ | 0.42±0.03$^{g}$ | 0.68±0.10$^{ef}$ | 0.73±0.17$^{ef}$ | 0.81±0.06$^{e}$ | 5.26±0.98$^{a}$ |
| **9.83** | 2-Heptanone | 2.70±0.06$^{f}$ | 7.68±0.09$^{de}$ | 11.77±1.36$^{bc}$ | 16.48±1.71$^{ab}$ | 20.93±1.23$^{a}$ | 468.37±0.88$^{a}$ |
| **10.15** | Heptanal | 7.78±0.28$^{h}$ | 21.94±0.60$^{cdefg}$ | 26.00±0.93$^{abc}$ | 30.87±4.85$^{ab}$ | 32.24±1.45$^{ab}$ | 248.29±23.32$^{a}$ |
| **11.80** | Benzaldehyde | 5.94±0.16$^{h}$ | 7.23±0.89$^{gh}$ | 9.80±2.07$^{f}$ | 12.92±1.78$^{de}$ | 13.60±0.79$^{cd}$ | 113.22±21.44$^{a}$ |
| **11.90** | 1-Octen-3-ol | 22.70±1.07$^{h}$ | 28.04±0.46$^{gh}$ | 36.75±3.12$^{cdef}$ | 43.65±0.18$^{abcd}$ | 46.09±0.77$^{ab}$ | 1400.54±112.85$^{a}$ |
| **12.05** | 1-Heptanol | 7.48±0.00$^{d}$ | 8.20±0.73$^{d}$ | 9.15±0.66$^{cd}$ | 10.26±1.92$^{bcd}$ | 9.47±0.32$^{cd}$ | 154.17±38.98$^{a}$ |
| **12.16** | 2-Octanone | 0.46±0.01$^{e}$ | 2.85±0.64$^{de}$ | 4.93±0.83$^{bc}$ | 6.68±0.91$^{ab}$ | 7.09±0.42$^{ab}$ | 46.63±3.92$^{a}$ |
| **12.49** | Octanal | 3.47±0.10$^{d}$ | 7.22±2.20$^{cd}$ | 10.53±0.98$^{ab}$ | 11.79±2.01$^{ab}$ | 12.59±0.29$^{a}$ | 198.00±10.55$^{a}$ |
| **12.75** | 2,4-Heptadienal | 5.37±0.13$^{defg}$ | 4.29±0.37$^{fgh}$ | 2.22±0.01$^{hi}$ | 1.72±0.15$^{i}$ | 2.39±0.27$^{hi}$ | 56.65±3.25$^{a}$ |
| **12.98** | 1-Hexanol, 2-ethyl- | 2.89±0.32$^{f}$ | 11.00±2.13$^{ef}$ | 12.48±1.17$^{def}$ | 12.85±2.30$^{cdef}$ | 13.75±2.03$^{cde}$ | 27.79±3.49$^{a}$ |
| **13.28** | Oct-3-en-2-one | 34.51±0.12$^{h}$ | 40.67±2.23$^{h}$ | 47.54±3.24$^{efg}$ | 61.31±2.64$^{abc}$ | 66.91±2.30$^{a}$ | 858.83±4.08$^{a}$ |
| **13.78** | 2-Octenal | 6.65±0.16$^{fgh}$ | 7.16±0.07$^{defgh}$ | 5.94±0.49$^{gh}$ | 5.73±0.51$^{h}$ | 7.45±0.17$^{cdefgh}$ | 3208.71±354.03$^{a}$ |
| **14.15** | Acetophenone | 1.42±0.93$^{h}$ | 2.49±0.29$^{gh}$ | 3.49±0.46$^{efg}$ | 3.83±0.76$^{def}$ | 3.83±0.39$^{def}$ | 25.59±3.86$^{a}$ |
| **14.78** | Nonanal | 10.81±0.04$^{bc}$ | 10.74±0.61$^{bc}$ | 10.44±0.01$^{bc}$ | 10.34±0.01$^{c}$ | 9.35±0.02$^{c}$ | 245.60±1.76$^{a}$ |
| **16.03** | 1-Nonanol | 1.29±0.17$^{d}$ | 2.91±0.34$^{cd}$ | 3.77±0.71$^{bc}$ | 4.10±0.59$^{ab}$ | 3.71±0.25$^{bc}$ | 33.85±11.06$^{a}$ |
| **16.36** | Benzaldehyde, 4-ethyl- | 0.19±0.16$^{f}$ | 0.37±0.08$^{f}$ | 0.55±0.08$^{ef}$ | 0.68±0.10$^{cde}$ | 0.76±0.01$^{bc}$ | 4.68±1.27$^{a}$ |
| **16.94** | Decanal | 0.32±0.01$^{f}$ | 1.17±0.12$^{ef}$ | 1.33±0.14$^{def}$ | 1.72±0.24$^{abcd}$ | 1.71±0.01$^{abcde}$ | 11.94±0.41$^{a}$ |
| **17.26** | 2,4-Nonadienal | 0.92±0.28$^{f}$ | 1.28±0.07$^{ef}$ | 1.40±0.15$^{def}$ | 1.71±0.15$^{cd}$ | 2.15±0.15$^{abc}$ | 152.10±29.54$^{a}$ |
| **18.15** | 2-Decenal | 0.95±0.01$^{a}$ | 0.28±0.09$^{de}$ | 0.00±0.00$^{f}$ | 0.00±0.00$^{f}$ | 0.00±0.00$^{f}$ | 49.90±1.81$^{a}$ |
| **18.36** | 1-Decanol | 1.53±0.00$^{abcd}$ | 1.10±0.17$^{d}$ | 1.55±0.32$^{bcd}$ | 1.73±0.26$^{abc}$ | 1.58±0.16$^{abcd}$ | 33.75±6.18$^{a}$ |
| **21.81** | Dodecanol | 0.12±0.01$^{h}$ | 0.64±0.08$^{gh}$ | 0.92±0.12$^{bcde}$ | 1.03±0.19$^{abc}$ | 0.92±0.04$^{bcd}$ | 2.41±0.89$^{a}$ |

Data are presented as mean (± SD) (n=3) $^{a-i}$Means within each row for each compound with different superscripts are significantly ($p<0.05$) different.

### *3.3 Sensory analysis*

Similarly to Frankel (2012a) and Clarke *et al.* (2020), the rancid off-odor was described by the panel as "painty" and that with all storage conditions. Rancidity started to develop first at 40°C from day 20, whereas rancidity at 30°C was detected starting from day 30 (Fig. 3).

At the lowest temperature, a rancid odor occurred from day 40. Further, from day 60 until the end of the test, a rapid 4-fold increase of rancidity in chips stored at 40°C was detected while samples held at lower temperatures had mild changes.

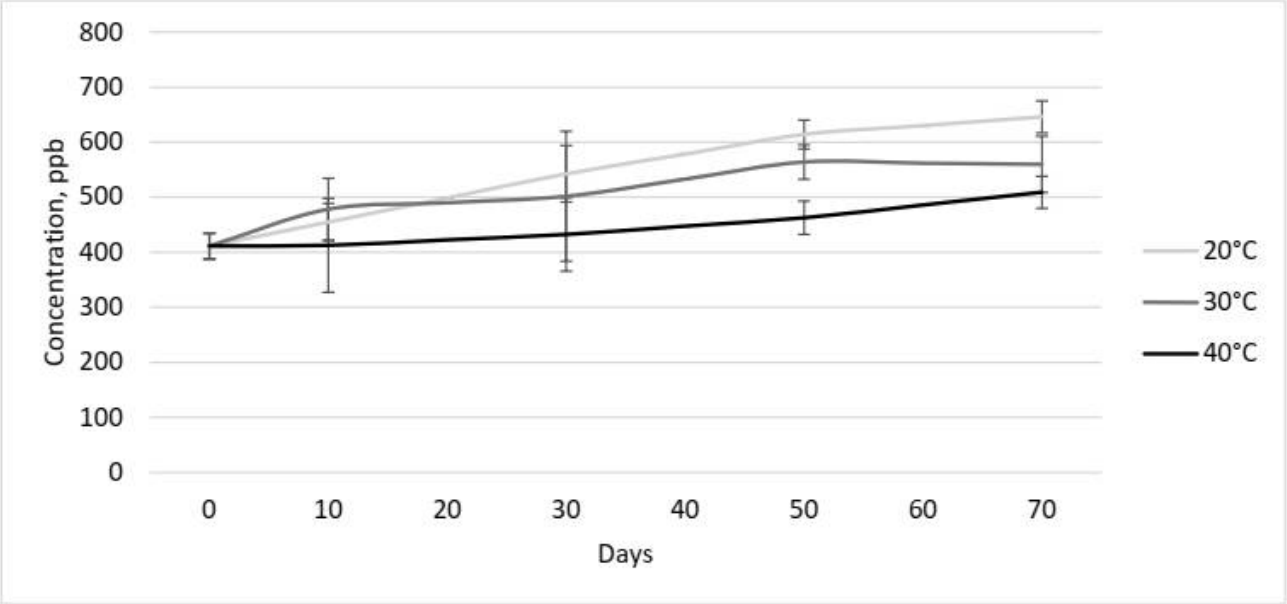


**Fig. 2.** The formation of hexanal in potato chips during 70 days of shelf-life test at 20°C, 30°C, and 40°C storage

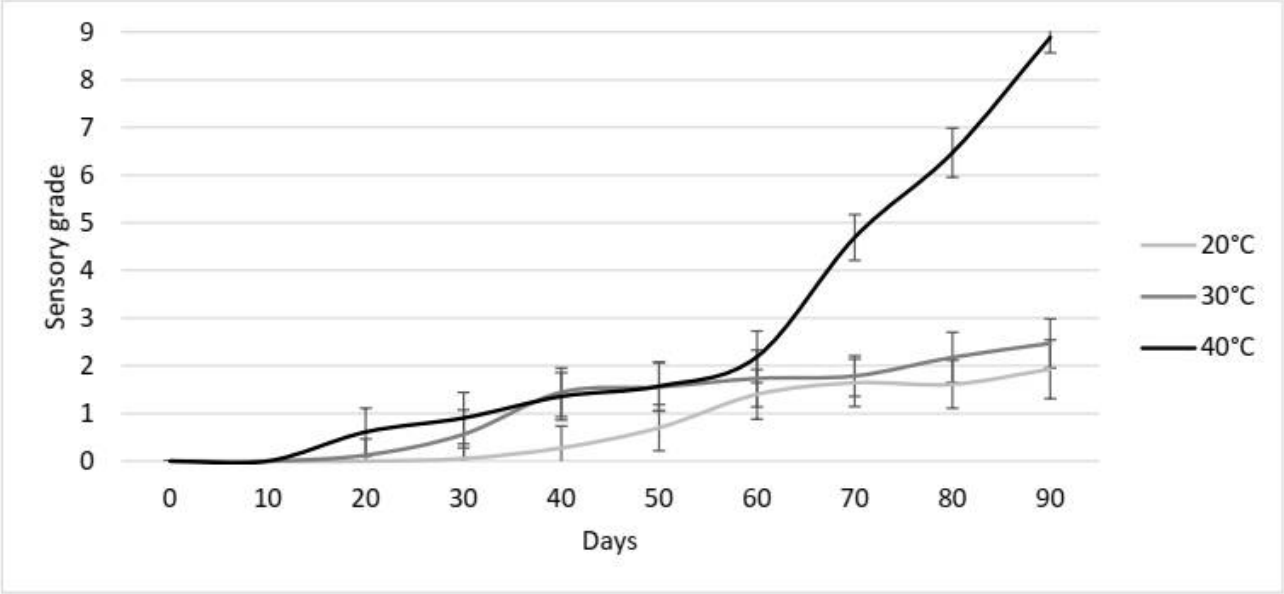


**Fig. 3.** Rancid odor of potato chips during 90 days of shelf-life test at 20°C, 30°C, and 40°C storage

These results confirm that the rate of lipid oxidation increases with temperature rise as temperature is the main catalyzer of autoxidation (Kong & Singh, 2016; Shahidi & Zhong, 2010). Therefore, rapid changes in the development of rancidity were detected only in samples stored at 40°C, reaching a rancidity score of 8.9 by the end of the experiment while the final rancidity scores for samples stored at 30°C and 20°C were 2.5 and 2, respectively.

**Table 6.** HS-SPME GC-TQMS/GC-Olfactometry results from volatiles isolated from potato chips stored at 40°C for 90 days

| Compound | Description | RT GC-O, min | LRI, exp | LRI, litr | Score |
|---|---|---|---|---|---|
| **Methyl acetate** | acidic | 2.20 | 507 | 515 | 1 |
| **Butanal, 2-methyl- OR Butanal, 3-methyl-** | chemical, green, acetone-like | 2.96 | 653 | 661 | 1.5 |
| **1-Penten-3-ol** | rancid butter, potato-like | 3.05 | 666 | 673 | 2 |
| **Pentanal** | grass, green apple | 3.13 | 677 | 696 | 2 |
| **2-Pentenal** | chemical, green bug | 3.53 | 724 | 744 | 1 |
| **Butanoic acid** | cheesy | 3.62 | 732 | 800 | 1.5 |
| **1-Pentanol** | green, fruity, grassy | 3.88 | 758 | 756 | 3 |
| **Hexanal** | green grass | 4.13 | 782 | 800 | 4 |
| **Pentanethiol** | potato-like, paint | 4.26 | 795 | 815 | 2 |
| **Pentanoic acid** | cheese, acidic | 4.84 | 839 | 887 | 3.5 |
| **2-Heptanone** | metallic, hay, woody | 5.14 | 861 | 890 | 3.5 |
| **Heptanal** | hay, rubbery, paint | 5.33 | 875 | 903 | 2 |
| **Unknown 1** | paint, chemical, medicinal | 5.53 | 890 | - | 3 |
| **Unknown 2** | mushroom, moldy | 6.10 | 927 | - | 2 |
| **1-Heptanol** | green, grassy | 6.32 | 941 | 975 | 1.5 |
| **Hexanoic acid** | rancid, sweaty, wet cloth | 6.37 | 945 | 981 | 4 |
| **1-Octen-3-ol** | mushroom | 6.61 | 960 | 979 | 3 |
| **Octanal** | floral, fresh, soapy | 6.98 | 988 | 1001 | 3 |
| **2,4-Heptadienal** | green, metallic | 7.25 | 1001 | 1015 | 1.5 |
| **2-Acetylthiazole OR 5-Methyl-2-furfurylthiol** | coffee, acidic, dump | 7.57 | 1020 | 1020/1016 | 2 |
| **3-Octen-2-one** | hay, green, fatty | 7.77 | 1032 | 1040 | 3 |
| **2-Ethyl-3-methylpyrazine** | herbal, nutty, boiled | 7.82 | 1035 | 1000 | 2 |
| **2-Octenal** | herbal, green | 8.00 | 1046 | 1062 | 3.5 |
| **1-Nonen-3-one** | mushroom, paint | 8.28 | 1063 | 1076 | 2 |
| **Acetophenone** | floral | 8.32 | 1065 | 1072 | 2 |
| **3-Ethyl-2,5-dimethyl- pyrazine** | hay-like, vegetables, roasted | 8.46 | 1074 | 1078 | 2 |
| **Nonanal** | fresh, waxy, chemical | 8.52 | 1078 | 1102 | 1 |
| **Unknown 3** | cooked, fried, fatty | 8.61 | 1083 | - | 2.5 |
| **2-Ethenyl-3,5-dimethylpyrazine** | mushroom | 8.86 | 1098 | 1102 | 2 |
| **2-Nonenal** | fresh, green, nice | 9.54 | 1139 | 1147 | 3 |
| **Octanoic acid** | hay, green, soapy | 9.66 | 1146 | 1156 | 1 |
| **4-Ethylphenol** | dry, rubbery, phenolic, leather | 9.74 | 1151 | 1161 | 2.5 |
| **Decanal** | fatty, fresh | 10.29 | 1184 | 1207 | 1.5 |
| **2,4-Nonadienal** | fatty, cooked, fried, soup | 10.61 | 1204 | 1210 | 3 |
| **γ-Octalactone** | coconut, sweet, baked | 10.99 | 1228 | 1261 | 3 |
| **Unknown 4** | forest-like, strange coconut, fat | 11.32 | 1248 | - | 3 |
| **(E)-2-Decenal OR 1-Decanol** | green, pungent | 11.58 | 1265 | 1262/1271 | 1 |
| **(E,E)-2,4-Decadienal** | fatty, vegetable, rancid, hay | 12.22 | 1305 | 1317 | 2 |
| **γ-Nonalactone** | coconut, sweet, baked | 12.60 | 1330 | 1366 | 2 |
| **Decanoic acid** | rubbery, dry, clay | 12.91 | 1350 | 1373 | 1.5 |
| **Unknown 5** | green pepper, onions, plant | 13.18 | 1368 | - | 2.5 |

Based on sensory analysis, it can be said that the end of the oxidation induction period for samples stored at 40°C was observed on day 60, while samples stored at 30°C and 20°C did not reach the end of the induction period and therefore did not have a rapid increase in rancidity. These results were in agreement with the conclusions from GC-TQMS analysis which also showed a rapid increase in volatiles causing rancidity for samples stored only at 40°C (Table 2).

However, for samples stored at 40°C, there were differences between the detected end of the induction period based on sensory analysis and the analysis of volatile compounds. While rancidity increased steeply from day 60, hexanal content, as one of the main indicators of oxidation (Azarbad & Jeleń, 2014; Marasca *et al*., 2016), started increasing rapidly after day 70. This difference could be explained by the non-linear relations between molecule concentrations and sensory perception together with the potential role of other key odor-active components contributing to organoleptically perceived rancidity. For example, the amounts of heptanal and 2-heptanone were the biggest at 40°C throughout the experiment. On the other hand, the production of octanal and pentanal started increasing from day 50. It was revealed from GC-O analysis that heptanal, octanal, and 2-heptanone were perceived with high, and pentanal with medium intensity. These results are in accordance with those of Franklin *et al*. (2017) who showed that these compounds contribute to the development of rancid odor during lipid oxidation. The GC-TQMS analysis showed that the amounts of 1-pentanol, 1-octen-3-ol, 3-octen-2-one, and 2,4-nonadienal started increasing from day 50 at 40°C, having high intensities in GC-O results as well. According to literature (Franklin *et al*., 2017; Fu *et al*., 2020; Lee & Choe, 2012), these compounds have been associated with rancid notes in different matrices. These findings confirm that although hexanal is considered to be the main indicator of rancidity during lipid oxidation, different alcohols, aldehydes, and ketones also contribute to the development of unwanted off-odors which can be organoleptically perceived before a rapid increase in hexanal content takes place. Therefore, it has been argumented by Coppin & Pike (2001) that the rancidity determined by human perception is the most important test for calculating induction period. Irwin & Hedges (2004) added that it is important to validate sensory results with analytical measurement since the latter can give additional information about the mechanism of organoleptically perceived rancidity.

### *3.4. Modeling the rate of lipid oxidation indicators*



The reaction rates for each oxidation indicator monitored throughout the experiment were calculated by using Equation (1) (Table 7). As linoleic and oleic acids are both contributing to the formation of volatiles associated with rancidity, their amounts and reaction rates at each temperature and time point were summed. It is seen that the reaction rate of the decomposition of chosen FAMEs increased with the rise in storage temperature. In addition, the rates of this process at 20°C and 30°C were approximately 2.3 and 1.4 times slower than at 40°C, respectively. Also, the reaction rate of rancid odor development increased at higher temperatures, with the rate at 20°C being approximately 3.6 times and at 30°C 3 times slower than in storage at 40°C. On the other hand, the rates of the formation of hexanal differ from other oxidation indicators.

**Table 7.** Reaction rates of different oxidation indicators

| Storage temperature | Linoleic and oleic acid methyl esters | | Rancid odor | | Hexanal | |
|---|---|---|---|---|---|---|
| | $k_{FAME}$ (mg/g day$^{-1}$) | $R^2$ | $k_{rancidity}$ (score/day) | $R^2$ | $k_{hexanal}$ (ppb/day) | $R^2$ |
| **20°C** | 0.9446 | 0.9957 | 0.0250 | 0.8998 | 2.8143 | 0.9223 |
| **30°C** | 1.5748 | 0.9977 | 0.0299 | 0.9454 | 2.0519 | 0.9234 |
| **40°C** | 2.2085 | 0.9599 | 0.0908 | 0.8290 | 124.07 | 0.4664 |

**Table 8.** Activation energy, frequency factor, and coefficient of determination of monitored oxidation indicators

| Oxidation indicator | $E_a$ (kJ/mol) | $k_0$ | $R^2$ |
|---|---|---|---|
| **Hexanal** | 142.58 | $7.58 \times 10^{24}$ | 0.67 |
| **Rancid odor** | 48.81 | $7.70 \times 10^{6}$ | 0.84 |
| **Linoleic and oleic acid methyl esters** | 32.47 | $6.20 \times 10^{5}$ | 0.99 |

The reaction rate of hexanal formation at 30°C was approximately 1.4 times slower than at 20°C, which is probably due to the formation of methyl ketones from hexanal. However, the rate of hexanal at 40°C was 44 times faster than at 20°C. As described previously, at 40°C, the induction period reached the end, resulting also in an increased reaction rate of hexanal production. A similar trend was followed for other volatiles.

To further study the temperature dependence of different oxidation indicators describing lipid oxidation in potato chips, the reaction rates were visualized in the Arrhenius plot (Fig. 4). It can be seen that the development of rancidity and the degradation of chosen FAMEs followed Arrhenius's behavior. Although, it has to be noted that the latter analysis was done from three storage time points which may not give the whole overview of the oxidation process. However, while the results of FAME and rancidity showed similar trends, the rate of hexanal formation had the biggest fluctuations. It is seen from the plot that at 20°C and 30°C, the production of hexanal throughout the shelf-life test was in lag phase, while at 40°C, it reached the endpoint of the induction period, having a rapid increase in the reaction rate as well.

The activation energies and frequency factors (Table 8) of monitored oxidation indicators were calculated, using Equations (2) and (3). It is seen that the activation energy of each parameter is within the range described by Calligaris *et al.* (2019). However, there is a clear difference between the values as the development of rancidity and the decomposition of chosen FAMEs had 3-4. 5 times smaller activation energy values than the formation of hexanal. Based on the results from the Arrhenius plot (Fig 4) and calculated activation energies (Table 8), it can be concluded that both the degradation of unsaturated fatty acids and the formation of

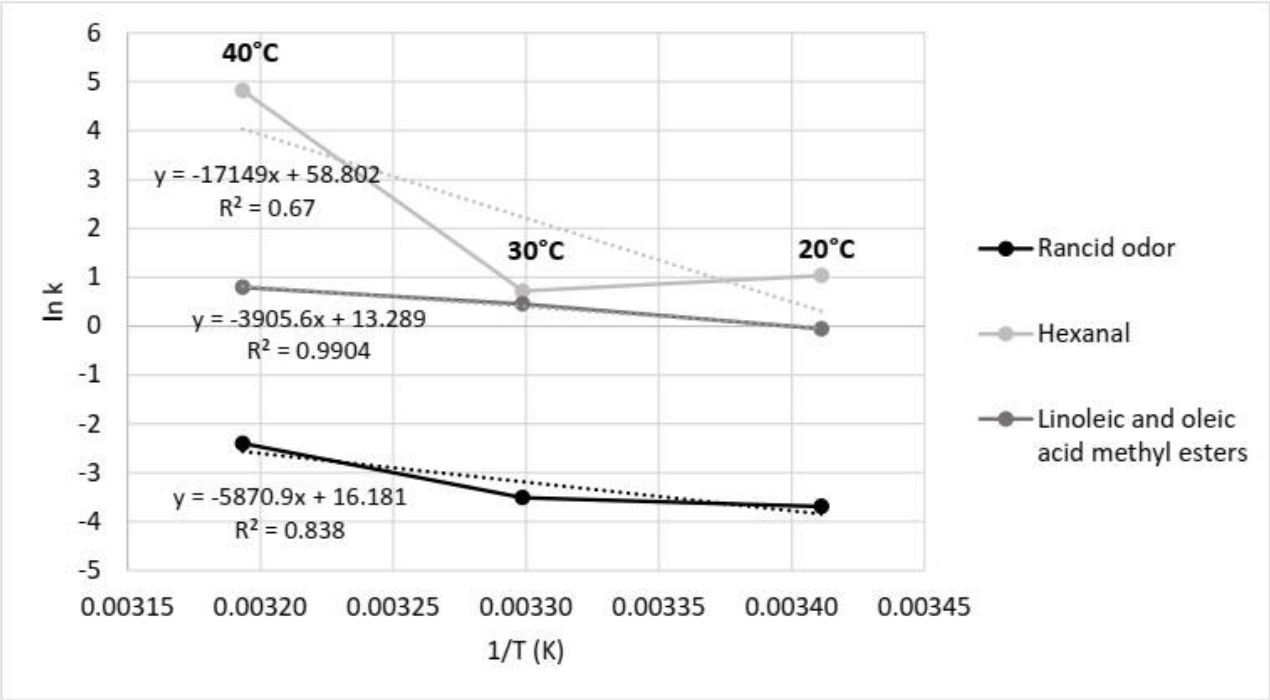


**Fig. 4.** Arrhenius plot of monitored oxidation indicators



rancid odor are indicators that can be used to describe oxidation processes in potato chips. However, as the decomposition of fatty acids does not provide any information about the organoleptical quality deterioration caused by lipid oxidation, the development of rancidity is the most suitable indicator to use when developing methodologies for ASLTs. In addition, as the formation of hexanal did not follow Arrhenius's behavior, it is an unsuitable indicator to assess quality degradation during ASLTs. However, it can be used to detect the end of the induction period.

## Conclusions

The results revealed that the rates of the degradation of fatty acids and the development of organoleptically perceived rancidity increased at higher storage temperatures throughout the experiment, following Arrhenius's behavior. On the contrary, the content of hexanal did not follow this trend for the majority of the testing time, due to the formation of methyl ketones from hexanal. However, the content of hexanal increased rapidly from day 70 only at 40°C, showing the end of the oxidation induction period.

In conclusion, sensorially assessed rancidity is the most suitable oxidation indicator to monitor the shelf-life of potato chips when conducting ASLTs due to its compliance with Arrhenius equation. The reaction rate of hexanal as the commonly known oxidation indicator could not be used to monitor lipid oxidation during ASLTs but it is beneficial for determining the end of the induction period. In addition, it is still important to validate sensory analysis results with instrumental findings to detect the time point after which rapid deterioration takes place since not only hexanal but also other volatiles

contribute to the development of unwanted off-odors. Next to that, as the degradation of fatty acids followed Arrhenius's behavior, it is suitable for assessing the rate of oxidation, although it does not provide any information about organoleptical quality.

To extend the knowledge gained from this experiment, it is important to continue with additional studies where the end of the induction period for samples stored at 20°C and 30°C would be detected as well. With this, lipid oxidation and its various indicators at different storage temperatures could be monitored more precisely to develop an accurate ASLT model for potato chips.

## Author Contributions

Kärt Leppik: Conceptualization, Methodology, Validation, Investigation, Resources, Data Curation, Writing – Original Draft, Writing – Review and Editing, Visualization, Supervision, Project administration, Funding acquisition. Hanna Lang: Methodology, Validation, Formal analysis, Software, Investigation, Resources, Data Curation, Writing – Original Draft. Maria Kuhtinskaja: Methodology, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing – Review and Editing, Supervision. Sirli Rosenvald: Conceptualization, Writing – Review and Editing, Supervision. All authors have read and agreed to the published version of the manuscript.

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## Conflict of interest

The authors declare that there are not conflicts of interest.

## Ethics

This Study does not involve Human or Animal Testing.

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